THE MINISTRY OF SCIENCE AND HIGHER EDUCATION OF THE RUSSIAN FEDERATION



ST. PETERSBURG STATE POLYTECHNICAL UNIVERSITY JOURNAL

Physics and Mathematics

VOLUME 16, No. 3.2, 2023

Peter the Great St. Petersburg Polytechnic University 2023

ST. PETERSBURG STATE POLYTECHNICAL UNIVERSITY JOURNAL. PHYSICS AND MATHEMATICS

JOURNAL EDITORIAL COUNCIL

A.I. Borovkov - vice-rector for perspective projects;

V.A. Glukhikh – full member of RAS;

V.K. Ivanov – Dr. Sci.(phys.-math.), prof.;

A.I. Rudskoy – full member of RAS, deputy head of the editorial council;

R.A. Suris – full member of RAS;

A.E. Zhukov - corresponding member of RAS, deputy head of the editorial council.

JOURNAL EDITORIAL BOARD

V.K. Ivanov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia, - editor-in-chief;

A.E. Fotiadi - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia, - deputy editor-in-chief;

V.M. Kapralova – Candidate of Phys.-Math. Sci., associate prof., SPbPU, St. Petersburg, Russia, – executive secretary;

V.I. Antonov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

I.B. Bezprozvanny – Dr. Sci. (biology), prof., The University of Texas Southwestern Medical Center, Dallas, TX, USA;

A.V. Blinov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

A.S. Cherepanov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

D.V. Donetski - Dr. Sci. (phys.-math.), prof., State University of New York at Stony Brook, NY, USA;

V.V. Dubov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

D.A. Firsov – Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

P.A. Karasev - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

A.S. Kheifets - Ph.D., prof., Australian National University, Canberra, Australia;

O.S. Loboda - Candidate of Phys.-Math. Sci., associate prof., SPbPU, St. Petersburg, Russia;

J.B. Malherbe - Dr. Sci. (physics), prof., University of Pretoria, Republic of South Africa;

V.M. Ostryakov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

V.E. Privalov - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

E.M. Smirnov – Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia;

A.V. Solov'yov – Dr. Sci. (phys.-math.), prof., MBN Research Center, Frankfurt am Main, Germany;

A.K. Tagantsev - Dr. Sci. (phys.-math.), prof., Swiss Federal Institute of Technology, Lausanne, Switzerland;

I.N. Toptygin - Dr. Sci. (phys.-math.), prof., SPbPU, St. Petersburg, Russia.

The journal is included in the List of leading peerreviewed scientific journals and other editions to publish major findings of theses for the research degrees of Doctor of Sciences and Candidate of Sciences.

The publications are presented in the VINITI RAS Abstract Journal and Ulrich's Periodical Directory International Database.

The journal is published since 2008 as part of the periodical edition 'Nauchno-tekhnicheskie vedomosti SPb-GPU'.

The journal is registered with the Federal Service for Supervision in the Sphere of Telecom, Information Technologies and Mass Communications (ROSKOMNADZOR). Certificate $\Pi M \ \Phi C77-52144$ issued December 11, 2012.

The journal is distributed through the CIS countries catalogue, the «Press of Russia» joint catalogue and the «Press by subscription» Internet catalogue. The subscription index is **71823.**

The journal is in the **Web of Science** (Emerging Sources Citation Index), **Scopus**, the **Russian Science Citation Index** (RSCI) and the **Directory of Open Access Journals** (DOAJ) databases.

© Scientific Electronic Library (http://www.elibrary.ru).

No part of this publication may be reproduced without clear reference to the source.

The views of the authors may not represent the views of the Editorial Board.

Address: 195251 Politekhnicheskaya St. 29, St. Petersburg, Russia.

Phone: (812) 294-22-85. http://ntv.spbstu.ru/physics

> © Peter the Great St. Petersburg Polytechnic University, 2023

PREFACE



10-я Международная школа-конференция по оптоэлектронике, фотонике, инженерии и наноструктурам / 10th International School and Conference on Optoelectronics, Photonics, Engineering and Nanostructures (SPb OPEN - 2023)



The Anniversary 10th International School and Conference on Optoelectronics, Photonics, Engineering and Nanostructures (SPb OPEN-2022) was held from May 23 to May 26, 2023. It continues the annual schools and seminars for young scientists on physics and technology of nanostructures for young scientists, organized since 2009, spearheaded by Zhores Alferov, RAS Academician and winner of the 2000 Nobel Prize in Physics.

The School was organized by the St. Petersburg Higher School of Economics, Peter the Great St. Petersburg Polytechnic University and the Alferov University with the support of Photonics Russia, Special Systems Photonics LLC, NT-MDT, Photonic Technologies.

The Programme Committee of the School and Conference selected 275 papers by young scientists, graduate and undergraduate students from 22 cities. The average age of this and last year's attendees was slightly under 27. Presentations were given in six panels:

- Synthesis and structural properties of semiconductor materials and nanostructures,
- Lasers, solar cells, other optoelectronic devices,
- Nanophotonics, spectroscopy, microresonators, optical properties, plasmonics,
- Biophysics, nanobiotechnology, biophotonics,
- Electrical, magnetic and microwave characteristics and devices,
- Other aspects of nanotechnology.

In addition to poster presentations from young scientists, the programme included a series of keynote speeches by prominent researchers, outlining the main advances and challenges in various fields of physics and technology. In total, 79 leading scientists participated in the conference. The keynote speakers included:

- Wang Qi (Beijing University of Posts and Telecommunications, China),
- Alexander Dubinov (Institute for Physics of Microstructures RAS, Nizhny Novogorod),
- Sergey Shcherbak (Peter the Great Polytechnic University, St. Petersburg),
- Grigory Sokolovsky (Ioffe Institute, St. Petersburg),
- Alexey Nadtochiy (St. Petersburg Higher School of Economics, St. Petersburg),
- Sergey Karpov (Soft Impact, St. Petersburg),
- Rodion Reznik (St. Petersburg State University, St. Petersburg),
- Sergey Polulyakh (V.I. Vernadsky Crimean Federal University, Simferopol),
- Sergey Blokhin (Ioffe Institute, St. Petersburg),
- Vladimir Mikhrin (Innolume, Germany).

The same as last year, the peer-reviewed reports from the conference are to be published in St. Petersburg State Polytechnical University Journal: Physics and Mathematics. The Programme Committee of SPbOPEN-2023 hopes that the range of subjects presented at the conference will be of interest to the journal's audience. We would like to thank the journal for giving us the opportunity to publish the proceedings, and thank the reviewers for useful recommendations and constructive criticism. We express our gratitude to all participants of the conference.

We invite young scientists, graduate and undergraduate students to take part in the next School and Conference in 2024. Please visit https://spb.hse.ru/spbopen/ for more details.

A. E. Zhukov

National Research University Higher School of Economics, St. Petersburg aezhukov@hse.ru

© Peter the Great St. Petersburg Polytechnic University, 2023

CONTENTS

Physical optics

Kovach Ya.N., Blokhin S.A., Bobrov M.A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Gladyshev A.G., Novikov I.I., Karachinsky L.Ya., Voropaev K.O., Egorov A.Yu., Ustinov V.M. Emission linewidth and α -factor of 1.3 μ m-range vertical cavity surface emitting laser based on InGaAs/InAlGaAs superlattice	9
Blokhin S.A., Kovach Ya.N., Bobrov M.A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Zadiranov Yu.M., Kulagina M.M., Guseva Yu.A., Vasil'ev A.P., Ustinov V.M. Vertical-cavity surface- emitting lasers for compact atomic sensors	16
Ignatev A.N., Fomin A.V., Usmanov S.R., Kadigrob E.V. Laser diode module over 350 W power output with 200 μm/NA 0.22 fiber	23
Dryazgov M.A., Biriukov Yu.A., Taratorin K.V., Dyakonov I.V., Korneev A.A., Straupe S.S. Pockels cell performance in N-photon demultiplexer	28
Goranskaia S.A. A new method for calculating spectral diffractive lenses for focusing laser radiation of various wave lengths	33
Zacharenko Yu.G., Kononova N.A., Kurkova A.D., Logvinuk E.I., Fomkina Z.V. Application of lasers of metrological appropriation as working standards	39
Deng Y., Davydov V.V. Features of photovoltaic cell degradation of solar power plants in Hong Kong and Saint Petersburg	44
BabichevA.V., NadtochiyA.M., TkachYu.S., KryzhanovskayaN.V., BlokhinS.A., NevedomskyV.N., Gladyshev A.G., Maleev N.A., Karachinsky L.Ya., Novikov. I.I. Photoluminescence study of InGaAs/GaAs quantum dots with bimodal inhomogeneous broadening	50
Arinushkina K.G., Adadurov A.S., Savelev I.Yu., Davydov V.V. Features of the operation of a laser profilometer in an automated rolling stock control system	56
Kashapov A.I., Bezus E.A., Bykov D.A., Doskolovich L.L. Generation of spatiotemporal optical vortices using Kretschmann setup for transverse magnetic and transverse electric polarizations	63
Kupriyanov P.A., Rudavin N.V., Gerasin I.S., Dvurechenskiy A.A., Petrov I.V., Menskoy D.D., Shakhovoy R.A. Influence of quantum states imperfections on the error rate in measurement- device-independent quantum key distribution	69
Kadigrob R.V. Design and simulation of an optical system of high-power fiber-coupled laser module	75
Popovskiy N.I., Davydov V.V., Rud V.Yu. Features of the construction photonic tensor cores for neural networks	81
Vovk N.A., Shibalov M.V., Mumlyakov A.M., Korneeva Ju.P., Asharchuk I.M., Smirnov K.V., Tarkhov M.A. Modelling the influence of planar waveguide cladding thickness on the absorption efficiency of a superconducting NbN strip	87
Bazhanova V.A, Davydov V.V. Features of monitoring the state of viscous media by refraction	92
Rudavin N.V., Gerasin I.S., Kupriyanov P.A., Dvurechenskiy A.P., Shakhovoy R.A. Real-time calibration methods for a commercial MDI-QKD system	97

Savelyev D.A. The subwavelength optical elements with a nonlinear dependence of the refractive index change for the formation of specified diffraction patterns using high-performance computer systems)3
Astafiev A.A., Shakhov A.M., Syrchina M.S., Nadtochenko V.A. <i>Analysis of size-dependent optical properties of lysine carbon dots produced by femtosecond laser synthesis</i>)9
Neelova A.D., Shepilova E.M., Nosova E.I., Rongonen S.L., Parfenov V.A. <i>A study of chemical and mechanical properties of paper under its laser cleaning</i> 11	_4
Naumova V.V., Orlov O.A. Compact solid-state laser with diode optical pumping and high frequency stability	20
Shuklov I.A., Milenkovich T., Mardini A.A. <i>Phosphine-free synthesis of selenide colloidal quantum dots</i>	25
Anikina M.A., Kuznetsov A., Toksumakov A.N., Dremov V.V., Ghazaryan D.A., Fedorov V.V., Arsenin A.V., Volkov V.S., Bolshakov A.D. Photoluminescence anisotropy in hybrid nanostructures based on gallium phosphide nanowire and 2D transition metal dichalcogenides	30
Stepanenkov G.V., Vakorina V.D., Davydov V.V., Davydov R.V. <i>Features of express control of volatile hydrocarbon media and their mixtures in visible light</i> 13	37
Reznikov B.K., Stepanenkov G.V., Isaenko D.I., Logvinova E.A., Pachin A.V., Kolybelnikov N.Yu. <i>Peculiarities of telemetry information transmission using analog fiber-optic communication line</i> <i>over long distances in a complex electromagnetic environment</i>	13
Vilchenko S.A., Gribko V.V. KDP crystals as an optical element in high-power laser system	50
Oaserele D.V., Gordeeva A.F., Davydov R.V. Development of a photodetector for an analog extended fiber-optic communication line	54
Mitrofanova A.E., Skuratov I.D., Svetikov V.V. Investigation of phase shift in waveguides with chalcogenide glasses	51
Murzagalina S.M., Skuratov I.D. The research of nonlinear optical phenomena in silicon slot waveguide structures	57
Jabr Y.J., Smirnova L.A., Parfenov V.A. Study of color characteristics of pigments and paints by spectrophotometer	'1
Physical Materials Science	
Komarov I.A., Danilov E.A. On the wetting of polyethylene terephthalate substrates with multicomponent graphene oxide dispersions	7
Stovpiaga E.Yu., Grudinkin S.A., Eurov D.A., Kurdyukov D.A. <i>A facile low-temperature approach for organics removal from SiO</i> ₂ -CTAB mesoporous particles	33
Eurov D.A., Kirilenko D.A., Stovpiaga E.Yu., Kurdyukov D.A. Hard-template synthesis of monodisperse spherical microporous SiO ₂ particles	38
Litovchenko N.A., Martynova I.K., Gavrilin I.M., Kudrvashova Y.O., Ryazanov R.M., Lebedev F.A.	

Litovchenko W.A., Wartynova I.K., Gavrinn I.W., Kuuryashova I.O., Kyazanov K.W., Lebeuev E.A.	
The method of formation of planar lithium-ion batteries with composite electrode materials	194

Kamalov A.M., Borisova M.E. Charge relaxation after exposure to barrier and corona discharge of polylactide films	200
Isokjanov Sh.Sh., Ryazanov R.M., Kitsyuk E.P., Lebedev E.A. Study of composite electrode material formation features based on Super C45/RuO ₂ and Super C45/MnO ₂ for asymmetric planar supercapacitors.	206
Mumlyakov A.M., Pershina E.A., Shibalova A.A., Shibalov M.V., Anufriev Yu.V., Filippov I.A., Sen' V.V., Tarkhov M.A. Study of n-diamond and carbon nanowalls structure synthsized by the RF-PECVD.	211
Nekrasov N.P., Romashkin A.V., Barsukov L.A., Nikitin K.G., Levin D.D., Bobrinetskiy I.I., Nevolin V.K. Mechanisms of residual polymer removal in solvent mixtures after the graphene transfer and effects on channel conductivity gate control	217
Grashchenko A.S., Kukushkin S.A., Sharofidinov Sh.Sh. Structural surface characteristics of aluminum-gallium nitride films on silicon carbide nanolayers on silicon	223
Khakhulin S.A., Lakuntsova O.E., Firsov D.D., Komkov O.S. Optical anisotropy of black phosphorus characterized by FTIR spectroscopy methods	228
Kamalov A.M., Kraft V.E., Vaganov G.V., Nesterova A.S., Borisova M.E., Ivankova E.M., Yudin V.E. Production of polyimide nonwoven fabric with low dielectric permittivity	233
Kapustin S.N., Volkov A.S., Tsykareva Yu.V. Icing and chemical pollution sensor based on carbon nanoparticles-based superhydrophobic coating	239
Toikka A.S., Kamanina N.V. Formation of the anisotropic ITO-based orienting layers for the liquid crystal devices	244
Lenshin A.S., Zolotukhin D.S., Seredin P.V., Mizerov A.M. Study of morphology and composition of nanoscale AlGaN heterostructures obtained by PA MBE technique on the silicon substrates with the use of porous silicon as buffer layer	249
Shugabaev T., Gridchin V.O., Reznik R.R., Khrebtov A.I., Melnichenko I.A., Kulagina A.S., Kotlyar K.P., Lendyashova V.V., Kryzhanovskaya N.V., Cirlin G.E. Quantum dot-induced photoluminescence enhancement of InGaN nanowires.	255
Malo D., Lizunova A.A., Vershinina O.V., Filalova E.M., Ivanov V.V. Ultraviolet photoluminescence enhancement of zinc oxide nanocrystals in colloidal mixtures with spark discharge aluminum nanoparticles	261
Shiryaev M.E., Ryazanov R.M., Sysa A.V., Lebedev E.A. Effect of Al-CuO multilayer thermite structures thickness on combustion behavior	267
Maksimova A.A., Uvarov A.V., Pozdeev V.A., Kirilenko D.A., Baranov A.I., Vyacheslavova E.A., Gudovskikh A.S. Boron phosphide grown by PECVD and its optical properties	273
Pesniakov V.V., Ignatiev A.I., Nikonorov N.V. <i>Optical properties of photo-thermo-refractive glasses doped with terbium</i>	278
Kameneva E.I., Lizunova A.A., Filalova E.M., Malo D., Kornyushin D.V., Ivanov V.V. Technology of manufacturing thin-film aluminum nanostructures by dry aerosol printing	282

Biophysics and medical physics

Levin A.I., Pecherskaya E.A., Varenik Yu.A., Shepeleva J.V. Implementation of electrical impedance tomography	288
Antipenko V.V., Pecherskaya E.A., Tuzova D.E., Yakushov D.V., Artamonov D.V. Development of an automated system for measuring bioimpedance for the study of body composition	294
Shipovskaya A.B., Rudenko D.A., Shmakov S.L., Gegel N.O. Optical activity anisotropy in thin films of chitosan L- and D-ascorbate	301
Zaichenko K.V., Afanasenko A.S., Kordyukova A.A., Denisova E.A., Sevakov D.O. Development of an algorithm for preprocessing ultra-high resolution electrocardiosignals	307
Sidorov E.A., Troshkina N.N, Gribova E.D., Gladyshev P.P., Polotnyanko N.A. Coating of hydrophilic chalcogenide quantum dots with carboxymethyl chitosan for lateral flow immunoassay applications	312
Kuzyaeva V.I., Sochilina A.V., Savelyev A.G., Akasov R.A., Generalova A.N. Fabrication of porous hydrogels containing hyaluronic acid by photoinduced crosslinking	318
Romanova V.V., Sibirtsev V.S., Zaitceva A.Yu. <i>Miniature potentiometric system for determination</i> of H^+ , K^+ , Na^+ , Cl^- , NO_3^- - and Ca^{2+} ions in liquid biological environment	323
Msokar S., Davydov R.V., Mazing M.S., Isakova D.D., Yakusheva M.A. New opportunities for studying the oxygen saturation of blood hemoglobin in capillaries and tissues	328
Kharlamova A.A. Mathematical modeling of determination of "Premeltons" sites in DNA by ultra short laser pulses	333
Ryabkin D.I., Suchkova V.V., Gerasimenko A.Yu. Development of an algorithm for predicting the strength of laser reconstruction of biological tissue	338
Ryabkin D.I., Suchkova V.V., Gerasimenko A.Yu. Modelling of laser welding of biological tissues using focused radiation	344
Zanevskaya M.Yu., Mazing M.S., Zaitceva A.Yu., Romanova V.V. Application of optical methods for quality control of dairy products using data mining	349
Stepanov M.E., Demina P.A., Akasov R.A., Babayeva G., Egorova T.V., Generalova A.N., Parodi A., Khaydukov E.V. In vivo visualization of albumin nanoparticles loaded with cyanine dyes	354
Physics of molecules	
Rudnykh S.K., Gribova E.D., Kholmurodov K.T., Gladyshev P.P., Polotnyanko N.A. Determination of the isoelectric point of the antibody to Sars-Cov-2 by molecular modeling for conjugation with quantum dots	360
Mathematical physics	
Gerasin I.S., Rudavin N.V., Kupriyanov P.A., Dvurechenskiy A.A., Shakhovoy R.A. <i>Experimental evaluation of imperfections of quantum states for time-bin encoding</i>	366

Radiophysics

Lvov A.V., Prikhodko A. N., Shurakov A.S., Goltsman G.N. Reconfigurable reflectarrays for 5/6G	
wireless systems with linear polarization	372

St. Petersburg Polytechnic University Journal. Physics and Mathematics. 16 (3.2) 2023

Nazarova K.S., Davydov V.V. Creation of an automated system for adjusting the position of the laser radiation axis for the air communication channel	377
Burtsev V.D., Bulatov N.O., Nikulin A.V., Semkin P.V., Kuznetsov S.A., Filonov D.S. Magneto- electric dipole antenna as a transceive element in a phased array	383
Mikheev I.I., Burtsev V.D., Vosheva T.S., Yusupov I.M., Filonov D.S. Using mobile phone as a ripeness sensor	389
Isupova E.V., Shvetsov S.Yu., Davydov V.V. Improvement of the thermoregulator of the quantum frequency standard on rubidium-87 atoms	394
Gryaznova E.M., Semicheva E.D. Two-channel fiber-optic communication line for measuring the parameters of active phased antenna arrays in the far zone a landfill conditions	400
Seliverstov S.V., Svyatodukh S.S., Prikhodko A.N., Shurakov A.S., Sheveleva E.D., Goltsman G.N. Optimization of a prism coupler for a THz photonic integrated metamaterial Si waveguide: simulation and experiment	406
Yaropolov T.A., Prikhodko A.N., Rozhkova P.V., Shurakov A.S., Goltsman G.N. Hardware- and user- induced micromobility effects in in-door radio access at 140 GHz	411
Boldarev D.A., Arinushkina K.G., Valov A.P., Dmitriev R.A. Modernization of quantum frequency standard with optical pumping	417
Fadeenko V.B., Ryzhova D.A., Valov A.P., Shavshin A.V. Fiber-optic system development for the output frequency setting of a voltage-controlled oscillator at the radar station antenna complex	423
Shavshin A.V. Improving microwave output in rubidium-87 atomic frequency standard with new automatic gain control	428
Valov A.P., Dmitriev R.A., Davydov V.V., Shavshin A.V. Investigation of a method for improving phase noise in the frequency standard generator block	434
Theoretical Physics	

Babukhin D.V., Sych D.V. Excess leakage of information in quantum key distribution with passive	
side channels	439

PHYSICAL OPTICS

Conference materials UDC 621.373.8 DOI: https://doi.org/10.18721/JPM.163.201

Emission linewidth and α -factor of 1.3 µm-range vertical cavity surface emitting laser based on InGaAs/InAlGaAs superlattice

Ya.N. Kovach^{1,2}, S.A. Blokhin¹, M.A. Bobrov¹, A.A. Blokhin¹, N.A. Maleev¹, A.G. Kuzmenkov¹, A.G. Gladyshev², I.I. Novikov², L.Ya. Karachinsky², K.O. Voropaev³, A.Yu. Egorov⁴, V.M. Ustinov¹

¹ Ioffe Institute, St. Petersburg, Russia;

² ITMO University, St. Petersburg, Russia;

³ JSC OKB-Planeta, Veliky Novgorod, Russia;

⁴ Connector Optics LLC, St. Petersburg, Russia

⊠ j-n-kovach@itmo.ru

Abstract. Static, spectral and linewidth measurements of 1.3 µm-range vertical-cavity surface-emitting lasers based on InGaAs/InAlGaAs superlattice are presented. Minimum emission linewidth about 40-45 MHz was obtained at output power of ~3.3 mW and operating current of ~8 mA using the Fabry-Perot interferometer method. During a further increase in the output optical power the emission linewidth broadening could be observed due to the rise of a laser internal temperature (self-heating). Based on the analysis of the internal optical losses and internal quantum efficiency the linewidth enhancement factor (α -factor) was evaluated at about 7.7–9 depending on population inversion factor of 2-1.5.

Keywords: vertical-cavity surface-emitting laser, superlattice, wafer fusion, linewidth, α -factor

Funding: The authors from ITMO University acknowledge support in part by Advanced Engineering Schools Federal Project for the optical spectra experiments and in part by the Ministry of Science and Higher Education of the Russian Federation, the research project 2019–1442, for the static characteristic and polarization measurements. S.A. Blokhin acknowledges support for laser emission linewidth measurements from RFBR project 20-52-12006.

Citation: Kovach Ya.N., Blokhin S.A., Bobrov M.A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Gladyshev A.G., Novikov I.I., Karachinsky L.Ya., Voropaev K.O., Egorov A.Yu., Ustinov V.M., Emission linewidth and α -factor of 1.3 µm-range vertical cavity surface emitting laser based on InGaAs/InGaAlAs superlattice, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 9–15. DOI: https://doi.org/10.18721/JPM.163.201

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Kovach Ya.N., Blokhin S.A., Bobrov M.A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Gladyshev A.G., Novikov I.I., Karachinsky L.Ya., Voropaev K.O., Egorov A.Yu., Ustinov V.M., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 621.373.8 DOI: https://doi.org/10.18721/JPM.163.201

Ширина линии излучения и α-фактор вертикально-излучающего лазера спектрального диапазона 1.3 мкм на основе сверхрешетки InGaAs/InAlGaAs

Я.Н. Ковач^{1,2⊠}, С.А. Блохин¹, М.А. Бобров¹, А.А. Блохин¹, Н.А. Малеев¹, А.Г. Кузьменков¹, А.Г. Гладышев², И.И. Новиков², Л.Я. Карачинский², К.О. Воропаев³, А.Ю. Егоров⁴, В.М. Устинов¹

¹ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

² Университет ИТМО, Санкт-Петербург, Россия;

3 АО «ОКБ-Планета», Великий Новгород, Россия;

4 ООО «Коннектор Оптикс», Санкт-Петербург, Россия

^{III} j-n-kovach@itmo.ru

Аннотация. В работе представлены результаты измерений статических и спектральных характеристик вертикально-излучающего лазера спектрального диапазона 1.3 мкм на основе сверхрешетки InGaAs/InAlGaAs. Минимальное значение ширины линии излучения, измеренное с помощью Фабри-Перо интерферометра, составило 40-45 МГц при выходной оптической мощности ~3,3 мВт и рабочем токе ~8 мА. При дальнейшем повышении выходной мощности наблюдается уширение линии излучения из-за роста внутренней температуры лазера (саморазогрев с током). Анализ внутренних оптических потерь и эффективности токовой инжекции позволил оценить значение α -фактора на уровне 7.7-9 в зависимости от значения фактора инверсной заселенности 2-1.5.

Ключевые слова: вертикально-излучающий лазер, сверхрешетка, технология спекание пластин, ширина линии, α-фактор

Финансирование: Работа авторов из Университета ИТМО выполнена при поддержке федерального проекта «Передовые инженерные школы» в части исследований оптических спектров, а также при поддержке Министерства науки и высшего образования Российской Федерации, проект тематики научных исследований № 2019-1442 в части ряда исследований статических и поляризационных характеристик. С.А. Блохин выражает благодарность РФФИ № 20-52-12006 в части измерений ширины линии излучения лазера.

Ссылка при цитировании: Ковач Я.Н., Блохин С.А., Бобров М.А., Блохин А.А., Малеев Н.А., Кузьменков А.Г., Гладышев А.Г., Новиков И.И., Карачинский Л.Я., Воропаев К.О., Егоров А.Ю., Устинов В.М., Ширина линии излучения и α-фактор вертикальноизлучающего лазера спектрального диапазона 1.3 мкм на основе сверхрешетки InGaAs/ InGaAlAs // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 9–15. DOI: https://doi.org/10.18721/JPM.163.201

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Today vertical-cavity surface-emitting lasers (VCSELs) and VCSEL-based matrixes are used in optical data communication systems, industrial heating, 3D sensing for consumer electronics, and LIDAR object recognition [1]. Recently, much attention has been paid to the possible implementation of single-mode VCSELs for optical spectroscopy and real-time analysis of industrial gases. However, the development of long-wavelength VCSELs is associated with a number of fundamental problems of the material systems InAlGaAs-GaAs and InAlGaAsP-InP. Today, the most promising approach to the creation of 1.3 μ m-range VCSELs is the hybrid integration of the active region based on the InAlGaAsP-InP material system with semiconductor distributed

© Ковач Я.Н., Блохин С.А., Бобров М.А., Блохин А.А., Малеев Н.А., Кузьменков А.Г., Гладышев А.Г., Новиков И.И., Карачинский Л.Я., Воропаев К.О., Егоров А.Ю., Устинов В.М., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Bragg reflectors (DBR) GaAs/AlGaAs using the wafer fusion technology (WF-VCSEL) or with hybrid metal-dielectric mirrors based on high-contrast materials (HI-VCSEL) [2]. As the result of optimization of photon lifetime by variation of mirror losses and enhancement of differential gain by implementation of InAlGaAs quantum well active region the WF-VCSEL devices with the modulation bandwidth more than 12 GHz and error-free data transmission up to 10 km at 25 Gbps without any equalization technique were obtained [3]. As for the state-of-the-art HI-VCSEL, record modulation bandwidth more than 15 GHz [4] with the error-free data transmission at 30 Gbps over 10 km [5] and up to 50 Gbps [6] over 15 km without and with pre-equalization, respectively, were demonstrated for the devices with minimized mode volume (with shorter effective cavity length and smaller current aperture). Recently, we successfully tested the use of an InGaAs/InAlGaAs short-period superlattice (SL) as an active region of 1.3 µm-range WF-VCSELs [7,8].

In this paper, the results of studying the emission linewidth of 1.3 μ m-range single-mode InGaAs SL-based WF-VCSEL are presented, and estimation of the α -factor is carried out.

Materials and Methods

WF-VCSEL designed in the geometry of a vertical microcavity with carrier injection through *n*-InP intracavity contacts and a composite tunnel junction (TJ) n^+ -InGaAs/ p^+ -InGaAs/ p^+ -InAlGaAs. For optical and current confinement, the concept of a buried tunnel junction (BTJ) was used, where mesas with 4 µm diameter were formed in the InGaAs layers of composite TJ. The active region was a short-period SL consisting of 24 pairs of In_{0.57}Ga_{0.43}As/In_{0.53}Ga_{0.20}Al_{0.27}As layers with thicknesses of 0.8 and 2 nm accordingly [7]. A detailed description of the WF-VCSEL heterostructure and the fabrication of the WF-VCSEL chips are presented in [8]. After dicing into individual chips, the devices were mounted in TO-can package.

Results and Discussion

The investigation of WF-VCSELs demonstrated lasing with a threshold current of ~3 mA and a differential efficiency of ~0.68 W/A. Due to the laser self-heating effect, output optical power reached saturation at operating currents above 10 mA (Fig. 1,*a*). According to analysis of the emission spectra of the WF-VCSELs, those devices demonstrate lasing through the fundamental mode with a side-mode suppression ratio (SMSR) of more than 30 dB in the entire current range (Fig. 1,*b*). In addition, the polarization degeneracy of the fundamental mode was observed, which can be explained by the transverse asymmetry of BTJ mesa and/or the elasto-optical effect. Polarization-resolved study revealed the predominance of short wavelength mode with polarization along short axis of BTJ mesa with an orthogonal polarization suppression ratio (OPSR) of more than 20 dB in the entire operating range of currents and without the presence of polarization switching (Fig. 1,*a*).

To measure WF-VCSEL emission linewidth a SA30-144 scanning Fabry–Perot interferometer was used; a chemical current source was used to minimize noise, and an optical isolator was used to suppress optical feedback. According to the Schawlow-Townes-Henry theory, the emission linewidth of the semiconductor injection lasers could be described by the following equation, which considers the dependence of the refractive index on the carrier density [9]:

$$\Delta v = \frac{n_{sp} n_{SE} \overline{e}}{4\pi P_{out} n_j \tau_p^2} (1 + \alpha^2) + \Delta v_0, \tag{1}$$

where n_{sp} is the population inversion factor, n_{SE} is the slope efficiency, *e* is the elementary charge, P_{out} is the output optical power, n_j is the internal quantum efficiency, Δv_0 is the residual linewidth, τ_p is the photon lifetime.

According to Fig. 2, at first, the laser emission linewidth of the WF-VCSEL decreased inversely proportional with increase in the output optical power down to 40–45 MHz (at ~3.3 mW and operating current of ~8 mA). The linear approximation gives the value of the residual linewidth Δv_0 about 6.5 MHz, which can be associated with 1/*f*-noise (fluctuations of the charge carriers) and/or mode competition. However, with a further increase in the output optical power a broadening of the laser emission line could be observed, which, apparently, connected with the laser self-heating.



Fig. 1. Evolution of an output optical power with OPSR as functions of current (a) and optical spectra for different operating currents (b) measured at 20 °C



Fig. 2. Emission linewidth measured at 20 °C and the estimated internal laser temperature against inverse output optical power

With the intension to verify such assumption the study of the laser internal temperature was conducted. In accordance with [10], internal temperature rise of VCSELs could be evaluated as:

$$\Delta T_{int} = R_{th} \left(P_{diss} - P_{out} \right), \tag{2}$$

where R_{th} is the thermal resistance, P_{diss} is the dissipated electrical power. Device R_{th} is defined by the resonance wavelength shifts with temperature $\Delta \lambda_0 / \Delta T$ and with dissipated electrical power $\Delta \lambda_0 / \Delta P_{diss}$. With the study of optical spectra for different operating current and different heat-sink temperatures the dissipated power shift $\Delta \lambda_0 / \Delta P_{diss}$ at fixed heat-sink temperature T (Fig. 3,*a*) and the temperature shift $\Delta \lambda_0 / \Delta T$ at fixed dissipated electrical power P_{diss} (Fig. 3,b) were evaluated as 0.22 nm/mW and 0.09 nm/°C accordingly. So, calculated thermal resistance value $R_{th} = (\Delta \lambda_0 / \Delta P_{diss}) / (\Delta \lambda_0 / \Delta T)$ was 2.46 °K/mW, which is significantly lower than thermal resistance of long-wavelength HI-VCSELs with the same BTJ mesa diameter [11]. It should be noted that such high calculated value of R_{th} compared with work [7] could be explained by higher P_{diss} value (lower slope efficiency) and peculiarities of chip packaging. As shown in Fig. 2, the sharp rise of laser internal temperature ΔT_{int} revealed for output optical power more than 2 mW (operating current over than 5.5 mA).



Fig. 3. Dependences of the wavelength shift on dissipated electrical power at fixed heat-sink temperature of 20 °C (*a*) and the wavelength shift on heat-sink temperature at fixed dissipated electrical power (*b*)

Dependence of photon lifetime in cavity on mirror losses T_m and internal optical losses A_{int} could be described as follows [9]:

$$\tau_p = 1/\nu_g \left(T_m + A_{int} \right),\tag{3}$$

where v_g is the group velocity (~10¹⁰ cm/s). Values of A_{int} and n_j were found from iterative varying of mirror losses by the deposition of the thin dielectric layer on the top DBR mirror as was conducted in [12]. According to Fig. 4., rise of heat-sink temperature leads to the increased internal optical losses of WF-VCSEL, which could be explained by stronger free-carrier absorption in the doped region and/or interband absorption in the InGaAs layers. As for the drop in the internal quantum efficiency, it may be due to the overflow of charge carriers as the threshold currents increase with temperature.

Note that the population inversion factor n_{sp} is difficult to determine separately from the α -factor. Using expressions (1) and (3) the value of the α -factor was estimated to be about 7.7–9 at 20 °C for n_{sp} in range 2–1.5, respectively.



Fig. 4. Estimated internal quantum efficiency and internal optical losses as function of heat-sink temperature

Additionally, it can be observed that the gradual decrease in the internal quantum efficiency and the increase in the internal optical losses due to a rise in the laser internal temperature led to the decrease in the slope efficiency and the photon lifetime, which, according to expression (1), could potentially cause the laser emission linewidth broadening. However, it is more likely that the observed broadening is associated with the gain saturation at the higher operating currents and the decrease in the material gain at the higher laser internal temperature. Both effects led to the reduction of the differential gain at the higher carrier density and/or laser internal temperature [9],which finally resulted to the rise of the α -factor [13] despite the further increase in the output optical power [14].

Conclusion

In this work, we analyzed the emission linewidth of 1.3 μ m-range InGaAs/InAlGaAs SL-based WF-VCSELs. For 20 °C, the linewidth drops to 45-40 MHz at 3.3 mW. The linewidth enhancement factor of 9–7.7 was estimated assuming population inversion factor of 2-1.5.

REFERENCES

1. Padullaparthi B.D., Tatum J.A., Iga K., VCSEL industry: communication and sensing. Wiley-IEEE Press, 2021. 352 p.

2. Babichev A., Blokhin S., Kolodeznyi E., Karachinsky L., Novikov I., Egorov A., Tian S.-C., Bimberg D., Long-Wavelength VCSELs: Status and Prospects // Photonics. 2023. Vol. 10, N_{0} 3. P. 268. 10.3390/photonics10030268.

3. Caliman A., Sirbu A., Iakovlev V., Mereuta A., Wolf P., Bimberg D., Kapon E., 25 Gbps direct modulation and data transmission with 1310 nm waveband wafer fused VCSELs // Optical Fiber Communication Conference. Washington, D.C.: OSA, 2016. P. Tu3D.1. 10.1364/OFC.2016.Tu3D.1.

4. Müller M., Grasse C., Saller K., Gründl T., Böhm G., Ortsiefer M., Amann M.C., 1.3 μm High-Power Short-Cavity VCSELs for High-Speed Applications // Conference on Lasers and Electro-Optics 2012. Washington, D.C.: OSA, 2012. P. CW3N.2. 10.1364/CLEO_SI.2012.CW3N.2.

5. Spiga S., Muller M., Amann M.-C., Energy-efficient high-speed InP-based 1.3 um short-cavity VCSELs // 2013 15th International Conference on Transparent Optical Networks (ICTON). IEEE, 2013. P. 1–4. 10.1109/ICTON.2013.6602683.

6. Breyne L., Verplaetse M., Neumeyr C., De Keulenaer T., Soenen W., Yin X., Ossieur P., Torfs G., Bauwelinck J., DSP-Free and Real-Time NRZ Transmission of 50 Gb/s Over 15-km SSMF and 64 Gb/s Back-to-Back With a 1.3-μm VCSEL // J. Light. Technol. 2019. Vol. 37, № 1. P. 170–177. 10.1109/JLT.2018.2885619.

7. Blokhin S.A., Babichev A. V., Gladyshev A.G., Karachinsky L.Y., Novikov I.I., Blokhin A.A., Bobrov M.A., Maleev N.A., Andryushkin V. V., Denisov D. V., Voropaev K.O., Zhumaeva I.O., Ustinov V.M., Egorov A.Y., Ledentsov N.N., High Power Single Mode 1300-nm Superlattice Based VCSEL: Impact of the Buried Tunnel Junction Diameter on Performance // IEEE J. Quantum Electron. 2022. Vol. 58, N_2 2. P. 1–15. 10.1109/JQE.2022.3141418.

8. Blokhin S., Babichev A., Gladyshev A., Karachinsky L., Novikov I., Blokhin A., Rochas S., Denisov D., Voropaev K., Ionov A., Ledentsov N., Egorov A., Wafer-fused 1300 nm VCSELs with an active region based on superlattice // Electron. Lett. 2021. Vol. 57, № 18. P. 697–698. 10.1049/ell2.12232.

9. Coldren L.A., Corzine, S. W. Mashanovitch M.L., Diode lasers and photonic integrated circuits. John Wiley & Sons, 2012. 583 p.

10. **Michalzik R.,** VCSELs: Fundamentals, Technology and Applications of Vertical-Cavity Surface-Emitting Lasers // Springer Series in Optical Sciences. Springer Verlag, 2013. 10.1007/978-3-642-24986-0_2.

11. Spiga S., Schoke D., Andrejew A., Boehm G., Amann M.-C., Effect of Cavity Length, Strain, and Mesa Capacitance on 1.5-μm VCSELs Performance // J. Light. Technol. 2017. Vol. 35, № 15. P. 3130–3141. 10.1109/JLT.2017.2660444.

12. Blokhin S.A., Bobrov M. A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Vasyl'ev A. P., Rochas S. S., Babichev A. V., Novikov I. I., Karachinsky L. Ya., Gladyshev A. G., Denisov D. V., Voropaev K. O., Egorov A. Yu., Ustinov V. M., Analysis of internal optical loss of 1.3 μ m vertical-cavity surfaceemitting laser based on n^{++} -InGaAs/ p^{++} -InGaAs/ p^{++} -InAlGaAs tunnel junction // Tech. Phys. Lett. 2022. Vol. 48, No 15. P. 3. 10.21883/TPL.2022.15.53808.18938. 13. Halbritter H., Riemenschneider F., Jacquet J., Provost J.-G., Symonds C., Sagnes I., Meissner P., Chirp and linewidth enhancement factor of tunable, optically-pumped long wavelength VCSEL // Electron. Lett. 2004. Vol. 40, № 4. P. 242. 10.1049/el:20040173.

14. Shau R., Halbritter H., Riemenschneider F., Ortsiefer M., Rosskopf J., Buhm G., Maute M., Meissner P., Amann M.-C., Linewidth of InP-based 1.55 [micro sign]m VCSELs with buried tunnel junction // Electron. Lett. 2003. Vol. 39, № 24. P. 1728. 10.1049/el:20031143.

THE AUTHORS

KOVACH Yakov N. j-n-kovach@itmo.ru ORCID: 0000-0003-4858-4968

BLOKHIN Sergey A. blokh@mail.ioffe.ru ORCID: 0000-0002-5962-5529

BOBROV Mikhail A. bobrov.mikh@gmail.com ORCID: 0000-0001-7271-5644

BLOKHIN Alexey A. bloalex91@yandex.ru ORCID: 0000-0002-3449-8711

MALEEV Nikolai A. Maleev@beam.ioffe.ru ORCID: 0000-0003-2500-1715

KUZMENKOV Alexander G. Kuzmenkov@mail.ioffe.ru ORCID: 0000-0002-7221-0117 GLADYSHEV Andrey G. andrey.gladyshev@connector-optics.com ORCID: 0000-0002-9448-2471

NOVIKOV Innokenty I. innokenty.novikov@itmo.ru ORCID: 0000-0003-1983-0242

KARACHINSKY Leonid Ya. leonid.karachinsky@connector-optics.com ORCID: 0000-0002-5634-8183

VOROPAEV Kirill O. kirill.voropaev@novsu.ru ORCID: 0000-0002-6159-8902

EGOROV Anton Yu. anton.egorov@connector-optics.com ORCID: 0000-0002-0789-4241

USTINOV Victor M. Vmust@beam.ioffe.ru ORCID: 0000-0002-6401-5522

Received 30.06.2023. Approved after reviewing 31.07.2023. Accepted 01.08.2023.

Conference materials UDC 621.373.8 DOI: https://doi.org/10.18721/JPM.163.202

Vertical-cavity surface-emitting lasers for compact atomic sensors

S.A. Blokhin¹^[2], Ya.N. Kovach¹, M.A. Bobrov¹, A.A. Blokhin¹, N.A. Maleev¹, A.G. Kuzmenkov¹, Yu.M. Zadiranov¹, M.M. Kulagina¹, Yu.A. Guseva¹, A.P. Vasil'ev², V.M. Ustinov²

¹ Ioffe Institute, Saint Petersburg, Russia;

² SHM R&E Center, Saint Petersburg, Russia

□ blokh@mail.ioffe.ru

Abstract. The design features of 8XX nm-range vertical-cavity surface-emitting lasers for providing single-mode and polarization-stable lasing, narrowing the spectral linewidth of laser emission and achieving high modulation bandwidth are considered The special intra-cavity contacted design and the rhomb-shaped oxide-confined aperture can simultaneously provide single-mode output optical power above 1 mW, fixed polarization direction, emission linewidth below 50 MHz and modulation bandwidth more than 5 GHz.

Keywords: vertical-cavity surface-emitting laser, single-mode, polarization, linewidth, modulation bandwidth

Funding: Research was supported in part by the Ministry of Science and Higher Education of the Russian Federation (project reference number FFUG-2022-0011).

Citation: Blokhin S.A., Kovach Ya.N., Bobrov M.A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Zadiranov Yu.M., Kulagina M.M., Guseva Yu.A., Vasil'ev A.P., Ustinov V.M., Vertical-cavity surface-emitting lasers for compact atomic sensors, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 16–22. DOI: https://doi.org/10.18721/JPM.163.202

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.373.8 DOI: https://doi.org/10.18721/JPM.163.202

Вертикально-излучающие лазеры для компактных атомных сенсоров

С.А. Блохин¹⊠, Я.Н. Ковач¹, М.А. Бобров¹, А.А. Блохин¹, Н.А. Малеев¹, А.Г. Кузьменков¹, Ю.М. Задиранов¹, М.М. Кулагина¹, Ю.А. Гусева¹, А.П. Васильев², В.М. Устинов²

¹ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

² Научно-технологический центр микроэлектроники и субмикронных гетероструктур,

Санкт-Петербург, Россия

□ blokh@mail.ioffe.ru

Аннотация. Рассмотрены особенности конструкций вертикально-излучающих лазеров спектрального диапазона 8XX нм с целью обеспечения одномодового режима генерации с фиксированным направлением поляризации излучения, заужения ширины спектральной линии излучения и реализации высокой частоты эффективной модуляции. Специальная конструкция микрорезонатора с внутрирезонаторными контактами и

© Blokhin S.A., Kovach Ya.N., Bobrov M.A., Blokhin A.A., Maleev N.A., Kuzmenkov A.G., Zadiranov Yu.M., Kulagina M.M., Guseva Yu.A., Vasil'ev A.P., Ustinov V.M., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

оксидная токовая апертура ромбовидной формы позволяет одновременно обеспечить оптическую мощность более 1мВт в одномодовом режиме генерации с фиксированным направлением поляризации, шириной линии изучения менее 50 МГц и частотой эффективной модуляции более 5 ГГц.

Ключевые слова: вертикально-излучающий лазер, одномодовое излучение, поляризация, ширина линии, частота модуляции

Финансирование: Исследования выполнены при частичной поддержке Министерства науки и высшего образования Российской Федерации (FFUG-2022-0011).

Ссылка при цитировании: Блохин С.А., Ковач Я.Н., Бобров М.А., Блохин А.А., Малеев Н.А., Кузьменков А.Г., Задиранов Ю.М., Кулагина М.М., Гусева Ю.А., Васильев А.П., Устинов В.М., Вертикально-излучающие лазеры для компактных атомных сенсоров // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 16–22. DOI: https://doi.org/10.18721/JPM.163.202

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Recently, increased attention has been paid to the issue of minimizing the size and power consumption of various types of atomic sensors, and the only possible solution is to replace gas discharge lamps, which are used for optical pumping and/or detection, with injection laser diodes [1]. In such devices, alkali metal atoms are used either as a working medium that senses macroscopic magnetization due to the optical orientation of atoms (quantum magnetometers [2]); or as an intermediate medium for the nuclear paramagnets optical orientation due to the spin-exchange interaction (nuclear magnetic gyroscopes [3]); or as a medium for the registration of the so-called dark resonance (formation of a non-absorbing superposition of two states of alkali metal atoms under bichromatic light) due to the effect of coherent population trapping (atomic clocks [4]). As for laser sources for compact atomic sensors, they must simultaneously satisfy several specific requirements: the exact correspondence of the lasing frequency to a certain energy transition of the used alkali atom (¹³Cs, ⁸⁵Ru, or ⁸⁷Ru isotopes); single-mode lasing and narrow spectral width of the emission line; fixed direction of linearly polarized laser emission; large modulation bandwidth; reliable operation at elevated operating temperatures; low power consumption; the possibility of compact installation of the laser emitter and the optical focusing scheme on the gas cell. External cavity lasers, which are widely applied in spectroscopy, can be used to demonstrate an effect or to test one or another design of atomic sensors, but to a large extent, they are a limiting factor in the compact design. The characteristics of the existing edge-emitting lasers are not optimal for creating real devices because the presence of mode-hopping (due to different temperature shifts of the gain maximum and the cavity mode) even with the precise stabilization of the laser temperature and with current and optical means for linking the laser frequency to atomic resonance. And as for a distributed feedback laser, accurate tuning to the required wavelength is the main problem in their practical implementation.

A unique opportunity for compact atomic sensors is provided by vertical-cavity surface-emitting lasers (VCSELs), which have single-mode lasing without external feedback, sub-milliampere threshold currents, increased temperature stability, high spatial symmetry of the output emission, and are manufactured in a planar technology [5]. In this paper, various aspects of the VCSEL design are analyzed in order to meet the above requirements for laser emitters for use in compact atomic sensors.

Results and Discussion

The modern design of the VCSEL is comprised of a vertical optical Fabry-Perot microcavity with an active region, which is confined on both sides by distributed Bragg reflectors (DBRs) based on alternating quarter-wave layers of materials with refractive index contrast. As an active region, several quantum wells (QWs) located at the maximum of the longitudinal distribution of the electromagnetic field of the standing wave are usually used. There are various ways to inject

© Блохин С.А., Ковач Я.Н., Бобров М.А., Блохин А.А., Малеев Н.А., Кузьменков А.Г., Задиранов Ю.М., Кулагина М.М., Гусева Ю.А., Васильев А.П., Устинов В.М., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

charge carriers into the active region: through doped DBRs, through intracavity contacts, or a combination of both, which have their own advantages and disadvantages [6]. To reduce the threshold current, the region of charge carrier injection and radiative recombination is spatially limited by current apertures, formed mainly either within the concept of buried tunnel junction (BTJ) when the local region of the p^+n^+ -junction is usually created, surrounded by the blocking reverse biased p^+n -structure; or by the technology of ion (usually protons) implantation when highly-resistive regions are obtained, or by the selective oxidation technology of AlGaAs layers with a high content of Al in water vapor when a current-blocking layer is created.

To narrow the VCSEL emission linewidth, it is crucial to either increase the output optical power or increase the photon lifetime in the cavity. In the first case, the maximum output optical power of VCSEL is limited by self-heating (increase in the laser internal temperature with an increase in operating current). So, enhancement of the output optical power could be achieved for the VCSELs with higher mirror losses (higher slope efficiency), however, it simultaneously leads to a decrease in photon cavity lifetime and undesirable laser emission line broadening (see Fig.1, a). Moreover, with the rise of the carrier and photon density in the microcavity, it becomes necessary to take into account the effects of gain nonlinearity, which lead to an increase of α -factor [7] and, eventually, to the saturation and broadening of the laser emission line with the increasing output optical power [8]. In addition, the optimal current aperture size should be carefully chosen, as it strongly affects the thermal resistance of the VCSEL. Thus, a decrease in the size of the current aperture leads to an earlier (i.e., at smaller output optical power) transition to an anomalous behavior of the spectral linewidth not only due to an increase in scattering losses (and, as a consequence, a drop in the photon cavity lifetime and an increase in the threshold current), but also due to a faster rise of the laser internal temperature and the observable self-heating even at a low optical power (see Fig. 1,b). In the latter case, the photon lifetime can be increased either by reduction of mirror losses (see Fig. 1,a), which leads to an undesirable drop in slope efficiency and limits the maximum output power, or by increase of the optical cavity length, which leads to an increase in free-carrier absorption in the case of a monolithic VCSEL design and/or a complication of the manufacturing technology in the case of an external cavity implementation (so-called VECSELs).



Fig. 1. Emission linewidths of oxide-confined VCSELs based on doped DBRs as functions of inverse optical power for the 2- μ m devices with high and low mirror losses (*a*) and for the devices with different aperture size at fixed mirror loss (*b*). The heatsink temperature is 20 °C

A promising solution is to increase the effective cavity length by using the VCSEL design with intracavity contacts and low-Q doped DBRs [9]. As shown in Fig. 2,*b*, incorporation of low-Q doped AlGaAs DBRs between AlGaAs intracavity contact (IC) layers and AlGaAs microcavity with the active region based on InGaAs QWs, along with the modulated doping profile, allows to redistribute electromagnetic mode field. It could also be seen that fine adjustment of the latter allows to substantially increase effective cavity length L_{eff} and decrease the level of intrinsic optical losses, which are usually associated with the free carrier absorption in *p*-doped layers. This approach can simultaneously provide the laser emission line of less than 50 MHz and relatively high (above 2 mW) optical power (see Fig. 2,*b*).

In contrast to edge-emitting lasers, in VCSELs light propagates perpendicular to the active region, which imposes strict requirements on the DBR reflectivity in order to achieve the necessary gain and overcome the lasing threshold. Due to a vertical microcavity, lasing is possible only via one longitudinal mode, while the number of transverse modes is determined by the type of current and/or optical confinement. The most obvious way to achieve single-mode lasing is to reduce the area of carrier injection into the active region. However, in the case of proton-implanted apertures, transverse optical confinement is realized by both the gain guiding and the thermal lensing, which leads to unstable current-dependent mode behavior. BTJ-based apertures and oxide-confined apertures introduce fewer optical losses and provide effective optical confinement due to the built-in index guiding effect (effective index step at the BTJ mesa or oxide-semiconductor boundary). Note that the first one is most widely used for creating long-wavelength InAlGaAsP/InP-based VCSELs, while the second one is for short-wavelength InAlGaAs/GaAs-based VCSELs. The effective index step for the oxide-confined aperture depends on the oxide layer thickness and its positions relative to the maximum of the longitudinal distribution of the electromagnetic field of the fundamental mode. However, even if the oxide layer would be placed in the field minimum, the strong waveguiding effect would be present (since the lowest possible thickness of the oxide layer is limited by the rate of the AlGaAs layer oxidation [10]), which ultimately limits the aperture size at which single-mode laser generation could be obtained. To increase the output optical power in the single-mode regime, various methods have been proposed to insert additional optical losses for high-order transverse modes in inherently multimode VCSELs (with the larger aperture) by varying mirror losses, absorption losses, scattering/diffraction losses, or their combination [6].



Fig. 2. Oxide-confined VCSELs with intra-cavity contacts: longitudinal distribution of electromagnetic mode field intensity along the refractive index profile (a), the inset shows zoom-in of longitudinal distribution of doping concentration along with the refractive index profile in the VCSEL cavity (AR, AL denote active region and aperture layer, respectively) emission linewidth as functions of inverse

optical power for the 2- μ m devices (b), the inset shows light-current characteristic at 20 °C



Fig. 3. Effective index step and transverse profiles of the first allowed mode as a function of radial distance for $2-\mu m$ oxide-confined VCSELs with the abrupt aperture (a) and the tapered aperture (b) The inset shows the scanning electron microscopy images both apertures

Nevertheless, the simplest solution is to use a tapered oxide-confined aperture, which makes it possible to smooth the effective index step (due to the gradual reduction of the oxide thickness towards the current aperture) and form a gradient effective waveguide in which higher-order modes become allowed and spread under oxide taper (see Fig. 3). However, the region of charge carrier injection is defined by the tip of the oxide taper, hence, these modes have a lower transverse optical confinement factor (transverse overlap of the pumped active region with the mode field distribution) compared to the fundamental mode [11]. As a results, single-mode lasing can be achieved at larger oxide-confined aperture sizes (see Fig. 4,a).

Unfortunately, the intrinsic mechanism of polarization gain anisotropy does not exist for VCSELs (except for the growth on vicinal substrates), and partial removal of degeneracy due to internal electro-optical and/or elasto-optical effects does not provide reliable polarization stability of laser emission. Therefore, several methods to increase the polarization mode dichroism could be implemented: the formation of a subwavelength diffraction grating on the surface of the output mirror, the use of high-contrast gratings as an output mirror, and the formation of gain anisotropy due to asymmetric charge carrier injection or mechanical stresses [6]. Also, an interesting solution is the use of a rhomb-shaped oxide-confined current aperture formed due to the anisotropy in the selective oxidation process of AlGaAs layers. Our studies revealed that for the emission from 8XX nm-range intra-cavity contacted oxide-confined VCSELs based on InGaAs QWs polarization is typically fixed along the short axis (crystallographic direction [T10]) of the rhomb-shaped oxide-confined aperture [12]. We believe that the rhomb-shaped oxide-confined aperture simultaneously introduces asymmetry into the optical microcavity and forms an asymmetric mechanical stress field near the active region, which provides suppression of the orthogonal polarized fundamental mode (see Fig. 4,*b*).





For injection lasers, modulation bandwidth under direct current modulation is determined by three mechanisms: damping of relaxation oscillations, thermal effects and the parasitic cut-off frequency of the low-pass filter (formed by the elements of the equivalent electrical circuit of the laser) [6]. The influence of thermal effects could be reduced by increasing the thermal conductivity of the lower part of the microcavity (via using AlAs layers in the bottom DBR instead of low-index AlGaAs layers) as well as by choosing the optimal gain-to-cavity detuning to provide the high differential gain in the wide temperature range. To increase resonance frequency, the differential gain of the active region should be increased, which could be achieved not only by increasing the strain in the InGaAs QW-based active region (by increasing the mole fraction of In), but also by decreasing total optical loss (see Fig. 5,a), this, however, leads to a lower output power and a broader emission line. Resonance frequency could also be enhanced by the reduction of the mode volume, but in the case of intra-cavity contacted VCSELs this can be obtained only by reducing the size of the current aperture, since the larger effective cavity length is needed

for narrow linewidth. To reduce damping, the photon lifetime in the cavity should be decreased by increasing the mirror loss and/or the effective cavity length, which, however, again leads to broadening of the emission line, so a compromise between damping and linewidth must be found.

In the case of small-aperture VCSELs, the parasitic cut-off frequency could significantly impact the high-speed performance. According to the analysis of the laser equivalent electrical circuit, the parasitic cut-off frequency is mainly defined by the parasitic capacitance of the laser, where the main contribution is associated with the oxide-blocking layer region. However, the most common approach to increase the parasitic cut-off frequency by increasing the oxide-confined aperture thickness [6] will lead to an increase in the waveguide effect and an earlier switching to the multimode lasing. So one of the possible solutions is the minimization of the topological sizes of the intra-cavity contacted oxide-confined VCSELs to decrease the oxide region capacitance (see Fig. 5,*b*). The combination of the mentioned approaches made it possible to obtain a modulation bandwidth of more than 5 GHz at relatively low (~1 mA) currents (see Fig. 5,*a*).



Fig. 5. Intra-cavity contacted oxide-confined VCSELs with 2- μ m aperture: modulation bandwidth $f_{-3dB}(\bullet)$ and parasitic cut-off frequency $f_p(\circ)$ as function of current above threshold for 2- μ m oxide-confined VCSELs with different design (*a*); capacitance of the oxide-blocking layer region and the calculated parasitic cut-off frequency (at other fixed elements of the equivalent electrical circuit extracted from S_{11} data for the maximum operation current, when self-heating can be neglected) as function of oxide region area (*b*). The heatsink temperature is 20 °C

Conclusion

In this paper, various features of the VCSEL design that meets the requirements for laser emitters for use in compact atomic sensors were discussed and analyzed. Presented 8XXnm-range intra-cavity contacted VCSEL with the rhomb-shaped oxide-confined aperture simultaneously demonstrated single-mode output optical power above 1 mW, fixed polarization direction, emission linewidth below 50 MHz and modulation bandwidth more than 5 GHz.

REFERENCES

1. Kitching J., Chip-scale atomic devices, Applied Physics Reviews 5 (3) 031302 (2018).

2. Schwindt P.D.D., et al., Chip-scale atomic magnetometer with improved sensitivity by use of the Mx technique, Applied Physics Letters 90 (8) 081102 (2007).

3. Meyer D. et al., Nuclear magnetic resonance gyro for inertial navigation, Gyroscopy Navigation 5 (2) 75 (2014).

4. Knappe S., et al., A microfabricated atomic clock, Applied Physics Letters 85 (9) 1460 (2004).

5. Padullaparthi B.D., Tatum J.A., Iga K., VCSEL industry : communication and sensing, Wiley-IEEE Press, 2021.

6. Michalzik R., VCSELs: Fundamentals, Technology and Applications of Vertical-Cavity Surface-Emitting Lasers, Springer Verlag, 2013.

7. Halbritter H., et al., hirpand linewidth enhancement factor of 1.55µm VCSEL with buried tunnel junction, Electronics Letters 40 (20) 1266 (2004).

8. Shau R., et al., Linewidthof InP-based 1.55 mm VCSELs with buried tunnel junction, Electronics Letters 39 (24) 1728 (2003).

9. Blokhin S.A., et al., The Influence of Cavity Design on the Linewidth of Near-IR Single-Mode Vertical-Cavity Surface-Emitting Lasers, Technical Physics Letters 44 (1) 28 (2018).

10. Choquette K.D., et al., Advances in selective wet oxidation of AlGaAs alloys, Journal of Selected Topics in Quantum Electronics 3 (3) 916 (1997).

11. Blokhin S.A., et al., Vertical-Cavity Surface-Emitting Lasers Based on Sub-Monolayer InGaAs Quantum Dots, Journal of Quantum Electronics 42 (9) 851 (2006).

12. **Bobrov M.A., et al.,** Polarization characteristics of 850-nm vertical-cavity surface-emitting lasers with intracavity contacts and a rhomboidal oxide current aperture, Semiconductors 50 (10), 1390 (2016).

13. Blokhin S.A., et al., Vertical-cavity surface-emitting lasers with intracavty contacts and a rhomboidal current aperture for compact atomic clocks, Quantum Electronics 49 (2) 187 (2019).

THE AUTHORS

BLOKHIN Sergei A. blokh@mail.ioffe.ru ORCID: 0000-0002-5962-5529

KOVACH Yakov N. j-n-kovach@itmo.ru ORCID: 0000-0003-4858-4968

BOBROV Mikhail A. bobrov.mikh@gmail.com ORCID: 0000-0001-7271-5644

BLOKHIN Alexey A. bloalex91@yandex.ru ORCID: 0000-0002-3449-8711

MALEEV Nikolai A. Maleev@beam.ioffe.ru ORCID: 0000-0003-2500-1715

KUZMENKOV Alexander G. Kuzmenkov@mail.ioffe.ru ORCID: 0000-0002-7221-0117 ZADIRANOV Yurii M. zadiranov@mail.ioffe.ru ORCID: 0000-0002-7394-9749

KULAGINA Marina M. Marina.Kulagina@mail.ioffe.ru ORCID: 0000-0002-8721-185X

GUSEVA Yulia A. guseva.ja@gmail.com ORCID: 0000-0002-7035-482X

VASIL'EV Alexey P. vasiljev@mail.ioffe.ru ORCID: 0000-0002-2181-5300

USTINOV Victor M. Vmust@beam.ioffe.ru ORCID: 0000-0002-6401-5522

Received 30.06.2023. Approved after reviewing 11.08.2023. Accepted 15.08.2023.

Conference materials UDC 621.373.826 DOI: https://doi.org/10.18721/JPM.163.203

Laser diode module over 350 W power output with 200 µm/NA 0.22 fiber

A.N. Ignatev[⊠], A.V. Fomin, S.R. Usmanov, E.V. Kadigrob

FSUE "RFNC-VNIITF named after Academ. E. I. Zababakhin", Snezhinsk, Russia

⊠ dep5@vniitf.ru

Abstract: The paper reports the development of the 915 nm laser module (LM) based on high-power single-emitter InGaAs/AlGaAs laser diodes (LDs). The main options to increase the output LM power as compared to the previous sample were considered. The optical system was designed for coupling the beams into a silica-silica fiber with a core of 200 μ m in diameter and a numerical aperture of 0.22. The maximum reached CW output power was 368 W at a nominal current of 22 A and thermal stabilization temperature of 20 °C, the total LM efficiency of 47%.

Keywords: laser module, high-power laser diodes, optical fiber

Citation: Ignatev A.N., Fomin A.V., Usmanov S.R., Kadigrob E.V., Laser diode module over 350 W power output with 200 μ m/NA 0.22 fiber, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 23–27. DOI: https://doi.org/10.18721/JPM.163.203

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.373.826 DOI: https://doi.org/10.18721/JPM.163.203

Лазерный диодный модуль с волоконным выводом излучения мощностью более 350 Вт в 200 мкм волокне с числовой апертурой 0.22

А.Н. Игнатьев[⊠], А В. Фомин, С.Р. Усманов, Е.В. Кадигроб

РФЯЦ-ВНИИТФ им. академика Е.И. Забабахина, г. Снежинск, Россия

^{III} dep5@vniitf.ru

Аннотация. В работе представлены результаты разработки лазерного модуля спектрального диапазона 915 нм на основе мощных одиночных InGaAs/AlGaAs лазерных диодов. Рассмотрены основные пути увеличения выходной мощности ЛМ по сравнению с ранее представленным образцом. Выходная мощность лазерного модуля составила 368 Вт.

Ссылка при цитировании: Игнатьев А.Н., Фомин А.В., Усманов С.Р., Кадигроб Е.В. Лазерный диодный модуль с волоконным выводом излучения мощностью более 350 Вт в 200 мкм волокне с числовой апертурой 0.22 // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 23–27. DOI: https://doi. org/10.18721/JPM.163.203

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

© Ignatev A.N., Fomin A.V., Usmanov S.R., Kadigrob E.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Introduction

As compared to other laser radiation sources the key advantages of high-power laser diodes (LD) are high power, high reliability, and small size [1]. These products based on such LDs include fiber-coupled laser modules (LM). LMs can be used for pumping high-power fiber lasers. Recently, the intense development of laser technologies requires to continuously increase the output power of pumping modules to produce high-power fiber lasers; for this purpose, various LM designs are offered for combining beams from the maximum possible number of LDs involving spatial, polarization, and spectral beam combining [2]. The objective of the present work is to develop and manufacture a high-power 915 nm LM (not less than 350 W) with output silica-silica 200µm/NA 0.22 fiber.

Materials and methods

In [3], an LM is reported with spatial combining of beams from 6 LDs mounted at different heights in the direction of fast axis. The output power for 105 μ m core/NA 0.15 optical fiber was 43.6 W at operating current of 10 A. 975 nm LDs with emitter width of 94 μ m and maximum radiation power of 12 W were used as power sources.

Since the LDs have a good polarization purity (>90%), polarization combining of beams from two symmetrical LD arrays with mutually perpendicular polarization is an efficient and cost-effective technique which is relatively easy in implementation to further increase LM output power [4]. The polarization plane of an LD array was rotated by 90 ° by passing the laser beam through a half-wave plate; subsequent combining of beams from two LD arrays was performed by passing radiation through the polarized beam splitter (Fig. 1). The LM polarization combining design provides nearly double increase in LM power as compared to the design based exclusively on the spatial combining. In addition, since the absorption peak width for alumina-silicate optical fibers doped by ytterbium ions at 915 nm is several times larger than that at 975 nm [5], the developed LM does not require LD wavelength stabilization and use of the volume Bragg gratings which would result in additional losses of laser radiation power, as it was shown in [3].



Fig. 1. LM optical design with LD polarization beam combining: LD *1*; acylindrical micro lenses *2*; cylindrical lenses *3*; rotating mirrors *4*, half-wave plate *5*; mirror *6*; polarized beam splitter (PBS) *7*; focusing lenses *8*, *9*; optical fiber *10*

The obvious option to increase LM power is to use higher-power LDs that have been commercially available in recent years. In particular, the LDs simultaneously satisfying the requirements to high power and reliability include LDs with increased emitter width providing the maximum radiation power of 21 W at operating current of 22 A (Table 1).

According to Table 1, the LD emitter width is 190 μ m that is two times larger than that of the previously used LDs. High efficiency of laser radiation coupling into the optical fiber is determined by the conditions [6]:

$$N_{FA} \cdot d_{FA} \cdot \theta_{FA} \le d_{fb} \cdot NA, \tag{1}$$

© Игнатьев А. Н., Фомин А. В., Усманов С. Р., Кадигроб Е. В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

$$N_{SA} \cdot d_{SA} \cdot \theta_{SA} \le d_{fb} \cdot NA, \tag{2}$$

where N_{FA} , N_{SA} are the numbers of LDs aligned in series in the direction of the fast and slow axes, respectively; d_{FA} , d_{SA} are the LD emitter widths along the fast and slow axes; θ_{FA} , θ_{SA} are the beam divergences along the fast and slow axes; d_{fib} is the optical fiber core diameter; and NA is the fiber numerical aperture.

Eq. (2) shows that in case of twice increased LD emitter width laser radiation can be efficiently coupled into the fiber along the slow axis only with the appropriately increased fiber core diameter or fiber NA. For this purpose, 200 μ m/NA 0.22 fiber was used in the developed LM. Note that the optical fiber with the given parameters allows not only efficient coupling of laser radiation along the slow axis but also significantly increasing the number of LDs aligned in series in the direction of the fast axis. The required LM power was provided by the design with combining of beams from 24 LDs and with spatial combining of beams from 12 LDs mounted at different heights along the fast axis.

Table 1

Parameter	Value
Maximum operating current, A	22
Maximum output power, W (I=22 A)	21
Emitter width, µm	190
Efficiency, %	60
Center wavelength, nm	915±10
Wavelenght shift versus temperature, nm/°C	0.3
Beam divergence (FWHM) along the fast axis, °	29
Beam divergence (FWHM) along the slow axis, °	9

LD parameters

The advantage of using higher-power LDs in the LM design is keeping the minimal size of the developed product. However, keeping the high density of LD packing results in the problem of increasing the efficiency of heat removal from LD since insufficient heat removal can considerably constrain the growth of LM power during operation at maximal or near-maximal operating currents and affect the LM efficiency. The LDs used in the work were soldered to the heat-conducting ceramic substrate using AuSn solder, the substrate was soldered to the copper heat sink using indium solder. In [3], indium foil gaskets were used as a thermal interface material to provide the minimum thermal resistance between surfaces of the enclosure and heat sink with the mounted LDs. In the present work, the following heat-conducting materials were considered when assembling a new LM experimental design: indium foil gaskets with thermal conductivity of 80–90 W/m K, graphite sheet with thermal conductivity of 700 W/m K, and thermal paste with thermal conductivity of 0.65-1 W/m K. Due to its low thermal conductivity, the thermal paste was applied as a thin layer filling the microroughnesses on the heat-exchanging surfaces. Heat removal efficiency was estimated based on the watt-ampere characteristic measurements and dependency of wavelength on operating current at the heat sinks with 6 mounted LDs. During measurements heat sinks were mounted on the copper water-cooled base with thermal stabilization temperature of 20 °C, connected to the water cooling system with flow rate of 7 l/min. Watt-ampere characteristic measurements and dependencies of wavelength on operating current for different thermal interfaces are presented in Fig. 2. For graphite sheet used as a thermal interface material the maximum laser radiation power of 126 W at operating current of 22 A was achieved. For thermal paste and indium foil in similar modes radiation power was 125.2 W and 123.2 W, respectively. The maximal LD radiation wavelengths for graphite sheet and indium foil were 918.4 and 919.7, respectively, which corresponds to the operating temperature difference of ~ 4.3 °C in the LD active area.



Fig. 2. Characteristics of the heat sink with 6 mounted LDs: watt-ampere characteristic (*a*); LD radiation spectrum versus operating current (*b*)

Although no significant difference in laser beam characteristics for graphite sheet and thermal paste was revealed, the use of graphite sheet is more preferable since thermal paste coating of reproducible thickness is a technologically difficult process; besides, thermal paste characteristics can degrade with time.

The loss of LM laser radiation power is mainly caused by the losses on the elements of the optical system the total efficiency of which can be determined by the expression:

$$\eta_{opt} = \eta_{fr} \cdot \eta_{mirr} \cdot \eta_{pol} \cdot \eta_{coupl}, \qquad (3)$$

where η_{opt} is the total efficiency of the optical system; η_{fr} is the coefficient taking into account the reflection loss from the surfaces of the optical elements; η_{mirr} is the coefficient taking into account 'clipping' loss at the rotating mirrors; η_{pol} is the polarization combining efficiency; and η_{coupl} is the efficiency of laser radiation coupling into the fiber. The results of the loss assessment are presented in the following section.

Results and discussion

An additional antireflective coating was deposited onto the fiber's facet to reduce losses in the process of introduction of laser radiation into the fiber. To determine coefficient η_{fr} , technical characteristics of the optical elements used in the design were considered, i.e. reflection coefficients for the reflecting elements and antireflection coating coefficients for the transmissive optics; the value of coefficient η_{fr} was 0.98. The coefficient η_{pol} was determined experimentally by measuring radiation power from both LD arrays before and after the PBS; the value of coefficient η_{pol} was 0.95. To determine the loss coefficient η_{mirr} , LD radiation power was measured before and after the rotating mirrors were mounted; the value of coefficient η_{mirr} was 0.97. To determine coefficient was calculated as a ratio of radiation power at the optical fiber input to the output power; the value of coefficient η_{coupl} was 0.92. The loss at radiation coupling into the fiber could be conditioned by the errors in mounting the optical elements (installation inaccuracy, additional shifting during glue polymerization); the current work has not considered the individual influence of these parameters. The total efficiency of the optical system η_{opt} was 0.83. During the measurements the absence of beams from three LDs was noted that was, probably, due to their failure at the stage of mounting the focusing optics elements. When measuring the optical losses the initial power values for these LDs were not considered.

The maximum reached CW output power of LM was 368 W at nominal current of 22 A and thermal stabilization temperature of 20 °C, the total LM efficiency being of 47%. LM spectral characteristics are shown in (Fig. 3,*b*). The center wavelength at the maximum current was 923.8 nm, the spectrum width was 6 nm, the shift of wavelength versus current was ~ 0.7 nm/A that agrees with the similar values for laser modules of such type. At that, the predicted resulting maximum LM radiation power could achieve a value of 420 W providing that all the LDs operated properly.



Fig. 3. LM optical power and electro-optical efficiency versus drive current (*a*), radiation spectrum versus operating current (*b*)

Conclusion

The paper reports the development of the high-power 915 nm laser module based on the spatial and polarization combining of beams from high-power single-emitter InGaAs/AlGaAs LDs. The main options to obtain the maximum LM efficiency were considered which made it possible to significantly increase the output LM power as compared to the previously reported sample.

REFERENCES

1. Yan Y., Zheng Y., Sun H., Duan J., Review of Issues and Solutions in High-Power Semiconductor Laser Packaging Technology, Frontiers in Physics, Vol. 9, 2021.

2. Yu H., Liu Y., Braglia A., Rossi G., Perrone G., Investigation of collimating and focusing lenses' impact on laser diode stack beam parameter product, Applied Optics, 34 (54) (2015) 10240 10248.

3. **Ignatev A.N., Fomin A.V., Usmanov S.R.,** Wavelength stabilized laser module for high-power fiber laser pumping, St. Petersburg State Polytechnical University Journal: Physics and Mathematics. 3.2 (15) (2022) 190–195.

4. Kruschke B., Fritsche H., Kern H., Hagen T., Pahl U., Koch R., Grohe A., Gries W., Beam Combining Techniques for High-Power High-Brightness Diode Lasers, In: Proc. of SPIE, Vol. 9346, (2015).

5. Kohler B., Brand T., Haag M., Wavelength stabilized high-power diode laser modules, In: Proceedings of SPIE. High-Power Diode Laser Technology and Applications VII, Vol. 7198 (719810) (2009).

6. Karlsen S., Price K., Reynolds M., Brown A., Mehl R., Patterson S., Martinsen R.J., 100-W, 105-μm, 0.15 NA Fiber Coupled Laser Diode Module, In: Proc. of SPIE Photonics West, Vol. (2009) 7198–29.

THE AUTHORS

IGNATEV Andrei N. dep5@vniitf.ru ORCID: 0000-0002-3724-7221 USMANOV Sergei R. dep5@vniitf.ru

FOMIN Alexei V. dep5@vniitf.ru

KADIGROB Ekaterina V. dep5@vniitf.ru

Received 30.06.2023. Approved after reviewing 31.07.2023. Accepted 02.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535.14 DOI: https://doi.org/10.18721/JPM.163.204

Pockels cell performance in N-photon demultiplexer

M.A. Dryazgov¹^[2], Yu.A. Biriukov¹, K.V. Taratorin¹, I.V. Dyakonov¹, A.A. Korneev¹, S.S. Straupe^{1,2}, S.P. Kulik^{1,3}

¹ Quantum Technology Centre, Lomonosov Moscow State University, Moscow, Russia;

² Russian Quantum Center, Skolkovo, Moscow, Russia;

³ South Ural State University, Chelyabinsk, Russia

□ mdryazgov@hse.ru

Abstract. We investigate the efficiency of a loop scheme for the spatial demultiplexing of N successive photons using only one Pockels cell at the center of the loop scheme. The maximum operating frequency of the Pockels cell, due to technical limitations, is 13.5 MHz. We experimentally find the maximum achievable demultiplexing efficiency with a single Pockels cell using continuous-wave and pulsed lasers and analog fast photodetectors. The maximum efficiency achieved at the maximum switching frequency is 87%.

Keywords: photons demultiplexing, single-photon source, Pockels cell

Funding: This study was funded by Russian Science Foundation (RSF) Grant 22-12-00353.

Citation: Dryazgov M.A., Biriukov Yu.A., Taratorin K.V., Dyakonov I.V., Korneev A.A., Straupe S.S., Kulik S.P., Pockels cell performance in N-photon demultiplexer, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 28–32. DOI: https://doi.org/10.18721/JPM.163.204

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.14 DOI: https://doi.org/10.18721/JPM.163.204

Эффективность ячейки Поккельса для N-фотонного демультиплексора

М.А. Дрязгов¹[⊠], Ю.А. Бирюков¹, К.В. Тараторин¹, И. В. Дьяконов¹, А.А. Корнеев¹, С.С. Страупе^{1,2}, С.П. Кулик^{1,3}

¹ Центр квантовых технологий, Московский государственный университет имени М. В. Ломоносова, Москва, Россия;

² Российский Квантовый Центр, Сколково, Москва, Россия;

³ Южно-Уральский Государственный Университет, г. Челябинск, Россия

[™] mdryazgov@hse.ru

Аннотация. Мы исследуем эффективность петлевой схемы пространственного демультиплексирования N последовательных фотонов с использованием только одной ячейки Поккельса в центре петлевой схемы. Максимальная частоты работы ячейки Поккельса, обусловленная техническими ограничениями, составляет 13.5 МГц. Мы экспериментально находим максимально достижимую эффективность демультиплексирования с помощью одной ячейки Поккельса с помощью непрерывного и импульсного лазеров и аналоговых быстрых фотодетекторов. Максимальная эффективность, достигнутая при максимальной частоте переключения, составляет 87%.

© Dryazgov M.A., Biriukov Yu.A., Taratorin K.V., Dyakonov I.V., Korneev A.A., Straupe S.S., Kulik S.P., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: демультиплексирование фотонов, источник одиночных фотонов, ячейка Поккельса_

Финансирование: Работа выполнена при поддержке Российского Научного Фонда (РНФ) грант № 22-12-00353.

Ссылка при цитировании: Дрязгов М.А., Бирюков Ю.А., Тараторин К.В., Дьяконов И.В., Корнеев А.А., Страупе С.С., Кулик С.П. Эффективность ячейки Поккельса для N-фотонного демультиплексора // Научно-технические ведомости СПбГПУ. Физикоматематические науки. 2023. Т. 16. № 3.2. С. 28–32. DOI: https://doi.org/10.18721/ JPM.163.204

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Applied tasks of quantum optics, such as boson sampling, require operations on several photons [1]. However, the most common sources of single indistinguishable photons, such as quantum dots, generate one photon per pump pulse [2–4]. This leads to the need to use demultiplexing, that is, the separation of photon sequence into channels for operations on them [5]. The most effective way of demultiplexing is the use of a Pockels Cells (PC). PC changes the polarization of photons to orthogonal, which makes it possible to separate them using Polarization Beam Splitters (PBS). The downside of this scheme is the need to use N-1 PC for demultiplexing N photons [6–7].

We are studying a scheme [8] where linear optics elements are used for the spatial separation of photons, and only one PC is required to demultiplex N photons. The principle of operation of the PC at its maximum switching frequency is considered. The maximum efficiency of the PC for demultiplexing N photons is experimentally determined using a pulsed laser and fast analog detectors.

Principal scheme

Photons from a single-photon source of indistinguishable photons fall into a spatial loop formed by two mirrors and a triangular prism. Photons pass between two mirrors, through an inactive PC, through a PBS and hit a triangular prism. The triangular prism makes it possible to reflect photons with a spatial shift so that during the return flight they are reflected from the mirrors. Each flight around the loop spatially shifts the photons, which ultimately allows them to be led into separate channels. The total number of photons in the loop depends on the geometric dimensions of the mirrors, the prism, and the aperture of the Pockels cell.

The length of the loop L_{loop} is chosen in such a way that the next photon from the source with the pumping frequency f_{pump} falls into it when the previous one has passed a full circle. When a sufficient number of photons are accumulated in the loop, the PC is activated, the photon polarization changes to orthogonal, and they are deflected by the PBS and exit the loop. The optical scheme on the example of 3 photons is shown in Fig. 1. The output channels of the multiplexer are numbered starting from the central one, the photons from which did not pass through the loop and immediately fell on the PBS.

The described scheme is easily scaled to a larger number of photons, provided that the geometric dimensions of the reflectors and PBS are increased. The assembly and measurement of the characteristics of the described demultiplexer working with single unresolvable photons from a quantum dot are described in detail in [8].

Pockels Cell operating mode

The Pockels Cell (Leysop) is controlled by four keys with high voltage driver (BME Bergmann). The change in the polarization of the transmitted radiation occurs only at the moments when A_{on} is on and B_{off} is off, or A_{off} is on and B_{off} is off. Fig. 2, *a* shows the smallest possible switching period of the Pockels cell, declared by the manufacturer.

© Дрязгов М.А., Бирюков Ю.А., Тараторин К.В., Дьяконов И.В., Корнеев А.А., Страупе С.С., Кулик С.П., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Principal scheme of the spatial demultiplexer for 3 photons



Fig. 2. Voltage on the keys of the PC(a) and CW-laser radiation in and out of the optical loop (*b*) per time

It can be seen that at the limiting switching frequency, the time windows of the polarization rotation change periodically – each second switching is bit longer in time. When using a continuous-wave laser, the detected difference is more clearly visible as shown in Fig. 2,*b*. The output power of the CW laser varied from 350 μ W to 0.3 μ W, which was at the sensitivity limit of the analog detector. No effect of the radiation power on the width of the exit time windows from the optical loop was found. This can be explained by the fact that for the manifestation of negative nonlinear effects of the Pockels cell crystal, the radiation power must be much higher.

The difference in the duration of the time windows means that in the case of single photons, the probability of losing every second photon increases. The observed effect can be explained by the maximum possible frequency of operation of the PC. By carefully selecting the delay between the switching period of the Pockels cell and the laser synchronization pulse, it is possible to reduce this effect.

Intensity in the channels of the demultiplexer

A pulsed laser with a pulse frequency of 82.6 MHz was used to obtain the dependences of the intensity on time in the output channels of the demultiplexer. The laser wavelength of 918.83 nm coincides with the wavelength of single photons from the quantum dot intended for

use, the output power of the pulsed laser was 1 μ W. The Pockels cell rotated the polarization of pulses with a period of 72.5 ns, due to technical limitations. Fast analog semiconductor detectors were used to measure the signal.

The obtained radiation intensities for 3 output channels of the demultiplexer are shown in Fig. 3, a-c). It should be noted that despite the alignment of the period of operation of the cell with the laser synchronization pulse, each second peak has a lower amplitude. This means that even when using 6 channels (for period of PC 72 ns and period photons 12 ns used in described scheme), when all photons from the loop are spatially separated into channels, the maximum efficiency will be less than 100%.

The amplitudes of the voltage peak from the analog detector is directly proportional to the radiation power in the optical pulse and depends linearly on it. Assuming that if all the peaks were the same size, then the demultiplexing efficiency would be 100%, was the demultiplexing efficiency obtained as the ratio of the sum of the average amplitudes of the large and small peaks to the two average amplitudes of the large peak. The resulting demultiplexing efficiency with a single PC is $87\pm3\%$.

It is also worth noting the increase in the amplitude of side peaks, especially noticeable for channel 3 in Fig. 3,c, which is farthest from the main optical axis. They are associated with the spatial distance of the photon trajectory from the center of the nonlinear crystal inside the PC. This leads to a rotation of the polarization through small angles when the PC is turned off. This problem can be overcome by using a Pockels cell with a larger entrance aperture or by using lenses with a longer focal length to form a 1:1 telescope.



Fig. 3. Intensity at the output of the loop in the 1st (*a*), 2^{nd} (*b*) and 3^{rd} (*c*) channel of the demultiplexer

Conclusion

For the described spatial demultiplexing scheme with only one Pockels cell, the operation of the PC at the limiting switching frequency leads to optical losses. The maximum efficiency achieved by an accurate selection of the time delay between the switching period of the cell and the laser synchronization pulse is 87%. When increasing the number of channels of the demultiplexer, it is necessary, in addition to the geometric dimensions, to consider parasitic polarization rotations that occur when the photon trajectory in the loop moves away from the geometric center of the nonlinear crystal.

Acknowledgments

The authors thank F. Bergmann for providing consulting assistance regarding the high-voltage Pockels cell driver, and for helping to solve problems that arose during the work.

REFERENCES

1. Wang H., He Yu., Li Yu. -H., Su Z.-E., Li B., Huang H.-L., Ding X., Chen M.-Ch., Liu Ch., Qin J., Li J.-P., He Yu. -M., Schneider Ch., Kamp M., Peng Ch.-Z., Höfling S., Lu Ch.-Y., Pan J.-W., High-efficiency multiphoton boson sampling, Nature Photon 11 (2017) 361–365.

2. Cirlin G.E., Reznik R.R., Shtrom I.V., Khrebtov A.I., Samsonenko Yu.B., Kukushkin S.A., Kasama T., Akopian N., Leonardo L., Hybrid GaAs/AlGaAs Nanowire—Quantum dot System for Single Photon Sources, Semiconductors, 52 (2018) 462–464.

3. Schöll E., Hanschke L., Schweickert L., Zeuner K.D., Reindl M., Covre da Silva S.F., Lettner T., Trotta R., Finley J.J., Müller K., Rastelli A., Zwiller V., Jöns K.D., Resonance Fluorescence of GaAs Quantum Dots with Near-Unity Photon Indistinguishability, Nano Letter, 19(4) (2019) 2404–2410.

4. Helene O., Maillette I., Thomas S., Wein S., Harouri A., Coppola G., Hilaire P., Millet C., Lemaotre A., Sagnes I., Krebs O., Lanco L., Loredo J., Antyn C., Somaschi N., Senellart P., Reproducibility of High-Performance Quantum Dot Single-Photon Sources, ACS Photonics 7(4) (2020) 1050–1059.

5. Münzberg J., Draxl F., Filipe S., Karli Yu., Manna S., Rastelli A., Weihs G., Keil R., Fast and efficient demultiplexing of single photons from a quantum dot with resonantly enhanced electro-optic modulators, APL Photonics, 7(7) (2022) 070802.

6. Rakhlin M.V., Galimov A.I., Dyakonov I.V., Skryabin N.N., Klimko G.V., Kulagina M.M., Zadiranov Yu.M., Sorokin S.V., Sedova I.V., Guseva Yu.A., Berezina D.S., Serov Yu.M., Maleev N.A., Kuzmenkov A.G., Troshkov S.I., Taratorin K.V., Skalkin A.K., Straupe S.S., Kulik S.P., Shubina T.V., Toropov A.A., Demultiplexed single-photon source with a quantum dot coupled to microresonator, Journal of Luminescence, 253 (2023) 119496,

7. Hummel T., Ouellet-Plamondon C., Ugur E., Kulkova I., Lund-Hansen T., Broome M., Uppu R., Lodahl P., Efficient demultiplexed single-photon source with a quantum dot coupled to a nanophotonic waveguide, Applied Physics Letters, 115(2) (2019) 021102.

8. Dryazgov M.A., Biriukov Yu.A., Dyakonov I.V., Taratorin K.V., Korneev A.A., Rakhlin M.V., Galimov A.I., Klimko G.V., Sorokin S.V., Kulagina M.M., Zadiranov Yu.M., Toropov A. A., Bergmann F., Straupe S. S., Kulik S. P., Resource-efficient low-loss four-channel active demultiplexer for single photons, (2023) arXiv:2304.09622.

THE AUTHORS

DRYAZGOV Mikhail A. mdryazgov@hse.ru ORCID: 0000-0002-6280-4667

BIRUKOV Yury A. biriukov.ia18@physics.msu.ru ORCID: 0009-0007-1064-1564

TARATORIN Konstantin V. konstv1@yandex.ru ORCID: 0009-0009-2802-8308 DYAKONOV Ivan V. iv.dyakonov@physics.msu.ru ORCID: 0000-0002-1931-2173

KORNEEV Alexander A. alex.korneev78@gmail.com ORCID: 0000-0002-0116-9591

STRAUPE Stanislav S. straups@yandex.ru ORCID: 0000-0001-9810-1958

Received 24.07.2023. Approved after reviewing 31.07.2023. Accepted 01.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535.42 DOI: https://doi.org/10.18721/JPM.163.205

A new method for calculating spectral diffractive lenses for focusing laser radiation of various wave lengths

S.A. Goranskaia¹⊠

¹ Saint Petersburg State University of Telecommunications named after prof. M.A. Bonch-Bruevich, St. Petersburg, Russia

[⊠] svetlancho.zueva@yandex.ru

Abstract. The necessity of developing a new methodology for calculating diffractive spectral lenses for optical systems with variable wavelength laser radiation is substantiated. The method for calculating spectral diffraction lenses for focusing radiation of different wavelengths at specified focal points has been developed. The method for calculating cascade metal-dielectric layered structures for optical filtering has been developed, and a method for obtaining neural network descriptors applicable to the analysis of hyperspectral data has been developed. Calculation examples for various designs of optical diffractive lenses are presented. The optimal parameters for the designs of diffractive lenses are established.

Keywords: Spectral diffraction lenses, focus, focal plane, efficiency assessment, microrelief of spectral diffraction lenses

Citation: Goranskaia S.A., A new method for calculating spectral diffractive lenses for focusing laser radiation of various wave lengths, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 33–38. DOI: https://doi.org/10.18721/JPM.163.205

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.42 DOI: https://doi.org/10.18721/JPM.163.205

Новая методика расчета спектральных дифракционных линз для фокусировки лазерного излучения различных длин волн

С.А. Горанская¹⊠

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М. А. Бонч-Бруевича, Санкт-Петербург, Россия

[⊠] svetlancho.zueva@yandex.ru

Аннотация. Разработан метод расчета спектральных дифракционных линз для фокусировки излучения разных длин волн в заданных точках фокуса. Разработан метод расчета каскадных металлодиэлектрических слоистых структур для оптической фильтрации, а также метод получения нейросетевых дескрипторов, применимых для анализа гиперспектральных данных. Представлены примеры расчета для различных конструкций оптических дифракционных линз. Установлены оптимальные параметры для конструкций дифракционных линз.

Ключевые слова: спектральные дифракционные линзы, фокус, фокальная плоскость, длина волны, оценка эффективности, микрорельеф спектральных дифракционных линз

© Goranskaia S.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Горанская С.А. Новая методика расчета спектральных дифракционных линз для фокусировки лазерного излучения различных длин волн // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 33–38. DOI: https://doi.org/10.18721/JPM.163.205

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Various models of refractive lenses are actively being used in modern optical devices [1-7]. The increasing demand for precise measurements of various parameters using optical devices, such as night vision devices or refractometers, has led to several challenges [6-12]. Refractive lenses that focus incident radiation often suffer from a significant drawback – dispersion of focal length for different wavelengths of the incident radiation. Consequently, their usage is limited to only one radiation wavelength, especially when dealing with lasers [12-14].

Another drawback that restricts their use in compact optical systems is their thickness. To overcome this limitation, diffractive lenses (DL) are employed. These lenses have a diffraction relief thickness comparable to the incident wavelength of the radiation. They find application in the development of compact imaging systems for mobile devices and unmanned aerial vehicles, particularly when multiple wavelengths are emitted simultaneously – spectral diffractive lenses (SDLs).

One well-known type of diffraction lens operating at multiple wavelengths is the harmonic diffraction lens (HDL), which possesses m times higher diffraction microrelief and allows focusing several different wavelengths into the same focus using different orders of diffraction [13, 15–17]. However, the operating wavelengths of the SDL cannot be arbitrarily chosen; they must satisfy an analytical relation depending on m and the 'main' operating wavelength.

Calculation Method of the SDL for Focusing Radiation of Different Wavelengths. The calculation of the SDL is performed independently for each point using the formula:

$$h_{j} = h_{\max} \frac{q_{j}}{Q}, \ q_{j} = \underset{q \in \{0, \dots, Q^{-1}\}}{\operatorname{argmin}} \left[\sum_{l=1}^{L} w_{l} \left| T_{sl} \left(h_{\max} \frac{q}{Q}; \lambda_{l} \right) - T_{l} \left(u_{j}; \lambda_{l}, x_{l} \right) \right|^{2} \right].$$
(1)

The calculation of microrelief height at each point by full brute force is simple from the computational point of view, as it corresponds to the calculation of Q weighted sums L of differences of two exponents. In a particular case, the coordinates of the focal points may coincide: $x_i = (x_0, y_0), l = 1,..., L$. In this case, this method of calculating the SDL results in an 'achromatic' SDL, focusing radiation of different wavelengths to the same fixed point. This approach is most rational for short-focus lenses, which are used in fiber systems, optical fibers, optical correlators, and near-IR photodetectors. Works [18–21] utilize a zone approach to image formation at different wavelengths, which is more optimal for lenses with long and medium focus, used to solve different problems than those considered in my work.

Modified Infrared Slope Index

To evaluate the effectiveness of this method, we calculated the SDL focusing two wavelengths $\lambda_1 = 455$ nm and $\lambda_1 = 750$ nm into two points in the plane z = f = 750 mm at the coordinates $x_1 = (-x_1, 0)$ and $x_2 = (x_1, 0)$ where $x_1 = 0.266$ nm. The selected wavelengths are used to calculate a modified infrared slope index employed in smart agriculture for monitoring forests and identifying anomalies in the state of the vegetation cover. The SDL is located in the plane of the z = 0 and has an aperture radius R = 2 mm, maximum height of the microrelief $h_{max} = 4 \mu m$, number of quantization levels Q = 256.

The relief of the SDL, calculated using formula (1) for the selected parameters, is shown in Fig. 1. When calculating the value of microrelief height h_j are defined in the nodes $u_j = (u_j, v_j)$ of a square grid with a step $\Delta = 2 \ \mu m$.

[©] Горанская С. А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig.1. Microrelief of the SDL focusing wavelengths $\lambda_1 = 455$ nm and $\lambda_2 = 750$ nm at two points

To assess the efficiency of the SDL, we calculated the intensity distributions formed by the lens using the two-dimensional Fresnel-Kirchhoff integral:

$$I(x_{j}\lambda_{1}) = \left|w(x;\lambda_{l})\right|^{2} = \left|\frac{1}{\lambda_{l}f}\iint_{G}T_{Sl}(u;\lambda_{l})\exp\left\{i\frac{\pi}{\lambda_{l}f}(x-u)^{2}\right\}d^{2}u\right|^{2},$$
(2)

where $T_{SI}(u;\lambda_i)$ is the complex transmittance function of the SDL, h(u), $u \in G$ is the microrelief of the SDL presented in Fig. 1.

It should be noted that the works [18–21] use other integrals for calculation of $I(x_j;\lambda_1)$. Fig. 2, *a* shows the calculated distributions $I_{\text{norm}}(x;\lambda_1) = I(x;\lambda_1)/I_{id}(x_1;\lambda_1)$, normalized to the 'ideal' intensities in focus:

$$I_{i}(x_{l};\lambda_{l}) = \left|\frac{\pi R^{2}}{\lambda_{l}f}\right|^{2},$$
(3)

obtained by substituting the complex transmittance functions of the lenses $T_i(u;\lambda_i,x_i)$ in formula (2) instead of the functions $T_{s_i}(u;\lambda_i)$.

Fig. 2, b shows sections of two-dimensional distributions along the x-axis.



Fig. 2. Normalized two-dimensional intensity distributions formed by the calculated SDL at operating wavelengths λ_1 =455 nm (the top) and λ_1 =750 nm (the lower) (*a*); sections of normalized intensity distributions along the *x*-axis for wavelengths λ_1 , $\lambda_1 \pm 10$ nm and λ_2 , $\lambda_2 \pm 10$ nm (*b*)

Water index

Focusing radiation of two relatively close wavelengths $\lambda_1 = 900$ nm and $\lambda_2 = 970$ nm at two points $x_1 = (-x,0)$, $x_2 = (x_1,0)$, where $x_1 = 0.17$ mm, located in the plane z = f = 35 mm. The selected wavelengths are used to calculate the water index, which estimates changes in the water content of the vegetation cover [5]. The microrelief of the SDL is calculated using the formula (1), as shown in Fig. 3.



Fig. 3. Microrelief of the SDL, focusing wavelength $\lambda_1 = 900$ nm and $\lambda_2 = 970$ nm at two points

Fig. 4,*a* shows the normalized distributions $I_{\text{norm}}(x; \lambda_l) = I(x; \lambda_l)/I_{id}(x_l; \lambda_l)$, calculated in a rectangular area with cross-sectional dimension $\Delta_{y} = 3\lambda_{2}f/R \approx 50 \,\mu\text{m}$. These distributions show that the calculated SDL focuses the radiation of the two working wavelengths to specified points. Fig. 4,*b* shows the distributions along the *x*-axis calculated at wavelengths 890 nm, 910 nm, 960 nm and 980 nm, that differ from the calculated values by ± 10 nm. In this example, the operating wavelengths differ by 7.2%. The successful separation of such closely spaced wavelengths using a relatively low diffraction micro-relief with $h_{max} = 4 \,\mu\text{m}$ is an important result.



Fig. 4. Normalized two-dimensional intensity distributions formed by the calculated SDL at operating wavelengths $\lambda_1 = 900$ nm (the top) and $\lambda_2 = 970$ nm (the lower) (*a*); sections of normalized intensity distributions along the *x*-axis for wavelengths λ_1 , $\lambda_1 \pm 10$ nm and λ_2 , $\lambda_2 \pm 10$ nm (*b*)

Infrared and water indices

In this calculation, four wavelengths were chosen $\lambda_1 = 900$ nm, $\lambda_2 = 455$ nm, $\lambda_3 = 750$ nm and $\lambda_4 = 970$ nm to four points $x_1 = (-x_1,0)$, $x_2 = (-x_2,0)$, $x_3 = (x_2,0)$, $x_4 = (x_1,0)$, where $x_1 = 0.2$ mm, $x_2 = 0.1$ mm, located in the plane z = f = 35. This SDL can be used to simultaneously obtain information about two vegetation indices, with an aperture radius of R = 2 mm, maximum height of microrelief $h_{max} = 6 \mu m$, number of quantization levels Q = 256. The relief of the SDL calculated by the formula (1) is shown in Fig. 5.


Fig. 5. Microrelief of the SDL focusing wavelengths $\lambda_1 = 900$ nm, $\lambda_2 = 455$ nm, $\lambda_3 = 750$ nm and $\lambda_4 = 970$ nm at four points

Fig. 6, *b* shows cross sections of two-dimensional distributions along the *x*-axis. The maximum values are $0.48I_{id}(x_i;\lambda_1)$, $0.51I_{id}(x_2;\lambda_2)$, $0.56I_{id}(x_3;\lambda_3)$ and $0.47I_{id}(x_4;\lambda_4)$. The width of the focal peaks coincides with the diameter of the diffraction spots with high precision $D_i = 1.22 \lambda_i f/R$ 'ideal' diffraction lenses. Fig. 6, *b* shows that when the wavelength deviates from one of the calculated values by ± 10 nm, there is a significant decrease in the amplitude of the generated intensity distribution (the existing maximum normalized intensities do not exceed 0.025).



Fig. 6. Normalized two-dimensional intensity distributions formed by the calculated SDL at operating wavelengths $\lambda_1 = 900$ nm (top distribution), $\lambda_2 = 455$ nm (second distribution from the top), $\lambda_3 = 750$ nm (third from the top distribution) and $\lambda_4 = 970$ nm (lower distribution) (*a*); sections of normalized intensity distributions along the *x*-axis for wavelengths λ_1 , $\lambda_1 \pm 10$ nm, λ_2 , $\lambda_2 \pm 10$ nm, λ_3 , $\lambda_3 = 10$ nm and λ_4 , $\lambda_4 \pm 10$ nm (*b*)

Conclusion

An analysis of the obtained data shows that the calculated spectral lenses indeed focus the radiation of the operating wavelengths to the specified points, and the widths of the focal peaks coincide with high accuracy with the diameters of diffraction spots of 'ideal' diffractive lenses. This confirms the high efficiency of the developed calculation method. Additionally, the developed technique allows for the reduction of the dimensions of diffractive lenses, which is extremely important when using them in small-sized devices.

REFERENCES

1. Semenov V.V., Nikiforov N.F., Ermak S.V., Calculation of stationary magnetic resonance signal in optically oriented atoms induced by a sequence of radio pulses, Soviet journal of Communications Technology and Electronics. 36(4) (1991) 59–63.

2. Kuzmin M.S., Rogov S.A., On the use of a multi-raster input of one-dimensional signals in twodimensional optical correlators, Computer Optics. 43(3) (2019) 391–396. 3. Davydov V.V., Davydova T.I., A nondestructive method for express testing of condensed media in ecological monitoring, Russian Journal of Nondestructive Testing. 53(7) (2017) 520–529.

4. **Petrov A.A.**, Digital Frequency Synthesizer for 133Cs-Vapor Atomic Clock, Journal of Communications Technology and Electronics. 62(3) (2017) 289–293.

5. Myazin N.S., Smirnov K.J., Spectral characteristics of InP photocathode with a surface grid electrode, Journal of Physics: Conference Series. 929(1) (2017) 012080.

6. Logunov S.E., Vysoczky M.G., New method of researches of the magnetic fields force lines structure, Journal of Physics: Conference Series. 1038(1) (2018) 012093.

7. Kuzmin M.S., Rogov S.A., Experimental study of a joint-transform correlator, Quantum Electronics. 48(11) (2018) 1048–1054.

8. Smirnov K.J., Glagolev S.F., Tushavin G.V., High speed near-infrared range sensor based on InP/ InGaAs heterostructures, Journal of Physics: Conference Series. 1124(2) (2018) 022014.

9. Grebenikova N.M., Smirnov K.J., Rud V.Yu., Artemiev V.V., Features of monitoring the state of the liquid medium by refractometer, Journal of Physics: Conference Series. 1135(1) (2018) 012055.

10. Davydov V.V., Kruzhalov S.V., Method for Determining Defects on the Inner Walls of Tubing from the Velocity Distribution of the Flowing Fluid, Measurement Techniques. 61(4) (2018) 365–372.

11. Mazing M.S., Zaitceva A.Y., Kislyakov Y.Y., Kondakov N.S., Avdyushenko S.A., Analytical complex for study of the oxygen status of tissues of the human organism, Journal of Physics: Conference Series. 1695(1) (2020) 012065.

12. Davydov V., Gureeva I., Davydov R., Dudkin V., Flowing Refractometer for Feed Water State Control in the Second Loop of Nuclear Reactor. Energies. 15(2) (2022) 457.

13. Sweeney D.W., Sommargren G.E., Harmonic diffractive lenses. Applied Optics. 34(14) (1995) 2469–2475.

14. **Davydov V.V., Kruzhalov S.V., Vologdin V.A.,** Concerning some features of studying the flow of liquid media by a Doppler method, Journal of Optical Technology (A Translation of Opticheskii Zhurnal). 84(8) (2017) 568–573.

15. Rossi M., Kunz R. E., Herzig H.P., Refractive and diffractive properties of planar micro-optical elements. Vol. 34, Applied Optics. 34(26) (1995) 5996–6007.

16. Faklis D., Morris G.M., Spectral properties of multiorder diffractive lenses. Applied Optics. 34(14) (1995) 2462–2468.

17. Bannari A., Morin D., Bonn F., Huete A.R., A review of vegetation indices. Vol. 13, Remote Sensing Reviews. 13 (1995) 95–120.

18. Byzov E.V., Doskolovich L.L, Kravchenko S.V., Moiseev M.A., Kazanskiy N.L., Design of optical elements for an extended light source. Computer Optics, 2023, 47(1) 40–47.

19. Doskolovich L.L., Mingazov A.A., Byzov E.V., Bykov D.A., Bezus E.A., Method for calculating the eikonal function and its application to design of diffractive optical elements for optical beam shaping. Computer Optics, 2022, 46(2) 173–183.

20. Blank V., Skidanov R, Doskolovich L., Kazanskiy N., Spectral diffractive lenses for measuring a modified red edge simple ratio index and a water band index. Sensors, 2021, 21(22), 7694.

21. Bezus E.A., Bykov D.A., Doskolovich L.L., Integrated Gires-Tournois interferometers based on evanescently coupled ridge resonators. Optics Letters, 2020, 45(18) 5065–5068.

THE AUTHOR

GORANSKAIA Svetlana A. svetlancho.zueva@yandex.ru ORCID: 0009-0004-3728-9837

Received 01.07.2023. Approved after reviewing 24.07.2023. Accepted 26.07.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 53.082.5 DOI: https://doi.org/10.18721/JPM.163.206

Application of lasers of metrological appropriation as working standards

Yu.G. Zacharenko¹, N.A. Kononova¹, A.D. Kurkova^{1,2}, E.I. Logvinuk¹, Z.V. Fomkina¹

¹D.I. Mendeleyev Institute for Metrology (VNIIM), St. Petersburg, Russia;

² Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

⊠ kurkova.ad@edu.spbstu.ru

Abstract. Today laser measuring systems and sets, interferometers and other measuring units, which principle of operation is based on the use of stabilized laser radiation sources, are actively used to solve urgent problems in metrological laboratories of advanced enterprises of various industries and in leading scientific institutes. This article discusses the research results of a number of stabilized radiation sources with the aim of using them as working standards. The research was carried out on the basis of the D.I. Mendeleyev Institute for Metrology (next VNIIM).

Keywords: laser, measuring instrument, State Primary Standard of the unit of length, working standard

Citation: Zacharenko Yu.G., Kononova N.A., Kurkova A.D., Logvinuk E.I., Fomkina Z.V., Lasers of metrological appropriation, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 39–43. DOI: https://doi.org/10.18721/JPM.163.206

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.082.5 DOI: https://doi.org/10.18721/JPM.163.206

Применение лазеров метрологического назначения в качестве рабочих эталонов

Ю.Г. Захаренко¹, Н.А. Кононова¹, А.Д. Куркова^{1,2}, Е.И. Логвинюк¹, З.В. Фомкина¹

¹ ФГУП ВНИИМ им. Д.И. Менделеева, Санкт-Петербург, Россия;

² Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

⊠ kurkova.ad@edu.spbstu.ru

Аннотация. В настоящее время лазерные измерительные системы и установки, интерферометры и другие измерительные устройства, принцип работы которых основан на использовании стабилизированных источников лазерного излучения, активно используются для решения актуальных задач в метрологических лабораториях передовых предприятий различных отраслей промышленности и в ведущих научных институтах. В данной статье рассмотрены результаты исследований ряда стабилизированных источников излучения с целью применения их в качестве рабочих эталонов. Исследования проводились на базе Федерального государственного унитарного предприятия «Всероссийский научно-исследовательский институт метрологии им. Д. И. Менделеева» (далее ВНИИМ).

© Zacharenko Yu.G., Kononova N.A., Kurkova A.D., Logvinuk E.I., Fomkina Z.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: лазер, средство измерения, государственный первичный эталон единицы длины, рабочий эталон

Ссылка при цитировании: Захаренко Ю.Г., Кононова Н.А., Куркова А.Д., Логвинюк Е.И., Фомкина З.В. Лазеры метрологического назначения // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 39–43. DOI: https://doi. org/10.18721/JPM.163.206

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

With the advent of the first laser in the middle of the 20th century, the rapid development of laser technology immediately began, which continues to this day. The laser does not cease to conquer new areas of applications due to its properties and characteristics, it becomes a reliable assistant to doctors, builders, archaeologists, criminologists, etc.

Now lasers are successfully used in modern industry, helping to solve a wide variety of tasks. Lasers are also widely used in metrology. As working measuring instruments, the metrological services of most manufacturing enterprises use laser-based measuring instruments, such as linear displacement sensors, distance measuring equipment, laser systems for shaft alignment, and others, to control their products. The assortment of laser-based measuring instruments are constantly expanding, newly developed measuring equipment are appearing, already available on the market measuring instruments are improving, their accuracy is increasing. Along with unstabilized laser radiation sources, in modern high-precision measuring equipment stabilized lasers are used. The principle of operation of such modern high-precision measuring systems as interferometers, lasers trackers, scanners, total stations, etc. is based on the use of stabilized laser radiation sources. Being the most accurate and capable of solving many technical problems, measuring instruments based on stabilized lasers occupy an important place in the technical control services of products and services and successfully replace the traditional measuring instrument [1].

Stabilized laser radiation sources are successfully used to realize, store and transfer of the unit of length all over the world. Stabilized lasers and systems based on them are successfully used for transfer the unit of length both as independent measuring instruments and as a part of various measuring equipment and systems. This article is devoted to the study of the metrological characteristics of stabilized laser radiation sources with the aim of using them as working standards of 1st and 2nd echelons in accordance with the State verification schedule for measuring instruments of length in the range from $1 \cdot 10^{-9}$ to 100 m and wavelengths in the range from 0.2 to 50 microns, approved by Order No. 2840 of December 29, 2018 of the Federal Technical Regulation and Metrology Agency.

In accordance with the Recommendation of the International Bureau of Weights and Measures (next BIPM), leading scientific metrological institutes of the world use in national standards stabilized laser radiation sources. In Russia the realization of the unit of length is by two He-Ne/ I_2 and one Nd:YAG lasers from the State Primary Standard of the Unit of Length – metre GET 2-2021 (next GET 2). GET 2 provides realization of the unit of length at the wavelength of 0.633 µm with the standard deviation – $1.6 \cdot 10^{-12}$, and $1.3 \cdot 10^{-12}$ at 0.532 µm. GET 2-2021 also includes the set for measuring the frequency difference of laser radiation sources, the complex of equipment for measuring a frequency of lasers in the wavelength range from 500 to 1050 nm (optical frequency comb) with the hydrogen standard of frequency and four linear laser interferometers in the range from $1 \cdot 10^{-9}$ to 30 m, the basis of the measuring system of which are also frequency stabilized lasers [2, 3].

Stabilized laser radiation sources used for realization of the unit of length are developed directly by national metrological institutes or other scientific organizations. Today a serial production of frequency-stabilized lasers of such precision is carried out only by Winters Electro-Optics, Inc. (USA). In accordance with the Recommendation of the BIPM, the absolute frequency accuracy of such lasers is less than $2.5 \cdot 10^{-11}$ [4].

[©] Захаренко Ю.Г., Кононова Н.А., Куркова А.Д., Логвинюк Е.И., Фомкина З.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The metre as one of the seven basic units of the International System of Units is included in a number of derived units, so the realization of many derived units is impossible without the use of equipment of storing and transferring of the unit of length. In the Russia, stabilized laser radiation sources are a part of a number of such State Primary standards as the State Primary Standard of the Flat Angle Unit GET 22-2014, the State Primary Standard of the Unit of the Temperature Coefficient of Linear Expansion of Solids GET 24-2018, the State Primary Standard of the Unit of Pressure GET 101-2011, etc.

To store and transfer of the unit of length to frequency-stabilized lasers, wavelength meters, etc., stabilized laser radiation sources in the range from 0.4 to 11 microns are used as secondary standards. Stabilized laser radiation sources are also as a part of sets for calibration of linescales and gauge blocks are used as secondary standards, and as a part of laser displacement meters in the range from 10^{-9} to 10^{-2} m for transferring the unit of length to laser interferometers and laser displacement meters. The main manufacturers of such lasers today are JSC Plasma (Russia), Meßtechnik GmbH (Germany), Thorlabs Inc. (USA). The absolute frequency accuracy of such lasers is near $10\cdot2^{-8}$.

Stabilized lasers are a part of modern high-precision measuring equipment, such as laser measuring systems, mobile coordinate measuring machines (trackers), laser interferometers and others. The operating principle of such measuring equipment is based on the method of laser interferometry, which is one of the most highly accurate method of transferring of the unit of length. Laser measuring systems are widely used to solve a variety of scientific and technical problems in the most important sectors of the national industry. Laser measuring systems of the following manufacturers are mostly used: Renishaw PLC (Great Britain), Automated Precision Inc. (USA), Chotest Technology Inc. (China) [5].

Experimental procedure

Research was carried out using the iodine-stabilized He-Ne laser and the set for measuring the frequency difference of laser radiation sources from the GET 2-2021. The appearance of the laser and the set is shown in Fig. 1.



Fig. 1. Iodine-stabilized He-Ne laser and the set for measuring the frequency difference of laser radiation sources

The principle of operation of a iodine-stabilized laser is to automatically adjust the optical frequency of the laser radiation to the center of a certain component of the absorption line of molecular iodine vapor. The frequency of the iodine-stabilized He-Ne laser can be tuned without loss of accuracy within 463 MHz along the components a, b, c, d, e, f, g, h, i, j, k, l, m and n of the absorption line R(127) in iodine.

The cavity of the iodine-stabilized He-Ne laser is based on four invar rods. Ends of bars are connected with end plates with positioners for cavity's adjustment on both sides. There are a low-noise laser tube which length is 210 mm and a iodine cell which length is 100 mm are used in a cavity. A process of a cell is placed in a thermocooler. A thermocooler provide the temperature of the process $-(15.00 \pm 0.05)$ °C. The system of automatic frequency control of the laser includes: a low noise high voltage source for power of laser tube; the power supply system and thermistor; generator f-3f; 3f phase detector; a DC amplifier; integrator; sweep generator; an iodine peaks indication system [4].

To obtain and process measurement information, specialized software "Laser-Laser" developed by VNIIM was used. This software package allows you to automatically register the difference frequency of iodine-stabilized and investigated lasers, process the difference frequency and determine the frequency of the investigated laser, determine the stability of the frequency of the investigated laser for various time intervals.

Metrological characteristics of the reference stabilized He-Ne/I, laser:

- the frequency of the laser radiation is f = 473612353603.6 kHz, the combined uncertainty of the laser radiation frequency is $u_c = 0.2$ kHz (calibration certificate No. 8 by the BIPM, BIPM.L-K11. The key comparison of stabilized lasers at a wavelength of 633 nm [6]);

- output power of laser radiation $-100-125 \mu$ W.

Experimental researching of widely used stabilized lasers carried out by GET2 at the following conditions:

 20 ± 3 :

 100 ± 6 .

80;

- ambient temperature, °C
- max. temperature's transformation during an hour, °C 0.2;

- relative humidity of the air, %, no more

- atmospheric pressure, kPa

For the research, frequency-stabilized laser radiation sources were chosen: Stabilized He-Ne laser LGN-302, Stabilized He-Ne laser SIOS SL 02/1, Differential laser interferometer SIOS SP 2000, Laser measuring system Renishaw XL-80 and Stabilized He-Ne laser Thorlabs HRS015. The following results were obtained, which are presented in Table 1.

According to Part 1 of the State verification schedule, frequency-stabilized lasers with confidence limits from $2 \cdot 10^{-10}$ to $1 \cdot 10^{-8}$ can be used as working standards of the 1st category, and from $1 \cdot 10^{-8}$ to $1 \cdot 10^{-6}$ as working standards of the 2nd echelon. Thus, based on the data obtained, we can conclude that the stabilized He-Ne laser LGN-302 in its accuracy characteristics corresponds to the 1st echelon operating manual, and the stabilized He-Ne laser SIOS SL 02/1, differential laser interferometer SIOS SP 2000, laser measuring system Renishaw XL-80, stabilized He-Ne laser Thorlabs HRS015 correspond to the 2nd echelon.

Table 1

Model	Wavelength, nm	Relative
		frequency instability
Stabilized He-Ne laser LGN-302	632.99097	1.10-8
Stabilized He-Ne laser SIOS SL 02/1	632.99099	2.10-8
Differential laser interferometer	632.99083	2.10-8
SIOS SP 2000		
Laser measuring system Renishaw XL-80	632.99058	2.10-8
Stabilized He-Ne laser Thorlabs HRS015	632.99152	3.10-8

Results

Conclusion

The dynamics of the global market of metrological services is defined by constantly growing needs for changes in new areas of activity and increasing requirements for their accuracy. The development of new technologies requires constant improvement of the state standards base, the development of new measuring technologies and equipment for the traceability of measurements. Stabilized laser radiation sources are the reliable basis for these goals. Thus, the metrological characteristics of the lasers discussed in this article correspond to the characteristics declared by the manufacturers and can be successfully used as working standards, ensuring the transfer of a unit of length at a high level.

REFERENCES

1. Zackharenko Yu.G., Kononova N.A., Kosmina M.A., Fomkina Z.V., Chekirda K.V., The current state of the reference base of the Russian Federation in the field of measurements of length and angle measurements. Measurement Techniques, (2022) (7) 18–23.

2. Akimova T.P., Zackharenko Yu.G., Kononova N.A., Fedorin V.L., Fomkina Z.V., Chekirda K.V., The State primary standard of the unit of length – metre GET 2-2021. Measurement Techniques, (2021) (10) 3–7.

3. Kononova N.A., Zackharenko Yu.G., Fomkina Z.V., The State Primary Standard of the Unit of Length - the meter GET 2. International Conference Laser Optics (ICLO). Saint Petersburg, 2022.

4. Kononova N.A., Zackharenko Yu.G., Fedorin V.L., Fomkina Z.V., Investigations of metrological characteristics of the "Winters Electro-Optics, Inc." iodine-stabilized He-Ne laser by The State Primary Standard of the Unit of Length – GET 2-2010. 18th International Conference on Laser Optics (ICLO). Saint Petersburg, 2018.

5. Chekirda K.V., Zakharenko Yu.G., Kononova N.A., Fomkina Z.V., Current state and prospects for the developments of a reference base in the field of length measurements. IX International symposium "Metrology of time abd space" (September, 12-14). (2018) (4) 190–194.

6. Robertsson L., Zucco M., Ma L.-S., Terra O., Saraiva F., Gentil S., Chekirda C., Zakharenko Yu., Fedorin V., Mostert L. Results from the CI-2004 campaign at the BIPM of the BIPM.L-K11 ongoing key comparison. Metrologia, (2005) (42) 04002.

THE AUTHORS

ZACHARENKO Yuri G. y.g.zackharenko@vniim.ru

KONONOVA Natalia A. n.a.kononova@vniim.ru **LOGVINUK Elena I.** e.i.logvinuk@vniim.ru

FOMKINA Zoya V. z.v.fomkina@vniim.ru

KURKOVA Alexsandra D. kurkova.ad@edu.spbstu.ru ORCID: 0000-0002-3729-1943

Received 03.07.2023. Approved after reviewing 15.09.2023. Accepted 16.09.2023.

Conference materials UDC 53.04 DOI: https://doi.org/10.18721/JPM.163.207

Features of photovoltaic cell degradation of solar power plants in Hong Kong and Saint Petersburg

Deng Y.^{1,2}⊠, V.V. Davydov^{1,3}

¹ Peter the Great St. Polytechnic University, St. Petersburg, Russia;

² Jiangsu Normal University, Xuzhou, China;

³ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia

□ dyuanbiao@gmail.com

Abstract. This work investigates the degradation characteristics of PV modules in two different climates, Hong Kong and St. Petersburg, in order to better understand the coupling effects of temperature, thermal cycling, UV exposure, relative humidity and other environmental factors on the performance of PV systems. The solar development potential of Hong Kong and St. Petersburg are compared. Different optimization recommendations are given based on the different climates of Hong Kong and St. Petersburg.

Keywords: Photovoltaic Models, Solar Panels, degradation, damp-heat climate, humid continental climate, electroluminescence

Citation: Deng Y., Davydov V.V., Features of photovoltaic cell degradation of solar power plants in Hong Kong and Saint Petersburg, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 44–49. DOI: https://doi.org/10.18721/JPM.163.207

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УД 53.04 DOI: https://doi.org/10.18721/JPM.163.207

Особенности деградации фотоэлектрических элементов солнечных электростанций в Гонконге и Санкт-Петербурге

Дэн Ю.^{1,2⊠}, В.В. Давыдов^{1,3}

¹Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;

² Цзянсуский нормальный университет, Сюйчжоу, Китай;

³ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия

□ dyuanbiao@gmail.com

Аннотация. В данной работе исследуются характеристики деградации фотоэлектрических модулей в двух различных климатических условиях, Гонконге и Санкт-Петербурге, чтобы лучше понять влияние температуры, термоциклирования, ультрафиолетового облучения, относительной влажности и других факторов окружающей среды на производительность фотоэлектрических систем. Сравнивается потенциал развития солнечной энергетики Гонконга и Санкт-Петербурга. Даются различные рекомендации по оптимизации, основанные на различных климатических условиях Гонконга и Санкт-Петербурга.

Ключевые слова: фотоэлектрические модели, солнечные панели, деградация, влажный жаркий климат, влажный континентальный климат, электролюминесценция

© Deng Y., Davydov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Дэн Ю., Давыдов В.В., Особенности деградации фотоэлектрических элементов солнечных электростанций в Гонконге и Санкт-Петербурге // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 44–49. DOI: https://doi.org/10.18721/JPM.163.207

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In the 21st century, the three major problems of energy shortage, environmental pollution and the greenhouse effect have spurred the development of renewable and clean energy sources. Solar energy, as a representative of clean energy, is being utilized in an ever-expanding range. Photovoltaic power plants are emblematic of the use of solar energy. Photovoltaic modules are the core components of photovoltaic power plants, and with the increase in use time, the performance decline is significant [1-6].

The performance deterioration of PV modules is divided into two main categories, one is internal factors, such as defects in the material itself or inadequate manufacturing processes. The other category is external environmental factors, which are greatly influenced by climate. Currently, there is a lack of research into the coupled effects of temperature, thermal cycling, UV exposure, relative humidity and other factors on PV systems [7–9]. There is therefore a need for a global database to determine the factors and characteristics of PV module degradation under different climatic conditions [10]. This thesis compares the degradation characteristics of PV modules in Hong Kong and St. Petersburg. Different optimization suggestions are given according to the climate characteristics of Hong Kong and St. Petersburg.

Materials and optimization methods for degradation of PV modules in Hong Kong and St. Petersburg

Hong Kong is located in southern China and has a humid subtropical climate, with average maximum temperatures above 30 °C from June to September, rainfall greater than 300 mm and an average annual relative humidity of 78%, so the main problem facing PV modules in Hong Kong is the damp-heat climate.

Han et al. [11] carried out an analytical study of a PV module in a hot and humid region and Fig. 1 shows an EL image of this PV module. Three of the more obvious disadvantages can



Fig. 1. EL (electroluminescence) image of photovoltaic module [11]: PV module exposed in the field (*a*); PV module exposed in the field (*b*); PV module stored indoors (*c*)

© Дэн Ю., Давыдов В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

be observed in Fig. 1. Defect A there is a distinct dark area between the busbars in the middle of the cell. defect B, there is a bright spot in the busbars of the cell. Defect C, there is a black border in the cell. By comparing Fig. 1, a, b and Fig. 1,c, it can be seen that the defects in the PV modules were caused by prolonged exposure to the field. Cracking of the solder interconnects (defect B) and corrosion of the silver metallization (defects A and C) have been caused by the hot and humid climate.

UV Fluorescence is a relatively new characterization method for photovoltaic solar panels to detect defects such as cracked solar cells [12]. Gilleland [13] observed package delamination after UVF imaging of field exposed modules (Fig. 2,*a*) and Gabor [14] also observed package delamination after UVF imaging of outdoor mounted PV modules (Fig. 2,*b*). This phenomenon may be due to corrosion caused by the degradation of EVA, which is exacerbated by the damp-heat climate. Ways to reduce this hydrothermal degradation can be considered by using solders that do not contain tin or lead or by replacing EVA with new encapsulation materials.



Fig. 2. UVF image showing similar patterns from the busbar for field-exposed modules (*a*); UVF image showing patterns from the busbar for outdoor installed modules (*b*) [13]

St. Petersburg is located at around 60 degrees north latitude and has a humid continental climate. During the summer months, the average daily incident shortwave solar energy is higher in St. Petersburg than in Hong Kong, as shown in Fig. 3.The data is derived from NASA's meteorological model reconstructions(MERRA-2 (nasa.gov)).This may be due to St. Petersburg's higher latitude, and therefore shorter daylight hours in winter and longer daylight hours in summer.



Fig. 3. Average daily incident shortwave solar energy

PVsyst is a widely used simulation software commonly used to evaluate PV energy yield and facilitate system optimization. Fig. 4 shows a comparison of the annual yield of the same PV arrays in Hong Kong and St. Petersburg, simulated using PVsyst. The PV module used for the simulation is the LG 450 N2W-E6 from LG Electronics, which is a high power solar panel with a conversion power of 20.5%. It can be seen that in the summer the same PV system in St. Petersburg yields more electricity than in Hong Kong. The low yield of photovoltaic modules in St. Petersburg from October to April may be due to frequent snowfall resulting in snow, frost and ice.



Fig. 4. Comparison of the annual yield of PV array in Hong Kong and St. Petersburg

As shown in Fig. 5, Christopher's [15] study of PV modules in humid continental climates found that moisture infiltration was clearly observed at the edges of the cells adjacent to the module frames and that darkening occurred in the middle of the cells, with an average annual power loss of about 0.6% in the modules. The reason for this phenomenon may be related to the frequent snowfall in northern climates, and as this phenomenon occurs mainly in cells adjacent to the module frame, consideration could be given to improving the durability of the module edge seal and frame structure to reduce the degradation rate. Due to the low yield of photovoltaic modules in St. Petersburg in winter, the degradation of solar cells can also be reduced by removing the solar panels during the frost season [16, 17].



Fig. 5. Module showing moisture ingress at corners. Two selected cells are shown enlarged [15]

Results and Discussion

Degradation of PV modules in Hong Kong should take into account their hot and humid climate. The use of lead-free solder or thermoplastic polyolefin (TPO) instead of ethylene and vinyl acetate (EVA) reduces the degradation rate of PV modules to 0.3%. Degradation of PV modules in St. Petersburg should take into account frequent snowfall and can be reduced by considering improving the durability of module edge sealing and frame construction or by removing solar panels during the frost season. Data from the Pulkovo Observatory shows that the annual degradation rate of PV modules removed during frost periods is 2.3%, which is much lower than the annual operational degradation rate of 8.19%.

Conclusion

We have analyzed the effects of two climates on PV modules in the Hong Kong region and the St. Petersburg region by examining PV modules from different regions. Different methods should be used to optimise degradation rates depending on the climate of different regions. Especially negatively the degradation of solar panels is affected by the number of temperature transitions through the zero mark. At one point, everything will melt (water appears and it penetrates into all the cracks). Then it freezes and expands. This leads to the destruction of the solar panel starting from the edges. Further cracks can lead to current loss from the panel when it is transferred to the network (part of the photovoltaic cells will lose contact). For a number of regions of Russia, this is the main factor in the degradation of solar panels.

REFERENCES

1. Boudjemila L., Krasnoshchekov V., Olimov S., Diuldin M., Kasimakhunova A., Some features of photoelectrical properties of highly efficient solar cells based on si, Proceedings of the 2020 IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2020, vol. 9244000 (2020) 223–226.

2. Sachenko A.V., Kostylyov V.P., Bobyl A.V., Shvarts M.Z., Evstigneev M., The Effect of Base Thickness on Photoconversion Efficiency in Textured Silicon-Based Solar Cells, Technical Physics Letters. 44(10) (2018) 873–876.

3. **Boudjemila L.**, Characterization of Nitride Silicon Layers Sin:x Enriched in Silicon at Different Stoichiometries by Photocurrent Spectroscopy Method and Mass Spectrometry of Secondary Ions, Springer Proceedings in Physics. 255 (2021) 177–184.

4. Bobyl A., Malyshkin V., Dolzhenko V., Grabovets A., Chernoivanov V., Scientific activity in the problems of technical and economic modeling of solar stations. An example of unstable climatic conditions. IOP Conference Series: Earth and Environmental Science, 2019, 390 (1), 012047.

5. **Boudjemila L., Bobyl A., Davydov V., Malyshkin V.** On a Moving Average with Internal Degrees of Freedom, Proceedings of the 2022 International Conference on Electrical Engineering and Photonics, EExPolytech 2022, vol. 2022 (2022) 191–194.

6. **Boudjemila L., Davydov V.V., Aleshin A.N., Malyshkin V.M., Terukov E.I.,** Electrical characteristics of CsPbI₃ and CsPbBr₃ lead halide Pervoskvite nanocrystal films deposited on Si-c solar cells for high-efficiency photovoltaics, St. Petersburg State Polytechnical University Journal: Physics and Mathematics. 15(3-2) (2022) 91–96.

7. Soares G. A., David T. W., Anizelli H., Miranda B., Rodrigues J., Lopes P., Martins J., Cunha T., Vilaça R., Kettle J., Bagnis D., Outdoor performance of organic photovoltaics at two different locations: a comparison of degradation and the effect of condensation, J. Renew Sustain Energy. (12) (2020) 63502.

8. Oreski G., Ottersbock B., Omazic A., Degradation processes and mechanisms of encapsulants, Durab. Reliab. Polym. Other mater. Photovolt. Modul., Elsevier (2019) 135–152.

9. Fairbrother A., Phillips N., Gu X., Degradation processes and mechanisms of backsheets. Durab. Reliab. Polym. Other mater. Photovolt. Modul., Elsevier (2019) 153–74.

10. Phinikarides A., Kindyni N., Makrides G., Georghiou G.E., Review of photovoltaic degradation rate methodologies, Renew Sustain Energy Rev, (40) (2014) 143–152.

11. Han H., Dong X., Lai H., Yan H., Zhang K., Liu J., Verlinden P. J., Liang Z., Shen H., Analysis of the Degradation of Monocrystalline Silicon Photovoltaic Modules After Long-Term Exposure for 18 Years in a Hot–Humid Climate in China, IEEE Journal of Photovoltaics. vol. 8(3) (2021) 806–812.

12. Kontges M., Morlier A., Eder G., Fleib E., Kubicek B., Lin J., Review: Ultraviolet Fluorescence as Assessment Tool for Photovoltaic Modules, *IEEE Journal of Photovoltaics*, 2 (10) (2020) 616–633.

13. Gilleland B., Hobbs W.B., Richardson J. B., High throughput detection of cracks and other faults in solar pv modules using a high-power ultraviolet fluorescence imaging system, 2019 IEEE 46th Photovoltaic Specialists Conference (PVSC), IEEE (2019) 2575–2582.

14. Gabor A. M., Knodle P., Uv fluorescence for defect detection in residential solar panel systems, 2021 IEEE 48th Photovoltaic Specialists Conference (PVSC), IEEE (2021), 2575–2579.

15. Kichou S., Wolf P., Silvestre S., Chouder A., Analysis of the behavior of cadmium telluride and crystalline silicon photovoltaic modules deployed outdoor under humid continental climate conditions, Solar Energy. 171 (2018) 681–691.

16. Ulin V.P., Ulin N.V., Soldatenkov F.Y., Semenov A.V., Bobyl A.V., Surface of porous silicon under hydrophilization and hydrolytic degradation, Semiconductors. 48(9) (2014) 1211–1216.

17. Fisher L.M., Bobyl A., Johansen T.H., Bondarenko A.V., Obolenskii M.A., Anisotropic Origin of the Bending Instability of the Flux-Antiflux Interface in Type-II Superconductors, Physical Review Letters. 92(3) (2004) 370021–370024.

THE AUTHORS

DENG Yuanbiao dyuanbiao@gmail.com ORCID: 0009-0000-4342-766X DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: 0000-0001- 9530- 4805

Received 03.07.2023. Approved after reviewing 24.08.2023. Accepted 24.08.2023.

Conference materials UDC 535.37 DOI: https://doi.org/10.18721/JPM.163.208

Photoluminescence study of InGaAs/GaAs quantum dots with bimodal inhomogeneous broadening

A.V. Babichev^{1⊠}, A.M. Nadtochiy^{2,3}, Yu.S. Tkach¹, N.V. Kryzhanovskaya^{2,3},
 S.A. Blokhin¹, V.N. Nevedomsky¹, A.G. Gladyshev⁴,
 N.A. Maleev¹, L.Ya. Karachinsky⁴, I.I. Novikov⁴

¹ Ioffe Institute, St. Petersburg, Russia;

² Alferov University, St. Petersburg, Russia;

³ National Research University Higher School of Economics, St. Petersburg, Russia;

⁴ ITMO University, St. Petersburg, Russia

□ a.babichev@mail.ioffe.ru

Abstract. The comparative studies of optical and structural properties of InGaAs/GaAs quantum dots grown in Stranski–Krastanov growth mode by molecular-beam epitaxy and metal-organic chemical vapor deposition is presented. An analysis of the photoluminescence at ultralow pump levels resulted that the quantum dots ensemble grown by metal-organic chemical vapor deposition exhibits photoluminescence corresponding to quantum dots ground state and at the same time ensemble of quantum dots grown by molecular-beam epitaxy demonstrates the bimodal behavior which can be explained by the presence of two characteristic ensembles of InGaAs/GaAs quantum dots studying by transmission electron microscopy are presented and discussed as well.

Keywords: molecular-beam epitaxy, metal-organic chemical vapor deposition, gallium arsenide, InGaAs, Stranski–Krastanov growth mode

Acknowledgment: Optical properties were partly studied on the equipment of the large-scale research facilities Complex optoelectronic setup, HSE University.

Funding: The authors from Ioffe Institute acknowledge support in part by the grant of the Russian Science Foundation 22-19-00221, https://rscf.ru/project/22-19-00221/ for the structure design, MBE epitaxy, and the study of photoluminescence spectra of MBE-grown structures. A.M. Nadtochiy and N.V. Kryzhanovskaya thanks project FSRM-2023-0010 Ministry of Science and Higher Education of the Russian Federation for support of the study of photoluminescence spectra of MOCVD-grown structures. The authors from ITMO University acknowledge support in part by the Advanced Engineering Schools Federal Project for the TEM study of MOCVD-grown structures.

Citation: Babichev A.V., Nadtochiy A.M., Tkach Yu.S., Kryzhanovskaya N.V., Blokhin S.A., Nevedomsky V.N., Gladyshev A.G., Maleev N.A., Karachinsky L.Ya., Novikov I.I., Photoluminescence study of InGaAs/GaAs quantum dots with bimodal inhomogeneous broadening, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 50–55. DOI: https://doi.org/10.18721/JPM.163.208

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Babichev A.V., Nadtochiy A.M., Tkach Yu.S., Kryzhanovskaya N.V., Blokhin S.A., Nevedomsky V.N., Gladyshev A.G., Maleev N.A., Karachinsky L.Ya., Novikov I.I., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 535.37 DOI: https://doi.org/10.18721/JPM.163.208

Исследование фотолюминесценции квантовых точек InGaAs/GaAs с бимодальным неоднородным уширением

А.В. Бабичев ¹[⊠], А.М. Надточий ^{2,3}, Ю.С. Ткач ¹, Н.В. Крыжановская ^{2,3}, С.А. Блохин ¹, В.Н. Неведомский ¹, А.Г. Гладышев ⁴,

Н.А. Малеев¹, Л.Я. Карачинский⁴, И.И. Новиков⁴

¹ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

² Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия

³ Национальный исследовательский университет «Высшая школа экономики», Санкт-Петербург, Россия

⁴Университет ИТМО, Санкт-Петербург, Россия

a.babichev@mail.ioffe.ru

Аннотация. Представлены сравнительные исследования оптических и структурных свойств квантовых точек InGaAs/GaAs, выращенных методом Странски-Крастанова с использованием молекулярно-пучковой и газофазной эпитаксии. Анализ спектров фотолюминесценции при сверхнизких уровнях накачки показал, что массив квантовых точек, выращенных методом газофазной эпитаксии, проявляет фотолюминесценцию, соответствующую переходам через основные состояния, а массив квантовых точек, выращенных методом молекулярно-лучевой эпитаксии, проявляет бимодальное поведение - наличие двух характерных ансамблей квантовых точек с разными размерами, соответствующих двум пикам фотолюминесценции. Представлены и обсуждены результаты исследования квантовых точек InGaAs/GaAs методом просвечивающей электронной микроскопии.

Ключевые слова: молекулярно-лучевая эпитаксия, газофазная эпитаксия, арсенид галлия, InGaAs, механизм Странски-Крастанова

Финансирование: Авторы из ФТИ им. А.Ф. Иоффе выражают благодарность за поддержку проекту РНФ № 22-19-00221, https://rscf.ru/project/22-19-00221/ в части разработки структуры, эпитаксии методом молекулярно-пучковой эпитаксии и исследования спектров фотолюминесценции структур, выращенных методом молекулярно-пучковой эпитаксии. А.А. Надточий и Н.В. Крыжановская благодарят проект FSRM-2023-0010 Министерства науки и высшего образования Российской Федерации за поддержку в части исследований спектров фотолюминесценции структур, выращенных методом газофазной эпитаксии. Авторы из Университета ИТМО выражают благодарность за поддержку федеральный проект «Передовые инженерные школы» в части исследований методом просвечивающей электронной микроскопии структур, выращенных методом газофазной эпитаксии.

Ссылка при цитировании: Бабичев А.В., Надточий А.М., Ткач Ю.С., Крыжановская Н.В., Блохин С.А., Неведомский В.Н., Гладышев А.Г., Малеев Н.А., Карачинский Л.Я., Новиков И.И. Исследование фотолюминесценции квантовых точек InGaAs/GaAs с бимодальным неоднородным уширением // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 50–55. DOI: https://doi.org/10.18721/ JPM.163.208

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

[©] Бабичев А.В., Надточий А.М., Ткач Ю.С., Крыжановская Н.В., Блохин С.А., Неведомский В.Н., Гладышев А.Г., Малеев Н.А., Карачинский Л.Я., Новиков И.И., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Introduction

The usage of optically pumped quantum dots (QDs) micropillar lasers with vertical microcavities is preferable to realize the optical reservoir computing (RC) scheme [1–4] due to low power consumption of photonic RC, high spectral homogeneity, small pitch and diameters of microlasers in relation with vertical-cavity surface-emitting lasers (VCSELs) case [5]. Due to possibility of the precise control of microlasers diameter, it is possible to realize a dense array of spectrally homogeneous microlasers emitting in a frequency-range of about 50 GHz (~200 μ eV) required for RC [3].

This paper presents the results on study of the optical properties of 980 nm range InGaAs QDs grown by molecular-beam epitaxy (MBE) according to the Stranski-Krastanov growth mode and a comparison with the results for InGaAs QDs grown by metal-organic chemical vapor deposition (MOCVD).

Materials and Methods

For the first structure InGaAs QDs were formed by deposition of $In_{0.63}Ga_{0.37}As$ layer with thickness of 2.6 monolayers (ML) using the Stranski-Krastanov mode and MBE. A 300 nm thick GaAs matrix layer was located between two 35 nm thick Al_{0.23}Ga_{0.77}As barriers. The QD layers were placed in the middle of the matrix layer. The growth temperature of the barrier layers, as well as the matrix layer, was 580 °C. Epitaxy of the QDs layers was carried out at 490 °C. The growth rate was a 0.55 E/s. The exposure time in arsenic flow before the deposition of the 5 nm thick GaAs capping layer was 30 seconds. After the capping layer deposition, the temperature was increased up to 580 °C, and the samples were annealed for 240 seconds to reduce the inhomogeneous broadening of QDs in the ensemble. Arsine, tertiary butylarsine, trimethylgallium, trimethylaluminum, and trimethylindium were used as precursors for MOCVD growth of QDs (structure 2). A 320 nm thick GaAs matrix layer was located between two 35 nm thick $Al_{0,42}Ga_{0,58}As$ barriers. The QD layers were placed in the middle of the matrix layer. The growth temperature of the barrier layers, as well as the matrix layer, was 700 °C. Epitaxy of the QDs layers was carried out at low temperature (580 °C), and the growth rate was a 0.68 E/s. The thickness of the GaAs capping layer was fixed at 2 nm. The exposure time before the deposition of the capping layer was 30 seconds. After the capping layer deposition, the temperature of the substrate holder increased up to 615 °C aimed with realize the QDs high-temperature annealing. The photoluminescence (PL) spectra were studied at 13 K in a wide range of excitation power densities. Optical pumping was carried out by a Yag:Nd laser at a wavelength of 532 nm with a 150 mW CW output power, which corresponds to the excitation power density $\sim 5 \text{ kW/cm}^2$. The range of laser power attenuation using neutral filters was $(1-3\cdot10^{-6})$. Temperature studies of the PL spectra were also carried out in the temperature range of 13-325 K at a moderate excitation power of 4.5 mW.

Transmission electron microscopy (TEM) studies were carried out using a JEM2100F electron microscope (Jeol) at an accelerating voltage of 200 kV. Samples were prepared in cross-sectional geometry according to a conventional technique, including thinning by precision lapping and sputtering with argon ions at the final stage until perforation.

Results and Discussion

The results of TEM studies are shown in Fig. 1. In both cases, the estimated QDs surface density is about $7 \cdot 10^9$ cm⁻². In structure 1 grown by the MBE, one can see the QDs with 2.8–3.9 nm range height. The QD outer boundary has a thin darker contrast than the surrounding GaAs





matrix and the inner part of the QD. It can be assumed that the wetting layer (WL) composition estimated using a TEM contrast [6] has mole fraction of indium about 0.2 ($In_{0.2}Ga_{0.8}As$). The thickness of the WL is no more than 0.8 nm. The central part of QD has a less contrast, which corresponds to a higher indium mole fraction (more than 40%).

In structure 2 grown by the MOCVD, the InGaAs (layer 1, cf. Fig. 1, right panel) is visible on the GaAs layer (layer 0). This InGaAs layer has pyramid thickening, both contrast intensity corresponds to about 40% in mole fraction. The estimated thickness of planar part is about 1.5 nm, while the QDs height limited by the boundary between layers 1 and 3 and is about 4.1 nm. The small capping layer (layer 2) thickness (estimated to about 2.6 nm) result the evaporation of large QDs with thickness exceeded this value at high-temperature annealing.

The results of low-temperature PL studies are shown in Fig. 2. The study of PL spectra at low temperatures makes it possible to avoid the thermal escape of charge carriers from QDs and their subsequent redistribution over the ensemble. In this case, a decrease in the pump level leads to a weakening of the contribution of excited states in the PL spectra (cf. Fig. 2). Thus, the PL spectrum at ultralow excitation densities should be a superposition of emission through the ground states of the QD ensemble [7]. For the structure 1 grown by MBE, the presence of additional lines (shoulder) in the short-wavelength spectral region was observed, which remain unchanged when the pumping is reduced below a certain level (cf. Fig. 2). This behavior was discussed earlier [8, 9] and can be associated with the presence of two ensembles of QDs with different sizes. For the structure 2 grown by MOCVD, a decrease in the half-width of the PL spectrum was observed, and the shape of the spectra was more symmetrical in comparison with the results for structure 1 under identical pumping conditions, which indicates on more homogeneous size distribution of QDs (absence of bimodality).



Fig. 2. PL spectra of structure 1 (left panel) and structure 2 (right panel), measured at 13 K



Fig. 3. FWHM versus temperature (*a*) and integrated/peak intensity versus temperature (*b*). PL spectra of structure 1 (*c*) and structure 2 (*d*), measured at different temperatures

Temperature studies of the PL spectra behavior for both structures were carried out at a moderate excitation power (4.5 mW) as well when there is no contribution from the excited states. Temperature studies of the PL spectra (the behavior of the full width at half maximum, FWHM, value, as well as the integral intensity/amplitude of the PL peak versus temperature, cf. Fig. 3) also have confirmed the previously mentioned assumption about the presence of two characteristic ensembles of QDs in the structure 1 grown by the MBE. At low temperatures, in structure 1, a nonequilibrium distribution of charge carriers over QD states is observed and is determined by QDs density. The peak intensity ratio allows one to assume the present of two different QDs ensembles. As the temperature increases, it becomes possible the escape of the carriers from an ensemble with smaller QDs (with weak carrier localization), followed by their capture through a wetting layer into an ensemble with larger QDs, which was previously observed both for the case of bimodal InAs [10, 11] and InGaAs [12] QDs. This process is accompanied by increasing in the peak intensity with temperature for the long-wavelength peak (in studied structure, in the temperature range of 100-210 K, cf. Fig. 3,b). Simultaneously, this process is accompanied by a decrease in the intensity of the short-wavelength shoulder, which leads to decreasing in the width of the PL maximum in the given temperature range (100-210 K) and its shifting to lower photon energies [13]. The subsequent rise in temperature leads to suppression of the recapture mechanism.

As a result, an increase in the maximum width of the PL spectrum is observed in the given temperature range. As the temperature increases in structure 2 grown by the MOCVD, a weak temperature dependence of the FWHM values is demonstrated, which indicates a homogeneous distribution of QDs. Fig. 3,*b* also does not demonstrate the growth of the peak PL intensity with increasing temperature, which is typical for the case of bimodal QDs. At low temperatures (up to 120 K), the peak intensity remains constant. Further temperature growth results to a drop in peak intensity, which is typical for thermal escape and further nonradiative recombination of the charge carriers outside the QDs [13].

Conclusion

Low-temperature studies of the PL spectra in a wide range of excitation power densities have been carried out. It was shown that the structure with QDs grown by the MOCVD demonstrates PL through the ground states in the ensemble of QDs. It is shown that the structure with QDs grown by the MOCVD contains one ensemble of QDs. In turn, for the structure with QDs grown by the MBE, the presence of additional lines in the short-wavelength spectral region at a low temperature and pumping was observed, which can be associated with the presence of two ensembles of QDs. Although the MOCVD technique makes it possible to realize a single ensemble of QDs, the low wafer thickness uniformity (about 2% [3]) limits to use this method in the fabrication of highly homogenous QDs micropillar arrays suitable for optical RC. In opposite, the MBE technique demonstrate better wafer thickness uniformity. Further studies aimed at creating the single ensemble of QDs grown by MBE are related to use the submonolayer deposition mode.

REFERENCES

1. Heuser T., Grose J., Holzinger S., Sommer M. M., Reitzenstein S., Development of highly homogenous quantum dot micropillar arrays for optical reservoir computing, IEEE Journal of Selected Topics in Quantum Electronics. 26 (1) (2020) 1–9.

2. Andreoli L., Porte X., Heuser T., Große J., Moeglen-Paget B., Furfaro L., Reitzenstein S., Brunner D. Optical pumping of quantum dot micropillar lasers, Optics Express. 29 (6) (2021) 9084–9097.

3. Heuser T., Große J., Kaganskiy A., Brunner D., Reitzenstein S. Fabrication of dense diametertuned quantum dot micropillar arrays for applications in photonic information processing, APL Photonics. 3 (11) (2018) 116103.

4. Shih C.-W., Limame I., Krüger S., Palekar C. C., Koulas-Simos A., Brunner D., Reitzenstein S., Low-threshold lasing of optically pumped micropillar lasers with Al_{0.2}Ga_{0.8}As/Al_{0.9}Ga_{0.1}As distributed Bragg reflectors. Applied Physics Letters. 122 (2023) 151111.

5. Heuser T., Pflüger M., Fischer I., Lott J. A., Brunner D., Reitzenstein S., Developing a photonic hardware platform for brain-inspired computing based on 5×5 VCSEL arrays, Jphys Photonics. 2 (4) (2020) 044002.

6. Lemaotre A., Patriarche G., Glas, F., Composition profiling of InAs-GaAs quantum dots. Applied Physics Letters. 85 (17) (2004) 3717–3719.

7. Heitz R., Grundmann M., Ledentsov N. N., Eckey L., Veit M., Bimberg D., Ustinov V.M., Egorov A.Yu., Zhukov A.E., Kop'ev P.S., Alferov, Z.I., Multiphonon-relaxation processes in self-organized InAs/GaAs quantum dots, Applied Physics Letters. 68 (3) (1996) 361–363.

8. Wang H.L., Ning D., Feng S.L., Temperature dependence of the optical properties of InAs/GaAs self-organized quantum dots with bimodal size distribution, Journal of Crystal Growth. 209 (4) (2000) 630–636.

9. Liang S., Zhu H. L., Wang W., Temperature-dependent bimodal size evolution of InAs quantum dots on vicinal GaAs (100) substrates, Journal of Applied Physics. 100 (10) (2006) 103503.

10. **Rybalko D.A., Nadtochiy A.M., Maximov M.V., Zhukov A.E.,** Luminescence Excitation spectroscopy of InAs/InGaAs/GaAs quantum-dot arrays in the temperature range between 20 and 300 K, Optics and Spectroscopy. 128 (2020) 106–113.

11. Kryzhanovskaya N.V., Gladyshev A.G., Blokhin S.A., Maksimov M.V., Semenova E.S., Vasil'ev A.P., Zhukov A.E., Ledentsov N.N., Ustinov V. M., Bimberg D., Nonequilibrium room-temperature carrier distribution in InAs quantum dots overgrown with thin AlAs/InAlAs layers, Semiconductors. 39 (2005) 1188–1193.

12. Nadtochiy A. M., Mintairov S. A., Kalyuzhnyy N. A., Rouvimov S. S., Shernyakov Y. M., Payusov A. S., Maximov M. V., Zhukov A. E., Effect of the bimodality of a QD array on the optical properties and threshold characteristics of QD lasers, Semiconductors. 49 (2015) 1090–1094.

13. Saint-Girons G., Sagnes I., Photoluminescence quenching of a low-pressure metal-organic vapor-phase-epitaxy grown quantum dots array with bimodal inhomogeneous broadening, Journal of Applied Physics. 91 (12) (2002) 10115–10118.

THE AUTHORS

BABICHEV Andrey V. a.babichev@mail.ioffe.ru ORCID: 0000-0002-3463-4744

NADTOCHIY Alexey M. al.nadtochy@mail.ioffe.ru ORCID: 0000-0003-0982-907X

TKACH Yulia S. polubavkina@mail.ru ORCID: 0000-0003-0982-907X

KRYZHANOVSKAYA Natalya V. nataliakryzh@gmail.com ORCID: 0000-0002-4945-9803

BLOKHIN Sergei A. blokh@mail.ioffe.ru ORCID: 0000-0002-5962-5529 NEVEDOMSKY Vladimir N. Nevedom@mail.ioffe.ru ORCID: 0000-0002-7661-9155

GLADYSHEV Andrey G. glad@mail.ioffe.ru

ORCID: 0000-0002-9448-2471

MALEEV Nikolay A. maleev.beam@mail.ioffe.ru ORCID: 0000-0003-2500-1715

KARACHINSKY Leonid Ya. karach@switch.ioffe.ru ORCID: 0000-0002-5634-8183

NOVIKOV Innokenty I. novikov@switch.ioffe.ru ORCID: 0000-0002-5634-8183

Received 03.07.2023. Approved after reviewing 24.07.2023. Accepted 25.07.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 620.1.08, 681.786.5, 681.7.014.3 DOI: https://doi.org/10.18721/JPM.163.209

Features of the operation of a laser profilometer in an automated rolling stock control system

K.G. Arinushkina¹^{III}, A.S. Adadurov^{2,3}, I.Yu. Savelev³, V.V. Davydov¹

¹The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

² Emperor Alexander I St. Petersburg State Transport University, St. Petersburg, Russia;

³ LLC VNIIZHT-Engineering, St. Petersburg, Russia

[™] k-arinushkina@mail.ru

Abstract. Faulty wheelset treads were identified as one of the major problems in the early stages of car repairs. Defects of wheel sets that occur during the operation of the rolling stock of the Moscow Railway are analyzed. When scanning the tread surface of wheel pairs with an automatic complex of technical measurements, the principle of operation and control parameters are taken into account. To reduce the stopping time of passing trains, it is proposed to introduce laser profilers on the railway tracks. The control of the geometric parameters of wheel sets using a laser profilometer is an important element of railway transport maintenance. Incorrect wheel sets can lead to high wheel wear, track damage, and poor passenger comfort and safety. In the course of the work, data obtained from measurements of various profiles of the surfaces of freight cars, including wheelsets, were analyzed in comparison with reference profiles. An increase in measurement accuracy has been established by minimizing the human factor, global digitalization of technological processes and automation of rolling stock control along the route.

Keywords: laser profilometer, geometrical parameters, railway transport, wheelset

Citation: Arinushkina K.G., Adadurov A.S., Savelev I.Yu., Davydov V.V., Features of the operation of a laser profilometer in an automated rolling stock control system, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 56–62. DOI: https://doi.org/10.18721/JPM.163.209

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Arinushkina K.G., Adadurov A.S., Savelev I.Yu., Davydov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 620.1.08, 681.786.5, 681.7.014.3 DOI: https://doi.org/10.18721/JPM.163.209

Особенности работы лазерного профилометра в автоматизированной системе управления подвижным составом

К.Г. Аринушкина¹[™], А.С. Ададуров^{2,3}, И.Ю. Савельев³, В.В. Давыдов¹

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия;

² Петербургский государственный университет путей сообщения Императора Александра I, Санкт-Петербург, Россия;

³ ООО"ВНИИЖТ-Инжиниринг", Санкт-Петербург, Россия

^{III} k-arinushkina@mail.ru

Аннотация. Неисправные поверхности катания колесных пар были определены как одна из основных проблем на ранних этапах ремонта вагонов. Проанализированы дефекты колесных пар, возникающие в процессе эксплуатации подвижного состава Московской железной дороги. При сканировании поверхности катания колесных пар автоматическим комплексом технических измерений учитываются принцип работы и параметры контроля. Для сокращения времени остановки проходящих поездов предлагается внедрить на железнодорожных путях лазерные профилометры. Контроль геометрических параметров колесных пар с помощью лазерного профилометра является важным элементом технического обслуживания железнодорожного транспорта. Неправильно подобранные колесные пары могут привести к повышенному износу колес, повреждению гусеницы и ухудшению комфорта и безопасности пассажиров. В ходе работы были проанализированы данные, полученные при измерениях различных профилей поверхностей грузовых вагонов, в том числе колесных пар, в сравнении с эталонными профилями. Установлено повышение точности измерений за счет минимизации человеческого фактора, глобальной цифровизации технологических процессов и автоматизации управления подвижным составом в пути следования.

Ключевые слова: лазерный профилометр, геометрические параметры, железнодорожный транспорт, колесная пара

Ссылка при цитировании: Аринушкина К.Г, Ададуров А.С., Савельев И.Ю., Давыдов В.В. Особенности работы лазерного профилометра в автоматизированной системе управления подвижным составом // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 56–62. DOI: https://doi.org/10.18721/ JPM.163.209

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Currently, much attention is paid to the problems of monitoring the state of various transport [1-5]. One of the most difficult areas to control is the railway. The traffic safety of railway transport largely depends on the quality of wheelset materials, design, manufacturing technology, its inspection and repair [6, 7]. Due to large static and dynamic loads, as well as violations of the rules for the technical operation of rolling stock, various defects occur in the wheelset. Optical methods are often used to control the state of various moving parts of an object and detect defects [8–13]. The requirements for the parameters of wheel sets in the automated control system for the operation of rolling stock are met by laser profilometers.

A laser profilometer is a device that is used to control the geometric parameters of wheel sets. It operates on the principle of laser interferometry and measures wheel profile height, wheel spacing, wheel diameter, and other parameters that can affect the safety and efficiency of rail transport.

[©] Аринушкина К.Г, Ададуров А.С., Савельев И.Ю., Давыдов В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The control of the geometric parameters of wheel sets is an important element of the maintenance and safety of railway transport. For example, incorrect wheel spacing or worn wheels can lead to track damage and even an accident. Therefore, regular monitoring of wheel pair parameters using a laser profilometer allows you to identify and eliminate these problems in a timely manner. This improves the safety and reliability of railway transport, as well as reduces wear and tear and operating costs.

The aim of the work is to develop a new algorithm for describing and evaluating the wheel profile, taking into account such additional requirements as the smoothness and continuity of the resulting profile, including on data with partial gaps. This will allow more accurate determination of geometric parameters, and, consequently, also reduce the number of erroneous rejection decisions.

The point cloud is a set of pairs $\{(x_i, y_m)\}_{i=1}^n$ that defines the profile boundary, more precisely, the trajectory of the laser beam reflected from the profile boundary. Since the position of the profile boundary is measured with an error, and in some place's detection omissions are possible (for example, the beam turned out to be blocked by something), the regression problem becomes a natural continuation of the problem of finding the profile boundary. The solution of this problem is carried out by means of classical regression analysis.

Materials and Methods

The laser profilometer for determining the geometrical parameters of the surface profile contains a laser radiation source with a laser beam-to-line converter, an optical matrix receiver of reflected radiation, and an information processing device. The source of laser radiation is made in the form of a semiconductor laser operating in a pulsed mode. At least one narrow-band interference light filter is introduced along the reflected beam in front of the optical matrix receiver. In addition, a semiconductor laser operating in the visible red wavelength range was used, the temperature stabilization system was made on the basis of Peltier elements with a control controller and a temperature sensor. These systems are very often used in various optical instruments for accurate measurements [1, 6, 8, 9, 12, 14–16]. The information processing device is made in the form of a programmable logic controller with real-time signal processing and calculation of the surface profile. The block diagram of the laser profilometer is shown in Fig. 1.

The laser profilometer is designed to measure: flange height, rolling, flange thickness, flange steepness, tire thickness, it also provides for the removal and analysis of a complete wheel rolling profile, maintaining an electronic database of wheel pair wear, monitoring tolerances and sorting during technical inspection, certification, repair and formation of railway wheel sets of rolling stock.



Fig. 1. Laser profilometer. laser module *1*; line generator *2*; plane of laser radiation *3*; controller based on digital signal processor *4*; controlled object *5*; optical system *6* of the photodetector; image 7 of the probing laser radiation line on the photodetector; matrix photodetector *8*

In contrast to the previously used templates for controlling the parameters of the wheel tread, which were applied by employees of the railway transport structure, the laser profilometer in the automated rolling stock control system fully automates this process.

The profilometer consists of several laser sensors that are mounted on the track and aimed at the wheels of passing trains. Lasers measure the distance to the wheel and fix its profile. The received data are transferred to a computer, where they are processed and analyzed.

The laser signal leaves a wide line on the photomatrix covering several points at once. Based on the point cloud obtained on the basis of the image from the photodetector, the wheel profile is analyzed and control values are calculated. Since the wheel geometry changes during operation, it becomes impossible to describe the new profile shape with sufficient accuracy by the classes of initial functions.

To solve this problem, a polynomial model was developed. This model takes into account the features in the distortion of the reflected laser radiation from the changed profiles of the wheel during its movement. Accounting for these features makes it possible to realize the restoration of the shape of the wheel pair profile more clearly in comparison with previously used methods.

The solution of the regression problem was sought in the class of piecewise polynomial functions [17, 18]. In what follows, the boundaries of the domain of definition of each part of the piecewise function will be called points of discord or matching points. So, the solution takes the form given in Eq. (1).

On all sites, a polynomial of degree p is used. The coefficients for each section are their own and the section number is indicated by a subscript. The superscript means the *i*th component of the vector of coefficients. To obtain the formula for the *i*th interval, it is sufficient to substitute the corresponding values for x and β .

$$f(x) = \begin{cases} f(x;\beta_0), x < x_1, \\ f(x-x_1;\beta_1), x_1 \le x < x_2, \\ \dots \\ f(x-x_{k-1};\beta_{k-1}), x > x_{k-1}, \end{cases}$$
(1)

where p is the degree of the polynomial, k is the number of segments, $\beta = (\beta^{(0)}, ..., \beta^{(p)})$ are the polynomial coefficients,

$$f(x;\beta) = \beta^{(0)} + \beta^{(1)}x + \dots + \beta^{(p)}x^{p} = \sum_{j=0}^{p} \beta^{(j)}x^{j}$$

is a polynomial function,

$$f(x_i;\beta_i) = \beta_i^{(0)} + \beta_i^{(1)}x_i + \dots + \beta_i^{(p)}x_i^p = \sum_{j=0}^p \beta_i^{(j)}x_i^j$$

is a polynomial function in the *i*th interval.

The laser signal leaves a wide line on the photo matrix covering several points at once. The laser beam is located vertically relative to the matrix, that is, along its short side. In this case, the image processing objects will be a string. The inverted image on the matrix is shown in Fig. 2,*a*. The processed point cloud in Fig. 2,*b* is a set of $\{(x_i, y_u)\}_{i=1}^n$ pairs defining the trajectory of the laser beam reflected from the profile boundary, found by solving the regression problem using the mathematical formulas above.

Based on the point cloud obtained on the basis of the image from the charge-coupled device matrix, the wheel profile is analyzed and control values are calculated.

The analysis of these profiles makes it possible to establish the presence of defects in a pair of wheels during the movement of the car, which was previously more difficult to do.



Fig. 2. Wheel profile: inverted image on the matrix (a), processed point cloud (b)

Results and Discussion

The use of a new model made it possible, using a laser profilometer, to create an automated system that can more accurately control the geometric parameters of the surface profile, the contour dimensions of the object, the relative position of parts, and the deviation from flatness.

Based on a mathematical model built on a cloud of points, the key parameters of the wheel were calculated. As part of the work, only one wheel was considered, since its data are indicative and contained gaps.

The decision on the need to send the wheel set for repair (turning) can be made according to the allowable ranges defined in the regulatory documents, which are unique for each type of wheels.

According to the processed data of the wheel set, the output of the parameter T3 was found - the steepness of the ridge from the allowable limits.

The ridge steepness parameter is the horizontal distance measured between two points on the outer surface of the ridge, one of which is 2 mm from the top and the other is 13 mm from the wheel circle.

The steepness parameter or the dangerous shape of the ridge characterizes almost all types of tire wear. It is measured in millimeters and depends on the drawing height of the comb. From this, it should further be concluded that the wheel with a dangerous ridge shape is rejected.

The ridge steepness parameter is complex and characterizes changes in the shape and dimensions of the ridge and the entire profile of the wheel tread surface associated with wear during operation.

The defect is the steepness of the ridge and the unacceptable value of the parameter at which the operation of the wheel set is prohibited is less than 6 mm. The resulting value was 3.8 mm.

This parameter is calculated by software. From which it was assumed that this wheel set is subject to prolonged exposure when passing one-sided curved sections of the track.

From which follows the conclusion about the need to reject this wheel.

A restored profile with wheel parameters was also obtained. From which we can conclude that the data processing system is working correctly and the laser profilometer is working correctly.

Conclusion

Just as a template is applied to a real wheel for measurements during the technical inspection of a rolling stock car, so in the proposed method, measurements are made at points according to the template. The technical result is an increase in measurement accuracy by minimizing the human factor, global digitalization of technological processes and automation of rolling stock control along the route.

The automated profilometer system allows not only taking pictures, analyzing the data obtained based on their comparison with the basic standard, but also transmitting information. This helps to estimate the number of errors in the received measurements and allows them to be converted into digital data. This made it possible to integrate it into the universal digital hardware and software platform of the automatic system for the operation of the rolling stock. Thus, the use of a laser profilometer in an automated rolling stock control system is an effective way to control the geometric characteristics of freight cars and platforms. However, to achieve the best result, it is necessary to take into account a number of features of the laser profilometer, such as choosing the optimal installation height and scanning angle, as well as proper data processing.

In addition, it should be taken into account that the use of a laser profilometer is not the only way to control the geometric characteristics of the rolling stock, and in order to achieve maximum efficiency, it is recommended to combine its work with other control methods using an automated rolling stock control system.

Thus, it can be concluded that the use of a laser profilometer in an automated rolling stock control system is a promising and effective method for controlling the geometric characteristics of a rolling stock, subject to certain features of operation and taking into account technical and economic restrictions. In general, the use of this technology improves the quality of control and increases the efficiency of the rolling stock control system.

REFERENCES

1. Davydov V.V., Kruzhalov S.V., Grebenikova N.M., Smirnov K.Y., Method for Determining Defects on the Inner Walls of Tubing from the Velocity Distribution of the Flowing Fluid, Measurement Techniques. 61(4) (2018) 365–372.

2. Mihov E.D., Nepomnyashchiy O.V., Selecting informative variables in the identification problem Journal of Siberian Federal University - Mathematics and Physics. 9(4) (2016) 473–480.

3. **Ryzhenko I.N., Lutsenko A.E., Varygin O.G., Nepomnyashchiy O.V.**, Carrier compensation mode implementation in satellite communication channels. In: Proceedings of 2019 International Siberian Conference on Control and Communications, SIBCON 2019, vol. 8729665 (2019) 23–29.

4. **Tarasenko M.R., Lenets V.A., Akulich N.V.**, Features of use direct and external modulation in fiber optical simulators of a false target for testing radar station, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 10531 LNCS (2017) 227–232.

5. Davydov R.V., Dmitrieva D.S., Pilipova V.M., Dudkin V.M., The research of radioactive exposure compensation on optical material for optical fibers by powerful laser radiation," Proceedings – International Conference Laser Optics, (ICLO-2020), vol. 9285820 (2020) 376.

6. Chunsheng Li., Shihui L., Colin C., et al., An overview: modern techniques for railway vehicle on-board health monitoring systems, Vehicle System Dynamics. 55(7) (2017) 1045–1053.

7. Kutner M., Nachtsheim C., Neter J., Applied Linear Regression Model, Technometrics. 26(4) (2004) 165–171.

8. Zharikov I.A., Rud V.Yu., Rud Yu.V., Terukov E.I., Polarization sensitivity of ZnSe single crystals based structures, Journal of Physics: Conference Series. 1410(1) (2019) 012088.

9. Smirnov K.J., Glinushkin A.P., Long-range night vision camera based on SWIR photocathode, Journal of Physics: Conference Series. 1695(1) (2020) 012090.

10. Kosolapov V.M., Cherniavskih V.I., Zarudny V.A., Mazur K., Konieczna, A., Tseiko, L., Dumacheva E.V., Dumachev D.V. Observations on the Productivity of Breeding Specimens of Urtica dioica L. from European Russian Ecotopes in Comparison with the Breeding Variety under Field Crop Conditions, Agronomy. 12 (2022) 76–82.

11. Myazin N. S., Dudkin V. I., Grebenikova N. M., Davydov R. V., Podstrigaev A. S., Fiber - optical system for governance and control of work for nuclear power stations of low power, Lecture Notes in Computer Science. 11660 (2019) 744–756.

12. Smirnov K.J., Tushavin G.V., Glagolev S.F., Temperature investigations of inp/ingaas based photocathodes," Proceedings of the 2018 IEEE International Conference on Electrical Engineering and Photonics, (EExPolytech-2018), vol. 8564416 (2018) 209-211.

13. Wardal W.J., Mazur K.E., Roman K., Roman M., Majchrzak M., Assessment of Cumulative Energy Needs for Chosen Technologies of Cattle Feeding in Barns with Conventional (CFS) and Automated Feeding Systems (AFS), Energies. 14 (2021) 8584–8592.

14. Kuzmin M. S., Rogov S. A., On the use of a multi-raster input of one-dimensional signals in two-dimensional optical correlators, Computer Optics. 43(3) (2019) 391–396.

15. Yakusheva M. A., Davydov R. V., Isakova D. D., Features of signal absorption fronts of laser radiation in rapid diagnosis of human health. IEEE Proceedings 8th International Conference on Information Technology and Nanotechnology, (ITNT-2022). 23-27 Mat 2022. Samara, Russia. (2022). 145–149.

16. Kazanskiy N.L., Butt M.A., Degtyarev S.A., Khonina S.N., Achievements in the development of plasmonic waveguide sensors for measuring the refractive index. Computer Optics. 44(3) (2020) 295–318.

17. Gregory C., Tests of Equality Between Sets of Coefficients in Two Linear Regressions. Applied Mathematics. 28 (1960) 591–605.

18. Huber P. J., Robust statistics, New York: John Wiley & Sons, 1981.

THE AUTHORS

ARINUSHKINA KSENIYA G. k-arinushkina@mail.ru ORCID: 0000-0002-1156-2071

ADADUROV ALEKSANDR S. adadurov.aleksandr@vniizht-engineering.ru ORCID: 0000-0002-9520-4596 SAVELEV IGOR YU. savelev.igor@vniizht-engineering.ru ORCID: 0009-0002-7511-7740

DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: 0000-0001-9530-4805

Received 26.07.2023. Approved after reviewing 16.08.2023. Accepted 16.08.2023.

Conference materials UDC 535.3 DOI: https://doi.org/10.18721/JPM.163.210

Generation of spatiotemporal optical vortices using Kretschmann setup for transverse magnetic and transverse electric polarizations

A.I. Kashapov^{1,2}, E.A. Bezus^{1,2}, D.A. Bykov^{1,2}, L.L. Doskolovich^{1,2}

¹ Image Processing Systems Institute of RAS – Branch of the FSRC Crystallography and Photonics RAS, Samara, Russia;

² Samara National Research University, Samara, Russia

⊠ ar.kashapov@outlook.com

Abstract. We investigate optical properties of the Kretschmann setup, which contains a dielectric prism and a metal layer and may also contain an additional dielectric layer. We show that the investigated structure allows one to generate a transverse-magnetic- (TM-) polarized spatiotemporal optical pulse comprising an optical vortex using the "conventional" Kretschmann configuration without an additional layer. We also demonstrate that in the case of transverse electric (TE) polarization, the additional dielectric layer is necessary for satisfying the optical vortex generation condition. The results of rigorous numerical simulations demonstrate the possibility of generating spatiotemporal optical vortices with high quality for both TM- and TE-polarizations.

Keywords: Kretschmann setup, optical vortex, optical computing

Funding: This work was funded by the Russian Science Foundation (project 19-19-00514, design and investigation of structures for generating spatiotemporal optical vortices) and was performed within the State Assignment of FSRC Crystallography and Photonics RAS (implementation of the simulation software).

Citation: Kashapov A.I., Bezus E.A., Bykov D.A., Doskolovich L.L., Generation of spatiotemporal optical vortices using Kretschmann setup for transverse magnetic and transverse electric polarizations, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 63–68. DOI: https://doi.org/10.18721/JPM.163.210

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.3 DOI: https://doi.org/10.18721/JPM.163.210

Формирование пространственно-временных оптических вихрей с помощью схемы Кречмана для поперечной магнитной и поперечной электрической поляризаций

А.И. Кашапов^{1,2}, Е.А. Безус^{1,2}, Д.А. Быков^{1,2}, Л.Л. Досколович^{1,2}

¹ ИСОИ РАН – филиал ФНИЦ «Кристаллография и фотоника» РАН, г. Самара, Россия;

² Самарский национальный исследовательский университет имени академика С.П. Королёва, г. Самара, Россия

⊠ ar.kashapov@outlook.com

Аннотация. В работе исследуются оптические свойства схемы Кречмана, которая содержит диэлектрическую призму и металлический слой, но также может содержать дополнительный диэлектрический слой. Показано, что исследуемая структура позволяет формировать пространственно-временной оптический импульс с поперечной магнитной (TM-) поляризацией, содержащей оптический вихрь, используя «классическую»

© Kashapov A.I., Bezus E.A., Bykov D.A., Doskolovich L.L., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

схему Кречмана без дополнительного слоя. Также показано, что в случае поперечной электрической (TE) поляризации дополнительный диэлектрический слой необходим для выполнения условия формирования оптического вихря. Результаты строгого численного моделирования демонстрируют возможность формирования пространственновременных оптических вихрей с высоким качеством для TM- и TE-поляризаций.

Ключевые слова: геометрия Кречмана, оптический вихрь, оптические вычисления

Финансирование: Работа выполнена при поддержке Российского научного фонда (проект 19-19-00514, расчет и исследование структур для формирования пространственно-временных оптических вихрей) и в рамках Государственного задания ФНИЦ «Кристаллография и фотоника» РАН (разработка моделирующего программного обеспечения).

Ссылка при цитировании: Кашапов А.И., Безус Е.А., Быков Д.А., Досколович Л.Л. Формирование пространственно-временных оптических вихрей с помощью схемы Кречмана для поперечной магнитной и поперечной электрической поляризаций // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 63–68. DOI: https://doi.org/10.18721/JPM.163.210

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Spatiotemporal optical vortex pulses (STOV pulses) are a special type of optical signals that have unique properties and are promising for applications in various fields of science and technology. These pulses are defined by the presence of a zero in the amplitude and a discontinuity in the phase in the spatiotemporal domain, which results in an unusual 'doughnut-shaped' spatiotemporal field distribution. Prospective applications of STOV pulses are in such fields as optical communications, optical trapping, and micromanipulation [1-3]. In this regard, active research and development of new methods for STOV generation are ongoing [4-5]. In the present work, the possibility of generating TE- and TM-polarized STOVs using a simple differentiating structure corresponding to the Kretschmann setup is investigated.

Materials and Methods

The method of generating an STOV using a photonic structure performing analog optical differentiation (see the inset in Fig. 1) has been previously studied in [5–7], including the previous works of the present authors [6, 7]. The key issue in generating an STOV with a differentiating structure is the proper selection of the parameters of such a structure. As it was shown in [6, 7], the structures generating STOVs are a subset of differentiating structures having a transfer function (TF) $H_{\rm st}$ (which describes the transformation of a spatiotemporal optical pulse by the diffractive structure) of a special form. Namely, in the vicinity of the operating spatial ($k_{x,0} = k_0 n_{\rm s} \sin \theta$) and angular (ω_0) frequencies, the TF has to be proportional to their weighted sum with coefficients c_x and c_i : $H_{\rm st}(k_{x,\rm inc}, \omega_{\rm inc}) \approx c_x k_{x,\rm inc} + c_i \omega_{\rm inc}$, where $\omega_{\rm inc} = \omega - \omega_0$, $k_{x,\rm inc} = k_0 n_{\rm s} \sin \theta_{\rm inc}$, and $\theta_{\rm inc}$ is the 'local' angle of incidence in the coordinate system associated with the incident optical pulse. It is worth noting that the differentiating structure possesses a reflection zero at $k_x = k_{x,0}$ and $\omega = \omega_0$ (i.e., at $k_{x,\rm inc} = 0$ and $\omega_{\rm inc} = 0$). In [6], the following condition for the STOV generation by differentiating structures was obtained:

$$\arg c_r - \arg c_t = \pm \pi / 2. \tag{1}$$

The structure studied in this work for generating TE- and TM-polarized STOVs is a structure corresponding to the Kretschmann configuration, but optionally possessing an additional dielectric layer, hereafter referred to as the generalized Kretschmann setup (see the inset in Fig. 1). The parameters of the investigated structure, such as the thickness of the metal (h_{met}) and dielectric (h_c) layers, can be calculated for each pair of the wavelength λ (or the angular frequency ω_0) and the angle of incidence θ (or the in-plane wave vector component $k_{v,0}$) using the algorithm described in [7].

© Кашапов А.И., Безус Е.А., Быков Д.А., Досколович Л.Л., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The materials used in the studied structure are SF11 glass (prism), gold (Au) (metal layer), and silicon dioxide (SiO₂) (dielectric coating). The structure is located in air (free space) with refractive index $n_s = 1$. It is also important to note that the dispersion of the listed materials was taken into account in the numerical simulations. The dispersion data were taken from [8].

Results and Discussion

First, let us consider the generation of a TM-polarized STOV. As it was previously noted, the layer thicknesses $h_{\rm met}$ and $h_{\rm c}$ (see the structure in the inset in Fig. 1) are determined from the condition of obtaining a reflection zero at the central wavelength λ and the angle of incidence θ . The structure found in this way provides optical computation of the temporal derivative of the envelope of an incident pulse or of the spatial derivative of the profile of an incident beam (or works as a frequency or a spatial optical filter). It is convenient to find a structure that satisfies the condition of STOV generation (1) by considering the dependence of the difference of arguments of the coefficients c_{i} and c_{i} on wavelength and angle of incidence. Fig. 1, c shows this dependence for the case of TM-polarization, and Fig. 1, a and 1, b show the corresponding layer thicknesses $h_{\rm met}$ and $h_{\rm c}$ of such structures. Let us note that the angle of incidence and wavelength ranges are chosen in such a way that the area, in which the STOV generation condition is fulfilled, is clearly visible. The solid white line in Fig. 1, b indicates the condition $h_c = 0$, i.e., shows the structures corresponding to the conventional Kretschmann setup without an additional layer. It is important to note that the crosshatched area denotes the region, in which the calculated thicknesses of the dielectric coating are negative. In this case, according to the formulas presented in [7], the value π/k_z can be added to the dielectric layer thickness to make it positive, where k_z is the z-component of the wave vector in the dielectric layer. The dotted black line in Fig. 1, c shows, where the STOV generation condition is met, and the solid black line repeats the line in Fig. 1,b, where $h_c = 0$. Therefore, we can see from Fig. 1 that there exist structures in the conventional Kretschmann



Fig. 1. Thicknesses of the metal and the dielectric layers of the studied structure, and the quantity arg (c_x/c_p) , considered as functions of wavelength and angle of incidence, at which zero reflection is obtained (*a*, *b*, *c* and *d*, *e*, *f* for TM- and TE-polarizations, respectively); dotted lines in (*c*), (*f*) show, where the STOV generation condition is met; solid lines in (*b*), (*c*) show the structures in the conventional Kretschmann configuration $(h_c = 0)$; black dots indicate the parameters of the structures considered in the examples. The inset shows the geometry of the structure configuration that enable the STOV generation in reflection. Further, we will consider the example of the structure marked by the black dot in Fig. 1, *a*, *b*, *c* ($\lambda = 407 \text{ nm}$, $\theta = 44^{\circ}$, $h_{\text{met}} = 22.4 \text{ nm}$). Next, we will carry out a similar study for the case of TE-polarization. In order to do this, the

Next, we will carry out a similar study for the case of TE-polarization. In order to do this, the structures in the generalized Kretschmann configuration were also calculated as shown in Fig. 1, *d*, *e*, *f*. However, it should be noted that in this case, the condition of STOV generation is achievable only in the presence of an additional dielectric coating (see Fig. 1,*e*), in contrast to the case of TM-polarization. Let us also note that during the process of material selection for the studied structures in the generalized Kretschmann configuration, other common materials (e.g., BK7 and BAF10 glasses for the prism, Ag and Cu for the metal layer, and Al₂O₃ for the dielectric coating) were considered. However, a combination of materials providing the STOV generation in the case of TE-polarization at zero thickness of the dielectric coating could not be found. Indeed, in the case of TM-polarization, the effect of zero reflectance at zero thickness of the dielectric coating is caused by the excitation of a surface plasmon polariton at the so-called critical coupling condition [9], which, obviously, cannot be achieved in the case of TE-polarization without an additional dielectric layer. For the example considered below, the structure marked with the black dot in Fig. 1, *d*, *e*, *f* ($\lambda = 407$ nm, $\theta = 34^\circ$, $h_{met} = 15.9$ nm, $h_c = 54.3$ nm) was chosen. Consider an example of the structure indicated by the black dots in Fig. 1, *a*, *b*, *c*, which

Consider an example of the structure indicated by the black dots in Fig. 1, *a*, *b*, *c*, which generates a TM-polarized STOV. Fig. 2, *a*, *d* show the amplitude and phase of the TF of the investigated structure, from which it is clear that the TF can be well approximated by the TF of an 'ideal' differentiating filter $H_{st}(k_{x,inc},\omega_{inc}) = c_x k_{x,inc} + c_t \omega_{inc}$, and the condition (1) is fulfilled with a high accuracy. This is confirmed by Fig. 2, *b*, *c* and Fig. 2, *e*, *f*, which show the amplitude and phase of the reflected pulse envelope calculated numerically using the method [10], and the corresponding 'model' (analytically calculated) function [6, 7]. The root-mean-square error (RMSE) of the above mentioned magnitudes, normalized by the maximum amplitude of the reflected pulse, is only 0.17%.



Fig. 2. Amplitudes (*a*) of the transfer function of the structure in the conventional Kretschmann configuration generating a TM-polarized STOV, (*b*) of the envelope of the reflected spatiotemporal optical pulse calculated numerically, (*c*) of the model function [6, 7], and their arguments (*d*), (*e*), (*f*), respectively

Next, we consider an example of the generalized Kretschmann setup generating a TE-polarized STOV. The parameters of the structure were previously shown in Fig. 1, d, e, f by black dots. The TF of this structure is visually very similar to the TF of the structure considered in the previous example, so, for the sake of brevity, we do not show it in Fig. 3. At the same time, it is worth mentioning that the TF of this structure is also well approximated by the TF of an ideal differentiating filter. Fig. 3 shows the amplitude (Fig. 3,a) and phase (Fig. 3,b) of the reflected

TE-polarized spatiotemporal optical pulse envelope. Comparing the results of the numerical simulation with the model function in the same way as in the example above, we obtained that the normalized RMSE of the amplitude of the numerically calculated reflected pulse envelope from the model function amounts to 0.4%.



Fig. 3. Amplitude (a) and phase (b) of the reflected TE-polarized spatiotemporal optical pulse envelope

Conclusion

In this work, we investigated the Kretschmann configuration with an additional dielectric layer (generalized Kretschmann setup) enabling the generation of TM- and TE-polarized spatiotemporal optical vortex pulses. It was obtained that in the case of TM-polarization, it is sufficient to use the structure in the conventional Kretschmann geometry without an additional layer, whereas in the case of TE-polarization, the condition of optical vortex generation can be achieved only when an extra dielectric layer is added. The results of numerical simulations demonstrated a high quality of optical vortex generation by the investigated structure: in both cases (TM- and TE-polarizations), the values of the normalized root-mean-square error do not exceed 0.5%. The obtained results are promising for application in new optical communication and optical computing systems.

REFERENCES

1. Yan L., Gregg P., Karimi E., Rubano A., Marrucci L., Boyd R., Ramachandran S., Q-plate enabled spectrally diverse orbital-angular-momentum conversion for stimulated emission depletion microscopy, Optica. Vol. 2 (10) (2015) 900–903.

2. Djordjevic I.B., Arabaci M., LDPC-coded orbital angular momentum (OAM) modulation for free-space optical communication, Opt. Express. Vol. 18 (24) (2010) 24722–24728.

3. Ng J., Lin Z., Chan C. T., Theory of optical trapping by an optical vortex beam, Phys. Rev. Lett. Vol. 104 (2010) 103601.

4. Chong A., Wan C., Chen J., Zhan Q., Generation of spatiotemporal optical vortices with controllable transverse orbital angular momentum, Nat. Photonics. Vol. 14 (2020) 350–354.

5. Huang J., Zhang J., Zhu T., Ruan Z., Spatiotemporal differentiators generating optical vortices with transverse orbital angular momentum and detecting sharp change of pulse envelope, Laser Photonics Rev. Vol. 16 (5) (2022) 2100357.

6. Doskolovich L.L., Kashapov A.I., Bezus E.A., Bykov D.A., Spatiotemporal optical differentiation and vortex generation with metal-dielectric-metal multilayers, Phys. Rev. A. Vol. 106 (2022) 033523.

7. Kashapov A.I., Bezus E.A., Bykov D.A., Doskolovich L.L., Plasmonic generation of spatiotemporal optical vortices, Photonics. Vol. 10 (2) (2023) 109.

8. Refractive Index Database. URL: https://refractiveindex.info. Accessed Apr. 9, 2022.

9. Zhu T., Zhou Y., Lou Y., Ye H., Qiu M., Ruan Z., Fan S., Plasmonic computing of spatial differentiation, Nat. Commun. Vol. 8 (2017) 15391.

10. Moharam M.G., Pommet D.A., Grann E.B., Gaylord T.K., Stable implementation of the rigorous coupled-wave analysis for surface-relief gratings: enhanced transmittance matrix approach, J. Opt. Soc. Am. A. Vol. 12 (5) (1995) 1077–1086.

THE AUTHORS

KASHAPOV Artem I. ar.kashapov@outlook.com ORCID: 0000-0002-7367-6277

BEZUS Evgeni A. evgeni.bezus@gmail.com ORCID: 0000-0001-7496-8960 BYKOV Dmitry A. bykovd@gmail.com ORCID: 0000-0002-9576-2360

DOSKOLOVICH Leonid L. leonid@ipsiras.ru ORCID: 0000-0001-8649-028X

Received 04.07.2023. Approved after reviewing 18.07.2023. Accepted 19.07.2023.

Conference materials UDC 535 DOI: https://doi.org/10.18721/JPM.163.211

Influence of quantum states imperfections on the error rate in measurement-device-independent quantum key distribution

P.A. Kupriyanov^{1,2,3,4}, N.V. Rudavin^{1,3,4,5}, I.S. Gerasin^{1,2,3,4}, A.A. Dvurechenskiy^{1,2,3,4}, I.V. Petrov^{1,3}, D.D. Menskoy^{1,3}, R.A. Shakhovoy^{1,3,4}

¹QRate, Moscow, Russia;

² Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, Russia;

³ NTI Center for Quantum Communications, National University of Science and Technology MISiS, Moscow, Russia;

⁴ Russian Quantum Center, Skolkovo, Moscow, Russia;

⁵ HSE University, Moscow, Russia

[™] kupriianov.pa@phystech.edu

Abstract. Quantum key distribution (QKD) is a modern technology that allows two legitimate users obtaining a shared cryptographic key completely secure. Unfortunately, real implementations of QKD systems contain vulnerabilities, such that an eavesdropper can still get information about the key. Therefore, QKD protocols generally use privacy amplification procedures that reduce the size of the key depending on the level of errors that are generally assumed to be caused by a non-legitimate user. So, the quantum bit error rate (QBER) becomes an important parameter significantly affecting the rate of key distribution. In this work, we investigate the influence of quantum states imperfections on the QBER in the measurement-device-independent QKD protocol with time-bin encoding. We proposed a theoretical model that describes imperfect states, and derived formulas for the dependence of the error level on the degree of imperfection. We also conducted an experiment, the results of which are in good agreement with the predictions of the theory.

Keywords: measurement-device-independent quantum key distribution, imperfect states, time-bin phase-encoding

Funding: The study was commissioned by JSCo RZD.

Citation: Kupriyanov P.A., Rudavin N.V., Gerasin I.S., Dvurechensky A.P., Petrov I.V., Menskoy D.D., Shakhovoy R.A., Influence of quantum states imperfections on the error rate in measurement-device-independent QKD, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 69–74. DOI: https://doi.org/10.18721/JPM.163.211

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Kupriyanov P.A., Rudavin N.V., Gerasin I.S., Dvurechenskiy A.A., Petrov I.V., Menskoy D.D., Shakhovoy R.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 535 DOI: https://doi.org/10.18721/JPM.163.211

Влияние неидеальностей приготовления квантовых состояний на уровень ошибок в детектор-независимом квантовом распределении ключей

П.А. Куприянов^{1,2,3,4}, Н.В. Рудавин^{1,3,4,5}, И.С. Герасин^{1,2,3,4}, А.А. Двуреченский^{1,2,3,4}, И.В. Петров^{1,3}, Д.Д. Менской^{1,3}, Р.А. Шаховой^{1,2,3,4}

¹ КуРэйт, Москва, Россия;

² Московский физико-технический институт, Московская область, г. Долгопрудный, Россия;

³ НТИ Центр квантовых коммуникаций, Национальный исследовательский технологический университет «МИСИС», Москва, Россия;

⁴ Российский Квантовый центр, Сколково, Москва, Россия;

⁵ Национальный исследовательский университет «Высшая школа экономики», Москва, Россия

⊠ kupriianov.pa@phystech.edu

Аннотация: Квантовое распределение ключей (КРК) — современная технология, позволяющая двум законным пользователям безопасно получить общий криптографический ключ. К сожалению, реальные системы КРК содержат уязвимости, так что у перехватчика появляется потенциальная возможность получить информацию о ключе. Поэтому протоколы КРК обычно используют процедуры усиления секретности, которые уменьшают размер ключа в зависимости от уровня ошибок, которые, как правило, считаются вызванными нелегитимным пользователем. Таким образом, важным параметром, существенно влияющим на скорость распределения ключей, становится квантовый уровень битовых ошибок (QBER). В этой работе мы исследуем влияние несовершенства квантовых состояний на QBER в протоколе детектор-независимого КРК на фазово-временном кодировании. Мы предложили теоретическую модель, которая описывает неидеальные состояния, и вывели формулы зависимости уровня ошибок от степени неидеальности. Также был проведен эксперимент, результаты которого хорошо согласуются с предсказаниями теории.

Ключевые слова: квантовое распределение ключей, неидельность приготовления состояний, фазово-временное кодирование

Финансирование: Исследовательская работа выполнена по заказу ОАО «РЖД».

Ссылка при цитировании: Куприянов П.А., Рудавин Н.В., Герасин И.С., Двуреченский А.А., Петров И.В., Менской Д.Д., Шаховой Р.А., Влияние неидельностей квантовых состояний на уровень ошибок в детектор-независимом КРК // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 69–74. DOI: https://doi.org/10.18721/JPM.163.211

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Measurement-device-independent QKD protocol [1] is resistant to all detector-side attacks. The main feature of this protocol is that two transmitters (Alice and Bob), who want to distribute a secret key, prepare quantum states and send them to an untrusted central node (Charlie). Quantum states are entangled on the beam splitter and then Charlie performs Bell state measurement. Such measurements can give an eavesdropper information only about the mutual correlation of transmitters bits, not about values. This allows the protocol to eliminate all vulnerabilities associated with measurement devices. But there is still a gap between theory and practice that can be used by an eavesdropper to obtain information about the secret key. One of the vulnerabilities is the imperfect preparation of quantum states. In the article [2] QKD on polarization encoding with non-ideal sources was experimentally demonstrated.

© Куприянов П.А., Рудавин Н.В., Герасин И.С., Двуреченский А.П., Петров И.В., Менской Д.Д., Шаховой Р.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. Our experimental setup uses time-bin encoding [3], for which the intensity modulator cuts out short pulses from the continuous laser. If Alice prepares "0" in the X-basis, then equal pulses are created in both time slots (we refer them to E- and L-pulses, i.e., early and late). In case of sending "1", it is necessary to additionally apply the phase π between the pulses. For the X-basis, there is always a slight intensity difference between the pulses in different time slots as well as deviation of the phase difference from 0 or π . Preparing states in the Z-basis, intensity modulator creates a pulse in only one of the two time slots. Here, non-ideality is related to the fact that "empty" time slot still contains some non-zero intensity. These imperfections lead to false clicks of detectors and to an increase in quantum bit error rate (QBER).

Materials and Methods

We first considered the problem of the interference of weak coherent pulses on a beam splitter. Alice and Bob send *L*-pulses with intensities s_a and s_b , respectively, while the time slot corresponding to the *E*-pulse gets noise intensities ζ_a and ζ_b , caused by imperfect operation of the amplitude modulator. The mutual state of Alice and Bob can be thus written as

$$\left|Z_{1}Z_{1}\right\rangle_{ab} = \left|\sqrt{\zeta_{a}}e^{i\varphi_{a}}\right\rangle_{a_{E}}\left|\sqrt{s_{a}}e^{i\varphi_{a}}\right\rangle_{a_{L}}\left|\sqrt{\zeta_{b}}e^{i\varphi_{b}}\right\rangle_{b_{E}}\left|\sqrt{s_{b}}e^{i\varphi_{b}}\right\rangle_{b_{L}}.$$
(1)

Indices a and b denote states of Alice and Bob respectively, indices E and L denote early and late time modes.

As is known, complex amplitudes representing coherent pulses at the input of the beam splitter are added and subtracted at the output ports [3]. Thus, after passing through quantum channels with losses t_a and t_b respectively and after interference at the beam splitter, the states will have the form:

$$\begin{aligned} \left| Z_{1} Z_{1} \right\rangle_{cd} &= \left| e^{i\varphi_{a}} \sqrt{\frac{t_{a} \zeta_{a}}{2}} + e^{i\varphi_{b}} \sqrt{\frac{t_{b} \zeta_{b}}{2}} \right\rangle_{c_{E}} \right| e^{i\varphi_{a}} \sqrt{\frac{t_{a} S_{a}}{2}} + e^{i\varphi_{b}} \sqrt{\frac{t_{b} S_{b}}{2}} \right\rangle_{c_{L}} \otimes \\ &\otimes \left| e^{i\varphi_{a}} \sqrt{\frac{t_{a} \zeta_{a}}{2}} - e^{i\varphi_{b}} \sqrt{\frac{t_{b} \zeta_{b}}{2}} \right\rangle_{d_{E}} \right| e^{i\varphi_{a}} \sqrt{\frac{t_{a} S_{a}}{2}} - e^{i\varphi_{b}} \sqrt{\frac{t_{b} S_{b}}{2}} \rangle_{d_{L}}. \end{aligned}$$

$$(2)$$

Indices c and d denote output ports of beam splitter.

We calculated the gain corresponding to the clicking of detectors in orthogonal time modes. When sending the same bits in the Z-basis, such events will lead to errors:

$$Q_{s_{a}s_{b}}^{Z,err} = y_{s_{a},s_{b}} y_{\zeta_{a},\zeta_{b}} \left(2y_{s_{a},s_{b}} y_{\zeta_{a},\zeta_{b}} - 2y_{\zeta_{a},\zeta_{b}} I_{0}(x_{s_{a},s_{b}}) + I_{0}(x_{s_{a},s_{b}} - x_{\zeta_{a},\zeta_{b}}) - 2y_{s_{a},s_{b}} I_{0}(x_{\zeta_{a},\zeta_{b}}) + I_{0}(x_{s_{a},s_{b}} + x_{\zeta_{a},\zeta_{b}}) \right),$$
(3)

where $y_{\nu,\mu} = (1 - p_{dc})e^{-\eta(t_d\nu + t_b\mu)/4}$, $x_{\nu,\mu} = (\eta/2) \cdot \sqrt{t_d t_b \nu \mu}$, and $I_0(x)$ is a modified Bessel function of the first kind. In our model, we assume that probability of dark counts p_{dc} and efficiency η are the same for all detectors.

Similarly, considering the sending of different bits in the Z-basis, we calculated the gain for correct events $Q^{Z,corr}_{s_{\alpha},s_{0}}$.

$$Q_{s_{a}s_{b}}^{Z,corr} = y_{\zeta_{a},s_{b}} y_{s_{a},\zeta_{b}} \left(2y_{\zeta_{a},s_{b}} y_{s_{a},\zeta_{b}} - 2y_{s_{a},\zeta_{b}} I_{0}(x_{\zeta_{a},s_{b}}) + I_{0}(x_{\zeta_{a},s_{b}} - x_{s_{a},\zeta_{b}}) - 2y_{\zeta_{a},s_{b}} I_{0}(x_{s_{a},\zeta_{b}}) + I_{0}(x_{\zeta_{a},s_{b}} + x_{s_{a},\zeta_{b}}) \right),$$
(4)

QBER in Z-basis can be calculated with the formula:

$$E_{s_a,s_b}^{Z} = \frac{e_d Q_{s_a,s_b}^{Z,corr} + (1 - e_d) Q_{s_a,s_b}^{Z,err}}{Q_{s_a,s_b}^{Z,corr} + Q_{s_a,s_b}^{Z,err}},$$
(5)

71

where e_d denotes the probability of error in the detection system, which can be caused by distortions in the quantum channel that were not considered in our model.

In the X-basis, the imperfect phase between the E- and L-pulses leads to additional errors. If we do not accurately select the voltage supplied to the phase modulator, an erroneous phase difference $\delta \Theta_{ab}$ appears. In a similar way, we calculated QBER for the X-basis:

$$Q_{\gamma_{a},\gamma_{b}}^{X,err} = 2y_{\gamma_{a},\gamma_{b}}y_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}\left(y_{\gamma_{a},\gamma_{b}}y_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}} - y_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}I_{0}(x_{\gamma_{a},\gamma_{b}}) - y_{\gamma_{a},\gamma_{b}}I_{0}(x_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}) + I_{0}\left(\sqrt{x_{\gamma_{a},\gamma_{b}}^{2} + x_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}^{2} - 2x_{\gamma_{a},\gamma_{b}}x_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}\cos\delta\Theta_{ab}}\right)\right),$$

$$(6)$$

$$Q_{\gamma_{a},\gamma_{b}}^{X,corr} = 2y_{\gamma_{a},\gamma_{b}}y_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}\left(y_{\gamma_{a},\gamma_{b}}y_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}} - y_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}I_{0}(x_{\gamma_{a},\gamma_{b}}) - y_{\gamma_{a},\gamma_{b}}I_{0}(x_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}) + I_{0}\left(\sqrt{x_{\gamma_{a},\gamma_{b}}^{2} + x_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}^{2} + 2x_{\gamma_{a},\gamma_{b}}x_{\gamma_{a}+\delta\gamma_{a},\gamma_{b}+\delta\gamma_{b}}\cos\delta\Theta_{ab}}\right)\right),$$

$$(7)$$

$$E_{\gamma_a,\gamma_b}^X = \frac{e_d Q_{\gamma_a,\gamma_b}^{X,corr} + (1 - e_d) Q_{\gamma_a,\gamma_b}^{X,err}}{Q_{\gamma_a,\gamma_b}^{X,corr} + Q_{\gamma_a,\gamma_b}^{X,err}}.$$
(8)

Here γ denotes intensity in the Early time slot in X-basis, $\delta\gamma$ denotes the difference between intensities in Late and Early time slots.

In order to verify our model, we set up an experiment in which we measured QBER depending on the level of noise. Since the formula (3) includes detector parameters such as efficiency and probability of dark count, it was necessary to conduct auxiliary experiment, in which the dependence of the number of detector clicks N_d on the power of weak coherent pulses was investigated. This dependence is described by the formula:

$$N_{d} = \frac{(1 - (1 - p_{dc})e^{-\eta\mu})N_{t}}{1 + (1 - (1 - p_{dc})e^{-\eta\mu})f\tau},$$
(9)

where f is the pulse repetition frequency, N_t is the number of pulses, that were sent during the time t. Fitting the experimental data we found parameters of detectors: probability of dark count and efficiency (Fig. 1).



Fig. 1. Dependence of clicks on the power of pulse
The transmission function of the intensity modulator from the voltage is the cosine shifted up along the ordinate axis [5]. By changing the modulator bias, we can displace the operating point and vary the ratio of noise power to signal pulse power. For each bias value, we sent to Charlie pattern of the same *E*-pulses, scanned the detector phase (Fig. 2) by changing the position of the detector strobe relative to the arrival time of the pulses. From the graph, we obtained values N_s and N, i.e., the number of clicks corresponding to the signal pulses and the number of noise clicks, respectively. N_s is equal to the maximum number of clicks. N is equal to the average number of clicks that are shifted by half a period from the maximum, since the orthogonal detectors are shifted relative to each other by half a period. Then, using the calibration graph of the detector, we found the power values *s* and ζ that correspond to these numbers. Selecting shifts and attenuation in such a way that the signal pulse power and the noise power are equal for both transmitters, we have measured averaged QBER in key generation mode.



Fig. 2. Dependence of clicks on the arrival time of pulse Orange line denotes moving average



Fig. 3. Dependence of E_{s_a,s_b}^Z on the noise-to-signal ratio $e_d = 4.2 \pm 0.2\%$

Results and Discussion

Considering the interference of weak coherent pulses, we obtained dependences of the error rates on the imperfections of the preparation of states. The plot of this dependence for the Z-basis and experimental data are presented in Fig. 3.

The parameter e_d for the theoretical curve was chosen to minimize the deviation from the experimental data. We can say that e_d limits the value of QBER that we can achieve under the condition of perfect preparation of states. The factors affecting the parameter e_d include distortion in the optical fiber, intersymbol interference [6], errors in the polarization adjustment system.

Conclusion

In this work, we derived formulas that allow estimating the error rate in the MDI-QKD protocol. These formulas can be used to solve the inverse problem: to find the characteristics of experimental equipment that allow us not to exceed a certain QBER value. We also proposed an experimental way to evaluate the effects of error parameter e_d and non-ideal states on QBER.

REFERENCES

1. Gisin N., Ribordy G., Tittel W., Zbinden H., Quantum cryptography. Reviews of modern physics, 74.1 (2002) 145.

2. Tang Z., Wei K., Bedroya O., Qian L., Lo H. K., Experimental measurement-device-independent quantum key distribution with imperfect sources. Physical Review A, 93.4 (2016) 042308.

3. Chen H., An X. B., Wu J., Yin Z. Q., Wang S., Chen W., Han Z. F., Hong–Ou–Mandel interference with two independent weak coherent states. Chinese Physics B 25.2 (2016) 020305.

4. Tang G.Z., Sun S.H., Chen H., Li C.Y., Liang L.M., Time-bin phase-encoding measurementdevice-independent quantum key distribution with four single-photon detectors. Chinese Physics Letters 33.12 (2016) 120301.

5. Thomaschewski M., Bozhevolnyi S.I., Pockels modulation in integrated nanophotonics. Applied Physics Reviews, 9.2 (2022) 021311.

6. Yoshino K.I., Fujiwara M., Nakata K., Sumiya T., Sasaki T., Takeoka M., Tomita A., Quantum key distribution with an efficient countermeasure against correlated intensity fluctuations in optical pulses. npj Quantum Information 4.1 (2018) 8.

THE AUTHORS

GERASIN Ilya S. i.gerasin@goqrate.com ORCID: 0000-0001-5084-7056 PETROV Ivan V. i.petrov@goqrate.com ORCID: 0000-0002-5422-2886

MENSKOY Daniil D.

d.meskoy@goqrate.com

SHAKHOVOY Roman A.

r.shakhovoy@goqrate.com ORCID: 0000-0003-2750-0518

RUDAVIN Nikita V. n.rudavin@goqrate.com ORCID: 0000-0003-0264-5710

KUPRIYANOV Pavel A. p.kupriyanov@goqrate.com ORCID: 0009-0006-1663-6806

DVURECHENSKIY Alexander P. a. dvurechenskiy@goqrate.com ORCID: 0009-0008-7391-0079

Received 06.07.2023. Approved after reviewing 11.09.2023. Accepted 11.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 621.373.826 DOI: https://doi.org/10.18721/JPM.163.212

Design and simulation of an optical system of high-power fiber-coupled laser module

E.V. Kadigrob⊠, A.V. Fomin, S.R. Usmanov

Russian Federal Nuclear Center – Zababakhin All – Russia Research Institute of technical Physics, Snezhinsk, Russia

^{III} dep5@vniitf.ru

Abstract: The paper presents the simulation results for an optical system based on a high-power and high-brightness laser module. The module design implies spatial and polarization combining of beams from 24 single-emitter laser diodes. The theoretical design and computational simulation were conducted for the fiber-coupled optical system with the fiber of 200/225 μ m in diameter and numerical aperture of 0.22. The coupling efficiency is 89% which correlates with the results of experiments with the laboratory module prototype.

Keywords: laser-based diode module, coupling, optical system, spatial combining of beams, polarization combining of beams

Citation: Kadigrob E.V., Fomin A.V., Usmanov S.R., Design and simulation of an optical system of high-power fiber-coupled laser module, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 75–80. DOI: https://doi.org/10.18721/JPM.163.212

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.373.826 DOI: https://doi.org/10.18721/JPM.163.212

Расчет и моделирование оптической системы высокомощного лазерного модуля с волоконным выводом излучения

Е.В. Кадигроб[⊠], А.В. Фомин, С.Р. Усманов

Российский федеральный ядерный центр – Всероссийский научно-исследовательский институт технической физики им. академика Е. И. Забабахина, г. Снежинск, Россия

^{III} dep5@vniitf.ru

Аннотация. В работе представлены результаты моделирования оптической системы лазерного модуля с высокими показателями мощности и яркости излучения. Произведен теоретический расчет и компьютерное моделирование оптической системы ввода излучения в волокно диаметром 200/225 мкм с числовой апертурой 0,22. Эффективность ввода лазерного излучения в волокно составляет 89%.

Ключевые слова: лазерный диодный модуль, ввод лазерного излучения в волокно, оптическая система, пространственное объединение излучения, поляризационное объединение излучения

Ссылка при цитировании: Кадигроб Е.В., Фомин А.В., Усманов С.Р. Расчет и моделирование оптической системы высокомощного лазерного модуля с волоконным выводом излучения // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 75–80. DOI: https://doi.org/10.18721/JPM.163.212

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

[©] Kadigrob E.V., Fomin A.V., Usmanov S.R., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Introduction

Fiber-coupled laser modules (LMs) are mostly used as highly efficient sources for high-power fiber and solid-state laser pumping and also can be applied in material processing, medical equipment, and scientific studies.

The development and enhancement of laser technologies imposes the need in continuous power growth of fiber-coupled laser modules.

Both single-emitter laser diodes (LDs) and laser diode bars (LDBs) can be applied as radiation sources in laser modules. LDBs have the advantage over LDs due to the small number of elements and sufficiently high output power [1]. The principal constraining factor during LDB coupling is implied by the high degree of radiation astigmatism. Radiation reconfiguration systems based on microoptic elements (mirrors, cylindrical lenses, and prisms) are utilized to compensate the beam asymmetry along the fast and slow axes [1, 2]. Complex microoptics requires high shape accuracy, high surface quality and minimization of transition regions between the elements. In combination with significant mounting efforts it causes high cost of such transducers and is appropriate only for systems with a constrained number of LDBs. Besides, LDBs have another disadvantage: the bar 'smile' affects the radiation quality and increases the focused beam size.

LD-based modules are the most preferred radiation sources due to their high capacity, brightness, and efficiency. The opportunity to use optical elements for each emitter enables to form high-quality radiation with a dense beam packing, while the optimal design of the focusing system provides high coupling efficiency. The references [3, 4] present the developed LM based on spatial combining of beams from six or seven single-emitter LDs. In the given framework the above designs were applied as a prototype to develop a module with the power of > 350 W. Besides the spatial combining, polarization beam combining was also used. The work presents the computational simulation results for the module optical design.

Optical system design

Table 1 shows the LDs parameters for the task to develop a LM over 350 W with 200 $\mu m/NA$ 0.22 fiber.

Table 1

Parameters at 22 A and 25 °C	Value
Operating voltage, V	1.65
Laser radiation power, W	21
Center wavelength, nm	915 ± 5
Polarization (TE)	98%
Emitter width, µm	190
Beam divergence at the level of 1/e ² along the fast axis, °	27.4
Beam divergence at the level of 1/e ² along the slow axis, °	5.5

Laser diodes characteristics

Obtaining a high-quality beam corresponding to the fiber parameters is the key challenge during spatial combining of beams from single-emitter LDs.

Beam parameter product (BPP) is used to evaluate the beam quality:

$$BPP = \frac{\theta \cdot D}{2},$$

where *D* is the waist width, and θ is the beam divergence. BPPs of the selected diodes radiation are BPP_{FA} = 0.42 mm·mrad and BPP_{SA} = 8.6 mm·mrad for the fast and slow axes, respectively.

© Фомин А.В., Усманов С.Р., Кадигроб Е.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The limit number of diodes in the spatial combining of beams design is restricted by the fiber BPP:

$$BPP_f = \frac{\theta_f \cdot D_f}{2} = 22 \quad \text{mm} \cdot \text{mrad},$$

where D_f is the fiber core diameter, and θ_f is the fiber numerical aperture. The maximum LD number along the fast and slow axes cannot exceed the following value in the spatial combining of beams design in case of complete beam coupling with the fiber:

$$N_{FA,SA} = \frac{BPP_f}{2BPP_{FA,SA}} \gamma_{FA,SA},$$

where $\gamma_{FA,SA}$ is the filling factor along the fast and slow axes, respectively. The choice of 1 LD along the slow axis and 12 LDs along the fast axis completely satisfies the requirement.

Besides spatial combining, polarization combining of beams of two LD arrays with 12 pieces in each (Fig. 1) is used to increase the output power of the module.

LDs are stepwise positioned with a shift of 0.5 mm in vertical plane and of 4.5 mm in horizontal plane.

The beams from each LD (Fig. 1, item 1) are collimated using cylindrical lenses (Fig. 1, item 2), and then, reflected from the mirrors (Fig. 1, item 4), they are formed in a combined beam, consisting of vertical beams. The polarization direction of the second LD array is changed by 90° using phase half-wave plate (Fig. 1, item 5). The PBS (Fig. 1, item 7) combines the radiation with two perpendicular polarization directions. Finally, a specially designed focusing system (Fig. 1, items 8, 9) enables the formed beam to couple into the fiber (Fig. 1, item 10).



Fig. 1. Basic optical design of the laser module: LD *1*, acylindrical micro lenses *2*, cylindrical lenses *3*, rotating mirrors *4*, half-wave plate *5*, rotating mirror *6*, polarized beam splitter (PBS) *7*, focusing lenses *8*, *9*, and optical fiber *10*

Results and Discussion

The following expression describes the laser beam spatial parameters at the output of the ideal optical system [5]:

$$\alpha = \frac{z'_k}{z_k} = \frac{z'_p}{z_p} = \left(\frac{\theta}{\theta'}\right)^2 = \left(\frac{r'_p}{r_p}\right)^2 = \frac{f'^2}{z_k^2 + z_p^2},$$

2

where α is the coefficient of the longitudinal increase of the laser optical system; z_k , z'_k are the confocality parameters of the input and output beams; $z_k = r_p/\theta$, $z'_k = r'_p/\theta'$; z_p , z'_p are the segments, determining the waist plane position of the initial and transformed beam relative to the front and back element focuses; and $2r_p$, $2r'_p$, θ , θ' are the beam diameter in the waist cross-section and the angle divergence before and after the transformation, respectively. The given ratio was used to design the overall parameters of the optical system with the required output beam parameters corresponding to the fiber parameters.

Computational simulation was used to analyze and optimize the optical system with the consideration of spherical aberrations and beam defocusing of each emitter.

Two orthogonal lenses provide successive fast and slow axis radiation collimation. The acylindrical fast axis collimation lens (FAC lens) with a focal length of 0.3 mm is used for beam pattern narrowing along the fast axis, and cylindrical slow axis collimation lens (SAC lens) with a focal length of 13 mm is used for laser radiation collimation along the slow axis (Fig. 2).



Fig. 2. Fast and slow axis collimation of single-emitter laser diode (a):
LD 1; FAC lens 2, SAC lens 3; the beam profile after FAC and SAC lenses (b), output divergence just after fast-axis (c) and slow-axis (d) collimation

Table 2 demonstrates the parameters of the single-emitter LD after the collimation.

Table 2

Single emitter parameters after the collimation

Beam parameter	Fast axis	Slow axis
Beam width, mm	0.31	2.5
Divergence half-angle, °	0.127	0.42

The spatial combining of beams includes the LD beams reflection by the mirrors and their alignment above each other in the vertical plane. During the polarization combining of two arrays radiation, the power increases approximately twice without any changes in the geometry parameters of the beam. The combined beam sizes after the PBS are 5.9 mm and 2.6 mm along the fast and slow axes, respectively.

The search for optimal overall parameters of focusing lenses was performed in order to provide efficient coupling of the beam into the fiber. The maximum radiation power in the fiber and the correspondence of the waist dimensions and the beam divergence to the fiber parameters were taken into account when selecting the focal length. The computational simulation results showed the optimal focal lengths of 20 mm for the fast axis and of 9.3 mm for the slow one. The lenses being used, the laser radiation completely couples with 200 μ m/NA 0.22 fiber. Table 3 presents the parameters of the focusing spot in the waist plane.

Table 3

r r r r r r r r r r r r r r r r r r r			
Beam parameter	Fast axis	Slow axis	
Beam width, µm	104	130	
Divergence half-angle, °	8.6	8.1	

Beam parameters of focusing spot

Fig. 3 demonstrates the computational simulation results.



Fig. 3. 3D model of the optical system with ray tracing (a), the beam profile of focusing spot (b), output divergence just after fast-axis (c) and slow-axis (d) focusing, radiance distribution of focusing spot for the fast (e) and slow (f) axis

Conclusion

The simulated results show that the beam fully couples with the fiber in terms of the size and divergence. The coupling efficiency is 89% considering the Fresnel loss, and the losses on the mirrors and the polarized beam splitter. The given optical system was designed as a laser module prototype coupled with the fiber 200/225 μ m with a numerical aperture of 0.22, the coupling efficiency being of 83%. The CW output power of the module reached 368 W with the brightness of 7.7 MW/cm²·sr in the continuous operation mode.

REFERENCES

1. Wang J.W., Yuan Z.B., Zhang Y.X., Packaging of semiconductor laser arrays. Inner Report, (12) (2011) 12–17.

2. Bachmann F., Loosen P., Poprawe R., High Power Diode Lasers. Technology and Applications, Springer Science+Business Media, LLC, 2007, 539.

3. Kadigrob E.V., Usmanov S.R., Fomin A.V., Laser module and manufacturing method. RF Patent 2688888, IPC H01S 5/022, G02B 6/42, G02B 27/16 (2006.01), State Corporation Rosatom, FSUE "RFNC-VNIITF named after Academ. E.I. Zababakhin" Bulletin, (in Russian) (15) (2019).

4. Ignatev A.N., Kadigrob E.V., Usmanov S.R., Fomin A.V., Fiber coupled laser module with brightness exceeding 10 MW/cm²·sr. Technical Physics, (2022) (4) (92) 616–619.

5. **Pakhomov I.I., Tsybulya** A.B., Design of optical systems for laser devices, Moscow: Radio i svyaz [Radio and Communication], 1986, 152 p (in Russian).

THE AUTHORS

KADIGROB Ekaterina V. dep5@vniitf.ru

USMANOV Sergei R. dep5@vniitf.ru

FOMIN Alexei V. dep5@vniitf.ru

Received 06.07.2023. Approved after reviewing 07.08.2023. Accepted 08.08.2023.

Conference materials UDC 535.8 DOI: https://doi.org/10.18721/JPM.163.213

Features of the construction photonic tensor cores for neural networks

N.I. Popovskiy¹[™], V.V. Davydov^{1, 2}, V.Yu. Rud ^{3, 4}

¹ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

² Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

³ Ioffe Institute, St. Petersburg, Russia;

⁴All-Russian Research Institute of Phytopathology, Moscow Region, Russia

^{III} nikitanikita24@mail.ru

Abstract. The demand for efficient and high-performance computing systems has led to the development of photonic-based technologies for machine learning. One of the key components of these systems is the photonic tensor core, which performs matrix operations at high speed and low power consumption. In this article, we review the features of photonic tensor cores and their construction for use in neural networks. We discuss the advantages of photonic-based technologies over traditional electronic-based systems, as well as the challenges in their implementation. We also highlight recent advancements in the development of photonic tensor cores for machine learning applications.

Keywords: photonic tensor cores, neural networks, optical computing, photonics, machine learning, deep learning, data processing

Citation: Popovskiy N.I., Davydov V.V., Rud V.Yu., Features of the construction photonic tensor cores for neural networks, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 81–86. DOI: https://doi.org/10.18721/JPM.163.213

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.8 DOI: https://doi.org/10.18721/JPM.163.213

Особенности построения фотонных тензорных ядер для обучения нейронных сетей

Н.И. Поповский¹[№], В.В. Давыдов^{1,2}, В.Ю. Рудь^{3,4}

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М. А. Бонч-Бруевича, Санкт-Петербург, Россия;

² Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;

³ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

⁴ Всероссийский научно-исследовательский институт фитопатологии, Московская область, Россия

nikitanikita24@mail.ru

Аннотация. Спрос на эффективные и высокопроизводительные вычислительные системы привел к разработке основанных на фотонике технологий машинного обучения. Одним из ключевых компонентов этих систем является фотонное тензорное ядро, которое выполняет матричные операции с высокой скоростью и низким энергопотреблением. В этой статье мы рассмотрим особенности фотонных тензорных ядер и их конструкцию для использования в нейронных сетях. Мы обсуждаем преимущества технологий, основанных на фотонике, перед традиционными электронными системами, а также проблемы, связанные с их внедрением. Мы также подчеркиваем недавние достижения в разработке фотонных тензорных ядер для приложений машинного обучения.

© Popovskiy N.I., Davydov V.V., Rud V.Yu., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: фотонные тензорные ядра, нейронные сети, оптические вычисления, фотоника, машинное обучение, глубокое обучение, обработка данных

Ссылка при цитировании: Поповский Н.И., Давыдов В.В., Рудь В.Ю. Особенности построения фотонных тензорных ядер для обучения нейронных сетей // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 81–86. DOI: https://doi.org/10.18721/JPM.163.213

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The challenge of emulating brain functions continues to fascinate and inspire human ingenuity, and has also proven to be of practical value to modern societies. One approach that has gained popularity in Artificial Intelligence (AI) is Machine Learning (ML) through the use of neural networks (NN). This involves training a system to autonomously classify and make decisions about new data, and once trained, the NN can be utilized to recognize and categorize patterns and objects. This is applied in various areas of science and technology, especially those related to space systems [1-5].

Neural networks (NNs) typically consist of multiple layers of interconnected neurons or nodes, and the configuration of each layer, as well as the interconnectivity of the network as a whole, is crucial for the network's ability to perform its intended task. The processing within a NN's connected layers relies heavily on vector matrix math operations, involving the multiplication of large matrices of input data and weights based on the training data. As the complexity and depth of NNs increase, their ability to perform these large matrix multiplications efficiently and quickly requires substantial bandwidth and low latency. This is extremely important in many cases. For example, for fiber-optic communication lines (FOCL) in systems of radar stations, when it is necessary to accompany a large number of objects, these functions are in great demand [6-8].

Since the beginning of the computing era, researchers have been exploring efficient methods to multiply matrices due to its ubiquity in various applications, including neuromorphic computing. Developing a platform that can perform matrix multiplication faster and more energy-efficiently is crucial in solving linear algebraic problems like inverting matrices, solving linear equations, and finding determinants. In fact, even fundamental graph algorithms can be hindered by slow matrix multiplication. This creates a number of problems in information transmission systems with intelligent processing [4, 9-11].

Matrix operations on a general-purpose processor are performed serially and require continuous access to cache memory, which creates a bottleneck known as the "von Neumann bottleneck". Specialized architectures, such as Graphic Process Units (GPUs) and Tensor Process Units (TPUs), have been developed to reduce this bottleneck and enable advanced machine learning models. These architectures are designed with domain-specific optimizations, such as parallel processing for convolutions or Matrix-Vector Multiplications (MVM), allowing for the deployment of systolic algorithms unlike CPUs [2, 9, 12, 13].

The advantages of using electromagnetic signals may be limited due to the need for conversion by optoelectronic and electro-optical methods, as well as repeated access to digital and non-volatile memory, which can lead to slower operation and high energy consumption. In this regard, the use of heterogeneously integrated optimized photonic memory, which can store information in a non-volatile state, is a great advantage, especially for projects using neural networks, where weights are rarely updated.

Method of constructing photonic tensor cores

To achieve this functionality, a multi-state photonic memory device has been developed, in which a set of cells are located between two resonant rings to select the appropriate wavelength at the input and output. Once the memory states are set in this photonic core, it is possible to perform the calculation functions completely passively. Selective recording is achieved by changing the phase of a certain number of cells that have been deposited on the waveguides by local

[©] Поповский Н.И., Давыдов В.В., Рудь В.Ю., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

electrostatic heating, which leads to crystallization or amorphization and, accordingly, a change in the modal refractive index of the waveguide in a reversible process.

The dot product mechanism multiplies the i-th row of the input matrix A by the *j*th column of the kernel B. The input matrix is represented in Fig. 1 by WDM signals, which are modulated using high-speed modulators such as Mach-Zehnder [14]. The column of the core matrix is loaded into the photonic memory with a given weight state. The interaction of light matter with memory leads to a change in the phase of the input signals, which are spectrally filtered by micro-ring resonators, weighed using amplitude modulation and subjected to element-wise multiplication. The resulting products of the elements are summed using a photodetector that performs the MAX (Dij) operation. Quantization is used in the electrical absorption circuit.



Fig. 1. Block diagram of the photonic tensor cores

In our approach to the implementation of photonic neural networks, micro-rings are used only for passive selection of the frequency that will be modulated by photonic storage devices, unlike other implementations that use actively tuned micro-ring modulators for filtering [14, 15]. This allows us to control inter-channel crosstalk more precisely and potentially increases the number of wavelengths in the multiplexing scheme with dense wavelength separation without affecting the absorption coefficient and the associated fluctuations in the quality coefficient. In addition, our architecture includes programmable photonic storage devices with a low loss level and multiple states for each pair of micro-ring resonators, which are able to store information without static power consumption and do not significantly contribute to total losses.

The $Ge_2Sb_2Se_5$ material was chosen for the implementation of photonic memory cores, since in the amorphous state it has a wide area of transparency for telecommunication wavelengths and can be used to create high-performance non-volatile photonic storage devices with multiple states. This material has very low optical absorption, which makes it promising for multi-state devices and avoids the use of high-power lasers and extremely low noise detectors. To set the extracted weights, we use electrothermal switching, which reversibly records each memory state by selective transition between amorphous and crystalline phases. To do this, heat is supplied to the material from the outside using Joule heating, which is activated by successively supplying various pulses to the cell through connected devices.

To minimize losses, the choice of material and the location of the electrodes in relation to the waveguide were specially developed, which allowed the use of metal with excellent thermal properties and low optical losses. Adjustment of the frequency and intensity of electrical pulses applied to tungsten electrodes is necessary to provide the necessary thermal energy for phase switching in $Ge_2Sb_2Se_5$. To create an effective resistive heater that will not create losses, it is possible to use doped silicon, silicide, indium-tin oxide or graphene electrodes that will be located next to the waveguide. The change in the absorption coefficient during the phase transition is investigated using light signals associated with the memory of the phase transition.

During the network training process, the weights are derived by employing electrothermal switching of individual states of photonic memories, as opposed to the previously used optical pulses. This technique involves writing each memory state reversibly by selectively transitioning between amorphous and crystalline phases through electrothermal switching induced by Joule heating. In our approach, external heat is applied to the material using joule heating of a tungsten metal layer in direct contact with the wire. Different pulse train profiles, based on the type of transition required, are applied to the wire through connections in series to the device.

Results and Discussion

Our photonic memories consist of PCM (Phase-Change Memory) wires arranged in a grating pattern. Each wire represents a quantized state, and we use 30-nm-thin and 250-nm-wide reprogrammable PCM-wires. By considering the condition where all wires are in the amorphous state as the highest state, we can achieve a 4-bit memory for each element of the kernel (Bij) using just 15 reprogrammable wires. The total length of this memory is only 8 micrometers, not including the electrical circuitry.

The insertion loss, defined as the decrease in optical power transmitted when some wires are switched to the crystalline state, is approximately 1 dB for the 4-bit multilevel memory. This results in discrete power levels for each quantized state. When all wires are in the amorphous state, the transmitted optical power is denoted as P_0 .

In this configuration of photonic memory, uniform quantization is achieved, where each state corresponds to one quantization step. In 4-bit photon memory, the quantization step is 0.2 dB per state, and the maximum attenuation coefficient is approximately 3.5 dB, as shown in Fig. 2. The attenuation coefficient is calculated by dividing the optical power transmitted in two extreme configurations, that is, when all wires are in the crystalline state and when all wires are in the amorphous state.



Fig. 2. Extinction ratio (ER) for a 4-bit photonic memory as a function of digital states, for an increased number of crystalline wires, the ER increases linearly and uniformly

Instead of using separate wires for each state, a smaller number of films of different lengths can be used to generate the remaining states by recording these films in different combinations. When using the ratio of linear losses per unit length, it is possible to implement 4-bit memory using only four films of variable length, where the losses in the crystal state correspond to the states 1000, 0100, 0010 and 0001. This binary weighing approach reduces the number of heaters and tungsten contact pads while maintaining the total installation area. However, each suspended state will require different write/erase time and voltage, which requires further optimization.

Although it is important to note that when performing logical inference, due to the stability of the NNs achieved through timely training, low-bit quantization of weights is also possible, which allows you to get a really efficient and accurate output for quantized weights with low resolution. If the system is going to be used to perform relatively simple inference tasks at the edge of the network, it may not require high resolution.

Thus, we propose a tensor core module implemented in photonics, which relies on photonic multiplexing (WDM) signals weighted after filtering using a constructed multi-component photonic memory based on $Ge_2Sb_2Se_5$ cells formed on a waveguide. Photonic memory is reprogrammed by selectively changing the phase (amorphous/crystalline) of wires using electrothermal switching by Joule heating induced by tungsten electrodes. If necessary, the programming of the photonic memory can be implemented in parallel, if necessary, or, alternatively, this photonic

tensor core can work as a passive system with a given core matrix; that is, there will be neither dynamic nor static power dissipation. Another key technological feature of this design is that photonic memory does not introduce additional losses, which avoids repeaters and optical amplifiers, cumbersome intersections and transformations between electrical and optical domains. The architecture shows the execution time limited only by the photon flight time in the chip, which is a function of the number of wavelengths and the delay of the photodetector after programming the core matrix and processing optical input data. The simultaneous development of new materials and the development of integrated photonic memory can allow the implementation of mechanisms based on the proposed scheme, capable of inherently performing accumulation and matrix multiplication with floating point, and, consequently, open the way to the implementation of fully optical photonic tensor blocks, which can significantly accelerate the execution of integligent tasks at the network boundary, without requiring electro-optical transformations and access to external memory.

Conclusion

The proposed Photonic Tensor Core (PTC) operates based on the outlined scheme and is capable of passive matrix multiplication with 4-bit precision. This operation only needs to occur once, during the storage of weights in the photonic network. The PTC functions independently of any logical architecture and doesn't necessitate data transduction from external memory for inference. This characteristic positions it as a comprehensive analog processor, akin to recently developed counterparts. Specifically, during inference tasks, our architecture conducts tensor operations with a time complexity of O(1), and its static power consumption approaches negligible levels. This efficiency arises from the system acting as a passive filter, relying solely on light-matter interactions with pre-stored states in the photonic memory. Unlike logic operations that require optical switching, our system operates by leveraging these interactions and accessing inputs directly from the optical domain. The photonic memory retains previously saved kernels, assuming they were stored during a prior instance, and the inputs are readily accessible from the network's edge.

REFERENCES

1. Mihov E.D., Nepomnyashchiy O.V., Selecting informative variables in the identification problem Journal of Siberian Federal University - Mathematics and Physics. 9 (4) (2016) 473–480.

2. Lin X., Rivenson Y., Yardimci N.T., Veli M., Luo Y., Jarrahi M., Ozcan A., Science 361, 1004 (2018).

3. Miscuglio M., Mehrabian A., Hu Z., Azzam S.I., George J., Kildishev A.V., Pelton M., Sorger V.J., Opt. Mater. Express 8, 3851 (2018).

4. **Ryzhenko I.N., Lutsenko A.E., Varygin O.G., Nepomnyashchiy O.V.,** Carrier compensation mode implementation in satellite communication channels. In: Proceedings of 2019 International Siberian Conference on Control and Communications, SIBCON 2019, vol. 8729665 (2019) 23–29.

5. Shen Y., Harris N. C., Skirlo S., Prabhu M., Baehr-Jones T., Hochberg M., Sun X., Zhao S., Larochelle H., Englund D., Soljačicr M., Nat. Photonics 11, 441 (2017).

6. Miscuglio M., Mehrabian A., Hu Z., Azzam S.I., George J., Kildishev A. V., Pelton M., Sorger V.J., Opt. Mater. Express 8, 3851 (2018).

7. **Popovskiy N.I., Davydov V.V., Rud V.Y.,** Features of construction of fiber-optic communication lines with orthogonal frequency-division multiplexing, St. Petersburg Polytechnic University Journal. Physics and Mathematics. 15(3.2) (2022) 178–183.

8. Krivenko Y.E., Logunov S.E., Davydov M.N., Andreeva E.I., Andreev D.P., Selection Features of Different Standard Optical Fiber in CCTV Fiber-Optics Systems, Springer Proceedings in Physics. 268 (2022) 539–543.

9. **Popovskiy N.I., Davydov V.V., Rud V.Yu.,** Features of the construction of photonic integrated circuits for communication systems. Journal of Physics: Conference Series 2086(1) (2021) 012163.

10. Filatov D.I., Galichina A.A., Vysoczky M.G., Yalunina T.R., Features of transmission at analog intermediate frequency signals on fiber – optical communication lines in radar station, Journal of Physics: Conference Series. 917(8) (2017) 082005.

11. **Reznikov B., Rodin S., Popovskiy N., Isaenko D., Stepanenkov G., Vakorina D.,** Development to High-Rate Fiber Optic Communication Line with Orthogonal Frequency-Division Multiplexing. 2022 International Conference on Electrical Engineering and Photonics (EExPolytech) (2022).

12. Podstrigaev A.S., Lukiyanov A.S., Smolyakov A.V., Nikitina M.I., The expediency of fiber-optical communication line used in different schemes of receiver tract of the radio-monitoring complex, Journal of Physics: Conference Series. 1368(2) (2019) 022027.

13. **Tarasenko M.Y., Lenets V.A., Akulich N.V., Yalunina T.R.,** Features of use direct and external modulation in fiber optical simulators of a false target for testing radar station, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 10531 LNCS (2017) 227–232.

14. Isaenko D., Reznikov B., Rodin S., Stepanenkov G., Popovskiy N., Vakorina D., Development of Communication Channel for data Transmission Over Single-Mode Optical Fiber in Environmental Monitoring System from Remote Multifunctional Complexes. 2022 International Conference on Electrical Engineering and Photonics (EExPolytech) (2022).

15. Miscuglio M., Photonic tensor cores for machine learning, Applied Physics Reviews. 7(2020) 031404-1-031404-10.

THE AUTHORS

POPOVSKIY Nikita I. nikitanikita24@mail.ru ORCID: 0000-0003-3457-0370 RUD Vasiliy Yu. rudvas.spb@gmail.com ORCID: 0000-0002-5731-0849

DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: 0000-0001-9530-4805

Received 25.07.2023. Approved after reviewing 10.08.2023. Accepted 10.08.2023.

Conference materials UDC 681.782.473 DOI: https://doi.org/10.18721/JPM.163.214

Modelling the influence of planar waveguide cladding thickness on the absorption efficiency of a superconducting NbN strip

N.A. Vovk¹, M.V. Shibalov², A.M. Mumlyakov², Ju.P. Korneeva², I.M. Asharchuk², K.V. Smirnov¹, M.A. Tarkhov²

¹ National Research University Higher School of Economics, Moscow, Russia;

² Institute of Nanotechnologies of Microelectronics of the RAS, Moscow, Russia

^{III} vovkolg2011@gmail.com

Abstract. This paper reports simulation results for 1550 nm wavelength absorption efficiency of a superconducting NbN nanowire coupled to a single-mode Si_3N_4 waveguide depending on SiO₂ cladding thickness. Simulation results for straight, U- and W-shaped strips show that with perfect planarization (no top cladding) the absorption coefficient per unit length is 0.031, 0.07 and 0.11 dB/µm, respectively.

Keywords: CMP, cladding, superconducting, detectors

Funding: 1021061509690-0-1.2.1

Citation: Vovk N.A., Shibalov M.V., Mumlyakov A.M., Korneeva Ju.P., Asharchuk I.M., Smirnov K.V., Tarkhov M.A. Modelling the influence of planar waveguide cladding thickness on the absorption efficiency of a superconducting NbN strip, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 87–91. DOI: https://doi.org/10.18721/JPM.163.214

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 681.782.473 DOI: https://doi.org/10.18721/JPM.163.214

Моделирование влияния толщины буферного слоя планарного волновода на эффективность поглощения сверхпроводящей NbN полоской

Н.А. Вовк¹[⊠], М.В. Шибалов², А.М. Мумляков², Ю.П. Корнеева², И.М. Ашарчук², К.В. Смирнов¹, М.А. Тархов²

¹ Национальный исследовательский университет «Высшая школа экономики», Москва, Россия;

² Институт нанотехнологий микроэлектроники РАН, Москва, Россия

^{III} vovkolg2011@gmail.com

Аннотация. В данной работе представлены результаты моделирования эффективности поглощения на длине волны 1550 нм сверхпроводящей нанополоской NbN, интегрированной с одномодовым волноводом Si_3N_4 , в зависимости от толщины буферного слоя SiO_2 . Результаты моделирования для прямых, U- и W-образных полосок показывают, что при идеальной планаризации (без верхнего буферного слоя) коэффициент поглощения на единицу длины составляет 0,07,0,031 и 0,11 дБ/мкм соответственно.

Ключевые слова: ХМП, буферный слой, сверхпроводник, детектор

Финансирование: 1021061509690-0-1.2.1

© Vovk N.A., Shibalov M.V., Mumlyakov A.M., Korneeva Ju.P., Asharchuk I.M., Smirnov K.V., Tarkhov M.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Вовк Н.А., Шибалов М.В., Мумляков А.М., Корнеева Ю.П., Ашарчук И.М., Смирнов К.В. Моделирование влияния толщины буферного слоя планарного волновода на эффективность поглощения сверхпроводящей NbN полоской // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 87–91. DOI: https://doi.org/10.18721/JPM.163.214

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Planarization technology of multilayer CMOS structures is one of the key steps in nano- and microelectronics manufacturing. Without planarization, each successive layer applied follows the topology of the previous layers, creating undesirable steps and steep slopes on the surface of the new layer, which degrades its performance. Photonic integrated circuits (PIC), used for converting optical signals into electrical signals, are multilayer structures comprising such basic elements as waveguides, electro-optical modulators, photon detectors and quantum emitters [1]. The main element for planarization of such circuits is the waveguide cladding layer, on which the control and detection elements of radiation are placed. One of the practical implementations of cladding planarization technology in PICs is the creation of a multi-resonator structure and vertical inter-wavelength coupling [2]. Modern CMP (Chemical Mechanical Planarization) equipment has high precision processing, which allows not only to thin cladding but also to prepare the surface for further technological operations, e.g., for splicing wafers with SiO₂ cladding and LiNbO₂ electro-optical modulator [3].

Integrating the detector onto the upper cladding reduces the number of standard processing steps, such as etching process, spin coating photoresist, that modify the waveguide surface and the result in the losses increase in the entire optical system. Similarly, if the waveguide is etched after the detector has been fabricated, the possibility of the detector itself being modified by technological operations can be excluded.

Ideally, the planarization of the upper cladding to the Si_3N_4 surface would allow the detector to be placed on the waveguide itself, but due to different material planarization rates, recesses are formed in the Si_3N_4 , which degrades the surface and increases the roughness of the waveguide [4]. Due to the planarization rate of the PECVD SiO_2 layer, which varies from 1 nm/s to 2 nm/s, one cannot exclude a situation where a small thickness of the upper cladding will remain on the surface of the waveguide, which greatly affects the radiation detection efficiency.

In this paper, we calculate the effect of the residual SiO_2 cladding layer after planarization process [5] on the efficiency of pulling an evanescent wave from a Si_3N_4 waveguide by a super-conducting NbN nanostrip.

Materials and Methods

The first step in PIC design is to determine the compatibility of the operating wavelength with the waveguide material. At the telecommunication wavelength of 1550 nm, Si_3N_4 -based platforms (refraction index n = 2.01) exhibit record low optical absorption [6]. To localize the optical mode of radiation in the Si_3N_4 waveguide, a cladding layer with a lower refractive index, SiO_2 (n = 1.44) is used.

We consider a single-mode radiation propagation with a wavelength of 1550 nm, which is defined by the geometry of the waveguide cross section of $1 \times 1 \ \mu\text{m}^2$. As a superconducting material, NbN, which is widely used for single-photon detectors [7], is chosen. NbN refractive index at 1550 nm is 5.23-5.82i, where the multiplier of the imaginary part is responsible for light absorption by the material.

The transmittance characteristic of a planar waveguide is defined as $\ln(P_{out}/P_{in})$, where P_{out} is the output signal power, P_{in} is the input signal power. And according to the Boeger-Lambert-Bera law considering the superconducting strip as an absorbing medium, the transmittance is defined as:

$$-\alpha \cdot L_{NbN} = \ln\left(\frac{P_{out}}{P_{in}}\right),\tag{1}$$

where L_{NbN} is the strip length, α is the absorption coefficient.

© Вовк Н.А., Шибалов М.В., Мумляков А.М., Корнеева Ю.П., Ашарчук И.М., Смирнов К.В., Тархов М.А. 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. An alternative way to calculate the absorption index is an analytical formula that includes the effective refractive index n_{eff} , which determines the phase velocity of the surface wave in the waveguide, taking into account the integrated detector:

$$\alpha = -20 \lg \left(e^{\frac{\mathbf{a} \cdot imag(n_{eff}) \ L_{NbN}}{\lambda}} \right), \tag{2}$$

where $imag(n_{eff})$ is the imaginary part of the effective refractive index of the strip waveguide, λ is the operating wavelength.

The absorption of light by the detector is determined by the area of wave mode overlap with the superconducting strip, but there are limits to the width of the strip used. Since the most common superconducting device implementation is based on a superconducting nanowire with 50-100 nm width patterned from a thin film (thickness 5-10 nm), we use the width of the strip equal to 100 nm, the gap is 50 nm and the thickness is 5 nm. For the better absorption of electrical transverse TE-like modes, in order to decrease the detector length, a U-shaped and W-shaped meander can be used as an alternative to a single long strip.

Simulations are performed for different strip configurations (Fig. 1): a single strip (Fig. 1,a), a strip with one turn (U-shape) (Fig. 1,b) and a strip with two turns (W-shape) (Fig. 1,c).

Results

The simulation was performed in COMSOL Multiphysics software in the Electromagnetic Waves, Beam Envelopes (EWBE) physics section using the finite element method. The perfect electric conductor condition was used as the boundary conditions for the entire modelling scope, except for the input and output ports. The 2D cross section modelling of the waveguide gives the distribution of the optical mode field considering the integrated detectors and the residual cladding thickness. The simulation results are the values of the effective refractive index n_{eff} , which $imag(n_{eff})$ (Fig. 1,d) imaginary parts can be used to calculate the absorption index according to Eq. (2).



Fig. 1. 3D simulation of the absorption intensity for the radiation mode in waveguide with: NbN single strip (a), NbN strip with one turn (U-form shape) (b) and NbN strip with two turns (W-form shape) (c). The panel in (d) shows the imaginary part of the effective refractive index in the waveguide with a detector of various configurations as function of the thickness of the upper SiO₂ cladding calculated by Eq. (2)

St. Petersburg Polytechnic University Journal. Physics and Mathematics. 2023. Vol. 16. No. 3.2

Fig. 2 shows 3D simulation results demonstrating the effect of the thickness of the upper cladding of the waveguide, which varied between 0 and 50 nm on the trapping of the NbN evanescent wave by a 36 µm long strip, a 25 µm long U-shape strip and an 18 µm long W-shape strip. For given strip configurations and geometrical sizes with perfect planarization ($d_{clad} = 0$ nm) maximum absorption coefficients are 28% for straight strip, 44% for U-shape and 49% for W-shape strip, which gives absorption coefficient of 0.031 dB/µm, 0.07 dB/µm and 0.11 dB/µm per 1 micron length for above mentioned topologies, respectively.



Fig. 2. Simulation results of optical power distribution in a planar waveguide with different shapes of NbN strip at different thicknesses (d_{clad}) of the cladding layer. The zoom shows the topology of the detector with a waveguide

The electric field intensity decreases exponentially at the waveguide boundary as the upper cladding increases, which leads to decrease in the overlap integral of the propagating mode and the detector. Fig. 3 shows the simulation results, which allow one to choose required length of the detector strip to achieve 99% absorption of the input radiation, depending on the type of detector topology and the thickness of the residual upper SiO2 cladding. With an upper cladding thickness of 50 nm SiO₂ to achieve full internal absorption, the length of one strip should be 400 μ m, for U-type topology the length of each strip should be 186 μ m, for W-type topology 123 μ m. The choice of a compact W-type detector topology guarantees a combination of high detection efficiency and small footprint in the PIC.



Fig. 3. Length of NbN detector strips of different topology, providing 99% absorption of waveguide radiation, as function of the upper cladding thickness

Conclusion

In this work the dependence of waveguide mode absorption by a superconducting NbN strip of different topology on the thickness of waveguide cladding after technological planarization operation is demonstrated. Simulation results allowed determining absorption efficiency per 1 μ m length of superconducting NbN strip of different configuration. The proposed calculation can be used to design a single photon detector, matched to a single-mode waveguide, based on NbN strip, whose length determines 99% absorption efficiency, with a fixed thickness of waveguide cladding. Such a detector is used in quantum computing and quantum cryptography applications.

Acknowledgments

The work was supported by project 1021061509690-0-1.2.1. Ministry of Education and Science of the Russian Federation.

REFERENCES

1. Elshaari A., Pernice W., Srinivasan K., Benson O., Zwiller V., Hybrid integrated quantum photonic circuits, Nature Photonics. 14 (5) (2020) 285–298.

2. **Dooyoung Hah**, Analysis of optical gyroscopes with vertically stacked ring resonators, Turkish Journal of Electrical Engineering and Computer Sciences; 29 (3) (2021) 1554–1564.

3. Ghosh S., Yegnanarayanan S., Ricci M., Kharas D., Juodawlkis P., Low-loss Thin Film Lithium Niobate Bonded on Silicon Nitride Waveguides, 2020 Conference: CLEO: Science and Innovations 2020.

4. Ye Z., Jia H., Huang Z., Shen C., Long J., Shi B., Luo Y., Gao L., Sun W., Guo H., He J., Liu J., Foundry manufacturing of tight-confinement, dispersion-engineered, ultralow-loss silicon nitride photonic integrated circuit, Photonics Research. 11 (4) (2023) 558–568.

5. Pfeiffer M.H.P., Herkommer C., Liu J., Morais T., Zervas M., Geiselmann M., Kippenberg T.J. Photonic Damascene Process for Low-Loss, High-Confinement Silicon Nitride Waveguides, IEEE Journal of Selected Topics in Quantum Electronics. 24 (4) (2018).

6. Heck M., Bauters J., Davenport M., Spencer D., Bowers J., Ultra-low loss waveguide platform and its integration with silicon photonics, Laser & Photonics Reviews. 8 (5) (2014) 667–686.

7. Kahl O., Ferrari S., Kovalyuk V., Goltsman G., Korneev A., Pernice W., Waveguide integrated superconducting single-photon detectors with high internal quantum efficiency at telecom wavelengths, Scientific Reports. 5 (11) (2015) 1–11.

THE AUTHORS

VOVK Nikolay A. vovkolg2011@gmail.com ORCID: 0000-0002-8687-3202 ASHARCHUK Ilya M. ilyaasharchuk@gmail.com ORCID: 0000-0001-6445-0009

SMIRNOV Konstantin V.

skv2050@mail.ru ORCID: 0000-0003-1562-0520

TARKHOV Michael A.

tmafuz@mail.ru ORCID 0000-0001-8168-1917

SHIBALOV Maksim V. maxshibalov@gmail.com ORCID: 0000-0002-5818-4776

MUMLYAKOV Alexander M. irbit_oppozit@mail.ru ORCID: 0000-0002-1081-8338

KORNEEVA Julia P. korneeva_yuliya@mail.ru ORCID: 0000-0003-1576-265X

Received 09.07.2023. Approved after reviewing 17.07.2023. Accepted 24.07.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535.8 DOI: https://doi.org/10.18721/JPM.163.215

Features of monitoring the state of viscous media by refraction

V.A. Bazhanova¹, V.V Davydov¹

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

vieronika.bazhanova.2003@mail.ru

Abstract. The article grounds a necessity of liquid media control using refractometer. A method for monitoring liquid media, including mixtures, using refractometric measurements is proposed. A system of equations has been developed to determine the composition of the medium, which consists of components that have not reacted chemically. The results of experimental studies are presented.

Keywords: liquid, refraction, refractive index, concentration, light-shadow boundary, media state control

Citation: Bazhanova V.A., Davydov V.V., Features of monitoring the state of viscous media by refraction, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 92–96. DOI: https://doi.org/10.18721/JPM.163.215

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.8 DOI: https://doi.org/10.18721/JPM.163.215

Особенности контроля состояния вязких сред методом рефракции

В.А. Бажанова¹[™], В.В. Давыдов¹

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

[™] vieronika.bazhanova.2003@mail.ru

Аннотация. Обоснована необходимость контроля жидких сред с использованием рефрактометра. Предложена методика контроля жидких сред, включая смеси, с использованием рефрактометрических измерений. Составлена система уравнений для определения состава среды, которая состоит из компонент, не вступивших между собой в химическую реакцию. Представлены результаты экспериментальных исследований.

Ключевые слова: Жидкость, рефракция, показатель преломления, концентрация, граница свет-тень, контроль состояния среды

Ссылка при цитировании: Бажанова В.А., Давыдов В.В. Особенности контроля состояния вязких сред методом рефракции // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 92–96. DOI: https://doi.org/10.18721/ JPM.163.215

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

A person who takes care of his/her health [1-3] is constantly thinking about what foods he/she will eat and how it may affect his/her health. To do this, many carry out express control of their health [4, 5]. In the human diet, very popular dishes that require frying on vegetable oil or dishes that add the same oil (for example, vegetable salads). Thanks to the content of vitamin E and unsaturated fatty acids, vegetable oil is healthy for the prevention of atherosclerosis, myocardial infarction

© Bazhanova V.A., Davydov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

and other cardiovascular diseases. The rise in prices for all services and goods has led to a deterioration in the quality of oil for various reasons. The number of oil treatment cycles is reduced, less valuable oils (soy, cotton, rape and others) are brought into sunflower oil, and refined and unrefined oils are mixed with many others. It is very difficult to determine the substitution in such mixtures using express control devices. This is done using chemical techniques or high-resolution spectrometers [6 -9]. This control is possible only in a stationary laboratory. The X-ray rapid monitoring devices developed do not meet the requirements for this task, because the chemical composition and physical structure of the test sample must not change during the tests. This test, in the event of a detected deviation, should be further studied by a stationary laboratory for confirmation. This is especially true in the case of mixing refined and unrefined oil. Unrefined oil contains phosphates, fat-soluble vitamins (A, E, K), waxes, carotene, aromatics and other compounds. Unrefined oil cannot be stored for a long time, quickly becomes turbid and is not suitable for frying unlike refined. The use of such a mixture can lead to great harm to human health.

Currently, a large number of small and mobile refractometers of various types have been developed for express control of various liquid media with an error in measuring the refractive index n to 0.00005 [10 -14]. These instruments operate on the phenomenon of full internal reflection, and their measurement does not take into account a number of features. These features appear both in n measurements and in the composition of the mixture. This is especially true for the study of different oils. Therefore, the aim of the work is to establish these features for edible oils and add-on methods of controlling mixtures of edible oils with new ratios for unique determina-tion of mixture composition of two components.

Features of control of the mixture of edible oils

In the express control of edible oil it is important to take into account one of the features - refinement or unrefinement of oil. This will make it possible to properly process the results in the future to determine the composition of the mixture of two oils and their concentration. To do this, at the place of sampling it is necessary to determine this condition of the oil using refraction. We assume we don't know what kind of oil we're testing, except it's edible. The technique has been developed that allows the refinement of the oil to be determined using two measurements of the position of the light-shadow by using total internal reflection (TIR) and frustrated total internal reflection (FTIR). Measurements to determine the position of the border shadow-light on the frustrated total internal reflection in industrial structures refractometers for express control cannot be realized. Therefore, it will be necessary to use a different design of the refractometer. The unrefined oil contains various components and dyes. Due to the presence of these components, the border shadow-light on the FTIR will be significantly different from the border shadow-light for TIR. In a mixture of refined and unrefined oil, the difference in the structure of light-shadow boundaries will depend on the ratio between the concentrations of these oils in the test mixture. If the unrefined oil is expired, a turbid sediment is formed at the bottom of the bottle. In order not to change the color of the oil, usually drain the top transparent layer and add it to refined or unrefined oil. In the expired unrefined oil, heavy components and dyes fall into the precipitation. Waxes remain in the top layer of oil. The refractive index of wax $n_{\rm w}$ varies from 1.4445 to 1.4473. The original sunflower oil has a higher refractive index (on the order of 1.46–1.47 depending on the region of production). The top layer of expired unrefined oil will have a lower refractive index than the original expired oil due to the presence of wax. Since the size of the wax molecule in the oil is very small, the light scattering at $\lambda = 589.3$ nm will not be [15]. And another way is needed to determine the refinement of the oil and the presence of the component in the test mixture. It is proposed to implement this using the mass equation, because the density of the oil ρ changes when part of the elements precipitate. Also, the density of the oil depends on the degree of its treatment. For different varieties of oil, the value is ρ different. In addition, the value of ρ depends on the temperature T [16, 17]. In this case, can be used a system of two equations (1) to study the oil mixtures: refraction equations and mass equations:

$$\begin{cases} k_1 n_1 + k_2 n_2 = n_{12}, \\ V(k_1 \rho_1 + k_2 \rho_2) = m_{12}, \end{cases}$$
(1)

[©] Бажанова В.А., Давыдов В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

where n_{12} is the refractive index of investigation mixture, n_1 and n_2 are the refractive indices of the media of which the investigation mixture may consist, k_1 and k_2 are the coefficients that shows the relative content of different media in the studied mixture (if it is necessary to get the percentage content, these coefficients are multiplied by 100%), ρ_1 and ρ_2 are the values of densities of the two media which are contained to investigation mixture (considering the temperature), m_{12} is the mass of the research mixture, V is the volume of the research mixture from which the value of m_{12} is measured.

After solving the system of equations, it is possible to unequivocally determine the composition of the mixture of two edible oils and the concentration of components.

Optical part design of refractometer and experimental results

For implementing the developed technique for studying mixtures from edible oils, was developed a new optical design of mobile refractometer. The feature of the design is the presence of an additional light prism, thanks to which measurements can be made in daylight or artificial light. Also, the advantage of the device is the lack of power from the network, in order to explore a large number of viscous media. Fig. 1 presents the modernization of the optical design of the refractometer, allowing to measure the refractive index of condensed medium with the use of the upper and lower prism.

Fig. 1 presents the case of measuring the value of n_{12} using the TIR phenomenon. For the realization of the n_{12} value measurements using the phenomenon of FTIR cover 5 with mirror 6 closes (light stop entering to prism 1. The cover 5 opens without the mirror and the light enters the top prism 2, and also the refractive index is measured at the border of the light-shadow and changes are recorded.



Fig. 1. Schematic diagram of the optical part of the refractometer and ray path for lower prism: lower triangular prism 1 (material leucosapphire), upper triangular prism 2 (material leucosapphire), silicone gaskets 3, rotating prism mount 4, closing flap 5, mirror 6, eyepiece 7, lens on movable mount 8, mirror 9, plate for registration of the light-shade border 10, medium under study 11

In order to confirm the methods developed by us, studies have been carried out on mixtures of different oils. Fig. 2 shows the measurement of refractive index n_{12} of mixture of refined and unrefined oils.

Analysis of the measurements in Fig. 2 shows that the light-shadow border obtained by the TIR method is very different from the border obtained by the FTIR method. The light-shadow boundary is almost blurred. The presence of components in the mixture, which scattering the light, corresponds to the unrefined oil.

In the study of refined oil, the light-shadow boundary is clearer (Fig. 3)

In order to determine the concentration of oils in the mixture, the refractive values of refined and unrefined oils n_1 and n_2 , previously measured, were placed into the system of equations (1). The density values ρ_1 and ρ_2 of each oil were also placed into the system of equations. After weighing the sample, in which refined and unrefined oils were mixed in a ratio of 10 ml : 10 ml (V = 20 ml), it is possible to have the value of m_{12} , which is also placed into the system (1):

$$\begin{cases} k_1 \cdot 1.4703 + k_2 = 1.4695, \\ 2 \cdot 10^{-5} (k_1 \cdot 800 + k_2 \cdot 890) = 16.9 \cdot 10^{-3}. \end{cases}$$

The solutions to this equation system are the required oil concentration values $k_1 = 0.503$ and $k_2 = 0.497$. The obtained values correspond to the proportions in which the refined and unrefined oil were mixed within the measurement error.



Fig. 2. Measurement of refractive index n_{12} of mixture of refined and unrefined oils using the method of TIR (*a*) and FTIR (*b*)





Conclusion

The analysis of the obtained results shows the adequacy of the technique developed by us for express control. The values obtained from the study on the composition of the oils and the concentrations of the components are the same as the types of oils and their concentrations used for the preparation of the tested media.

Another feature of this method is the dependence on the resolution of the light shadow on the power (or intensity) of the light source in the oil mixture. This factor is also related to the oil concentrations in the mixture and requires separate studies.

Experiments have shown that the upgraded design of the refractometer can also be used to monitor the condition of other medium. It may also be possible to use it to control their mixtures, provided that these media do not react chemically. Of additional interest are liquid degreasing media. This will also be the subject of our next studies.

REFERENCES

1. Naumova V., Kurkova A., Zaitceva A., Davydov R., Method for the Analysis of Tissue Oxygen Saturation Disorders Using an Optical Analyzer of Visible and IR Spectra. IEEE Proceedings of International Conference on Electrical Engineering and Photonics, (EExPolytech-2022), 13-15 October 2022, Saint-Petersburg. Russia. (2022) 151–153.

2. Yakusheva M.A., Davydov R.V., Isakova D.D., Features of signal absorption fronts of laser radiation in rapid diagnosis of human health. IEEE Proceedings 8th International Conference on Information Technology and Nanotechnology, (ITNT-2022). 23-27 Mat 2022. Samara, Russia. (2022). 145 –149.

3. Marusina M.Ya., Karaseva E.A., Application of fractal analysis for estimation of structural changes of tissues on MRI images, Russian Electronic Journal of Radiology. 8(3) (2018) 107–112.

4. Mazing M.S., Zaitceva A.Yu., Kislyakov Yu.Ya., Kondakov N.S., Avdushenko S.A., Monitoring of Oxygen Supply of Human Tissues Using A Noninvasive Optical System Based on A MultiChannel Integrated Spectrum Analyzer, International Journal of Pharmaceutical Research. 12(2) (2020) 1974–1978.

5. Mazing M.S., Zaitceva A.Y., Davydov R.V., Application of the Kohonen neural network for monitoring tissue oxygen supply under hypoxic conditions, Journal of Physics: Conference Series. 2086(1) (2021) 012116.

6. Davydov V.V., Moroz A.V., Myazin N.S., Makeev S.S., Dukin V.I., Peculiarities of Registration of the Nuclear Magnetic Resonance Spectrum of a Condensed Medium During Express Control of Its State, Optics and Spectroscopy.128(10) (2020) 1678–1685.

7. Vakhin A.V., Khelkhal M.A., Mukhamatdinov I.I., Nasybullin A.R., Morozov O.G., Changes in Heavy Oil Saturates and Aromatics in the Presence of Microwave Radiation and Iron-Based Nanoparticles, Catalysts. 12(5) (2022) 514.

8. Davydov V.V., Dudkin V.I., Grebenikova N.M., On the Possibility of Express Recording of Nuclear Magnetic Resonance Spectra of Liquid Media in Weak Fields, Technical Physics. 63(12) (2018) 1845–1850.

9. Sadovnikova M.A., Murzakhanov F.F., Mamin G.V., Gafurov M.R., HYSCORE Spectroscopy to Resolve Electron–Nuclear Structure of Vanadyl Porphyrins in Asphaltenes from the Athabasca Oil Sands In Situ Conditions, Energies. 15(17) (2022) 6204.

10. Kashaev R.S., Kien N.C., Tung T V., Kozelkov O.V., Fast Proton Magnetic Resonance Relaxometry Methods for Determining Viscosity and Concentration of Asphaltenes in Crude Oils, Journal of Applied Spectroscopy. 86(5) (2019) 890–895.

11. Irfan M., Khan Y., Khonina S.N., Kazanskiy N.J., Plasmonic Refractive Index and Temperature Sensor Based on Graphene and LiNbO3. Sensors. 22(20) (2020) 7790-7802.

12. **Karabegov M.A.**, Ways of improving the accuracy of analytical instruments, Measurement Techniques. 52(1) (2009) 97–104.

13. **Karabegov M.A.,** On certain information capabilities of analytical instruments, Measurement Techniques. 54(10) (2012) 1203–1212.

14. **Provodin D.S., Davydov V.V.,** New technique for control of liquid media state by optical method in express mode, St. Petersburg State Polytechnical University Journal: Physics and Mathematics. 15(3.2) (2022) 124–129.

15. Kazanskiy N.L., Butt M.A., Degtyarev S.A., Khonina S.N., Achievements in the development of plasmonic waveguide sensors for measuring the refractive index. Computer Optics. 44(3) (2020) 295-318.

16. Chen J., Guo W., Xia M., Li W., Yang K., In situ measurement of seawater salinity with an optical refractometer based on total internal reflection method, Optics Express. 26(20) (2018) 25510–25523.

17. Davydov V.V., Kruzhalov S.V., Grebenikova N.M., Smirnov K.J., Method for Determining Defects on the Inner Walls of Tubing from the Velocity Distribution of the Flowing Fluid, Measurement Techniques. 61(4) (2018) 365–372.

THE AUTHORS

BAZHANOVA Veronika A. vieronika.bazhanova.2003@mail.ru ORCID: 0009-0007-9890-2262 DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: 0000-0001-9530-4805

Received 14.07.2023. Approved after reviewing 18.09.2023. Accepted 18.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535 DOI: https://doi.org/10.18721/JPM.163.216

Real-time calibration methods for a commercial MDI-QKD system

N.V. Rudavin^{3,5^{III}}, I.S. Gerasin^{1,2,3,4}, P A. Kupriyanov^{1,2,3,4}, A.P. Dvurechenskiy^{1,2,3,4}, R.A. Shakhovoy^{1,2,3,4}

¹QRate, Moscow, Russia;

²Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, Russia;

³NTI Center for Quantum Communications, National University of Science and Technology MISiS, Moscow, Russia;

⁴Russian Quantum Center, Skolkovo, Moscow, Russia;

⁵HSE University, Moscow, Russia

[™] n.rudavin@gograte.com

Abstract. Quantum key distribution (QKD) is a well-studied field of science and is becoming a common technology. Commercial systems become more available. Such systems require high level of automatization, so, the set of real-time and prior calibrations is required for them. In this work, we propose calibration algorithms that pre-tune the amplitude of pulses and the laser wavelength and also maintain phase and polarization of weak coherent pulses during generation. Described algorithms were implemented on a prototype of the commercial QKD system and demonstrated high results.

Keywords: quantum key distribution, phase fluctuation, polarization distortion

Funding: The study was commissioned by JSCo RZD.

Citation: Rudavin N.V., Gerasin I.S., Kupriyanov P.A., Dvurechenskiy A.P., Shakhovoy R.A., Features of the construction photonic tensor cores for neural networks, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 97–102. DOI: https://doi.org/10.18721/JPM.163.216

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535 DOI: https://doi.org/10.18721/JPM.163.216

Методы калибровки в реальном времени системы детектор-независимого КРК

Н.В. Рудавин^{3,5⊠}, И.С. Герасин^{1,2,3,4}, П.А. Куприянов^{1,2,3,4}, А.А. Двуреченский^{1,2,3,4}, Р.А. Шаховой ^{1,2,3,4}

¹ КуРэйт, Москва, Россия;

² Московский физико-технический институт, Московская область, г. Долгопрудный, Россия;

³ НТИ Центр квантовых коммуникаций, Национальный исследовательский технологический университет «МИСИС», Москва, Россия;

⁴ Российский Квантовый центр, Сколково, Москва, Россия;

⁵ Национальный исследовательский университет «Высшая школа экономики», Москва, Россия

[™] n.rudavin@goqrate.com

Аннотация. Квантовое распределение ключей (КРК) является хорошо изученной областью науки и становится распространенной технологией. Коммерческие системы становятся более доступными. Такие системы требуют высокого уровня автоматизации,

© Rudavin N.V., Gerasin I.S., Kupriyanov P.A., Dvurechenskiy A.P., Shakhovoy R.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

поэтому для них требуется набор предварительных калибровок, а также калибровок, которые поддерживают рабочее состояние системы в реальном времени. В данной работе мы предлагаем алгоритмы калибровки, которые предварительно настраивают амплитуду импульсов и длину волны лазера, а также поддерживают фазу и поляризацию слабых когерентных импульсов во время генерации. Описанные алгоритмы были реализованы на прототипе коммерческой системы КРК и показали высокие результаты.

Ключевые слова: квантовое распределение ключей, флуктуации фазы, искажения поляризации

Финансирование: Исследование выполнено по заказу ОАО «РЖД».

Ссылка при цитировании: Рудавин Н.В., Герасин И.С., Куприянов П.А., Двуреченский А.А., Шаховой Р.А., Методы калибровки в реальном времени системы детекторнезависимого КРК // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 97–102. DOI: https://doi.org/10.18721/JPM.163.216

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The amount of information transmitted via the Internet is rapidly increasing and this information needs to be protected. In contrast to quantum cryptography, classical cryptography has vulnerabilities that allow the eavesdropper to gain (at least, in principle) unauthorized access to sensitive data [1]. When this became clear, it became necessary to develop commercial quantum key distribution (QKD) systems.

From a technical point of view, modern QKD systems consisting of a receiver and a transmitter are complex devices that include many components, which are not calibrated by default. Therefore, before starting the key generation process, it is necessary to calibrate all its components. Moreover, it is necessary to develop calibration algorithms most appropriate for the selected QKD protocol and encoding methods and pertinent to the characteristics of the internal components. The calibration system must ensure the correct operation of the QKD setup corresponding to the security requirements of the key distribution. In the measurement-device-independent (MDI) QKD system [2], calibrations are required not only for the receiver and transmitter, but also for the untrusted node. The latter should be configured in such a way that both transmitters could interact with it properly.

Calibration of the QKD system can be divided into 2 stages: initial and real-time. During the initial calibration, one should conFig. the components, whose properties will be constant over time and will not require occasional reconfiguration. In contrast, the purpose of real-time calibrations is a periodic adjustment of the operating parameters of the system to ensure the correctness of the key generation process.

In this work, we describe the most essential calibration techniques needed to ensure maximum visibility of the interference of weak coherent pulses on the beam splitter of our experimental MDI-QKD system.

Materials and Methods

To obtain high interference visibility in the MDI QKD experiment, photons (or rather weak coherent pulses) from both transmitters must be fully indistinguishable. It means that it is necessary to align optical pulses in all their degrees of freedom: frequency, polarization, intensity, and spatiotemporal characteristics.

When using lasers with high thermal stability, their frequencies can be aligned just at the initial calibration. The corresponding calibration procedure we propose is based on measuring the beat frequency observed in the interference pattern of laser beams. To perform the calibration, we input the light from the lasers into a 50:50 beam splitter and acquire the beats with a photode-tector. The photodetector output is analyzed with an oscilloscope, where we perform the Fourier transform of the beats to determine the beat frequency. By changing the temperature of one of the lasers, we minimize the beat frequency thereby minimizing detuning between the lasers.

© Рудавин Н.В., Герасин И.С., Куприянов П.А., Двуреченский А.А., Шаховой Р.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. To obtain optical pulses from the continuous laser beam, we use fiber lithium niobate intensity modulators. It is well-known that one should control the bias voltage level of the lithium niobate intensity modulators during operation [3]. Due to the very low bias voltage drift of the modulators that we used in this work, we have decided to use an adjustment algorithm based on a simple proportional controller (P controller) to regulate it:

$$V_n = V_{n-1} - \alpha \left(P_t - P_n \right) ,$$

where V_n and V_{n-1} are the bias voltages at the current and previous steps respectively, α is the proportional coefficient, P_t is the target value of optical power, P_n is the average value of the optical power at step *n* of the algorithm. The values P_t and P_n are measured using power meters built into the transmitters. The target value of optical power P_t^n is determined by maximizing the signal-to-noise ratio measured on single photon detectors (SPD). This P_t choice allows us to achieve the best cutting of optical pulses. Since our setup uses time-bin quantum states encoding, the signal-to-noise ratio for the signal states gives a direct contribution to the quantum bit error rate (QBER) value.

As for the intensity calibration, we introduced the procedure that chooses one of the senders as a master and the second one as a slave and changes the attenuation on the slave to match the master's power. Instead of a power, we measure the total number of clicks on all SPDs for each transmitter separately. It is important for this calibration to make sure that all the SPDs work in linear mode, and that the transmitters send the same pulse sequences. Since the values of losses introduced by tunable optical attenuators on transmitters are constant in time, this calibration is carried out only at the stage of initial setup.

Since the quantum channel is generally a single-mode optical fiber that does not preserve polarization, the polarization of the optical pulse transmitted through such a channel is not correlated with the initial polarization by default. As mentioned earlier, to ensure acceptable visibility of interference, the pulses coming to the beam splitter from two transmitters must be indistinguishable in each degree of freedom including polarization. In the case of time-bin encoding, a polarizing filter coupler (a beam splitter with built-in polarizer) can be used to match the polarization at the receiver inputs. Then a change of polarization in each arm will lead to a change in relative intensities of incoming pulses. It can be shown that an acceptable level of polarization distortions in the case of time-bin encoding is noticeably higher than in the case of polarization encoding. Therefore, the use of time-bin encoding with interference on a polarizing filter coupler makes it possible to significantly reduce the sensitivity of the error level to polarization fluctuations in the channel. In addition, the polarizer guarantees the indistinguishability of independent pulses in the polarization mode, and the error of the polarization distortion compensation algorithm will affect only the intensity of interfering pulses, which does not significantly reduce the quality of interference.

To compensate for polarization distortions, we have designed a polarization control system with two piezo-controlled polarization controllers. Such controllers are driven by an external electrical voltage, are compact enough, and allow for good autonomy and reliability of QKD systems in real conditions. To regularly recover the state of polarization at the receiver by means of the polarization controllers, an active algorithm based on gradient descent was developed [4]. The adjustment is performed periodically in the key generation mode by alternately changing the voltage on the channels of the controllers.

From a mathematical point of view, compensation of polarization distortions is a task of optimizing the objective function. The QBER was used as the objective function in [4], which was estimated in the generation mode according to statistics obtained from the analysis of detected decoy states. In MDI QKD, we generally do not have large enough sifted keys (particularly at high distances); therefore, it is inconvenient to use QBER as the objective function. The task of the polarization control is reduced here to the task of maximizing the total number of clicks, which corresponds to the maximization of the pulse intensity. As usually, this can be done by selecting the optimal set of voltages on the piezo actuators of the polarization controller. Except for using a different objective function, the polarization adjustment algorithm is similar to the one proposed in [4].

SPDs in our setup operate in a gating mode - a sinusoidal voltage is applied to each SPD. When the voltage exceeds the threshold value, the detector switches to the operating mode and can register the pulses coming to it. The detector is in the open state for about 1 ns with a total period of 3.2 ns. The phase of the detector corresponds to the moment of opening the gate. Since we can register a signal pulse only when the detector is "open", it is necessary to calibrate the optimal phase value within the reference signal period. When calibrating, we change the value of the phase (the time of the gate appearance), scanning the entire period.

Also, to obtain good visibility of the interference pattern, it is necessary that the time of arrival (phase) of laser pulses from both transmitters was the same. To perform this, the phase (spatial) alignment is required [5]. At the first stage of calibration, optical pulses are sent only by the master transmitter, and the phases of all SPDs are adjusted to them. In the second stage, a similar sequence of pulses is sent by the slave transmitter, and the corresponding phase shift is determined. Further, using the difference in phase shifts for the two transmitters, the slave adjusts to the master by changing the values of the delay lines. For rough alignment of optical pulses, a time shift of the intensity modulator with a step of 400 ps is used. The 400 ps is determined by the DAC used to control the modulator. For more precise alignment, a tunable optical delay line (TODL) installed in one of the receiver arms is used. Thus, it is possible to achieve a high degree of alignment of the arrival time of optical pulses from two transmitters. This setting is performed at the initial stage of calibration.

However, temperature variations in the fiber and physical influences on it change the time of arrival of laser pulses, so, the phase calibration must be performed in real-time during the generation mode. Since the number of detector clicks is used as a feedback control parameter, together with the synchronizing sequences, we send short calibration pulse sequences between the signal pulse sequences [6]. Like the primary calibration, the transmitters are tuned alternately, using calibration sequences as feedback. The need for these sequences is due to the use of time-bin encoding, in which the SPDs are configured to register certain quantum states. Note that these sequences are not used to generate a secret key.

As a result of changing the pulse arrival time, it is also possible to change the numbering of packages. Synchronization of package numbering at all nodes of the QKD system is necessary for the subsequent sifting procedure provided for by the MDI-QKD protocol. The sifting procedure refers to the reconciliation of the bases of pulse numbers from the transmitters, which corresponds to a successful event at the receiver.

Initially, the numbering of packages is set up at the initial stage of calibration, two mechanisms have been developed for it to set the general numbering of parcels. The first uses a change in the delay time of the generation of the first laser pulse in the signal sequence on the transmitter, thereby changing the numbering of the parcels. As mentioned earlier, pulse generation is performed by the intensity modulator, so in this case, the moment when the high-frequency signal is applied to the modulator changes. The second mechanism allows to adjust of the delay in the SPD electrical channels, i.e., allows to shift of the numbering of packages on the receiver.

The electrical channels connecting the SPDs to the FPGA control board have different lengths, which is why pulses registered at the same time on different SPDs can reach the FPGA at times corresponding to different periods of the clock signal on the control board. To solve this problem, we use additional individual delays in the channel of each SPD with a maximum delay equal to 7 reference signal periods.

Calibration is performed alternately for each transmitter. It is important to note that to calibrate the package numbering, the transmitter should send a pseudo-random, not a periodic sequence of laser pulses. At the same time, the receiver needs to know in advance which sequences the transmitter will send to detect a correlation between the received and expected sequence by going through the period numbers. To do this, a pseudo-random calibration sequence of pulses is used, which is known to all nodes in the QKD system. The transmitter performs calibration by iterating over the period numbers using a 128-period delay line. Accordingly, the shift of the package numbering on the calibrated transmitter modulator should not exceed 128 periods. Then the found delays are applied to the intensity modulators of the transmitters. Delays for phase modulators are also determined based on the delays of intensity modulators.

The described package numbering calibrations are applied in the generation mode if the QBER level, estimated by decoy states statistics, becomes equal to 50%, which may indicate that there is no synchronization of numbers. Accordingly, for this calibration, the generation mode is interrupted, and the system switches to calibration mode. If, after numbers synchronization recalibration, the QBER level remains above the threshold value, the algorithm for the primary calibration of the QKD system is started.

Results and Discussion

With the described methods, we run the key generation procedure on the prototype of the MDI-QKD system and measured second order correlation function, click count and QBER. During the experiment, both Alice and Bob were connected to Charlie by 75 kilometers of standard single-mode telecommunication optical fiber SMF-28e. Alice and Bob's fiber was in the same room under the same conditions. As signal lasers with high-temperature stability we used Koheras BASIK from NKT Photonics. As power meters for bias control were used Thorlabs PM101A, as photodetector and oscilloscope for lasers frequency calibration were used Thorlabs RXM40AF and Lecroy Waverunner 8404MR respectively. We can see that the number of clicks on each SPD is kept at the level from 5500 to 5900 clicks throughout the experiment (see Fig. 1).



Fig. 1. Number of clicks on SPDs with total 150 km of fiber for 19 hours

Since we used weak coherent states with random phase, the minimum achievable value of second order correlation function was 50%, we obtained 52%. Fig. 2 shows the dependence of QBER estimated by signal states. The general level of error is about 6%, and an outlier of the error level of up to 8% was also recorded about 15 hours of the experiment. We believe that this outlier is due to the imperfection of the bios control algorithm used, which caused a temporary change of the signal-to-noise ratio for the signal states. Since the obtained values are appropriate for key generation, the experiment confirmed that the proposed calibration algorithms can be used in MDI-QKD experimental system.



Fig. 2. QBER with total 150 km of fiber for 19 hours

Conclusion

In this work, we demonstrated the most essential calibration techniques needed to ensure maximum visibility of the interference of weak coherent pulses on the beam splitter of our experimental MDI-QKD system. Using the described initial and real-time calibrations, we obtained stable QBER and number of clicks on SPDs, which allowed us to start key generation. Importantly, described algorithms allows us not to interrupt the key generation process with any change in the optical path length, which increases the speed of the secret key.

REFERENCES

1. Gisin N., Ribordy G., Tittel W., Zbinden H., Quantum cryptography, Reviews of modern physics 74.1 (2002) 145.

2. Lo H.K., Curty M., Qi, B., Measurement-device-independent quantum key distribution, Physical review letters 108.13 (2012) 130503.

3. Wooten E.L., Kissa K.M., Yi-Yan A., Murphy E.J., Lafaw D.A., Hallemeier P.F., et al., A review of lithium niobate modulators for fiber-optic communications systems, IEEE Journal of selected topics in Quantum Electronics 6.1 (2000) 69–82.

4. Mekhtiev E.E., Gerasin I.S., Rudavin N.V., Duplinsky A.V., Kurochkin Y.V., Polarization control algorithm for QKD systems, Journal of Physics: Conference Series. Vol. 2086. No. 1. IOP Publishing, 2021.

5. Hiskett P.A., Rosenberg D., Peterson C.G., Hughes R.J., Nam S., Lita A. E., et al., Longdistance quantum key distribution in optical fiber, New Journal of Physics 8.9 (2006) 193.

6. Rudavin N.V., Gerasin I.S., Mekhtiev E.E., Duplinsky A.V., Synchronization protocol for MDI-QKD systems, St. Petersburg State Polytechnical University Journal: Physics and Mathematics. 15.S3. 2 (2022) 56–60.

THE AUTHORS

RUDAVIN Nikita V. n.rudavin@goqrate.com ORCID: 0000-0003-0264-5710 **DVURECHENSKIY Alexander P.** a. dvurechenskiy@goqrate.com ORCID: 0009-0008-7391-0079

GERASIN Ilya S. i.gerasin@goqrate.com ORCID: 0000-0001-5084-7056 SHAKHOVOY Roman A. r.shakhovoy@goqrate.com ORCID: 0000-0003-2750-0518

KUPRIYANOV Pavel A. p.kupriyanov@goqrate.com ORCID: 0009-0006-1663-6806

Received 13.07.2023. Approved after reviewing 15.09.2023. Accepted 15.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535.42 DOI: https://doi.org/10.18721/JPM.163.217

The subwavelength optical elements with a nonlinear dependence of the refractive index change for the formation of specified diffraction patterns using high-performance computer systems

D.A. Savelyev^{1,2}

¹ Samara National Research University, Samara, Russia;

² Image Processing Systems Institute of RAS – Branch of the FSRC Crystallography and Photonics RAS, Samara, Russia

[⊠] savelev.da.2@ssau.ru

Abstract. The diffraction of optical vortices with circular polarization by subwavelength optical microelements with a nonlinear dependence of the change in the refractive index of the substrate was investigated in this paper. The relief height of the elements was varied, as well as the direction of change in the refractive index of the substrate. It was shown that it was possible to obtain a focal spot 37.8% smaller than the focal spot formed by a standard diffractive axicon. It is also shown that it was possible to obtain a light segment 29.7% longer than the light segment formed by the diffractive axicon. It was also demonstrated that it was possible to form a series of optical traps for all considered types of substrates using the ring gratings with a relief height $h = 4.24\lambda$ without central zones.

Keywords: subwavelength focusing, optical vortices, FDTD, high performance computer systems, subwavelength ring gratings

Funding: This research was funded by the expense of the program of strategic academic leadership Priority 2030 in the part "Introduction, "Materials and Methods", as well as the financial support of the Ministry of Science and Higher Education within the State assignment (project FSSS-2023-0006) in other parts.

Citation: Savelyev D.A., The subwavelength optical elements with a nonlinear dependence of the refractive index change for the formation of specified diffraction patterns using high-performance computer systems, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 103–108. DOI: https://doi.org/10.18721/JPM.163.217

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.42 DOI: https://doi.org/10.18721/JPM.163.217

Субволновые оптические элементы с нелинейной зависимостью изменения показателя преломления для формирования заданных дифракционных картин с использованием высокопроизводительных компьютерных систем

Д.А. Савельев^{1,2⊠}

¹ Самарский национальный исследовательский университет им. академика С.П. Королева, г. Самара, Россия;

² Институт систем обработки изображений – филиал ФНИЦ «Кристаллография и фотоника» РАН, г. Самара, Россия

□ savelev.da.2@ssau.ru

Аннотация. В данной работе исследована дифракция оптических вихрей с круговой поляризацией на субволновых оптических микроэлементах с нелинейной зависимостью изменения показателя преломления подложки. Варьировалась высота рельефа элементов, а также направление изменения показателя преломления подложки. Показана возможность оптимизации высоты рельефа субволновых элементов таким образом, что наблюдалось формирование как узкой световой иглы, так и оптической ловушки.

© Savelyev D.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: субволновая фокусировка, оптические вихри, FDTD, высокопроизводительные компьютерные системы, субволновые кольцевые решетки_

Финансирование: Работа выполнена за счет средств программы стратегического академического лидерства «Приоритет 2030» в части «Введение», «Материалы и методы», а также при финансовой поддержке Министерства науки и высшего образования в рамках государственного задания (проект № FSSS0006-2023-) в других частях.

Ссылка при цитировании: Савельев Д.А. Субволновые оптические элементы с нелинейной зависимостью изменения показателя преломления для формирования заданных дифракционных картин с использованием высокопроизводительных компьютерных систем // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 103–108. DOI: https://doi.org/10.18721/JPM.163.217

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Materials with a gradient refractive index (GRdient Index, GRIN) are used for communication [1-3], light collimation [1], in biology and medicine [2], and in other applications [3]. It is known that gradient photonic crystals can be used to control acoustic waves [4]. It is also known that metamaterials with a gradient refractive index are used to control the propagation of light in integrated photonic chips [5].

Optical vortices arouse considerable interest in the field of optics due to their special optical properties [6, 7], which can be used for advanced applications such as nonlinear optics [7], information transmission [8], high-order quantum entanglement [7], optical tweezers [9]. Optical vortices are known to solve problems of sharp focusing [11]. It should also be noted that optical vortices are used to form a reverse energy flow [10] using subwavelength axicons with different twist angles and metalens. The formation of a reverse flow using metalens has been demonstrated experimentally [11]. Also, the implementation of an optical trap using Hermite-Gauss beams and Laguerre-Gauss modes is known [6, 10].

Optical vortices are often generated using multi-order diffractive optical elements [12], spiral phase micro-plates, and axicons [13], including helical and twisted axicons. Metasurfaces are also known to generate optical vortices [11].

Respectively, the diffraction of optical vortices (3D) with circular polarization by subwavelength optical microelements with a nonlinear dependence of the change in the refractive index of the substrate is studied in this paper using high-performance computer systems. Two variants of these substrates were considered: an increase in the refractive index from the center to the edges and the reverse case. In addition, the change in the relief height of the ring gratings was considered at the same time. The solution was simulated numerically with the finite difference time domain method (FDTD).

Materials and Methods

The Laguerre–Gauss mode (1,0) with circular polarization was considered as the input laser radiation (the sign of the circular polarization is opposite to the sign of the introduced vortex phase singularity). The wavelength λ is equal to 0.532 µm ($\sigma = 1.5$).

The main modeling parameters: the size of the 3D computational region is 6 μ m, the thickness of the PML absorbing layer is 0.6 μ m. The absorbing layer surrounds the computing region from all sides. Spatial sampling step $-\lambda/20$, time step $-\lambda/(40c)$, where c is the speed of the light.

The lattice period of subwavelength ring gratings is equal to 1.05λ . The profiles of the considered subwavelength elements with the height of the relief $h = 1.06\lambda$ are shown in Fig. 1. The standard substrate (constant refractive index n = 1.47) and substrate with a nonlinear dependence of the change in the refractive index were considered. Such a variant of the substrate was called a quantized substrate (Q-substrate).

The refractive index of the Q-substrate varied from 1.47 to 2.7 (the thickness of the rings is the same and equal 0.7λ). The following values n were taken: 1.47, 1.74, 1.77, 1.98, 2.03, 2.17, 2.37, 2.7 (Fig. 1). The direct Q-substrate will be called the case of a change in the refractive index from

[©] Савельев Д.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

the maximum in the center (n = 2.7) to the minimum at the edges (n = 1.47) of the element. The reverse case (the refractive index varies from a minimum in the center to a maximum at the edges) will be called the reverse Q-substrate. The results were compared with the action of a diffractive axicon of the same period (i.e. with a numerical aperture NA = 0.95) with a standard substrate at n = 1.47.

The height of the substrates was fixed and amounted to one wavelength. The relief refractive index for all elements was equal to 1.47. The height of the relief h (corresponding to the phase jump π radians) is equal to 1.06 λ in this case.

It should be noted that the effect of the Q-substrate compared to the standard substrate should appear as the action of a collecting (at n = 2.7 at the center) and scattering (at n = 1.47 at the center) lenses. The size of the focal spot was estimated from the full width at half maximum (FWHM), the size of the longitudinal light segment was measured similarly, and will call such as depth of focus (DOF). The relief height h of optical microelements (Fig. 1) ranged from 1.06 λ to 4.24 λ in this paper.



Fig. 1. Profiles of subwavelength optical microelements with Q-substrate (a) and standard substrate, $h = 1.06\lambda$ (b)

Results and Discussion

The diffraction of optical vortices on the subwavelength optical microelements with a standard and Q-substrate at different relief heights (from 1.06λ to 4.24λ) was researched in this section. The results of studies for the standard substrate, direct Q-substrate, and reverse Q-substrate are shown in Fig. 2. The FWHM values (in the main) are given for intensity peaks (maximums) outside of the elements.

The minimum focal spot for standard substrate was obtained for the case $h = 4.24\lambda$: FWHM = 0.48 λ (intensity I = 100%), which is less than the focal spot formed by a standard diffractive axicon with a height $h = 1.06\lambda$ by 35.1%.

An extended light needle on the optical axis for standard substrate is formed for the cases of relief heights h corresponding to odd phase jumps π and 3π radians: $h = 1.06\lambda$ and $h = 3.18\lambda$, respectively. The longest light needle was obtained at a height of relief $h = 3.18\lambda$ (DOF = 2.22 λ), which was longer than the light needle obtained by a diffractive axicon with a height $h = 1.06\lambda$ by 4.7%.

The influence of the direct Q-substrate appears in the formation of more distinct maxima on the optical axis. The maximum intensity peak on the optical axis is formed outside the element for the cases $h = 1.06\lambda$ and $h = 2.12\lambda$. The main maxima for other cases $(h = 3.18\lambda$ and $h = 4.24\lambda)$ are formed inside the element and the values of FDTD and DOF are given for local maxima outside the element. It should be noted that with an increase in the height of the relief (Fig. 2), an increase in the number of local maxima on the optical axis is observed.

The minimum focal spot size for direct Q-substrate was obtained for the cases $h = 4.24\lambda$: FWHM = 0.46 λ (I = 77.9%), which was less than the focal spot formed by a diffractive axicon with a standard substrate and with a height $h = 1.06\lambda$ by 37.8%.



Fig. 2. Laguerre–Gaussian (1,0) modes diffraction on ring gratings (total intensity) with a standard substrate (a, d, g, j), direct Q-substrate (b, e, h, k), reverse Q-substrate (c, f, i, l)

The minimum value of the focal spot for a direct Q-substrate inside the element was obtained at a height $h = 4.24\lambda$ FWHM = 0.3 λ . It was obtained in the last local maximum (at a distance of 0.66 λ from the edge of the relief).

All maxima for reverse Q-substrate were formed outside the relief of the elements. Also, the intensity oscillations were observed on the optical axis with the height increases (the maximum was always formed outside the relief in this case). The minimum of the focal spot was obtained for the case $h = 4.24\lambda$ FWHM = 0.63 λ , which was less than the focal spot formed by a diffractive axicon with a height $h = 1.06\lambda$ and a standard substrate by 14.8%.

The best value of the light needle for reverse Q-substrate is 2.75 λ , which was longer than the light needle formed by a diffractive axicon with a standard substrate and height $h = 1.06\lambda$ by 29.7%.

It should be noted that narrower focal spot was formed inside the element than outside. The minimum focal spot values for the all substrate were obtained at a height $h = 4.24\lambda$. Let us fix this height and consider elements without central zones of the relief. The heights of individual relief zones were denoted as hi, $i \in [0, 5]$, where 0 is the center, 5 is the edge. Then the following cases will be considered ($h = 4.24\lambda$ for the remaining zones): $h_0 = 0$; $h_0 = h_1 = 0$. The main maxima were formed outside the optical elements for all considered cases. The results are shown in Fig. 3.

The minimum focal spot was obtained for a direct Q-substrate at $h_0 = 0$, FWHM = 0.47 λ . This result is comparable to the result for a direct Q-substrate with the same height of all zones $(h_i = 4.24\lambda)$.

An extended light needle on the optical axis was formed for the case of the relief height $h_0 = 0$ for reverse Q-substrate (DOF = 3.2 λ).

It should be noted that the formation of individual optical traps or their series was observed for all types of considered substrates.



Fig. 3. Laguerre-Gaussian (1,0) modes diffraction on ring gratings without central zones with standard substrate (a, d), direct Q-substrate (b, e), reverse Q-substrate (c, f)

Conclusion

The finite difference time domain method was used in this paper to study the diffraction of the Laguerre-Gauss (1,0) modes on subwavelength ring gratings with variable height for a standard substrate, a direct Q-substrate and a reverse Q-substrate. The relief height of the ring gratings varied from 1.06λ to 4.24λ . A significant decrease in the size of the focal spot, the formation of an extended light segment, and the formation of a series of optical traps were shown for some cases.

An analysis of the electric field intensity pattern showed that the smallest focal spot at the maximum on the optical axis outside the element was obtained for a ring grating with a direct Q-substrate and a relief height $h = 4.24\lambda$: FWHM = 0.46 λ . This result was less than the focal spot formed by a diffractive axicon with standard substrate and with height $h = 1.06\lambda$ by 37.8%.

The longest light needle (completely formed outside from the element) was obtained for the case of a ring grating with a reverse Q-substrate and a relief height $h = 4.24\lambda$, DOF = 2.75 λ . This result was longer than the light needle obtained by a diffractive axicon with a standard substrate and with a height $h = 1.06\lambda$ by 29.7%.

It was also demonstrated that it was possible to form both single optical traps and their series for the considered ring gratings with a relief height $h = 4.24\lambda$ without central zones.

REFERENCES

1. Lalanne P., Chavel P., Metalenses at visible wavelengths: past, present, perspectives, Laser & Photonics Reviews. 11 (3) (2017) 1600295.

2. Chien Y. F., Lin J. Y., Yeh P. T., Hsu K. J., Tsai Y. H., Chen S. K., Chu S.W., Dual GRIN lens two-photon endoscopy for high-speed volumetric and deep brain imaging, Biomedical Optics Express. 12 (1) (2021) 162–172.

3. Richardson K. A., Kang M., Sisken L., Yadav A., Novak S., Lepicard A., Martin I., Francois-Saint-Cyr H., Schwarz C.M., Mayer T.S., Rivero-Baleine C., Yee A.J., Mingareev I., Advances in infrared gradient refractive index (GRIN) materials: a review, Optical Engineering. 59 (11) (2020), 112602.

4. Jin Y., Djafari-Rouhani B., Torrent D., Gradient index phononic crystals and metamaterials, Nanophotonics. 8 (5) (2019), 685–701.

5. Luque-González J. M., Halir R., Wangüemert-Pérez J. G., de-Oliva-Rubio J., Schmid J.H., Cheben P., Molina-Fernández H., Ortega-Mocux A., An ultracompact GRIN-lens-based spot size converter using subwavelength grating metamaterials, Laser & Photonics Reviews. 13 (11) (2019), 1900172.

6. Savelyev D.A., Karpeev S.V., Development of 3D Microstructures for the Formation of a Set of Optical Traps on the Optical Axis, Photonics. 10 (2) (2023), 117.

7. Shen Y., Wang X., Xie Z., Mi, C., Fu X., Liu Q., Gong M., Yuan X., Optical vortices 30 years on: OAM manipulation from topological charge to multiple singularities, Light: Science & Applications. 8 (1) (2019), 1–29.

8. Khonina S.N., Karpeev S.V., Butt M.A., Spatial-light-modulator-based multi-channel data transmission by vortex beams of various orders, Sensors. 21 (9) (2021), 2988.

9. Wen J., Gao B., Zhu G., Liu D., Wang L.G., Precise position and angular control of optical trapping and manipulation via a single vortex-pair beam, Optics and Lasers in Engineering. 148 (2022), 106773.

10. Savelyev D.A., Peculiarities of focusing circularly and radially polarized super-Gaussian beams using ring gratings with varying relief height, Computer Optics. 46 (4) (2022) 537–546.

11. Kotlyar V.V, Stafeev S.S., O'Faolain L., Kotlyar M.V., High numerical aperture metalens for the formation of energy backflow, Computer Optics. 44 (5) (2020) 691–698.

12. **Khonina S.N., Ustinov A.V.**, Binary multi-order diffraction optical elements with variable fill factor for the formation and detection of optical vortices of arbitrary order, Applied Optics 58 (30) (2019), 8227–8236.

13. Khonina S.N., Kazanskiy N.L., Khorin P.A., Butt M.A., Modern types of axicons: new functions and applications, Sensors. 21 (19) (2021), 6690.

THE AUTHOR

SAVELYEV Dmitry A. dmitrey.savelyev@yandex.ru ORCID: 0000-0003-2282-3895

Received 13.07.2023. Approved after reviewing 31.07.2023. Accepted 01.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023
Conference materials UDC 544.536 DOI: https://doi.org/10.18721/JPM.163.218

Analysis of size-dependent optical properties of lysine carbon dots produced by femtosecond laser synthesis

A.A. Astafiev¹, A.M. Shakhov¹, M.S. Syrchina¹, V.A. Nadtochenko¹

¹ Semenov Institute of Chemical Physics, Moscow, Russia

□ wrongclue@gmail.com

Abstract. Pulsed laser synthesis of fluorescent nanoparticles from amino acids is promising technique for fluorescent imaging. Understanding relation between nanoparticle size and absorption and fluorescence characteristics sheds light on mechanism of fluorescence and enables control of optical properties of products. To study this relation, we separated products obtained by laser synthesis from L-lysine into fractions of different size and analyzed optical properties and chemical composition of these fractions.

Keywords: luminescent carbon dots, femtosecond laser pulses, nanomaterials, photostability

Funding: This study was funded by Russian Scientific Foundation grant 21-72-20169 "Fundamental physicochemical bases of design and application of carbon nanomaterials formed by nonlinear absorption in strong optical fields of femtosecond laser pulses".

Citation: Astafiev A.A., Shakhov A.M., Syrchina M.S., Nadtochenko V.A., Analysis of sizedependent optical properties of lysine carbon dots produced by femtosecond laser synthesis, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 109–113. DOI: https://doi.org/10.18721/JPM.163.218

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 544.536 DOI: https://doi.org/10.18721/JPM.163.218

Анализ оптических характеристик фракций углеродных точек, полученных из лизина методом фемтосекундого лазерного синтеза

А.А. Астафьев¹, А.М. Шахов¹, М.С. Сырчина¹, В.А. Надточенко¹

1 Институт химической физики им. Н.Н. Семёнова РАН, Москва, Россия

[™] wrongclue@gmail.com

Аннотация. Лазерный синтез углеродных точек с флуоресцентными свойствами на основе аминокислот — многообещающая методика для флуоресцентного имаджинга. Исследование соотношения размера точки с ее флуоресцентными параметрами является необходимым для понимания механизма флуоресценции и точного контроля характеристик продуктов лазерного синтеза. В данной работе мы разделили углеродные точки, полученные в ходе лазерного синтеза из лизина, на фракции в соответствии с их молекулярной массой (<2 kDa и >2 kDa), проанализировали ключевые оптические характеристики и химический состав соответствующих фракций.

Ключевые слова: люминесцентные углеродные точки, фемтосекундные лазерные импульсы, наноматериалы, фотостабильность

© Astafiev A.A., Shakhov A.M., Syrchina M.S., Nadtochenko V.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Финансирование: Работа была выполнена при поддержке гранта РНФ № 21-72-20169 "Фундаментальные физико-химические основы дизайна и применения углеродных наноматериалов, формируемых при нелинейном поглощении в сильных оптических полях фемтосекундных лазерных импульсов".

Ссылка при цитировании: Астафьев А.А. и др. Анализ оптических характеристик фракций углеродных точек полученных из лизина методом фемтосекундого лазерного синтеза // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 109–113. DOI: https://doi.org/10.18721/JPM.163.218

Статья открытого доступа, распространяемая по лицензии СС ВУ-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Production of fluorescent species from biomolecules in living cells and tissues *in situ* by femtosecond laser irradiation holds promise for targeted, localized, rapid and non-invasive fluorescent labelling of intracellular material [1-2]. Previously, we demonstrated that femtosecond laser synthesis of fluorescent carbon dots-like nanoparticles from essential amino acids, in particular, L-lysine provides a potential route of fluorescent species formation in living cells [3].

Hence, there is a practical interest in understanding and tailoring fluorescent properties of amino acid-derived carbon dots. Nanoparticle size is one of parameters through which optical properties of carbon dots can be controlled and manipulated. Also, relation between size and fluorescence characteristics is indicative of the fluorescence mechanism. When energy levels are controlled by quantum confinement effects, absorption and emission bands of carbon dots strongly depend on their diameter [4–5].

On the other hand, fluorescence of carbon dots can originate from specific organic fluorophore groups in their structure, in this case its spectra are independent of the nanoparticle diameter [6]. Fluorescence of these groups can be bright, when they exist as separate molecules in solution, but becomes strongly quenched when they combine into large nanoparticles [7].

In order to reveal the relation between nanoparticle size and optical properties and gain insight into fluorescence mechanisms, we employed dialysis to separate fluorescent products, obtained from L-lysine aqueous solution, into several fractions of different sizes. Absorption and emission spectra, fluorescence quantum yields and lifetimes and other optical characteristics were then registered for each fraction and effect of nanoparticle size on these properties was revealed.

Materials and Methods

Synthesis and separation of products. Aqueous solution of L-lysine (2 mL, 0.1 g/mL) in a quartz cuvette was irradiated with trains of femtosecond laser pulses focused by a spherical lens (f = 8 mm, 0.5NA). Central wavelength of laser pulses was 800 nm, repetition rate 1 kHz, duration 50 fs, pulse energy 1.4 mJ. Irradiation resulted in color change of solution and fluorescent carbon dots formation (Lys-CD). This solution was dialyzed for 72 hours in a 2,000 MWCO dialysis unit and separated into dialysate with molecular weight < ca. 2 kDa (Lys-CD-1) and retentate (Lys-CD-2, molecular weight > ca. 2 kDa) (Fig. 1).

Samples characterization. Absorption of photoluminescence spectra of samples in water were recorded with Shimadzu spectrophotometer (UV-3600) and spectrofluorometer (RF-5031 PC). Fluorescence quantum yield (350 nm excitation) was estimated with the slope method using ethanol solution of anthracene (quantum yield 0.27) as a standard.

Fluorescence decay and fluorescence anisotropy decay kinetics in aqueous solution were registered with femtosecond pulsed laser excitation at 360 nm at 450 nm emission wavelength using time-correlated single-photon counting module (SPC-150N, Becker&Hickl GmbH). Fluorescence lifetime and anisotropy decay time were calculated as amplitude-weighted averages from three-exponential fit of decay kinetics.

Photobleaching kinetics were recorded by exposure of carbon dots aqueous solutions of the same concentration to continuous irradiation with excitation light of the spectrofluorometer

[©] Астафьев А.А., Шахов А.М., Сырчина М.С., Надточенко В.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Synthesis and separation of lysine carbon dots

(central wavelength is 350 nm, spectral width is 20 nm); fluorescence intensity was recorded at 430 nm every 2 minutes for 80 minutes.

Infrared absorption spectra of dried samples were collected using Bruker Lumos II FTIR microscope-spectrometer in an attenuated total reflection mode.

Results and Discussion

As described previously, laser irradiation of L-lysine solution resulted in formation of water-soluble colored and fluorescent nanometer-sized particles (carbon dots). This solution was separated using dialysis into lower and higher weight fractions (Lys-CD-1 and Lys-CD-2 respectively). Effective separation of the sample into fractions was confirmed using measurements of fluorescence anisotropy decay time, which is proportional to the average hydrodynamic volume of carbon dots (Fig. 2,*a*, Table 1). Emission anisotropy of Lys-CD-1 decayed much faster and Lys-CD-2 – much slower than of Lys-CD which confirms their different volumes. Characteristically, Lys-CD-1 exhibited relatively long anisotropy decay corresponding to the hydrodynamic volume of approximately 3.1 nm³. Thus, even in the lower-weight fraction, fluorescence is mostly attributed to nanoparticles (carbon dots) and few, if any, fluorescent moieties exist as separate small molecules in solution.

Infrared spectra of irradiated solution, separated from unreacted L-lysine, demonstrated characteristic amide peaks (Fig. 2,b), indicating that carbon dots were formed by polymerization of



Fig. 2. Fluorescence anisotropy decay kinetics of Lys-CD, Lys-CD-1, and Lys-CD-2 (excitation at 360 nm, registration at 430 nm) (*a*). Comparison of infrared spectra of Lys-CD dialyzed using 2 and 10 kDa membranes (*b*)

amino acid monomers through formation of amide bonds. Additionally, there were also bands of hydroxyl, alkoxy-, methylene and carboxylate groups. We compared infrared spectra of carbon dots of different weights, dialyzed through 2 kDa and 10 kDa membranes, which were essentially similar (Fig. 2,*b*). Thus, chemical composition of carbon dots demonstrates little dependence on their size.

Absorption and emission spectra demonstrated, that, unlike original L-lysine, the Lys-CD exhibited a broad absorption spectrum in the near ultraviolet and visible range and excitation-dependent visible fluorescence with the maximal intensity at ca. 430 nm and excitation maximum at ca. 350 nm. Absorption and fluorescence characteristics of Lys-CD-1 and Lys-CD-2 fractions were generally the same as of Lys-CD. The small difference between them was in slightly larger visible absorption and broader emission spectrum of Lys-CD-2 (Fig. 3, a, b) and small shifts in the excitation and emission maxima (Table 1). Lack of obvious dependence of the absorption and emission bands position on the carbon dot size proves that quantum size effects do not make appreciable contribution to their optical characteristics. Rather absorption and fluorescence are attributed to organic chromophore groups, which are the same in carbon dots of different sizes.



Fig. 3. Comparison of UV-Vis absorption (a) and fluorescence emission (excitation at 350 nm) (b) spectra, fluorescence decay kinetics (c) and fluorescence photobleaching kinetics (d) of Lys-CD, Lys-CD-1 and Lys-CD-2

Unlike emission spectra, fluorescence lifetimes and quantum yields demonstrated a clear dependence on the nanoparticle size and declined with increase of the carbon dot size (Fig. 3,c, Table 1). The natural radiative lifetime, equal to the ratio of fluorescence lifetime to quantum yield, was approximately constant at 35-40 ns for all the three samples. Thus, the difference in yields and lifetimes originates from higher nonradiative relaxation rate in carbon dots of larger diameter. This fluorescence quenching effect in Lys-CD-2 is accompanied by broadening of the emission spectrum to the higher wavelengths area (Fig. 3,b).

These observations indicate that the quenching mechanism is likely related to resonance energy transfer between donor and acceptor chromophores within the same carbon dot [8]. Larger nanoparticles are more likely to include several chromophore groups and thus are exhibit stronger energy transfer effects which agrees with stronger fluorescence quenching in Lys-CD-2.

Table 1

Fluorescence characteristics of Lys-CD and its fractions Lys-CD-1 and Lys-CD-2

Sample	Em. minimum, nm	Ex. maximum, nm	Φ, %	Lifetime, ns	Anisotropy decay time, ns	I ₄₅₀ /I ₃₅₀
Lys-CD	429	351	6.5	2.29	1.39	0.109
Lys-CD-1	428	348	7.9	2.72	0.77	0.091
Lys-CD-2	433	352	4.6	1.85	2.68	0.149

Notations. Φ is the fluorescence quantum yield, I_{450}/I_{350} is the ratio of integral fluorescence intensities under 450 and 350 nm excitation

Finally, we analyzed photostability of lysine carbon dots. Under continuous wave irradiation at 350 nm fluorescence intensity of all the three samples decreased, the fastest photobleaching rate and the largest magnitude of decrease was observed for larger dots (Lys-CD-2) (Fig. 3,*d*). Thus, the smallest dots possessed the largest photostability.

Conclusion

Our results indicate that the same type of chromophores is responsible for absorption and emission of lysine carbon dots regardless of their size and quantum size effects do not contribute to their absorption and fluorescence. These chromophores are only formed within carbon dots and don't exist as separate molecules in solution. Quenching of blue fluorescence in carbon dots of large size indicates resonance energy transfer to acceptors within the same nanoparticle. Due to higher quantum yield and larger photostability smaller-sized lysine carbon dots are more attractive for practical applications.

REFERENCES

1. Sun Q., Qin Z., Wu W., Lin Y., Chen C., He S., Li X., Wu Z., Luo Y., Qu J., In vivo imagingguided microsurgery based on femtosecond laser produced new fluorescent compounds in biological tissues, Biomedical Optics Express. 9 (2018) 581–590.

2. Astafiev A.A., Shakhov A.M., Osychenko A.A., Syrchina M. S., Karmenyan A.V., Tochilo U.A., Nadtochenko V.A., Probing intracellular dynamics using fluorescent carbon dots produced by femtosecond laser in situ, ACS Omega. 5 (21) (2020) 12527–12538.

3. Astafiev A.A., Shakhov A.M., Gulin A.A., Vasin A.A., Gubina M.V., Syrchina M.S., Nadtochenko V.A., Femtosecond laser synthesis and comparative analysis of fluorescent carbon dots from L-lysine aqueous solution, Journal of Physics: Conference Series. 2086 (2021) 012121

4. Zhu S., Song Y., Zhao X., Shao J., Zhang J., Yang B., The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective, Nano Research. 8 (2015) 355–381.

5. Yuan F., Yuan T., Sui L., Wang Z., Xi Z., Li Y., Li X., Fan L., Tan Z., Chen A., Jun M., Yang S., Engineering triangular carbon quantum dots with unprecedented narrow bandwidth emission for multicolored LEDs, Nature Communications. 9 (2018) 2249.

6. Schneider J, Reckmeier C.J., Xiong Y., von Seckendorff M., Susha A.S., Kasák P., Rogach A.L., Molecular Fluorescence in Citric Acid-Based Carbon Dots, The Journal of Physical Chemistry C 121 (3) (2017) 2014–2022.

7. Essner J.B., Kist J.A., Polo-Parada L., Baker G.A., Artifacts and Errors Associated with the Ubiquitous Presence of Fluorescent Impurities in Carbon Nanodots, Chemistry of Materials. 30 (6) (2018) 1878–1887.

8. Astafiev A.A., Shakhov A.M., Nadtochenko V.A., Resonance Energy Transfer Reveals the Presence of Multiple Luminescence Emission Centers within a Carbon Nanodot, JETP Letters. 116 (2022) 505–513.

THE AUTHORS

ASTAFIEV Artyom A. astafiev.artyom@gmail.com

SHAKHOV Aleksander M. physics2007@yandex.com

SYRCHINA Maria S. wrongclue@gmail.com ORCID: 0000-0002-5318-8903

NADTOCHENKO Victor A. wrongclue@gmail.com

Received 17.07.2023. Approved after reviewing 24.08.2023. Accepted 30.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 544.032.65 DOI: https://doi.org/10.18721/JPM.163.219

A study of chemical and mechanical properties of paper under its laser cleaning

A.D. Neelova¹[∞], E.M. Shepilova², E.I. Nosova², S.L. Rongonen³, V.A. Parfenov¹

¹ St. Petersburg Electrotechnical University «LETI», St. Petersburg, Russia;

² Saint Petersburg Institute of History of the Russian Academy of Sciences, St. Petersburg, Russia;

³ The Archive of the RAS St. Petersburg Branch, St. Petersburg, Russia

⊠ angelina.neelova@gmail.com

Abstract. This paper is devoted to investigation of chemical and mechanical paper properties after laser cleaning. In recent years, laser technologies have been widely used in the preservation of Cultural Heritage (CH). One of the main fields of laser application in this area is the cleaning of surfaces of CH objects from natural and anthropogenic contaminations. However, cleaning of books and documents on paper basis requires intensive experimental studies. Comparison of paper properties before and after laser cleaning may prove the safety of laser cleaning. One of the most important parameters that characterize paper strength and durability are hydrogen ion concentration (pH) and absorptivity. We will present experimental results on pH value measurements of paper as well as results on paper absorptivity performed on model samples and real historical artefacts such as books and fragments of newspapers. The results of studies indicate on the neutralising effect of laser irradiation which can be used for the conservation of books and documents on paper base.

Keywords: heritage science, laser application, laser cleaning

Citation: Neelova A.D., Shepilova E.M., Nosova E.I., Rongonen S.L., Parfenov V.A., A study of chemical and mechanical properties of paper under its laser cleaning, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 114–119. DOI: https://doi.org/10.18721/JPM.163.219

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 544.032.65 DOI: https://doi.org/10.18721/JPM.163.219

Исследование химических и механических свойств бумаги после лазерной очистки

А.Д. Неелова¹[™], Е.М. Шепилова², Е.И. Носова², С.Л. Ронгонен³, В.А. Парфенов¹

¹ Санкт-Петербургский государственный электротехнический университет «ЛЭТИ»

им. В.И. Ульянова (Ленина), Санкт-Петербург, Россия;

² Санкт-Петербургский Институт истории РАН, Санкт-Петербург, Россия;

³ Санкт-Петербургский филиал архива РАН, Санкт-Петербург, Россия;

⊠ angelina.neelova@gmail.com

Аннотация. Данная работа посвящена исследованию химических и механических свойств бумаги после лазерной очистки. В последнее время лазерные технологии стали все шире применятся для сохранения культурно-исторического наследия. В реставрации используют технологию лазерной очистки, которая позволяет решать

© Neelova A.D., Shepilova E.M., Nosova E.I., Rongonen S.L., Parfenov V.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

задачи по удалению природных наслоений и антропогенных загрязнений с поверхности памятников. На сегодняшний день наиболее отработанной является очистка объектов из камня и металла, лазерная очистка органических материалов, например, бумаги находится в стадии проведения поисковых научно-исследовательских работ. Сравнение химических и механических свойств бумаги до и после воздействия лазера может доказать безопасность лазерной очистки. Наиболее важными параметрами, характеризующим сохранность бумаги являются концентрация ионов водорода (pH) и впитываемость бумаги. В данной работе будут приведены результаты измерения кислотности и впитываемости бумаги после лазерной очистки иттербиевым волоконным импульсным лазером с длиной волны 1064 нм модельных образцов и исторических артефактов. Результаты проведенных исследований указывают на нейтрализующий эффект лазерного излучения, что потенциально может быть использовано для реставрации книг и документов на бумажной основе.

Ключевые слова: культурно-исторические наследие, лазерная очистка, применение лазеров

Ссылка при цитировании: Неелова А.Д., Шепилова Е.М., Носова Е.И., Ронгонен С.Л., Парфенов В.А. Исследование химических и механических свойств бумаги после лазерной очистки // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 114–119. DOI: https://doi.org/10.18721/JPM.163.219

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Laser technologies have recently begun to be widely embedded not only in industrial and scientific applications but also in the field of restoration and conservation of Cultural Heritage. Laser restoration of stone and metal monuments is the most well developed, while laser cleaning of paper objects is still at the stage of experimental studies.

For the last decade many research groups have presented the possibility of using laser irradiation to remove paper deteriorations such as dust, soot, fungi, foxings, etc. [1-5]. These studies have shown that laser cleaning has a significant potential for removal of surface contaminations. However, currently there are still debates between professional restorers regarding the safety of laser cleaning for preservation of books and documents, especially in the long term. That is why proving the inalterability of chemical and mechanical properties of paper before and after laser cleaning might be considered as confirmation of its safety.

Most significant parameters of paper in conservation practice are hydrogen ion concentration and absorptivity. The hydrogen ion concentration or pH value of paper characterizes strength and durability of paper. Oxidation processes in paper have a negative effect on its properties, increasing the acidity. Increased acidity is one of the main factors that causes accelerated ageing [6]. Usually paper that is long in storage becomes acidic: pH 3.0–5.0. If the pH is less than 5.5 paper is neutralized. The ability of paper to absorb moisture from the air is determined by its absorptivity [7]. When being stored under conditions with a certain humidity level between the air and the paper there is established a balance. When the balance is disturbed robustness of paper is compromised. In conservation, absorptivity is very important. For example, it influences the possibility to absorb adhesives substances therefore the possibility of conservation itself. If the absorptivity decreases after laser cleaning it raises a question about capability of subsequent conservations of paper documents. Not to say that excessive dryness leads to fragility of paper and its early destruction for dry paper loses its mechanical durability.

Experiment

Earlier the authors of this work reported about laser cleaning of different kinds of paper using Ytterbium fiber laser [8–9]. It was shown that use of laser with following parameters: wavelength of 1064 nm, pulse duration of 100 ns, peak power density varies from $1.6 \cdot 10^5$ W/cm² to $3.2 \cdot 10^5$ W/cm², the pulse repetition frequency of 20 kHz makes possible effective removal of

[©] Неелова А.Д., Шепилова Е.М., Носова Е.И., Ронгонен С.Л., Парфенов В.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

contaminants. The purpose of this work is to investigate chemical and mechanical properties of paper after laser cleaning at 1064 nm with Ytterbium fiber laser performed on paper samples and real historical artefacts.

Three types of old paper samples from the Soviet era were cleaned during the experiments and further their chemical and mechanical properties were studied. These samples are: sample 1, thin paper of a light brown shade, sample 2, thicker paper similar in shade to sample 1, sample 3, thin nearly white paper. Soviet paper samples are presented in Fig. 1.

To simulate surface contamination of paper graphite or charcoal dust were rubbed onto the surface of samples.

The other artefacts are the books from the late third of the 18th century to the beginning of the 20th century. Such a choice of books was made to cover a large period of time and to have different kinds of book paper. On top of that, investigated books are relevant to conservation science, especially 19th century books since they were mass produced from raw materials of lesser quality, therefore they are more fragile and unstable towards ageing. In the selection there are books printed in European countries and in the Russian Empire. Contaminations that occur in studied artefacts are typical in conservation, they are worn-in dust, traces of grease and of unknown origin. A list of artefacts is presented in Table 1.

The pH value measurement was carried out by portable pH metres manufactured by Hanna Instruments and Ohaus with plane electrodes and temperature sensitive elements. For the paper absorptivity measurement, analytical balance was utilized.

Table 1

#	Title	Year of printing	Place of printing	
1	Sonnets by Petrarca	1778	London, England	
2	The Dramatick Writings of Will. Shakspere, Volume the Thirteenth	1788	London, England	
3	Application de l'Analyse à la géométrie by M. Monge	1809	Paris, France	
4	Collected volume of works by F.M. Dostoyevsky	1866	St. Petersburg, Russia	
5	The Complete Works of M.E. Saltykov-Shchedrin, Volume One	1905	St. Petersburg, Russia	
6	What are we living for? by L. Tolstoy	1906	Moscow, Russia	
7	History of Greece in the classical period. 9th–4th century BC by R. Vipper	1913	St. Petersburg, Russia	
8	History of Western Europe, Contemporary Times by N. Kareev	1916	Moscow, Russia	
9	Newspaper dated June, 1943	1943	USSR	

List of historical artefacts

Results and Discussion

The pH test was performed by the method of aqueous extract in concordance with *Direction* of pH value measuring using the contact method by Mamaeva and Velikova [6] with electronic pH-meter. The measurement was performed in two points on the page of a given sample or artefact: one in the area (Fig. 1) that was treated by the laser and another in the untreated area. Results of pH value measuring are shown in Table 2.

As seen in Table 2, alkalic modern copy paper became more neutral after laser cleaning, pH value decreased. For the samples 1 and 2, pH value increased whereas for the sample 3, it stayed nearly the same.



Fig. 1. Books after laser cleaning. Fragment of book *Application de l'Analyse* a la géométrie (a). Fragment of *The Complete Works of M.E. Saltykov-Shchedrin, Volume One* (b). Laser-treated areas are marked in red

Consider further pH value measurement of historical artefacts. Sample numbers match document titles presented in Table 1. As seen in the table, all of the artefacts excluding 2 became more neutral, their pH values increased after laser treatment. As for artefact 3 its initial pH value is quite neutral and it becomes slightly more acidic. Probably further investigation is needed. Overall pH value tending to neutrality is a positive fact. In general, initially acidic paper became less acidic after laser treatment or did not change its pH value, alkali paper became more neutral. There is no change in pH value for the newspaper after laser cleaning.

To conclude, pH measurement showed overall the tendency for neutralizing of paper after laser irradiation, initially acidic paper became less acidic, alkalic one became less alkalic, although paper samples that had neutral pH-value became more acidic. To ensure general rule it is suggested that another experiment taking place with a sample collection method of pH value measuring. Given results could raise a question about the possibility of neutralizing paper by laser which is an actual conservation task.

While performing pH value measuring it was noted that laser treated areas absorb water differently than non-treated areas (Fig. 2). It was suggested that the absorptivity of paper declines due to processes that happen under laser irradiation. This phenomenon will be considered in the following part.

As it was noted in the previous part that paper presumably loses its ability to absorb moisture, it was decided to perform an experiment to evaluate the absorptivity of paper.

Table 2

Sample	Without cleaning	After cleaning	Sample	Without cleaning	After cleaning
Model samples			2	4.29	4.55
Copy paper	9.15	8.89	3	6.56	6.23
#	Soviet paper samples		4	5.57	5.66
1	4.75	5.32	5	5.83	6.05
2	4.75	5.32	6	4.20	4.40
3	4.91	4.90	7	4.40	4.60
	Artefacts		8	4.00	4.40
1	5.55	5.88	9	5.55	5.55

Summary table of measured pH values of paper samples

ROLEMENT Фашистами тел прабро. Его танк русеницами раздавил рай мётных гнезда и орнём своего чил орудия вражеских противотанковых Лен HVILLEN. машены ранили, но и раненый он проъся, пока не выполния приказ коман-781 пвшесь из госпеталя, Чауский принял ую машину. Он тщательно полготовляет ощим боям. Мих. ШЕФЕР ющая ариня

Fig. 2. Fragment of the newspaper wetted with distilled water for pH value estimation. Less absorbent areas are noticeably lighter, they were treated with laser irradiation

The experiment was carried out in accordance with the Soviet Union State Standard 12605-97 *Paper and board. Method for determination of surface water absorptiveness at one-sided wetting (Cobb method).* Three samples 10 by 10 cm in size of old soviet paper (paper that goes by sample 1 in previous parts) were cleaned from charcoal dust, they were weighed on an analytical balance in dry and wet states and compared with three samples of the same paper which did not undergo the laser treatment. Laser treated samples were wetted from the cleaned side.

The surface water absorptivity of paper with one-sided wetting for each sample is calculated by the following formula

$$Cobb_{x} = 100(m_{2} - m_{1}),$$
 (1)

where m_1 is the mass of the sample before the experiment; m_2 is the mass of the sample after the experiment.

There is no difference in values, thus it could not be unambiguously said that paper loses its absorptivity after laser cleaning. Nevertheless, the result observed in Fig. 2 with the piece of a newspaper is significant enough to proceed the investigation of a given question for paper differ drastically in properties depending on many factors. In conclusion, further investigation is needed.

Conclusion

pH measurement of paper samples and artefacts showed overall the tendency for neutralizing of paper after laser irradiation, initially acidic paper became less acidic, alkalic one became less alkalic, although paper samples that had neutral pH-value became more acidic. Considering that generally paper that has been in storage for a long time is acidic and has pH of 3.0–5.0 the tendency of neutralizing paper after laser irradiation is a positive fact. It could raise a question about the possibility of neutralizing paper by laser which is a topical conservation task.

The investigation of the absorptivity of paper gave no unequivocal result, it could be speculated that some paper really loses its absorptivity after laser impact as it was suggested happened with the newspaper fragment, which is a negative fact for it leads to fragility of paper, though some paper does not lose it.

To conclude, laser cleaning of paper has its own benefits, it is a very precise and fast conservation method, though it has a narrow applicability, it could be used in specific conservation tasks and only for surface contaminations. Nevertheless, further investigations of the laser irradiation influence on paper and its chemical and mechanical as well as other properties are needed.

REFERENCES

1. Zekou E., Tsilikas I., Chatzitheodoridis E., Serafetinides A., Laser paper cleaning: the method of cleaning historical books. Proceedings of 19th International Conference and School on Quantum Electronics: Laser Physics and Applications, V. 10226, (2017) 1022605.

2. Brandt N.N., Chikishev A.Y., Itoh K., Rebrikova N.L., ATR-FTIR and FT Raman spectroscopy and laser cleaning of old paper samples with foxings. Laser physics, (2009) (19) (3) 483–492.

3. Atanassova V., Yankov G., Zahariev P., Grozeva M., Laser treatment of contaminations on paper: a preliminary study. Proceeding of the Conference "Applicazioni Laser nel Restauro (APLAR)", (2019) (6) 433–445.

4. Mokrushin Yu. M., Parfenov V. A., Use of copper-vapor laser for restoration of artworks. Journal of Optical Technology, (2008) (75) (7) 476–477.

5. **Parfenov V.A., Titov S.V.,** Technical and Technological Aspects of Laser Cleaning for Books and Documents. Proceedings of the IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus). (2019) 903–906.

6. **Dobrusina S.A.**, Laboratornye metodiki i tekhnologicheskie instruktsii v konservatsii dokumentov. [Laboratory procedures and technological directions in conservation of documents]. St. Petersburg, RNB Publ., (2016).

7. Flyate D.M., Svoystva bumagi [Properties of paper]. Lesn. Promysh. Publ., (2012) 440.

8. Neelova A.D., Vasilieva A.V., Rongonen S.L., Vasiliev O.S., Safronov D.V., Parfenov V.A., Laser Cleaning of Paper. Proceedings of the IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus). (2022) 1134–1137.

9. Parfenov V., Galushkin A., Tkachenko T., Aseev V., Laser Cleaning as Novel Approach to Preservation of Historical Books and Documents on a Paper Basis. Quantum Beam Science, (2022) (6) (3) 23.

THE AUTHORS

Received 17.07.2023. Approved after reviewing 10.08.2023. Accepted 31.08.2023.

NEELOVA Angelina D. angelina.neelova@gmail.com ORCID: 0009-0004-8098-2055

SHEPILOVA Elena M. yelena_sch@mail.ru ORCID: 0009-0007-8081-4758

NOSOVA Ekaterina I. katerinanossova@gmail.com ORCID: 0000-0002-9050-3239 RONGONEN Sofia L. sofiagonobobleva@mail.ru ORCID: 0000-0002-9050-3239

PARFENOV Vadim A. vadim_parfenov@mail.ru ORCID: 0000-0002-2048-4677

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 53.082.534 DOI: https://doi.org/10.18721/JPM.163.220

Compact solid-state laser with diode optical pumping and high frequency stability

V.V. Naumova^{1,2}, O.A. Orlov²

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² D.I. Mendeleev Institute for Metrology, St. Petersburg, Russia

^{III} vika_025898@mail.ru

Abstract. Continuous single-frequency solid-state lasers with intracavity frequency doubling Nd⁺³/YVO/KTP, whose frequency is stabilized along the absorption lines of molecular iodine, are currently widely used in laser interferometers. The paper describes a small-sized laser with frequency instability at the level of 10-12 with an averaging time of 1 second. It has been shown that this level of stability is limited by the amplitude noise of the laser, which in turn are determined by fluctuations in the laser pumping. Reducing the amplitude noise and increasing the signal-to-noise ratio in the stabilization system made it possible to further increase the frequency stability of laser radiation.

Keywords: solid-state laser, laser diode, amplitude noise, Bragg grating

Citation: Naumova V.V., Orlov O.A., Compact solid-state laser with diode optical pumping and high frequency stability, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 120–124. DOI: https://doi.org/10.18721/JPM.163.220

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.082.534 DOI: https://doi.org/10.18721/JPM.163.220

Компактный твердотельный лазер с диодной оптической накачкой и высокой частотной стабильностью

В.В. Наумова^{1,2}, О.А. Орлов²

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;

² Всероссийский НИИ метрологии имени Д. И. Менделеева, Санкт-Петербург, Россия

⊠ vika_025898@mail.ru

Аннотация. Непрерывные одночастотные твердотельные лазеры с внутрирезонансным удвоением частоты $Nd^{+3}/YVO/KTP$, частота которых стабилизирована по линиям поглощения молекулярного йода, в настоящее время широко используется в лазерных интерферометрах. В работе описан малогабаритный лазер с нестабильностью частоты на уровне 10-12 при времени усреднения в 1 секунду. Было показано, что это уровень стабильности ограничивается амплитудными шумами лазера, которые в свою очередь определяются флуктуациями лазерной накачки. Уменьшение амплитудных шумов и повышение отношения сигнал/шум в системе стабилизации позволило дополнительно повысить частотную стабильность лазерного излучения

Ключевые слова: твердотельный лазер, лазерный диод, амплитудный шум, решетка Брэгга

© Naumova V.V., Orlov O.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Наумова В.В., Орлов О.А. Компактный твердотельный лазер с диодной оптической накачкой и высокой частотной стабильностью // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 3.2 № .16. С. 120–124. DOI: https://doi.org/10.18721/JPM.163.220

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In modern science and technology, optical measurements are increasingly being used to solve various tasks [1-5]. A special place among them is occupied by measurements using various lasers [7-10]. An iodine-stabilized diode-pumped solid-state laser (DPSS laser) with a wavelength of 532 nm is not only a good secondary frequency standard but is also a good laser source with a wavelength (frequency) for implementing a meter using laser interferometry.

Many of the lasers usually described in all references are quite large (all the optical parts of the laser systems were arranged on a 45 cm \times 45 cm breadboard) [11–13]. The compactness and low weight of the laser (the dimensions of the laser head, which includes an iodine spectroscopy scheme, are 80 mm \times 116 mm \times 130 mm with a mass of about 1.5 kg) can be critical parameters for use in laser displacement interferometry, for example, in industrial laser interferometers and in absolute ballistic gravimeters.

The paper describes a small-sized laser with frequency instability at the level of 10^{-12} with an averaging time of 1 second.

It has been shown that this level of stability is limited by the amplitude noise of the laser, which in turn are determined by fluctuations in the laser pumping. Reducing the amplitude noise and increasing the signal-to-noise ratio in the stabilization system made it possible to further increase the frequency stability of laser radiation.



Fig. 1. Optical scheme of Nd⁺³/YVO/KTP/I₂ iodine stabilized laser resonator with a wavelength of 532 nm

Solid-state laser design

Fig. 1 shows the optical scheme of the developed laser resonator.

This linear resonator consists of a laser diode LD with a wavelength of 808 nm, a plate of the active medium Nd: YVO_4 AM, a Brewster plate B, a nonlinear crystal KTP (KTiOPO_4) with frequency doubling and a mirror of the output coupler M mounted on a piezoelectric disk PZT (lead zirconate titanate). The active medium Nd: YVO_4 , illuminated by a laser diode, generates radiation with a wavelength of 1064 nm. The Single-Frequency TO-Can Laser Diode is based on quantum well epitaxial layer growth and a highly reliable ridge waveguide structure with external volume holographic grating (VHG)

feedback. This single-transverse mode laser diode features high optical output power and produces a wavelength stabilized spectrum with a single frequency narrow linewidth (0.8 pm) over the operating power range of approximately 400 to 500 mW (SMSR 42.5 dB). The intracavitary KTP crystal doubles the frequency of this radiation. PD is a photodetector.

The optical length of the linear resonator is about 17 mm, which corresponds to an intermode frequency interval of about 10 GHz. Single-mode generation at a single frequency is provided in the range of about 400 GHz (along the luminescence line) by a birefringent interference Lyot filter formed by a birefringent KTP crystal and a Brewster plate.

[©] Наумова В. В., Орлов О. А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 2. Allan deviations of Nd:YVO $_4$ /KTP/I $_2$ compact laser at 532 nm

The temperatures of the active medium plate, the KTP crystal, the laser diode and the resonator are regulated with instability within 2 mK. The frequency tuning range with the KTP temperature is about 100 GHz (at twice the frequency, which corresponds to a wavelength of 532 nm).

The dimensions of the laser head, which includes an iodine spectroscopy scheme, are $80 \text{ mm} \times 116 \text{ mm} \times 130 \text{ mm}$ with a mass of about 1.5 kg.

The third harmonic method [14, 15] with a modulation frequency of 3.3 kHz is used to stabilize the frequency. An electronic unit for the power supply, five temperature control systems for laser elements and an iodine cell element, as well as servo electronics for frequency stabilization.

Amplitude noise

Several such type lasers were developed [11-13]. But in general, it was a laboratory installation, mounted on optical tables which are difficult for transportation.

To stabilize the frequency of the output radiation in these lasers, the binding of the output radiation to the absorption lines of molecular iodine is used. For the stable operation of the servo system, it is necessary to ensure a sufficient signal-to-noise ratio. In stationary installations, the length of the iodine cell is increased for these purposes. The best results were achieved with a 2m iodine cell (BIPM).

In our case, the length of the iodine cell is limited by the size of the transported radiator and is 10 cm. On such a cell, it was possible to stabilize the laser frequency at the level of 10^{-12} with an averaging time of 1 s. The frequency stability of the compact laser was measured using a stationary Nd:YAG/MgO:LiNbO₃/I2 BIPM laser at 532 nm.

The Allan deviations of the compact $Nd:YVO_4/KTP/I_2$ laser, stationary BIPM laser and He-Ne/I₂ WEO 131 laser at 633 nm (manufactured by Winters Electro-Optics, Inc.) are shown in Fig. 2.

As studies have shown, the main contribution to the amplitude noise of the laser, which limits the SNR ratio, is the parasitic modulation of optical pumping in DPSS lasers.

Typically, DPSS lasers use multimode LDs with a power of 0.5 - 2 W for pumping. The generation spectrum of these diodes is wider than the absorption line of the active medium of 0.1 nm. Several LD modes are placed in the absorption line.

In these lasers, the phenomenon of mode competition is observed, which leads to a change in the amplitude of individual longitudinal modes. At the same time, the total intensity of the LD radiation remains constant and is determined by the pump current.

To observe this phenomenon and the selection of LD, an installation was assembled in which the level and modulation of the power absorbed in the active medium can be recorded and recorded. It has been shown that the relative parasitic modulation of radiation in the pump radiation increases greatly after passing through the active medium. The level of this modulation differs for different LD batches. In Fig. 3, the spectrum of parasitic modulation of the pumping power of a typical multimode LD is shown.



Fig. 3. Spectrum of parasitic modulation of the pumping power of typical multimode LD

In addition, it should be noted that SS lasers are characterized by the presence of relaxation oscillations caused by Q-factor modulation of the resonator or pumping. The frequency of the peak of relaxation oscillations is determined by the laser parameters. The presence of these oscillations causes additional amplification of parasitic modulation, which at its peak can reach several orders of magnitude.

All this can negatively affect the operation of the servo system, which stabilizes the frequency by a signal of 1 and 3 harmonics at a modulation frequency of 10 kHz.

Recently, single-frequency LDs with a power of 0.5 watts have appeared. To ensure the selection of longitudinal modes, a volumetric Bragg lattice is used. In Fig. 4, the spectrum of parasitic modulation of the pumping power for a single-frequency LD is shown. They are significantly lower than those of conventional LDs.



Fig. 3. Spectrum of parasitic modulation of pumping power for single-frequency LD

Conclusion

A compact solid-state Nd: $YVO_4/KTP/I_2$ diode-pumped, iodine-stabilized laser at a wavelength of 532 nm was developed and investigated. Metrological (frequency stability and reproducibility) and technical (laser power, size and weight of laser blocks) characteristics suggest that such lasers will find wide application in laser displacement interferometry, including laser interferometers for absolute ballistic gravimeters, as well as portable secondary frequency standards in the visible optical frequency range.

REFERENCES

1. Mazing M., Zaitceva A., Kislyakov Y., Kondakova N., Avdyushenko S., Monitoring of oxygen supply of human tissues using a noninvasive optical system based on a multi-channel integrated spectrum analyzer, International Journal of Pharmaceutical Research. 12(2020) 1974–1978.

2. Davydov V., Vakorina D., Provodin D., Ryabogina N., Stepanenkov G., New Method for State Express Control of Unstable Hydrocarbon Media and Its Mixtures, Energies, 16 (6) (2023) 2529.

3. Smirnov K.J., Glinushkin A.P., Long-range night vision camera based on SWIR photocathode, Journal of Physics: Conference Series. 1695(1) (2020) 012090.

4. Smirnov K.J., Tushavin G.V., Glagolev S.F., Temperature investigations of inp/ingaas based photocathodes," Proceedings of the 2018 IEEE International Conference on Electrical Engineering and Photonics, (EExPolytech-2018), vol. 8564416 (2018) 209-211.

5. Yakusheva M.A., Davydov R.V., Isakova D.D., Features of signal absorption fronts of laser radiation in rapid diagnosis of human health, Proceedings of 8th International Conference on Information Technology and Nanotechnology (2022) 1–5.

6. Davydov V. V., Dudkin V. I., E.N. Velichko E. N., Karseev A.Yu., Fiber-optic system for simulating accidents in the cooling circuits of a nuclear power plant, Journal of Optical Technology (A Translation of Opticheskii Zhurnal). 82(3) (2015) 132–135.

7. Davydov V.V., Kruzhalov S.V., Grebenikova N.M., Smirnov K.Y., Method for Determining Defects on the Inner Walls of Tubing from the Velocity Distribution of the Flowing Fluid, Measurement Techniques. 61(4) (2018) 365–372.

8. Davydov V., Porfir'eva E., Davydov R., Nondestructive Method for Testing Elasticity of Walls of Human Veins and Arteries, Russian Journal of Nondestructive Testing. 58(9) (2022) 847–857.

9. Davydov R., Zaitceva A., Davydov V., Isakova D., Mazing M., New Methodology of Human Health Express Diagnostics Based on Pulse Wave Measurements and Occlusion Test, Journal of Personalized Medicine. 13(3) (2023) 443.

10. Grevtseva A.S., Smirnov K.J., Greshnevikov K.V., Davydov V.V., Rud V.Yu., Glinushkin A.P., Method of assessment the degree of reliability of the pulse wave image in the rapid diagnosis of the human condition, Journal of Physics: Conference Series. 1368(2) (2019) 022072.

11. Feng-Lei H., Ishikawa J., Yoon T. H., Ma L-S., Ye J., Hall J., Portable I2-stabilized Nd:YAG laser for wavelength standards at 532 nm and 1064 nm, Recent Developments in Optical Gauge Block Metrology. 1 (1998) 2–10.

12. Feng-Lei H., Ishikawa J., Yoda J., Ye J., Ma L-S., John L., Portable I2-stabilized Nd:YAG laser for wavelength standards at 532 nm and 1064 nm, IEEE Transaction of instrumentation and measurement. 48(2) (1999) 532–536.

13. Gaizerano G., Bava E., Bisi M., Bertinetto F., Svelto C., Frequency stabilization of frequencydoubled Nd:YAG lasers at 532 nm by frequency modulation spectroscopy technique, IEEE Transaction of instrumentation and measurement. 48(2) (1999) 540–543.

14. Okhapkin M.V., Skvortsov M.N., Belkin A.M., Kvashnin N.L., Bagaev S.N., Tunable single-frequency diode-pumped Nd:YAG ring laser at 1064/532 nm for optical frequency standard applications, Optics communications. 203(2002) 359–362.

15. Bitou Y., Sasaki K., Iwasaki S., Hong F-L., Compact I2-stabilized frequency doubled Nd:YAG laser for long gauge block interferometer, Japanese Journal of Applied Physics. 42(2) (2003) 2867–2871.

THE AUTHORS

NAUMOVA Victoria V. vika_025898@mail.ru ORCID: 0000-0002-6577-1223 **ORLOV Oleg A.** oorl@mail.ru

Received 24.07.2023. Approved after reviewing 17.08.2023. Accepted 02.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 544.77 DOI: https://doi.org/10.18721/JPM.163.221

Phosphine-free synthesis of selenide colloidal quantum dots

I.A. Shuklov¹[™], T. Milenkovich¹, A.A. Mardini¹

¹ Moscow Institute of Physics and Technology (State University), Dolgoprudny, Moscow, Russia

⊠ shuklov.ia@mipt.ru

Abstract. Metal selenide colloidal quantum dots have promising properties for applications in many fields such as gas sensing, food quality control, car accessories for orientation under low-visibility conditions, Infrared detectors for spectrometers. The wide application of selenide nanoparticles is limited due to a number of reasons. High requirements to the equipment for preparation of these materials in an inert atmosphere as well as poor reproducibility of modern synthetic procedures are some of the major reasons for very limited application of the selenide quantum dots today. Preparation of mercury and lead selenide colloidal nanoparticles by standard phosphine based procedures are especially affected by these problems. In this paper we report the application of selenium precursor prepared by dissolution of elemental selenium by action of sodium borohydride in oleylamine in the synthesis of lead selenide and mercury selenide quantum dots. The optical properties of the obtained quantum dots are investigated. This reagent is more easily prepared and less affected by conditions as a common phosphine based precursors. The impact of the reaction conditions and isolation procedures on the size distribution is reported. The work-up procedures are developed.

Keywords: quantum dots, nanoparticles, selenides, hot-injection synthesis

Funding: RNF 23-23-00300.

Citation: Shuklov I.A., Milenkovich T., Mardini A.A., Phosphine-free synthesis of selenide colloidal quantum dots, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 125–129. DOI: https://doi.org/10.18721/JPM.163.221

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 544.77 DOI: https://doi.org/10.18721/JPM.163.221

Синтез квантовых точек селенидов металлов с использованием безфосфиновых прекурсоров

И.А. Шуклов¹, Т. Миленкович¹, А.А. Мардини¹

¹ Московский физико-технический институт (государственный университет), г. Долгопрудный, Московская обл., Россия

^{IIII} shuklov.ia@mipt.ru

Аннотация. Коллоидные квантовые точки селенидов металлов, благодаря своим оптическим свойства, имеют потенциал для применений во многих областях, таких как сенсоры газов, системы контроля качества пищевых продуктов, системы для ориентации в условиях пониженной видимости, ИК-детекторы для спектрометров. Обширное применение наночастиц селенидов сдерживается рядом факторов. К таким факторам относится высокая стоимость оборудования для их получения в инертной атмосфере, а также плохая воспроизводимость существующих методик ссинтеза. Получение коллоидных наночастиц селенидов ртути и свинца с использованием стандартных прекурсоров на основе фосфинов особенно сильно страдают от вышеуказанных проблем.

© Shuklov I.A., Milenkovich T., Mardini A.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

В рамках данной статьи показана возможность применения прекурсоров селена, полученных растворением элементарного селена в присутствии боргидрида натрия, для получения коллоидных квантовых точек селенидов ртути и свинца. Для полученных наночастиц исследованы их оптические свойства. Данный реагент менее требователен к оборудованию и его легче использовать чем селениды фосфинов, используемые в настоящее время в качестве прекурсоров. Проведено исследование влияния условий синтеза и способа выделения на наночастицы.

Ключевые слова: квантовые точки, наночастицы, селениды, высокотемпературный коллоидный синтез

Финансирование: РНФ 00300-23-23.

Ссылка при цитировании: Шуклов И.А., Миленкович Т., Мардини А.А. Синтез квантовых точек селенидов металлов с использованием безфосфиновых прекурсоров // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 125–129. DOI: https://doi.org/10.18721/JPM.163.221

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Metal chalcogenide colloidal quantum dots (CQDs) is promising materials for applications in many fields based on their physical properties. Cadmium selenide CQDs is already found application in QLED TVs. Very recently SWIR-video cameras based on PbS CQDs were commercialized by several firms. Many other applications like solar cells, bioimaging markers, lasers, gas sensors, food quality control, Infrared detectors for spectrometers are under development.

Selenide nanoparticles are interested for application in near-IR. PbSe has band gap 0.28 eV and exciton Bohr radius about 46 nm. These properties allow to obtain PbSe CQDs with a first absorption peak from 800 to 3200 nm [1]. Band gap of lead selenide CQDs and therefor optical properties could be estimated by following formula reported by Moreels et al

$$E_0 = 0.278 + \frac{1}{0.016d^2 + 0.209d + 0.45},$$

where d is diameter of nanocrystal in nanometers [2].

HgSe is a semimetal in bulk with bang gap 0 eV, HgSe has spectral tunability from 800 up to 12000 nm based on intra- or interband adsorption.

The wide application of selenide nanoparticles is limited due to a number of reasons. They are more air-sensitive and less developed than PbS CQDs [3–5]. High requirements to the equipment for preparation of these materials in an inert atmosphere as well as poor reproducibility of modern synthetic procedures are some of the major reasons for very limited application of the selenide quantum dots today.

Preparation of mercury and lead selenide colloidal nanoparticles with commonly used trioctylphosphine suffer from these problems. Herein we report the application of selenium precursor prepared by dissolution of elemental selenium by action of sodium borohydride in oleylamine in the synthesis of PbSe and HgSe quantum dots.

Results and Discussion

Synthesis of mercury selenide. Mercury precursor is prepared by dissolution of 20 mg mercury chloride in 6 ml of dry oleylamine in two-necked flask at 120 °C within 1 h in Ar-flow. Selenium-precursor is prepared in a Schlenk-tube from selenium powder (58 mg) and sodium borhydride (27 mg) in 6.5 ml of dry oleylamine. 1 ml of selenium-precursor is added swiftly to the solution of cooled mercury-precursor at 100 °C. Reaction time by vigorous stirring is 5 minutes. Reaction is quenched by adding 1 ml 1-dodecanethiol and immediate cooling with ice bath. Nanoparticles are purified by 2x redispersing in tetrachloroethylene and precipitation with methanol. Sample of HgSe are dispersed in tetrachloroethylene for storage and characterization.

© Шуклов И.А., Миленкович Т., Мардини А.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Synthesis of lead selenide. Lead precursor is prepared by dissolution of 20 mg mercury chloride in 5 ml of dry oleylamine in two-necked flask at 150 °C within 1 h in Ar-flow. Selenium-precursor is preC pared in a Schlenk-tube from selenium powder (40 mg) and sodium borhydride (19 mg) in 5 ml of dry oleylamine. 1 ml of selenium-precursor is added swiftly to the solution of cooled mercury-precursor at 150 °C. Reaction time by vigorous stirring is 5 minutes. Reaction is quenched by cooling with ice bath and adding cold toluene. Nanoparticles are purified by 2 x redispersing in toluene and precipitation with ethanol. Sample of PbSe are dispersed in tetrachloroethylene for storage and characterization.

Two selenium precursors could be prepared by dissolution of selenium in oleylamine (OLA). One by heating to the temperatures about 200 °C and the second one by addition of sodium borohydride [6-7].

We successfully applied OLA/NaBH₄/Se reagent for the preparation of both HgSe and PbSe CQDs. Mercury selenide CQDs prepared at 100 °C possess absorption peak about 5200 nm (Fig. 1). From the absorption spectra could be assumed intraband transition nature of this signal. The interband peak is not present in the absorption spectra. TEM analysis revealed spherical nanoparticles with a mean size of 23 nm.

The electron diffraction (SAED) pattern revealed a crystalline structure of studied material. The lattice dimension are typical for tiemannite (HgSe), which is isostructural to metacinnabar (β -HgS) (Fig. 1,*c*). first rings in SAED match up perfectly with the 111, 220, and 311 diffraction lines of the Fd3m structure of HgSe with a = 6.08 E.

Absorption spectrum in the near-IR/visible range doesn't possess any absorption peaks, these could be attributed as an excitonic peak. This pattern is common for HgSe nanocrystals with intraband absorption peaks. Band edge is about 1500 nm (Fig. 2).



Fig. 1. HgSe CQDs: TEM image (a) and absorption spectrum (b)
in 5000-1000 cm⁻¹ range on the HATR Ge-plate , selected-area electron diffraction (SAED) pattern (c), size-distribution histogram (d)



Fig. 2. HgSe CQDs absorption spectrum

Lead selenide CQDs require higher temperatures for synthesis. Reaction proceed at the temperature as high as 150 °C with this selenium precursor. Reaction rate of the PbSe CQDs is much higher then with trioctylphosphine selenide. The sample with a first absorption peak at 2100 nm could be obtained after 3 minutes of synthesis.

Conclusion

Selenium precursor prepared by dissolution of elemental selenium by action of sodium borohydride in oleylamine could be interesting alternative for the preparation of lead selenide and mercury selenide quantum dots. The obtained PbSe CQDs possess first absorption peak at 2200 nm. The obtained HgSe CQDs possess intraband absorption peak at 5000 nm.

REFERENCES

1. Shuklov I.A., Razumov V.F., Lead chalcogenide quantum dots for photoelectric devices, Russian Chemical Reviews. 89 (2020) 379–391.

2. Moreels I., Lambert K., De Muynck D., Vanhaecke F., Poelman D., Martins J.C., Allan G., Hens Z., Composition and Size-Dependent Extinction Coefficient of Colloidal PbSe Quantum Dots, Chem. Mater. 19 (25) (2007) 6101–6106.

3. Ganeev R.A., Shuklov I.A., Zvyagin A.I., Dyomkin D.V., Smirnov M.S., Ovchinnikov O.V., Lizunova A.A., Perepukhov A.M., Popov V.S., Razumov V.F., Synthesis and low-order optical nonlinearities of colloidal HgSe quantum dots in the visible and near infrared ranges, Optics Express. 29 (11) (2021) 16710–16726.

4. Ganeev R.A., Kim V.V., Shuklov I.A., Popov V.S., Lavrentyev N.A., Ponomarenko V.P., Mardini A.A., Dyomkin D.V., Milenkovič T., Bundulis A., et al., Third harmonic generation in the thin films containing quantum dots and exfoliated nanoparticles. Applied Physics B. 128 (2022) 202.

5. Shuklov I.A., Toknova V.F., Lizunova A.A., Razumov V.F., Controlled aging of PbS colloidal quantum dots under mild conditions. Materials Today Chemistry. 18 (2020) 100357.

6. Goubet N., Jagtap A., Livache C., Martinez B., Portalus H., Xu X.Z., Lobo R.P.S.M., Dubertret B., Lhuillier E., Terahertz HgTe Nanocrystals: Beyond Confinement. Journal of the American Chemical Society. 140 (15) (2018) 5033–5036.

7. Hou B., Benito-Alifonso D., Webster R., Cherns D., Galan M.C., Ferman D.J., Rapid phosphinefree synthesis of CdSe quantum dots: promoting the generation of Se precursors using a radical initiator. Journal of Materials Chemistry A. 2 (2014) 6879–6886.

THE AUTHORS

SHUKLOV Ivan A. shuklov.ia@mipt.ru ORCID: 0000-0001-5537-5609 MARDINI Alaa Aladdin aladdin.mardini@phystech.edu

MILENKOVICH Teodora tmilenkovich@phystech.edu

Received 25.07.2023. Approved after reviewing 11.09.2023. Accepted 12.09.2023.

Conference materials UDC 537.876.4 DOI: https://doi.org/10.18721/JPM.163.222

Photoluminescence anisotropy in hybrid nanostructures based on gallium phosphide nanowire and 2D transition metal dichalcogenides

M.A. Anikina^{1,2}, A. Kuznetsov^{1,2}, A.N. Toksumakov^{1,3},
 V.V. Dremov¹, D.A. Ghazaryan^{1,4}, V.V. Fedorov^{2,5},
 A.V. Arsenin^{1,4}, V.S. Volkov^{1,4}, A.D. Bolshakov^{1,2,4}

¹ Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russia;

² Alferov University, St. Petersburg, Russia;

³ Emanuel Institute of Biochemical Physics RAS, Moscow, Russia;

⁴ Yerevan State University, Yerevan, Armenia;

⁵ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

🖾 anikina_mar@spbau.ru

Abstract. Integration of nanophotonic structures having different geometry is a wellestablished way to promote desired optical effects. This work is aimed at study of the optical properties of a hybrid structure based on a transition metal dichalcogenides (TMDC) thin layer and III-V nanowires. The structures were studied by μ -Raman and μ -photoluminescence spectroscopy at room temperature. We demonstrate experimentally guiding of the TMDC photoluminescence through the individual nanowires and analyze this phenomenon. The results of the work shed a light on new ways for fabrication of integrated optical circuitry components.

Keywords: photonics, photoluminescence, 2D TMDC, III–V semiconductors, nanowires

Funding: Ministry of Science and Higher Education of the Russian Federation (Agreement 075-03-2023-106, project FSMG-2021-0005; Grant FSRM-2023-0009). Russian Science Foundation (grant No. 22-19-00738).

Citation Anikina M.A., Kuznetsov A., Toksumakov A.N., Dremov V.V., Ghazaryan D.A., Fedorov V.V., Arsenin A.V., Volkov V.S., Bolshakov A.D., Photoluminescence anisotropy in hybrid nanostructures based on gallium phosphide nanowire and 2D transition metal dichalcogenides, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 130–136. DOI: https://doi.org/10.18721/JPM.163.222

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Anikina M.A., Kuznetsov A., Toksumakov A.N., Dremov V.V., Ghazaryan D.A., Fedorov V.V., Arsenin A.V., Volkov V.S., Bolshakov A.D., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 537.876.4 DOI: https://doi.org/10.18721/JPM.163.222

Анизотропия фотолюминесценции в гибридных наноструктурах на основе нитевидных нанокристаллов фосфида галлия и двумерных дихалькогенидов переходных металлов

М.А. Аникина^{1,2}, А. Кузнецов^{1,2}, А.Н. Токсумаков^{1,3},
 В.В. Дремов¹, Д.А. Казарян^{1,4}, В.В. Федоров^{2,5},
 А.В. Арсенин^{1,4}, В.С. Волков^{1,4}, А.Д. Большаков^{1,2,4}

¹ Московский физико-технический институт (НИУ), Долгопрудный, Россия;

² Академический университет им. Ж.И. Алферова, Санкт-Петербург, Россия;

³ Институт биохимической физики им. Н.М. Эмануэля РАН, Москва, Россия;

⁴ Ереванский государственный университет, Ереван, Армения

⁵ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

⊠ anikina_mar@spbau.ru

Аннотация. Создание гибридных наноструктур на основе матриалов с различной геометрией является одним из способов получения оптических элементов с заданными параметрами. Данная работа направлена на исследование оптических свойств гибридных структур на основе тонких слоев дихалькогенидов переходных металлов и нитевидных нанокристаллов фосфида галлия. Структуры исследовалась методами микроспектроскопии комбинационного рассеяния и фотолюминесценции. Благодаря совмещению излучательных свойств тонких слоев ТМDC и волноводных свойств полупроводниковых ННК была получена анизотропная фотолюминесценция. Результаты работы могут быть использованы для изготовления компонентов интегральных оптических схем.

Ключевые слова: фотоника, фотолюминесценция, 2D TMDC, полупроводники А3Б5, нитевидные нанокристаллы

Финансирование: Работа выполнена в рамках Государственного задания Министерства науки и высшего образования Российской Федерации (Соглашение -075 106-2023-03 от 13.01.2023; проект FSMG-2021-0005 (01.2021 - 12.2023); грант FSRM-2023-0009). Также исследование выполнено за счет гранта Российского научного фонда (№ 22-19-00738).

Ссылка при цитировании: Аникина М.А., Кузнецов А., Токсумаков А.Н., Дремов В.В., Казарян Д.А., Федоров В.В., Арсенин А.В., Волков В.С., Большаков А.Д., Анизотропия фотолюминесценции в гибридных наноструктурах на основе нитевидных нанокристаллов фосфида галлия и 2D дихалькогенидов переходных металлов // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 130–136. DOI: https://doi.org/10.18721/JPM.163.222

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Thin layers of transition metal dichalcogenides (TMDCs) are a large family of two-dimensional materials with a number of unique physical properties. It is especially interesting that some of these materials exhibit an efficient photoluminescence in the visible and near-infrared ranges [1]. One of the problems limiting the usage of these materials for the development of devices is the low absorption capacity due to their small thickness [1]. It is possible to optimize absorption by using resonant optical structures [2]. Such structures include nanowires (NWs) of semiconductor compounds [3] providing several pathways for device applications [4, 5] including flexible devices

© Аникина М.А., Кузнецов А., Токсумаков А.Н., Дремов В.В., Казарян Д.А., Федоров В.В., Арсенин А.В., Волков В.С., Большаков А.Д., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

[6]. Due to the transparency and high refractive index [7] Gallium phosphide (GaP) NWs promote several peculiar effects [8, 9] promising for nanophotonic applications. It should be noted that these structures are able to support both resonant modes and waveguide modes [10], that makes them perfectly suitable for anisotropic signal outcoupling [11]. So, it becomes possible to fabricate nanoscale radiation sources for optical data processing on-chip systems. This work is focused on fabrication and study of the TMDC (molybdenum disulfide MoS_2 and molybdenum diselenide $MoSe_2$) and GaP NWs based hybrid structure for exploration of the field confinement and light guiding of the TMDC photoluminescence (PL).

Materials and Methods

Thin layers of TMDC were mechanically exfoliated from bulk crystals. GaP NWs were grown on a Si (111) substrate by molecular beam epitaxy using the vapor-liquid-solid mechanism according to the protocol reported previously [12].

The transfer of GaP NWs to TMDC layers was carried out via drop-cast technique: a small piece of the Si substrate with a vertical array of as-grown NWs was placed into Eppendorf tube filled with isopropanol and treated in an ultrasonic bath. A small volume of the suspension was dropped onto the Si/SiO_x substrate with thin TMDC layers. NWs were additionally positioned with an atomic force microscope (AFM) probe to achieve a desired geometry of the fabricated structure.

The structures were studied by μ -Raman and μ -photoluminescence (μ -PL) techniques at room temperature. The measurements were carried out on Horiba LabRAM HR 800 spectrometer equipped with confocal microscope with 100x magnification objective (N.A. = 0.9). Stage with piezoelectric controllers facilitated precise positioning of the laser beam, making it possible to measure PL maps with a high spatial resolution with a step of less than 100 nm. The excitation source was a 532-nm solid-state YAG:Nd continuous wave laser (455 μ W) with diode pump. Scanning probe microscope Solver NEXT (NT-MDT) was used to obtain topography maps.

Results and Discussion

MoS₂ layer based hybrid structure. The optical image (Fig. 1,*a*) shows the obtained sample with the GaP NW and the thin MoS_2 layer. Intensity of the Raman signal is found uniform over the entire MoS_2 layer (Fig. 1,*f*). The shape of the gray area correlates with the optical image. It indicates that the thickness is homogeneous throughout the layer. The spectral distance between MoS_2 vibrational modes E_{2g}^1 and A_{2g} on the Raman spectrum (Fig. 1,*k*) can be used to estimate a number of TMDC layers [13]. The spectral distance is found at 21.2 cm⁻¹, corresponding to the MoS₂ bilayer. The PL intensity map of the hybrid structure (Fig. 1,*c*) demonstrates the PL emission from the MoS_2 layer. The corresponding PL spectra (Fig. 1i) show two features: emission occurs as a result of direct A and B exciton transitions at the K point of the Brillouin zone according to the electronic band structure [14]. It should be noted, that a decrease in the PL signal is observed along the NWs lying on the MoS_2 layer (Fig. 1,*c*). This can be related to the field localization inside the NWs, which will be discussed in detail hereafter.

One of the NWs depicted in Fig. 1, a was moved with an AFM probe for a detailed study of the light propagation along it. The corresponding image of the final structure is depicted in Fig. 1,b. The diameter of the GaP nanowire was determined via analysis of AFM image and vary along its length (Fig. 1,g, h). The length of the NW is approximately 16.5 μ m. The Raman integral intensity map of area 2 (Fig. 1,e) and Raman spectrum of the NW tip in area 2 (Fig. 1,e) with only GaP vibrational modes indicate that there are no TMDC layers under the NW at the top segments of the NW. However bright spots can be seen on the PL integral intensity map of area 2 (Fig. 1,d) obtained in the MoS_2 emission range (600–715 nm) manifesting the waveguiding promoted by GaP NWs reported earlier for various wavelengths [10, 15]. The thickness of NW promotes waveguiding for both the excitation radiation and PL signal, which is the response of the MoS₂ layer under the laser excitation. The PL spectrum of the transmitted signal (Fig. 1,*j*) correlates with the result shown in Fig. 1,*i*, which confirms the earlier suggestion about the waveguiding of the NW. The tip of the neighboring NW was moved only in area 1 (Fig. 1,b) as a result of manipulating by the AFM probe. Therefore, the presence of the second spot on the PL integral intensity map of area 2 can be explained by the presence of an additional bundled NW optical coupled to the first one [16].



Fig. 1. Characterization of hybrid structures based on MoS₂ and GaP NWs: Optical image of the hybrid structure before (a) and after manipulation with the AFM probe (b); room temperature (RT) PL integral intensity maps of area 1 before manipulation with the AFM probe (c) and area 2 (d) in 600–715 nm range; RT Raman integral intensity maps of areas 2 (e) and 1 (f); AFM images of the upper (g) and lower (h) parts of the NW in 340–420 cm⁻¹ range; PL spectra of the MoS₂ layer and GaP NW in area 1 (i); PL spectrum of the transmitted signal: with excitation at area 1, and signal collection in area 2 (j); Raman spectra of MoS₂ layer and GaP NW in area 1 (k) and NW tip in area 2 (l)

MoSe₂ **layer based hybrid structure.** A similar approach was proceeded to study hybrid structure with MoSe₂ layer and GaP NW. The optical and AFM images (Fig. 2, *a* and 2, *e*, respectively) show the features of this structure: the NW has morphological defects at both ends. The thickness of the NW varies sufficiently along the length, which is approximately 18 μ m. A NW splitting (presence of additional NW) is observed in area 1, which is also confirmed by Raman integral intensity map (Fig. 2, *f*). The Raman spectrum obtained in area 1 has a characteristic shape for GaP NW (Fig. 2, *h*) and no any MoSe₂ vibration modes.

MoSe₂ layer thickness is found nonuniform demonstrated by the Raman integral intensity map in area 2 (Fig. 2,g). MoSe₂ layer thickness can be estimated not only by the Raman peaks position, but also by their presence. The presence and position of the A_{1g} and E^{1}_{2g} modes on the Raman spectrum (Fig. 2,*i*) correspond to a single-layer material [17]. There is a slight shift in the peak relating to the MoSe₂ bilayer [18] near the GaP NW tip, which indicates a fluctuation of the TMDC layer thickness. In the range of 750–825 nm (Fig. 2,*d*), the PL peak corresponding to the direct K-K transition in the monolayer is observed, and a long-wavelength shoulder corresponding to the K-K transition in the bilayer appears as a result of the thickness variation [19]. The peak in the shorter wavelength range (675–725 nm) appears due to spin-orbit splitting of the valence band at the K point of the MoSe₂ Brillouin zone [20].



Fig. 2. Characterization of hybrid structures based on MoSe₂ and GaP NWs: Optical image of the hybrid structure (*a*); RT PL integral intensity maps of area 1 (*b*, with related PL spectrum of NW tip) and area 2 (*c*) in 650–830 nm range; PL spectra of the MoSe₂ layer and GaP NW in area 2 (*d*); AFM image of the of the hybrid structure (*e*); RT Raman integral intensity maps of areas 1 (*f*) and 2 (*g*) in 230–415 cm⁻¹ range; Raman spectra of NW tip in area 1 (*h*) and MoSe₂ layer and GaP NW in area 2 (*i*)

The increase of the PL signal in the area 2 near the NW (Fig. 2, c, d) can be explained by light scattering on the structure defects. The shape of the PL spectrum obtained in the area 1 near the NW tip (spectrum relating to Fig. 2,b) corresponds to the PL spectrum shown in Fig. 2,d, which confirms the presence of the NW waveguiding and optical coupling with the MoSe, layer.

Conclusion

We demonstrate that both hybrid structures based on thin TMDC layers and GaP NWs exhibit anisotropic photoluminescence due to the combination of the TMDC layers radiative properties and the semiconductor NWs waveguiding. This result proves the possibility of directional transmission of optical signals at the nanoscale, which makes such structures promising for applications in integrated photonics.

Acknowledgments

M.A.A. thanks the Ministry of Science and Higher Education of the Russian Federation (agreement 075-03-2023-106, project FSMG-2021-0005) for support of the structures fabrication. V.S.V. acknowledges support of the spectroscopy by the Russian Science Foundation (grant No. 22-19-00738). A.K. thanks the Ministry of Science and Higher Education of the Russian Federation (Grant FSRM-2023-0009) for support of the data analysis.

REFERENCES

1. Li H., Pam M. E., Shi Y., Yang H. Y., A review on the research progress of tailoring photoluminescence of monolayer transition metal dichalcogenides, FlatChem. 4 (2017) 48–53.

2. Tonkaev P., Sinev I. S., Rybin M. V., Makarov S. V., Kivshar Y., Multifunctional and transformative metaphotonics with emerging materials, Chemical Reviews. 122 (19) (2022) 15414–15449.

3. Dubrovskii V. G., Timofeeva M. A., Tchernycheva M., Bolshakov A.D., Lateral growth and shape of semiconductor nanowires, Semiconductors. 47 (2013) 50–57.

4. Wong-Leung J., Yang I., Li Z., Karuturi S. K., Fu L., Tan H. H., Jagadish C., Engineering III–V semiconductor nanowires for device applications, Advanced Materials. 32 (18) (2020) 1904359.

5. Kondratev V. M., Morozov I. A., Vyacheslavova E. A., Kirilenko D. A., Kuznetsov A., Kadinskaya S. A., Nalimova S. S., Moshnikov V. A., Gudovskikh A. S., Bolshakov A. D., Silicon Nanowire-Based Room-Temperature Multi-environment Ammonia Detection, ACS Applied Nano Materials. 5 (7) (2022) 9940–9949.

6. Khayrudinov V., Remennyi M., Raj V., Alekseev P., Matveev B., Lipsanen H., Haggren T., Direct growth of light-emitting III–V nanowires on flexible plastic substrates, ACS nano. 14 (6) (2020) 7484–7491.

7. Bolshakov A.D., Shishkin I., Machnev A., et al., Single GaP nanowire nonlinear characterization with the aid of an optical trap, Nanoscale. 14 (3) (2022) 993–1000.

8. Roy P., Bolshakov A.D., Ga-GaP nanowire hybrid optical system for enhanced coupling, focusing and steering of light, Journal of Physics D: Applied Physics. 53 (29) (2020) 295101.

9. Assali S., Zardo I., Plissard S., et al., Direct band gap wurtzite gallium phosphide nanowires, Nano letters. 13 (4) (2013) 1559–1563.

10. Kuznetsov A., Moiseev E., Abramov A.N., Fominykh N., Sharov V.A., Kondratev V.M., Shishkin I.I., Kotlyar K.P., Kirilenko D.A., Fedorov V.V., Kadinskaya S.A., Vorobyev A.A., Mukhin I.S., Arsenin A.V., Volkov V.S., Kravtsov V., Bolshakov A.D., Elastic Gallium Phosphide Nanowire Optical Waveguides – Versatile Subwavelength Platform for Integrated Photonics, Small. (2023) 2301660.

11. Lorenzo L., Jacob H., Rodion R., George C., Nika A., Resonant excitation of nanowire quantum dots, NPJ Quantum Information. 6 (1) (2020) 93.

12. Fedorov V.V., Bolshakov A.D., Dvoretckaia L.N., et al., Self-catalyzed mbe-grown gap nanowires on Si(111): V/III ratio effects on the morphology and crystal phase switching, Semiconductors. 52 (2018) 2092–2095.

13. Ye M., Winslow D., Zhang D., Pandey R., Yap Y. K., Recent advancement on the optical properties of two-dimensional molybdenum disulfide (MoS_2) thin films, Photonics. 2 (1) (2015) 288-307.

14. Splendiani A., Sun L., Zhang Y., Li T., Kim J., Chim C. Y., Galli G., Wang F., Emerging photoluminescence in monolayer MoS₂, Nano letters. 10 (4) (2010) 1271–1275.

15. Kuznetsov A., Roy P., Grudinin D. V., et al., Self-assembled photonic structure: A Ga optical antenna on GaP nanowires, Nanoscale. 15 (5) (2023) 2332–2339.

16. Anikina M. A., Roy P., Kadinskaya S. A., Kuznetsov A., Kondratev V. M., Bolshakov A.D., Numerical Study of GaP Nanowires: Individual and Coupled Optical Waveguides and Resonant Phenomena, Nanomaterials. 13 (1) (2023) 56.

17. Tonndorf P., Schmidt R., Buttger P., Zhang X., Burner J., Liebig A., Albrecht M., Kloc C., Gordan O., Zahn D. R., de Vasconcellos S. M., Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂, Optics express. 21 (4) (2013) 4908–4916.

18. Chen S.-Y., Zheng C., Fuhrer M. S., Yan J., Helicity-resolved Raman scattering of MoS₂, MoSe₂, WS₂, and WSe₂ atomic layers, Nano letters. 15 (4) (2015) 2526–2532.

19. Yang Y., Li X., Wen M., Hacopian E., Chen W., Gong Y., Zhang J., Li B., Zhou W., Ajayan P. M., Chen Q., Brittle fracture of 2D MoSe₂, Advanced Materials. 29 (2) (2017) 1604201.

20. Zhang Y., Chang T. R., Zhou B., Cui Y. T., Yan H., Liu Z., Schmitt F., Lee J., Moore R., Chen Y., Lin H., Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe₂, Nature nanotechnology. 9 (2) (2014) 111–115.

THE AUTHORS

ANIKINA Maria A. anikina_mar@spbau.ru ORCID: 0000-0002-5522-5026

KUZNETSOV Alexey alkuznetsov1998@gmail.com ORCID: 0000-0001-7143-6686

TOKSUMAKOV Adilet N. adilet.toksumakov@phystech.edu ORCID: 0000-0001-5016-1054

DREMOV Viacheslav V. dremovs54@gmail.com ORCID: 0000-0000-0000-0000

GHAZARYAN Davit A. dav280892@gmail.com ORCID: 0000-0002-8620-8560 FEDOROV Vladimir V. burunduk.uk@gmail.com ORCID: 0000-0001-5547-9387

ARSENIN Aleksey V. arsenin.mipt@gmail.com ORCID: 0000-0002-7506-4389

VOLKOV Valentin S. vsv.mipt@gmail.com ORCID: 0000-0003-2637-1371

BOLSHAKOV Alexey D. bolshakov@live.com ORCID: 0000-0001-7223-7232

Received 25.07.2023. Approved after reviewing 17.08.2023. Accepted 21.08.2023.

Conference materials UDC 535-7 DOI: https://doi.org/10.18721/JPM.163.223

Features of express control of volatile hydrocarbon media and their mixtures in visible light

G.V. Stepanenkov¹, V.D. Vakorina¹, V.V. Davydov², R.V. Davydov²

¹The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

² Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

^{III} 261199g@gmail.com

Abstract. The necessity of development of new methods of express control of hydrocarbon media and their mixtures, especially volatile ones is proved. The problems arising when controlling the condition of volatile hydrocarbon media using the phenomenon of refraction are noted. A new method for determining the components and the ratio between their concentrations in a mixture of volatile hydrocarbon media has been developed. The use of the new method makes it possible to determine the composition and percentage content of the components in hydrocarbon mixtures. The design of a small-size refractometer for the implementation of the new method has been developed. There are no analogs of the new method and refractometer design. The developed instrument can also measure n with an error of ± 0.0004 in the range from 1.250 to 1.740. This is sufficient for express control of the state of all hydrocarbon media and their mixtures. The results of studies of gasoline and oil mixtures are presented.

Keywords: hydrocarbon medium, mixture, refraction, express control, refractive index, visible light, light-shadow boundary, concentration, measurement error

Citation: Stepanenkov G.V., Vakorina V.D., Davydov V.V., Davydov R.V., Features of express control of volatile hydrocarbon media and their mixtures in visible light, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 137–142. DOI: https://doi.org/10.18721/JPM.163.223

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535-7 DOI: https://doi.org/10.18721/JPM.163.223

Особенности экспресс-контроля летучих углеводородных сред и их смесей в видимом свете

Г.В. Степаненков¹[∞], Д.В. Вакорина¹, В.В. Давыдов², Р.В. Давыдов²

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия;

²Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

^{III} 261199g@gmail.com

Аннотация. Обоснована необходимость разработки новых методов экспрессконтроля углеводородных сред и их смесей, особенно летучих. Отмечены проблемы, возникающие при контроле состояния летучих углеводородных сред с использованием явления рефракции. Разработан новый метод определения компонентов и соотношения между их концентрациями в смеси летучих углеводородных сред. Использование нового метода позволяет определять состав и процентное содержание компонентов в углеводородных смесях. Разработана конструкция малогабаритного рефрактометра для реализации нового метода. Аналогов новому методу и конструкции рефрактометра нет.

© Stepanenkov G.V., Vakorina V.D., Davydov V.V., Davydov R.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Разработанным прибором также можно проводить измерения n с погрешностью ±0.0004 в диапазоне от 1.250 до 1.740. Этого достаточно для экспресс-контроля состояния всех углеводородных сред и их смесей. Представлены результаты исследований смесей бензинов и масла.

Ключевые слова: углеводородная среда, смесь, преломление, экспресс-контроль, показатель преломления, видимый свет, светотеневая граница, концентрация, погрешность измерения

Ссылка при цитировании: Степаненков Г.В., Вакорина Д.В., Давыдов В.В., Давыдов Р.В. Особенности экспресс-контроля летучих углеводородных сред и их смесей в видимом свете // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 137–142. DOI: https://doi.org/10.18721/JPM.163.223

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The reduction of energy resources in the world, as well as high prices of raw materials have led to the need for them careful use [1-6]. One of the priority directions in the field of their rational use is the development of fast and reliable methods of express - control of the state of condensed media [3, 7-10]. It should be noted that express - control is now in demand in many areas of human activity. In recent years, a number of rather stringent requirements have become imposed on the instruments and methods of express control. The main of them is connected with the fact that measurements of various parameters of the medium did not introduce irreversible changes in it [3, 5, 8, 10]. Almost for all liquid media - it is necessary to obtain a confirmation of the results of express control on devices of high resolution in a special laboratory. In addition, the methods used in express control should be applicable to the study of a large number of media. The error of measurement of parameters should be no more than 1.5%. These requirements are currently satisfied by only two methods: nuclear magnetic resonance (NMR) and refraction [3, 4, 9-12]. Refractometers have an undeniable advantage over small-sized NMR spectrometers and relaxometers in size, mass, and cost [5, 11-13].

There is a significant disadvantage in the currently used in the designs of industrial refractometers for express control when working with mixtures of different media. It is impossible to determine the composition of the mixture and the concentrations of its components (even if the mixture consists of media that have not reacted chemically with each other) from the measured n value. This problem is especially relevant for hydrocarbon media and their mixtures. Desktop NMR spectrometers allow to solve this problem. Therefore, the purpose of our work is to develop a new method and design of refractometer for its realization, so that by measured values of n it is possible to determine the composition of hydrocarbon mixtures and the concentration of components. And also to identify the medium if it is free of impurities.

Materials and Methods

For the light-shade boundary, by which we will measure the refractive index nm we will use daylight (for example, radiation from the Sun). In its spectrum there is a yellow line Na $(\lambda = 589.3 \text{ nm})$, on which measurements of refractive indices of condensed media are made for comparison with standard ones made in laboratories. This requires that light enters only the face of one of the prisms. The second prism must not receive light. As a result, the light-shadow boundary is formed at the output of prism 1 (lower prism) and nb is measured. Then the light coming to prism 1 is blocked and the light goes to prism 2 (upper prism) and nt is measured. The temperature T of the medium under study is constantly monitored. During our measurements of nt and nb it is necessary to realize everything very quickly (in 6–8 seconds), so that significant movements between the media in the measured layers do not occur. In our proposed sealed volume evaporation of volatile hydrocarbon media will not occur in such a time. The temperature also does not change so quickly. To determine the concentrations of the media in the mixture, we use the refraction equation:

© Степаненков Г.В., Вакорина Д.В., Давыдов В.В., Давыдов Р.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

$$n_m = F_1 n_1 + F_2 n_2 + \dots + F_n n_n, \tag{1}$$

where n_m is the refractive index of the medium measured at the initial moment $(n_m = n_t = n_b)$, n_1 , $n_2, ..., n_n$ are the refractive indices of the media of which the mixture under study may consist, F_1 , $F_2, ..., F_n$ are the coefficients that characterize the relative content of various media in the mixture under study (in case it is necessary to determine the percentage content, these coefficients are multiplied by 100%). Them also characterize the concentrations of components in the mixture.

Experience with volatile hydrocarbon media and analysis of the results of various studies showed that in equation (1) two terms should be left initially:

$$n_m = F_1 n_1 + F_2 n_2. (2)$$

Taking into account our developed measurement technique and the data obtained, equation (2) takes the following form:

$$n_m = F_1 n_b + F_2 n_t. \tag{3}$$

The values of n_{t} , and n_{b} are determined for equation (3). Note that (according to Fig. 1) the value of n_{t} is the refractive index of the upper layer of the investigated mixture, the value of n_{b} is the refractive index of the lower layer in the investigated mixture. The indices t and b will be further used to define the ratio of the measured refractive index value nm to the upper or lower layer of the investigated mixture.

In hydrocarbon mixtures in a closed volume, stratification of the media into layers occurs. Light media rise to the top, heavy media sink to the bottom. By measuring the values of n_t and n_b after stratification, the temperature T of the components can be determined. Then (3) is solved and the concentrations of components in the mixture are determined.

For practical implementation of our developed method, we assembled a new optical design of the laboratory refractometer layout. In the design, the possibility of placing the liquid medium in a sealed volume, which is located between two prisms, was realized. Also, control of the visible light entering the two prisms was realized (possibility to measure the refractive index of the medium using the upper or lower prism). Fig. 1, *a*, *b* shows the refractometer block diagram and the course of optical beams for two cases of measurement, $n_{i}(a)$ and $n_{b}(b)$.

The light flux that falls on the prisms is controlled using the flaps 5. Fig. 1 shows two positions of flaps 5 during measurements.



Fig. 1. Schematic diagram of the optical part of the refractometer and ray path for the upper (a) and lower (b) prisms: lower triangular prism 1 (material leucosapphire), upper triangular prism 2 (material leucosapphire), silicone spacers 3, rotating prism mount 4, closing flap 5, mirror 6, eyepiece 7, lens 8 on movable mount, mirror 9, plate 10 for registration of the light-shade border, medium 11 under study

Results and Discussion

Fig. 2, *a*, *b* and *c* shows, for example, the research results for mixtures, which consists of two gasoline Ai-92 and Ai-95 in the proportion 0.3 to 0.7 using two prisms. At the initial measurement time $n_t = n_b = 1.4252 \pm 0.0004$ at T = 301.2 K (Fig. 2,*a*). Next (after 140 seconds), two measurements were performed using upper and lower triangular prisms 2 and 1 (Fig. 1, *a*, *b*). The results of these measurements are presented in Fig. 2,*b* and Fig. 2,*c* at respectively. These measurements were carried out at a temperature $T_1 = 301.1$ K. The difference between T and T_1 is within the measurement error and does not have a significant impact on the final result.

According to Fig. 2, *b* and Fig. 2, *c* were determined two values of n_m^t and n_m^b . Value $n_m^t = 1.4112 \pm 0.0004$ corresponds to Ai-95 gasoline. Value $n_m^b = 1.4262 \pm 0.0004$ corresponds to Ai-92 gasoline. These three measurements are marked in Fig. 2 with a circle with a red arrow.

Further, using (3) for the measured values of refractive indices n_i , n_m^t and n_m^b , coefficients $F_1 = 0.7017$ and $F_2 = 0.2983$ were obtained. The values of coefficients F_1 and F_2 correspond with an insignificant error to the content of gasoline Ai-95 and Ai-92 in the mixture prepared. This mixture was prepared by using 70 ml of Ai-95 gasoline and 30 ml of gasoline Ai-92. This confirms the adequacy of our proposed methodology.



Fig. 2. Light-shade boundary and refractometer scale a during the measuring a mixture of two gasoline Ai-95 and Ai-92 in the proportion 0.7 to 0.3 (a, b, c)

Table 1

<i>Т</i> , К	Laboratory model of developed refractometer	Industrial refractometer Abbe NAR - 2T
277.2 ± 0.1	1.5328 ± 0.0004	1.5326 ± 0.0002
282.1 ± 0.1	1.5322 ± 0.0004	1.5320 ± 0.0002
287.1 ± 0.1	1.5314 ± 0.0004	1.5312 ± 0.0002
290.0 ± 0.1	1.5308 ± 0.0004	1.5306 ± 0.0002
293.1 ± 0.1	1.5300 ± 0.0004	1.5298 ± 0.0002
298.1 ± 0.1	1.5282 ± 0.0004	1.5280 ± 0.0002
303.1 ± 0.1	1.5262 ± 0.0004	1.5260 ± 0.0002
307.0 ± 0.1	1.5240 ± 0.0004	1.5238 ± 0.0002
312.0 ± 0.1	1.5213 ± 0.0004	1.5213 ± 0.0002

Dependence of change a refractive index n_m on temperature T

To check the reliability of the optical design developed by us, a comparison of the measured refractive indices n_m of synthetic oil at a small change of temperature T in the laboratory was implemented. These oils are highly viscous and are used in machine tools for metal working. Volatile solvents are often added to them. These solvents evaporate from the open oil into the air, just as with gasoline. This makes the research we are conducting close in terms of the aggregate state of the media. The change of nm from T was measured with an industrial Abbe NAR-2T refractometer (measuring error ± 0.0002). Table 1 shows the results of n_m studies using two refractometers.

The obtained results coincide within the measurement error. This confirms the reliability in conducting measurements of refractive indices using our developed refractometer design. The results of these studies show great functional possibilities of application of the developed refractometer design in comparison with the previously used ones.

Conclusion

The analysis of the obtained new results of the study of media with high viscosity (synthetic oils, which require special high degree purification), as well as complex mixtures of media by fuel (gasoline Ai-92 and Ai-95, a similar situation may occur with aviation kerosene) showed the reliability of our methodology and the design of the developed refractometer for its implementation. The quality of synthetic oil is determined unambiguously. The absence of impurities in it, which are removed by purification at the end of the technological cycle of production, is also unambiguously determined. For the most complex two-component fuel mixture, which is a mixture of gasoline Ai-92 and Ai-95 (the density of gasoline Ai-92 is greater than that of Ai-95, and the quality of gasoline Ai-92 is lower than that of gasoline Ai-95) the composition of the mixture and the concentrations of components in it are determined unambiguously. When comparing other brands of gasoline with each other, there is no such thing (the higher the quality of gasoline, the higher its density). Such a fact in density, which is related to the structure of the molecule in two gasolines, creates a number of problems in express control of such a mixture by various spectrometers at the place of sampling (before that the mixture was subjected to intensive treatment with additives). It is impossible to get an unambiguous answer on the composition of the mixture and concentration of components in it by chemical shift in spectra at (concentration of gasoline Ai-92 in the mixture 5 - 10 %) unlike the method developed by us.

It should be noted that the developed design of a small-size refractometer allows measuring nm values in visible light with an error of ± 0.0004 . During the measurements we took the maximum value of the error (40 % of the scale discreteness).

The obtained results allowed us to determine the further direction of research. This direction will be connected with the study of three-component fuel mixtures. Nowadays there are frequent cases of making a mixture from gasoline Ai-92, Ai-95 and Ai-98, which is passed off as gasoline Ai-98. Intensive treatment with additives makes it possible to raise the octane number of this mixture to the required level with small additions of the other two gasolines to Ai-98 gasoline. When layers are formed in the refractometer, the Ai-92 gasoline will be placed between the Ai-95 and Ai-98 gasolines, creating difficulties. This layer will not be measured by the refractometer. In the future we will try to solve this problem using our method and instrument to get an unambiguous answer on the composition of such a mixture and concentrations.

REFERENCES

1. Kosolapov V.M., Cherniavskih V.I., Zarudny V.A., Mazur K., Konieczna, A., Tseiko, L., Dumacheva E.V., Dumachev D.V., Observations on the Productivity of Breeding Specimens of Urtica dioica L. from European Russian Ecotopes in Comparison with the Breeding Variety under Field Crop Conditions, Agronomy. 12 (2022) 76–82.

2. Wardal W.J., Mazur K.E., Roman K., Roman M., Majchrzak M., Assessment of Cumulative Energy Needs for Chosen Technologies of Cattle Feeding in Barns with Conventional (CFS) and Automated Feeding Systems (AFS), Energies. 14 (2021) 8584–8592.

3. Kashaev R.S., Kien N.C., Tung T.V., Kozelkov O.V., Fast Proton Magnetic Resonance Relaxometry Methods for Determining Viscosity and Concentration of Asphaltenes in Crude Oils. Journal of Applied Spectroscopy. 86(5) (2019) 890–895.

4. Sadovnikova M.A., Murzakhanov F.F., Mamin G.V., Gafurov M.R., HYSCORE Spectroscopy to Resolve Electron–Nuclear Structure of Vanadyl Porphyrins in Asphaltenes from the Athabasca Oil Sands In Situ Conditions, Energies. 15(17) (2022) 6204.

5. Davydov V., Gureeva I., Davydov R., Dudkin V., Flowing Refractometer for Feed Water State Control in the Second Loop of Nuclear Reactor. Energies. 15(2) (2022) 457.

6. Verbitskii V.N., Panaiotti I.E., Nikitin S.E., Bobyl A.V., Shelopin G.G., Andronikov D.A., Abramov A.S., Sachenko A.V., Terukov E.I., Electroluminescent study of the efficiency of silicon heterostructural solar cells. Tech. Phys. Lett. 43(9) (2017) 779–782.

7. Naumova V., Kurkova A., Davydov R., Zaitceva A., Method for the Analysis of Tissue Oxygen Saturation Disorders Using an Optical Analyzer of Visible and IR Spectra, Proceedings of the 2022 International Conference on Electrical Engineering and Photonics, EExPolytech 2022, vol. 2022 (2022) 151–153.

8. Yakusheva M., Davydov R., Isakova D., Features of signal absorption fronts of laser radiation in rapid diagnosis of human health, Proceeding of 2022 8th International Conference on Information Technology and Nanotechnology (ITNT 2022). vol. 2022 (2022) 145–149.

9. Davydov V.V., Dudkin V.I., Grebenikova N.M., On the Possibility of Express Recording of Nuclear Magnetic Resonance Spectra of Liquid Media in Weak Fields, Technical Physics. 63(12) (2018) 1845–1850.

10. Vakhin A.V., Khelkhal M.A., Mukhamatdinov I.I., Nasybullin A.R., Morozov O.G., Changes in Heavy Oil Saturates and Aromatics in the Presence of Microwave Radiation and Iron-Based Nanoparticles, Catalysts. 12(5) (2022) 514.

11. Kazanskiy N.L., Butt M.A., Degtyarev S.A., Khonina S.N., Achievements in the development of plasmonic waveguide sensors for measuring the refractive index. Computer Optics. 44(3) (2020) 295–318.

12. Karabegov M.A., On certain information capabilities of analytical instruments, Measurement Techniques. 54(10) (2012) 1203–1212.

13. Davydov V., Vakorina D., Provodin D., Ryabogina N., Stepanenkov G., New Method for State Express Control of Unstable Hydrocarbon Media and Its Mixtures, Energies, 16(6) (2023) 2529.

THE AUTHORS

STEPANENKOV Gregory V. 261199g@gmail.com ORCID: 0000-0002-8924-5033

VAKORINA Darya D. cementary.ley@gmail.com ORCID: 0000-0001-5303-5387 DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: -0000-0001-9530-4805

DAVYDOV Roman V. davydov_vadim66@mail.ru ORCID: -0000-0003- 1958- 4221

Received 26.07.2023. Approved after reviewing 27.09.2023. Accepted 27.09.2023.

Conference materials UDC 621.372.2:621.398 DOI: https://doi.org/10.18721/JPM.163.224

Peculiarities of telemetry information transmission using analog fiber-optic communication line over long distances in a complex electromagnetic environment

B.K. Reznikov¹[⊠], G.V. Stepanenkov¹, D.I. Isaenko¹ E.A. Logvinova¹, A.V. Pachin¹, N.Yu. Kolybelnikov¹

¹ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia

[™] rznkff@gmail.com

Abstract. To implement the environmental monitoring program, it is proposed to use the upper parts of power line towers for the placement of measuring sensors of various kinds. The analysis of possibilities of application of various ways of telemetric information transmission over long distances in the presence of powerful electromagnetic interference is carried out. It was found that the most appropriate in this situation for the transmission of information to use analog fiber-optic communication lines. The use of analog FOCL, which takes into account a number of features we have established the peculiarities of the transmission of analog optical signals, allows you to transmit information at distances greater than 500 km without amplification. According to the results of calculation of the FOCL parameters and experimental studies, the limiting distances for information transmission and the permissible power for the used laser radiation are determined.

Keywords: telemetry information, electromagnetic environment, optical signal, fiber, attenuation, distance, laser radiation power, analog information transmission format, signal-to-noise ratio

Citation: Reznikov B.K., Stepanenkov G.V., Isaenko D.I., Logvinova E.A., Pachin A.V., Kolybelnikov N.Yu., Peculiarities of telemetry information transmission using analog fiberoptic communication line over long distances in a complex electromagnetic environment, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 143–149. DOI: https://doi.org/10.18721/JPM.163.224

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.372.2:621.398 DOI: https://doi.org/10.18721/JPM.163.224

Особенности передачи телеметрической информации с использованием аналоговой волоконно-оптической линии связи на большие расстояния в сложной электромагнитной обстановке

Б.К. Резников¹⊠, Г.В. Степаненков¹, Д.И. Исаенко¹ Е.А. Логвинова¹, А.В. Пачин¹, Н.Ю. Колыбельников¹

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия

[⊠] rznkff@gmail.com

Аннотация. Для реализации программы экологического мониторинга предлагается использовать верхние части опор линий электропередач для размещения измерительных датчиков различного типа. Проведен анализ возможностей применения различных

© Reznikov B.K., Stepanenkov G.V., Isaenko D.I., Logvinova E.A., Pachin A.V., Kolybelnikov N.Yu., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

способов передачи телеметрической информации на большие расстояния при наличии мощных электромагнитных помех. Установлено, что наиболее целесообразно в данной ситуации для передачи информации использовать аналоговые волоконно-оптические линии связи. Использование аналоговой ВОЛС, учитывающей ряд установленных нами особенностей передачи аналоговых оптических сигналов, позволяет передавать информацию на расстояния более 500 км без усиления. По результатам расчета параметров ВОЛС и экспериментальных исследований определены предельные расстояния передачи информации и допустимая мощность используемого лазерного излучения.

Ключевые слова: телеметрическая информация, электромагнитная обстановка, оптический сигнал, волокно, затухание, расстояние, мощность лазерного излучения, аналоговый формат передачи информации, отношение сигнал/шум

Ссылка при цитировании: Резников Б.К., Степаненков Г.В., Исаенко Д.И., Логвинова Е.А., Пачин А.В., Колыбельников Н.Ю. Особенности передачи телеметрической информации с использованием аналоговой волоконно-оптической линии связи на большие расстояния в сложной электромагнитной обстановке // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 143–149. DOI: https://doi.org/10.18721/JPM.163.224

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The rapid development of mankind has led to a sharp deterioration of the ecological situation on the planet [1-7]. This, in turn, greatly affects the activities of people and the behavior of living organisms [8-10]. In such a situation, environmental monitoring systems that are placed in different parts of the territory become extremely important [11-13]. When placing environmental monitoring complexes in remote from settlements, there are many problems, which are associated with the provision of electric power equipment, its protection from various negative influences and stable transmission of information about the state of the environment in real time over long distances [14-15]. The solution to these problems, in addition to transmitting information, is to place a multifunctional complex for environmental monitoring on top of the power line (transmission line). In this case the information will have to be transmitted in a complex electromagnetic environment. One of the options for solving this problem is the use of fiber optic communication lines (FOCL) [1, 11]. Developed designs of digital fiber-optical communication lines (FOCL) allow information to be transmitted without the use of optical amplifiers for distances up to 500 km. It is proposed to use a 150 mW laser for transmission. If the terrain changes, the distance between the complexes can be reduced. Therefore, it is necessary to search for new solutions for transmitting information from multifunctional complexes of environmental monitoring over long distances. One of the variants of such a solution is presented in the current work.

Construction of analog fiber-optic communication line and its parameters for transmitting telemetric information over long distances

Analog signals with amplitude-pulse modulation are the most appropriate for the transmission of telemetry information. It is proposed that each number (e. g., temperature value) be represented as a sequence of pulses, the amplitude of each of which carries a certain digit. Such sequences are used in radio monitoring and radiolocation systems. Amplitude values in relative units (0.95, 0.955, 0.96, 0.965, ..., 0.995) correspond to digits (0, 1, 2, ..., 9), the comma is transmitted with a relative amplitude of 0.4, and marks the beginning and stopping of transmission - with relative amplitude 1. The duration of the information components of the parcel is 1 ms, the duration of the transmission start and stop marks is 2 ms. The interval between pulses is 2 ms. When using such temporal characteristics of the sequence the overrun of chromatic dispersion at $\lambda = 1550$ nm on the optical fiber length L = 500 km is about 2.2 ns. Fig. 1 shows an example signal for transmitting a temperature value T = 294.5 K.

© Резников Б.К., Степаненков Г.В., Исаенко Д.И., Логвинова Е.А., Пачин А.В., Колыбельников Н.Ю., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.


Fig. 1. Sequence of command codes in the form of rectangular pulses to transmit the temperature value T = 294.3 K in analog form over the FOCL

The proposed method of information transmission is fundamentally new in the field of telemetry information transmission via fiber-optic transmission system using amplitude-pulse modulation. This method also allows the use of radiation sources with internal modulation by pump current. In this case it is possible to vary the depth of modulation within a large range. In experiments a laser source of radiation with a power of 150 mW is used, the depth of modulation of which varies in the range from 30% to 70%. The level of optical power p_{in} injected into the optical fiber is about 20 dBm. To avoid manifestation of nonlinear effects, further increase in optical power is inexpedient.

Since the telemetry information is transmitted as a sequence of pulses with pulse amplitude modulation, this allows the use of a subcarrier frequency F_s in the range from 100 kHz to 200 MHz. This improves the characteristics of the proposed transmission system, in particular, to provide a large pass-through time of the FOCL when transmitting a signal over long distances, as well as improving the signal-to-noise ratio (SNR), which increases the optical budget of the transmission line. The signal reception bandwidth in this case is from 0.1 to 1 MHz.

Existing digital fiber-optic transmission systems require an *SNR* on the receiving side of at least 20 dB. The proposed system shows that SNR = 6 dB is sufficient. In this case the error in determining the amplitude of the pulse is 0.1%, and bit error ratio $BER \approx 10^{-3}$. Modern photodetectors have a sensitivity of up to 90 dB.



Fig. 2. Structure diagram of the fiber-optic transmission system: semiconductor laser 1 with $\lambda = 1550$ nm, direct modulated laser power supply 2, optical fiber 3, photodetector 4, tunable LC-filter 5, electronic key 6, frequency tunable high-stability quartz generator 7, multifunction power supply 8, information processing device 9, control device 10, sensors for measuring various physical quantities in the environment 11-16, personal computer 17

When transmitting an optical signal over a fiber optic line, the length of which in this case is 500 km, it accumulates noise, which usually does not exceed 8 dB. It is also necessary to take into account the operating margin of 3 dB.

The structural diagram of the proposed fiber-optic transmission system is shown in Fig. 2.

Calculation of fiber-optic communication line

The most important parameters of the designed FOCL are: the rise time τs of the optical system, the time of the signal transmitted through the optical fiber τ_0 and the energy balance a_{Σ} .

The energy balance a_{Σ} is the predicted sum of the optical signal losses on all components of the fiber-optic communication line. The energy balance of a fiber-optic communication line is calculated mainly at the stage of line design and selection of channel-forming equipment.

Information is transmitted at a wavelength of $\lambda = 1550$ nm. Optical power P_1 of the transmitting laser module (Emcore company) is 150 mW (21.8 dBm), modulation depth is 70%, line width $\Delta \lambda = 0.112$ nm at this P_1 laser bandwidth $\Delta F_1 = 600$ MHz, subcarrier frequency $F_s = 100$ MHz. G.653 standard single-mode optical fiber with offset zero dispersion (triangular profile) M = 0.3 ps/(nm·km) with attenuation coefficient 0.195 dB/km is used for information transmission. Optical signal reception is carried out by a photodetector module, which has the following characteristics: bandwidth $\Delta F_2 = 1$ GHz, Noice-equivalent power $NEP = 10^{-13}$ W/Hz^{1/2}.

$$\tau_0 = B/F_s = 0.35/100 \cdot 10^6 = 3.50 \text{ ns.}$$
 (1)

The time τ_s is calculated as follows: $\tau_1 = B/\Delta F_1$ is the rise time at the transmitter; $\tau_2 = B/\Delta F_2$ is the rise time at the receiver; $\tau_3 = B/\Delta F_3$ is the rise time on optical fiber; B = 0.35 is the coefficient, taking into account the nature of the linear analog signal.

$$\Delta F_{2} = 0.35/(M \cdot \Delta \lambda \cdot L) \approx 18.5 \text{ GHz}, \tag{2}$$

$$\tau_1 = 0.35/600 \cdot 10^6 = 0.58 \text{ ns},$$

$$\tau_2 = 0.35/1 \cdot 10^9 = 0.35 \text{ ns},$$
 (3)

$$\tau_3 = 0.35/22 \cdot 10^9 = 0.017 \text{ ns}$$

$$\tau_s = \sqrt{(\tau_1^2 + \tau_2^2 + \tau_3^2)} = 0.519 \text{ ns}.$$
 (4)

The energy balance is calculated as follows:

$$a_{s} = a_{1} - (a_{2} + N \cdot a_{3} + a_{4} + a_{5}), \tag{5}$$

where $a_1 = p_{Tx} - p_{Rx} = 104.8$ dB is the optical loss budget; $p_{Tx} = p_{in} - 2$ dB = 19.8 dBm is the level of power injected into the optical fiber; $p_{in} = 21.8$ dBm is the transmitted power; $p_{Rx} = -87$ dBm is the the sensitivity level of the photodetector. Calculated for *SNR* (dB) = 10, with a bandwidth of $\Delta F_i = 1$ MHz according to the formula (6):

$$p_{Rr} = 10 \cdot \log(NEP/10^{-3}) + 5 \cdot \log(\Delta F_{r}) + 0.5 \cdot SNR \text{ (dB)};$$
 (6)

 a_2 is the FOCL losses; $\alpha_{1550} = 0.195$ dB/km is the attenuation coefficient at a wavelength of 1550 nm; L = 500 km is the FOCL length;

$$a_2 = 0.195 \cdot 500 = 107.25 \text{ dB};$$
 (7)

 $a_3 = 0.05 \text{ dB}$ is the losses at welded joints; N = 50 is the number of connections; $a_4 = 1.5 \text{ dB}$ is the losses at the 70% modulation depth of the signal on the transmitting side; $a_5 = 3 \text{ dB}$ is the operating reserve.

$$a_{\Sigma} = 106.8 - (97.5 + 50 \cdot 0.05 + 1.5 + 3) = 2.3 \text{ dB.}$$
 (8)

The data obtained show that at distances L = 500 km the conditions necessary for information transfer are fulfilled: $\tau_0 > \tau_s$ and $a_s > 0$.

Experimental results and discussion

The main characteristic of FOCL for the transmission of analog signals is the dynamic range. Fig. 3 shows as an example the results of measuring the output power P_{out} from changes in the laser radiation power P_{in} , which enters the optical fiber for different values of L.

Analysis of the results showed that the dynamic range of our developed FOCL for L = 100 km is 85 dB, for L = 150 km is 76 dB. The established tendency of changing the value of the dynamic range shows that the developed FOCL allows to provide a stable transmission of information with an increase in L up to 500 km.



Fig. 3. Amplitude response of the FOCL. Graphs 1 and 2 correspond to the value of L in km: 100 and 150

Fig. 4 shows, as an example, the results of studies of transmission over the developed FOCL of rectangular pulses with durations of 2 ms (start and stop number counting) with an interval between pulses of 2 ms for different values of L.

Analysis of the results shows the stable operation of the FOCL when transmitting information in the form of a sequence of command codes at a power $P_{in} = 100$ mW.



Fig. 4. Pulses for sending start commands and completion of number counting at input 3 and at output 9 for different values of L in km: 100 (a); 150 (b)

Conclusion

Analysis of the experimental and calculated data confirms the adequacy of the proposed developments to implement the design of the FOCL to transmit information from multifunctional complexes placed on power lines for distances from 4 to 500 km and more (with different configurations). Modernization of multifunctional complexes will affect only the control system.

The most realistic direction is the search for solutions related to increasing the value of L for information transmission using the photodetector module with lower $NEP < 10^{-13}$ W/Hz^{1/2}, and the development of inexpensive optical fiber with $\alpha_{1550} < 0.195$ dB/km. At present, it is possible to increase the L to 600 km when using a pure quartz core fiber, if necessary.

REFERENCES

1. Dmitrieva D.S., Pilipova V.M., Davydov V.V., Dudkin V.I., Fiber-Optic Sensor for Monitoring Radiation Level. Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), 2022, 13158 LNCS, pp. 230–239.

2. **Ryzhova D., Davydov V.,** Monitoring of emergency situations on water objects using remote sensing of the Earth IEEE 2022 VIII International Conference on Information Technology and Nanotechnology (ITNT). Samara, Russian Federation, 2022, V. 21992029, pp. 23–27.

3. Davydov V.V., Davydov R.V., Myazin N.S., Nuclear-Magnetic Flowmeter-Relaxometer for Monitoring the Flow Rate and State of the Coolant in the First Loop of the Nuclear Reactor of a Moving Object. Measurement Techniques, 2022, 65 (4), pp. 279–289.

4. Davydov V., Gureeva I., Davydov R., Dudkin V., Flowing Refractometer for Feed Water State Control in the Second Loop of Nuclear Reactor Energies, 15 (2) (2022) 457.

5. Sadovnikova M.A., Murzakhanov M.A., Mamin F.F., Gafurov G.V., Hyscore M.R., Spectroscopy to Resolve Electron–Nuclear Structure of Vanadyl Porphyrins in Asphaltenes from the Athabasca Oil Sands In Situ Conditions," Energies, vol. 15(17), 6204. June 2022.

6. **Ponomareva O., Nepomnyashchaya E., Velichko E., Victor K., Petukhov A.,** Spectroscopic Method for Studying the Characteristics of Human Skin, Proceedings of the 2021 International Conference on Electrical Engineering and Photonics, EExPolytech, (2021) 244–247.

7. Davydov V.V., Grebenikova N.M., Smirnov K.J., An Optical Method of Monitoring the State of Flowing Media with Low Transparency That Contain Large Inclusions. Measurement Techniques 62 (6) (2019) 519–526.

8. Mazing M.S., Zaitceva A.V., Davydov R.V., Application of the Kohonen neural network for monitoring tissue oxygen supply under hypoxic conditions. Journal of Physics: Conference Series, (2021) 2086(1), 012116.

9. Grevtseva A.S., Smirnov K.J., Greshnevikov K.V., Davydov V.V., Rud V.Yu., Glinushkin A.P., Method of assessment the degree of reliability of the pulse wave image in the rapid diagnosis of the human condition. Journal of Physics: Conference Series, 1368 (2) (2018) 022072.

10. Mazing M.S., Zaitceva A.Yu., Kislyakov Yu.Ya., Kondakov N.S., Avdushenko S.A., Davydov V.V., Monitoring of oxygen supply of human tissues using a noninvasive optical system based on a multichannel integrated spectrum analyzer, International Journal of Pharmaceutical Research, (12) (2020), 1974–1978.

11. Davydov R., Antonov V., Moroz A., Parameter Control System for a Nuclear Power Plant Based on Fiber-Optic Sensors and Communication Lines. Proceedings of IEEE International Conference on Electrical Engineering and Photonics (EExPolytech -2019), 8906791, (2019) 295–297.

12. Irfan M., Khan Y., Rehman A.U., Khonina S.N., Kazanskiy N.J., Plasmonic Refractive Index and Temperature Sensor Based on Graphene and LiNbO₃, Sensors, vol. 22 (20), (2022) 7790–7802.

13. Myazin N.S., Davydov V.V., Compact nuclear magnetic spectrometer for non-destructive condition testing of biological objects. Journal of Physics: Conference Series, 1124 (3) (2018) 031004.

14. **Rukin E.V., Myazin N.S., Davydov V.V., Rud, V.Y.,** Modeling of non-stationary processes in the study of liquid media by the method of nuclear magnetic resonance in a weak field. Journal of Physics: Conference Series, 1368(4), (2019) 042011.

15. Karseev A., Vologdin V., Davydov V., Features of nuclear magnetic resonance signals registration in weak magnetic fields for express - Control of biological solutions and liquid medium by nuclear magnetic spectroscopy method. Journal of Physics: Conference Series, 643 (1) (2015) 012108.

THE AUTHORS

REZNIKOV Bogdan K. rznkff@gmail.com ORCID: 0000-0003-3866-6265

STEPANENKOV Gregory V. 261199g@gmail.com ORCID: 0000-0002-8924-5033

ISAENKO Dmitriy I. isaenko-d@mail.ru ORCID: 0000-0002-4714-5675 LOGVINOVA Ekaterina A. katua.logvinova@gmail.com

PACHIN Andrey V. pachin.andrej@bk.ru

KOLYBELNIKOV Nikolai Yu. ya.nikolai-kolyb@yandex.ru

Received 28.07.2023. Approved after reviewing 17.08.2023. Accepted 20.08.2023.

Conference materials UDC 535 DOI: https://doi.org/10.18721/JPM.163.225

KDP crystals as an optical element in high-power laser system

S.A. Vilchenko¹[⊠], V.V. Gribko²

¹Lobachevsky State University of Nizhni Novgorod, Nizhny Novgorod, Russia;

² Institute of Applied Physics RAS, Nizhny Novgorod, Russia

^{III} sergey.vilchenko@yandex.ru

Abstract. This research presents a study of the dependence of the addition of ethylenediaminetetraacetic acid to the KDP crystal on the crystal growth kinetics and its physical-optical properties: width of the dead zone, growth rate of crystal faces, and transmission spectra. Obtained data on the change of dead zone width of growth solutions with concentrations of 0, 0.001, 0.005, 0.015, 0.02 mol% EDTA. KDP crystal was grown by the method of high-speed growth of oriented crystals, its transmission spectra in the range from 200 to 1100 nm were obtained. The possibility of adding EDTA when growing KDP crystals by the high-speed method is discussed.

Keywords: KDP crystal, potassium dihydrophosphate, EDTA, high-power lasers

Funding: Supported by the Priority 2030 Strategic Academic Leadership Program of the Ministry of Science and Higher Education of the Russian Federation.

Citation: Vilchenko S.A., Gribko V.V., KDP crystals as an optical element in high-power laser system, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 150–153. DOI: https://doi.org/10.18721/JPM.163.225

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535 DOI: https://doi.org/10.18721/JPM.163.225

Кристаллы КDP как оптические элементы в мощных лазерных системах

С.А. Вильченко¹[⊠], В.В. Грибко²

¹Нижегородский государственный университет им Н.И. Лобачевского

² Институт прикладной физики Российской академии наук

^{III} sergey.vilchenko@yandex.ru

Аннотация. В работе исследуется влияние этилендиаминтетрауксусной кислоты (EDTA) на кинетику роста кристалла KDP и его физико-оптические свойства. Получены данные изменения ширины мертвой зоны ростовых растворов с концентрациями 0, 0,001, 0,005, 0,015, 0,02 mol% EDTA. Методом скоростного роста профилированных, заданным образом ориентированных кристаллов выращен кристалл KDP, получены его спектры пропускания в диапазоне от 200 до 1100 нм. Обсуждается возможность добавления EDTA при выращивании скоростным методом кристаллов KDP.

Ключевые слова: кристаллы KDP, дигидрофосфат калия, EDTA, мощные лазеры

Финансирование: При поддержке программы стратегического академического лидерства «Приоритет 2030» Министерства науки и высшего образования Российской Федерации.

© Vilchenko S.A., Gribko V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Вильченко С.А., Грибко В.В. Кристаллы КDP как оптические элементы в мощных лазерных системах // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 150–153. DOI: https:// doi.org/10.18721/JPM.163.225

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Potassium dihydrogen phosphate (KDP) crystals are a non-alternative material for optical elements in high power laser sources. As a rule, such lasers generate radiation in the infrared range. Optical elements made from KDP crystals are used for conversion to the visible and ultraviolet ranges. Also, optical elements made of KDP crystals play the role of a laser pulse shaper.

The main advantages of optical elements based on KDP crystals are their transparency in a wide frequency range, high threshold laser-induced damage and non-linearity coefficients. Another important factor is the nature of KDP crystals. They are grown from aqueous solutions based on the KH_2PO_4 salt at temperatures near to room temperature. The peculiarities of KDP growth made it possible to develop methods of growing large crystals, up to 1 m in cross-section [1]. Rapid growth techniques are used for growing KDP crystals up to 1 m in cross-section [1, 2]. Studies have shown that rapid growth techniques are more sensitive to the presence of trivalent metal impurities (e.g., AI^{3+} , Fe^{3+}) in the growth solutions. It is known that the addition of chelating agents to the growth solution leads to reduce the influence of such impurities on the growth process. One of such chemical compounds are ethylenediaminetetetraacetic acid (EDTA). Also experiments show that addition of EDTA to the solution leads to leads to higher growth rate of the boundary prism face that is why there is interest in detailed study of EDTA influence on morphology and properties of crystals [3].

Results and Discussion

The following concentrations of impurity in the solution were chosen for the study: 0, 0.001, 0.005, 0.015, 0.02 mol%, the low concentration of EDTA is a consequence of the poor degree of solubility in water. Elemental analyses of growth solutions are in the table below (Table 1). The dependences of crystal growth rate on the value of solution supersaturation were determined. It follows from the data obtained that the addition of EDTA to decrease in the dead zone and an increase in the growth rate of the prism faces depending on supersaturation. The dead zone is the inert interval of the face growth rate at which the relative supersaturation of the solution grows, but there is no crystal face growth.

At low supersaturations (up to 0.3 °C) all investigated samples show the increase of prism face growth rate. At increasing supersaturations, the greatest increase in the growth rate of the prism face shows solutions with concentrations of 0.001, 0.005, and 0.015 mol%. Such supersaturation is corresponding to the supersaturation region used in the rapid methods of growth.



Fig. 1. Dependence of dead zone width (T_d) on solution concentration (C). (Green is the solution without holding, blue holding for 2 weeks, red holding for 4 weeks))

[©] Вильченко С.А., Грибко В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

To study the degradation of the solution over time after two and four months from the first study, the samples were retested. The results of the three studies are summarized in Fig. 1.

It can be seen that the dead zone width and saturation temperature change insignificantly with time in the solution. It can be noticed that the solution with EDTA concentration of 0.005 mol% in the second run has an anomalous value of the dead zone width. This is due to experimental errors: formation of stray crystals in the cuvette, laser beam moving away from the crystal or passing through the interface, hardware errors in data processing. It can be seen from the plot that the solution over time has retained the same values of the width of the dead zone.



Fig. 2. Obtained KDP crystal (size of 80×80×56 mm³)

A crystal KDP with 0.005 mol% EDTA in the growth solution was grown by the method of high-speed growth of oriented crystals profiled in a certain way. A dimension of the obtained crystal was $80 \times 80 \times 56$ mm³ (Fig. 2). The growth took place in a 10-liter crystallizer. The whole growth process took about a month.

Transmission spectrums for KDP crystal with EDTA addition in the growth solution were obtained (Fig. 3) with the UV-3600i Plus high-sensitivity spectrophotometer. The values correspond to the bipyramid sector with the orientation of the optical element of the type 1 frequency converter.

The impurity increased the transmittance threshold in the range of 5% in the 300-1100 nm. A characteristic 'pit' was formed at the beginning of the graph. Comparing the values we obtained with [3], we can see that the graphs have a general character of dependence in the studied area.

Table 1

Impurity	Mass fraction of impurity, ppm(wt)	Impurity	Mass fraction of impurity, ppm(wt)
Al	≤0.02	Pb	< 0.01
As	< 0.04	Pr	< 0.03
Au	< 0.05	Rb	0.14
В	< 0.1	S	<0.5
Bi	< 0.05	Sb	< 0.06
Ca	0.08	Se	< 0.04
Ce	< 0.04	Si	1.0
Cs	< 0.01	Sm	< 0.03
Fe	≤0.01	Sn	< 0.01
Ga	< 0.05	Та	< 0.05
Gd	< 0.01	Tb	< 0.03
Ge	< 0.06	Те	< 0.09
Na	0.06	Th	< 0.04
Nb	<0.01	Tl	< 0.05

Impurity composition of the prepared solution



Fig. 3. Transmission spectra of the obtained crystal (red is the KDP crystal with EDTA addition, black is the clean KDP crystal).

Conclusion

A study of the effect of EDTA on KDP crystal morphology and properties showed that the addition of EDTA to the growth solution leads to an increase in the growth rate of faces (both prism and pyramid) while not disturbing the crystal structure. Within four months, the impurity solution retained the original width of the dead zone, which may indicate a long degradation time of its properties.

Analyzing the obtained transmittance spectra, we can conclude about the increase of the transmittance threshold in the wavelength region of interest. In the future it is also planned to study the threshold voltage value.

The addition of EDTA to the KDP growth solution leads to the improvement of its optical characteristics and positively affects the growth morphology and kinetics. The increase of crystal growth rate, in turn, makes the process cheaper by reducing the technological costs, which also has a positive effect on the growth technology at all. Without the influence of EDTA on the structure of the KDP crystal, EDTA can be used for fast growth of large KDP crystals. In this way, the effect of chelating agents on the morphology and properties of KDP crystals remains a promising topic for more detailed research in the future.

REFERENCES

1. Zaitseva N., Carman L., Rapid Growth of KDP-type Crystals.

2. Bespalov V.I., Bredikhin V.I., Ershov V.P., Katsman V.I., Kiseleva N.V., Kuznetsov S.P., Optical properties of KDP and DKDP crystals grown with high speed. Quantum Electronics, (9) (11) (1982).

 Vinh Trung Phan, Khanh Duy Nguyen, Hung Vu Tuan Le, Effect of some hydroxyl additives on the growth and optical properties of KDP crystals, Journal of Crystal Growth, Vol. 587 (2022) 126643.
 Ershov E.V., High-speed growth of monosectoral profiled single crystals of the KDP group. RAS,

2007.

5. Chuprunov V.N., Portnov V.N., The appearance and growth of crystals. M.: fizmatlit, 2006.

THE AUTHORS

VILCHENKO Sergey A. sergey.vilchenko@yandex.ru

GRIBKO Vladimir V. sergey.vilchenko@yandex.ru ORCID: 0009-0003-9101-9718

Received 28.07.2023. Approved after reviewing 30.08.2023. Accepted 31.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 621.383.5 DOI: https://doi.org/10.18721/JPM.163.226

Development of a photodetector for an analog extended fiber-optic communication line

D.V. Oaserele¹, A.F. Gordeeva¹, R.V. Davydov²

¹ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

² Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

^{III}oasereledenis@gmail.com

Abstract. Different designs of analog fiber-optic lines (FOCL) for transmitting information at different distances in different frequency ranges are considered. The peculiarities of optical analog signals transmission, which will influence its registration in the FOCL photodetector module, are noted. The format of analog signals to be transmitted over a FOCL over a distance of more than 500 km without the use of optical amplifiers was determined. A photodetector module of the type PDA 400 Thorlabs with a peak response of 0.95 A/W at 1550 nm is considered. The bandwidth of which is from DC to 10 Mhz. Response: from 800 to 1750 nm. Based on the calculation of various parameters of the FOCL and its energy balance, the requirements to the design and characteristics of the photodetector module were determined. A laboratory mockup of the photodetector module was assembled. The results of its operation as a part of the analog FOCL with different ranges of information transmission are presented.

Keywords: Analog optical signal, photodetector, laser radiation, wavelength, line width, dynamic range, registration bandwidth, signal/noise ratio

Citation: Oaserele D.V., Gordeeva A.F., Davydov R.V., Development of a photodetector for an analog extended fiber-optic communication line, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 154–160. DOI: https://doi. org/10.18721/JPM.163.226

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.383.5 DOI: https://doi.org/10.18721/JPM.163.226

Разработка фотоприемника для аналоговой протяженной волоконно-оптической линии связи

Д.В. Оасереле¹, А.Ф. Гордеева¹, Р.В. Давыдов²

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия;

²Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

^{III} oasereledenis@gmail.com

Аннотация. Рассмотрены различные конструкции аналоговых волоконно-оптических линий (ВОЛС) для передачи информации на различные расстояния в разном диапазоне частот. Отмечены особенности передачи оптических аналоговых сигналов, которые окажут влияние на его регистрацию в фотоприемном модуле ВОЛС. Определен формат аналоговых сигналов, которые необходимо передать по ВОЛС на расстояния более 500 км без использования оптических усилителей. Рассмотрен фотоприемный модуль типа PDA 400 Thorlabs с пиковым откликом 0,95 A/BT при 1550 нм. Полоса пропускания которого от постоянного тока до 10 Мгц. Отклик: от 800 до 1750 нм. На основании расчета различных параметров ВОЛС и ее энергетического баланса определены требования к

© Oaserele D.V., Gordeeva A.F., Davydov R.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

конструкции и характеристикам фотоприемного модуля. Собран лабораторный макет фотоприемного модуля. Представлены результаты его работы в составе аналоговой ВОЛС с различной дальностью передачи информации.

Ключевые слова: Аналоговый оптический сигнал, фотоприемник, лазерное излучение, длина волны, ширина линии, динамический диапазон, ширина полосы регистрации, отношение сигнал/шум

Ссылка при цитировании: Оасереле Д.В., Гордеева А.Ф., Давыдов Р.В. Разработка фотоприемника для аналоговой протяженной волоконно-оптической линии связи // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. .16 3.2 №. С. 154–160. DOI: https://doi.org/10.18721/JPM.163.226

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Currently, in various optical systems photodetectors for short wave infrared (SWIR) or near-infrared region of the radiation spectrum find great application [1-8]. In some cases, their use is the only solution for obtaining accurate results in research using laser radiation [9-13], for information transmission over fiber-optic communication lines (FOCL) and much more [14-18]. A large number of different photodetectors have been developed for various designs of analog and digital FOCLs [19-21]. To calculate the parameters of digital and analog communication lines, methods have been proposed that take into account the typical conditions of information transmission. Taking into account these conditions, as well as the need to adapt the FOCL design to the required wavelength of laser radiation, a photodetector is selected and a photodetector module is developed [22, 23].

In the case of the use of FOCL to solve special problems associated with the transmission of analog signals, there are a number of features, both in the choice of the photodetector, and on the design of the photodetector module itself. These features are related to the operating conditions of the photodetector module, the frequency of transmission and form of optical signals, as well as the level of signal to noise ratio, which ensures reliable decoding of information and the recorded signal. Therefore, despite the small number of applications of analog optical signals, there are many designs of photodetector modules. This is due to the fact that the features of working with analog signals change dramatically depending on the tasks to be solved [19-25]. In most cases it is required to develop or modernize the design of photodetector module to solve new problems. One of such tasks is the transmission of telemetry information about the state of the environment along the FOCL in the power line area for distances over 500 km. In these conditions the use of optical amplifiers is excluded, since powerful spark induction on the power line, which occurs for various reasons, changes the polarization of laser radiation, which is used for pumping. This leads to distortion of information in the transmitted optical signal. During a thunderstorm the optical amplifier stops its work to ensure the functioning of the line. Therefore, optical amplifiers are not used in the transmission line system. This imposes certain restrictions on the transmitting module, because in digital FOCL the laser radiation of low power is amplified to a certain level by the optical amplifier (everything is in one transmitting module). In FOCL it is necessary to use powerful laser radiation, which has a number of features both in terms of line width and formation of information in the optical signal.

Therefore, for the new FOCL design, which is used in the transmission line system, it is necessary to develop a photodetector module, which takes into account the features of transmitted signals with information at $\lambda = 1550$ nm for long distances.

Selection of a photodetector for recording weak signals in the form of rectangular pulses with variable amplitude

The main requirement for the photoreceptor material to realize absorption at the desired wavelengths is the width of the band gap. Fig. 1 shows the absorption coefficients of various structures [22, 24, 26]. This analysis is necessary to choose a structure with maximum absorption near 1.55 μ m. It is more reasonable to use In_{0.53}Ga_{0.47}As based structure in the photodetector.

© Оасереле Д.В., Гордеева А.Ф., Давыдов Р.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Absorption coefficient of semiconductor materials

This composition has a large absorption coefficient at a wavelength of 1.55 μ m and a relatively low intrinsic concentration of charge carriers. This ternary compound is lattice constant matched to InP substrates, has a bandgap width of 0.74 eV, and covers the wavelength range of 0.9 to 1.7 μ m. The layer thickness of about 2 μ m provides a high quantum efficiency, specifically, about 90% [19].

Analysis of the data shows that two photodiode designs with materials based on $In_n Ga_{1-n}$ As and $In_{0n} Ga_{1-n} AsP$ are suitable for optical signal registration in analog FOCLs. InGaAsP structure based on InP, *n*-type substrate, highly doped. Two types of photodetectors, P-I-N and avalanche photodiodes (APD), have been mainly developed based on different combinations in terms of concentrations in these materials. These devices have a number of disadvantages and premiums in different applications depending on the tasks to be solved. As well as the design of the FOCL and the format of the signals that are transmitted over it. Fig. 2 shows the design of the analog FOCL to transmit telemetry signals over long distances from various systems installed on power lines, as well as control commands of these systems. The distances can be up to about 500 km.

In such a situation, a photodetector will receive a weak by power signal with low speed. The signal frequency will be of the order of tens of kHz. In this case the important elements in such registration will be the minimum detectable input power (NEP) of the photodiode and the spectral sensitivity. Tables 1 and 2 give the characteristics of currently produced photodiodes for comparison.



Fig. 2. Structural diagram of analog FOCL for control and monitoring of key elements: semiconductor laser 1; optical fiber 2; photodetector module 3; laser power supply with direct current modulation 4; multifunctional power supply 5; tunable LC-filter 6; analog-digital converter 7; electronic key 8; signal generator of subcarrier frequency 9; device 10 for generation of rectangular pulse sequence; information processing device 11, obtained using a sequence of command codes; central controller's

computer 12; device for formation of signals of the key elements 13; switch position signal 14

Table 1

Material	Si	Ge	In _{0.53} Ga _{0.47} As	In _{0.53} Ga _{0.3} As _{0.6} P _{0.4}
Spectral sensitivity range, µm	0.4–1.1	0.6-1.65	1.2–1.6	1.2–1.4
Photosensitive window area, cm ²	10-2	10-5	n/a	n/a
Diameter of the photosensitive window, mm	n/a	n/a	0.06–2	0.06–2
Dark current, nA	1-100	100-1000	1	1
Speed, ns	< 1	0.1	0.1	0.1

Parameters of some commercially available *p-i-n* PDs

Table 2

Parameters of some commercially available avalanche PDs (APDs)

Tashniasl Spesifications	Photodiodes			Avalanche photodiodes		
Technical Specifications	FD-252			FD-317L		
Semiconductor material	Si	InGaAsP	InGaAs	Si	Ge	Ge
Spectral sensitivity	400–1100	1200–1400	1200–1600	400–1100		
range, nm						
Working wavelength, nm	850	1300	1550	850	1300	1550
Operating voltage, V	24	5 (10)	5 (10)	70–400	30–50	30–50
Current sensitivity, A/W	0.35	0.6–0.8	0.6–0.8	50	8-10	8-10
Dark current, nA	10	1–5	0.1–1			
Capacity, pF	5	1	1	2	< 2	< 2
Rise time, fall time, ns	5	0.15-0.3	0.1–0.2	< 2	0.3/0.6	0.5/0.7
Noise current				5.10-13	5.10-12	5.10-12
density, AGH–0.5				5.10 "	5.10 .2	5.10 .2

The presented results allow a comparison of PD by NEP and photosensitivity R.

When transmitting information over long distances it is necessary to ensure energy balance in the used FOCL. In this case it is necessary to use PD with the lowest NEP and maximum R value. According to these criteria two types of PDs from Tables 1 and 2 (e.g. G12180-003A or IAG-080X) can be used for photodetector module design. The difference in these PDs between the two marked parameters is insignificant.

The primary criterion in the selection of the PD in the used analogue FOCL is its stable operation at significant temperature changes. The photodetector module used by the FOCL is placed on top of the power line and is exposed to various temperature modes. These regimes with changes in vert and precipitation can change dramatically.

Avalanche PDs (LFDs) have internal amplification, which is due to the avalanche multiplication of charge carriers in the high field region in the diode base. Photodiodes of this design have increased sensitivity. A negative quality of avalanche photodiodes is that their parameters strongly depend on temperature changes and the magnitude of the reverse voltage [27].

Therefore, it is more reasonable to use PDA P-I-N type photodetectors for photodetector module design. In the heterostructure of these photodetectors with partially depleted absorption layer (Partially Depleted Absorber) the spatial charge effect is reduced by reducing the thickness of the i-InGaAs drift layer and aligning the electron and hole fluxes in this layer. For this purpose, additional absorbing layers of InGaAs of p-type and n-type conductivity are included in the heterostructure. When PDA *p-i-n*-FD light is illuminated, photogenerated electrons are injected from the absorbing p-InGaAs layer into the i-InGaAs layer, and photogenerated holes are injected from the absorbing n-InGaAs layer. If the thickness of the n-InGaAs absorbing layer is greater than the thickness of the p-InGaAs layer, the flux of electrons is greater than the flux

of holes. The advantage of p-i-n-FD PDAs is that high quantum efficiency, high photocurrent, fast response, and low thermal resistance are achieved at low reverse voltages by minimizing the spatial charge accumulation effect, short span time, and smaller drift region thickness [24, 28].

In PDA p-i-n-PDs, there are a number of limitations on the photodiode bandwidth. This problem in such PDs is solved by reducing the thickness of the absorption layer. However, such a modification of the structure will lead to a decrease in the sensitivity of the structure. In the analog FOCL used for transmission of information signals frequencies of the order of 1-10 kHz are used, so there are no significant limitations on bandwidth, which allows the thickness of the absorbing layer of the order of 2 microns less sensitive to temperature changes at its departure in the thermal stabilization system.

Photodetector module design, recorded information signals and discussion

The optical signal formed using direct modulation of laser radiation in the form of a rectangular pulse at a carrier frequency is transmitted along the optical fiber 2.

Fig. 3 shows the optical signal that comes after the transmitting laser module 1 (Fig. 2) to the input of the optical fiber 2 and after its registration by the developed photodetector module 1.



Fig. 3. Rectangular pulses for transmitting information as a sequence of command codes. Graph 1 corresponds to the signal at the input to 2. Graph 2 corresponds to the signal at the output of 1

Then the optical signal at a subcarrier frequency of 200 MHz is fed through the fiber 2 to the input of the photodetector module 1. At the output of the photodetector module a rectangular pulse is formed with the filling of a sinusoidal signal with a frequency of 200 MHz (Fig. 3, graph 2). The load of the photodetector is a resonant LC-filter. The filter is tuned to a frequency of 200 MHz.

After the filter the signal at the subcarrier frequency is removed from the pulse and goes to the ADC 7. Then after the ADC the signal goes to the processing device to decode the transmitted information. It should be noted that with this scheme of registration of optical signal can be carried out its registration at signal/noise ratio of the order of 4 times, when in digital fiber-optic networks it is necessary to ensure at least 20 dB.

Conclusion

The analysis of the conducted studies of sequences of rectangular pulses of different duration with different subcarrier frequencies showed the stable operation of the developed photodetector with the following characteristics: bandwidth $\Delta F_f = 1$ GHz, NEP = 10–14 W·Hz^{1/2}. Placement of resonant LC-filter and ADC in the design of the developed photodetector module is one of its features of operation in conditions of power lines. This design of the photodetector module allows to register information optical signals with linear frequency modulation (LFM), which are used as subcarriers in them. This increases the base of the signal during its registration by several orders of magnitude and allows the recognition of information when the optical signal is registered below the noise level. The use of these signals in the designs of analogue fiber-optic lines is one of the future scientific directions of our development and research.

REFERENCES

1. Myazin N.S., Smirnov K.J., Logunov S.E., Spectral characteristics of InP photocathode with a surface grid electrode. Journal of Physics: Conference Series, 929 (1) (2017), 012080.

2. Logunov S.E., Vysoczky M.G., Mazing M.S., New method of researches of the magnetic fields force lines structure. Journal of Physics: Conference Series, 1038 (1) (2018), 012093.

3. Davydov V.V., Kruzhalov S.V., Vologdin V.A., Concerning some features of studying the flow of liquid media by a Doppler method, Journal of Optical Technology (A Translation of Opticheskii Zhurnal), 84 (8) (2017), 568–573.

4. Logunov S.E., Koshkin A.Y., Petrov A.A., Visualizer of magnetic fields," Journal of Physics: Conference Series. 741 (1) (2016) , 012092.

5. Mazing M.S., Zaitceva A.Yu., Kislyakov Yu.Ya., Kondakov N.S., Avdushenko S.A., Monitoring of oxygen supply of human tissues using a noninvasive optical system based on a multichannel integrated spectrum analyzer. International Journal of Pharmaceutical Research, 12 (2020), 1974–1978.

6. Kuzmin M.S., Rogov S.A., On the use of a multi-raster input of one-dimensional signals in twodimensional optical correlators. Computer Optics, 43 (3) (2019), 391–396.

7. Yakusheva M.A., Davydov R.V., Isakova D.D., Features of signal absorption fronts of laser radiation in rapid diagnosis of human health. 2022 8th International Conference on Information Technology and Nanotechnology, ITNT, (2022), 234–239.

8. Davydov R.V., Rud V.Y., Yushkova V.V., On the possibility of analysis using the wavelet transform of the pulse waveform from the bloodstream. Journal of Physics: Conference Series, 1695 (1) (2020), 012064.

9. Savelyeva A.A., Kozlova E.S., Comparison of the shape of focal spots in terms of intensity and energy flux for a high-aperture zone plate and a spiral zone plate. Computer Optics, 46 (4) (2022), 531–536.

10. Davydov R.V., Antonov V.I., Computer simulation of femtosecond pulsed laser ablation of aluminium and copper. Journal of Physics: Conference Series, 1124 (8) (2018), 081037.

11. Kozlova E., Kotlyar V., Ultrashort Laser Pulse Focusing by Amplitude and Phase Zone Plates. Photonics, 9 (9) (2022), 662.

12. Kotlyar V.V., Kovalev A.A., Kalinkina D.S., Kozlova E.S., Fourier-Bessel beams of finite energy. Computer Optics, 45(4) (2021), 506–511.

13. Savelyeva A.A., Kozlova E.S., Simulation of laser light focusing with two-layer dielectric microcylinders. Computer Optics, 45(2) (2021), 208–213.

14. **Davydov R., Antonov V., Moroz A.,** Parameter Control System for a Nuclear Power Plant Based on Fiber-Optic Sensors and Communication Lines. Proceedings of IEEE International Conference on Electrical Engineering and Photonics (EExPolytech -2019), 8906791(2019), 295–297.

15. Grebenikova N.M., Davydov R.V., Rud V.Y., Features of the signal registration and processing in the study of liquid flow medium by the refraction method. Journal of Physics: Conference Series, 1326(1) (2019), 012012.

16. Davydov V.V., SharovaN.V., Fedorova E. V., Vologdin V. A., Karseev A. Y., Fiber-optics system for the radar station work control Lecture Notes in Computer Science (including subseries, Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), 9247 (2015), 712–721.

17. Isaenko D., Reznikov B., Rodin S., Multifunctional ecological monitoring complex with optical communication channel. 2022 8th International Conference on Information Technology and Nanotechnology, ITNT (2022), 182151.

18. Arinushkina K., Valov A., Isupova E., Improvement of the frequency standard on cesium atoms used in spacecraft for remote sensing of the Earth. 2022 8th International Conference on Information Technology and Nanotechnology, ITNT (2022), 182151.

19. Tarasenko M. Y., LenetsV. A., AkulichN. V., YaluninaT. R., Features of use direct and external modulation in fiber optical simulators of a false target for testing radar station, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), LNCS, 10531 (2017), 227–232.

20. Davydov R., Logunov S., Nikolaev D., Dudkin V., Fiber Optic System for Monitoring Coolant Parameters in Nuclear Power Plants. Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), LNCS 13158 (2022), 221–229.

21. Rodin S.A., Reznikov B.K., Features of modulation of high-power laser radiation for optical space control systems. Journal of Physics: Conference Series, 2086 (1) (2021), 012050.

22. **Burlakov I.D.,** InGaAs-based short-wave infrared detectors (review) / D.I. Burlakov // Uspekhi Applied Physics. 2 (2) (2014) 131–162.

23. **Pereira J.M.T.,** Frequency response optimization of dual depletion InGaAs/InP PIN photodiodes / J.M.T. Pereira, J.P.N. Torres // Photonic Sensors. 6 (1) (2016), 63–70.

24. Chen J., Optimization of InGaAs/InAlAs Avalanche Photodiodes / J. Chen // Nanoscale Res Lett. 12(1) (2017), 123–131.

25. Myazin N., Neronov Y., Petrov A., On the need for express control of the quality of consumer goods within the concept 'Internet of things, IOP Conference Series: Materials Science and Engineering, 497 (1) (2019), 12111.

26. **Campbell J.C.**, Recent advances in telecommunications avalanche photodiodes // Journal of Lightwave Technology. Institute of Electrical and Electronics Engineers Inc. 25 (1) (2007), 109–121.

27. Li J., et al., Mid-wavelength infrared avalanche photodetector with AlAsSb/GaSb superlattice // Sci Rep. Nature Research, 11 (1) (2021), 453–459.

28. Lin L., et al., Theoretical study of separate absorption, grading, charge, and multiplication InGaAs/InP single photon avalanche diode //2008 International Conference on Numerical Simulation of Optoelectronic Devices (NUSOD). IEEE, (2008) 38–5.

THE AUTHORS

OASERELE Denis V. oasereledenis@gmail.com ORCID: 0009-0003-2742-0515 DAVYDOV Roman V. davydovroman@outlook.com ORCID: 0000-0003-1958-4221

GORDEEVA Aleksandra F. alexgordeeva99@mail.ru

Received 28.07.2023. Approved after reviewing 19.09.2023. Accepted 19.09.2023.

Conference materials UDC 621.383 DOI: https://doi.org/10.18721/JPM.163.227

Investigation of phase shift in waveguides with chalcogenide glasses

A.E. Mitrofanova¹,²,⁴, I.D. Skuratov¹,², V.V. Svetikov³,⁴

¹JSC Molecular Electronics Research Institute, Moscow, Russia;

² Moscow Institute of Physics and Technology, Dolgoprudny, Russia;

³ Prokhorov General Physics Institute, RAS, Moscow, Russia;

⁴ JSC Zelenograd Nanotechnology Center, Moscow, Russia

⊠ mitrofanova.ae@phystech.edu

Abstract. The paper presents a numerical study of the propagation of the waveguide mode in a waveguide with films of chalcogenide glasses, a numerical analysis of the phase change of the waveguide mode depending on the phase state of chalcogenide glass and geometric parameters of the structure.

Keywords: integrated optics, chalcogenide glasses, phase shift

Citation: Mitrofanova A.E., Skuratov I.D., Svetikov V.V., Investigation of phase shift in waveguides with chalcogenide glasses, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 161–166. DOI: https://doi.org/10.18721/JPM.163.227

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Mitrofanova A.E., Skuratov I.D., Svetikov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 621.383 DOI: https://doi.org/10.18721/JPM.163.227

Исследование фазового сдвига в волноводах с халькогенидными стеклами

А.Е. Митрофанова¹,²,⁴, И.Д. Скуратов¹,², В.В. Светиков³,⁴

¹ АО «НИИМЭ», Москва, Россия;

² Московский физико-технический институт (национальный исследовательский университет), г. Долгопрудный, Россия;

³ Институт общей физики им. А.М. Прохорова РАН, Москва, Россия;

⁴ АО «Зеленоградский нанотехнологический центр», Москва, Россия

^{III} mitrofanova.ae@phystech.edu

Аннотация. В статье представлено численное моделирование распространения волноводной моды в волноводе с пленками из халькогенидных стекол, численный анализ изменения фазы волноводной моды в зависимости от фазового состояния халькогенидного стекла и геометрических параметров структуры.

Ключевые слова: интегральная фотоника, халькогенидные стекла, сдвиг фазы

Ссылка при цитировании: Митрофанова А.Е., Скуратов И.Д., Светиков В.В. Исследование фазового сдвига в волноводах с халькогенидными стеклами // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 161–166. DOI: https://doi.org/10.18721/JPM.163.227

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Currently, chalcogenide materials are widely used to create memory cells. Such devices are based on the principle of changing optical and electrical properties when the phase state of the glass film changes from amorphous to crystalline. The phase state is switched using heat from laser or electric pulses.

Special attention is paid to the study of Ge–Sb–Te (GST) glasses, which have high optical contrast [1] and short phase-state switching time (< 50 ns) [2]. GST-225 has a high refractive index in both crystalline (n = 8.03) and amorphous (n = 4.69) phase states [3, 4]. In the work, the possibility of creating a discrete phase shift using elements based on GST-225 thin films was investigated.

The idea of generating a discrete phase change employing materials based on GST-225 thin films was studied during the course of the investigation. Calculations were performed for waveguide architectures based on SOI for wavelength $\lambda = 1.55$. The BPM numerical calculation was used to undertake a numerical analysis of the phase shift based on the geometric parameters of the structure and the GST-225 film's phase state. The obtained results provided the optimal thickness of the film and the buffer layer separating it from the waveguide. A numerical model of the Mach-Zehnder interferometer with discrete phase adjustment was built based on the study's findings.

[©] Митрофанова А.Е., Скуратов И.Д., Светиков В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Results and Discussion

The major goal of the research investigation was to find the optimal shape for a waveguide with a thin GST film that could provide the required phase shift while minimizing absorption losses in the GST layer. When the GST layer is on the surface of the waveguide, there is a rapid (on the length about 0.1 micron) transfer of signal into the GST layer [5]. A buffer layer is put between the waveguide and the thin film to prevent this. The GST layer therefore 'captures' only the mode's edge, preventing signal from passing into a thin layer and reducing losses. Fig. 1 shows the final geometry of the structure and the distribution of the field in the plane of the waveguide's cross-section.



Fig. 1. Waveguide geometry (a) and field distribution in the waveguide (b)

The study presents computational analysis of the phase change of the waveguide mode and waveguide losses as variables of the phase state of the GST film and the geometric parameters of the structure: the thickness of the film (10-30 nm) and the thickness of the buffer layer (0-100 nm). The graph of the relative phase shift (Fig. 2,*a*) in two channels has a stepped structure for all variants with a buffer layer. This is explained by the fact that light propagation takes a zigzag shape in the area with GST (Fig. 2,*c*). The "capture" of the mode's edge by the glass increases the size of the waveguide with the film, and it changes the profile of the main mode. As a result, the phase difference between the two channels rises where the mode approaches the GST layer and remains nearly constant where the mode returns to the silicon waveguide.

The GST film's width might vary within extremely tight limitations. It is technically challenging to create a layer thinner than 10 nm. Losses grow significantly when the layer thickness is increased to 20 nm or greater.

The buffer layer thickness was selected with the features of propagation and the amount of the necessary phase shift. The research investigated the feasibility of producing a customizable phase shift within 15° by using numerous sections coated with a GST film. The graphs show results of numerical modeling of structures coated with a thin GST coating. Fig. 2,*a* shows the phase shift dependence on the thickness of the buffer layer between the waveguide and the GST layer. The phase difference is calculated at the output of two waveguides, one with a crystalline layer of GST and the other with an amorphous layer of GST. Figure 2,*b* shows dependence of losses in a waveguide with a GST layer in the crystalline phase of the thickness of the buffer layer; losses in the amorphous phase layer are significantly lower. At a length of about 2 microns, the buffer layer width of 75 nm enables a phase shift of up to 5° with relatively low losses. A buffer layer with a thickness of 75 nm was chosen for this particular task because the resulting shift diminishes dramatically with slightly reducing losses as the layer thickens. A significant rise in losses takes place in a thinner layer, limiting the final interferometer model from being built.



St. Petersburg Polytechnic University Journal. Physics and Mathematics. 2023. Vol. 16. No. 3.2

Fig. 2. Dependence of the phase shift on the width of the buffer layer (a) and dependence of the amplitude loss on the width of the buffer layer (b); propagation of the waveguide mode in a waveguide with GST (c)



Fig. 3. Scheme of optical switching device based on Mach–Zehnder interferometer with GST (*a*) and dependence of the intensity in the channels on the distance from the entrance (*b*)

Based on the results, a model of switch device based on the Mach-Zehnder interferometer was created (Fig. 3,*a*). The phase difference between signals traveling in different arms must be 45 degrees for the switch to function correctly. However, generating an exact phase difference is challenging since it requires an optical path difference between the two channels of just /8, which in the case of a wavelength h = 1.55 microns is approximately 0.2 microns. To implement the correction, separate sections of GST film were produced in both arms of the interferometer. It is possible to shift phase by 5-15 degrees by switching phase state of the GST, providing the exact final phase shift of 45 degrees required for switch operation. In the model phase shift about 35° is implemented geometrically and 10° phase shift is implemented by using GST. Fig. 3,*b* shows the intensity in the interferometer channels as a function of distance from the input. Significant intensity losses appear when reaching areas with GST in the crystalline phase state.

Conclusion

An investigation of the effectiveness of structures with different geometry was performed using mathematical modeling. The dependence of the resulting phase shift and losses in waveguide configurations on the thickness of the buffer layer between the waveguide and the GST thin film is studied. It is demonstrated that the ideal width of the buffer layer is 75nm due to the peculiarities of light propagation in the suggested structure. This makes it possible to achieve the highest phase shift with the fewest losses in the area containing GST in the crystalline phase. Based on the results, an optical switch model based on a Mach–Zehnder interferometer with a customizable discrete phase shift is created.

REFERENCES

1. Guo P., Sarangan A. M., Agha I., A review of germanium-antimony-telluride phase change materials for non-volatile memories and optical modulators, Applied sciences, 9 (3) (2019) 530.

2. Kozyukhin S. A., et al., Phase change memory materials and their applications //RUSSIAN CHEMICAL REVIEWS, 91(9) (2022).

3. Krasnikov G.Ya. et al., contemporary situation in the field of non-volatile memory development // Electronic engineering. Series 3: microelectronics, (2) (2015) 38–44.

4. Kim H. J., et al., PCM-net: a refractive index database of chalcogenide phase change materials for tunable nanophotonic device modelling //Journal of Physics: Photonics, 3 (2) (2021) 024008.

5. **Rudé M., et al.,** Optical switching at 1.55 μm in silicon racetrack resonators using phase change materials //Applied Physics Letters, 103 (14) (2013), 141119.

THE AUTHORS

MITROFANOVA Anastasia E. mitrofanova.ae@phystech.edu ORCID: 0009-0004-5306-278X **SVETIKOV Vladimir V.** vl.svetikov@gmail.com

SKURATOV Ilya D. ilya.skuratov@phystech.edu ORCID: 0000-0002-4045-2883

Received 29.07.2023. Approved after reviewing 01.08.2023. Accepted 03.08.2023.

Conference materials UDC 621.372.8 DOI: https://doi.org/10.18721/JPM.163.228

The research of nonlinear optical phenomena in silicon slot waveguide structures

S.M. Murzagalina^{1,2,3}, I.D. Skuratov^{1,2}

¹ JSC Molecular Electronics Research Institute, Moscow, Russia;

² Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russia;

³ JSC Zelenograd Nanotechnology Center, Moscow, Moscow, Russia

[™] murzagalina.sm@phystech.edu

Abstract. This work is devoted to the study of nonlinear phenomena in silicon waveguides, as well as in silicon-organic hybrids, which help to obtain improved characteristics of the initial device by compensating for the limitations imposed by second- and third-order nonlinearities in Si. The slot waveguide model is analyzed using computational methods such as the finite element method, the finite difference method in the time domain, and the singular perturbation method.

Keywords: nonlinearity, doped polymers, slot waveguides, FEM, FDTD, SPT

Citation: Murzagalina S.M., Skuratov I.D., The research of nonlinear optical phenomena in silicon slot waveguide structures, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 167–170. DOI: https://doi.org/10.18721/JPM.163.228

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.372.8 DOI: https://doi.org/10.18721/JPM.163.228

Исследование нелинейных эффектов в кремниевых щелевых волноводных структурах

С.М. Мурзагалина^{1,2,3}, И.Д. Скуратов^{1,2}

¹ АО «Научно-исследовательский институт молекулярной электроники», Москва, Россия;

² Московский физико-технический институт (национальный исследовательский университет), г. Долгопрудный, Россия;

³ ЗАО «Зеленоградский нанотехнологический центр», Москва, Россия

[⊠] murzagalina.sm@phystech.edu

Аннотация. Работа посвящена исследованию нелинейных явлений в кремниевых щелевых волноводах, а также в кремнийорганических гибридах, при интеграции которых возможно получить улучшенные характеристики исходного устройства за счет компенсации ограничений, налагаемых нелинейностями второго и третьего порядка в Si. Модель щелевого волновода анализируется с использованием таких вычислительных методов, как метод конечных элементов (МКЭ), метод конечных разностей во временной области (FDTD) и метод сингулярных возмущений (SPT).

Ключевые слова: нелинейные эффекты, легированные полимеры, щелевые волноводы, МКЭ, FDTD, SPT

© Murzagalina S.M., Skuratov I.D., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Мурзагалина С.М., Скуратов И.Д. Исследование нелинейных эффектов в кремниевых щелевых волноводных структурах // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 167–170. DOI: https://doi.org/10.18721/JPM.163.228

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The silicon technological foundation has the great potential in conjunction with electronics, photonics and quantum technologies. It has opportunities in performing as solution for growing demands in such applications as data processing and telecommunications industry. Using the linear optical phenomena significant quantity of devices have been implemented on the SOI platform, for example optical buffers, interconnections [1] and sensors.

The second and third-order nonlinearities provide optical power losses, but in same time nonlinear optical effects may lead to new applications such as multiplexing and modulating signals. Therefore, researchers come across with the new challenge – to create the device with minimal losses and best functional characteristics.

Materials and Methods

The second-order nonlinearity in silicon is lower due to the centrosymmetric crystal structure, while the third-order nonlinearity is high and caused by such effects as two-photon absorption, forced scattering, four-wave mixing and the Kerr effect [2]. To solve that problem was carried out an analysis of various materials, among them silicon-organics hybrids (SOH), which also has strong second and third-order nonlinearities [3]. The propagation of optical radiation in wave-guide structures is influenced by both the properties of silicon and SOH materials [4].

Currently, the model of slot waveguide with nonlinear properties is under development. It consists of silicon strips with a high refractive index and a nanoscale gap with a low refractive index, which formed between them as shown in Fig. 1.



Fig. 1. Planar overview of waveguide parameters

This configuration is capable of providing new applications, such as optical capture, optical switching and sensors technology. In order to adapt the model to new applications, waveguides are coated with dopped polymer or other organic substances, such as the Ormocore polymer, in which both second- and third-order nonlinearities are demonstrated. Such waveguides are good candidates for electro-optical modulators with high data transfer rates and optical signal processing devices [5]. These devices have advantages such as high efficiency and integration with new materials conformant with CMOS.

The nonlinear phase shift was caused in the slit waveguide by the nonlinear optical Kerr effect. The analysis of this structure is carried out using software for modeling based on the finite element method (FEM) and the finite difference method in the time domain (FDTD).

In order to minimize optical losses, it was decided to optimize the geometric parameters of the model using machine learning methods. An analytical approach to obtain the parameters of a slot waveguide with nonlinear characteristics using the singular perturbation technique (SPT) is also considered. SPT is used to study the behavior of waveguides with spatial perturbation [6] and weak second- and third-order nonlinearities, leading to solutions with sufficiently high accuracy [7].

© Мурзагалина С.М., Скуратов И.Д., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 2. Mode profile

Results and Discussion

In this paper, an analysis of silicon-organic compounds with second- and third-order nonlinearities was carried out, the polymer Ormocore was selected as a coating for waveguides. Nonlinear index coefficient n_{NL} and third-order susceptibility $\chi^{(3)}$ are interrelated as follows:

$$n_{NL} = \operatorname{Re}\left(\chi^{(3)}\right) / \left(4\varepsilon_0 c n_L^2\right),$$

where ε_0 and c are dielectric constant and velocity of light in vacuum and n_L is the linear refractive index of the selected nonlinear material. For polymer Ormocore, the nonlinear refractive index is $2 \cdot 10^{-17} \text{ m}^2/\text{W}$, while for Si it is $6 \cdot 10^{-18} \cdot \text{m}^2/\text{W}$.

A nonlinear material's relevance is influenced by its nonlinear losses as well as its nonlinear index coefficient. Two photon absorption (TPA) tends to be the cause of significant power losses. Unfortunately, excited band states are occupied by the carriers produced by TPA. These nanosecond lifetime carriers then take on the role of a highly absorbent plasma, lowering optical power and impairing nonlinear performance. Figure of merit (FOM), which relates the nonlinear phase shift to the associated intensity change, is defined as:

$$FOM = \frac{1n_{NL}}{\lambda \alpha_{NL}},$$

where a_{NL} is the nonlinear absorption coefficient. Si although has a relatively large n_{NL} is the coefficient but unfortunately it has a low, caused by TPA, figure of merit. However, silica has a large FOM yet weak nonlinear characteristics. On the other hand, polymer Ormocore shows both a large nonlinear index n_{NL} and a small nonlinear absorption coefficient a_2 , thus leading to a good FOM.

To obtain maximal nonlinearity in slot waveguides, not only the material dependent refractive index but also the mode confinement must be optimized. The nonlinearity parameter is:



Fig. 3. Effective areas of nonlinear interaction $A_{eff}^{(3)}$ for a cover material with a linear refractive index *n*

To attain the highest possible nonlinearity in waveguides, it is necessary to optimize both the confinement of the mode and the material-dependent refractive index. It heavily depends on the third-order nonlinear interaction's effective area $A_{eff}^{(3)}$

The silicon slot waveguide structure of Fig. 1 has $A_{eff}^{(\ell)}$ smaller than 0.1, which can be obtained with such geometry parameters as slot width of 50 nm, a core width 180 nm, and a core height 350 nm as shown in Fig. 3. The unique advantage of the slot waveguide structure is that it concentrates the field inside the slot as shown in Fig. 2., so that the nonlinearities in the silicon material become less important, and the slot material determine the nonlinear behavior.

Conclusion

In the conducted research, silicon-organic hybrids materials were analyzed. The modeling of the structure was carried out during which the distribution of fields in the structure was revealed depending on the characteristics of the source and the geometric parameters of the slot waveguide. A value for the minimum effective area of nonlinear interaction was also obtained, which will further help to improve the characteristics of waveguides by optimizing geometric parameters, increasing FOM of the device.

It is planned to build model's optimization based on the genetic algorithm in order to improve its characteristics. The problem of a bent silicon slot waveguide is also under consideration, it will solve the common issue of reducing rotation losses. It is also intended to develop biological sensors based on slot waveguide structures that use nonlinear optical phenomena.

REFERENCES

1. Valeev A.S., Krasnikov G.Y., Manufacturing technology of intracrystal and intercrystal interconnections of modern ASIC// Microelectronics, 44 (3) (2015) 180–201.

2. Fujisawa T., Koshiba M., Guided modes of nonlinear slot waveguides. IEEE Photonics Technology Letters 18 (2006) 1530–1532.

3. Leuthold J., et al., Silicon Organic Hybrid Technology—A Platform for Practical Nonlinear Optics, in Proceedings of the IEEE, 97 (7) (2009)1304–1316.

4. Lipson M., et al., Guiding, modulating, and emitting light on Silicon-challenges and opportunities, in Journal of Lightwave Technology, 23 (12) (2005) 4222–4238.

5. **Palmer R., et al.,** Low power Mach–Zehnder modulator in silicon-organic hybrid technology // IEEE Photonics Technology Letters, 25 (13) (2013) 1226–1229.

6. Nayfeh A.H., Asfar O.R., Parallel-plate waveguide with sinusoidally perturbed boundaries // Journal of Applied Physics, 45 (11) (1974) 4797–4800.

7. Yokota M., et al., Guided transverse-magnetic waves supported by a weakly nonlinear slab waveguide // JOSA B, 10 (6) (1993) 1096-1101.

THE AUTHORS

MURZAGALINA Sofya M. murzagalina.sm@phystech.edu SKURATOV Ilya D. ilya.skuratov@phystech.edu

Received 30.07.2023. Approved after reviewing 11.09.2023. Accepted 12.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535 DOI: https://doi.org/10.18721/JPM.163.229

Study of color characteristics of pigments and paints by spectrophotometer

Y.J. Jabr¹[™], L.A. Smirnova², V.A. Parfenov¹

¹ St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia;

² Academy of Fine Arts, St. Petersburg, Russia

⊠ yara.jabr.1996@gmail.com

Abstract. Nowadays, in restoring and examining paintings, the search for effective analytical methods for studying paint pigments is very actual. The identification of poor pigments is important itself, but it is also important for the determination of pigments in paints with different binders. Many studies were done in this field by means of Raman and IR Fourier spectroscopy, X-ray fluorescence spectrometry and some others. However, all the mentioned methods require the use of complex and expensive equipment, sampling, and preparation of samples. For this reason, the search for new simple non-destructive, and inexpensive testing methods is still very actual. In this work for studying color characteristics of pigments, the spectrophotometry method was used. In the experiments, the color characteristics of model samples were studied. It was shown that the color characteristics of pigments and paints, including, for example, whitewash (lead, zinc, and titanium), have characteristic individual values of the color coordinates $L^*a^*b^*$ that may be used for their identification.

Keywords: spectrophotometry, pigments, paints, color characteristics

Citation: Jabr Y.J., Smirnova L.A., Parfenov V.A., Study of color characteristics of pigments and paints by spectrophotometer, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 171–176. DOI: https://doi.org/10.18721/JPM.163.229

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535 DOI: https://doi.org/10.18721/JPM.163.229

Исследование цветовых характеристик пигментов и красок с помощью спектрофотометра

Я. Джабр¹[™], Л.А. Смирнова², В.А. Парфенов¹

¹ Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» имени В.И. Ульянова (Ленина), Санкт-Петербург, Россия;

² Санкт-Петербургская академия художеств имени Ильи Репина, Санкт-Петербург, Россия

^{III} yara.jabr.1996@gmail.com

Аннотация. В настоящее время при реставрации и экспертизе картин очень актуален поиск эффективных аналитических методов изучения пигментов красок. Идентификация чистых пигментов важно само по себе, но также важно определение пигментов в красках с различным связующим. В данной предметной области было проведено много исследований с помощью методов рамановской и ИК-фурьеспектроскопии, рентгеновской флуоресцентной спектрометрии и некоторых других. Однако все упомянутые методы требуют использования сложного и дорогостоящего оборудования, отбора проб и подготовки образцов. По этой причине поиск новых простых, неразрушающих и недорогих методов контроля по-прежнему является актуальной задачей. В данной работе для изучения цветовых характеристик пигментов

© Jabr Y.J., Smirnova L.A., Parfenov V.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

был использован метод спектрофотометрии, с помощью которого экспериментов были изучены цветовые характеристики модельных образцов пигментов красок. Было показано, что цветовые характеристики пигментов и красок, включая, например, белила (свинцовые, цинковые и титановые), имеют характерные индивидуальные значения цветовых координат L*a*b*, что может быть использовано для их идентификации.

Ключевые слова: спектрофотометрпz, пигменты, краски, картины, цветовые характеристики.

Ссылка при цитировании: Джабр Я., Смирнова Л.А., Парфенов В.А., Исследование цветовых характеристик пигментов и красок с помощью спектрофотометра // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 171–176. DOI: https://doi.org/10.18721/JPM.163.229

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Preserving art and artifacts is crucial for our history. Spectrophotometry measures reflection at different wavelengths, helping identify pigments without sampling. Analyzing the unique shapes of the spectrum curve reveals the colorants and pigments present. Visual reflectance spectrum and colorimetric coordinates provide vital information. The CIELAB system is widely used for chromatic coordinates and color visualization.

The CIELAB system analyzes reflectance spectrum differences influenced by pigments. Factors like deterioration, material content, and particle size affect color measurements. This study focuses on spectral curve measurements within the visible spectrum to understand color perception. Colorimetry considers illuminants, observers, and CIE standards [1]. Spectral analysis and CIE colorimetric data are used in studying colored objects. This paper discusses color science applications, including monitoring material changes, yellowing, gloss, fading or darkening. The studyexplores challenges and approaches with new binder materials like glue dispersion K9 acrylic and modern restoration materials such as Loropal (carbamide ormaldehyde resin resistant to yellowing) and iridescent pigments. Color measurement helps to document the color palette of some objects, so that we can see any changes in color. Routinely, there is a focus on identifying the oldest pigments by different methods of analysis. A direct and rapid identification of the minerals contained in tiny samples can be achieved by vibration and spectroscopic techniques.

The CIE (Commission International de l'Eclairage) 1976 (L*a*b*), or the CIE LAB system, is widely used for recording the chromatic coordinates. This system, referred to as colorimetry, is an effective tool for visualizing the color. The characteristics of a painted surface may have been found to be determined based on differences in reflectance spectrum, which is commonly characteristic of each pigment. Various possible factors, such as deterioration processes in the image area, materials content, surface hardness and particle size, can influence measurements of colors [2].

Color measurement helps to document the color palette of some objects, so that we can see any changes in color. Routinely, there is a focus on identifying the oldest pigments by different methods of analysis. A direct and rapid identification of the minerals contained in tiny samples can be achieved by vibration and spectroscopic techniques. Raman microscopy is a sensitive, nondestructive tool for the study of single grains in pigment samples and has been able to achieve some successful results [3-4]. In addition, a wide variety of advantages have been demonstrated when scanning electron microscopes are used to characterize painted objects. For pigment and microchemical analysis, we could use a scanned electron microscope that is able to identify morphologic microstructure features. Several studies were carried out on the importance of color measurements in terms of conservation of Cultural Heritage, with a view to determining whether they are relevant. Different art works of easel painting and murals have successfully been captured using colorimetry. Document, oil painting, wall art and stone structures [5]. Marchiafava et al. [6] have reported that measurement of color is useful in monitoring the conservation process applied to the mural Tuttomondo (1989) painted by Keith Haring (1958-1990) on the wall of the Church of Sant'Antonio Abate in Pisa (Italy).

© Джабр Я., Смирнова Л.А., Парфенов В.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Materials and Methods

To study the color characteristics of paint pigments, model samples were prepared, which represented the coloring of natural pigments. The model samples are pigment stains on sheets of paper about 2×2 cm in size, ground with various binders. In the experiments, both natural (yellow and red ochres, black ivory – production of Kremer Pigmente GmbH & Co. KG) and synthetic (various whitewash) pigments were used, as well as their mixtures. They have been rubbed with binders including traditional materials (for example, linen oil) and modern restoration ones (such as dispersion K9 acrylic–carbamide formaldehyde resin resistant to yellowing and used in restoration as a binder when tinting the loss of painting).

Since the properties of the paper itself can influence the color characteristics of pigments, careful paper selection was required. In particular, the paper should not contain excessive amounts of titanium, lead and zinc, since the presence of these chemical elements may subsequent influence of model samples, and therefore lead to inaccuracies in the analysis of their color. The fact is that some pigments (for example, titanium, lead and zinc white) contain them in their composition. For this reason, the paper used to create model samples underwent elemental analysis, which was performed using the X-ray fluorescence spectroscopy method. XRF spectrometric analyzer Niton XL3t GOLD + (Thermo Fisher, USA) was used.

Color measurements of model samples were carried out by means of spectrophotometer BYK Gardner Spectro-guide 45/0. In the CIE L*a*b* color system, color differences, and locations were determined based on L*, a*, and b* color coordinates. The symbols represent the following: a* for red-green, b* for yellow-blue, and L* for black-white (L* = 0 for black, L* = 100 for white). To assess the impact of changes in color tone, evaluations were conducted separately for red tone (+a*), yellow tone (+b*), and brightness value (L*). In our study, D65° illuminance was employed, representing daylight and encompassing the entire visual spectrum from around 400 nm to slightly over 700 nm of light. The chosen observer degree, 10°, corresponds better with human color perception.

The next step, a insulating layer has been laid upon it before drying to form the protective coating which is essential for wrapping this paper up so that it stays for longer time. Then it was covered by the glue dispersion K9 acrylic, which has a good binding capacity and widely used because of its low surface contamination without ammonia, formaldehyde free.

When thinned, it is possible to achieve a very matte finish. Then the pigments" (French Ochre, lead white, zinc white, red pole, terra Ercolano red natural land Ercolano Ivory black), were applied on the covered paper, measurements were collected by the spectrophotometer on each paint moving within the 4 cm \times 4 cm area.

Results and Discussion

The CIE L*a*b* values recorded on the studied paint samples are given in Table 1 and demonstrates the BYK elemental analysis obtained on the studied samples.

Table 1

on the studied pigment samples mixed with K9					
	L*	a*	b*		
zinc white	97.04	0.42	3.93		
lead white	97.00	-0.22	2.61		
Titanium white	97.02	-0.78	2.74		
French Ochre	55.95	13.65	41.61		
Black Ivory	6.61	0.55	1.22		
Red Bole	33.32	22.65	22.07		
Red Terra	40.50	36.21	35.35		

Chromatic coordinates (L*a*b*) recorded on the studied pigment samples mixed with K9



Fig. 1. CIELAB color differences (ΔL^*) (*a*); CIELAB color differences (ΔL^* , $\Delta b^* \Delta a^*$) Δa^* , Δb^*) for difference between the standard for the difference between the standard Red black and black ivory pole and red Terra Ercolano (*b*)

The dependence of Δb versus Δa is illustrated in Fig. 1,*a*. It is apparent that black ivory is redder than standard black. The color differences calculated for black ivory versus black as standard are from these values it can be seen that the major difference between these two blacks is in lighting (L). From graphing the chromaticity coordinates Fig. 1,*b* of the Red Terra Ercolano, with the standard "Red Pole", the red Terra have determined that it is redder and more yellowness than the others, and the values of L indicate it is lighter than the other two reds pigments.

This paper substrate involves the main class color spaces, CIE $L^*a^*b^*$ color space, which is recommended to use in the case of our study instead of LIELCH, and the reason is that $L^*a^*b^*$ and LCH can both done manually, but it depends on which if you have chromatic or non-chromatic colors, so $L^*a^*b^*$ usually used for colors that are under a chroma of 10 and anything over that we could use both LCH and $L^*a^*b^*$, so what it does because of the way the calculations are set up when you switch to LCH, some variations are gained on the chroma axis.

The plotted as percent reflectance on the vertical axis (y) versus wavelength on the horizontal axis (x) at a scale of 400-700 nm is presented with the used pigments (Fig. 2). Fig. 2, a shows the reflectance spectrum of the yellow French ochre pigment, which is mixed with K9 glue, the curve shape at 540–560 nm is characteristic of yellow paint which started to show high reflection intensity shoulders and above 560 nm, the chemical composition of this yellow is SiO₂, Al₂O₃, Fe₂O.The average values for a* and b* were (13.65) and (41.61), respectively. In terms of black pigment, a low reflectance intensity has been detected. The observation of the reflectance spectrum curve registered on the black pigment sample (Fig. 2,b) A slope on the wavelength of 400 nm was shown. Besides, there is a characteristic absorption band 420 nm was observed. The changes in the structure of the pigment and its composition are most likely to be the cause of this band. The closer a curve approaches this flat shape, the brighter it looks as neutral color and the lower its saturation or Chroma, which is Munsell's designation that corresponds exactly to saturation. On the pigment, an a* and b* value of 0.58 was recorded. Both numbers are 0.55 and 1.22.

In addition to the positive a* values, the microscopic observations showed that the sample tends towards yellow and red areas. In previous studies, the comparison of CIE L*a*b* coordinates and reflection spectrum has allowed us to differentiate between standard black and Ivory Black. Conversely, the more contrast there is between the maximum and minimum reflectance, the higher is the saturation (Chroma), as seen in the reds pigments and, yellow, in Fig. 2a,c, which is Red terra has the highest saturation (chroma) between the red. Fig. 3,c illustrates the spectrophotometric curves for reds, spectrum showed an increase at 560–700 nm (Fig. 2,c, d), and the band at 650 nm is for the Fe³⁺absorption in red ochres, in Fig. 2,e. where each measurement was carried out three times with different surface homogeneity. Red bole is a natural, ferruginous aluminum silicate. It is similar to ochres in its chemical composition but is softer and more unctuous. The a* and b* average values for the red sample were (22.65) and (32.17) for the Red Bole, respectively and (36.21) and (35.35) for Red Terra and (34.80) and (32.17) for Red Ercolano.



Fig. 2. Reflectance spectra of yellow French ochre pigments (mixed with glue K9) (a); reflectance spectra of Black ivory pigments (mixed with glue K9) (b); reflectance spectra of powders red pigments (red terra, ercolano land K9) (c); reflectance spectra of powders red pigments (red terra, Ercolano land) mixed with glue (d); reflectance spectra of powders white pigments (zinc-lead-tit) (e); reflectance spectra of powders white pigments mixed with K9 (zinc-lead-tit) (f)

Fig. 2, *e*, *f* shows the reflectance spectrum of the three white pigments(lead, zinc, and titanium), in Fig. 2, *f*, where each measurement was carried out three times with different surface homogeneity, the curve shape at beginning of the percent reflectance is characteristic of the titanium white pigment(PW6), in both dry and mixed with pure acrylic dispersion K9. The chromaticity coordinates (x, y) and the luminous reflectance, or lightness (L), of the three whites are given in Table 1. The L tristimulus value indicates that zinc white (PW4) is the lightest.

Conclusion

In conclusion, the interpretation of spectrophotometry reflectance curves in visible wavelengths serves a broader purpose beyond pigment identification. It encompasses a wide range of functions related to colors, making accurate interpretation of spectrophotometric data crucial.

By correctly interpreting such data, valuable assistance can be provided in identifying the pigments and paints used in paintings, enabling the implementation of optimal care and preservation methods. In the present study, both colorimetric and spectral reflectance analyses were conducted to examine the pigments. These analyses yield valuable information regarding the physical characteristics of cultural heritage objects, which can be documented through color documentation. To record color values, a BYK spectrophotometer was utilized, specifically capturing L*a*b* values. This color space is typically employed for colors with a chroma below 10. Considering the chosen pigments and their chroma values, the use of $L^*a^*b^*$ calculations and coordinates proved to be the most suitable approach in our study. The investigation of the reflectance spectrum of the pigments played a significant role in their identification. This technique provides insights into the unique spectral characteristics exhibited by different pigments, aiding in their differentiation and classification.

Our future work will be focused on further optimizing, by looking at visible reflectance spectra of pigment powders to the ones of their mixed paints with the white pigments. In the case of red pigment containing zinc white and lead white pigments, this is intended to assess differences in reflectance spectrum which started at 30%, 50% and 70% respectively of percentage of the red pigment, also Controlling the homogeneity content of the pigment surface to be measured is important because homogeneity content does affect the pigments' spectral reflectance and (CIE L*a*b*) values.

REFERENCES

1. Klockenkämper R., Von BohlenA., Moens, L., Analysis of pigments and inks on oil paintings and historical manuscripts using total reflection x-ray fluorescence spectrometry. X-Ray Spectrometry: An International Journal, 29 (1) (2000) 119–129.

2. Budakçı M., Karamanoğlu M., Effect of bleaching on hardness, gloss, and color change of weathered woods", BioResources, 9 (2) (2014) 2311–2327.

3. Perardi A., Zoppi A., Castellucci E., Micro-Raman spectroscopy for standard and in situ characterisation of painting materials, Journal of Cultural Heritage, (1) (2000) 269–272.

4.Vandenabeele P., Wehling B., Edwards H.G.M., De Reu M., Van Hooydonk G., Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art, Analytica Chemical Acta, 407 (1) (2000) 261–274.

5. Lorusso S., Natali A., Matteucci C., Colorimetry applied to the field of cultural heritage: Examples of study cases, Conservation Science in Cultural Heritage, 7 (2007) 187–208.

6. Marchiafava V., Bartolozzi G., Cucci C., Colour measurements for monitoring the conservation of contemporary artworks, Journal of the International Colour Association, 13 (2014) 36–42.

7. Feller R.J., Color science in the Examination of museum objects. Los Angeles: The J. Paul Getty Trust. (2001) 100–180.

THE AUTHORS

JABR Yara J. yara.jabr.1996@gmail.com

PARFENOV Vadim A.

SMIRNOVA Lyudmila A.

Received 31.07.2023. Approved after reviewing 31.08.2023. Accepted 28.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

PHYSICAL MATERIALS SCIENCE

Conference materials UDC 620.3 DOI: https://doi.org/10.18721/JPM.163.230

On the wetting of polyethylene terephthalate substrates with multicomponent graphene oxide dispersions

I.A. Komarov¹[⊠], E.A. Danilov¹

¹ JSC Research Institute Graphite, Moscow, Russia

⊠ master_kom@mail.ru

Abstract. In this work, we investigate wetting properties of polymer polyethylene terephthalate (PET) substrates with graphene oxide multicomponent dispersions. Overcoming poor wettability polymer substrates like PET, promising for flexible electronics applications, with commercially available water graphene oxide suspensions is proposed to solve by adding organic components. We used dimethylacetamide (DMA) and thinner for lacquer paints (LT) to successfully show the decrease of wetting angle. Moreover, we showed stability of multicomponent dispersion with DMA within more than 6 months and LT within more than several weeks and also found out that drying time of droplets of mixed dispersions with different additives may vary more than 15 times that is important for choice of the preferred deposition method.

Keywords: Graphene oxide, mixed dispersions, organic solutions, DMA, PET substrate

Citation: Komarov I.A., Danilov E.A., On the wetting of polyethylene terephthalate substrates with multicomponent graphene oxide dispersions, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 177–182. DOI: https://doi.org/10.18721/JPM.163.230

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 620.3 DOI: https://doi.org/10.18721/JPM.163.230

О смачивании подложек полиэтилентерефталата многокомпонентными дисперсиями оксида графена

И.А. Комаров¹⊠, Е.А. Данилов¹

¹ АО «Научно-исследовательский институт конструкционных материалов на основе графита «НИИграфит», Москва, Россия

⊠ master_kom@mail.ru

Аннотация. В данной работе исследуется смачивание полимерных подложек из полиэтилентерефталата (ПЭТ) многокомпонентными дисперсиями оксида графена. Для обеспечения улучшения смачиваемости полимерных подложек, таких как ПЭТ, являющихся перспективныим для применения в гибкой электронике, с помощью коммерчески доступных водных суспензий оксида графена предлагается пойти путем добавления органических растворителей. Мы использовали диметилацетамид (ДМА) и разбавитель для эмалевых красок (LT). Было успешно продемонстрировано уменьшение угла смачивания. Кроме того, показано, что стабильность многокомпонентной дисперсии с ДМА составляет более 6 месяцев и с LT – более нескольких недель. Также установлено, что время высыхания капель смешанных дисперсий с разными добавками может различаться более чем в 15 раз, что важно для выбора предпочтительного метода нанесения.

Ключевые слова: Оксид графена, смешанные дисперсии, органические растворы, ДМА, ПЭТ подложки

© Komarov I.A., Danilov E.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Комаров И.А., Данилов Е.А. О смачивании подложек полиэтилентерефталата многокомпонентными дисперсиями оксида графена // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 177–182. DOI: https://doi.org/10.18721/JPM.163.230

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Carbon nanomaterials, especially graphene derivatives that include graphene oxide (GO) and reduced graphene oxide (rGO) are very promising materials for different applications in flexible electronics [1], chemical and biological sensors [2], energy storage systems [3], drug delivery platforms [4] etc. One of the main requirements for flexible devices is large-area uniform conductive and dielectric nanomaterials-based layers. Highly uniform films can be formed on polymer substrates via different methods such as Langmuir–Blodgett technique [5], dip-coating [6], spin-coating [7], spray coating [8] or roll-to-roll technology [9] and many others, but only the latter three are compatible with at least small batch production. On the other hand, most of commercially available GO forms are water suspension with poor wettability of polymer substrates. This limitation can be overcome by mechanical or plasma pre-treatment, but in case of need of nanometer thick films those cannot be applied. On the other hand, wettability can be improved by the dispersion's properties themselves.

In the current study, we tried to introduce additional organic components to the water-based GO suspension to improve its wettability characteristics. Additional components in the dispersion media should at least provide good dispersibility of GO. According to the data obtained from [10], GO can form long-time stable dispersions in such organic solvents (besides water) as dimethylformamide (DMF), N-methylpyrrolidone (NMP) and tetrahydrofuran (THF), and less stable in ethylene glycol, acetone and toluene. On the other hand, it is known that dimethylacetamide (DMA) is a good dispersion media for carboxylized carbon nanotubes [11].

Thus, we tried to form a multicomponent mixed dispersion media that contains water-based GO suspension, DMA and thinner for lacquer paints (LT) that is a mixture of ethyleneglycol, butylglycol, methylisobutylketone at different GO concentrations. We investigated wettability of these multicomponent GO dispersions with respect to PET substrates. We also study morphology and Raman spectra of the dried up droplets of multicomponent dispersions.

Materials and Methods

Dispersions were prepared from commercially available GO water suspension (4,7 mg/ml) produced by improved Hummer's method (LLC MIP Graphene, Russian Federation). Additional components: ultrapure DMA (EKOS-1, Russian Federation), thinner for lacquer and enamel paints (Tamiya Inc., Japan) were mixed with initial suspension with 50 : 50 ratio. We made five concentrations for each additive: 0.01; 0.025; 0.05; 0.1 and 0.25 mg/ml.

As a substrate for film deposition, we used high opacity PET film without additional surface treatment. Substrates with 5×10 mm dimensions were cleaned with 2-propanol and water and dried in the 2 bar airflow.

For wetting angle investigations, we used home-made device with $3.5 \times \text{lens}$, digital camera for optical photos of dispersion droplets with further image processing using ImageJ software. Dispersions were deposited on substrates by drop-casting (drop volume was 0.25 µl)

Optical images of morphology and Raman spectra were obtained by InVia Raman spectrometer (Renishaw, UK). SEM images were obtained with Hitachi TM-3000 (Hitachi Ltd, Japan).

Results and Discussion

For wettability investigation of multicomponent dispersions, we used ImageJ software that can calculate wetting angle from photos (Fig. 1). Submitted data for each concentration and additional component was averaged over eight samples. Dependence of wetting angle on the additional organic component of the dispersion, GO concentration and drying time is shown in Fig. 2,a. Initial GO water suspension wetting angle is 41.6°. From the obtained data, one can

[©] Комаров И.А., Данилов Е.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

see that dispersion with LT as additional component has two shoulders with approximate linear dependence of wetting angle (under and above 0.05 mg/ml concentration). Drying time on the concentration dependence can be approximated with linear function. This result, on the one hand, means that we reached basic goal to reduce wetting angle. In case of LT as an additional component we clearly see the decrease of wetting angle by 2–8 times to the initial GO water suspension. The effect of the relatively strong dependence of wetting angle of dispersion with LT as additional component may be related to different surface charges of these particles and their Hamaker constants, which characterize the particle–water dispersion interaction same as observed in this article [12].



Fig. 1. Photos of GO dispersions droplets on PET substrate: 0.01 mg/ml in LT (*a*); 0.05 mg/ml in LT (*b*); 0.25 mg/ml in LT (*c*); 0.01 mg/ml in DMA (*d*); 0.05 mg/ml in DMA (*e*); 0.25 mg/ml in DMA (*f*)



Fig. 2. Dependence of wetting angle and drying time on the type of the additional component and GO concentration (*a*); dependence of main Raman bands ratios of deposited films on the GO concentration (*b*)

On the other hand, pronounced dependence of wetting angle may be used to efficiently control wetting properties. High volatility (low drying time) of LT-based dispersion is due to the basic purpose of the LT as a thinner for lacquer or enamel paints for airbrush applications. We can see that the use of the LT as a second component makes this dispersion perspective for spray coating of thin GO films.

Dispersion with DMA on the contrary did not show strong dependence of the wetting angle or time on the GO concentration. This mixture also showed decrease in wetting angle, but the decrease is much lower than in case of LT and only 1.18 - 1.38 times lower than initial wetting angle. We suppose this effect is due to the high evaporation time of both pure water and DMA. In fact the evaporation time of GO water suspension mixture with DMA is more than 1800 seconds is more than 20 times bigger than in case of LT addition.

Drying time in range of tenth of minutes means that DMA-containing dispersion will be better for spin-coating deposition due to the characteristic time of spin-coating process (few minutes). But spin-coating unit should have option of camera heating. In conclusion of this block we can claim that in general addition of organic components to the commercially available graphene oxide suspension leads to the reduction of the wetting angle and in case of lacquer thinner – to reduction of drying time.

We also study morphology (Fig. 3) and Raman spectra (insets to Fig. 3) of thin films formed from the multicomponent dispersion droplets. By analyzing morphology and Raman we can in some approximation predict future film properties in case of spin-coating or aerosol deposition.

As it was mentioned before, in case of deposition from LT with concentration 0,01 mg/ml we observed few separate multilayered graphene oxide flakes without any interconnections between it on the 200×150 μ m area. Same situation with film deposited from 0,01 mg/ml DMA dispersion. In case of deposition from 0.05 mg/ml multicomponent dispersions we observed formation of thin film with larger than 100 μ m lateral dimensions in case of LT as additional component and more than 50 μ m in case of DMA. In our prediction this concentration will be useful for large area formation by aerosol deposition. Such films may be useful for flexible display formation or photonics applications. In case of largest concentration – 0.25 mg/ml we observed formation of large area films with more than 0.5 mm lateral dimensions in both LT and DMA cases. This



Fig. 3. SEM images of GO dispersions droplets on PET substrate (attributed Raman spectra are on inserts): 0.01 mg/ml in LT (*a*);
0.05 mg/ml in LT (*b*); 0.25 mg/ml in LT (*c*); 0.01 mg/ml in DMA (*d*);
0.05 mg/ml in DMA (*e*); 0.25 mg/ml in DMA (*f*)
concentration may be used for thicker film formation by aerosol deposition and by spin-coating for such applications as flexible electronics and sensors.

As it can be observed from Raman data general view of spectra matches well with known spectra of GO [13]. On the all samples we observed three main peaks: G (~1580 cm⁻¹) that represents the in-plane stretching vibrations of the sp2 bonded carbon atoms, D (~1350 cm⁻¹) is the peak which highlights defects in the sample, so the more intensive this band is, the higher the level of disorder within the sample and 2D (~2950 cm⁻¹) that indicates the number of layers present in the sample. The 2D-band originates from a double resonance enhanced two-phonon lateral vibrational process.

On spectra obtained from 0.01 mg/ml and 0.05 mg/ml concentrations we can see presence of Raman peaks at 860 cm⁻¹, 1097 cm⁻¹, 1728 cm⁻¹, 3083 cm⁻¹ that can be attributed to PET with good congruence to the literature [14]. Thus in case of low concentrations film thickness is relatively low (few nanometers) due to the presence of PET peaks.

Analysis of morphology images and intensity of main Raman bands of GO (I_D is the intensity of D band, I_G is the intensity of G band and I_{2D} is the intensity of 2D band) shows that concentration of GO under the 0.05 mg/ml leads to the island-type film formation. Difference is that in case of LT we observe islands as mixture of many small flakes, whereas in case of DMA islands are relatively large individual multilayered GO flakes. Over the 0,05 mg/ml concentration films are uniform. Raman spectra and band ratio are classic for thin GO films [15].

Stability of the multicomponent dispersions was investigated by visual observations. Stability criteria was presence of macrosized agglomerates. In case of LT agglomerates were observed after two months of holding in test tube rack. On the contrary, dispersions with DMA showed absence of agglomerates within more than 6 months even in case of 0.25 mg/ml concentration.

Conclusion

In this work, we showed the possibility to decrease and control wetting angle on GO suspension/PET interface by adding organic components to the commercially available GO water-based suspension. We found out that addition of the thinner for lacquer and enamel paints leads to the formation of highly volatile dispersion that can form relatively large area (up to 0.5 mm) thin film that will be perspective for deposition by spray coating due to the fast drying time. According to formation or relatively thin film, thinner for lacquer or enamel paint may by useful for flexible displays and photonics applications. In case of DMA as the second component drying time is about 20 times larger that may be useful for spin-coating deposition but in case of additional heating. DMA as additional component may be used in flexible electronics applications and sensors. Also multicomponent dispersions have good time stability from few weeks to few months that is important for mass production applications.

REFERENCES

1. Gilshteyn E.P., Romanov S.A., Kopylova D.S., Savostyanov G.V., Anisimov A.S., Glukhova O.E., Nasibulin A.G., Mechanically Tunable Single-Walled Carbon Nanotube Films as a Universal Material for Transparent and Stretchable Electronics. ACS Appl. Mater. Interfaces. 11 (2019) 27327–27334.

2. Freddi S., Emelianov A.V., Bobrinetskiy I.I., Drera G, Pagliara S., Kopylova D.S., Chiesa M., Santini G., Mores N., Moscato U., Nasibulin A.G., Montuschi P., Sangaletti L., Development of a Sensing Array for Human Breath Analysis Based on SWCNT Layers Functionalized with Semiconductor Organic Molecules. Advanced Healthcare Materials. 9 (2020) 2000377.

3. Liu Y., Zhu Y., Cui Y., Challenges and Opportunities Towards Fast- Charging Battery Materials. Nat. Energy. 4 (2019) 540–550.

4. Oliveira A.M.L., Machado M., Silva G.A., Bitoque D.B., Ferreira J.T., Pinto L.A., Ferreira Q., Graphene Oxide Thin Films with Drug Delivery Function. Nanomaterials. 12 (2022) 1149.

5. Holm A., Wrasman C.J., Kao K.-C., Riscoe A.R., Cargnello M., Frank C.W., Langmuir-Blodgett Deposition of Graphene Oxide — Identifying Marangoni Flow as a Process that Fundamentally Limits Deposition Control. Langmuir. 34(33) (2018) 9683–9691.

6. Gelamo R.V., Lima A.B., Machuno L.G.B., Moraes L.C., Furlan R.H., Oliveira A.R., Multilayer Graphene Films Obtained by Dip Coating Technique. Materials Research. 18(4) (2015) 775–780.

7. Nguyen A.N., Solard J., Nong H.T.T., Osman C.B., Gomez A., Bockelée V., Tencé-Girault S., Schoenstein F., Simyn-Sorbed M., Carrillo A.E., Mercone S., Spin Coating and Micro-Patterning Optimization of Composite Thin Films Based on PVDF. Materials. 13 (2020) 1342.

8. Struchkov N.S., Alexandrov E.V., Romashkin A.V., Silakov G.O., Rabchinskii M.K., Uniform graphene oxide films fabrication via spray-coating for sensing application. Fullerenes Nanotubes and Carbon Nanostructures. 28 (2020) 214–220.

9. Wells R.A., Johnson H., Charles R.L., Sachin K., Kevin S., Roll-to-Roll Deposition of Semiconducting 2D Nanoflake Films of Transition Metal Dichalcogenides for Optoelectronic Applications. ACS Appl. Nano Mater. 2 (2019) 7705–7712.

10. Konios D., Stylianakis M.M., Stratakis E., Kymakis E., Dispersion behaviour of graphene oxide and reduced graphene oxide. Journal of Colloid and Interface Science. 430 (2014) 108–112.

11. Komarov I.A., Rubtsova E.N., Lapashina A.S., Golovin A.V., Bobrinetskiy I.I., Chemiresistive Sensors for Thrombin Assay Based on Nanosize Carbon Nanotube Films on Flexible Supports. Biomedical Engineering. 51 (2018) 377–380.

12. Molchanov S.P., Roldughin V., Chernova-Kharaeva I.A., Initial Contact Angles of Dispersion Droplets and Structure of Ring-Shaped Deposits Resulting from Capillary Self-Assembling of Particles. Colloid Journal. 77(6) (2015) 761–769.

13. Wu J-B., Lin M-L., Cong X., Liu H-N., Tan P-H., Raman spectroscopy of graphene-based materials and its applications in related devices. Chem. Soc. Rev. 47 (2018) 1822.

14. Johra F.T., Lee J-W, Jung W.-G., Facile and safe graphene preparation on solution based platform. Journal of Industrial and Engineering Chemistry. 20 (2014) 2883–2887.

15. Zhu C., Tong N, Song L., Zhang G., Investigation of Raman spectra of polyethylene terephthalate. Proceedings of the SPIE. 9656 (2015) 96560E.

THE AUTHORS

KOMAROV Ivan A. master_kom@mail.ru ORCID: 0000-0002-6397-6671 DANILOV Egor A. danilovegor1@gmail.com ORCID: 0000-0002-1986-3936

Received 15.06.2023. Approved after reviewing 07.09.2023. Accepted 08.09.2023.

Conference materials UDC 54.057 DOI: https://doi.org/10.18721/JPM.163.231

A facile low-temperature approach for organics removal from SiO,-CTAB mesoporous particles

E.Yu. Stovpiaga¹[⊠], S.A. Grudinkin¹, D.A. Eurov¹, D.A. Kurdyukov¹

¹ Ioffe Institute, St. Petersburg, Russia

⊠ kattrof@gvg.ioffe.ru

Abstract. A simple, fast and efficient method has been developed for removing pore-forming organic substances from MCM-41 type materials without affecting their shape, structural and adsorption characteristics. The method is based on express annealing of the synthesized silica materials in vacuum at low temperatures. It was shown that the synthesized particles do not sinter during annealing in vacuum and are monodisperse and aggregatively stable.

Keywords: Mesoporous silica, template method, organics removal, CTAB, vacuum annealing

Funding: This work was funded by the Russian Science Foundation, project 22-23-20104 and by the St. Petersburg Science Foundation, agreement 27/2022 (14.04.2022), https://rscf. ru/project/22-23-20104/.

Citation: Stovpiaga E.Yu., Grudinkin S.A., Eurov D.A., Kurdyukov D.A., A facile low-temperature approach for organics removal from SiO₂-CTAB mesoporous particles, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 183–187. DOI: https://doi.org/10.18721/JPM.163.231

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 54.057 DOI: https://doi.org/10.18721/JPM.163.231

Низкотемпературный метод удаления органических веществ из мезопористых частиц SiO,-ЦТАБ

Е.Ю. Стовпяга¹[™], С.А. Грудинкин¹, Д.А. Еуров¹, Д.А. Курдюков¹

1 Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия

⊠ kattrof@gvg.ioffe.ru

Аннотация. Разработан простой, быстрый и эффективный способ удаления порообразующих органических веществ из материалов типа MCM-41 без изменения их формы, структурных и адсорбционных характеристик. Метод основан на экспрессотжиге синтезированных кремнеземных материалов в вакууме при низких температурах. Показано, что синтезированные частицы не спекаются в процессе отжига в вакууме, остаются монодисперсными и агрегативно устойчивыми.

Ключевые слова: мезопористый кремнезем, темплатный метод, удаление органики, ЦТАБ, отжиг в вакууме

Финансирование: Исследование выполнено за счет гранта Российского научного фонда №22-23-20104 и гранта Санкт-Петербургского научного фонда в соответствии с соглашением от 14.04.2022 г. № 27/2022, https://rscf.ru/project/22-23-20104/.

© Stovpiaga E. Yu., Grudinkin S.A., Eurov D.A., Kurdyukov D.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Стовпяга Е.Ю., Грудинкин С.А., Еуров Д.А., Курдюков Д.А. Низкотемпературный метод удаления органических веществ из мезопористых частиц SiO₂-ЦТАБ // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 183–187. DOI: https://doi.org/10.18721/JPM.163.231

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

MCM-41 type porous silica materials are actively studied owing to the wide range of their possible applications as adsorbents, in catalysis and biomedicine [1, 2]. A template method is applied to obtain such materials with the use of micelles of alkylamines as a template. Control over the internal structure, particle and pore size is carried out by varying the synthesis conditions and the structure of surfactant template. The elimination of these organic templates from the pores is a crucial step in the synthesis of mesoporous silica materials. Thermal calcination is a common method for template removal in the laboratory due to high efficiency, easy operation, and requirement of simple equipment. However, the significant reduction of silanol concentrations happens during calcination (which renders the sample unsuitable for post-modification), besides, the structural shrinkage is invariably detected following template removal. In addition to the removal of organics by calcination, various post synthetic methods are also used to wash particles from surfactant in organic solvents under the action of ultrasound or microwaves [3, 4]. As a rule, all of the above template removal methods include several successive stages, for example, washing, centrifugation, drying, etc., which significantly increases the time required to obtain the final product [3-5]. Thus, the development of a procedure for a fast, efficient, low-temperature and one-stage removal of the template from the pores of MCM-41 type particles is still a crucial task.

Materials and Methods

Materials. Cetyltrimethylammonium bromide (CTAB), $C_{16}H_{33}N(CH_3)_3Br$, 99+% (Acros); aqueous ammonia (NH₃), 24% wt., \geq 99.99%; ethanol (C_2H_5OH), 95% wt.; deionized water (H₂O) 10 M Ω ; tetraethoxysilane (TEOS), Si(OC₂H₅)₄, 99+% (Acros), hydrochloric acid (HCl), 37% wt., ACS reagent grade.

Methods. In the present study we used spherical mesoporous silica particles (MSP) with a diameter of 550 ± 25 nm. MSP were synthesized according to the method developed by us via hydrolysis of TEOS in a mixture of NH₃-H₂O-C₂H₅OH containing a pore-forming agent – CTAB [6]. The removal of organics from the pores of MSP-CTAB particles was carried out in three different ways and then the structural characteristics of the resulting particles were compared. The first way was a traditional calcination of MSP-CTAB at 550 °C in air for 6 h. In the second one organics were removed in two stages. The synthesized MSP-CTAB particles were first washed in an alcoholic solution of HCl (0.01 M) for 10 h. Then the washed particles were annealed at 400 °C in air for 5 h. The third way to remove pore-forming substance was fast (within 1 h) annealing of particles at 300 °C in dynamic vacuum under pressure of 0.1 Torr.

IR transmission spectra were measured using an IFS Bruker 113v Fourier spectrometer. Spectra were recorded in vacuum in the range of 450–4000 cm⁻¹ with the use of DTGS detector. Spectral resolution was 4 cm⁻¹. Spectra were obtained from the sample area of 1.25×1.25 mm. The nitrogen adsorption was performed using a Micromeritics 3FLEX at a temperature of 77 K. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was found using the nonlocal density functional theory (NLDFT). Transmission electron microscopic measurements were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm). The preparation of particles for TEM studies is described in Ref. [7]. Microscopic studies also were carried out using an NT-MDT SMENA atomic force microscope (AFM) in a tapping mode. Particle size distribution and the electrophoretic light scattering methods, respectively, at 25 °C with the use of a Zetasizer Nano analyzer. The particle size distribution and the electrokinetic potential were calculated using the built-in analyzer software.

© Стовпяга Е.Ю., Грудинкин С.А., Еуров Д.А., Курдюков Д.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Results and Discussion

Monodisperse spherical MSP are synthesized via basic hydrolysis of TEOS in a $NH_3-H_2O-C_2H_5OH-CTAB$ medium [6]. CTAB molecules are present mainly in the form of cylindrical micelles in the chosen reaction medium. Negatively charged products of TEOS hydrolysis interact with positively charged trimethylammonium groups, which are located on the surface of CTAB micelles. As a result, the micelles are covered with a layer of amorphous SiO₂ [6,8]. Furthermore, these silica-coated micelles form clusters ~10-15 nm in size in the reaction mixture due to van der Waals forces. As the number of clusters grows, the aggregative stability of the system decreases and, as a result, the clusters coagulate to form submicrometer spherical aggregates.

The organics removal from the pores of the synthesized particles was carried out by several methods (Fig. 1). In the first case organics are removed by a long-term (6 h) high-temperature (550 °C) annealing of particles in air (the thus obtained particles were designated as MSP-a). During annealing an oxidation of CTAB molecules occurs followed by the formation of CO, CO_2 , and NO_x oxides, which are subsequently removed from the pores by surface diffusion. When calcination can affect the composition and/or structure of the material low-temperature methods are required to remove pore-forming substances. For example, multiple (2 to 5 times) washing of MSP from CTAB in an alcoholic HCl solution is applied. Then, the resulting particles are annealed at 400 °C in air for 5 h (MSP-w) to remove water and CTAB molecules remaining after washing. In order to further reduce the annealing temperature and the number of stages required to remove organic pore-forming substances from MSP we propose a new low-temperature method for CTAB removing, which is annealing of particles at 300 °C in vacuum for 1 h (MSP-vac).



Fig. 1. Schematic representation of different approaches for CTAB removal from MSP





Fig. 2,*a* shows the size distributions measured by the DLS method for all synthesized particles. The average diameter of all obtained particles is the same and found to be 555 nm, the standard size deviation does not exceed 5%. The zeta potential value of MSP-vac was found to be -34 mV at pH = 5.5, which is close to the values obtained for MSP-a (-35 mV) and MSP-w (-38 mV). The results obtained indicate that all the particles are aggregatively stable in aqueous suspensions regardless the method of CTAB removal. AFM image of a monolayer of MSP-vac (Fig. 2,*b*) shows that they form a hexagonal close packing similar to opal-like structure [6], which additionally confirms that the particles are monodisperse and not coalesced. The average particle diameter determined by AFM was found to be 545 ± 25 nm, which is consistent with the DLS data (Fig. 2,*a*). There are 3-nm pores visible on the TEM image of the particles (Fig. 2,*c*), besides, a roughness of ~10 nm can be seen on the surface of the particles, which is comparable to the size of the clusters forming the particles [6]. Apparently, during vacuum annealing CTAB is removed both from the pores and from the outer surface of the particles, otherwise the presence of organics decomposition products on the particle surface would lead to a decrease in roughness. Thus, according to the results of DLS, AFM and TEM (Fig. 2), the synthesized MSP-vac particles do not sinter during annealing in vacuum and are monodisperse and aggregatively stable.

Fig. 3, a shows the results of the FTIR study of silica particles right after the synthesis and after removal of CTAB by various methods. The spectral bands were identified based on the given in Ref. [9]. The band at 1630 cm⁻¹ present in the spectra of all MSPs corresponds to bending vibrations of H–O–H. The transmission spectra of the particles also contain a broad band at 3450 cm^{-1} (Fig. 3, a, curves 2-5), to which OH stretching vibrations in hydrogen-bound molecules of physically adsorbed water mainly contribute. There is a weak broad band in the region $3650-3700 \text{ cm}^{-1}$ and the narrow band at 3745 cm⁻¹, which correspond to vibrations of terminal and single silanol groups, respectively. Thus, all types of particles contain surface hydroxyl groups, which allows for further functionalization. The absorption bands corresponding to the vibrations of carbon-containing organic groups are almost absent in the spectra of MSP-w (Fig. 3, a, curve 3) and MSP-a (Fig. 3,*a*, curve 5). At the same time, a set of weak absorption bands in the regions 1300-1500 cm⁻¹ and 2750-3025 cm⁻¹ is observed in the spectrum of MSP-vac (Fig. 3, a, curve 4). These bands are more pronounced in the spectra of CTAB and as-synthesized MSP-CTAB (Fig. 3, a, curves 1, 2) and attributed to the different vibrational modes of CH, CH, CH, and N-CH, groups characteristic of CTAB. The band in the range 1540-1570 cm⁻¹ (Fig.3, *a*, curves 2, 4) results from simultaneous N-H and C-N vibrations. The N-H vibrations are caused by the CTAB decomposition products containing amino groups present in the sample. The presence of these groups causes a slight decrease in the porosity of MSP-vac particles compared to MSP-w and MSP-a (Fig. 3,b).



Fig. 3. FTIR spectra: (1) bulk CTAB, (2) MSP-CTAB as-synthesized, (3) MSP-w, (4) MSP-vac, (5) MSP-a (a). N_2 adsorption and desorption isotherms at 77 K and NLDFT pore size distribution (inset) for synthesized particles: MSP-w (1), MSP-a (2), MSP-vac (3) (b)

The nitrogen adsorption and desorption isotherms of the MSP after removing of CTAB by different methods are shown in Fig. 3,*b*. For all the samples the adsorption isotherms have a step-like shape, which is typical of mesoporous materials [10]. The BET specific surface area and pore volume values were found to be: 838 m²g⁻¹, 0.64 cm³g⁻¹ for MSP-w; 822 m²g⁻¹, 0.54 cm³g⁻¹ for MSP-a; 770 m²g⁻¹, 0.52 cm³g⁻¹ for MSP-vac. Pore size distribution calculated by NLDFT for all the samples has a well pronounced peak at 3.1 nm (Fig. 3,*b*, inset). It can be seen that the porosity characteristics of all types of particles are comparable.

Conclusion

A method of low temperature vacuum annealing is developed for CTAB removal from as-synthesized MCM-41-like mesoporous silica particles, which does not affect their size and porous structure. The measured value of the zeta potential of the particles annealed in vacuum was found to be -34 mV, which determines their aggregative stability in an aqueous suspension. The obtained values of specific surface area and pore volume were found to be ~800 m²g⁻¹ and ~0.5 cm³g⁻¹, respectively, which is comparable with the values for MCM-41 type materials obtained by traditional annealing in air. The proposed approach for the pore-forming template removal from MCM-41-like materials in vacuum is fast, facile and alternative to the thermal calcination and chemical treatment methods.

Acknowledgments

The authors thank D.A. Kirilenko for TEM measurements.

REFERENCES

1. Chircov C., Spoială A., Păun C., Crăciun L, Ficai D., Ficai A., Andronescu E., Turcule S.C., Mesoporous silica platforms with potential applications in release and adsorption of active agents. Molecules 25 (2020) 3814.

2. Tang F., Linlin L., Chen D., Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery. Adv. Mater. 24 (12) (2012) 1504–1534.

3. Ghaedi H., Zhao M., Review on template removal techniques for synthesis of mesoporous silica materials. Energy Fuels 36 (2022) 2424–2446.

4. Tian B., Liu X., Yu C., Gao F., Luo Q., Xie S., Tu B., Zhao D., Microwave assisted template removal of siliceous porous materials. Chem. Commun. 11 (2002) 1186–1187.

5. Zanjanchi M., Jabariyan S., Application of ultrasound and methanol for the rapid removal of surfactant from MCM-41 molecular sieve. J. Serb. Chem. Soc. 79 (2014) 25–38.

6. Trofimova E.Yu., Kurdyukov D.A., Yakovlev S.A., Kirilenko D.A., Kukushkina Yu.A., Nashchekin A.V., Sitnikova A.A., Yagovkina M.A., Golubev V.G., Monodisperse spherical mesoporous silica particles: fast synthesis procedure and fabrication of photonic crystal films. Nanotechnology 24 (2013) 155601.

7. Eurov D. A., Volkova E. A., Kirilenko D. A., Kurdyukov D. A., Stovpiaga E. Yu., TEM contrast enhancement by adsorption of erbium ions on the inner surface of micro-mesoporous silica particles. St. Petersburg State Polytechnical University Journal. Physics and Mathematics, 15 (3.3) (2022) 239–243.

8. Eurov D.A., Kurdyukov D.A., Medvedev A.V., Kirilenko D.A., Tomkovich M.V., Golubev V.G., Micro-mesoporous submicron silica particles with pore size tunable in a wide range: synthesis, properties and prospects for LED manufacturing. Nanotechnology 32 (2021) 215604.

9. Lin-Vien D., Colthup N.B., Fateley W.G., Grasselli J.G., The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules. Academic Press, San Diego, California 503 p., (1991).

10. Gregg S. J., Sing. K.S.W., Adsorption, Surface Area and Porosity. 2nd Ed. Academic Press, London, (1982).

THE AUTHORS

STOVPIAGA EKATERINA YU. kattrof@gvg.ioffe.ru ORCID: 0000-0003-0434-5252

GRUDINKIN SERGEY A. grudink@gvg.ioffe.ru ORCID: 0000-0003-1344-9483 EUROV DANIIL A. eurov@gvg.ioffe.ru ORCID: 000-0002-7471-4028

KURDYUKOV DMITRY A. kurd@gvg.ioffe.ru ORCID: 0000-0002-3041-9609

Received 07.07.2023. Approved after reviewing 24.07.2023. Accepted 25.07.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 54.057 DOI: https://doi.org/10.18721/JPM.163.232

Hard-template synthesis of monodisperse spherical microporous SiO, particles

D.A. Eurov¹^{III}, D.A. Kirilenko¹, E.Yu. Stovpiaga¹, D.A. Kurdyukov¹

¹ Ioffe Institute, St. Petersburg, Russia

⊠edan@mail.ru

Abstract. A simple and facile method for the synthesis of monodisperse microporous spherical silica particles is proposed. The method is based on a traditional Stöber technique with the use of ammonium metavanadate acting as a hard template for the micropore formation. The thus obtained silica particles possess an interconnected system of micropores that determines high values of their specific surface area (up to 320 m² g⁻¹) and pore volume (up to 0.25 cm³ g⁻¹). The use of the Stöber method allows obtaining highly monodisperse spherical particles with the standard size deviation not exceeding 5%. The particles with an average diameter of 250 nm exhibit high sedimentation and aggregation stability and form stable hydrosol, which is important from the practical point of view.

Keywords: Porous silica, monodispersity, template method, ammonium metavanadate, microporosity

Funding: This work was funded by the Russian Science Foundation, project 23-79-00018.

Citation: Eurov D.A., Kirilenko D.A., Stovpiaga E.Yu., Kurdyukov D.A., Hard-template synthesis of monodisperse spherical microporous SiO₂ particles, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 188–193. DOI: https://doi.org/10.18721/JPM.163.232

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 54.057 DOI: https://doi.org/10.18721/JPM.163.232

Темплатный метод синтеза монодисперсных сферических микропористых частиц SiO,

Д.А. Еуров¹⊠, Д.А. Кириленко¹, Е.Ю. Стовпяга¹, Д.А. Курдюков¹

¹ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия

⊠edan@mail.ru

Аннотация. Предложен простой и технологичный метод синтеза монодисперсных микропористых сферических частиц аморфного кремнезема. Метод основан на традиционной методике Штобера с применением метаванадата аммония в качестве темплата, используемого для формирования микропор. Показано, что полученные частицы содержат внутреннюю систему взаимосвязанных микропор, что обуславливает их большую удельную поверхность (320 м² г⁻¹) и объем пор (0.25 см³ г⁻¹). Использование метода Штобера позволяет получать монодисперсные сферические частицы со среднеквадратичным отклонением размеров, не превышающим 5%. Частицы со средним размером 250 нм обладают седиментационной и агрегативной устойчивостью и образуют стабильную водную суспензию, что важно с практической точки зрения.

© Eurov D.A., Kirilenko D.A., Stovpiaga E.Yu., Kurdyukov D.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: пористый кремнезем, монодисперсность, темплатный метод, метаванадат аммония, микропористость

Финансирование: Работа выполнена за счет гранта Российского научного фонда № 23-79-00018.

Ссылка при цитировании: Еуров Д.А., Кириленко Д.А., Стовпяга Е.Ю., Курдюков Д.А., Темплатный метод синтеза монодисперсных сферических микропористых частиц SiO₂ // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 188–193. DOI: https://doi.org/10.18721/JPM.163.232

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In today's world high-capacity inflammable and ecologically safe microporous materials are in high demand across various industries [1]. Materials of this kind are used, for example, in selective adsorption [2], catalysis [3], and as molecular sieves [4]. Zeolites and AlPO₄ are widely used microporous materials possessing a specific surface area (SSA) of up to 600 $m^2 g^{-1}$ and pore volume (V_{a}) of up to 0.4 cm³g⁻¹ [5]. Amorphous silica $(a-SiO_{2})$ has a number of advantages such as fast and facile synthesis, high thermal and chemical stability [6], low toxicity [7], which makes it promising as an alternative for creating microporous materials. The main way to synthesize silica particles (SP) is the Stöber method [8], which is based on a hydrolysis of tetraethyl orthosilicate (TEOS) in an NH₂-H₂O-C₂H₅OH medium and allows obtaining highly monodisperse (with standard size deviation less than 3%) spherical particles of a-SiO₂. However, the thus obtained particles are nonporous. There are two approaches to forming micropores within the silica particles: post-synthetic treatment of nonporous SPs or modification of the Stöber process by changing the composition of the reaction mixture. For example, the authors of [9] showed that a treatment of nonporous SPs in alcoholic solutions yields microporous silica particles with micropore V of up to 0.16 cm³g⁻¹ and SSA of up to 380 m²g⁻¹. It was shown in [10] that the replacement of 80% of TEOS with aminopropyltriethoxysilane containing an unhydrolyzable pore-forming aminopropyl group yields microporous silica particles with SSA ~130 m²g⁻¹ and V_p ~0.1 cm³g⁻¹. Addition of [3-(methacryloyloxy)propyl] trimethoxysilane with an unhydrolyzable methacryloyloxypropyl (MP) group to the reaction mixture made it possible to obtain particles with SSA of up to 950 m^2g^{-1} and V_p of up to 0.8 cm³g⁻¹ [11,12]. Micropores within the particles obtained are frequently isolated from each other, which makes it difficult to obtain large values of specific surface area and pore volume. Molecules of adsorbate (e.g., N₂) cannot penetrate inside the pores and they are not included into the useful volume of the particles. Thus, the development of a method for obtaining microporous silica particles with interconnected pore structure is an urgent technological problem. In the present study, an approach is implemented to synthesizing monodisperse spherical microporous silica particles by Stöber process with the use of ammonium metavanadate as a porogen for the first time.

Materials and Methods

Materials. Vanadium (V) oxide, V_2O_5 , 99.95% (Sigma-Aldrich, Germany); tetraethyl orthosilicate, Si(OC₂H₅)₄, 99% (Acros Organics, Germany); aqueous ammonia, NH₃, 24 wt%, 99.99%; ethanol, C₂H₅OH, 95 wt%; deionized (DI) water, H₂O with a resistance of 10 M Ω . All the chemicals were of analytical purity grade commercially available. There was no need to additionally purify the reagents.

Methods. The procedure used for synthesis of microporous silica particles with the use of ammonium vanadate as a hard template is similar to that employed for synthesis of submicron monodisperse silica particles (Stöber-Fink-Bohn method [8]). A weighed portion of TEOS (2 g) was added to a concentrated solution (0.5 L) of ammonium metavanadate in a mixture $C_2H_5OH-NH_3-H_2O$ under stirring at room temperature. After 5 h of further stirring, the particles obtained were centrifuged, washed with DI water, and dried under the ambient conditions at 100 °C for 2 h.

© Еуров Д.А., Кириленко Д.А., Стовпяга Е.Ю., Курдюков Д.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Transmission electron microscopic measurements were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm) equipped with Bruker XFlash 6T-30 energy dispersive X-ray (EDX) spectrometer. The nitrogen adsorption was performed using a Micromeritics 3FLEX at a temperature of 77 K. The specific surface area was calculated by the Brunauer – Emmett – Teller (BET) method, and the pore size distribution was found using the nonlocal density functional theory (NLDFT). The hydrodynamic diameter of the particles was determined at 25 °C by dynamic light scattering (DLS) using a Zetasizer Nano ZS analyzer.

Results and Discussion

The silica particles were synthesized by hydrolysis of TEOS in a concentrated solution of ammonium metavanadate in a $H_2O-C_2H_5OH-NH_3$ mixture traditionally used in Stöber process [8]. To obtain a solution of NH_4VO_3 a weighed portion of commercially available V_2O_5 powder was dissolved in a $H_2O-C_2H_5OH-NH_3$ mixture heated to 60°C under ultrasonic agitation, which leaded to the formation of saturated aqueous-alcoholic solution of ammonium metavanadate. After that TEOS was added to the obtained solution, as a result of hydrolysis of which spherical particles of amorphous silica were formed.

The synthesis conditions similar to those in the Stöber process (namely reaction mixture composition, temperature and time) allowed obtaining highly monodisperse spherical silica particles. Fig. 1 shows typical TEM images of the particles obtained. It can be seen (Fig. 1,*a*) that the particles have spherical shape and the same size. The large object in the bottom left corner is, most likely, comprised of several particles lying on top of each other. An average diameter of the particles was found to be 250 nm with the size deviation less than 5%. On the enlarged image of a single particle (Fig. 1,*b*) one can clearly see that the synthesized silica particles possess a spongy structure, which indicates the presence of pores. This is confirmed by the results of nitrogen porosimetry.



Fig. 1. TEM images of silica particles synthesized using NH_4VO_3 as a hard template

Fig. 2,*a* shows N₂ adsorption-desorption isotherms for the particles obtained. It can be seen that the isotherm has a shape characteristic of microporous materials. The specific surface area of the particles calculated in the pressure range $0.05 \le p/p_0 \le 0.20$ by the BET method was found to be 320 m² g⁻¹. The pore volume was 0.25 cm³ g⁻¹. The pore size distribution (Fig. 2,*b*) demonstrates a well pronounced peak with a maximum at ~1 nm. Apparently, NH₄VO₃ present in the solution acts as a template for the formation of micropores. During SiO₂ formation the polycondensation of silicic acid monomers with non-hydrolyzed $\equiv V-O^-$ and hydrolyzed $\equiv V-OH$ groups present in solution, presumably, can take place. In an alkaline medium condensation can proceed as follows:



Fig. 2. N_2 adsorption and desorption isotherms at 77 K (*a*) and pore size distribution (*b*) for silica particles synthesized using NH_4VO_3 as a hard template

$$\begin{split} & \equiv V - O^- + H_4 SiO_4 \leftrightarrow \equiv V - O - Si(OH)_3 + OH^- \\ & \equiv V - OH + H_3 SiO_4^- \leftrightarrow \equiv V - O - Si(OH)_3 + OH^- \\ & \equiv V - OH + H_4 SiO_4 \leftrightarrow \equiv V - O - Si(OH)_3 + H_2O \end{split}$$

Similar interaction with the formation of V-O-Si bonds was observed for various silica-supported vanadium complexes [13].

Next, the silica produced as a result of TEOS hydrolysis can adsorb ions from a saturated ammonium metavanadate solution with the formation of associates of hydrated amorphous SiO_2 with VO_3^- and NH_4^+ . Due to the high concentration of NH_4VO_3 in the reaction mixture the silica contains, apparently, not individual ions but associated complexes of several vanadium-containing species. After the synthesis the obtained particles are washed with water, as a result of which the dissolution of the complexes occurs with the formation of voids in their place – micropores. The results of the elemental EDX analysis confirm the complete removal of the vanadium from the particles at the washing stage. Moreover, the obtained values of specific surface area and pore volume of the particles synthesized allow concluding that they contain not isolated micropores, but their interconnected system.



Fig. 3. DLS size distribution for the obtained silica particles

Fig. 3 shows the results of the DLS measurements. An average diameter of the particles was found to be 265 nm, while the PDI value was as low as 0.07. Note, that the value of the particle diameter measured from DLS data correlates with that obtained from TEM measurements. According to DLS the standard size deviation of the fabricated particles does not exceed 5%, which together with the results of TEM and nitrogen porosimetry measurements confirms that the applied approach allows obtaining highly monodisperse spherical silica particles with an interconnected system of micropores.

It is worth noting that the synthesized particles exhibit high sedimentation and aggregative stability, which provides the formation of a stable hydrosol. These advantages together with high monodispersity of the particles make them promising materials for use, for example, as sorbents, which will have identical properties such as adsorption capacity, selectivity, kinetics of adsorption/desorption and hydrodynamic properties.

Conclusion

An approach was proposed for the synthesis of SiO₂ particles by Stöber method with the use of ammonium metavanadate as hard template, which made it possible to obtain highly monodisperse spherical silica particles possessing microporous structure. The standard deviation of the particle diameter does not exceed 5%. Micropores within the particles form an interconnected system resulting in high values of SSA (~320 m² g⁻¹) and V_p (~0.25 cm³ g⁻¹) of the particles. The monodispersity and the high sedimentation and aggregative stability of the particles provide the formation of a stable hydrosol and allow obtaining materials with identical geometrical and hydrodynamic characteristics, which makes the obtained particles promising, for example, in adsorption or catalytic applications.

Acknowledgments

The TEM study was carried out on equipment of the Federal Joint Research Center "Material science and characterization in advanced technology".

REFERENCES

1. Doustkhah E., Ide Y., Microporous layered silicates: old but new microporous materials. New J. Chem. 44 (24) (2020) 9957–9968.

2. Uguina M., Serrano D., Van Grieken R., Venes S., Adsorption, acid and catalytic changes induced in ZSM-5 by coking with different hydrocarbons, Appl. Catal. A Gen. 99 (18) (1993) 97–113.

3. Khan W., Jia X., Wu Z., Choi J., Yip A. C. K., Incorporating hierarchy into conventional zeolites for catalytic biomass conversions: a review, Catalysts 9 (2) (2019) 127.

4. Marcilly C. R., Where and how shape selectivity of molecular sieves operates in refining and petrochemistry catalytic processes, Top. Catal. 13 (2000) 357–366.

5. Schüth F., Sing K., Weitkamp J. (Eds.), Handbook of Porous Solids, Wiley, Weinheim, 2002.

6. Schwanke A.J., Balzer R, Pergher S., Microporous and mesoporous materials from natural and inexpensive sources. Handbook of Ecomaterials, (2019) 3379–3399,

7. Dong X., Wu Z., Li X., Xiao L., Yang M., Li Y., Duan J., Sun Z., The size-dependent cytotoxicity of amorphous silica nanoparticles: a systematic review of in vitro studies, Int. J. Nanomedicine 15 (2020) 9089–9113.

8. Stöber W., Fink A., Bohn E., Controlled growth of monodisperse silica spheres in the micron size range, J. Colloid Interface Sci. 26 (1) (1968) 62–69.

9. Bazula P. A., Arnal P. M., Galeano C., Zibrowius B., Schmidt W., Schüth F., Highly microporous monodisperse silica spheres synthesized by the Stöber process, Microporous Mesoporous Mater. 200 (2014) 317–325.

10. Vacassy R., Flatt R. J., Hofmann H., Choi K. S., Singhy R. K., Synthesis of microporous silica spheres, J. Colloid Interface Sci. 227 (2000) 302–315.

11. Kurdyukov D. A., Eurov D. A., Kirilenko D. A., Sokolov V. V., Golubev V.G., Tailoring the size and microporosity of Stöber silica particles, Microporous Mesoporous Mater. 258 (2018) 205–210.

12. Stovpiaga E.Y., Eurov D.A., Kurdyukov D.A., Glebova N.V., Kirilenko D.A., Tomkovich M.V., Golubev V.G., Formation of spherical microporous silica particles from organosilane and quat molecules, Colloids Surf. 650 (2022) 129633.

13. Feher F. J., Walzer J. F., Synthesis and characterization of vanadium-containing silsesquioxanes, Inorg. Chem. 30 (1991) 1689–1694.

THE AUTHORS

EUROV Daniil A. edan@mail.ru ORCID: 000-0002-7471-4028

KIRILENKO Demid A. zumsisai@gmail.com ORCID: 0000-0002-1571-209X STOVPIAGA Ekaterina Yu. kattrof@gvg.ioffe.ru ORCID: 0000-0003-0434-5252

KURDYUKOV Dmitry A. kurd@gvg.ioffe.ru ORCID: 0000-0002-3041-9609

Received 07.07.2023. Approved after reviewing 19.07.2023. Accepted 27.07.2023.

Conference materials UDC 541.138:621.315 DOI: https://doi.org/10.18721/JPM.163.233

The method of formation of planar lithium-ion batteries with composite electrode materials

N.A. Litovchenko¹[⊠], I.K. Martynova¹, I.M. Gavrilin³, Y.O. Kudryashova³, R.M. Ryazanov², E A. Lebedev¹,²

¹ National Research University of Electronic Technology, Moscow, Zelenograd, Russia;

² Scientific-Manufacturing Complex Technological Centre, Moscow, Zelenograd, Russia;

³ A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Zelenograd, Russia

□ natlitovch@gmail.com

Abstract. A novel approach was developed to locally fabricate planar lithium-ion batteries using composite electrode materials. The method involved electrophoretic deposition to create a composite cathode material comprising NCA and Super C45, while the anode was formed through localized electrochemical deposition of germanium nanofibers. This technique successfully formed planar batteries with heterogeneous composite electrode polarization, and enhanced electrochemical performance. The integration of electrochemical and electrophoretic deposition methods allowed for precise control of layer composition and deposition parameters, optimizing the properties of planar batteries in terms of specific capacitance and electrical conductivity. The study also focused on laser engraving topology and optimized modes for planar battery structures, enabling the integration of multiple processes in a single manufacturing cycle. Capacitive characteristics were assessed using specialized polypropylene tooling, and the planar battery prototypes demonstrated comparable capacity (4 μ Ah) to existing commercial alternatives.

Keywords: planar lithium-ion battery, electrophoretic deposition, electrochemical deposition, cathode material, anode material

Funding: This work was supported by State Assignment № FSMR-2023-0003.

Citation: Litovchenko N.A., Martynova I.K., Gavrilin I.M., Kudryashova Y.O., Ryazanov R.M., Lebedev E.A., The process of forming a planar battery with composite electrode materials, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 194–199. DOI: https://doi.org/10.18721/JPM.163.233

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Litovchenko N.A., Martynova I.K., Gavrilin I.M., Kudryashova Y.O., Ryazanov R.M., Lebedev E.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 541.138:621.315 DOI: https://doi.org/10.18721/JPM.163.233

Метод формирования планарных литий-ионных аккумуляторов с композитными электродными материалами

Н.А. Литовченко¹⊠, И.К. Мартынова¹, И.М. Гаврилин³, Ю.О. Кудряшова³, РМ. Рязанов², Е.А. Лебедев¹,²

¹ Национальный исследовательский университет «Московский институт электронной техники», Москва, Зеленоград, Россия;

² Научно-производственный комплекс «Технологический центр», Москва, Зеленоград, Россия;

² Институт физической химии и электрохимии им. А.Н. Фрумкина РАН, Москва, Россия

□ natlitovch@gmail.com

Аннотация. В данной работе был исследован метод формирования планарных литийионных аккумуляторов с композитными электродными материалами. Для формирования композитного катодного материала на основе NCA (LiNi_xCo_yAl_zO₂) и Super C45 был использован процесс электрофоретического осаждения, а анод был сформирован путем локального электрохимического осаждения германия в виде нановолокон. Была продемонстрирована принципиальная возможность формирования и работоспособность планарных литий-ионных аккумуляторов с гетерогенными композитными электродными материалами, расположенными на одной плоскости.

Ключевые слова: планарный литий-ионный аккумулятор, электрофоретическое осаждение, электрохимическое осаждение, анодный материал, катодный материал

Финансирование: Работа выполнена в рамках государственного задания 2025-2023 гг. соглашение FSMR-2023-0003.

Ссылка при цитировании: Литовченко Н.А., Мартынова И.К., Гаврилин И.М., Кудряшова Ю.О., Рязанов Р.М., Лебедев Е.А. Метод формирования планарных литийионных аккумуляторов с композитными электродными материалами // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 194–199. DOI: https://doi.org/10.18721/JPM.163.233

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Microsized lithium-ion batteries (μ LIB) with a sandwich structure have been developed for wearable electronics and microsystem devices [1]. These batteries, composed of superimposed electrodes and electrolytes, are compact and lightweight. However, integrating them with other miniature devices can be challenging.

Transition metal oxide systems like NCA offer high energy density, stability, and durability, making them ideal for wearable microelectronics [2]. Planar batteries with an interdigitated design provide an attractive alternative [3]. This architecture offers increased electrode surface area, leading to improved electrochemical reactions and battery performance. It also ensures uniform voltage and current distribution, enhancing efficiency and cyclic stability. Furthermore, planar batteries with interdigitated topology exhibit high mechanical strength and stability, making them resistant to deformation and damage.

To achieve optimal implementation of planar batteries with an interdigitated topology, selecting the appropriate method for forming the cathode material is crucial. Electrophoretic deposition is a promising approach, offering simplicity, cost-effectiveness, and precise control over structure and composition [4]. It enables uniform and stable deposition of cathode material layers, ensuring homogeneity and effectiveness in battery operation.

© Литовченко Н.А., Мартынова И.К., Гаврилин И.М., Кудряшова Ю.О., Рязанов Р.М., Лебедев Е.А, 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

This study proposes a method for creating a planar μ LIB structure on a conductive substrate. It involves local electrophoretic deposition (EPD) of composite cathode materials (NCA and Super C45) on one current collector and local electrochemical deposition (ECD) of germanium nanofibers on the other. This approach allows for the fabrication of a planar battery in a single process cycle with a power consumer.

Overall, this research explores the optimization of deposition parameters, selection of suitable suspensions or solutions, and characterization of the electro-physical properties of planar battery samples.

Materials and Methods

The substrates for the planar batteries were sitall plates with a 250 nm Cr conductive layer. Using laser engraving on a CNC machine, the structures of planar batteries were formed, representing the structures of a counter-pin converter - two combs nested into each other.

An electrophoretic cell consisting of two electrodes connected to a power supply and immersed in a beaker with a suspension was used for local formation of composite cathode materials by the EPD method. The electric field strength was varied from 30 V/cm to 110 V/cm and the process duration was 2 minutes. The suspension used in this work contained 1.8 mg of NCA and 0.2 mg of the carbon conductive additive Super C45 per 1 ml of isopropyl alcohol and acetone-based solvent in a 1:1 ratio. To improve the electrophoretic mobility of the active material, nickel nitrate hexahydrate at a concentration of 0.1 per 1 ml of solvent was used.

Germanium nanofiber structure was formed on one current collector. Indium catalyst arrays were deposited on the substrate surface using electrochemical deposition. The indium deposition solution contained citric acid, indium chloride (InCl₃), and a wetting agent dissolved in deionized water. The deposition was performed at room temperature with a constant stirring and a current density of 1 mA/cm² for 5 minutes. The germanium nanofibers were deposited in an electrolyte solution containing germanium oxide (GeO₂), ammonium sulfate (NH₄)₂SO₄, and succinic acid. The solution pH was adjusted to 6.5 using NH₄OH. The deposition process was carried out at 85°C with a current density of 2 mA/cm² for 30 minutes, followed by an additional hour at 4 mA/cm².

To control the composition of the obtained samples, the method of energy dispersive X-ray spectroscopy was used. The morphology of the obtained layers was studied using a scanning electron microscope. The capacitive characteristics of the planar battery samples were studied on the basis of charge-discharge characteristics and cyclic sweeps.

To create a planar battery, a polypropylene tolling was designed to prevent damage to the electrode materials. The working electrodes were pre-dried under vacuum at 120°C for 8 hours to remove any traces of water. The electrolyte used was a mixture of 1M LiClO₄ in a propylene carbonate-dimethoxyethane (7:3) solution. The water content in the electrolyte, measured by Fischer coulometric titration, was no more than 15 ppm.

The assembly of the electrochemical cells was carried out in a sealed glove box with an argon atmosphere. The water and oxygen content in the box was approximately 1 ppm. Electrochemical investigations of the electrodes were conducted in a galvanostatic mode with a current of 0.5 μ A.

Results and Discussion

In this study, the influence of various additives on the stability and deposition rate of the composite cathode materials NCA and Super C45 was investigated. Specifically, dispersing and surfactant additives such as nickel nitrate hexahydrate and hydroxypropyl cellulose were used. Nickel nitrate hexahydrate served as a source of nickel ions, which adsorb onto the particle surfaces and change their zeta potential. Hydroxypropyl cellulose was used as a dispersant and for viscosity modification of the suspension.

Experiments showed that at a nickel concentration of 0.1 mg/mL, the deposition rate was $0.7 \text{ mg/cm}^2\text{min}$ (Fig. 1,*a*). At higher concentrations of nickel ions, charged particles can collide with each other, leading to electrostatic repulsion. Hydroxypropyl cellulose prevents particle agglomeration, thereby increasing the deposition rate at an optimal concentration of 0.03 mg/mL. However, increasing the cellulose concentration results in higher viscosity, which slows down particle movement.



Fig. 1. Dependency (*a*) of deposition rate on the concentration of nickel nitrate hexahydrate and hydroxypropyl cellulose in the suspension, and (*b*) of carbon conducting additive concentration in the active material on its quantity in the suspension

The concentration of carbon in the cathode material influences the electrochemical properties and electrical conductivity. The impact of Super C45 concentration on the graphite content in the composite cathode material was investigated (Fig. 1,b). It was shown that the carbon additive concentration in the active material is directly proportional to the Super C45 content in the suspension, enabling the regulation of the composition of the composite cathode material for specific needs.

In order to create planar accumulators in this study, both the anode and the cathode electrodes were formed in the same plane and in close proximity to each other on the surface of thin-film current collectors. It was necessary to ensure electrical isolation between the formed electrodes. For this purpose, a set of planar accumulator samples with deposited cathode and anode materials was prepared to study the localization of electrode deposition.

The correct sequence of electrode material deposition was experimentally determined for creating planar battery samples. Thus, localized electrochemical deposition of germanium nanofibers was performed first, followed by localized electrophoretic deposition of the composite cathode material. Since water-based solution is used in localized electrochemical deposition, the deposited layer of cathode material is separated from the substrate due to the capillary effect.

A distribution map of elements was constructed using energy-dispersive X-ray spectroscopy to determine the localization of deposition of different electrode materials (Fig. 2). The map reveals that carbon, nickel, cobalt, aluminum, and oxygen (components of NCA) are concentrated on one electrode, while germanium (anode component) is uniformly distributed on the other electrode. The absence of overlap between the two materials indicates the localized formation of electrode materials.



Fig. 2. Distribution map of elements in a planar battery



Fig. 3. Charge-discharge curves (*a*) and variation of discharge capacity of the NCA-Ge battery prototype (*b*)

The charge-discharge curves of the battery (Fig. 3,a) and the dependence of discharge capacity during cycling at a constant current density (Fig. 3,b) reflect the characteristics of the battery.

It can be observed that the average voltage during charging is approximately 3.8, while during discharging, it is around 1.3. The low voltage during discharging is not typical for the NCA-Ge electrochemical system and may be attributed to high internal resistance of the battery. The discharge capacity increases in the initial cycles and stabilizes around the 8th to 10th cycle. The increase in discharge capacity may be associated with the increase in the discharge capacity of germanium in the initial cycles [5].

Conclusion

This study developed a method for fabricating composite cathode materials for integrated batteries. The main focus was on optimizing the suspension composition and investigating the influence of dispersing and surfactant additives on the stability of the suspension and the electro-phoretic mobility of the active material.

The conducted experiments showed that the optimal suspension recipe includes a 1:1 ratio of acetone and isopropyl alcohol as the solvent. The addition of nickel nitrate hexahydrate at a concentration of 0.1 mg/mL of the solvent resulted in a deposition rate of the active material at a level of 0.7 mg/cm²·min. The addition of hydroxypropyl cellulose at a concentration of 0.03 mg/mL of the solvent increased the stability of the suspension by 25%. It was also confirmed that the concentration of carbon conductive additive is directly proportional to its content in the composite cathode material.

To form the structure of a planar battery, a methodology was developed, which includes creating a topological pattern using laser engraving on the conducting coating, local electrochemical deposition of germanium nanofibers, and local electrophoretic deposition of the composite cathode material.

The results of cyclic voltammetry measurements showed that the specific capacity of the planar lithium-ion accumulator is 4 μ Ah, which corresponds to the level of commercial analogs.

Acknowledgments

This work was supported by State Assignment FSMR-2023-0003.

REFERENCES

1. Li X., Xie P., Xiang W., Wei X., Huang Y., Shen G., Micro-sized lithium-ion battery with sandwich structure, Nano Energy, 60 (2019) 772-779.

2. Tu J., Zhao X.B., Cao G.S., Zhuang D.G., Zhu T.J., Enhanced cycling stability of $LiMn_2O_4$ by surface modification with melting impregnation method, Electrochimica Acta, 51 (2015) 6456–6462.

3. Li H., Liang J., Interfacial Engineering Toward Efficient and Stable Inverted Planar Perovskite Solar Cells, Journal of Power Sources, 81 (1999) 547–553.

4. Boccaccini A.R, Cho J., Roether J. A., Electrophoretic deposition of carbon nanotubes, Carbon N Y, 44 (2006) 3149–3160.

5. Lebedev E.A., Gavrilin I.M., Kudryashova Y.O., Martynova I.K., Volkov R.L., Kulova T.L., Skundin A.M., Borgardt N.I., Gavrilov S.A., Effect of Vinylene Carbonate Electrolyte Additive on the Process of Insertion/Extraction of Na into Ge Microrods Formed by Electrodeposition, Batteries, 9 (2022) 109.

THE AUTHORS

LITOVCHENKO Natalya A. natlitovch@yandex.ru ORCID: 0000-0001-7568-5655

MARTYNOVA Irina K. Irisha-windsurfer@yandex.ru ORCID: 0000-0002-6128-5244

GAVRILIN Ilya M. gavrilin.ilya@gmail.com ORCID: 0000-0002-0278-1598 KUDRYASHOVA Yulia O. yulia.kudryashova@mail.ru ORCID: 0000-0003-1359-0700

RYAZANOV Roman M. r.m.ryazanov@gmail.com ORCID: 0000-0002-2464-8712

LEBEDEV Egor A. dr.beefheart@gmail.com ORCID: 0000-0002-5085-5408

Received 30.06.2023. Approved after reviewing 01.09.2023. Accepted 04.09.2023.

Conference materials UDC 620.22 DOI: https://doi.org/10.18721/JPM.163.234

Charge relaxation after exposure to barrier and corona discharge of polylactide films

A.M. Kamalov¹[⊠], M.E. Borisova¹

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

⊠ kamalov_am@spbstu.ru

Abstract. In this work, it is shown that the effect of a corona discharge and a dielectric barrier discharge differs in depth of charge penetration and relaxation time. The relaxation time and the mechanism of charge relaxation in polylactide films were determined using thermally stimulated depolarization current (TSDC). Experimental data are analyzed based on modern ideas about the mechanism of charge relaxation. The activation energies are calculated based on a model that considers the intrinsic conductivity of the dielectric. By the method of computer modeling, the complex TSDC spectra are decomposed into separate elementary maxima, which are described by first-order kinetics, and the activation energies corresponding to them are determined.

Keywords: polylactide, relaxation, charge, plasma, film

Funding: Grant for young scientists the Ministry of Education and Science Russia MK-4346.2022.4.

Citation: Kamalov A.M., Borisova M.E., Charge relaxation after exposure to barrier and corona discharge of polylactide films, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 200–205. DOI: https://doi.org/10.18721/JPM.163.234

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 620.22 DOI: https://doi.org/10.18721/JPM.163.234

Релаксация заряда после воздействия барьерного и коронного разрядов на полилактидные пленки

А.М. Камалов¹⊠, М.Э. Борисова¹

¹Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

⊠ kamalov_am@spbstu.ru

Аннотация. В этой работе показано, что воздействие коронного разряда и разряда с диэлектрическим барьером различается по глубине проникновения заряда и времени релаксации. Экспериментальные данные проанализированы на основе современных представлений о механизме релаксации заряда.

Ключевые слова: полилактид, релаксация, заряд, плазма, пленка_

Финансирование: Работа выполнена в рамках гранта для молодых ученых при Министерстве науки и высшего образования РФ МК4346.2022.4-.

Ссылка при цитировании: Камалов А.М., Борисова М.Э. Релаксация заряда после воздействия барьерного и коронного разрядов на полилактидные пленки // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 200–205. DOI: https://doi.org/10.18721/JPM.163.234

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

© Kamalov A.M., Borisova M.E., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Introduction

Environmental, economic, and safety issues have initiated the work of scientists and manufacturers dealing with packaging problems to partially replace petrochemical-based polymers with biodegradable polymers.

It is known that under the influence of an electric field, the activity of microbial cells decreases, and consequently, metabolic processes slow down. In this regard several studies have been carried out, which confirmed that the polymer film, which has undergone preliminary electric charge, significantly increases the shelf life of various food products [1].

To modify polymer films, different forms of gas discharge are used: Townsend [2], barrier [3], sliding and corona. Corona discharge and barrier discharge at atmospheric pressure in the air are the most common methods of activation (charging) of dielectric materials [4].

Atmospheric pressure plasma can be created using an alternating electric field source from ultra-low to ultra-high frequencies. An increase in the frequency of discharge repetition leads to a more uniform modification of the polymer film surface.

The nature of the ions coming from the corona discharge at a constant electric field in the air to the surface of the dielectric is determined by the polarity of the corona electrode. The main ions to be considered in the reactive non-thermal plasma of dry air include cations O_2^{++} , N_2^{++} , O^{+} , N⁺, NO⁺ and anions O⁻⁻, O₂⁻⁻ O₃⁻⁻ [5]. The average kinetic energy of ions in the corona discharge coming to the surface of the film can reach values of 0.01-0.1eV [6]. When ions interact with the polymer surface, charging is carried out due to ion-electron emission (Auger neutralization).

Charges that are fixed in the near-surface region or in the volume of the dielectric are captured at energy levels (traps) located in the forbidden zone. In polymers, the existence of a set of many discrete capture levels with different 'depths' is assumed. Dielectric materials have either a purely amorphous or partially crystalline structure. The heterogeneity of the structure in these materials leads to an increase in many years.

The energy distribution of traps depends on the degree of ordering of the polymer structure, the lower the ordering, the more capture levels with high activation energy are formed.

The appearance of traps in the volume is due to the presence of defects and impurities in the polymer. Defects can be associated with the irregularity of the chain, the appearance of the boundaries of the amorphous and crystalline phase.

The accumulation of charge at the interface of phases with different values of conductivity and permittivity may be due to the Maxwell-Wagner-Sillars polarization. These boundaries can appear at the junction of the near-surface layer and the volume of the polymer, as well as between amorphous and crystalline phases.

The purpose of this work is to study the relaxation of the charge accumulated under the action of corona and barrier discharges in polylactide films. Determine the effective depth of the charge accumulated under the action of various discharges.

Materials and Methods

The objects of this study are samples of polylactide films, which thickness was $25\pm5 \,\mu\text{m}$.

A dielectric barrier discharge (DBD) was created in an ionization cell, which consists of ceramic plates with electrodes divided by an air gap (1 mm thick). The method of DBD film surface treatment was shown in the previous work [7]. The PLA film was charged in DBD for 2 minutes at a voltage of 3 kV with a frequency of 25 kHz.

Corona discharge method allows to produce electrets with homocharge. The sample is placed on a ground electrode, the other electrode is a needle with a negative potential. A metal grid is placed between the needle and the sample. Biased by a negative potential supply, the grid limits the maximum voltage on the sample. The charging process ends with the potentials of the grid and the surface of the sample becoming equal [8]. The PLA film was charged in a corona discharge for 1 minute, there was a voltage of -6 kV on the corona electrode and -400V on the grid. The charging level is regulated by the grid potential.

To determine the electret potential difference, a compensation method with a vibrating electrode was used. The electret potential difference for the PLA film charged in DBD was -200V, and for the film charged in corona discharge -400V.

Charge relaxation processes were studied by the method of thermally stimulated depolarization current (TSDC) under heating of samples at a constant rate of 2 K/min. The TSDC was measured

© Камалов А.М., Борисова М.Э., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. 201 in an open circuit, as provided by an insulating layer of PTFE film 40 μ m thick arranged between the charged film and the electrode.

Results and Discussion

When charging in a gas discharge, a homocharge will accumulate in the glassy state of the polylactide. The effect of the polylactide charging method on the relaxation of the homocharge has been studied by thermal activation spectroscopy. The spectra of TSDC are shown in Fig. 1.



Fig. 1. TSD current for PLA film after: corona discharge (1), barrier discharge (2)

As can be seen from Fig. 1 (Curve *I*), three relaxation maxima are observed on the TSD spectrum for a PLA film pre-charged in a corona discharge. The position of the first (anomalous) sharp peak at 54 °C corresponds to the beginning of the transition process from a glassy state to a highly elastic one. The glass transition temperature T_g of polylactide is 50–60 °C [9], T_g determines the defrosting of the segmental mobility of the polymer. It can be assumed that the low-temperature peak is due to the relaxation of the homocharge in the region of the glass transition temperature. A similar result was obtained in the work [10].

The second (67 $^{\circ}$ C) and third (82 $^{\circ}$ C) peaks on the TSD spectrum can be associated with various relaxation processes. The main mechanisms of relaxation of the homocharge can be carried out either by releasing charge carriers from traps, or due to the intrinsic conductivity of the polymer.

The spectrum of the TSD current of a film charged in a barrier discharge is shown in Fig. 1 (Curve 2). The spectrum has 2 distinct relaxation maxima in the region of 53 °C and 60 °C. Similarly, the low-temperature peak is caused by the relaxation of the homocharge in the region of the glass transition temperature of the PLA. To determine the mechanism of charge relaxation in polylactide films in high-temperature peaks, it is necessary to carry out a mathematical calculation of activation energies and relaxation times.

Mathematical analysis

The theoretical analysis of the TSDC spectra is based on the 'fitting method'. The calculated spectrum of TSDC is compared with the experimentally measured by varying three parameters, J_m , T_m , W. Complex curves of TSDC can be analyzed using the sum of discrete elementary Debye maxima $\Sigma n_{1,2,3}J_k$, described by first-order kinetics [11]. The current density of the TSDC J_{TSD} can be described by the expression

$$J_{TSD} = \frac{d\sigma_{ind}}{dt} = J_m \exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right] \exp\left\{-\frac{W}{kT_m^2}\int_{T_m}^T \exp\left[\frac{W}{k}\left(\frac{1}{T_m} - \frac{1}{T'}\right)\right] dT'\right\}.$$
 (1)

Current density value J_m by T_m :

$$J_{m} = \frac{\varepsilon \varepsilon_{0} \varepsilon_{lay} U_{e0}}{\left(\varepsilon h_{lay} + \varepsilon_{lay} h\right)} \exp\left\{-\frac{W}{k T_{m}^{2}} \int_{T_{0}}^{T_{m}} \exp\left[\frac{W}{k} \left(\frac{1}{T_{m}} - \frac{1}{T'}\right)\right] dT'\right\},\tag{2}$$

where ε_{lay} , h_{lay} are the dielectric constant and thickness of gasket; k is the Boltzmann coefficient; T_0 , T are the initial and current temperature; T_m is the maximum current density temperature J_m ; ε , h are the dielectric constant and thickness of experimental film; U_{e0} is the initial value of electret potential difference; τ_m is the relaxation time at maximum temperature, ε_0 is the permittivity.

The relaxation time is expressed as

$$\tau = \tau_m \exp\left(\frac{W}{kT} - \frac{W}{kT_m}\right). \tag{3}$$

Temperature dependence U_{ρ} expressed:

$$U_{e}(t) = U_{e}(0) \exp\left(-\int_{0}^{\infty} \frac{dt}{\tau_{e}}\right).$$
(4)

The theoretical calculation of the TSD current spectra was carried out based on the values of the current density J_m at the maximum and the temperature of the maximum T_m , determined from the experimental spectra of the TSD currents. In this case, the value of the activation energy W varies. Activation energies and relaxation times were calculated from ratio 4, which are presented in Table 1.

High values of activation energies may indicate the inapplicability of the Debye model in the field of defrosting of segmental mobility of polylactide. In the region of the glass transition temperature, there is a sharp increase in electrical conductivity, which causes an increase in the TSDC in this region.

The spectra of films pre-charged in corona discharge and DBD were measured by the method of TSDC in a closed circuit. The experimental data presented (Fig. 2) confirm the fact that the specific conductivity of the inner layers of the film is lower than the conductivity of the near-surface layers.

According to the TSD current curves (Fig. 2) measured at close contact, the effective depth δ of charge localization was calculated by the ratio based on the model of a three-layer electret [12]:

$$\delta = h \left[1 + \frac{\varepsilon \varepsilon_0 U_E S}{Qh} \right]^{-1},$$

where $h = h_1 + \delta$ is the film thickness, ε is the its dielectric constant, U_E is the initial value of the electret potential difference, Q is the charge calculated from the TSDC curve by integrating.

Table 1

r					
Calculated maxima	$J_m \cdot 10^{-8}, \mathrm{A/m^2}$	T_m, \mathbf{K}	W, eV	τ_m, s	
Corona charging					
J_{11}	3.3	327	9.5	30	
$J_{12.}$	0.7	340	2.0	110	
J_{13}	0.35	355	1.2	301	
DBD charging					
J_{21}	0.9	326	7.0	346	
	1.8	333	4.0	97	

Calculation parameters TSDC



Fig. 2. TSDC at short circuit contact for PLA films charged in corona discharge (1) and DBD (2)

As a result of the calculations carried out, it was found that the value of δ depends on the method of charging polylactide films. The effective depth of the charge after treatment in the corona discharge is 1.5 ± 0.1 microns, and after charging in the dielectric barrier discharge 2.7 ± 0.2 microns.

Conclusion

It has been demonstrated that when polylactide films are charged at room conditions at atmospheric pressure, a homocharge accumulates in the corona and barrier discharge. Using the method of TSDC in the open circuit mode, it was found that the relaxation of the homocharge in the region of the glass transition temperature of the polylactide is due to the defrosting of segmental mobility (an increase in electrical conductivity). Likely the remaining peaks are associated with the release of the homo charge from the traps. When measuring the TSDC in an open and closed circuit, the currents have the opposite direction, therefore, the specific conductivity of the inner layers of the film is lower than the conductivity of the surface layers of the film. Using a three-layer dielectric model, the depth of the charge after treatment in the corona discharge is 1.5 ± 0.1 microns, and after charging in the dielectric barrier discharge 2.7 ± 0.2 microns.

However, it should be noted that under the action of a corona discharge in the presence of a grid, the polymer film is charged, while the action of the DBD in an alternating electric field leads to the processes of polymer destruction and its simultaneous charging, which is indirectly confirmed by the spectra of TSDC.

Acknowledgments

Grant for young scientists the Ministry of Education and Science Russia MK-4346.2022.4.

REFERENCES

1. Sun Z., Wang H., Guo X., Xu J., Liang J. Jiang J., Liang Y., Electret prevents the formation of bacterial biofilm. IET Nanodielectr. 6(2), (2023) 57–63.

2. Sessler G.M., West J.E., Production of High Quasipermanent Charge Densities on Polymer Foils by Application of Breakdown Fields // J. Appl. Phys. 43.3 (1972) 922–926.

3. Borisova M.É., Koikov S.N., Electret effect in dielectrics. Soviet Physics Journal 22, 58–69 (1979).

4. Gorokhovatskiy Yu. A., Galikhanov M. F., Ignatyeva D. A., Karulina E.A., Sotova Yu.I., Charge Relaxation Mechanisms in Composite Films Based on Polylactide // University Scientific Journal. 27 (2017) 46–55.

5. Marotta E., Callea A., Ren X., Rea M., Paradisi C., DC Corona Electric Discharges for Air Pollution Control, 2–Ionic Intermediates and Mechanisms of Hydrocarbon Processing. Plasma Processes Polym., 5 (2008) 146–154.

6. Chen J., Davidson J.H., Model of the Negative DC Corona Plasma: Comparison to the Positive DC Corona Plasma / // Plasma Chemistry and Plasma Processing. 23 (2003) 83–102.

7. Kamalov A., Smirnova N., Kolbe K., Borisova M., Bystrov S., Didenko A., Vlasova E., Yudin V., Activation of R-BAPB polyimide with cold plasma dielectric barrier discharge for improvement of cell-material interaction V., J. Appl. Polym. Sci. 139(42), (2022), e53024.

8. **Borisova M., Kamalov A., Jayasinghe N., Chiriateva A.**, Charge Relaxation and Kinetic Accumulation of Non-woven Polypropylene and Polyimide Films, 2022 Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus), Saint Petersburg, Russian Federation, (2022) 1332–1334.

9. Saeidlou S., Huneault M. A., Li H., Park C. B., Park, Poly(lactic acid) crystallization, Progress in Polymer Science, 37, 12 (2012) 1657–1677.

10. Gorokhovatskiy Yu.A., Galikhanov M.F., Ignatyeva D.A., et al., Ways to increase the stability of the electret state in composite polylactide films, Bulletin of Kazan University of Technology. 20 (4) (2017) 27–30.

11. Borisova M.É., Koikov S.N., Physics of dielectrics, Russian, Publishing Office of Leningrad University, Leningrad, 1979.

12. Borisova M.É., Koikov S.N., Tihomirov A.F., Effective depth of charge in polycarbonate film electretes. // Izvestiya vuzov. Ser. Physics., 4 (1981).

THE AUTHORS

KAMALOV Almaz M. spb.kamalov@gmail.com ORCID: 0000-0003-2044-957X BORISOVA Margarita E. vladimirl.borisov@gmail.com ORCID: 0000-0003-0761-6302

Received 01.07.2023. Approved after reviewing 03.08.2023. Accepted 03.08.2023.

Conference materials UDC 621.359.3 DOI: https://doi.org/10.18721/JPM.163.235

Study of composite electrode material formation features based on super C45/RuO₂ and super C45/MnO₂ for asymmetric planar supercapacitors

Sh.Sh. Isokjanov¹[™], R.M. Ryazanov², E.P. Kitsyuk², E.A. Lebedev¹

¹National Research University of Electronic Technology, Moscow, Russia;

² Scientific-Manufacturing Complex "Technological Centre", Zelenograd, Moscow, Russia

[™] isakjanov2997@gmail.com

Abstract. A method for fabricating an asymmetric planar supercapacitor with dissimilar electrodes based on Super C45/RuO₂ and Super C45/MnO₂ using the electrophoretic deposition method has been developed. The electrode topology was formed using laser engraving. The electrophoretic deposition method was chosen for deposition of the composite onto the surface of nickel-coated sitall plates. The features of sequential deposition of composite materials onto the substrate surface were studied, as well as the influence of electrophoresis modes on the composition and morphology of the formed electrode layers. The research was conducted to identify the dependence of the capacitance characteristics of the formed electrode materials on the process parameters. A technology for producing compact planar supercapacitors with an asymmetric configuration for a wide range of microelectronics applications has been developed.

Keywords: planar supercapacitor, asymmetric supercapacitor, laser engraving, electrode material, electrophoretic deposition, suspension

Funding: This work was supported by State Assignment FSMR-2023-0003.

Citation: Isokjanov Sh.Sh., Ryazanov R.M., Kitsyuk E.P., Lebedev E.A., Study of composite electrode material formation features based on Super C45/RuO₂ and Super C45/ MnO_2 for asymmetric planar supercapacitors, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 206–210. DOI: https://doi.org/10.18721/JPM.163.235

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.359.3 DOI: https://doi.org/10.18721/JPM.163.235

Исследование особенностей формирования композитного электродного материала на основе Super C45/RuO₂ и Super C45/MnO, для асимметричных планарных суперконденсаторов

Ш.Ш. Исокжанов¹⊠, Р.М. Рязанов², Е.П. Кицюк², Е.А. Лебедев¹

¹ Национальный Исследовательский Университет «МИЭТ», Москва, Россия;

² НПК «Технологический центр», Зеленоград, Москва, Россия

^{III} isakjanov2997@gmail.com

Аннотация. Разработан метод изготовления асимметричного планарного суперконденсатора с разнородными электродами на основе Super C45/RuO₂ и Super C45/MnO₂ методом электрофоретического осаждения. Топология электродов была сформирована с помощью лазерной гравировки. Для осаждения композита на поверхность

© Isokjanov Sh.Sh., Ryazanov R.M., Kitsyuk E.P., Lebedev E.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

ситалловых пластин с никелевым покрытием был выбран метод электрофоретического осаждения. Были изучены особенности последовательного осаждения композиционных материалов на поверхность подложки, а также влияние режимов электрофореза на состав и морфологию формируемых электродных слоев. Исследования проводились с целью выявления зависимости емкостных характеристик сформированных электродных материалов от параметров процесса. Разработана подход для получения миниатюрных планарных суперконденсаторов с асимметричной конфигурацией для широкого применения в микроэлектронике.

Ключевые слова: планарный суперконденсатор, асимметричный суперконденсатор, лазерная гравировка, электродный материал, электрофоретическое осаждение, суспензия

Финансирование: Работа выполнена в рамках Государственного Задания на 2023-2025 гг., соглашение FSMR-2023-0003.

Ссылка при цитировании: Исокжанов Ш.Ш., Рязанов Р.М., Кицюк Е.П., Лебедев Е.А. Исследование особенностей формирования композитного электродного материала на основе Super C45/RuO₂ и Super C45/MnO₂ для асимметричных планарных суперконденсаторов // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 206–210. DOI: https://doi.org/10.18721/ JPM.163.235

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Supercapacitors (also known as electrochemical capacitors or ultracapacitors) are particularly attractive for microelectronic devices and renewable energy production because they have excellent power and outstanding service life. The current trend in the development of miniature portable electronic devices has greatly increased the demand for ultra-thin, flexible, and durable micro-supercapacitors on a chip, which have enormous potential to complement or even replace microbatteries and capacitors. Asymmetric planar supercapacitors with dissimilar electrodes based on carbon-containing materials and transition metal oxides are promising electrochemical energy storage devices that can fully utilize the advantages of the unique properties of composite materials through combinations of different charge storage mechanisms or different redox reactions [1-5].

This paper presents the results of research and development of a method to form asymmetric planar counter-pin supercapacitors from representative materials based on carbon material, Super C45, transition metal oxides such as RuO_2 , MnO_2 , by electrophoretic deposition, and a method to create the topological pattern of a planar supercapacitor by laser engraving. The morphology and composition of Super C45/MnO₂ and Super C45/RuO₂ composite samples, as well as the capacitive characteristics of asymmetric planar supercapacitors based on them, were studied.

Materials and Methods

As electrodes of the planar supercapacitor, a $20 \times 12 \times 0.6$ mm cut sitall substrate was used, on which a 200 nm thick layer of nickel was deposited by magnetron sputtering. As an adhesion layer between the substrate and the nickel layer, a 40 nm-thick chromium layer was deposited. Laser engraving was used to create two electrically isolated supercapacitor electrodes, which allows high accuracy in reproducing the topological pattern of the device.

Two suspensions, 50 ml each, were prepared. A dispersant was used to achieve the most uniform dispersion of the suspension and to improve the quality of the final product. A mixture of isopropyl alcohol and acetone in a 1 : 1 ratio was used as a solvent. The components were mixed in a test tube with a mixture of acetone and isopropyl alcohol (Table 1).

The deposition process took place in the electrophoretic cell in two stages: sequential deposition of the composite on one half and deposition of the composite on the second half of the counter-pin electrode. The EDP process was performed in the galvanostatic mode. The electrodes were connected to the power supply by reversing polarity. The main stages of creating the planar supercapacitor are schematically shown in Fig. 1.

© Исокжанов Ш.Ш., Рязанов Р.М., Кицюк Е.П., Лебедев Е.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Table 1

Suspension composition				
Components	Suspension 1	Suspension 2		
Super C45, g/l	0.04	0.04		
$RuO_2*xH_2O, g/l$	0.2	_		
MnO ₂ , g/l	_	0.4		
Hydroxypropyl cellulose, g/l	0.2	0.2		
Iodine, g/l	0.4	0.6		
Acetone, 1	0.025	0.025		
Isopropyl alcohol, 1	0.025	0.025		







In the power supply, the upper voltage limit was set to 200 V and the current was varied in the range of 5–15 mA. First, deposition was performed for the electrode based on a suspension with RuO_2 in two cycles of 60 seconds each. Then, composite with MnO_2 was deposited in three cycles of 60 seconds for the second electrode.

The morphology and surface composition of the obtained coatings were studied using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy, and measurements were taken to determine the capacitive characteristics of the supercapacitors.

The capacity of the cell was calculated by the formula (1):

$$C = \frac{\Delta I}{2\vartheta},\tag{1}$$

where ΔI is the current swing, ϑ is the scanning speed.

The specific capacitance is calculated by the formula (2):

$$C_{specific} = \frac{c}{m},\tag{2}$$

where C is the capacity of the device, m is the mass of the sediment.

Results and Discussion

The experimental sample of asymmetric planar supercapacitor with Super C45/RuO₂-based composite on one half and Super C45/MnO₂-based composite on the other half was prepared according to the technique. The results of the morphology and composition study are shown in Fig. 2.

The porous surface structure observed in SEM images is important in increasing the capacitance and power characteristics of supercapacitors. Surface porosity provides a large contact surface between electrode and electrolyte, which promotes efficient ionic diffusion and maximum electrolyte absorption.



Fig. 2. SEM image and element distribution maps of asymmetric planar supercapacitor

The element distribution maps show a uniform distribution of the components of the electrode material over the surface of the sample, and, importantly, the composites were deposited clearly in their area and did not cross the interface into the opposite electrode. The composite with RuO_2 was deposited only on the left electrode, and the composite with MnO_2 was deposited only on the right electrode. Carbon, which is part of both composites, is present on the two electrodes. Iodine, an auxiliary component that is also present in both suspensions, was equally deposited.

To study the electrophysical characteristics, the supercapacitors were placed in a 1 M KOH electrolyte solution and volt-ampere cyclic sweeps were taken using a potentiostat, after which their capacitive characteristics were measured (Fig. 3).



Fig. 3. Graph of the cyclic volt-amperogram (a), and the dependence of the scanning speed on the specific capacity of supercapacitors (b)

It is well seen, in the asymmetric planar supercapacitor not only a different form of sweep, but also increases the area of the figure, which is directly proportional to the electrical capacitance in contrast to the capacitor with a double electric layer (Fig. 3,a). If we compare their shapes, we can see the presence of peaks that correspond to reversible redox reactions.

The specific capacitance of the obtained sample of asymmetric planar supercapacitor was 19.8 F/g, exceeding the specific capacitance of the capacitor with an electric double layer 18 times, which was 1.1 F/g.

Conclusion

In the course of the study, by varying the composition of the suspension and deposition modes, the composition of the composite electrodes was optimized. The peculiarities of the sequential local deposition of composites onto electrodes of planar supercapacitors were studied. These investigations allowed demonstrating the fundamental possibility of creating asymmetric planar supercapacitors with improved capacitance and power characteristics that are compatible with traditional integrated circuit production technology. Further development of new electrode materials, optimization of the synthesis and assembly processes of supercapacitors, and improvement of their electrochemical properties are possible.

REFERENCES

1. Wu N., Bai X., Pan D., Dong B., Wei R., Naik N., Rangrao R. P., Guo Z., Recent Advances of Asymmetric Supercapacitors, Advanced Materials Interfaces. 8 (1) (2021) 2001710.

2. Kakovkina Yu.I., Isokjanov Sh.Sh., Ryazanov R.M., Lebedev E.A., Kitsyuk E.P., Features of the formation Super C45-RuO₂ based planar supercapacitor structures, St. Petersburg Polytechnic University Journal: Physics and Mathematics. 15 (3.2) (2022) 336–339.

3. Muzaffara A., Ahameda B.M., Deshmukha K., Thirumalai J., A review on recent advances in hybrid supercapacitors: Design, fabrication and applications. Renewable and Sustainable Energy Reviews. 101 (2019) 123–145.

4. Zhu J., Tang Sh., Xie H., Dai Y., Meng X., Hierarchically porous MnO_2 microspheres doped with homogeneously distributed Fe_3O_4 nanops for supercapacitors. ACS Applied Materials & Interfaces. 6 (20) (2015) 17637–17646.

5. Tang Y., Guo W., Zou R., Nickel-based bimetallic battery-type materials for asymmetric supercapacitors. Coordination Chemistry Reviews. 451 (2022) 214242.

THE AUTHORS

ISOKJANOV Shakhboz Sh. isakjanov2997@gmail.com ORCID: 0000-0001-6009-9039

RYAZANOV Roman M. r.m.ryazanov@gmail.com ORCID: 0000-0002-2464-8712 KITSYUK Evgeny P. Kitsyuk.e@gmail.com ORCID: 0000-0002-4166-8408

LEBEDEV Egor A. dr.beefheart@gmail.com ORCID: 0000-0002-5085-5408

Received 02.07.2023. Approved after reviewing 03.08.2023. Accepted 07.08.2023.

Conference materials UDC 539.2 DOI: https://doi.org/10.18721/JPM.163.236

Study of n-diamond and carbon nanowalls structure synthsized by the RF-PECVD

A.M. Mumlyakov[⊠], E.A. Pershina, A.A. Shibalova, M.V. Shibalov, Yu.V. Anufriev, I.A. Filippov, V.V Sen', M.A. Tarkhov

Institute of Nanotechnologies of Microelectronics of the RAS, Moscow, Russia

□ mumlyakov.a@inme-ras.ru

Abstract. In this work, a hybrid n-diamond-carbon nanowalls structure was synthesized on a 100 mm diameter silicon wafer using RF-PECVD (CCP type). This structure was analyzed by transmission microscopy, electron microscopy and X-ray diffraction. It was found that the addition of carbon monoxide (CO) to a gas mixture of methane (CH₄), argon (Ar), and hydrogen (H₂) leads to the formation of n-diamond nanocrystals in the basal layer. Using plasma surface treatment techniques, the carbon nanowalls were fully removed and the lower layer consisting of n-diamond was studied separately, for which X-ray diffraction results of a separate n-diamond phase were obtained for the first time.

Keywords: n-diamond, carbon nanowalls, X-ray diffraction, allotropic form, hybrid material

Funding: This study was funded by Ministry of Science and Higher Education of the Russian Federation grant number FFFG-2022-0003.

Citation: Mumlyakov A.M., Pershina E.A., Shibalova A.A., Shibalov M.V., Anufriev Yu.V., Filippov I.A., Sen' V.V, Tarkhov M.A. Study of n-diamond and carbon nanowalls structure synthsized by the RF-PECVD, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 211–216. DOI: https://doi.org/10.18721/JPM.163.236

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 539.2 DOI: https://doi.org/10.18721/JPM.163.236

Исследование гибридной структуры n-алмаза и углеродных наностенок, синтезированной методом RF-PECVD

А.М. Мумляков[⊠], Е.А. Першина, А.А. Шибалова, М.В. Шибалов, Ю.В. Ануфриев, И.А. Филиппов, В.В. Сень, М.А. Тархов

Институт нанотехнологий микроэлектроники РАН, Москва, Россия

□ mumlyakov.a@inme-ras.ru

Аннотация. В данной работе на кремниевой пластине диаметром 100 мм была синтезирована методом RF-PECVD (тип CCP) гибридная структура n-алмаз — углеродные наностенки. Для данной структуры был проведен анализ методами просвечивающей микроскопией, сканирующей микроскопией и рентгеновской дифракцией. Установлено, что добавление угарного газа (CO) в газовую смесь метана (CH₄), аргона (Ar) и водорода (H₂) приводит к образованию частиц n-алмаза в базальном слое. Используя плазмохимическое травление в кислород-содержащей среде, были успешно удалены углеродные наностенки и отдельно изучен нижний слой, состоящий из n-алмаза, для которого впервые были получены результаты рентгеновской дифракции отдельной фазы n-алмаза.

Ключевые слова: п-алмаз, углеродные наностенки, рентгеновская дифракция, аллотропная форма, гибридный материал

© Mumlyakov A.M., Pershina E.A., Shibalova A.A., Shibalov M.V., Anufriev Yu.V., Filippov I.A., Sen' V.V, Tarkhov M.A, 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Финансирование: Работа выполнена при финансовой поддержке Министерства науки и высшего образования Российской Федерации № FFFG-2022-0003.

Ссылка при цитировании: Мумляков А.М, Першина Е.А., Шибалова А.А., Шибалов М.В., Ануфриев Ю.В., Филиппов И.А., Сень В.В., Тархов М.А. Исследование гибридной структуры п-алмаза и углеродных наностенок, синтезированной методом RF-PECVD // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 211–216. DOI: https://doi.org/10.18721/JPM.163.236

Статья открытого доступа, распространяемая по лицензии СС ВУ-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Carbon nanowalls (CNWs) are structures consisting of graphite-like two-dimensional sheets oriented almost perpendicular to the substrate surface. The exceptional morphological and structural properties of CNWs, including their vertical orientation, open and ultra-thin edges of graphene sheets, large specific surface area and open areas between graphene sheets, have attracted significant interest. [1]. Due to their important properties, such as high electrical conductivity, thermal conductivity, and chemical stability, CNWs have been successfully applied in nanoelectronics, photoelectronics, and electrochemistry. [2–5].

CNWs are mainly grown using Plasma Enhanced Chemical Vapor Deposition (PECVD) from various types of hydrocarbons with different plasma sources. The interfacial layer formed between a substrate and CNWs, i.e., the basal layer, is an important phase of CNWs synthesis. The basal layer ensures a uniform heat and current distribution within the substrate plane and remains significant for interface resistance and CNW formation. Studying the basal layer has demonstrated that it can be represented by a layer of graphite sheets growing parallel to a substrate, a layer of amorphous carbon, or various carbides formed during interaction with the substrate material. The type of the formed basal layer depends on both the synthesis technique and gas precursors applied during the growth.

Throughout our research, we found that feeding an additional carbon source in the form of carbon monoxide (CO) to a gas mixture $(Ar/CH_4/H_2)$ induces the formation of a unique interface layer consisting of a new-diamond (n-diamond, FCC-carbon). A new diamond crystalline phase (carbon γ phase) was first produced during the low-temperature annealing of a carbon film exposed to Ar ions during deposition [6]. Various methods have been developed to generate nano-sized n-diamond crystallites, including hydrothermal synthesis [7], hydrogen plasma treatment of a diamond surface [8], microwave plasma enhanced chemical vapor deposition (MW-PECVD) [9] and other.

There is no detailed study of the n-diamond structure using X-ray diffraction in the scientific papers due to the small size of nanoscale crystallites and by-products arising during synthesis. Therefore, most of the data on the n-diamond structure has been obtained based on electron diffraction results from TEM studies, which is insufficient to determine the exact structure of the n-diamond. Thus, the n-diamond crystalline structure remains uncertain and requires further scientific investigation [10].

The study of n-diamond-CNWs hybrid structure formation is important fundamental research for producing applied micro- and nanodevices, optoelectronic systems, energy storage and conversion systems, various sensors and other tools. Understanding the factors affecting the development of hybrid structures facilitates the control of the synthesis and growth processes, as well as the phase composition.

Materials and Methods

The n-diamond-CNWs hybrid structure was synthesized in the Oxford Instruments Nanofab 1200 Agile reactor. At room temperature, the wafers were placed at a grounded graphite base electrode, which is used with an upper electrode to generate high-frequency capacitively coupled plasma (CCP). The heating to 750 °C was performed in a hydrogen flow at a pressure of 1 Torr, and an average heating rate of 14 °C/min. The depositing phase comprised the feeding of Ar, CH_4 , CO, and H₂ process gases (ratio 200:10:7.5:2.5), at a pressure of 250 mTorr and the RF source power of 300 W. Synthesis was performed on a silicon wafer for 3600 seconds without and with feeding carbon monoxide (CO) to a gas mixture.

© Мумляков А.М, Першина Е.А., Шибалова А.А., Шибалов М.В., Ануфриев Ю.В., Филиппов И.А., Сень В.В., Тархов М.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Scanning electron microscopy (SEM) was performed using FEI Helios, a dual beam FIB-SEM (focused ion beam) system. Images (patterns, micrographs) were acquired using the secondary electron imaging mode while scanning the surface of analyzed objects with an electron beam. Imaging parameters were selected experimentally according to the criteria of sufficient resolution for visualizing relevant characteristics and an acceptable signal-to-noise ratio

The microstructure of the samples was studied by transmission electron microscopy with high resolution (TEM and HRTEM) using a JEOL JEM-2100 Plus microscope at an accelerating voltage of 200 kV. The two-dimensional Fourier transform technique (FFT) was used to obtain diffraction patterns of separate nanoparticles and minimize the noise of high-resolution TEM images.

The samples were analyzed on an X-ray diffractometer using the X-ray diffraction (XRD) technique at a grazing incidence of X-ray radiation to a sample (incident angle $\approx 0.5^{\circ}$, selected based on the maximum intensity of peaks from CNWs and n-diamond). X-ray diffraction patterns were taken in the scanning mode at an angle of 20 using Cu K_a radiation ($\lambda = 1.540605$ E) under the X-ray source parameters of 45 kV and 40 mA. A paraboloidal reflector with a divergence slit of j and an anti-scatter slit of j was set on a primary beam. A parallel plate collimator with a divergence amounting to 0.19° was set on a diffracted beam. The value of Soller slit divergence was equal to 0.04°. A point-linear detector was used as a detector.

Results and Discussion

The phase composition of samples synthesized with and without CO was determined using the X-ray diffraction technique. To analyze the surface layer of the samples, the Grazing Incidence X-ray Diffraction (GIXRD) method was applied. The X-ray diffraction pattern of the sample synthesized without CO (see Fig. 1, blue chart) displays peaks at 20 angles equal to 25.4° , 43.0° , $45-46^{\circ}$, and 78.5° , which refer to CNWs [11]. The lack of (004) reflex at $20 \approx 53.3^{\circ}$ on the diffraction pattern can be explained by a low number of graphene layers in nanowalls along [0001] or their aperiodicity. However, the diffraction pattern of the sample synthesized with CO (Fig. 1, dark-red chart) displays additional peaks at 20 angles equal to 44.6° , 52.1° , 76.7° , 93.2° , and 98.8, which were identified as the n-diamond phase according to scientific literature [12].



Fig. 1. Grazing incidence X-ray diffraction patterns for the samples synthesized without CO (blue chart) and with CO feeding (red chart). The location of peaks for the CNWs phase and n-diamond phase are marked on a line diagram

Several peaks in the diffraction pattern overlap with each other. Since experimentally obtained X-ray diffraction patterns for the n-diamond phase without overlapping peaks from accompanying phases are not presented in the literature, we removed CNWs from the hybrid structure by treatment in oxygen plasma. The diffraction pattern (Fig. 2) for the range of 20 angles from 25° to 105° distinctively displays peaks at 20 angles equal to 44.6°, 51.8°, 76.4°, 93.0°, and 98.5° for the Kal position. The value of integral FWHM (integral breadth) for all peaks is \approx 1.3, which corresponds to an average size of crystallites equal to \approx 10 nm and calculated according to the



Fig. 2. Experimental X-ray diffraction pattern of a nanocrystalline n-diamond phase indicating the fractional intensity of each peak. The diffraction pattern background was removed

Scherrer formula. The intensity ratio of each peak is given in the insert to Fig. 2. The number of reflexes, their relative position, and intensity ratio substantiate that the n-diamond structure can be described by a crystallographic set Fm3m, as it was suggested in a series of scientific papers [8]. According to the diffraction pattern interpretation using the Fm3m structure, the n-diamond

According to the diffraction pattern interpretation using the $Fm_{2}m$ structure, the n-diamond lattice parameter is equal to a = 3.52E, which is in agreement with the literature data [6].

A general cross-section view of the sample containing the hybrid structure grown with and without CO for the same synthesis duration of 3600 seconds is shown in Fig. 3, *a*, *b* in SEM images of secondary electrons. It can be seen that at the same synthesis time, adding CO to the reaction mixture leads to the growth of higher CNWs. The increase in CNWs growth rate is associated with a shift in the balance between the process of etching in the oxygen plasma and the deposition towards deposition, which occurs when a small amount of CO is added to the gas mixture.

The morphology and structural differences of the obtained samples samples were also analyzed using the TEM technique. The general view of the CNWs-Si interface for samples grown without CO and with CO feeding is provided in Fig. 3, *c* and Fig. 3, *d*, respectively. The TEM images show



Fig. 3. Cross-sectional (*a*) SEM and *c*) TEM images of CNWs grown on Si substrate for 3600 seconds without CO. Cross-sectional (*b*) SEM and (*d*) TEM images of CNWs grown on Si substrate for 3600 seconds with CO

a distinctive feature of the sample grown with CO, i.e., the presence of individual nanoparticles formed on the CNWs-Si boundary. According to TEM images, the average size of the particles is 10 nm. The presence of graphene layers of CNWs growing around the observed nanoparticles is also apparent in Fig. 3,*d*. By contrast, in the sample grown without CO, only graphene layers with an interplanar spacing of 3.74-3.77 E can be visible at the CNWs–Si boundary (Fig. 3 (*c*), insert) corresponding to the interplanar spacing for the (0001) plane of turbostratic graphite [13] and capable of responding to an unformed CNWs structure.

High-resolution TEM images of the CNWs-Si section were taken in several areas of the sample grown with CO to study the nanoparticle's structure. An example of those areas is given in the insert to Fig. 3,*d*, i.e., an enlarged image of a yellow square. Some particles overlapped or were composed of several crystallites, while most of them represented individual monocrystals. To identify the phase, we only used FFT images of monocrystals. Significantly, different allotropes of carbon may exist simultaneously and possess the same value of interplanar d-spacings. Therefore, to ensure precise identification of a phase of carbon nanoparticles under study, we determined interplanar d-spacing and angles between directions in the lattice on FFT images and compared them with values defined for registered allotropes of carbon according to the ICDD database.

A typical HRTEM image of a particle taken for the evaluation and a relevant FFT pattern can be found in the insert to Fig. 3,*d*. The reflection positions on the displayed FFT pattern indicate that this electron diffraction pattern corresponds to the [101] cross-section of the lattice structure [14], and the lattice parameters correspond to the n-diamond phase. By summarizing the electron diffraction data of various individual nanoparticles in the sample, it can be concluded that during synthesis with CO feeding, randomly oriented crystals with an n-diamond structure and lattice are formed. The obtained data are consistent with the results of the investigation by the XRD technique.

Conclusion

The n-diamond-CNWs hybrid structure was successfully synthesized in capacitively coupled plasma discharge using a mixture of carbon monoxide, methane, hydrogen, and argon. The study has demonstrated that feeding CO to the gas mixture is an essential factor in the n-diamond formation. Selective removal of CNWs from the hybrid structure has allowed to experimentally obtain X-ray diffraction patterns for the n-diamond phase, free of overlapping peaks of accompanying phases. The average size of the n-diamond particles was approximately 10 nm at 3600 seconds of synthesis. Having grown the n-diamond-CNWs hybrid structure on 4-inch silicon wafers offers opportunities for large-scale integration and wide practical application.

Acknowledgments

The authors are grateful to Grant FFFG-2022-0003 in support of the Ministry of Science and Higher Education of the Russian Federation. Fabrication and characterization were carried out at large-scale facility complexes for heterogeneous integration technologies and silicon + carbon nanotechnologies.

REFERENCES

1. Chen, Junhong, Zheng Bo, Ganhua Lu., Vertically-oriented graphene. Springer International Publishing Switzerland, DOI 2015) 10) 978–3.

2. Zhou, Quan, et al., The controlled growth of graphene nanowalls on Si for Schottky photodetector. AIP Advances 7 (12) (2017) 125317.

3. Mumlyakov A. M., et al., Fabrication and characterization of quasi-three-dimensional capacitor structure based on carbon nanowalls. Carbon 2021) 184) 698–705.

4. Stratakis E., et al., Three-dimensional carbon nanowall field emission arrays. Applied Physics Letters 96 (4) (2010) 043110.

5. Evlashin Stanislav A., et al., N-doped carbon nanowalls for power sources." Scientific Reports 9 (1) (2019) 1–7.

6. Palatnik L. S., et al., y carbon. Zh. Eksp. Teor. Fiz 87 (9) (1984) 14-9.

7. Ma Xuanxuan, et al., Influence of crystallization temperature on fluorescence of n-diamond quantum dots. Nanotechnology 31 (50) (2020) 505712.

8. Fatow M., et al., Carbon modification with the fcc crystal structure. Vacuum 68 (1) (2002) 75–78.

9. Thomas Joseph P., et al., Preferentially grown ultranano c-diamond and n-diamond grains on silicon nanoneedles from energetic species with enhanced field-emission properties. ACS Applied Materials & Interfaces 4 (10) (2012) 5103–5108.

10. Kondrin M.V., et al., Diamond subhydride: unraveling the mystery of "n-diamond". CrystEngComm 24 (38) (2022) 6724–6729.

11. **Yoshimura Hirofumi, et al.,** Grazing incidence X-ray diffraction study on carbon nanowalls. Chemical Physics Letters 482 (1-3) (2009) 125–128.

12. Yamada K., Sawaoka A. B., Very small spherical crystals of distorted diamond found in a detonation product of explosive/graphite mixtures and their formation mechanism. Carbon 32 (4) (1994) 665–673.

13. Franklin Rosalind E., The interpretation of diffuse X-ray diagrams of carbon. Acta crystallographica 3 (2) (1950) 107–121.

14. **Oberlin A.**, Electron microscopy of thin crystals by PB Hirsch, A. Howie, RB Nicholson, DW Pashley and MJ Whelan. Acta crystallographica 21 (3) (1966) 454–454.

THE AUTHORS

MUMLYAKOV Alexander M. mumlyakov.a@inme-ras.ru ORCID: 0000-0002-1081-8338

PERSHINA Elena A. squirrel_red@mail.ru ORCID: 0000-0002-2455-7941

SHIBALOVA Anastasia A. shibalova.a@inme-ras.ru ORCID: 0000-0001-9792-3968

SHIBALOV Maksim V. maxshibalov@gmail.com ORCID: 0000-0002-5818-4776 ANUFRIEV Yuri V. hf_super@mail.ru

FILIPPOV Ivan A. ivnfilippov@gmail.com ORCID: 0000-0002-6209-0086

SEN' Vasiliy V. dlcmsu@gmail.com ORCID: 0000-0003-3583-2643

TARKHOV Mikhail A. tmafuz@mail.ru ORCID: 0000-0001-8168-1917

Received 03.07.2023. Approved after reviewing 13.07.2023. Accepted 14.07.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023
Conference materials UDC [66.061.16;544.163.2:621.793]:681.586.72 DOI: https://doi.org/10.18721/JPM.163.237

Mechanisms of residual polymer removal in solvent mixtures after the graphene transfer and effects on channel conductivity gate control

N.P. Nekrasov[⊠], A.V. Romashkin, L.A. Barsukov, K.G. Nikitin, D.D. Levin, I.I. Bobrinetskiy, V.K. Nevolin

National Research University of Electronic Technology, Moscow, Russia

☑ 8141147@gmail.com

Abstract. After graphene transfer, solvent mixtures were used to remove residual PMMA, which efficiency was estimated by AFM, Raman spectroscopy, and CVC. That post-treatment gives: stress relaxation (2D peak shift, compared to trichloroethylene), 2D/G intensity ratio 1.1 changes to 2.6, clean graphene regions exceed 100–150 nm size; threshold point shifts to zero but the conductivity and mobility reduce. Ethanolamine functionalizes both PMMA and graphene.

Keywords: graphene transfer, polymer removal, sensor, polymethyl methacrylate

Funding: This work was supported by Russian Science Foundation, agreement No. 19-19-00401 (development of PMMA removing techniques); grant of the President of the Russian Federation MK-4010.2022.4 (AFM, Raman study).

Citation: Nekrasov N.P., Romashkin A.V., Barsukov L.A., Nikitin K.G., Levin D.D., Bobrinetskiy I.I., Nevolin V.K., Mechanisms of Residual Polymer Removal in Solvent Mixtures after the Graphene Transfer and Effects on Channel Conductivity Gate Control, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 217–222. DOI: https://doi.org/10.18721/JPM.163.237

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК [66.061.16;544.163.2:621.793]:681.586.72 DOI: https://doi.org/10.18721/JPM.163.237

Механизмы удаления остаточного полимера в смесях растворителей после переноса графена и влияние на проводимость и управление канала

Н.П. Некрасов[⊠], А.В. Ромашкин, Л.А. Барсуков, К.Г. Никитин, Д.Д. Левин, И.И. Бобринецкий, В.К. Неволин

Национальный исследовательский университет «МИЭТ», Москва, Россия

≅ 8141147@gmail.com

Аннотация. Остаточный ПММА удалялся в смеси растворителей, эффективность оценивали по ACM, спектроскопии КР и ВАХ. При обработке: напряжения релаксируют (смещение 2D пика); 2D/G меняется: с ~1,1 до 2,6; чистые области становятся 100-150 нм; пороговая точка смещается к нулю, но проводимость и подвижность снижаются. Этаноламин функционализирует и ПММА и графен.

Ключевые слова: перенос графена, сенсор, удаление полимера, ПММА

Финансирование: Работа выполнена в рамках гранта РНФ, № 19-19-00401 (методы удаления полимера); гранта Президента РФ № МК-4010.2022.4 (АСМ и спектроскопия).

© Nekrasov N.P., Romashkin A.V., Barsukov L.A., Nikitin K.G., Levin D.D., Bobrinetskiy I.I., Nevolin V.K., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Некрасов Н.П., Ромашкин А.В., Барсуков Л.А., Никитин К.Г., Левин Д.Д., Бобринецкий И.И., Неволин В.К. Механизмы удаления остаточного полимера в смесях растворителей после переноса графена и влияние на проводимость и управление канала // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 217–222. DOI: https://doi.org/10.18721/JPM.163.237

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The removal of polymer residuals, that are left after the graphene transfer used for the sensor channel, is still an important problem [1]. Residual PMMA blocks the active sensor area and decreases its efficiency, affecting the limit of detection, sensitivity, response time, and sensor parameters reproducibility [2–4]. PMMA tends to strongly interact with graphene in the near-surface layer [5], therefore needs new ways to delete it from graphene, rather than the methods based on bulk material dissolution. We suggest some new methods to remove the near-surface layer using: rinsing in solvent/non-solvent mixture; swelling or functionalization of the PMMA layer. Although the use of mixtures of solvents [6] and some special [1] for removing PMMA, provides a sufficiently high quality of CVD graphene transferred to the target substrate. Nevertheless, some mechanisms for removing PMMA molecules from the graphene and the solvent molecules' interaction with PMMA remain unclear. Despite the use of low molecular weight PMMA and other polymers, plasma modification, etc. [7] the functionalization of residual PMMA with the role of polar side groups increase for its subsequent more efficient removal has not been found in the literature. Thus, the study of the mechanisms of residual PMMA removal from graphene using different solvent mixtures and the PMMA functionalization, as well as graphene characteristics changes as the results of that cleaning, were the goals of this work. The rinsing efficiency and PMMA layer parameters change were estimated by AFM, Raman spectroscopy, and CVC measurements of the graphene layer.

Materials and methods

CVD graphene (Graphenea, Spain) on Cu foil was used. PMMA with $M_{\nu} \sim 495$ kDa 2 % in anisole (MicroChem, USA) was used as the supporting layer required for transfer onto Si substrate with 300 nm SiO₂ layer with Cr/Au microelectrodes (50 µm gap with 100 µm channel width). PMMA was spin-coated onto graphene at 2.5 krpm, then annealed at 110 °C. To remove polymer residuals film on SiO₂/Si substrate was rinsed in different solvents or mixtures: firstly, trichloroeth-ylene (TCE) at room temperature, and then consequently diacetone alcohol (DAA):water (H₂O) (4:1), tetrahydrofuran (THF):H₂O (Komponent-Reaktiv, Russia) (7:3), ethanolamine (EA) (Sigma-Aldrich):THF (3:7) for half an hour at ~60 °C to increase the dissolution rate. Residual PMMA removing efficiency was investigated using AFM (Solver-Pro, NT-MDT, Russia) and Raman spectroscopy (Centaur U HR, 532 nm laser, Nano Scan Technology, Russia). CVC measurements (IPPP5/1, MNIPI, Belarus) were carried out using a liquid gate (Ag/AgCl in 0.1x PBS 7.0 pH) with PDMS mask with well diameter 700 µm to localize liquid area, drain-source voltage was 10 mV.

Results and Discussion

In comparison with trichloroethylene (TCE), for DAA:H₂O there is stress relaxation or doping (2D peak shifts from 2696 to 2690 cm⁻¹), but with no 2D/G ratio change (~1.1, Fig. 1), although the layer thickness increased (from 3.7 to 4 nm, Fig. 2, *a*, *c*). This behavior can be explained by polymer swelling in the solvent with polymer molecular chain conformations changing relative to each other and graphene. That leads to the stress relaxation formed before: during the graphene transfer with an initially continuous PMMA layer and their heat treatment on the substrate. However, such PMMA swelling is not enough to redistribute PMMA molecules and remove them from graphene. Increasing solvent temperature potentially can improve PMMA removal efficiency. But used temperature already results in the graphene being partially removed from SiO₂, which appears as the curled edge of the graphene layer with residual PMMA (Fig. 2,*c*). Thus, due to the more energy-favorable PMMA-graphene interaction compared to PMMA-PMMA,

© Некрасов Н.П., Ромашкин А.В., Барсуков Л.А., Никитин К.Г., Левин Д.Д., Бобринецкий И.И., Неволин В.К., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Raman spectra (a), 2D position (b), 2D/G peak ratio (c) of graphene rinsed in various solvents

instead of easy removal of PMMA in TCE, which is one of the best solvents for PMMA [8], the removal of the near-surface PMMA layer from graphene does not occur. And as the temperature increases, only the graphene removal along with the residual PMMA layer occurs, especially if a large part of graphene was covered by PMMA. Thus, a two-stage treatment was carried out: (i) the main PMMA layer thickness was gradually removed in TCE at 25 °C, (ii) the residual near-surface PMMA layer was removed in a solvents mixture not exceed 60 °C.

For THF:H₂O, 2D/G increases to 1.6-1.9, which with AFM data (thickness ~2.2 nm), indicates that graphene regions without PMMA increased to ~50 nm. In our previous work [9], similar processing led to the graphene areas formation on Cu foil, on the contrary, with residual PMMA on that areas with slightly smaller sizes, with fluorescence from such quantum dots. In current work also small graphene regions, but without PMMA, don't provide fluorescence on SiO₂, but also suppress 2D/G. Due to its small specific area contribution, they can't change 2D/G ratio in the case of TCE compared to full PMMA-covered graphene. If its contribution and at the same time its size would be larger, 2D/G should be ~5 [9]. Graphene regions contribution, locally with high quality (2D/G ~5 [1, 9]), could be suppressed by the larger proportion of areas with PMMA (2D/G ~1) that total contribution is more than 2/3 of the whole area (Fig. 2,d).



Fig. 2. AFM of graphene cleaned by: TCE (a), AFM (b), DAA:H₂O (c), THF:H₂O (d, e),
(e) correspond to another sample, EA:THF (f). Scale bars are 1 μm

At the same time, with a small size of such small islands of graphene with PMMA or, similarly, without PMMA limited by PMMA, due to the possibility of fluorescence in them on copper foil [9], the energy levels position can also significantly change for them, even in the case of graphene on SiO_2 , accompanied by significant suppression of the 2D intensity for such regions. Thus, even in the presence of a large proportion of graphene without PMMA, the 2D/G ratio will be significantly suppressed when the regions with and without PMMA are small in size. Observed changes in the shape and area of the graphene regions without PMMA when using THF, points to the redistribution and only partial PMMA removal, especially on SiO_2 at an increased annealing temperature after transfer.

2D/G of AFM-cleaned graphene was higher: ~2.7. The thickness of the graphene layer is still larger (0.7–1 nm) than that observed for exfoliated graphene, transferred without polymers and solvents. The increased thickness is associated with the residual water molecules on SiO₂ under graphene for PMMA-transferred CVD graphene [10]. A further 2D/G ratio increase in comparison with the AFM-cleaned graphene is possible using a different substrate containing fewer residual water molecules and functional groups (such as Si-OH) on the surface or with special cleaning of the substrates [1]. Similar is realized for exfoliated graphene, which interacts weakly with an underlying graphene sublayer separating the upper layer from SiO₂, in comparison with the graphene directly on SiO₂ [11]. The decrease in 2D/G is due to the formation of graphene regions with different types and charge densities [12]. It leads to a broadening and, accordingly, a 2D peak intensity decrease. That is a result of the graphene interaction with a similar substrate in our case also containing regions with different potential.

For EA:THF, the 2D peak is shifted from 2690 to 2681 cm⁻¹ and 2D/G increases to 2.6 which points to extended graphene regions without PMMA. Therefore, EA functionalization of PMMA helps to remove PMMA, but graphene is functionalized too (D/G~0.7). Although the AFM thickness is ~5 nm. The ethanolamine functionalization of PMMA [13] makes it capable of retaining a sufficient number of solvent and H₂O molecules [14]. That forms the effective layer thickness increase. Additionally, graphene functionalization also occurs, which is specific, without long-term heat treatment and catalyzing agents [15]. A possible explanation for the graphene functionalization is the formation of reactive radicals during the PMMA functionalization, which as a result leads, together with ethanolamine, to the graphene functionalization. Such modification is not acceptable for some sensors.

Despite the PMMA partial removal with the 2D/G increasing (>1.5 is considered acceptable [2]) and the threshold point shifting to zero (Fig. 3), the conductivity and mobility decrease. That is explained by the formation of alternating regions with (\sim 30–60 % of the surface) and without PMMA along the channel after THF:water cleaning, which differs in properties. The alternating can even reduce the CVC slope (Fig. 2,*d*, 3, *a*, *b*) in contrast to TCE cleaning, and to some known results. Although the AFM probe partially removes most of the PMMA from the graphene and shifts the threshold point closer to zero. Nevertheless, it does not lead to a significant increase in the CVC slope [16], in comparison with graphene purified by more efficient methods [1]. Thus even a small PMMA residual amount reduces the CVC slope.



Fig. 3. CVC measuring scheme (a), CVC (b) of initial graphene with PMMA and rinsed in solvents and the inset is the I_D changes relative to I_{D0} depending on V_G , where I_{D0} is $I_D(V_G = 0 \text{ V})$

Hole mobility was estimated from CVC slope using a simple field-effect transistor equation: $\mu_h = [(\Delta I_D / \Delta V_G)(L/W)]/(C_{ox}/V_D)$, where *L*, *W* are the channel length and width; $C_{ox} = 5 \,\mu\text{F/cm}^2$ is the gate electrolyte double-layer specific capacitance [17–19]. The estimated μ_h for different structures are: 107 cm²/Vs for PMMA covered, 249 cm²/Vs for TCE, 202 cm²/Vs for THF:H₂O. Significant μ_h decrease for graphene cleaned by THF:H₂O can be explained by the integrity destruction of the PMMA layer, remained after TCE, with the formation of an island character of the residual PMMA layer (Fig. 2, *a*, *d*). These graphene regions' alternation with and without polar groups of PMMA molecules can form charge density level or even conductivity type differences along the channel. It can significantly reduce gate control [20, 12]. Nevertheless, the I_D change relative to I_{D0} depending on V_G has a higher slope than for TCE (Fig. 3, *b*, inset), so the THF:H₂O cleaned graphene resistive sensor has potentially higher sensitivity.

Conclusions

Trichloroethylene (TCE) cannot remove the near-surface PMMA layer. In comparison with TCE, for DAA:water there are: stress relaxation (2D peak shifts) with layer thickness increased due to swelling, but no 2D/G ratio change (~1.1). Also, graphene was partially removed due to the solvent high temperature (60 $^{\circ}$ C) while maintaining a high interaction energy of the remaining PMMA layer with graphene. For tetrahydrofuran (THF):water treatment, 2D/G increases to 1.6-1.9, and graphene regions without PMMA increase to ~50 nm and more. And according to AFM, redistributed PMMA still occupies about half of the graphene surface. 2D/G of AFM cleaned graphene was higher: ~ 2.7 which is consistent with pure graphene Raman data. Although at AFM PMMA remains in several regions. Thus, the graphene cleaning control only by Raman is not enough, AFM is required. For ethanolamine (EA):THF, the 2D peak is shifted and 2D/G is 2.6 which points to extended graphene regions without PMMA. Although the AFM thickness is ~5 nm due to swelling. Thus, EA functionalization helps to remove PMMA, but graphene is functionalized too (D/G~0.7). Despite the PMMA partial removal after THF:water treatment with the 2D/G increasing and the threshold point shifting to zero, the conductivity and mobility decrease. The alternating of with and without PMMA regions forms different charge density levels or even conductivity types along the channel, which in turn significantly reduces channel control from the gate. Nevertheless, such resistive sensors might have better sensitivity.

REFERENCES

1. Tyagi A., Mišeikis V., Martini L., Forti S., Mishra N., Gebeyehu Z. M., Giambra M. A., Zribi J., Frégnaux M., Aureau D., Romagnoli M., Beltram F., Coletti C. Ultra-clean high-mobility graphene on technologically relevant substrates, Nanoscale. 14 (6) (2022) 2167–2176.

2. Nekrasov N., Jaric S., Kireev D., Emelianov A. V., Orlov A. V., Gadjanski I., Nikitin P. I., Akinwande D., Bobrinetskiy I., Real-time detection of ochratoxin A in wine through insight of aptamer conformation in conjunction with graphene field-effect transistor, Biosensors and Bioelectronics. 200 (2021) 113890.

3. Romashkin A. V., Struchkov N. S., Lashkov A. V., Shpakov D. S., Nekrasov N. P., Emelianov A. V. Ammonia Recognition at Different Humidity with a Graphene Sensors Array Modified by a Focused Ion Beam. Proceedings of the 2022 International Conference on Actual Problems of Electron Devices Engineering, Saratov, IEEE, (2022) 186–190.

4. Hong J., Lee S., Seo J., Pyo S., Kim J., Lee T., A highly sensitive hydrogen sensor with gas selectivity using a PMMA membrane-coated Pd nanoparticle/single-layer graphene hybrid, ACS applied materials & interfaces. 7(6) (2015) 3554–3561.

5. An R., Huang L., Mineart K. P., Dong Y., Spontak R. J., Gubbins K. E., Adhesion and friction in polymer films on solid substrates: conformal sites analysis and corresponding surface measurements, Soft Matter. 13(19) (2017) 3492–3505.

6. Miller-Chou B. A., Koenig J. L., A review of polymer dissolution, Progress in Polymer Science 28(8) (2003) 1223–1270.

7. Zhuang B., Li S., Li S., Yin J., Ways to eliminate PMMA residues on graphene – superclean graphene, Carbon. 173 (2021) 609–636.

8. Evchuk I. Y., Musii R. I., Makitra R. G., Pristanskii R. E., Solubility of polymethyl methacrylate in organic solvents, Russian journal of applied chemistry. 78 (10) (2005) 1576–1580. 9. Barsukov L. A., Nekrasov N. P., Romashkin A. V., Bobrinetskiy I. I., Levin D. D., Nevolin V. K., Improved polymer residuals removing after the graphene transfer to enhance sensors performance, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.3) (2023) 44–49.

10. Bobrinetskiy I., Emelianov A., Nasibulin A., Komarov I., Otero N., Romero P. M., Photophysical and photochemical effects in ultrafast laser patterning of CVD graphene, Journal of Physics D: Applied Physics. 49(41) (2016) 41LT01.

11. Ferrari A. C., Basko D. M., Raman spectroscopy as a versatile tool for studying the properties of graphene, Nature nanotechnology. 8 (4) (2013) 235–246.

12. Martin J., Akerman N., Ulbricht G., Lohmann T., Smet J. V., Von Klitzing K., Yacoby A., Observation of electron-hole puddles in graphene using a scanning single-electron transistor, Nature physics. 4(2) (2008) 144–148.

13. Yu Y., Brown G. R., Carbon-13 NMR study of the kinetics of the functionalization of poly (methyl acrylate) by reaction with ethanolamine, Macromolecules. 25(24) (1992) 6658–6663.

14. Lewis C. L., Anthamatten M., Synthesis, swelling behavior, and viscoelastic properties of functional poly (hydroxyethyl methacrylate) with ureidopyrimidinone side-groups. Soft Matter, 9 (15) (2013) 4058–4066.

15. Dao T. D., Hong J. E., Ryu K. S., Jeong H. M., Super-tough functionalized graphene paper as a high-capacity anode for lithium ion batteries, Chemical Engineering Journal. 250 (2014) 257–266.

16. Choi W., Shehzad M. A., Park S., Seo Y., Influence of removing PMMA residues on surface of CVD graphene using a contact-mode atomic force microscope, RSC advances. 7(12) (2017) 6943–6949.

17. Ruslinda A. R., Tanabe K., Ibori S., Wang X., Kawarada H., Effects of diamond-FETbased RNA aptamer sensing for detection of real sample of HIV-1 Tat protein. Biosensors and Bioelectronics, 40 (1) (2013) 277–282.

18. **Takagi S. I., Toriumi A.,** Quantitative understanding of inversion-layer capacitance in Si MOSFET's. IEEE Transactions on Electron Devices, 42 (12) (1995) 2125–2130.

19. Chen P. W., Tseng C. Y., Shi F., Bi B., Lo Y. H., Measuring electric charge and molecular coverage on electrode surface from transient induced molecular electronic signal (TIMES). Scientific reports, 9(1) (2019) 1–10.

20. Zhang Y., Yuan Y., Cao G., Han C., Li X., Wang X., Zhang G., Geng Li, Liu W., A freshbias photoresponse of graphene field-effect transistor: An electrical tunable fast dipole moment generation, Carbon. 173 (2021) 322–328.

THE AUTHORS

NEKRASOV Nikita P. 8141147@gmail.com ORCID: 0000-0003-1417-0177

LEVIN Denis D. skaldd@yandex.ru ORCID: 0000-0002-8414-6191

ROMASHKIN Al exey V. romaleval@gmail.com ORCID: 0000-0002-0101-6122

BOBRINETSKIY Ivan I. bobrinet@mail.ru ORCID: 0000-0003-2380-2594 BARSUKOV Leonty A. leonty.barsukov@gmail.com ORCID: 0000-0002-4802-0014

NEVOLIN Vladimir K.

vkn@miee.ru ORCID: 0000-0003-4348-0377

NIKITIN Konstantin G.

halkwww@mail.ru ORCID: 0000-0002-0457-4568

Received 05.07.2023. Approved after reviewing 24.08.2023. Accepted 26.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 621.315.592 DOI: https://doi.org/10.18721/JPM.163.238

Structural surface characteristics of aluminum-gallium nitride films on silicon carbide nanolayers on silicon

A.S. Grashchenko¹, S.A. Kukushkin¹, Sh.Sh. Sharofidinov²

¹Institute for Problems in Mechanical Engineering RAS, St. Petersburg, Russia;

² Ioffe Institute, St. Petersburg, Russia

^{III} asgrashchenko@bk.ru

Abstract. Experimental studies of the surface morphology of AlGaN films formed on nanometer-thick SiC layers synthesized on Si by atom substitution were performed. Structural characteristics of the surface of AlGaN/SiC/Si and AlGaN/AlN/SiC/Si heterostructures grown on Si with orientations (001), (011) and (111) were studied by atomic force microscopy. It is shown that the Si orientation has a significant influence on the surface morphology of AlGaN films. The surface roughness and characteristic dimensions of the AlGaN surface structure on nano-SiC/Si with and without an AlN buffer layer were measured. It is shown that the buffer AlN layer leads to a change in the surface structure dimensions of AlGaN layers._

Keywords: AFM, thin films, heterostructures, nano-SiC/Si, AlGaN

Funding: The work was performed within the framework of the state order of FSUE IPME RAS FFNF-2021-0001 of the Ministry of Science and Higher Education of the Russian Federation.

Citation: Grashchenko A.S., Kukushkin S.A., Sharofidinov Sh.Sh., Structural surface characteristics of aluminum-gallium nitride films on silicon carbide nanolayers on silicon, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 223–227. DOI: https://doi.org/10.18721/JPM.163.238

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.315.592 DOI: https://doi.org/10.18721/JPM.163.238

Структурные характеристики поверхности пленок нитрида алюминия-галлия на нанослоях карбида кремния на кремнии

А.С. Гращенко¹⊠, С.А. Кукушкин¹, Ш.Ш. Шарофидинов²

¹Институт проблем машиноведения РАН, Санкт-Петербург, Россия;

² Физико-технический институт имени А. Ф. Иоффе РАН, Санкт-Петербург, Россия

[⊠] asgrashchenko@bk.ru

Аннотация. В работе проведены экспериментальные исследования морфологии поверхности пленок AlGaN, сформированных на слоях SiC нанометровой толщины, синтезированных на Si методом замещения атомов. Методом атомно-силовой микроскопии изучены структурные характеристики поверхности гетероструктур AlGaN/SiC/Si и AlGaN/AlN/SiC/Si, выращенных на Si с ориентациями (011) ,(001) и (111). Показано, что ориентация Si оказывает существенное влияние на морфологию поверхности пленок AlGaN. Измерена шероховатость поверхности и характерные размеры структуры поверхности AlGaN на нано-SiC/Si с буферным слоем AlN и без него. Показано, что буферный слой AlN приводит к изменению характерных размеров элементов структуры поверхности слоев AlGaN.

Ключевые слова: ACM, тонкие пленки, гетероструктуры, нано-SiC/Si, AlGaN

[©] Grashchenko A.S., Kukushkin S.A., Sharofidinov Sh.Sh., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Финансирование: Работа выполнена в рамках государственного задания ФГУП ИПМаш РАН № ФСНФ-2021-0001 Министерства науки и высшего образования Российской Федерации.

Ссылка при цитировании: Гращенко А.С., Кукушкин С.А., Шарофидинов Ш.Ш. Структурные характеристики поверхности пленок нитрида алюминия-галлия на нанослоях карбида кремния на кремнии // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 223–227. DOI: https://doi. org/10.18721/JPM.163.238

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Thin films of aluminum-gallium nitride (AlGaN) have unique physical and mechanical properties that make them an ideal material for creating high-performance electronic and optoelectronic devices such as LEDs, lasers, and transistors [1]. They have high thermal stability, high electrical conductivity, and a wide range of optical properties. Optimization of growth conditions and crystal direction can further improve the properties of these structures for various practical applications. Integration of AlGaN layers with silicon technologies is an important step in microelectronics development. It enables enhanced capabilities and performance of devices, creating high-performance LEDs, lasers, transistors, and other devices that are ideal for use in lighting, displays, and optical communications. Integrating AlGaN layers with silicon technologies also enables the creation of high-frequency transistors and other electronic devices with high performance and reliability, which reduces manufacturing costs and improves the cost-effectiveness of electronic device production. However, the growth of AlGaN layers on Si silicon crystals causes problems with mismatch of lattice parameters and thermal expansion coefficients between AlGaN and Si. This leads to the appearance of defects in the structure such as dislocations and disturbances in crystal orientation. In addition, the growth of AlGaN layers on Si wafers creates problems with controlling the composition and concentration of impurities in the structure, which can lead to changes in the optical and electrical properties of the material and reduce the performance of devices. High growth temperature of high quality AlGaN layers on Si crystals can also lead to structure degradation and device performance degradation. To solve these problems, various methods are used to compensate for inconsistencies in lattice parameters, in particular, various kinds of buffer layers are created on the silicon surface [2, 3].

To solve these problems, it is proposed to use Si substrates with a nanometer-thick silicon carbide layer (nano-SiC) synthesized by the atom substitution method [4] for the growth of AlGaN thin films. This nano-SiC/Si hybrid substrate configuration allows the growth of AlGaN layers on a SiC layer with a surface roughness of 0.5 nm, which is comparable to industrial SiC crystals. This solution avoids the appearance of defects in the structure and controls the composition and concentration of impurities in the structure. In this work AlGaN layers grown directly on nano-SiC/Si and on nano-SiC/Si with a buffer layer of aluminum nitride (AlN) are investigated. Studies of the surface morphology of AlGaN on nano-SiC thin films on Si with orientations (001), (011) and (111) is an important task for materials science.

Materials and Methods

Growth of AlGaN layers was performed on Si crystals with nanometer-thick SiC layers nano-SiC. The nano-SiC structures were synthesized using the atomic substitution method [5] on Si *p*-type conductivity substrates doped with boron with crystallographic directions (001), (011), and (111). The Si crystal with the (001) orientation was deflected from the base direction by 4° to the (111) direction. The SiC layers were synthesized in an atmosphere of carbon monoxide (CO) and silicon tetrahydride (SiH₄) for 10 minutes at 1100°C. The pressure inside the reactor during the synthesis was 0.5, 0.7, and 2.3 Torr for Si substrates with crystallographic orientations (001), (011), and (111), respectively. The thickness of the synthesized SiC layers was determined by analyzing spectra obtained by spectral ellipsometry on a Woollam M-2000D instrument. The surface roughness of the SiC films was measured by optical profilometry on a Zygo New View 6000. Thin films of AlGaN

© Гращенко А. С., Кукушкин С. А., Шарофидинов Ш.Ш., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

were grown by the HVPE method [6] on hybrid SiC/Si substrates with and without an AlN buffer layer. Layers of AlGaN were grown at 1020 °C in an ammonia and argon atmosphere with a total flux of 1 and 4 liters per minute, respectively. Aluminum and gallium atoms were delivered to the growth zone using a hydrogen chloride flow of 0.2 and 0.1 liter per minute, respectively. In the case of AlGaN films grown directly on hybrid SiC/Si substrates, the AlGaN layer thickness was 6-9 μ m. Buffer layers of AlN thickness 2-3 μ m were grown by the HVPE method immediately before the AlGaN films were formed. In the case of AlGaN/AlN/SiC/Si heterostructures, the thickness of AlGaN layers was 3-5 μ m. The surface morphology of the AlGaN films was studied by atomic force microscopy AFM in contact mode on an Easy Scan Nanosurf microscope.

Results and Discussion

The study of nano-SiC/Si hybrid substrates by spectral ellipsometry showed that the thicknesses of all SiC layers synthesized on Si substrates are the same and equal to 3 nm. According to optical profilometry data, the surface roughness of all nano-SiC/Si hybrid substrates is 0.4–0.6 nm.

A study of the surface morphology of AlGaN thin films by AFM showed that the morphology of AlGaN layers is significantly different, depending on which orientation of the Si substrates these layers were grown on. This is not surprising since it was shown in [7] that when growing by the coordinated atom substitution method, a smooth SiC surface of orientation (111) is formed only on the Si substrate (111). In the case of SiC growth on the (001) and (011) Si faces, the SiC layer surface is covered by pyramids with inclined orientation faces (111). As a result, these surfaces resemble sawtooth structures. AlN, GaN and AlGaN films grow on these surfaces in the form of hexagonal c-axis blocks inclined with respect to the substrate plane, which will be directed perpendicular to the SiC(111) structure plane, that is, parallel to the SiC(111) plane will form (0001) planes of blocks consisting of Al_xGa_{1-x}N with different composition. Such inclined hexagonal layers are called semi-polar layers [8]. Semipolar structures grow on SiC/Si hybrid substrates, both with and without an AlN buffer layer.

Morphology studies have shown that the characteristic geometric dimensions of the AlGaN layer surface structural elements on nano-SiC/Si substrates and on AlN/SiC/Si substrates are different (Fig. 1).



Fig. 1. AFM surface images of AlGaN/SiC/Si(001) (*a*) and AlGaN/AlN/SiC/Si(001) (*b*) heterostructures

Thus, the size of the sawtooth structures grown on the AlN/SiC/Si(001) substrate is smaller than the geometrical size of the structures grown on the nano-SiC/Si substrate. In the case of AlGaN films grown on Si substrates with (001) orientation, the surface has a sawtooth structure which consists of ridge-like clusters. The average surface roughness of the AlGaN/SiC/Si(001) and AlGaN/AlN/SiC/Si(001) heterostructures is 810 and 680 nm, respectively. The slope planes in the case of the AlGaN/SiC/Si(001) heterostructure are inclined $45\pm5^{\circ}$ and $20\pm3^{\circ}$ relative to the general plane of the sample surface, whereas they are inclined $40\pm5^{\circ}$ and $25\pm2^{\circ}$ for the AlGaN layer on AlN/SiC/Si(001). The height of the ridge-like clusters on the AlGaN surface on nano-SiC/Si(001) and AlN/SiC/Si(001) is 2–4 µm and 1–3 µm, respectively. Thus, in the case of growth of AlGaN films on nano-SiC/Si(001), the use of the AlN buffer layer leads to changes in the characteristic sizes and orientations of the crystal structural elements of the surface.

The surface of AlGaN films grown on Si substrates with orientation (011) has a mosaic structure with pronounced steps (Fig. 2). The surface structure of AlGaN films formed on hybrid nano-SiC/Si(011) substrate presents smooth terraces up to 20 μ m2 with sharp slopes at the edges. The terraces occupy 70% and 55% of the total AFM image area of AlGaN/SiC/Si(011) and AlGaN/AlN/SiC/Si(011) heterostructures, respectively. The slope of the terraces and slopes relative to the general plane of the sample surface in the case of AlGaN on SiC/Si(011) is 5±1° and 25±5°, respectively. The height of the slopes of the AlGaN/SiC/Si(011) surface structure according to AFM data is 2.0±0.3 μ m. The slope of the terraces and slopes relative to the general plane of the sample surface in the case of AlGaN on AlN/SiC/Si(011) is 5.3±0.2° and 28±5°, respectively. The height of the slopes of the AlGaN/AlN/SiC/Si(011) surface structure is 2–5 μ m according to AFM data. According to AFM data, the RMS roughness of AlGaN films formed on SiC/Si(011) and AlN/SiC/Si(011) substrates is 480 and 700 nm, respectively, that is, in contrast to SiC/Si(001) and AlN/SiC/Si(001) substrates, pre-grown AlN layer resulted in increased roughness.

Analysis of AFM images (Fig. 3) of AlGaN layers grown on nano-SiC/Si(111) and AlN/SiC/Si(111) heterostructures showed that the surface was formed in the form of hills during growth. According to AFM data, the hills have a rounded shape. The surface of AlGaN film on nano-SiC/Si is covered by ridge-like clusters with base diameter of $10-30 \mu m$ and height of 200-400 nm. In the case of the AlGaN/AlN/SiC/Si heterostructure, the ridge-like structure has a base diameter of $20-50 \mu m$ and a height of 300-500 nm. The RMS surface roughness of AlGaN films in both cases is 60 nm. The slope of the side hillsides of the AlGaN layer surface on nano-SiC/Si relative to the general sample plane is $1.5\pm0.5^{\circ}$. The slope of lateral slopes of hilly structure of AlGaN on AlN/SiC/Si layers relative to the general plane of the sample is from $2.0\pm0.5^{\circ}$. In AlGaN films on nano-SiC/Si (111) growth defects in the form of growth pits (pit) were found, the formation of which is associated with the peculiarities of growth of AlGaN films on defective and not perfect in crystal quality, places of nano-SiC/Si hybrid substrates.



Fig. 2. AFM surface images of AlGaN/SiC/Si(011) (*a*) and AlGaN/AlN/SiC/Si(011) (*b*) heterostructures



Fig. 3. AFM surface images of AlGaN/SiC/Si(111) (*a*) and AlGaN/AlN/SiC/Si(111) (*b*) heterostructures

Conclusion

Thus, in the present work the structural characteristics of AlGaN thin films formed by the HVPE method on nano-SiC/Si substrates with Si (001), (011) and (111) orientation was studied for the first time. The characteristic structural parameters of the surface of AlGaN layers on nano-SiC/Si have been determined by AFM method. It is shown that the surface structure of AlGaN layers grown on Si substrates with orientations (001), (011) and (111) is fundamentally different. As a result of studies, it was found that the buffer AlN layer grown on nano-SiC layers formed on Si substrates of orientation (001), leads to a decrease in the characteristic dimensions of the structural elements of the surface. When AlGaN films grow on nano-SiC layers formed on Si orientation (011) substrates, studies have shown that the opposite situation occurs, namely, the presence of a buffer AlN layer grown on nano-SiC layers formed on Si orientation (111) substrates the characteristic sizes of crystal clusters on the surface. The buffer AlN layer grown on nano-SiC layers formed on Si orientation (111) substrates characteristic sizes of crystal clusters on the surface.

Acknowledgments

Experimental studies were carried out using the unique scientific facility "Physics, chemistry, and mechanics of crystals and thin films" (Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences, St. Petersburg).

REFERENCES

1. Alhassan A. I., Farrell R. M., Saifaddin B., Mughal A., Wu F., DenBaars S. P., Nakamura S., Speck J. S., High luminous efficacy green light-emitting diodes with AlGaN cap layer, Optics express. 24 (16) (2016) 17868–17873.

2. Zhang Q., Yin X., Martel E., Zhao S., Molecular beam epitaxy growth and characterization of AlGaN epilayers in nitrogen-rich condition on Si substrate, Materials Science in Semiconductor Processing. 135 (2021) 106099.

3. Arifin P., Sutanto H., Subagio A., Plasma-assisted MOCVD growth of non-polar GaN and AlGaN on Si(111) substrates utilizing GaN-AlN buffer layer, Coatings. 12 (1) (2022) 94.

4. Kukushkin S.A., Osipov A.V., Theory and practice of SiC growth on Si and its applications to wide-gap semiconductor films, Journal of Physics D: Applied Physics. 47 (31) (2014) 313001.

5. Grashchenko A.S., Kukushkin S.A., Osipov A.V., Coating of a nanostructured profiled Si surface with a SiC layer, Technical Physics Letters. 46 (2020) 1012–1015.

6. Sharofidinov S.S., Kukushkin S.A., Red'kov A.V., Grashchenko A.S., Osipov A.V., Growing III–V semiconductor heterostructures on SiC/Si substrates, Technical Physics Letters. 45 (2019) 711–713.

7. Kukushkin S.A., Osipov A.V., Soshnikov I.P., Growth of epitaxial SiC layer on Si (100) surface of n- and p-type of conductivity by the atoms substitution method, Reviews on Advanced Materials Science. 52 (2017) 29–42.

8. Bessolov V.N., Konenkova E.V., Kukushkin S.A., Osipov A.V., Rodin S.N., Semipolar gallium nitride on silicon: technology and properties, Reviews on Advanced Materials Science. 38 (1) (2014) 75–93.

THE AUTHORS

GRASHCHENKO Aleksandr S. asgrashchenko@bk.ru ORCID: 0000-0002-4746-4238 SHAROFIDINOV Shukrillo Sh. shukrillo71@mail.ru ORCID: 0000-0003-0354-5981

KUKUSHKIN Sergey A. sergey.a.kukushkin@gmail.com ORCID: 0000-0002-2973-8645

Received 14.07.2023. Approved after reviewing 30.08.2023. Accepted 30.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 538.958 DOI: https://doi.org/10.18721/JPM.163.239

Optical anisotropy of black phosphorus characterized by FTIR spectroscopy methods

S.A. Khakhulin[⊠], O.E. Lakuntsova, D.D. Firsov, O.S. Komkov

St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia

⊠khsmn@ya.ru

Abstract. The present study employs the FTIR spectroscopy methods, such as polarized transmittance measurements and the reflectance anisotropy spectroscopy technique, to characterize the optical properties of black phosphorus - a layered semiconductor with a narrow band gap. Our results reveal a notable crystal absorption anisotropy within the 0.26-0.42 eV range with strong linear dichroism, wherein a polarization-dependent feature is observed in the reflectance anisotropy spectra with a maximum near 0.33 eV. This feature is believed to be related to a direct interband transition E_0 , which is permitted for linearly polarized incident radiation along the AC crystal direction and forbidden for the ZZ direction.

Keywords: Black phosphorous, reflectance anisotropy spectroscopy, in-plane anisotropy, FTIR spectroscopy

Funding: The study was supported by the Russian Science Foundation, grant 22-29-20141 and the St. Petersburg Science Foundation (grant under agreement 18/2022 dated April 14, 2022).

Citation: Khakhulin S.A., Lakuntsova O.E., Firsov D.D., Komkov O.S., Optical anisotropy of black phosphorus characterized by FTIR spectroscopy methods, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 228–232. DOI: https://doi.org/10.18721/JPM.163.239

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 538.958 DOI: https://doi.org/10.18721/JPM.163.239

Характеризация анизотропии оптических свойств черного фосфора методами ИК фурье-спектроскопии

С.А. Хахулин[⊠], О.Е. Лакунцова, Д.Д. Фирсов, О.С. Комков

Санкт-Петербургский государственный электротехнический университет «ЛЭТИ», Санкт-Петербург, Россия

⊠khsmn@ya.ru

Аннотация. Методами ИК фурье-спектроскопии, такими как поляризованное пропускание и анизотропное отражение, охарактеризован кристалл черного фосфора – узкозонного слоистого полупроводника. Получены результаты существенной анизотропии вблизи края поглощения материала, а также поляризационно-зависимый сигнал при энергии, соответствующей прямому межзонному переходу.

Ключевые слова: черный фосфор, спектроскопия анизотропного отражения, ИК фурье-спектроскопия, узкозонные полупроводники, слоистые полупроводники

Финансирование: Работа выполнена при поддержке Российского научного фонда (грант № 22-29-20141) и Санкт-Петербургского научного фонда (грант по договору № 18/2022 от 14 апреля 2022 г.).

© Khakhulin S.A., Lakuntsova O.E., Firsov D.D., Komkov O.S., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Хахулин С.А., Лакунцова О.Е., Фирсов Д.Д., Комков О.С. Характеризация анизотропии оптических свойств черного фосфора методами ИК фурьеспектроскопии // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 3.2 № .16. С. 228–232. DOI: https://doi.org/10.18721/JPM.163.239

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Black phosphorus is a direct-gap layered semiconductor crystal with an interband transition energy of approximately 0.3 eV [1], which corresponds to the mid-IR range. The crystal consists of atomic layers connected to each other by weak van der Waals forces, enabling the production of single semiconductor layers via exfoliation. As the number of layers in the structure decreases, the material's band gap increases, with a monolayer having a value of approximately 2 eV. This property makes it possible to create photonic devices with a broad optical range from mid-IR to visible using black phosphorus layers [2, 3].

In the plane of layer, the black phosphorus crystal has two orthogonal nonequivalent crystallographic directions known as 'zigzag' (ZZ) and 'armchair' (AC). Differences in chemical bond lengths and atomic arrangement [4] result in significant anisotropy of optical properties. According to literature data, when the incident radiation is polarized along the AC direction, the absorption of optical radiation is orders of magnitude more intense [1]. This feature is crucial for creating polarization-sensitive emitters, detectors and modulators of optical radiation based on the material under consideration [5].

Despite the extensive research on the optical properties of black phosphorous, recent studies [6, 7] using photoluminescence have yielded varying bandgap energy values. The application of transmittance and reflectance spectroscopies [1, 8] in the corresponding studies has been limited due to the smooth nature of the spectra, making it challenging to obtain precise information about optical transition values.

As a result, we present an investigation of the optical properties of black phosphorus near its absorption edge using various Fourier-transform infrared (FTIR) spectroscopy methods with linearly polarized probe light. Additionally, to improve the accuracy of measurements and obtain more detailed information we use a novel modulation method of FTIR reflectance anisotropy spectroscopy (RAS).

Materials and Methods

In this work, a synthetic black phosphorus crystal bulk manufactured by HQGraphene was studied. To study the practically significant band structure characteristics of semiconductor black phosphorus, we employ polarization-sensitive optical spectroscopy techniques. Specifically, we utilize transmittance and reflectance spectroscopy while varying the direction of incident radiation polarization along the AC and ZZ crystallographic directions. By utilizing these methods, we are able to determine the absorption edge of black phosphorus and analyze its dependence on the polarization direction of the incident radiation.

To obtain detailed information regarding the in-plane anisotropy of black phosphorus optical properties, we employ a novel method of modulation FTIR reflectance anisotropy spectroscopy [9]. This method involves modulating the direction of probe radiation linear polarization within the sample plane along two orthogonal directions, namely x and y. Consequently, the measured value in this technique is the normalized difference in reflectance coefficients, expressed as $\Delta R/R = 2(R_x - R_y)/(R_x + R_y)$. In the case of black phosphorus, the two orthogonal directions are AC and ZZ.

All measurements were carried out using the Vertex 80 FTIR spectrometer. An InSb photodetector with the effective spectral range of 0.23-1.55 eV (0.8-5.4 um) was employed. ZnSe wire grid polarizers, operating within the spectral range of 0.062-0.827 eV (1.5-20 um), were utilized. Modulation of linear polarization was achieved with a ZnSe photoelastic modulator PEM-100 manufactured by Hinds Instruments.

© Хахулин С.А., Лакунцова О.Е., Фирсов Д.Д., Комков О.С., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Results and Discussion

The obtained transmittance spectra of black phosphorus are presented in Fig. 1. There are two different absorption edges for different polarization directions of the incident radiation. A sharp absorption edge was observed within the range of 0.26-0.3 eV with the position of linear polarization along the AC direction (Fig. 1, dash-dotted line). In the case of the ZZ direction, a uniform decrease was obtained within the range of 0.32-0.44 eV (Fig. 1, dotted line).



Fig. 1. Transmittance spectra of black phosphorous crystal. Spectrum obtained with direction of polarization along AC is dot-dashed, along ZZ is dotted. Spectrum with unpolarized probe radiation is solid

The dissimilarity in the transmittance curves' behavior is attributed to the variance in previously discussed oscillator strength, leading to intense absorption in the AC direction. Similarly, the polarized reflectance curves exhibit analogous behavior when the polarization of the incident radiation aligns with the corresponding crystallographic directions. As a result of such strong linear dichroism, transmittance spectrum with unpolarized incident radiation has a complicated form (Fig. 1, solid line). It should be noted that the spectrometer radiation is partially polarized, and the corresponding transmittance spectrum has a slightly reduced amplitude compared to the average of the spectra obtained for the AC and ZZ polarizations.

The presented transmittance spectra exhibit weak spectral features near an energy of 0.29 eV, which is attributed to the absorption of carbon dioxide CO_2 in the atmosphere. The state of the surface of industrially obtained black phosphorus crystals poses a significant challenge in the registration and interpretation of ordinary reflectance spectra, as well as the specifics of the mid-IR range in which studies are conducted. For this reason, reflectance spectra with linearly polarized probe light exhibit low signal-to-noise ratio wherein demonstrate the same spectral behavior with strong linear dichroism as transmittance spectra.

The use of a FTIR reflectance anisotropy spectroscopy modulation technique significantly enhances the signal-to-noise ratio and enables the detection of relatively small changes in the reflectance coefficient. This is made possible by modulating the direction of linear polarization along two in-pane orthogonal crystallographic axes described earlier in the *Materials and Methods* section.

The reflectance anisotropy (RA) spectrum obtained by the FTIR RAS method has a broad negative peak in the range of 0.26-0.42 eV (Fig. 2). This signal is associated with a significant anisotropy of the reflectance coefficients of black phosphorus in two orthogonal directions, ZZ and AC. This result correlates with polarized transmittance and reflectance measurements discussed earlier.



Fig. 2. Reflectance anisotropy spectrum of black phosphorous crystal. The peak associated with the main direct interband optical transition E_0 is marked by arrow

A relatively narrow peak of a different sign stands out against the background of a broad spectral line in the RA spectrum. An extremum of that peak is at an energy of 0.33 eV. Such a feature with an amplitude about several percent can be associated with a direct interband transition, which is allowed when the polarization of the incident light is along the AC direction and forbidden in the case of ZZ. In the study by Chen et al. (2019) [6], the energy of this transition was determined via photoluminescence and found to be 0.334 eV, while Zhang et al. (2020) [7] reported it to be 0.343 eV.

Conclusion

Thus, we have experimentally characterized the optical properties of black phosphorus that are related to the anisotropy of optical transitions in this material by methods of FTIR spectroscopy including the FTIR-RAS method. Within the 0.26–0.42 eV range, there exists a pronounced linear dichroism, accompanied by a polarization-dependent characteristic at 0.33 eV associated with the direct interband transition. The information obtained is in great demand for the development of polarization-sensitive photodetectors and light emitters in the mid-IR range based on black phosphorus.

REFERENCES

1. Wang X., Lan S., Optical properties of black phosphorus, Advances in Optics and photonics. 8 (4) (2016) 618–655.

2. Xia F., Wang H., Hwang J.C., Neto A.C., Yang L., Black phosphorus and its isoelectronic materials, Nature Reviews Physics. 1 (2019) 306-317.

3. Huang L., Dong B., Guo X., Chang Y., Chen N., Huang X., Liao W., Zhu C., Wang H., Lee C., Ang K-W., Waveguide-Integrated Black Phosphorus Photodetector for Mid-Infrared Applications, ACS Nano 13 (913 (2019) (1–921.

4. Akahama Y., Endo S., Narita S., Electrical properties of black phosphorus single crystals, Journal of the Physical Society of Japan. 52 (6) (1983) 2148–2155.

5. Deng B., Frisenda R., Li C., Chen X., Castellanos-Gomez A., Xia F., Progress on black phosphorus photonics, Advanced Optical Materials. 6 (19) (2018) 1800365.

6. Chen C., Chen F., Chen X., Deng B., Eng B., Jung D., Guo Q., Yuan S., Watanabe K., Taniguchi T., Lee M. L, Xia F., Bright Mid-Infrared Photoluminescence in Thin-Film Black Phosphorus. 19 (3) (2019) 1488–1493.

7. Zhang Y., Wang S., Chen S., Zhang Q., Wang X., Zhu X., Zhang X., Xu X., Yang T., He M., Yang X., Li Z., Chen X., Wu M., Lu Y., Ma R., Lu W., Pan A., Wavelength-Tunable Mid-Infrared Lasing from Black Phosphorus Nanosheets. 32 (17) (2020) 1808319.

8. Xin W., Jiang H.B., Sun T.Q., Gao X.G., Chen S.N., Zhao B., Yang J.L., Liu Z.B., Guo C.L., Optical anisotropy of black phosphorus by total internal reflection, Nano Materials Science. 1 (4) (2019) 304–309.

9. Firsov D.D., Khakhulin S.A., Komkov O.S., Fourier-Transform Infrared Reflection Anisotropy Spectroscopy of Semiconductor Crystals and Structures: Development and Application in the Mid-Infrared, Applied Spectroscopy. 77 (5) (2023) 470–481.

THE AUTHORS

KHAKHULIN Semyon A. khsmn@ya.ru ORCID: 0000-0002-1780-2013

LAKUNTSOVA Olga E. olya-lakuncova@mail.ru ORCID: 0000-0000-0000-0000 FIRSOV Dmitrii D. ddfirsov@gmail.com ORCID: 0000-0001-7608-9580

KOMKOV Oleg S. okomkov@yahoo.com ORCID: 0000-0002-8999-1175

Received 05.07.2023. Approved after reviewing 09.08.2023. Accepted 09.08.2023.

© Хахулин С.А., Лакунцова О.Е., Фирсов Д.Д., Комков О.С., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Conference materials UDC: 691.175.5/.8 DOI: https://doi.org/10.18721/JPM.163.240

Production of polyimide nonwoven fabric with low dielectric permittivity

A.M. Kamalov^{1,2,} V.E. Kraft¹[⊠], G.V. Vaganov², A.S. Nesterova², M.E. Borisova¹, E. M. Ivan'kova², V.E. Yudin²

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² Institute of Macromolecular Compounds RAS, St. Petersburg, Russia,

⊠ kraft.ve@edu.spbstu.ru

Abstract. This work is devoted to the production of nonwoven polyimide material by electroforming from aqueous solutions of polyamide acid salts based on pyromellitic dianhydride (PMDA) and 4,4'-oxydiphenylenediamine (ODA). The dielectric and mechanical properties of the nonwoven material were determined over a wide frequency and temperature range. The dielectric permittivity of the material at 20 °C and a frequency of 1 Hz was 1.5.

Keywords: electroforming, polyimide, nonwoven material, relative permittivity, elastic modulus

Citation: Kamalov A.M., Kraft V.E., Vaganov G.V., Nesterova A.S., Borisova M.E., Ivankova E.M., Yudin V.E., Production of polyimide nonwoven fabric with low dielectric permittivity, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 233–238. DOI: https://doi.org/10.18721/JPM.163.240

Funding: The work was performed within the framework of RSF grant 23-79-01112.

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК: 691.175.5/.8 DOI: https://doi.org/10.18721/JPM.163.240

Получение полиимидного нетканого материала с низкой диэлектрической проницаемостью

А.М. Камалов^{1,2,} В.Е. Крафт¹[⊠], Г.В. Ваганов², А.С. Нестерова², М.Э. Борисова¹, Е. М. Иванькова², В.Е. Юдин²

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия,

² Институт высокомолекулярных соединений РАН, Санкт-Петербург, Россия,

[⊠] kraft.ve@edu.spbstu.ru

Аннотация. Данная работа посвящена получению нетканого полиимидного материала методом электроформования из водных растворов солей полиамидокислоты на основе пиромеллитового диангидрида (ПМ) и 4,4'-диаминдифенилового эфира (ДАДФЭ). Были определены диэлектрические и механические свойства нетканого материала в широком интервале частот и температур. Диэлектрическая проницаемость материала при температуре 20 °C и частоте 1 Гц составила 1.5.

Ключевые слова: электроформование, полиимид, нетканый материал, диэлектрическая проницаемость, модуль упругости

© Kamalov A.M., Kraft V.E., Vaganov G.V., Nesterova A.S., Borisova M.E., Ivankova E.M., Yudin V.E., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Камалов А.М., Крафт В.Е., Ваганов Г.В., Нестерова А.С., Борисова М.Э., Иванькова Е.М., Юдин В.Е., Получение полиимидного нетканого материала с низкой диэлектрической проницаемостью // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 233–238. DOI: https:// doi.org/10.18721/JPM.163.240

Финансирование: Работа выполнена в рамках гранта РНФ 23-79-01112.

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In modern integrated circuits, materials with low dielectric constant ε are needed to reduce resistive capacitance delay and minimize crosstalk. Flexible printed circuit boards (FPCs) are widely used in complex electronic products because of their outstanding characteristics such as light weight, size and flexibility. Polyimide is most commonly used for flexible printed circuit boards as an insulating dielectric layer between metals because of its high mechanical and heat resistance properties [1]. However, polyimide films have a relatively high dielectric permittivity (3–3.5), which does not meet the requirements for the design of modern integrated circuits. Thus, the creation of composites based on polyimides with low dielectric permittivity has become one of the actual problems in the field of high-frequency and high-speed signal transmission.

Recently, the technology of electroforming nanofibers from polymer solutions, in particular polyimides, has been increasingly developed. Thus, composite materials with unique properties are produced. High values of specific surface (porosity of the material) enable their application in power engineering and medicine: porous electrodes, interelectrode separators, filters and sensors [2,3].

In this research we study a nonwoven polyimide (PI) material obtained by electroforming (EF) from aqueous solutions of triethylammonium salt of poly (amic acid) (SPAA) based on pyromellite dihydride (PMDA) and 4,4'-diamindiphenyl ether (ODA) [4,5].

The aim of the work is to obtain and study the dielectric and mechanical properties of polyimide nonwoven materials obtained by electroforming.

Materials and Methods

The synthesis of PAA salts (SPAA) was performed at Laboratory № 1 (Synthesis of High-Temperature Resistant Polymers) of the Institute of Macromolecular Compounds Russian Academy



Fig. 1. Chemical formula of polyimide PMDA-ODA

of Sciences (IMC RAS); the detailed synthesis process is described in our previous work [4]. The process of electroforming is significantly affected by the parameters presented in Table 1.

Table 1

Process parameters (experiment)	Optimal values according to literature data [1]		
$\gamma = 10^{-2} \mathrm{S/m}$	$\gamma = 10^{-6} - 10^{-2} \text{ S/m}$		
$\sigma = 0.031 \text{ N/m}$	σ < 0.05 N/m		
U = 20.5 kV	U = 20 - 30 kV		

Parameters of electroforming of nonwoven material

© Камалов А.М., Крафт В.Е., Ваганов Г.В., Нестерова А.С., Борисова М.Э., Иванькова Е.М., Юдин В.Е., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Here γ is the specific volumetric conductivity. Low conductivity leads to slowing down of the EF process, due to fast relaxation of the free charge under the influence of an external electric field. High specific conductivity contributes to reduction of fiber diameters due to greater tensile force in the electric field.

The surface tension coefficient of the solution σ is one of the determining parameters of the electroforming process, because in the initial stage of the electroforming process, the deformation of the solution drop together with the formation of the primary jet leads to an increase in the surface area.

Viscosity affects the EF process and determines the fiber thickness. When using low viscosity solutions, the formation of defects such as droplets is inevitable, which deteriorates the properties of the obtained material. However, with excessive viscosity of the solution, energy losses for overcoming internal friction of the solution at its exit from the nozzle increase.

There are also other parameters: the geometry of the process in the unit, the rate of delivery of the solution, and so on. The optimum selection of all of the above properties of the spinning solution and the process parameters is a research task for each individual case. The study of this process is still ongoing.

It was found experimentally that the most suitable for EF is 12 wt.% SPAA in an alcohol-water solvent with an ethyl alcohol content of 70% and 30% water.

The EF can be performed on different grounded electrodes: on the flat electrode and on the rotating collector drum (Fig. 2) The EF process was performed in the NANON-01 Ver. 1.33 MECC Co. 2010. Electroforming was done on a grounded rotating drum.



Fig. 2. Schematic diagram of the installation for electroforming: feed rate control *1*; solution *2*; high voltage source *3*; nozzles *4*; grounded rotating collector drum 5

The microstructure of the nonwoven samples was studied by scanning electron microscopy (SEM). In this work, a Supra 55VP-32-49 microscope (Carl Zeiss, Germany) was used in the secondary electron detection mode. Before placing the samples inside the microscope chamber, a thin conductive layer of platinum was sprayed on their surface using an Eiko-IB3 unit. The diameter of the fibers was determined from microphotographs using the ImageJ software product.

The temperature dependences of the dynamic modulus of elasticity (E'), and the tangent of the angle of mechanical loss (tg δ) were measured to estimate the temperatures of relaxation transitions of nonwoven polyimide materials. The measurements were performed on a Dynamic Mechanical Analysis (DMA) DMA 242 C (NETZSCH, Germany) at a frequency of 1 Hz, the strain amplitude of the films was 0.1%, and the temperature rise rate was 5 °C/min.

Dielectric spectra were obtained on a broadband dielectric spectrometer Concept-21 (Novocontrol Technologies GmbH) with an automatic frequency analyzer of high resolution ALPHA-ANB. Temperature-frequency dependences of dielectric permittivity ϵ and dielectric loss angle tg δ were obtained in the frequency range of 1 Hz–15 kHz and temperatures 20–400 °C.

Results and Discussion

Fibers oriented along the axis of rotation were investigated using SEM (Fig. 3.). The thickness of the fibers averaged 500 nm, which corresponds to the industrial criterion, according to which the thickness of the fibers is taken less than 500 nm [1]. This is due to the effect of thickness on consumer properties - hydrophobicity, tribological properties, mechanical strength and others [1]. With a decrease in fiber diameter, the mechanical properties of the material, such as tensile strength, tensile strength, elastic modulus, increase.



Fig. 3. Microphotograph of polyimide nonwoven material obtained from the rotating drum

The obtained PAA nonwovens were subjected to imidization in a thermostat according to the following regime: heating from 25 °C to 250 °C for 2 hours with isothermal exposure at 250 °C for 1 hour [6]. The thickness of the obtained nonwoven material after heat treatment was 24 μ m.

The dielectric and DMA dependences of polar polymers are convenient to consider together because of the relationship between the maximums of their relaxation transitions: α , β , and γ . This is due to the coincidence of their losses associated with dipole-group and dipole-segmental relaxations. The low-temperature γ -transition depends on the method of polymer preparation, on the thermal background, and on the degree of moisture penetration into the polyimide [7]. The low-temperature γ peak is observed around -50 °C on the tg δ (*T*) dependence, the medium-temperature β -transition has a local relaxation character and is determined by the unfreezing of dipole groups, the maximum is in the region of 50 °C. The high-temperature α -transition (383 °C) is related to the unfreezing of the segmental mobility of the polymer.



Fig. 4. Temperature dependence of Young's modulus E' and tg δ of mechanical losses at a frequency of f = 1 Hz

Fig. 4 shows the temperature dependence of E' and tg δ . The modulus of elasticity E' has values of the order of 600 MPa at 25 °C. The modulus of elasticity on the temperature dependence has three relaxation regions, the first (in the region of -50 °C), the second (in the region of 50 °C) reflects the non-cooperative movement of the diamine fragment in the structure of the PMDA-ODA polyimide under consideration, and the third (in the region of 350 °C) is associated with the defrosting of the polymer segmental mobility. The curve tg $\delta(T)$ of nonwoven polyimide PMDA-ODA is characterized by distinct maximum at 383 °C that corresponds to glass transition temperature T_g of polyimide. According to the literature [8] the glass transition temperature of PMDA-ODA film lies in the range from 360–410 °C depending on the research method.

The dielectric properties of the nonwoven PI are shown in Fig. 5. As can be seen from the dependence $\varepsilon'(T)$ the dielectric permittivity at frequency f = 1 Hz is $\varepsilon' = 1.5$. On the temperature dependence $tg\delta(T)$ three relaxation regions can be distinguished, the first β -transition is due to



Fig. 5. Temperature dependence of tg δ and ε' in frequency range f = 1Hz-15kHz (growth of frequency from left to right)

local mobility in the dianhydride part of the macromolecule, rotation of the para-phenylene links in the diamine part or local motions in both parts of the macromolecule simultaneously. The high-temperature α -transition is associated with the transition from a glassy to a highly elastic state and is defined by T_{α} .

Dielectric spectroscopy and DMA results identify the β and α relaxation processes in the glassy and highly elastic states of PI PMDA-ODA respectively.

Fig. 6 presents a comparison of the dielectric permittivity of the film and nonwoven material of the same chemical structure PMDA-ODA. The graph illustrates a significant difference ε' , so the nonwoven material has $\varepsilon' = 1.5$, and the film has $\varepsilon' = 3.5$. Thus, it is possible to justify the use of materials obtained by the electroforming process in modern integrated circuits, which have requirements for low dielectric permittivity.



Fig. 6. Comparison of dielectric permittivity of film (1) and nonwoven material (2) at 1Hz electric field frequency

Conclusion

A nonwoven polyimide material PMDA-ODA with low dielectric permittivity $\varepsilon' = 1.5$ and low loss tg δ was obtained, which will significantly expand the use of polyimide in modern integrated circuits.

REFERENCES

1. Ding Y., Hou H., Zhao Y., Zhu Z., Electrospun polyimide nanofibers and their applications // Progress in Polymer Science. 2016. (61) 67–103.

2. Matveev A.T., Afanasov. I.M., Nanofibers production by electroforming. - Moscow: Lomonosov Moscow State University, (2010) 83.

3. Matrenichev V.V., Popryadukhin P.V., Sklizkova V.P., Svetlichnyi V.M., Obtaining nanofibers from aromatic polyimides and materials based on them for cell technologies // High Molecular Compounds. 2018. 4 (60) 296–303.

4. Svetlichnyi V.M., Vaganov G.V., Myagkova L.A., Electrospinning of Aqueous Solutions of a Triethylammonium Salt of Polyamic Acid and Properties of the Nonwoven Polyimide Materials // Russian Journal of Applied Chemistry. 1 (93) (2020) 35–44.

5. Svetlichny B. M., Miagkova L. A., Sukhanova T. E., Ivankova E. M., Synthesis of water-soluble salts of polyamide acid // High Molecular Compounds. - SPb: (2020) 83–95.

6. Karamancheva I., Dimov.D, Spassova E., Georgiev A., FTIR spectroscopy and FTIR microscopy of vacuum-evaporated polyimide thin films // Vibrational spectroscopy. 2 (19) (1999) 369–374.

7. Kamalov A.M., Borisova M.E., Didenko A.L., Relaxation Behavior of Thermoplastic Polyimide R-BAPB in the Amorphous State // Polymer Science, Series A. 62 (2) (2020) 107–115.

8. Bessonov, M.I. and William W. Wright., "Polyimides: thermally stable polymers." (1987).

THE AUTHORS

KAMALOV Almaz M. spb.kamalov@gmail.com ORCID: 0000-0003-2044-957X

KRAFT Vadim E. Sparta3006@inbox.ru BORISOVA Margarita E. vladimirl.borisov@gmail.com ORCID: 0000-0003-0761-6302

IVANKOVA Elena M. ivelen@mail.ru ORCID: 0000-0002-4823-0695

VAGANOV Gleb V. glebvaganov@mail.ru ORCID: 0000-0002-0210-7456 YUDIN Vladimir E. yudinve@gmail.com ORCID: 0000-0002-5517-4767

NESTEROVA Anna S. annest.2107@yandex.ru ORCID: 0000-0002-5834-5357

Received 05.07.2023. Approved after reviewing 01.09.2023. Accepted 02.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 620.22 DOI: https://doi.org/10.18721/JPM.163.241

Icing and chemical pollution sensor based on carbon nanoparticles-based superhydrophobic coating

S.N. Kapustin¹^{III}, A.S. Volkov¹, Yu.V. Tsykareva¹

¹ Northern (Arctic) Federal University named after M.V. Lomonosov, Arkhangelsk, Russia

^{III} hare22@yandex.ru

Abstract. A method of using a section of a superhydrophobic coating based on xerogel made out of carbon nanotubes and carbon-like onions as an icing sensor was suggested. The obtained dependencies of the conductivity of the coating on the state of the environment are not linear, but unambiguous. They allow to track changes in the environmental conditions. The sensitivity of the coating to volatile substances adsorbed by the surface of the carbon nanoparticles was revealed. Selection ways of the influence of ice and pollutants were suggested. The coating area serves as a protective surface and a detector, and its dual purpose not only simplifies the anti-icing system, but also allows it to potentially work as a chemical sensor aimed at detecting contaminants. The dimensions of the sensitive areas are determined by the reliability of local data and the sensitivity of the surface resistance measurement circuit, and therefore can vary quite freely. Samples with an area from 10 to 0.5 square centimeter were used in the work.

Keywords: carbon nanotubes, anti-icing coatings, superhydrophobicity, icing

Funding: Russian Science Foundation grant 22-22-20115.

Citation: Kapustin S.N., Volkov A.S., Tsykareva Yu.V., Icing and chemical pollution sensor based on carbon nanoparticles-based superhydrophobic coating, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 239–243. DOI: https://doi.org/10.18721/JPM.163.241

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 620.22 DOI: https://doi.org/10.18721/JPM.163.241

Датчик обледенения и химического загрязнения из сверхгидрофобного покрытия на основе углеродных наночастиц

С.Н. Капустин¹[™], А.С. Волков¹, Ю.В. Цыкарева¹

¹ Северный (Арктический) федеральный университет им. М.В. Ломоносова, г. Архангельск, Россия

^{III} hare22@yandex.ru

Аннотация. Предложен способ использования участка сверхгидрофобного покрытия на основе ксерогеля из углеродных нанотрубок и углерода луковичной структуры как датчика обледенения. Полученные зависимости проводимости покрытия от состояния окружающей среды не являются линейными, но однозначны и позволяют отследить изменение условий окружающей среды. Выявлена чувствительность покрытия к летучим веществам, сорбируемыми поверхностью углеродных наночастиц. Предложены пути селекции влияния льда и загрязнителей. Двойное назначение участка покрытия — защитная поверхность и датчик, не только упрощает антиобледенительную систему, но и потенциально способна работать как химический сенсор для определения загрязнений.

© Kapustin S.N., Volkov A.S., Tsykareva Yu.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Размеры чувствительных площадок определяются достоверностью локальных данных и чувствительностью схемы измерения поверхностного сопротивления, а значит может варьироваться достаточно свободно. В работе использовались образцы площадью от 0.5 до 10 квадратных сантиметров.

Ключевые слова: углеродные нанотрубки, антиобледенительные покрытия, сверхгидрофобность, обледенение

Финансирование: Russian Science Foundation grant number 22-22-20115.

Ссылка при цитировании: Капустин С.Н., Волков А.С., Цыкарева Ю.В. Датчик обледенения и химического загрязнения из сверхгидрофобного покрытия на основе углеродных наночастиц // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 239–243. DOI: https://doi.org/10.18721/ JPM.163.241

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Development of the North, work in areas with poor climatic conditions and the climate change itself require devising ways to protect structures, communication lines and equipment from corrosion, pollution and icing. One of the passive methods of protection that does not require energy is the use of hydrophobic and superhydrophobic coatings. Due to the small contact area of the droplet with the surface for such coatings heat exchange with the cold surface is greatly slowed down: the droplet has time to slide off the coating without having time to freeze [1].

In work [2], we proposed an anti-icing superhydrophobic coating based on carbon nanoparticles xerogel. The coating was presented as a two-layer coating - a heating layer of carbon nanotubes (CNTs) and a hydrophobic one of onion-like carbon (OLC). This combination allows you to save energy due to anti-icing properties at temperatures down to -10° C and de-ice the coating at lower temperatures, when the lotus effect is lost upon the icing of the surface.

During testing of the heating layer, the dependence of its electrophysical properties on the presence of volatile substances in the air, its humidity and temperature was noticed. This leads to the idea of using coating areas to determine environmental conditions and control the operation of the heating layer. The task of detecting icing is equivalent to the task of detecting a chemical substance (water and its vapors) in a certain range of conditions (temperature and humidity). The most common way to monitor icing processes is to measure the conductivity of the surface being iced.

In article [3], the authors grew carbon nanotubes on a silicon substrate using the chemical vapor deposition (CVD) method. The authors then functionalized the surface of the grown nanotubes to increase their sensitivity to ice formation. To do this, they used sulfonating agents such as concentrated sulfuric acid or a mixture of sulfuric acid and sulfuric anhydride. This made it possible to increase the sensitivity to ice formation. The resulting sensors were tested on a model aircraft in an ice chamber.

In article [4], the authors present a similar type of icing sensors. The principle of their manufacture is the same, however, CNTs were subjected to secondary functionalization. Initially, oxygen-containing functional groups were created on the surface of carbon nanotubes. Then sulfonating agents were used. This made it possible to increase the affinity of nanotubes for water and increase their sensitivity to ice formation. In [4], the authors also used the polymer polyvinylaminourea (PVIm), which was chemically bonded to the surface of carbon nanotubes. Polymers such as polyethyleneimine (PEI), polyaminoimidazole (PAI), polyamine (PAM), polyacrylamide (PAAm) and others have been used.

In work [5], the authors describe the development of icing sensors based on carbon nanotubes with improved sensitivity and selectivity. Copper nanoparticles were deposited on CNTs. The sensors are highly sensitive and selective to the formation of ice on the surface, and also show a fast response to changes in temperature and humidity.

© Капустин С.Н., Волков А.С., Цыкарева Ю.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Materials and Methods

In the course of the work, carbon nanoparticles with known characteristics from the manufacturer were used (OLC [6], CNT–Nanotechcenter LLC [7]).

Taunit-M, if necessary, was subjected to oxidative functionalization in hydrogen peroxide to obtain -OH groups on their surface. To do this, 250 mg of purified CNTs were added to 250 ml of hydrogen peroxide (30%) heated to 100°C, and kept at atmospheric pressure at a temperature of 100 C in a water bath. The reaction lasted 120 minutes.

Coating samples were prepared according to the procedure in work [2]. The sputtering device consisted of a flask where nanoparticles were deagglomerated by the cavitation effect caused by an MEF 93.1 ultrasonic disperser with an effective power of 0.5 kW. Dispersion lasted about ten minutes, after which the resulting sol was fed into an airbrush mounted on a programmable coordinate device. By smoothly moving the airbrush over the sample, uniformity and homogeneity of the deposition of the sol with nanoparticles onto the sample were achieved.

Getinaks was used as a substrate. 2 mm thick tinned copper conductive tracks with an interval of 2 cm were glued on top of it. About 7-8 layers of coating were applied one after another as the previous one dried. The parameters for applying the hydrophobic layer were as follows: surface roughness, 28 μ m; concentration of nanoparticles in the dispersion suspension, 0.05 g of nanoparticles per 60 mL of hexane.

This is how the heating layer of the coating [2] was created on the basis of the Taunit CNT. To obtain a two-layer coating, an already obtained sample with a heating layer was coated with a hydrophobic layer of OLC. This layer was applied in exactly the same way as described above. Before the measurements, the samples were kept in a dry room for a week for a final drying. For measurements, the samples were placed under a sealed glass cap, which, in turn, was installed in an Espec PG-2J climate chamber (Japan). The electrical properties of the samples were measured using the Novocontrol Concept 80 dielectric spectrometer.

Results and Discussion

The dependence of the resistance of the coating from a single heating layer based on Taunit-M, Taunit-M with hydroxyl groups and from a two-layer sample consisting of a Taunit-M heating layer and a superhydrophobic layer (OLC) are shown in Fig. 1.

It is clear that the resistance of the proposed coating [2] is sensitive to humidity and temperature. The obtained dependencies are not linear, but are unambiguous and allow tracking changes in environmental conditions. Of particular note is the moment of intersection of the dependences in Fig. 1,b, which should correspond to the moment of formation of the conditions for the development of icing.

The main difficulty in using the proposed coating as a sensor is that the sensitivity of the resistance of carbon nanoobjects does not only apply to water in certain phases. Other volatile substances also change the resistance of carbon nanoobjects. For example, work [8] shows the sensitivity of CNTs to nitrogen dioxide and work [9], to ammonia. We measured the effect of ethanol and hexane vapor concentration on coating resistance at room temperature, the results are shown in Fig. 2. The data are normalized to the percolation network resistance in the absence of volatiles.



Fig. 1. Dependence of the resistance of the hydrophobic coating area depending on humidity and temperature:(a) is a heating layer based on the Taunit-M CNT, (b) a heating layer based on CNT-OH, (c) a two-layer coating of a heating layer and a superhydrophobic layer based on OLC. The data are normalized to sample readings at n.c. The red line is the sample at 5% humidity, the blue line is at 95% humidity



◆ Carbon nano onion ● CNT Taunit M - OH ▲ CNT Taunit - M ■ CNT Taunit-MD

Fig. 2. Dependence of the resistance of the hydrophobic coating area (onion-like carbon (violet rhombuses), Taunit-M with hydroxyl groups (green circles), Taunit-M (red triangles) and Taunit-MD (pink squares) without functional groups) at different concentrations of volatile substances in the air. Volatile substances: (a) hexane, (b) mixtures of ethanol and hexane in a ratio of 1: 1, (c) ethanol.

The values along the vertical axis are normalized for the resistance of the sample in clean air

It is clear that OLCs respond to an increase in the concentration of impurities in the atmosphere faster than non-functionalized CNTs. To change the resistance, a carbon nanoobject must be covered with a sorbed impurity so that the areas where the impurity affects the band structure of the nanoparticle are in contact and do not leave alternative paths for the movement of charge carriers. This assumption is indirectly confirmed by the higher sensitivity of Taunit-M over Taunit-MD.

It is interesting that CNT-OH react faster not only to polar impurities, but also to non-polar ones. We explain this by the fact that the functional groups play the role of protrusions that widen the gaps between individual CNTs during xerogel formation. As a result, the sorption of the impurity occurs faster due to facilitating the penetration of vapors into the CNT agglomerates. The reason for the decrease in the sensitivity of CNT-OH to a mixture of hexane and alcohol is not clear to us. One could assume that polar and nonpolar molecules interfere with each other's sorption.

The easiest way to organize the operation of the sensor is by comparing two sections of a two-layer coating - one that is protected from external moisture (inside the case) and an external one that is exposed to atmospheric influences and tracks the moment of intersection of the dependences in Fig. 1,b. Several approaches can be taken to avoid false positives that could cause volatiles in the air.

It is possible to protect the sensor area with a selective membrane that passes mainly water vapor. The downside of this method is that the coating area will no longer be superhydrophobic. Several additional sensitive sites from CNTs of other brands and functionalized CNTs could serve as an alternative. By processing the readings of additional areas, it is possible to determine the presence of contaminants and avoid false positives. However, this requires additional research.

The dimensions of the sensitive areas are determined by the reliability of local data and the sensitivity of the surface resistance measurement circuit, and therefore can vary quite freely. We used samples with areas ranging from 10 cm^2 to 0.5 cm^2 .

Conclusion

The novelty of the proposed approach lies in the fact that the icing sensor can be organized on the basis of the existing technology for creating a superhydrophobic coating based on carbon nanoparticles. In the works listed in the review, the sensor was formed by growing a CNT percolation network by the CVD method on a substrate and connecting the contacts to it. This approach limits the available materials, as it requires the substrate to be heated to high temperatures. The technology we offer allows you to spray a coating on a wide range of substances - metals, plastics, polymers, wood. In fact, there is no need for the sensor as a separate part. The dual purpose of the coating area - a protective surface and a sensor, not only simplifies the anti-icing system, but also has the potential to work as a chemical sensor to detect contaminants. The complexity of the practical application of this approach lies in the fact that the percolation networks of carbon nanoobjects are sensitive to the presence of air pollutants such as ammonia, alcohol vapor and gasoline. We assume that the presence of additional sections of sputtered nano-tubes of other brands and types of functionalization (-OH, -COOH, -NH2 groups) sensitive to volatile substances will make it possible to detect the presence of impurities in the atmosphere and subtract their effect on the conductivity of the coating. Undoubtedly, separate studies are needed for this. An alternative to this would be the search for a functional group that has a high selective sensitivity to ice formation, similar to work [5].

REFERENCES

1. **Boinovich L.B., Emelyanenko A.M.,** Anti-icing potential of superhydrophobic coatings, Mendeleev Commun. 23 (1) (2013) 3–10.

2. Kapustin S., Zabolotny S., Eseev M., Tsykareva Y., Double-layer superhydrophobic anti-icing coating based on carbon nanoparticles, Crystals. 12. (10) (2022) 1501.

3. Homola M.C., Nicklasson P.J., Sundsbur P.A., Ice sensors for wind turbines, Cold Regions Science and Technology. 46 (20) (2006) 125–131.

4. Ko W.-Y., Huang L.-T., Lin K.-J., Green technique solvent-free fabrication of silver nanoparticle– carbon nanotube flexible films for wearable sensors, Sensors and Actuators A: Physical.317 (2021).

5. Han T., Nag A., Chandra Mukhopadhyay S., Xu Y., Carbon nanotubes and its gas-sensing applications: A review, Sensors and Actuators A: Physical. 291 (2019) 107–143.

6. Mordkovich V.Z., Lugvishchuk D.S., Mitberg E.B., et al., Formation of concentric shell carbon by homogeneous partial oxidation of methane // Chem. Phys. Lett. 2018. V. 713. P. 242–246.

7. CNTs «Taunit» and Synthesis Thereof. URL: http://eng.nanotc.ru/producrions/87-cnm-taunit. Accessed June 14, 2023.

8. Wongwiriyapan W., Inoue S., Okabayashi Yu., Ito T., Shimazaki R., Maekawa T., Suzuki K., Ishikawa H., Honda Sh., Mori H., Oura K., Katayama M., Highly Stable and Sensitive Gas Sensor Based on Single-Walled Carbon Nanotubes Protected by Metal-Oxide Coating Layer, Applied Physics Express. 2 (2009) 095008.

9. Chopra S., Pham A., Gaillard J., Parker A., Rao A. M., Carbon-nanotube-based resonant-circuit sensor for ammonia, Applied Physics Letters. 80 (24) (2002) 4632–4634.

THE AUTHORS

KAPUSTIN Sergey N. hare22@yandex.ru TSYKAREVA Yuliana V. aisonoka@gmail.com

VOLKOV Alexandr S. a.s.volkov@narfu.ru

Received 05.07.2023. Approved after reviewing 22.09.2023. Accepted 24.09.2023.

Conference materials UDC 53.043, 532.6 DOI: https://doi.org/10.18721/JPM.163.242

Formation of the anisotropic ITO-based orienting layers for the liquid crystal devices

A.S. Toikka^{1,2,3}, N.V. Kamanina^{1,2,3}

¹St. Petersburg Electrotechnical University, St. Petersburg, Russia;

² Petersburg Nuclear Physics Institute, Gatchina, Russia

³ Vavilov State Optical Institute, St. Petersburg, Russia

⊠ astoikka.nano@gmail.com

Abstract. In this paper, the influence of the CO₂ laser ablation on the indium-tin oxide (ITO) and ITO with carbon nanotubes (CNTs) was considered. The ITO and CNTs were deposited on the Crown K8 substrates via the laser-oriented deposition technique. The anisotropy of the wetting angle for the laser-ablated pure ITO and ITO with the CNTs thin films was considered and compared. The ablation of pure ITO thin films under the CO₂-laser provides the arithmetical mean deviation of the profile in the range of 1.0-1.3 nm (in parallel direction relative to laser ablation) and in the range of 1.6.-1.7 nm (in perpendicular direction). In the case for the ITO with CNTs the mean deviation of the profile corresponds to the ranges of 6.2-9.1 nm and of 10.9-24.3 nm for the parallel and perpendicular directions respectively. The anisotropy of the height distribution leads to the same tendency in the wetting angle. The mean value of the wetting angle anisotropy for pure ITO is 31.6° and for ITO with CNTs it is 48.3°. The possibility to control the anisotropy of the wetting angle via the deposition of the CNTs and the laser ablation allow considering the ITO modifications as the universal electrical contacts and alignment layers for the twisted-nematic liquid crystal devices.

Keywords: indium-tin oxides, wetting angle, laser processing, liquid crystal devices_

Funding: This study has initiative character.

Citation: Toikka A.S., Kamanina N.V., Formation of the anisotropic ITO-based orienting layers for the liquid crystal devices, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 244–248. DOI: https://doi.org/10.18721/JPM.163.242

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.043, 532.6 DOI: https://doi.org/10.18721/JPM.163.242

Формирование анизотропных ориентирующих слоев на основе ITO для жидкокристаллических устройств

А.С. Тойкка^{1,2,3}, Н.В. Каманина^{1,2,3}

¹Санкт-Петербургский государственный электротехнический университет, Санкт-Петербург, Россия;

² Петербургский институт ядерной физики, Гатчина, Россия;

³ Государственный оптический институт им. С.И. Вавилова, Санкт-Петербург, Россия

⊠ astoikka.nano@gmail.com

Аннотация. В текущей работе рассмотрена возможность изменения анизотропии смачивания тонких пленок на основе оксидов индия и олова (ITO) при помощи лазерной абляции CO₂-лазером. Среднее значение анизотропии угла смачивания для чистых ITO пленок составило 31,6°, а для ITO с лазерно-осажденными углеродными нанотрубками

© Toikka A.S., Kamanina N.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

среднее значение этого параметра равно 56,5°. Возможность перестройки анизотропии смачивания при помощи лазерной абляции и осаждения углеродных нанотрубок позволяет рассматривать тонкие пленки на основе ITO в качестве электрических контактов и ориентирующих покрытий при разработке жидкокристаллических устройств с конфигурацией скрученного нематика.

Ключевые слова: оксиды индия и олова, угол смачивания, лазерная обработка, жидкокристаллические устройства

Финансирование: Работа имеет инициативный характер.

Ссылка при цитировании: Тойкка А.С., Каманина Н.В. Формирование анизотропных ориентирующих слоев на основе ITO для жидкокристаллических устройств // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 244–248. DOI: https://doi.org/10.18721/JPM.163.242

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Liquid crystal (LC) mesophase is an important material for the electro-optical applications (display elements, modulation and conversion devices, laser techniques, etc.) due to the easy change of the mechanical, electrical and optical properties under the external field. The basic electrically tunable nematic LC device consists of the mesophase, orienting layers, transparent contacts and optical substrates. In case for the application of the external electric field, the nematic LC molecules change the orientation among the field. As the results, the devices based on the LC have much usage in the display technologies, opto-electronic techniques and biomedical systems [1–3]. The properties of the LC devices extremely depend on the distribution of the LC molecules versus the volume and interface [4–5]. The design of the orienting layers is an important problem, because their properties influence on the pre-tilt angles of the LC alignment could be considered in the LC devices. In nowadays the significant numbers of the researches are connected with the development of the alignment layers based on the organic structures [6–8]. However, these organic structures increase the electrical consumption in the devices. Moreover, the additional layers lead to the optical losses, thus, the brightness and related parameters are also limited.

In the recent researches, the ITO thin films were considered as a universal layer in the LC cells, which simultaneously performed functions of the contacts, anti-reflective coatings and orienting layers [9-11]. In the current paper, the formation of the ITO modifications for the twist-nematic configurations of the LC cells was considered.

Materials and Methods

ITO thin films were deposited on the Crown K8 substrates via the laser-oriented deposition (LOD) method. For these issues, the CO₂ laser (operated at the wavelength of $\lambda = 10.6 \mu m$, power of P = 30 W) with the conjugated electro-mechanical modules were used [12]. The thickness of the ITO films was approximately 100 nm. For the modification of the ITO thin films, the SWCNTs (Sigma-Aldrich, No. 704121, CAS: 308068-56-6) with chirality <7,6> (>77% content of the CNTs) were used. Taking into account the chirality indices, these CNTs have semiconductor properties, the average diameter was 0.83 nm. In order, to provide the anisotropy conditions, the ITO modifications were patterned via the CO₂-marker ($\lambda = 10.6 \mu m$; P = 21 W; modulation frequency, f = 1 kHz; beam diameter, $d = 150 \mu m$; the velocity of the processing, v = 50 mm/s). The pattern consisted of the parallel stripes with the length of 10 mm and step of 5 mm (Fig. 1, a).

For the relief characterization in the micro-scale the atomic force microscope Solver Next NT-MDT (contact mode, scan area of $30 \ \mu m \times 30 \ \mu m$, scan rate of 1 Hz) with the data processing software (Image Analysis P9) were used. The characterization of the orienting properties was estimated via the measurement of the wetting angle in the *xz*- and *yz*-projections. The *y*-axis is parallel and *x*-axis is perpendicular to the direction of the ablation (Fig. 1,*a*). For these issues, the OCA-15 EC (Dataphysics) measurement system with the sessile drop method were used.

[©] Тойкка А.С., Каманина Н.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The parameters of the drop were the following: volume of $0.5-0.7 \ \mu$ L, the material was distilled water, surface free tension was 72.8 mN/m (total), 48.1 mN/m (polar component), 24.7 mN/m (dispersive component).

Results and Discussion

Thin films based on the ITO with the CNTs have higher laser strength in comparison with the pure ITO, due to the increased surface of the heat dissipation [9]. Due to this reason, under the same conditions of the laser ablation, the traces in the ITO with CNTs are more ordered (Fig. 1, a, b).



Fig. 1. Laser ablation of the ITO modifications: schematic image of the samples (*a*); microscopy image of the laser ablated ($\lambda = 10.6 \ \mu m$, $P = 10 \ W$, $d = 0.15 \ mm$, $v = 50 \ mm/s$) pure ITO (*b*) and ITO with the CNTs (*c*) thin films

The orientation of the liquid crystals in the volume depends on the pre-tilt angle and the roughness of the alignment relief respectively. The laser ablation performs the anisotropic conditions of the relief. According to the AFM data from Table 1, the arithmetical mean deviation of the profile (R_a) of pure ITO in the ablated areas rises from 1.0-1.3 nm (for yz-projections) to 1.6-1.8 nm (for xz-projections). The mean height of the CNTs clusters is approximately 40-60 nm (depends), due to this fact, the maximum profile peak height (R_p) and valley depth (R_p) for the ITO with the CNTs in 1 order higher in comparison with the pure ITO. As a result, the anisotropy $\Delta R_a = R_a(x)-R_a(y)$ for the ITO with the CNTs under the laser the higher as well.

The anisotropy of the alignment properties in the ITO modifications could be visualized via the wetting angle measurements. Fig. 2,*a* demonstrates the initial distribution of the wetting angle for pure ITO without the laser ablation. In this case the relief is isotropic, thus the wetting angle in the *xz*-projection (perpendicular, θ_{\perp}) and *yz*-projection (parallel, θ_{\parallel}) are equal to each other for the same drops. The laser ablation leads to the decrease of the wetting angle to $\theta_{\parallel} = 39.1-59.6^{\circ}$ (Fig. 2,*b*) and $\theta_{\perp} = 75.8-85.6^{\circ}$ (Fig. 2,*c*).

In order to increase the anisotropy of the wetting, the relief based on the ITO with the CNTs could be used. Due to the rise of the surface area under the deposition of the CNTs [11], the wetting angle becomes bigger as well (Fig. 3,*a*). The rise of initial wetting angle and the higher values of the relief's anisotropy (Table 1) lead to greater anisotropy of the wetting angle: $\theta_{\parallel} = 46.7-65.4^{\circ}$ (Fig. 3,*b*) and $\theta_{\perp} = 75.8-85.6^{\circ}$ (Fig. 3,*c*).



Fig. 2. Contact angle distribution of pure ITO: before the laser ablation (*a*); after the laser ablation: parallel (*b*) and perpendicular (*c*) components



Fig. 3. Contact angle distribution of the ITO with the CNTs: before laser ablation (*a*); after the laser ablation: parallel (*b*) and perpendicular (*c*) components

It should be noticed, that the green markers in Figs. 2-3 correspond to the non-ablated region (the space between). The discussed information regarding to the wetting angle of the ITO modification is demonstrated below.

Table 1

Structure	No.	x-coordinate			y-coordinate		
		R_q , nm	R_{p} , nm	R_{v} , nm	R_q , nm	R_{p} , nm	R_{v} , nm
Pure ITO	1	1.7	5.1	3.8	1.0	2.3	1.8
	2	1.8	4.9	3.7	1.0	2.5	2.2
	3	1.8	4.8	3.8	1.0	2.1	2.9
	4	1.6	5.2	3.6	1.2	3.0	1.9
	5	1.6	5.2	3.6	1.3	3.3	2.0
ITO with CNTs	1	24.3	68.4	73.9	9.1	21.3	16.4
	2	15.7	45.7	48.7	9.1	19.7	17.8
	3	21.9	62.3	52.1	8.5	15.3	18.0
	4	22.0	71.9	49.5	7.1	12.5	17.3
	5	10.9	46.4	32.5	6.2	14.4	13.6

Relief parameters of the ablated areas in the ITO thin films

Table 2

Contact angles of the ITO modifications

	Value	Contact angle				
Structure		(min/mean/max), degrees				
			After			
		Initial $(\theta \approx \theta)$	laser processing			
			θ	θ_{\perp}		
Pure ITO	Min.	95.7	39.1	75.8		
	Mean	99.5	49.5	81.1		
	Max.	101.2	59.6	85.6		
ITO with CNTs	Min.	115.8	46.7	92.2		
	Mean	120.2	56.5	104.8		
	Max.	124.4	65.4	112.0		

Conclusion

The ablation of pure ITO thin films under the CO_2 -laser provides the mean anisotropy of the wetting angle $\Delta \theta = 31.6^{\circ}$, where $\theta_{\parallel} = 39.1-59.6^{\circ}$ (mean value of 49.5°) and $\theta_{\perp} = 75.8-85.6^{\circ}$ (mean value of 81.1°). In case for the ITO with the LOD-deposited CNTs, the mean anisotropy $\Delta \theta = 48.3$, where the parallel and perpendicular component correspond to the ranges 46.7-65.4° (mean of 56.5°) and 92.2-112.0° (mean of 104.8°) respectively. These results can be reasoned via the rise of the relief's anisotropy, what depends on the CNTs clusters impact under the laser ablation. The anisotropy of the wetting angle demonstrates the possibility to change the conditions of the alignment of the LC molecules in order to realize the twisted-nematic configurations in the LC devices.

Acknowledgments

The authors would like to thank their colleagues from the Lab for Photophysics of media with nanoobjects at Vavilov State Optical Institute for productive discussions and seminars.

REFERENCES

1. Ma Z., Gao Y., Cao H., The Effect of Chemically Modified Multi-Walled Carbon Nanotubes on the Electro-Optical Properties of a Twisted Nematic Liquid Crystal Display Mode, Crystals. 12(10) (2022) 1–8.

2. d'Alessandro A., Asquini R., Light Propagation in Confined Nematic Liquid Crystals and Device Applications, Applies Sciences. 11(18) (2021) 1–17.

3. Abadla M.M., Elsayed H.A., Mehaney A., Sensitivity enhancement of annular one dimensional photonic crystals temperature sensors with nematic liquid crystals, Physica Scripta. 95(085508) (2020) 1–25.

4. Frank F.C., Liquid crystals: On theory of liquid crystals, Discuss. Faraday Soc. 25 (1958) 19–28.
5. Ericksen J.L., Truesdell C., Exact theory of stress and strain in rods and shells, Archive for Rational Mechanical and Analysis. 1 (1957) 295–323.

6. Sato O., Okuno H., Adachi I., Watanabe J., Tokita M., Sakakibara K., Kinose Y., Goto A., Tsujii Y., Novel in-plane switching liquid crystal display with an extremely high transmittance using a well-designed bottlebrush as a zero-azimuth anchoring material, Japanese Journal of Applied Physics. 58(066503) (2019) 1–7.

7. Son S.R., An J., Choi J.W., Kim S., Park J., Lee J.H., Surface-anchored alkylated graphene oxide as a two-dimensional homeotropic alignment layer for nematic liquid crystals, Materials today: Communications. 28(102539) (2021) 1–8.

8. Nimmy J.V., Karumuthil S.C., Varghese S., Nano P(VDF-TrFE) doped polyimide alignment layers for twisted nematic liquid crystal devices, Liquid Crystals. 47(1) (2020) 36–41.

9. Kamanina N.V., Kukharchik A.A., Kuzhakov P.V., Zubtsova Yu.A., Stepanov R.O., Baryshnikov N.V., Carbon Nanotubes Modification of the Conductive ITO-Layer for Orientation of Liquid Crystals Used in Electro-Optical Devices For Information Processing, Liq. Cryst. and their Appl. 15(3) (2015) 109–118.

10. Kamanina N., Toikka A., Gladysheva I., ITO conducting coatings properties improvement via nanotechnology approach, Nano Express. 2(010006) (2021) 1–7.

11. Toikka A.S., Kamanina N.V., The control of ITO conductive coating relief via laser-oriented deposited carbon nanotubes, Journal of Advanced Materials and Technologies. 7(1) (2022) 58–67.

12. Patent RU 2405177, 2008. Authors: Kamanina N.V., Vasilyev P.Ya., Studenov V.I.

THE AUTHORS

TOIKKA ANDREI S. astoikka.nano@gmail.com ORCID: 0000-0002-8694-8497 KAMANINA NATALIA V. nvkamanina@mail.ru ORCID: 0000-0002-2903-2685

Received 05.07.2023. Approved after reviewing 04.08.2023. Accepted 06.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 538.9 DOI: https://doi.org/10.18721/JPM.163.243

Study of morphology and composition of nanoscale AlGaN heterostructures obtained by PA MBE technique on the silicon substrates with the use of porous silicon as buffer layer

A.S. Lenshin¹[™], D.S. Zolotukhin¹, P.V. Seredin¹, A.M. Mizerov²

¹ Voronezh State University, Voronezh, Russia;

² Alferov University, St. Petersburg, Russia

[™] lenshinas@mail.ru

Abstract. In this work, we study the morphology, composition and optical properties of AlGaN epilayers grown by plasma-assisted molecular beam epitaxy on the AlN buffer layer which was performed on regular Si substrate and compliant Si substrate with a preformed buffer porous silicon layer (*por*-Si) and carbonized porous layer(SiC/*por*-Si). The AlGaN layers formed on the *por*-Si buffer revealed a 15% higher intensity of photoluminescence spectra in visible range in comparison with ones formed on regular Si substrate.

Keywords: AlGaN, epitaxy, buffer layer, porous silicon

Funding: The study was carried out with the financial support of the Russian Foundation for Basic Research within the framework of scientific project 19-72-10007.

Citation: Lenshin A.S., Zolotukhin D.S., Seredin P.V., Mizerov A.M., Study of morphology and composition of nanoscale AlGaN heterostructures obtained by PA MBE technique on the silicon substrates with the use of porous silicon as buffer layer, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 249–254. DOI: https://doi. org/10.18721/JPM.163.243

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 538.9 DOI: https://doi.org/10.18721/JPM.163.243

Исследование морфологии и состава наноразмерных гетероструктур AlGaN, полученных методом ПА МПЭ, на кремниевых подложках с использованием пористого кремния в качестве буферного слоя

А.С. Леньшин¹⊠, Д.С. Золотухин¹, П.В. Середин¹, А.М. Мизеров²

¹ Воронежский государственный университет, г. Воронеж, Россия;

² Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия

[™] lenshinas@mail.ru

Аннотация. В работе были проведены исследования морфологии, состава и оптических свойств эпитаксиальных слоев AlGaN, выращенных методом плазменной молекулярнолучевой эпитаксии на буферном слое AlN, сформированном на обычной подложке монокристаллическогос-Siиподатливыхподложкахс-Siспредварительносформированными на них буферными слоями пористого кремния (*por*-Si) и карбидизированным пористым слоем (SiC/*por*-Si). Слои AlGaN, сформированные на буфере *por*-Si, показали на 15% более высокую интенсивность спектров фотолюминесценции в видимом диапазоне, по сравнению со слоями, сформированными на обычной подложке Si.

© Lenshin A.S., Zolotukhin D.S., Seredin P.V., Mizerov A.M., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: AlGaN, эпитаксия, буферный слой, пористый кремний

Финансирование: Работа выполнена при финансовой поддержке гранта РНФ № 19-72-10007.

Ссылка при цитировании: Леньшин А.С., Золотухин Д.С., Середин П.В., Мизеров А.М. Исследование морфологии и состава наноразмерных гетероструктур AlGaN, полученных методом ПА МПЭ, на кремниевых подложках с использованием пористого кремния в качестве буферного слоя // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 3.2 № .16. С. 249–254. DOI: https://doi.org/10.18721/ JPM.163.243

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Heterostructures on the basis of (Al, Ga) N system attract great interest since they are currently used as for the fabrication of radiation-hardened high temperature high mobility transistors, as for the application of optoelectronic devices. Basic techniques for the growth of heterostructure devices are known to be vapor-phase epitaxy from metal-organic compounds (MOS VPE) and molecular beam epitaxy (MBE). Combination of AIIIN materials with silicon devices for signal processing opens new ways for appearance of the new functional units that could merge high-quality optoelectronic characteristics of AIIIN and the developed more profit-proved technologies on the basis of Si substrates. Moreover, the use of silicon substrates for the growth of III-N heterostructures is useful from the practical point of view due their commercial availability and maturity of Si-technologies.

However, the formation of III-N/Si heterostructures is yet impeded due to the differences in the thermal expansion coefficient and lattice parameters that results in the generation of the threading dislocations with high density, delaminating and cracking of heterostructures, thus impairing the instrument characteristics of the terminal devices. One of the perspective technological processes providing possibility of obtaining high functional properties in the fabricated hybrid heterostructures can be based on the usage of the compliant structured silicon substrate composed of porous silicon [1-3].

The aim of our work was to determine the effect of incorporation of the transition layer, nanoporous silicon *por*-Si, into technological process of $Al_xGa_{1-x}N/AlN/por$ -Si/Si(111) heterostructure growth as well as carbonized porous silicon on the structural-morphological characteristics and atomic composition of the surface layers applying microscopy and X-ray photoelectron spectroscopy technique.

Materials and Methods

In order to grow $Al_xGa_{1-x}N/AIN$ heterostructures, silicon substrates Si (111) were used with different kinds of surface modification: standard smooth substrates of *c*Si, Si (111) substrates with the layer of porSi/*c*Si formed on the substrate surface, as well as SiC/*por*Si/cSi substrates. The layers of porous silicon (~50 nm) were obtained by electrochemical etching of single-crystalline silicon wafers of KDB type with (111) orientation in fluorine acid solution, similar to that one described in [4, 5] and SiC layer was formed with the use of the atom replacement technique [6].

AlGaN epitaxial layers on the substrates of three types (c-Si, por-Si and SiC/por-Si/c-Si) were grown in a common growth process by molecular beam epitaxy with the addition of plasma-activated nitrogen (PA MBE) in the Veeco Gen 200 facility.

Al_xGa_{1-x}N/AlN/Si(111) heterostructures (HS) without transition layer and also with transition layer of *por*-Si were grown at on and the same time. Just before the growth process of heterostructure the substrates were annealed and nitridized for 30 minutes at the substrate temperature of $T \sim 670$ °C in the growth chamber of the facility. The growth processes of formation for all of the HS layers were realized in metal-enriched conditions. The growth rate was controlled and limited by nitrogen flow and it was equal to $F_N \sim 0.05 \,\mu$ m/hour. In order to prevent etching of silicon substrate with liquid Ga accompanied with formation of Ga-Si eutectic buffer layer of AlN was formed

[©] Леньшин А.С., Золотухин Д.С., Середин П.В., Мизеров А.М., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

on the surface of the substrates. Epitaxial synthesis of heterostructures started from the formation of nucleus AlN layers at $T \sim 800$ °C, $F_{Al} \sim 0.02 \,\mu\text{m/hour grown}$ for 60 minutes on the surface of substrates. After that, temperature of the substrates was reduced up to the value of $T \sim 700$ °C for the growth of the main Al Ga_{1-x}N layer implemented for four hours at the constant layers of $F_{Al} \sim 0.01 \,\mu\text{m/hour}$, $F_{Ga} \sim 0.4 \,\mu\text{m/hour}$ and $F_N \sim 0.04-0.05 \,\mu\text{m/hour}$. The morphology of the grown heterostructures was examined with a JEOL JSM 6380LV scanning electron microscope (SEM).

The samples were studied by X-ray photoelectron spectroscopy (XPS) on a SPECS spectrometer. The spectra were excited with Mg K α -irradiation (E = 1253.6 eV). The depth of the XPS analysis of the sample surface is 1–2 nm. When processing the measurement results, Shirley algorithms were used to determine the background line and subtract the background values. To determine the binding energy of the heterostructure elements, we used the C1s line of natural hydrocarbon impurities of the sample surface not subjected to special cleaning as a reference line, the binding energy $E_b[C1s] = 285$ eV. The core levels of the elements and their chemical state were determined using the X-ray photoelectron spectra database of the US National Institute of Standards [7].

The luminescence spectra of the samples were obtained with the unit measuring photoluminescence and optical reflection spectra Accent RPM Sigma. The studies were made at room temperature under laser excitation having a wavelength of 266 nm and a power density of W = 5W/cm².

Results and Discussion

Certain inhomogeneities of the structure with sub-micrometer sizes can be seen on the surface of the samples which are attributed to the columnar structure of the films, observed in SEM images of the sample chips. Similar columnar structure of the films we have also observed in $In_xGa_{1-x}N/Si(111)$ heterostructures [8]. Total thickness of the grown heterostructures was of ~100–120 nm. Comparison of heterostructures morphology demonstrated that the growth on porous layer provided less scattering in the sizes of inhomogeneities on the surface. It means that the structure of the film is more homogeneous as compared with heterostructure grown without the buffer layer. At the same time even more homogeneous fine-grained structure is observed for the structure grown on the carbonized porous layer. Mean lateral sizes of inhomogeneities/globules for heterostructures grown on the crystalline silicon were of about 130 nm, while those ones on porous silicon were of about ~100 nm, and on the carbonized porous buffer layer they were of ~60 nm.



Fig. 1. SEM images of Al_xGa_{1-x}N/AlN/Si (*a*), Al_xGa_{1-x}N/AlN/*por*-Si/Si (*b*) and Al_xGa_{1-x}N/AlN/SiC/*por*-Si/*c*-Si (*c*) heterostructures surfaces and cross-sections respectively

Fig. 2 represents XPS spectra of the core levels of Al 2p, Ga 2p and N1s for heterostructures obtained directly on single-crystalline silicon c-Si(111) (Fig. 2,*a*), with porous sublayer (Fig. 2,*b*) and with carbonized sublayer (Fig. 2,*c*).

Analysis of XPS spectra shows that on the surface of the samples for all heterostructures Al and Ga atoms form chemical bonds with nitrogen and they display practically the same binding energies (just as the half-widths) of the core-level spectra for all of the elements in $Al_xGa_{1-x}N$ alloy close to the values of the binding energies of aluminum and gallium in pure nitrides [7].

Besides, a contribution of low-intensity component characteristic for the oxidized aluminium Al₂O₃ $(E_b = 75.5 \text{ eV})$ formed on the surface of the samples under their contact with the oxygen air can be seen in Al 2p core level spectra. Note, that Al_2O_3 contribution is most clearly seen for heterostructures grown on the carbonized porous layer while it is least noticeable in heterostructures grown on c-Si. Similar component is not observed for Ga 2p3/2 spectrum, however, Auger-line of nitrogen N KLL is superimposed on the low-energy part of gallium spectra thus masking gallium oxide contribution. N1s spectra of nitrogen correspond to the binding energies of Al and Ga nitrides [7].



Fig. 2. XPS spectra of the core Al2p and Ga3d levels in heterostructures with different types of the substrates (a) c-Si, (b) por-Si/c-Si and (c) SiC/por-Si/c-Si)

Similar to the results of [8] aluminum content in the film can be calculated basin on the relationship (1):

$$x_{\rm Al} = \frac{I_{\rm Al2p3}/F_{\rm Al2p3}}{\left(I_{\rm Al2p3}/F_{\rm Al2p3} + I_{\rm Ca2p3}/F_{\rm Ca2p3}\right)},\tag{1}$$

where I is integrated intensity of photoelectron peaks for the corresponding lines in the spectrum

and *F* is a sensitivity factor ($F_{Ga2p3} = 2.75$ and $F_{Al2p3} = 0.54$). The values of Al atoms concentration in the alloys determined on the basis of relation-ship (1) were of $x_{a_cryst} = 0.49$, $x_{a_por} = 0.54$, and $x_{sic} = 0.42$ for the samples grown on sin-gle-crystalline silicon, namely, Al Ga_{1-x}N/AlN/Si(111), and also with the use of porous buffer layer Al₂Ga₁₋₂N/AlN/Si/por-Si/Si(111) and Al₂Ga₁₋₂N/AlN/SiC/por-Si/c-Si, respectively. The obtained values are in a good agreement with the expected technological value of $x \sim 0.50$ specified previously for the process of synthesis. The difference in x values of heterostructures can be due their structural-morphological distinctions and the attributed aluminium oxidation under sample storage in the atmosphere. Note, that most fine-grained surface of the samples grown on carbonized porous silicon just involves the greater amount of the oxidized aluminium.


Fig. 3. PL spectra at T ~ 300 °C from AlxGa1-xN/AlN heterostructures, grown on cSi, porSi/cSi and SiC/porSi/cSi substrates

Photoluminescence spectra of the epitaxial AlxGa1-xN/AlN heterostructures for all types of the samples are presented in Fig. 3. One can see that the luminescence spectra of the samples in the range of 300–900 nm depend on the type of a substrate used for film growth.

These spectra show the presence of ultraviolet spectral band only for heterostructure grown on SiC/porSi/cSi substrate with the maximum energy of $E_g = 3.99$ eV (near 310 nm), which can be attributed to the transitions of band-to-band type in Al_xGa1-xN alloy. Moreover, in all of the spectra, additional broad yellow spectral band can be observed. It is attributed to the spurious defect that appeared due to the impurities incorporated in the process of growth [9]. For all of the structures grown on porous silicon, PL band is the most intensive one and it is by ~ 15% higher than for heterostructures with buffer layer formed with carbonized porous silicon and is by 25-30% higher than for those ones grown on crystalline silicon. One should note that in the experimental spectrum of the film obtained on the hybrid SiC/porSi/cSi substrate, the peak is present near 2.34 eV. This maximum can be attributed to 3*C*-SiC sublayer, with the energy value of the band-gap approximately equal to $E_g \sim 2.24-2.39$ eV [10].

Conclusion

In the work original $Al_xGa_{1-x}N/AlN/por-Si/Si(111)$ heterostructures were fabricated by molecular-beam epitaxy technique using buffer layer of porous silicon *por-Si* and carbonized porous silicon.

Formation of $Al_x Ga_{1-x} N/AIN$ heterostructures with the use of porous silicon layers was shown to facilitate more homogeneous distribution of the alloy nanocolumns over their sizes and orientation in the base direction as compared with similar alloy grown at the same time in single-crystalline silicon without porous layer implying that the growth process was performed in the same technological conditions. It was found that variations of Al content over the samples surface can be attributed to the different intensity of the oxidation processes of the surface due to the differences in heterostructures morphology.

Applying the scanning electron microscopy, photoelectron and photoluminescence spectroscopy it was shown that thin AlGaN/AlN heterostructures formed on the *por*-Si substrate were characterized up to 15-25% more intensive photoluminescence in a visible range as compared with those ones formed on the carbonized porous buffer layer and regular Si substrate.

REFERENCES

1. Oh J-T., Moon Y-T., Jang J-H., Eum J-H., Sung Y-J., Lee S. Y., Song J-O., Seong T-Y., Highperformance GaN-based light emitting diodes grown on 8-inch Si substrate by using a combined lowtemperature and high-temperature-grown AlN buffer layer, J. Alloys Compd. 732 (2018) 630–636.

2. Kohen D., Nguyen X.S., Yadav S., Kumar A., Made R.I., Heidelberger C., Gong X., Lee K.H., Lee K.E. K., Yeo Y.C., Yoon S.F., Fitzgerald E.A., Heteroepitaxial growth of In_{0.30}Ga_{0.70}As high-electron mobility transistor on 200 mm silicon substrate using metamorphic graded buffer, AIP Advances. 6 (2016) 085106.

3. Sugawara Y., Ishikawa Y., Watanabe A., Miyoshi M., Egawa T., Observation of reaction betweena-type dislocations in GaN layer grown on 4-in. Si(111)substrate with AlGaN/AlN strained layer superlattice after dislocation propagation, Journal of CrystalGrowth. 468 (2017) 536–540.

4. Seredin P.V., Lenshin A.S., Kashkarov V.M., Lukin A.N., Arsentiev I.N., Bondarev A.D., Tarasov I.S., Ultrathin nano-sized Al₂O₃ strips on the surface of *por*-Si, Mater. Sci. Semicond. Process. 39 (2015) 551–558.

5. Seredin P.V., Goloshchapov D.L., Lenshin A.S., Mizerov A.M., Zolotukhin D.S., Influence of *por*-Si sublayer on the features of heteroepitaxial growth and physical properties of $In_xGa_{1-x}N/Si(111)$ heterostructures with nanocolumn morphology of thin film, Physica E Low Dimens. Syst. Nanostruct. 104 (2018) 101–110.

6. Kukushkin S.A., Osipov A.V., Feoktistov N.A., Synthesis of epitaxial silicon carbide films through the substitution of atoms in the silicon crystal lattice: A review, Phys. Solid State. 56 (2014) 1507–1535.

7. **Moulder J.F., Chastain J.,** Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics Division, Perkin-Elmer Corporation, Minnesota, 1992.

8. Fang Z.L., Li, Q.F. Shen X.Y., Cai J.F., Kang J.Y., Shen W.Z., Modified InGaN/GaN quantum wells with dual-wavelength green-yellow emission. J. Appl. Phys. 115(4) (2014) 043514.

9. Serban E., Palisaitis J., Junaid M., Tengdelius L., Högberg H., Hultman L., Persson P.O.A., Birch J., Hsiao C-L., Magnetron Sputter Epitaxy of High-Quality GaN Nanorods on Functional and Cost-Effective Templates/Substrates, Energies. 10 (9) (2017) 1322.

10. **Zhao G.L., Bagayoko D.,** Electronic structure and charge transfer in 3*C*- and 4H-SiC, New J. Phys. 2 (2000) 16.

THE AUTHORS

LENSHIN Aleksandr S. lenshinas@mail.ru ORCID: 0000-0002-1939-253X

ZOLOTUKHIN Dmitriy S. zolotukhinspb@gmail.com ORCID: 0000-0002-1939-253X SEREDIN Pavel V. paul@physvsu.ru ORCID: 0000-0002-6724-0063

MIZEROV Andrey M. miserov@mail.ru ORCID: 0000-0002-9125-6452

Received 10.07.2023. Approved after reviewing 07.08.2023. Accepted 07.08.2023.

Conference materials UDC 535.3 DOI: https://doi.org/10.18721/JPM.163.244

Quantum dot-induced photoluminescence enhancement of InGaN nanowires

T. Shugabaev^{1,2⊠}, V.O. Gridchin¹⁻⁴, R.R. Reznik¹, A.I. Khrebtov^{1,2},
 I.A. Melnichenko⁵, A.S. Kulagina^{1,2}, K.P. Kotlyar¹⁻⁴,
 V.V. Lendyashova¹⁻³, N.V. Kryzhanovskaya⁵, G.E. Cirlin¹⁻⁴

¹ St. Petersburg State University, St. Petersburg, Russia;

² Alferov University, St. Petersburg, Russia;

³ Ioffe Institute, St. Petersburg, Russia;

⁴ Institute for Analytical Instrumentation RAS, St. Petersburg, Russia;

⁵ HSE University, St. Petersburg, Russia

[™] talgashugabaev@mail.ru

Abstract. In this work, we propose a simple method to enhance the photoluminescence of InGaN nanowires using CdSe/ZnS colloidal quantum dots. It is found that decoration the surface of InGaN NWs with QDs leads to an increase in the integral and peak photoluminescence intensity by more than 3 times. The observed enhancement is attributed to the nonradiative energy transfer between quantum dots and nanowires.

Keywords: InGaN nanowires, CdSe/ZnS quantum dots, photoluminescence, hybrid nanostructures

Funding: The samples growth and optical properties studies were done under the financial support of Russian Science Foundation grant 23-79-00012. The morphological properties of grown samples were studied under the financial support of St. Petersburg State University under research grant 94031047.

Citation: Shugabaev T., Gridchin V.O., Reznik R.R., Khrebtov A.I., Melnichenko I.A., Kulagina A.S., Kotlyar K.P., Lendyashova V.V., Kryzhanovskaya N.V., Cirlin G.E. Optical properties of hybrid structures based on InGaN nanowires and colloidal quantum dots, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 255–260. DOI: https://doi.org/10.18721/JPM.163.244

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Peter the Great St. Petersburg Polytechnic University, 2023

Материалы конференции УДК 535.3 DOI: https://doi.org/10.18721/JPM.163.244

Усиление фотолюминесценции нитевидных нанокристаллов InGaN с помощью квантовых точек CdSe/ZnS

Т. Шугабаев^{1,2⊠}, В.О. Гридчин¹⁻⁴, Р.Р. Резник¹, А.И. Хребтов^{1,2}, И.А. Мельниченко⁵, А.С. Кулагина^{1,2}, К.П. Котляр¹⁻⁴, В.В. Лендяшова¹⁻³, Н.В. Крыжановская⁵, Г.Э. Цырлин¹⁻⁴

¹ Санкт-Петербургский государственный университет, Санкт-Петербург, Россия;

² Академический университет им. Ж.И. Алферова, Санкт-Петербург, Россия;

³ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

⁴ Институт аналитического приборостроения РАН, Санкт-Петербург, Россия;

⁵ НИУ ВШЭ – Санкт-Петербург, Санкт-Петербург, Россия

^{III} talgashugabaev@mail.ru

Аннотация. В данной работе предлагается простой метод усиления фотолюминесценции нитевидных нанокристаллов InGaN с использованием коллоидных квантовых точек CdSe/ZnS. Установлено, что декорирование поверхности нитевидных нанокристаллов InGaN с помощью квантовых точек приводит к увеличению интегральной и пиковой интенсивностей фотолюминесценции более чем в 3 раза. Наблюдаемое усиление фотолюминесценции связывается с безызлучательным переносом энергии между квантовыми точками и нитевидными нанокристаллами.

Ключевые слова: нитевидные нанокристаллы InGaN, квантовые точки CdSe/ZnS, фотолюминесценция, гибридные наноструктуры

Финансирование: Синтез экспериментальных образцов и исследования их оптических свойств были выполнены при финансовой поддержке Российского научного фонда (проект № 00012-79-23). Исследования морфологических свойств синтезированных наноструктур были выполнены при финансовой поддержке Санкт-Петербургского государственного университета в рамках исследовательского гранта № 94031047.

Ссылка при цитировании: Шугабаев Т., Гридчин В.О., Резник Р.Р., Хребтов А.И., Мельниченко И.А., Кулагина А.С., Котляр К.П., Лендяшова В.В., Крыжановская Н.В., Цырлин Г.Э. Оптические свойства гибридных структур на основе нитевидных нанокристаллов InGaN и коллоидных квантовых точек CdSe/ZnS // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 255–260. DOI: https://doi.org/10.18721/JPM.163.244

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Nowadays, the hybrid systems consisting of various dimension semiconductor nanostructures are actively studied [1, 2]. A special place is occupied by hybrid nanostructures based on nanowires (NWs) [3–5] since the latter exhibit high surface-to-volume ratio [6] and can be grown with high crystal quality on lattice-mismatched substrates, for example on cost-efficient Si [7–9]. In addition, NWs are suitable for growing ternary compounds, in particular, InGaN, which are of considerable interest for creating micro-RGB LEDs and nanolasers [10–12].

It was previously shown that hybrid nanostructures based on NWs and colloidal quantum dots (QDs) allows one to create efficient infrared sources, white light-emitting diodes (LED), solar cells, photocatalysts, photodetectors and gas sensors, etc. [3, 5, 13–16]. The interaction between the parts of the hybrid nanosystem can manifest itself in Förster Resonance Energy Transfer (FRET). Experimental and theoretical validity of FRET in semiconductor nanostructures with

© Шугабаев Т., Гридчин В.О., Резник Р.Р., Хребтов А.И., Мельниченко И.А., Кулагина А.С., Котляр К.П., Лендяшова В.В., Крыжановская Н.В., Цырлин Г.Э., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

different dimensions was described in the [3, 17]. We have recently shown that the deposition of a trioctylphosphine oxide (TOPO)-CdSe/ZnS QDs on the arrays of InP/InAsP/InP NWs leads to a significant increase in the duration and intensity of the photoluminescence (PL) of the InAsP nanoinsertion [3, 18].

In this work, we fabricate NW/QD hybrid nanostructures based on InGaN NWs and study their photoluminescent properties. The initial InGaN NWs exhibit a PL at room temperature (RT) in the red region of the spectrum. We show that the deposition of CdSe/ZnS QDs on InGaN NWs results in the significant PL enhancement. The results open the ways to increase the photoluminescence efficiency of the high In content InGaN NWs by colloidal QDs.

Materials and Methods

The InGaN NWs were grown on 1-inch *n*-type Si(111) substrate using Riber Compact 12 MBE system equipped with In and Ga effusion cells and a nitrogen plasma source. Prior to the growth, the substrate was thermally treated at 920 °C to remove silicon oxide from the growth surface. The substrate temperature was then decreased to 605 °C. At this moment, an atomically clean growth surface was detected by in-situ reflection high-energy electron diffraction showing (7×7) surface reconstruction. After stabilization of the substrate temperature, the nitrogen plasma source was ignited and the Ga and In shutters were simultaneously opened. The growth lasted 20h. The nitrogen flux and power of the nitrogen plasma source were set at 0.4 sccm and 450 W, respectively. Beam equivalent pressures of In and Ga measured by the Bayard-Alpert vacuum gauge were equal to each other and amounted to $1 \cdot 10^{-7}$ Torr.

The synthesized NWs have a core/shell structure [8]. To achieve FRET between the TOPO-CdSe/ZnS QDs and the InGaN core, we subjected the initial NW arrays to chemical treatment. Wet chemical etching was carried out in the solution KOH:H₂O (1:5) at a temperature of 75 °C for 2 minutes to remove the GaN shell. 12 µl of the QDs solution in toluene ($C \approx 10^{-6}$ M) were deposited on a substrate with InGaN NWs using a micropipette to create hybrid nanostructures. Deposed QDs had a structure with a CdSe core (about 3 nm in diameter) covered with a ZnS shell and TOPO ligand layer.

The initial NW array was placed in isopropyl alcohol and subjected to ultrasonic treatment for estimating the absorption properties of InGaN NWs. The absorption properties of the resulting suspension were detected by measuring optical density spectra with a spectrophotometer Thermo Scientific Multiskan GO. The PL measurements of QDs were performed at room temperature (RT) using a He-Cd laser with a wavelength of 325 nm at 15.5 mW. The laser spot diameter was approximately 100 μ m. The PL signal was detected using a MS5204i Sol instruments monochromator and a single-channel Si detector.

The optical properties of InGaN NWs and hybrid nanostructures were studied using an Integra Spectra (NT-MDT) confocal microscope at room temperature. The Nd:YLF laser operating in continuous mode (527 nm wavelength) was used for excitation. The excitation laser beam was focused using a 100x objective (Mitutoyo, M Plan APO NIR) with a numerical aperture NA = 0.5. The same objective was used to collect the photoluminescence of nanostructures. The radiation was directed to the entrance slits of the monochromator (Sol Instruments MS5204i) using mirrors. Detection was performed using a cooled InGaAs CCD array (iDus). Morphological properties of the samples were examined using a SUPRA 25 C. Zeiss scanning electron microscope (SEM).

Results and Discussion

Several conditions should be performed simultaneously for FRET between a donor and an acceptor. The PL spectrum of the donor should overlap with the absorption spectrum of the acceptor (condition 1), and the distance between the donor and acceptor should be approximately 1-10 nm (condition 2) [5]. In our case, donors are CdSe/ZnS QDs, and acceptors are InGaN NWs. Fig. 1,*a* shows the fulfillment of the condition 1. The QD PL band (wavelength of PL maxima 530 nm) completely falls within the absorption region of InGaN NWs.

As it was mentioned above, the synthesized NWs have a core/shell structure with a shell thickness of about 20 nm [8]. Therefore, to carry out condition 2, the shell was removed. The initial diameter of the NW core/shell is 110-120 nm, and the diameter of the InGaN NWs is 65-75 nm (see Fig. 1, *b*, *c*).

Fig. 1,d shows a typical SEM image after deposition QDs to an array of InGaN NWs. It can be seen that QDs predominantly fill the space between NWs, thus being deposited on their lateral surface.



Fig. 1. Implementation of conditions for effective FRET; overlap between the optical density spectrum of InGaN NWs and the PL spectrum of CdSe/ZnS QDs (*a*), plan-view SEM images: core/shell InGaN/GaN NWs (*b*), InGaN NWs (*c*), InGaN NWs with QDs (*d*)



Fig. 2. Micro-PL maps; InGaN NW array before deposition of QDs (*a*), InGaN NW array after deposition of QDs (*b*)



Fig. 3. PL spectra before and after deposition QDs

In general case, nonradiative energy transfer manifests itself in a decrease in the PL intensity of the donor and an increase in the PL of the acceptor [3]. Fig. 2 shows the PL distribution of InGaN NWs before and after QD deposition. The relative inhomogeneity of the NW PL distribution before QD deposition does not exceed 2. The surface decoration of the NW array leads to an increase in the PL signal over the entire area of the sample.

Fig. 3 shows the PL spectra at the maximum points of the micro-PL maps (black circles in Fig. 2). The InGaN NWs exhibit a PL at RT in the range of 600–700 nm. The PL spectrum contains short-wavelength (625 nm) and long-wavelength (645 nm) maxima. The two pronounced maxima and relatively broad PL can be explained by the different composition of indium in InGaN NWs.

After decoration the NW surface with QDs, the following is observed. The full width at half maximum of PL decreases by 10 nm, and the ratio between the short- and long-wavelength peaks decreases slightly. The peak and integrated PL intensity increases by more than 3 times. Thus, the reason for the PL enhancement is apparently the FRET mechanism. Moreover, another reason for this may be the passivation of surface states by the TOPO-QDs layer [18]. A detailed study of the nature of PL enhancement will be carried out in further works.

Conclusion

To conclude, we have synthesized InGaN NWs on the Si substrate by plasma-assisted MBE. The obtained sample has RT PL peaks in the red region of the visible spectrum. The deposition of colloidal TOPO-CdSe/ZnS on the surface of InGaN NWs allowed to enhance the PL of the initial nanostructures. The results obtained are of interest for the development of optically efficient devices based on InGaN NWs.

REFERENCES

1. Tang S.-Y., Yang C.-C., Su T.-Y., Yang T.-Y., Wu S.-C., Hsu Y.-C., Chen Y.-Z., T Lin.-N., Shen J.-L., Lin H.-N., Design of core-shell quantum dots-3d WS2 nanowall hybrid nanostructures with high-performance bifunctional sensing applications, ACS Nano. 14 (2020) 12668–12678.

2.Nizamoglu S., Sari E., Baek J., Lee I., Demir H.V., Nonradiative resonance energy transfer directed from colloidal CdSe/ZnS quantum dots to epitaxial InGaN/GaN quantum wells for solar cells, Physica Status Solidi (RRL)–Rapid Research Letters. 4 (2010) 178–180.

3. Khrebtov A.I., Reznik R.R., Ubyivovk E.V., Litvin A.P., Skurlov I.D., Parfenov P.S., Kulagina A.S., Danilov V.V., Cirlin G.E., Nonradiative energy transfer in hybrid nanostructures with varied dimensionality, Semiconductors. 53 (2019) 1258–1261.

4. Khrebtov A., Talalaev V., Samsonenko Y.B., Werner P., Rutskaya V., Artem'ev M., Tsyrlin G., A hybrid system of GaAs whisker nanocrystals and PbS quantum dots on silicon substrate, Technical Physics Letters. 40 (2014) 558–561.

5. Lu M.-L., Lai C.-W., Pan H.-J., Chen C.-T., Chou P.-T., Chen Y.-F., A facile integration of zero-(I–III–VI quantum dots) and one-(single SnO2 nanowire) dimensional nanomaterials: fabrication of a nanocomposite photodetector with ultrahigh gain and wide spectral response, Nano Letters. 13 (2013) 1920–1927.

6. Agarwal R., Heterointerfaces in semiconductor nanowires, Small. 4 (2008) 1872-1893.

7. Cirlin G., Dubrovskii V., Soshnikov I., Sibirev N., Samsonenko Y.B., Bouravleuv A., Harmand J., Glas F., Critical diameters and temperature domains for MBE growth of III–V nanowires on lattice mismatched substrates, Physica Status Solidi (RRL)–Rapid Research Letters. 3 (2009) 112–114.

8. Gridchin V.O., Kotlyar K.P., Reznik R.R., Dragunova A.S., Kryzhanovskaya N.V., Lendyashova V.V., Kirilenko D.A., Soshnikov I.P., Shevchuk D.S., Cirlin G.G., Multi-colour light emission from InGaN nanowires monolithically grown on Si substrate by MBE, Nanotechnology. 32 (2021) 335604.

9. Tabata T., Paek J., Honda Y., Yamaguchi M., Amano H., Growth of InGaN nanowires on a (111) Si substrate by RF-MBE, Physica Status Solidi c. 9 (2012) 646–649.

10. Guo W., Zhang M., Banerjee A., Bhattacharya P., Catalyst-free InGaN/GaN nanowire light emitting diodes grown on (001) silicon by molecular beam epitaxy, Nano Letters. 10 (2010) 3355–3359.

11. Liu X., Sun Y., Malhotra Y., Pandey A., Wu Y., Sun K., Mi Z., High efficiency InGaN nanowire tunnel junction green micro-LEDs, Applied Physics Letters. 119 (2021) 141110.

12. Lu Y.-J., Wang C.-Y., Kim J., Chen H.-Y., Lu M.-Y., Chen Y.-C., Chang W.-H., Chen L.-J., Stockman M.I., Shih C.-K., All-color plasmonic nanolasers with ultralow thresholds: autotuning mechanism for single-mode lasing, Nano Letters. 14 (2014) 4381–4388.

13. Shin D.-Y., Kim T., Akyuz O., Demir H.V., Lee I.-H., $Ag@SiO_2$ -embedded InGaN/GaN nanorod array white light-emitting diode with perovskite nanocrystal films, Journal of Alloys and Compounds. 898 (2022) 162974.

14. Wang H., Kubo T., Nakazaki J., Segawa H., Solution-processed short-wave infrared PbS colloidal quantum Dot/ZnO nanowire solar cells giving high open-circuit voltage, ACS Energy Letters. 2 (2017) 2110–2117.

15. Li Y., Zhuang T.-T., Fan F., Voznyy O., Askerka M., Zhu H., Wu L., Liu G.-Q., Pan Y.-X., Sargent E.H., Pulsed axial epitaxy of colloidal quantum dots in nanowires enables facet-selective passivation, Nature Communications. 9 (2018) 4947.

16. Hou D., Dev A., Frank K., Rosenauer A., Voss T., Oxygen-controlled photoconductivity in ZnO nanowires functionalized with colloidal CdSe quantum dots, The Journal of Physical Chemistry C. 116 (2012) 19604–19610.

17. Hernóndez-Marthnez P.L., Govorov A.O., Demir H.V., Furster-Type Nonradiative Energy Transfer for Assemblies of Arrayed Nanostructures: Confinement Dimension vs Stacking Dimension, The Journal of Physical Chemistry C. 4958–4951 (2014) 118.

18. Khrebtov A.I., Danilov V.V., Kulagina A.S., Reznik R.R., Skurlov I.D., Litvin A.P., Safin F.M., Gridchin V.O., Shevchuk D.S., Shmakov S.V., Influence of TOPO and TOPO-CdSe/ZnS Quantum Dots on Luminescence Photodynamics of InP/InAsP/InPHeterostructure Nanowires, Nanomaterials. 11 (2021) 640.

THE AUTHORS

SHUGABAEV Talgat talgashugabaev@mail.ru ORCID: 0000-0002-4110-1647

KULAGINA Anastasia S. a.s.panfutova@gmail.com ORCID: 0000-0002-9668-6398

GRIDCHIN Vladislav O. gridchinvo@yandex.ru ORCID: 0000-0002-6522-3673

KOTLYAR Konstantin P. konstantin21kt@gmail.com ORCID: 0000-0002-0305-0156

REZNIK Rodion R. moment92@mail.ru ORCID: 0000-0003-1420-7515 LENDYASHOVA Vera V. erilerican@gmail.com ORCID: 0000-0001-8192-7614

KHREBTOV Artyom I. khrebtovart@mail.ru ORCID: 0000-0001-5515-323X

KRYZHANOVSKAYA Natalia V. nataliakryzh@gmail.com ORCID: 0000-0002-4945-9803

MELNICHENKO Ivan I. imelnichenko@hse.ru ORCID: 0000-0003-3542-6776

CIRLIN George E. cirlin.beam@mail.ioffe.ru ORCID: 0000-0003-0476-3630

Received 16.07.2023. Approved after reviewing 17.08.2023. Accepted 17.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 544.7 DOI: https://doi.org/10.18721/JPM.163.245

Ultraviolet photoluminescence enhancement of zinc oxide nanocrystals in colloidal mixtures with spark discharge aluminum nanoparticles

D. Malo^{1,2}, A.A. Lizunova¹, O.V. Vershinina¹, E.M. Filalova¹, V.V. Ivanov¹

¹ Moscow Institute of Physics and Technology, Dolgoprudny, Moscow region, Russia;

² Damascus University, Damascus, Syria

[™] malo.d@mipt.ru

Abstract. Currently, nanoplasmonics is considered one of the most appealing areas of nanophotonics for researchers especially in studies on aluminum as one of the most attractive metal for pushing plasmonics into ultraviolet (UV) devices. Aluminum plasmonics has been shown to be effective for several applications including ultraviolet enhanced fluorescence, optoelectronics, photocatalysis, imaging and biosensing. This work investigated ultraviolet photoluminescence enhancement in mixture colloids of zinc oxide with aluminum nanoparticles. Where aluminum nanoparticles, synthesized by spark discharge method, were with an average size 22.3 ± 7.7 nm and five aluminum colloids with various concentrations of metal from 0.001 to 0.015 g/L were obtained in isopropyl alcohol solution. At the same time, zinc oxide colloids were with two concentrations 0.022 and 0.22 g/L with an average size of the nanocrystals 26.6 \pm 7.4 nm. In our research, we have achieved photoluminescence enhancement up to 2.4-fold of zinc oxide emission at wavelength 377 nm in mixture colloids of zinc oxide with aluminum nanoparticles at excitation wavelengths of 300 nm and 325 nm.

Keywords: Photoluminescence (PL), ultraviolet (UV), colloidal mixture, spark discharge method, aluminum nanoparticles (Al NPs), zinc oxide nanoparticles (ZnO NPs)

Funding: This work was financially supported by the Russian Science Foundation (project no. 22-19-00311, https://rscf.ru/en/project/22-19-00311/).

Citation: Malo D., Lizunova A.A., Vershinina O.V., Filalova E.M., Ivanov V.V., Ultraviolet photoluminescence enhancement of zinc oxide nanocrystals in colloidal mixtures with spark discharge aluminum nanoparticles, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 261–266. DOI: https://doi.org/10.18721/JPM.163.245

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Malo D., Lizunova A.A., Vershinina O.V., Filalova E.M., Ivanov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 544.7 DOI: https://doi.org/10.18721/JPM.163.245

Ультрафиолетовое усиление фотолюминесценции нанокристаллов оксида цинка в коллоидных смесях с наночастицами алюминия, синтезированных в газовом разряде

Д. Мало^{1,2}, А.А. Лизунова¹, О.В. Вершинина¹, Э.М. Филалова¹, В.В. Иванов¹ ¹ Московский физико-технический институт, Долгопрудный, Московская область, Россия

² Дамасский университет, Дамаск, Сирия

□ malo.d@mipt.ru

Аннотация. В данной работе исследовано усиление ультрафиолетовой фотолюминесценции в смеси коллоидных растворов нанокристаллов оксида цинка с наночастицами алюминия. Наночастицы алюминия, синтезированные методом газового разряда, имели средний размер 22,3 ± 7,7 нм. Из них были получены пять коллоидов алюминия с концентрацией наночастиц металла от 0,001 до 0,015 г/л в растворе изопропилового спирта, а коллоиды оксида цинка средним размером кристаллов 26,6 ± 7,4 нм использовались с двумя концентрациями 0,022 и 0,22 г/л. В нашим исследовании, мы добились усиления фотолюминесценции до 2,4 раза эмиссии оксида цинка на длине волны 377 нм в смеси коллоидов оксида цинка с наночастицами алюминия при длинах волн возбуждения 300 нм и 325 нм.

Ключевые слова: Фотолюминесценция (ФЛ), ультрафиолет (УФ), коллоидная смесь, метод газового разряда, наночастицы алюминия, наночастицы оксида цинка

Финансирование: Исследование выполнено за счет гранта Российского научного фонда (проект № 22-19-00311, https://rscf.ru/en/project/22-19-00311/).

Ссылка при цитировании: Мало Д., Лизунова А.А., Вершинина О.В., Филалова Э.М., Иванов В.В. Ультрафиолетовое усиление фотолюминесценции нанокристаллов оксида цинка в коллоидных смесях с наночастицами алюминия, синтезированных в газовом разряде // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 261–266. DOI: https://doi.org/10.18721/JPM.163.245

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Nowadays, interest in the synthesis of aluminum nanoparticles and structures has especially increased after the theoretical substantiation of the use of aluminum as a cheap and promising material with surface plasmon resonance in ultraviolet region which makes it possible to enhance the photoluminescence of organic dyes and semiconductor structures by several times. This phenomenon actively can be used in various fields of science and technology such as in medicine, solar cells, fluorescent lamps and microelectronics [1-3].

Spark discharge synthesis, it is considered to be a simple and potential method to produce plasmonic aluminum nanoparticles in the UV region [4]. Additionally, stabilization suspensions of Al nanoparticles is a challenging process for researchers to obtain nano-inks, study their morphological, physicochemical and optical properties [5-8] that can be used for the nanostructures' and film fabrication [9].

In this research, we obtained colloids of plasmonic Al NPs, synthesized by spark discharge method, and their mixtures with an ultraviolet phosphor, namely, ZnO NPs and we studied the effect of plasmonic Al NPs to enhance the photoluminescence in liquid dispersions in the UV region of the spectrum.

© Мало Д., Лизунова А.А., Вершинина О.В., Филалова Э.М., Иванов В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Materials and Methods

ZnO NPs colloids were prepared by the method which is described in [8, 9] by dilution using chromatographically pure isopropyl alcohol (Scharlau) to get concentrations 0.022 and 0.22 g/L.

Aerosol aluminum nanoparticles were synthesized using the spark discharge generator [4], that used in atmosphere of argon of purity 6.0 at pressure 1.2 atm with Al electrodes (solid cathode 8 mm in diameter, anode with the hole 3.5 mm), discharge voltage 1.5 kV, discharge period 2 ms, gas flow 600 mL/min and one hour for passivation with argon 4.8.

For Al NPs colloids, citric acid in chromatographically isopropyl alcohol (0.01 g/L) (buffer solution) was used as surface active agents to form stable Al dispersions with the desired dimensional parameters. Then, ultrasonic treatment of dispersion (0.4 g/L) of Al NPs was carried out for 30 minutes to crush agglomerated particles.

Five suspensions of Al NPs were prepared with different concentrations 0.001, 0.003, 0.005, 0.010 and 0.015 g/L by dilution with buffer solution.

At room temperature, to study photoluminescence enhancement at excitation wavelengths of 300 nm and 325 nm, mixtures of ZnO NPs with Al NPs (v:v) (1:1) were prepared and compared with mixture of ZnO NPs with pure isopropanol (1:1).

The size and crystal structure of primary NPs were received by transmission electron microscope (TEM) Jeol JEM 2100 (200 kV) and energy dispersive X-ray (EDX) spectrometer X-MAXN OXFORD Instruments. UV-vis-NIR spectra and luminescence emission were obtained using JASCO V-770 and JASCO FP-8300 spectrometers, correspondingly.

The photoluminescence inner filter correction of the colloidal mixture and pure ZnO NPs colloids according to the approach described in our previous work [8] was used.

Results and Discussion

According to TEM and electron diffraction images, spherical shape and core-shell structure with metal crystal core and oxide shell for aluminum nanoparticles were observed.

The average primary particle size of Al nanoparticles, which formed large agglomerates, was 22.3 ± 7.7 nm including the shell thickness (about 3 nm), while 26.6 ± 7.4 nm for ZnO nanocrystals.

EDX maps of several agglomerates confirmed the formation of Al-ZnO complexes presented in (Fig. 1). Elemental line profile (Fig. 1,c) of the agglomerate confirms the presence of separate ZnO (yellow peaks) and metal Al nanoparticles (red peaks).



Fig. 1. Typical TEM image with corresponding SAED pattern (on the insert) for an Al-ZnO complex found in the colloidal mixture of Al 0.003 g/L with ZnO 0.22 g/L (*a*); STEM image of an Al-ZnO agglomerate found in the colloidal mixture of Al 0.015 g/L with ZnO 0.022 g/L and corresponding EDX elemental maps (*b*); EDX line profile (*c*)

The photoluminescence spectra of ZnO NPs colloids (0.022 and 0.22 g/L) and their mixtures with Al NPs colloids of different concentrations were obtained at excitation wavelengths of 300 nm and 325 nm (Fig. 2,a). Fig. 2,*b* showed the increase of the luminescent enhancement factor from 1.21 to 2.4 for the colloidal mixtures of ZnO and Al NPs when the concentration of metal nanoparticles grows up regardless of the mass fraction of semiconductor nanocrystals. The enhancement factor was calculated by dividing the corrected intensity of the PL peak at 377 nm for a solution mixture of ZnO and Al NPs by the corrected PL intensity of a ZnO NPs colloid with the same fluorophore concentration using inner filter effect correction [10].



Fig. 2. Photoluminescence emission spectra of pure ZnO NPs colloids (red line) and their mixtures with Al NPs colloids of various concentrations (from 0.001 to 0.015 g/L) (a);
PL enhancement factor for mixtures with different concentrations of ZnO and Al NPs (b); at excitation wavelengths of 300 nm (left) and 325 nm (right)

It was found that an increase in photoluminescence intensity of ZnO nanoparticles up to 240% at an emission wavelength 377 nm was observed with an increase in the concentration of Al nanoparticles from 0.001 to 0.015 g/L with an average size 22.3 ± 7.7 nm. In our previous study using other aluminum nanoparticles [8], we achieved PL enhancement up to 2.9- and 3.0-fold at excitation wavelengths of 300 nm and 325 nm, correspondingly. That was in colloi-dal mixtures using Al nanopowder, produced by electrical explosion of wires with an average size 54.6 ± 25.1 nm. Where concentrations of Al NPs colloids were from 0.00285 to 0.057 g/L while ZnO nanoparticles colloids with concentrations from 0.022 to 0.44 g/L. The best achieved enhancement up to 7 times in solutions was shown by Staruknin et al. in colloids of silver nanoparticles and phthalocyanines metallocomplexes [11]. On the other side, A. Muravitskaya et al. [12] presented in 2020 the maximum possible enhancement of ZnO nanocrystals (9.7-fold) on the array of oval Al nanoparticles.

Based on the obtained results, we have observed the effect of particle size and concentration on the PL enhancement factor related to the formation of Al-ZnO complexes in mixture colloids.

Conclusion

We demonstrated that photoluminescence enhancement of ZnO NPs in presence of plasmonic metal Al NPs, synthesized by spark discharge method, at excitation wavelengths of 300 nm and 325 nm was achieved up to 2.4-fold in UV region at an emission wavelength 377 nm in colloid solutions. So, these promising colloids can be used as nano-inks to fabricate biomedical and optoelectronic sensors in ultraviolet region of the spectrum based on Al nanostructures.

Acknowledgments

This work was financially supported by the Russian Science Foundation (project № 22-19-00311, https://rscf.ru/en/project/22-19-00311/).

REFERENCES

1. Gérard D., Gray S. K., Aluminium plasmonics, Journal of Physics D: Applied Physics. 48 (18) (2015) 184001.

2. Li Y.F., Kou Z.L., Feng J., Sun H.B., Plasmon-enhanced organic and perovskite solar cells with metal nanoparticles, Nanophotonics. 9 (10) (2020) 3111–3133.

3. Li W., Ren K., Zhou J., Aluminum-based localized surface plasmon resonance for biosensing, TrAC Trends in Analytical Chemistry. 80 (2016) 486–494.

4. Borisov V.I., Lizunova A.A., Mazharenko A.K., Malo D., Ramanenka A.A., Shuklov I.A., Ivanov V.V., Aluminum nanoparticles synthesis in spark discharge for ultraviolet plasmonics, Journal of Physics: Conference Series, IOP Publishing. 1695 (2020) 012021.

5. **Mahdieh M.H., Mozaffari H.,** Characteristics of colloidal aluminum nanoparticles prepared by nanosecond pulsed laser ablation in deionized water in presence of parallel external electric field, Physics Letters A. 381 (38) (2017) 3314–3323.

6. Ramanenka A.A., Lizunova A.A., Mazharenko A.K., Kerechanina M.F., Ivanov V.V., Gaponenko S.V., Preparation and optical properties of isopropanol suspensions of aluminum nanoparticles, Journal of Applied Spectroscopy. 87 (4) (2020) 662–667.

7. Castilla M., Schuermans S., Gérard D., Martin J., Maurer T., Hananel U., Markovich G., Plain J., Proust J., Colloidal synthesis of crystalline aluminum nanoparticles for UV plasmonics, ACS photonics. 9 (3) (2022) 880–887.

8. Lizunova A.A., Malo D., Guzatov D.V., Vlasov I.S., Kameneva E.I., Shuklov I.A., Urazov M.N., Ramanenka A.A., Ivanov V.V., Plasmon-enhanced ultraviolet luminescence in colloid solutions and nanostructures based on aluminum and ZnO nanoparticles, Nanomaterials. 12 (22) (2022) 4051.

9. Malo D., Lizunova A.A., Nouraldeen M., Borisov V.I., Ivanov V.V., Aluminum nanostructures produced by aerosol dry printing for ultraviolet photoluminescence enhancement, St. Petersburg Polytechnic University Journal. Physics and Mathematics. 15 (3.3) (2022) 276–280.

10. Lakowicz J.R., Principles of Fluorescence Spectroscopy, 3rd ed, University of Maryland School of Medicine: Baltimore, MD, USA, 2006.

11. Starukhin A., Apyari V., Gorski A., Ramanenka A., Furletov A., Plasmon enhancement of fluorescence of phthalocyanines metallocomplexes in solutions of silver nanoparticles, In EPJ Web of Conferences. 220 (2019) 03003. EDP Sciences.

12. Muravitskaya A., Gokarna A., Movsesyan A., Kostcheev S., Rumyantseva A., Couteau C., Lerondel G., Baudrion A.L., Gaponenko S., Adam P.M., Refractive index mediated plasmon hybridization in an array of aluminium nanoparticles, Nanoscale. 12 (11) (2020) 6394–6402.

THE AUTHORS

MALO Dana malo.d@mipt.ru ORCID: 0000-0001-6310-9183

LIZUNOVA Anna A. lizunova.aa@mipt.ru ORCID: 0000-0002-2895-4696

VERSHININA Olesya V. seraia.ov@phystech.edu ORCID: 0000-0001-6945-4818 FILALOVA Emilia M. filalova.em@phystech.edu ORCID: 0000-0002-3391-4576

IVANOV Victor V. ivanov.vv@mipt.ru ORCID: 0000-0002-9149-0468

Received 17.07.2023. Approved after reviewing 19.07.2023. Accepted 24.07.2023.

Conference materials UDC 621.793.182 DOI: https://doi.org/10.18721/JPM.163.246

Effect of Al-CuO multilayer thermite structures thickness on combustion behavior

M.E. Shiryaev¹⊠, R.M. Ryazanov², A.V. Sysa², E.A. Lebedev^{1,2}

¹ National Research University of Electronic Technology (MIET), Zelenograd, Moscow, Russia;

² Scientific-Manufacturing Complex "Technological Centre", Zelenograd, Moscow, Russia

□ shiryaevme@bk.ru

Abstract. This study investigates multilayer structures of Al-CuO formed on the surfaces of sitall substrates using magnetron sputtering. The influence of changing the total thickness of the multilayer structure on the character and speed of the combustion front, characteristics of the reaction products, and gas emission levels is analyzed. Increasing the total thickness of the multilayer structure leads to changes in the speed and behavior of the combustion wave, as well as variations in the quantity, size, and form of the combustion products. The analysis includes theoretical data obtained using the Thermo software and experimental investigations. Gas emission values at different reaction temperatures have been evaluated.

Keywords: multilayer structure, Al-CuO, thermite, combustion

Funding: The study was supported by the Russian Science Foundation grant 22-29-01177, https://rscf.ru/project/22-29-01177/.

Citation: Shiryaev M.E., Ryazanov R.M., Sysa A.V., Lebedev E.A., Effect of Al-CuO multilayer thermite structures thickness on combustion behavior, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 267–272. DOI: https://doi.org/10.18721/JPM.163.246

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.793.182 DOI: https://doi.org/10.18721/JPM.163.246

Влияние толщины многослойных термитных структур Al-CuO на характеристики горения

М.Е. Ширяев¹[™], Р.М. Рязанов², А.В. Сыса², Е.А. Лебедев^{1,2}

¹ Национальный исследовательский университет «МИЭТ», Зеленоград, Москва, Россия;

² «Научно-производственный комплекс «Технологический центр», Зеленоград, Москва, Россия

^{III} shiryaevme@bk.ru

Аннотация. В данном исследовании изучаются многослойные структуры Al-CuO, формируемые на поверхности ситалловых подложек методом магнетронного распыления. Анализируется влияние изменения общей толщины многослойной структуры на характер и скорость фронта горения, характеристики продуктов реакции, а также величины газовыделения. При увеличении общей толщины многослойной структуры наблюдается изменение скорости волнового горения и его характера, а также варьируются количество продуктов горения, их размер и форма. Приведен анализ теоретических данных, полученных с помощью программы Thermo и экспериментальных исследований. Оценены значения газовыделения при различных температурах реакции.

Ключевые слова: многослойные структуры, Al-CuO, термиты, горение

© Shiryaev M.E., Ryazanov R.M., Sysa A.V., Lebedev E.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Финансирование: Исследование выполнено при поддержке гранта Российского научного фонда No. 22-29-01177, https://rscf.ru/project/22-29-01177/.

Ссылка при цитировании: Ширяев М.Е., Рязанов Р.М., Сыса А.В., Лебедев Е.А. Влияние толщины многослойных термитных структур Al-CuO на характеристики горения // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 267–272. DOI: https://doi.org/10.18721/JPM.163.246

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Currently, extensive research is being conducted on various nanostructured thermite materials. Reactive compositions utilizing thin-film multilayer reactive structures as local heat sources offer efficient solutions for a range of technological challenges in microelectronics. In such structures, self-propagating exothermic reactions can occur after local initiation. The temperatures reached in these reactions can reach several thousand degrees Celsius, making thermite materials valuable for various applications, including welding, reactive bonding, and the aerospace industry.

Most thermite materials used in electronics consist of powder mixtures and multilayer thin films of aluminum combined with various oxidizers (MoO₃, CuO, WO₃, Fe₂O₃, I₃O₄, and Bi₂O₃) [1, 2]. Typically, these materials are fabricated by mixing nanoscale particles of pure metal (fuel) with nanoscale particles of metal oxide (acting as the oxidizer) in the form of powders [3, 4], granules [5], or thin films [5, 6].

Al-CuO thermite systems are widely used due to their high specific heat of combustion (approximately 4.1 kJ/g) and adiabatic reaction temperature (2843 K). Multilayer Al-CuO materials can be formed using magnetron sputtering. Control over the characteristics of combustion reaction products, including composition and morphology, is crucial in many application areas. Furthermore, the ability to control the propagation rate of the combustion front in wave thermite reactions, as well as gas emission, can be crucial for specific applications.

In this study, we investigated the influence of the thickness of the Al-CuO multilayer film on gas emission, combustion front propagation velocity, and characteristics of the reaction products.

Materials and Methods

The multilayer Al-CuO thermite structure was fabricated using magnetron sputtering on the URM-71 system. The aluminum and copper oxide layers were deposited sequentially by sputtering the respective targets in an argon environment at a pressure of 3×10^{-3} Torr. The copper oxide and aluminum targets were operated under a constant current mode at powers of 250 W and 500 W, respectively.

The geometric characteristics and combustion products of the multilayer structures were examined using scanning electron microscopy (SEM).

In this study, samples with different total structure thicknesses were considered, where the bilayer thickness (the combined thickness of one aluminum layer and one copper oxide layer) was 100 nm. The multilayer structure consisted of 20, 30, and 40 layers, resulting in total thicknesses of 2 μ m, 3 μ m, and 4 μ m, respectively.

The combustion front propagation speed was measured using high-speed video recording. The combustion of the structures was recorded using a high-speed camera at a frame rate of 10,000 fps. Wave-like combustion was initiated using an electrical spark at the lower part of the sample. Based on the recorded combustion videos, the distance traveled by the combustion front, the time taken to cover that distance, and the velocity were calculated.

The Thermo program was used to obtain gas emission values at different reaction temperatures. The mole amounts of the components were calculated based on a total volume of 1 cm³. The Thermo program, developed at the Institute of Structural Macrokinetics of the Russian Academy of Sciences, is designed to calculate thermodynamic equilibrium in complex multicomponent heterophase systems. The calculation results include the composition of equilibrium products (both condensed and gaseous) and adiabatic temperature [7].

© Ширяев М.Е., Рязанов Р.М., Сыса А.В., Лебедев Е.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Results and Discussion

Fig. 1 shows a storyboard of the combustion process of multilayer thermite structures with a total thickness of 2, 3 and 4 μ m. The calculated values of the propagation velocity of the combuso tion front were 6.7, 10.2 and 7.8 m/s, respectively. The maximum speed of the front was achieved by combustion structures thickness of 3 μ m.

The study of the combustion process revealed differences in the propagation speed of the wave combustion front depending on the structure thickness. For the sample with a thickness of 2 μ m, as shown in Fig. 1,*a*, the reaction products were practically not expelled, and there was no gas emission. In the case of the sample with a thickness of 3 μ m, Fig. 1,*b*, gas emission and a significant amount of various-sized reaction products expelled from the surface were observed. Meanwhile, the combustion of the structure with a thickness of 4 μ m, Fig. 1,*c*, was characterized by intense gas emission and a large quantity of expelled reaction products, which were larger in size compared to those expelled from the 3 μ m thick structure.



Fig. 1. Storyboard of the combustion process of multilayer Al-CuO thermite structures with a total thickness of 2 μ m (*a*), 3 μ m (b) and 4 μ m (*c*)

Investigation of combustion products in multilayer thermite structures (MTS) using scanning electron microscopy yielded the results presented in Fig. 2.

For MTS with a total thickness of 2 and 3 μ m, Fig. 2, *a*, *b*, respectively, the combustion products appeared as elongated droplet-shaped objects with spherical inclusions. However, for MTS with a total thickness of 3 μ m, the reaction products exhibited significantly larger sizes, reaching several tens of μ ms. In addition to the larger particles, smaller particles were uniformly distributed on the substrate surface. In contrast, for MTS with a total thickness of 4 μ m, Fig. 2,*c*, large objects with inclusions were practically absent. Instead, smaller droplet-shaped objects formed on the substrate surface, exhibiting similar structures to the reaction products in the other two cases, and they were covered with short and thin fibers.

To justify the differences in the form and quantity of reaction products, modeling was performed using the Thermo program. Theoretical values of gas emission were obtained within the specified temperature range of the reaction, ranging from 2250 K to 2850 K. The obtained data is depicted in Fig. 3.

In the analysis of multilayer thermite structure combustion, it's crucial to consider heat dissipation through the substrate, as some energy will disperse, leading to a decrease in reaction temperature. The substrate's influence on heat dissipation depends on the total thickness of the multilayer structure - the thinner the structure, the stronger the substrate's influence. This study experimentally found that multilayer thermite structures with a total thickness of less than 1.5 μ m cannot sustain self-propagating combustion.



Fig. 2. Results of SEM studies of reaction products on the surface of multilayer Al-CuO thermite structures with thicknesses of 2 μ m (*a*), 3 μ m (*b*), 4 μ m (*c*)

The comparison of experimental results obtained through SEM and high-speed video recording with theoretical gas emission calculations (presented in Fig. 3) allows us to estimate the change in reaction temperature depending on the total thickness of the multilayer thermite structure. The upper temperature limit is constrained to 2666 K (the adiabatic reaction temperature of Al + CuO, corresponding to the chosen component ratio, obtained in the Thermo program). This temperature value (marked in Fig. 3 as T_{adiab}) is below the melting points of aluminum (2743 K, Al T_{boil}), copper (2835 K, Cu T_{boil}), and aluminum oxide (3250 K), meaning these components do not contribute to gas emission.



Fig. 3. Relationship between gas emission and the temperature of the reaction

The combustion of a 2 μ m thick multilayer thermite structure visually does not accompany gas emission (Fig. 1,*a*), and SEM images clearly show that most reaction products remain on the substrate surface. The reaction products are hardened droplets of aluminum oxide with copper inclusions. Thus, for a multilayer thermite structure with a total thickness of 1.5 μ m, the reaction temperature lies in the range from 2345 K (melting temperature of aluminum oxide) to 2400 K, when gas emission is still insignificant.

The combustion processes of multilayer thermite structures with a total thickness of 3 and 4 μ m visually differ little from each other according to high-speed video recording results (Fig. 1,*b* and 1,*c*). However, compared to 2 μ m thick multilayer thermite structures, significant gas emission is observed. SEM images clearly show that after the combustion of thicker multilayer structures, significantly fewer reaction products remain on the substrate surface, which may be associated with more intense gas emission.

Analyzing the character of the graph presented in Fig. 3, it can be assumed that the front temperature values for multilayer structures with a total thickness of 3 and 4 μ m should be on different sides of the plateau observed in the range from 2450 to 2550 K, where significant changes in gas emission intensity do not occur. Thus, the reaction temperature for a 3 μ m thick multilayer structure may lie in the range from 2400 to 2450 K, and for a 4 μ m thickness from 2550 to 2666 K. It can also be assumed that further increase in the total thickness of the multilayer structure (more than 4 μ m) will not lead to a significant change in the combustion character, as the adiabatic reaction temperature cannot be exceeded.

Conclusion

During the study, the influence of the thickness of the multilayer Al-CuO thermite structures on the characteristics of combustion reaction products was investigated. The results showed that the thickness of the multilayer structure had a significant impact on both the reaction characteristics and its products. High-speed video analysis revealed that the combustion front velocity increased with increasing thickness, while SEM analysis demonstrated changes in the morphology and composition of the reaction products. An analysis of theoretical calculated characteristics and obtained experimental data was conducted, revealing a relationship between them. This study provides an estimation of reaction temperature values for multilayer thermite structures of various thicknesses, contributing to a better understanding of their combustion behavior.

REFERENCES

1. Nellums R., Terry B., Tappan B., Son S., Groven L.G., The effect of silicon powder characteristics on the combustion of silicon/teflon/viton nanoenergetics // Propellants, Explosives, Pyrotechnics. 39 (3) (2014) 337–347.

2. Yarrington C., Son S., Foley T., Obrey S., Pacheco A., Nano aluminum energetics: The effect of synthesis method on morphology and combustion performance // Propellants, Explosives, Pyrotechnics. 36 (6) (2012) 551–557.

3. Guidotti R., Odinek A., Reinhardt F., Characterization of $Fe/KClO_4$ Heat Powders and Pellets // Journal of Energetic Materials. 24 (4) (2006) 271–305.

4. **Petrantoni M., Rossi C., Salvagnac L., Conedera V., Esteve A.**, Multilayered Al/CuO thermite formation by reactive magnetron sputtering: Nano versus micro // Journal of Applied Physics. 108 (8) (2010) 84–32.

5. Fritz J., Grzyb A., Knio O., Grapes M., Weihs T., Characterizing solid-state ignition of runaway chemical reactions in Ni-Al nanoscale multilayers under uniform heating // Journal of Applied Physics. 118 (13) (2015) 101–135.

6. Grapes M., Weihs T., Exploring the reaction mechanism in self-propagating Al/Ni multilayers by adding inert material // Combustion and Flame. 172 (2016) 105–115.

7. Institute of Structural Macrokinetics of the Russian Academy of Sciences. "Thermo". URL: https://ism.ac.ru/thermo/. Accessed Mar. 20, 2023.

THE AUTHORS

SHIRYAEV MAKSIM E. shiryaevme@bk.ru ORCID: 0000-0002-0028-4061

RYAZANOV ROMAN M. r.m.ryazanov@gmail.com ORCID: 0000-0002-2464-8712 SYSA ARTEM V. sysa.artem@yandex.ru ORCID: 0000-0002-5010-7071

LEBEDEV EGOR A. dr.beefheart@gmail.com ORCID: 0000-0002-5085-5408

Received 21.07.2023. Approved after reviewing 17.08.2023. Accepted 17.08.2023.

Conference materials UDC 621.315.592 DOI: https://doi.org/10.18721/JPM.163.247

Boron phosphide grown by PECVD and its optical properties

A.A. Maksimova^{1,2^{IZI}}, A.V. Uvarov¹, V.A. Pozdeev¹, D.A. Kirilenko³, A.I. Baranov¹, E.A. Vyacheslavova¹, A.S. Gudovskikh^{1,2}

¹ St. Petersburg Alferov Academic University, St. Petersburg, Russia;

² St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia;

³Ioffe Institute, St. Petersburg, Russia

[™] maksimova_alina@spbau.ru

Abstract. This article presents a study of the growth of boron phosphide (BP) thin films by plasma enhanced chemical vapor deposition (PECVD) and its optical properties. BP thin films were deposited on a fused silica and silicon substrates using a mixture of diborane (B_2H_6) and phosphine (PH₃) with hydrogen as precursors. The optical properties were investigated using optical spectroscopy, which showed excellent optical transparency in the visible and near-infrared regions. The BP films exhibited a bandgap of approximately 1.9 eV, indicating its potential for use in optoelectronic applications. The results demonstrate that PECVD is a promising technique for growing BP thin films with desirable optical properties.

Keywords: boron phosphide, PECVD, plasma enhanced chemical vapor deposition, optical spectroscopy

Funding: This study was funded by Russian Science Foundation under the grant RSF 21-79-10413.

Citation: Maksimova A.A., Uvarov A.V., Pozdeev V.A., Kirilenko D.A., Baranov A.I., Vyacheslavova E.A., Gudovskikh A.S., Boron phosphide grown by PECVD and its optical properties, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 273–277. DOI: https://doi.org/10.18721/JPM.163.247

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.315.592 DOI: https://doi.org/10.18721/JPM.163.246

Плазмохимическое осаждение фосфида бора и его оптические свойства

А.А. Максимова^{1,2⊠}, А.В. Уваров¹, В.А. Поздеев¹, Д.А. Кириленко³, А.И. Баранов¹, Е.А. Вячеславова¹, А.С. Гудовских^{1,2}

¹ Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия;

² Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова (Ленина), Санкт-Петербург, Россия;

³ Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия

□ maksimova_alina@spbau.ru

Аннотация. В этой статье представлено исследование роста тонких пленок фосфида бора (ВР) методом плазмохимического осаждения и его оптических свойств. Тонкие пленки ВР осаждались на кварцевую подложку с использованием смеси диборана

© Maksimova A.A., Uvarov A.V., Pozdeev V.A., Kirilenko D.A., Baranov A.I., Vyacheslavova E.A., Gudovskikh A.S., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

(B₂H₆) и фосфина (PH₃) с водородом в качестве прекурсоров. Оптические свойства были исследованы с помощью оптической спектроскопии, которая показала высокую оптическую прозрачность в видимой и ближней инфракрасной областях. Пленки ВР имели ширину запрещенной зоны примерно 1,9 эВ, что указывает на их потенциал для использования в производстве оптоэлектронных приборов. Результаты показывают, что плазмохимическое осаждение является многообещающим методом выращивания тонких пленок ВР с требуемыми оптическими свойствами.

Ключевые слова: фосфид бора, плазмохимическое осаждение, оптическая спектроскопия

Финансирование: Работа выполнена в рамках проекта РНФ №10413-79-21.

Ссылка при цитировании: Максимова А.А., Уваров А.В., Поздеев В.А., Кириленко Д.А., Баранов А.И., Вячеславова Е.А., Гудовских А.С. Плазмохимическое осаждение фосфида бора и его оптические свойства // Научно-технические ведомости СПбГПУ. Физикоматематические науки. 2023. Т. 16. № 3.2. С. 273–277. DOI: https://doi.org/10.18721/ JPM.163.247

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Boron phosphide (BP) is a novel material for use in photovoltaics that has a number of attractive characteristics. BP is chemically inert, resistant to oxidation at high temperatures, has high thermal conductivity, low toxicity and mechanical stability [1]. It has also been theoretically shown that BP is one of the most promising materials for creating transparent conductive p-type coatings, since it is an indirect-gap semiconductor with a band gap of 2.1 eV, while the band gap for a direct transition is 4 eV, which implies low optical losses [2].

Due to these properties, the use of boron phosphide to create solar cells can increase the short circuit current compared to the use of amorphous hydrogenated silicon (a-Si:H). On the other hand, the negative $(-0.3 \pm 0.1 \text{ eV})$ valence band gap offset (ΔE_v) for the BP/Si interface [3] provides the necessary selectivity, which makes boron phosphide an excellent candidate for a selective hole contact without requiring an additional indium tin oxide layer (ITO) [4].

One of the key challenges in producing high-quality BP thin films is the availability of a suitable deposition technique. Among the various deposition methods, plasma-enhanced chemical vapor deposition (PECVD) has emerged as a promising technique for growing BP thin films due to its advantages such as scalability, low deposition temperatures, cost-effectiveness, and compatibility with large-area substrates.

In this article, we present a study on the growth of BP thin films by PECVD and their optical properties. The optical properties of BP thin films are critical to their performance in optoelectronic devices. Therefore, their characterization is essential for assessing their potential applications in energy-related fields. The results of this study provide valuable insights into the use of PECVD as a method for growing BP thin films with desired optical properties, which could facilitate its integration into various optoelectronics applications.

Materials and Methods

The growth of BP films was carried out in a standard Oxford PlasmaLab 100 PECVD (13.56 MHz) plasma chemical deposition unit using capacitive coupled RF plasma with a precursors flow control and temperature control of a heating table. Gas mixtures of 100 sccm hydrogen with 20 sccm of diborane (B_2H_6) and 10 sccm of phosphine were used as precursors. BP layers were deposited on fused silica and silicon substrates with orientation (100) at a low temperature (350 °C). The deposition was carried out at a plasma power of 100 W for 30 minutes with 600 mTorr chamber pressure.

Structural properties and surface morphology of the BP layer deposited on the silicon substrate was studied by means of transmission electron microscopy (TEM) using Jeol JEM-2100F set-up with 200 kV acceleration voltage (point resolution 0.19 nm). Cross-section specimens

[©] Максимова А.А., Уваров А.В., Поздеев В.А., Кириленко Д.А., Баранов А.И., Вячеславова Е.А., Гудовских А.С., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

for TEM were prepared by conventional route involving mechanical grinding with subsequent ion milling by Ar^+ at 2–4 kV. Energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) implemented in the TEM were used for the BP layers composition evaluation.

Optical transmission and reflection spectra were obtained on BP film deposited on fused silica substrates with Avantes ULS2048 spectrometer and Xe light source. Optical band gap parameters for BP thin layers were evaluated by a Tauc plot for indirect band gap semiconductors [5].

Results and Discussion

Fig. 1 shows Electron Energy Loss Spectra (EELS) and Transmission Electron Microscopy (TEM) image of the BP film on silicon substrate. According to EELS layer has semi-stoichiometric composition of elements with ratio of 60% of boron and 40% of phosphorus. TEM images of BP sample (Fig. 1) demonstrate the amorphous structure the film compared to the clearly distinguishable crystalline state of the Si substrate. The BP layer has a smooth surface and homogeneous structure with lack of visible defects. Heterointerfaces between Si substrate and BP layer are sharp and smooth. No initial epitaxy or any intermediate layer are observed.



Fig. 1. Electron Energy Loss Spectra (EELS) and Transmission Electron Microscopy (TEM) image of the BP film

Fig. 2, a shows absorbance spectra, boron phosphide is quite transparent in the long wavelength region (from 600-1100 nm), while in the short-wavelength region absorbance increases.

Fig. 2, *b* shows the Tauc plot for indirect bandgap, in which the gap value can be extracted. The gap value for the BP layer is 1.93 eV, which is in agreement with literature data. According to [3], the band gap for a-BP:H is in the range of 2.0-2.1 eV and depends on both the hydrogen and phosphorus proportion. The layer thickness was determined, the value of which is about 300 nm.

Т	а	b	1	e	1

Deposition properties										
Temperature, °C	Deposition	Pressure,	Plasma	Growth rate,	B ₂ H ₆ /PH ₃ /H ₂ ,					
	time, min	mTorr	power, W	nm/min	sccm					
350	30	600	100	12.3	20/10/100					



Fig. 2. Absorbance specter of BP film (a), Tauc plot for the indirect bandgap (b)

Conclusion

Thus, for the first time, boron phosphide was successfully deposited at low temperature (350 °C) by the plasma enhanced chemical vapor deposition (PECVD) method and its optical properties were studied. Film demonstrated high transparence in a long wavelength range and its band gap value extracted from the Tauc plot is in a good agreement with the literature.

This study provides a valuable contribution to the field of materials science, as BP is a promising material for various optoelectronic and photovoltaic-related applications. The use of PECVD as a deposition technique facilitates the integration of BP thin films into various device architectures, as it is scalable, cost-effective, and compatible with large-area substrates. Further research can leverage the results of this study to optimize the deposition process of BP by PECVD and explore its potential applications in optoelectronics, photovoltaics, and catalysis. Furthermore, the electronic properties of BP needs to be investigated.

Acknowledgements

TEM studies were performed using equipment of the Federal Joint Research Center "Material science and characterization in advanced technology" supported by the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Neuberger M., III-V Semiconducting Compounds. Springer US, 1971.

2. Varley J.B., High-Throughput Design of Non-oxide p-Type Transparent Conducting Materials: Data Mining, Search Strategy, and Identification of Boron Phosphide, Chemistry of Materials. American Chemical Society (ACS). 29 (6) (2017) 2568–2573.

3. **King S.W.**, Valence Band Offset at a-B:H and a-BP:H/Si Interfaces, ECS Journal of Solid State Science and Technology. The Electrochemical Society. 1 (5) (2012) 250–253.

4. **Гудовских А.С.,** Формирование селективного контакта BP/Si с помощью низкотемпературного плазмохимического осаждения, Письма в журнал технической физики. Ioffe Institute Russian Academy of Sciences. 47 (2) (2021) 49.

5. Tauc J., Grigorovici R., Vancu A., Optical Properties and Electronic Structure of Amorphous Germanium, Phys. Status Solidi B. 15 (2) (1966) 627–637.

THE AUTHORS

MAKSIMOVA Alina A. deer.blackgreen@yandex.ru ORCID: 0000-0002-3503-7458

UVAROV Alexander V. lumenlight@mail.ru ORCID: 0000-0002-0061-6687

POZDEEV Vyacheslav A. pozdeev99va@gmail.com ORCID: 0000-0002-4894-6503

KIRILENKO Demid A. demid.kirilenko@mail.ioffe.ru ORCID: 0000-0002-1571-209X BARANOV Artem I. itiomchik@yandex.ru ORCID: 0000-0002-4894-6503

VYACHESLAVOVA Ekaterina A. cate.viacheslavova@yandex.ru ORCID: 0000-0001-6869-1213

GUDOVSKIKH Alexander S. gudovskikh@spbau.ru ORCID: 0000-0002-7632-3194

Received 23.07.2023. Approved after reviewing 26.07.2023. Accepted 31.07.2023.

Conference materials UDC 535.341.08 DOI: https://doi.org/10.18721/JPM.163.248

Optical properties of photo-thermo-refractive glasses doped with terbium

V.V. Pesniakov¹[™], A.I. Ignatiev¹, N.V. Nikonorov¹

¹ ITMO University, St. Petersburg, Russia

^{III} v.pesnyackoff@yandex.ru

Abstract. In this study two types of photo-thermo-refractive glasses were investigated. First one was the classical photo-thermo-refractive glass doped with 0,007 mol.% Ce^{3+} co-doped with 1 mol.% Tb^{3+} and the second one did not contain any Ce^{3+} but only 1 mol.% Tb^{3+} . These types of glass were exposed to the mercury lamp using a cut-off filter that do not transmit wavelengths shorter than 350 nm. After the heat treatment such glasses did not show any plasmon resonance absorption peak. But in samples of photo-thermo-refractive glass without any Ce^{3+} but only containing Tb^{3+} plasmon resonance absorption peak corresponded to silver nanoparticles was appeared at 430 nm after mercury lamp exposure without filter and subsequent heat treatment.

Keywords: PTR glass, plasmon resonance, silver nanoparticles, terbium

Citation: Pesniakov V.V., Ignatiev A.I., Nikonorov N.V., Optical properties of photo-thermorefractive glasses doped with terbium, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 278–281. DOI: https://doi.org/10.18721/JPM.163.248

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.341.08 DOI: https://doi.org/10.18721/JPM.163.248

Оптические свойства фото-термо-рефрактивных стекол, активированных тербием

В.В. Песняков¹ , А.И. Игнатьев¹, Н.В. Никоноров¹

¹Университет ИТМО, Санкт-Петербург, Россия

[⊠] v.pesnyackoff@yandex.ru

Аннотация. В данной работе были исследованы два типа фото-термо-рефрактивных стекол. Первое представляло собой классическое фото-термо-рефрактивное стекло, легированное 0,007 мол.% Се³⁺ с добавлением 1 мол.% Тb³⁺. Второе содержало только 1 мол.% Tb³⁺. Эти стекла подвергались воздействию ртутной лампы с использованием фильтра, не пропускающего длины волн короче 350 нм. После термообработки в таких стеклах не наблюдался пик поглощения плазмонного резонанса. Но в образцах фото-термо-рефрактивного стекла, содержащего только Tb³⁺ после облучения ртутной лампой без фильтра при последующей термической обработке появлялся пик плазмонного резонанса на 430 нм, соответствующий наночастицам серебра.

Ключевые слова: ФТР-стекло, плазмонный резонанс, наночастицы серебра, тербий

Ссылка при цитировании: Песняков В.В., Игнатьев А.И., Никоноров Н.В. Оптические свойства фото-термо-рефрактивных стекол, активированных тербием // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 278–281. DOI: https://doi.org/10.18721/JPM.163.248

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

[©] Pesniakov V.V., Ignatiev A.I., Nikonorov N.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Introduction

Photo-thermo-refractive (PTR) glasses are photosensitive glasses that are widely used in various optical schemes due to the possibility of recording volume Bragg gratings [1-2]. But for now, there is one significant drawback - the inability to record a hologram using visible light. Overcoming this obstacle will allow using cheaper and more affordable light sources for hologram recording [3] as well as open a new branch of holography for PTR glasses - image holography. Also, there will be possible to create complex holographic optical elements such as holographic lenses.

In this work classical PTR glasses co-doped with Tb_4O_7 as well as with replaced CeO_2 by Tb_4O_7 were studied. The choice of Tb^{3+} ions is explained by its energy levels which allow obtaining phototo-electron in two stages. On the first stage UV exposure under 370 nm excite electron to ${}^{5}D_3$ level. From this energy level it relaxes to the lower metastable ${}^{5}D_4$ level and then, on the second stage, due to the excited state absorption (ESA) process, absorbs photon and excites to the $5d4f^2$ level which provides photoelectron to start a classical PTR photochemical process [4].

Materials and Methods

In this research PTR glasses with Na₂O-ZnO-Al₂O₃-SiO₂ matrix doped with photosensitizers such as Tb₄O₇ (1 mol.%), Sb₂O₃ (0,04 mol.%), Ag₂O (0,06 mol.%) and CeO₂ (0,007 mol.%) were studied. To find the value of glass transition temperature (T_g the scanning calorimeter STA 449 F1 Jupiter (Netzsch) was used. The obtained T_g for the glasses under the study was around 490 °C. Absorption spectra in UV-vis regions were measured with Perkin Elmer Lambda 650 spectrophotometer.

The glass was melted in an electrical furnace in a quarts crucible at the temperature of 1480°C. Optical homogeneity was provided by platinum stirrer. After annealing in muffle furnace glass was cut in form of small plates 2 mm width which then were polished. Samples were UV irradiated with mercury lamp and then thermally treated in muffle furnace under 500 °C for 10 hours.

Results and Discussion

First part of the study included only PTR glass with replaced CeO₂ by Tb_4O_7 (1 mol.%). Absorption spectra were measured before (initial), after UV irradiation to mercury lamp for 10 minutes and after heat treatment for 10 hours under the temperature of 500 °C. Results are presented in Fig. 1. To exclude contribution of heat treatment in the silver nanoparticles formation, the same glass plate sample was partly UV irradiated and fully heat treated in a furnace. It can be seen that in irradiated part of a sample (Tb 1 mol.%10H 500C UV) there is a broad plasmon



Fig. 1. Absorption spectra for Tb 1 mol.% (init), after UV irradiation (UV) and subsequent heat treatment (10H 500C UV) and after additional treatment (after add. treatment) (a) and spectrum of the mercury lamp (b)

© Песняков В.В., Игнатьев А.И., Никоноров Н.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. resonance absorption peak correlated with silver nanoparticles in glass. For previously processed sample these stages were done twice which resulted in enhanced plasmon resonance absorption peak located at around 430 nm (Tb 1 mol.% after add. treatment).

From the mercury lamp spectrum (Fig. 1,*b*) it can be concluded that it has exactly the needed wavelength at around 365 nm to excite electron firstly from the ground state to ${}^{5}D_{3}$ and then at around 490 nm to excite further from ${}^{5}D_{4}$ level to 5d4f⁷ as was described above.

Second part of this study also included PTR glass co-doped with Ce³⁺ and Tb³⁺ ions. First, samples of this glass were UV-exposed and thermally treated under the same conditions as the one without Ce³⁺. Results are presented in Fig. 2.



Fig. 2 Absorption spectra for the PTR glass co-doped with Ce^{3+} and Tb^{3+} ions that was UV exposed to mercury lamp and thermally treated for 10 hours under 500 °C

It can be clearly seen the plasmon resonance absorption peak at 445 nm corresponded to the silver nanoparticles. This result was expected because of the Ce³⁺ presence that initialize all photochemical processes under the UV lamp. Then it was used a filter to cut-off the wavelengths shorter than 350 nm. That was not let the Ce³⁺ ions release electrons because the absorption band is in the filtered band. For this purpose, C3C 21 glass from the standard catalog was used. Using this filter, two samples of PTR glass were irradiated: containing only Tb³⁺ and codoped with Ce³⁺. Due to the fact that filter also partly cut-off needed band around 365 nm the time of the irradiation was increased from 10 minutes to 90 minutes. Absorption spectra after the heat treatment for 10 hours for 520 °C are presented in Fig. 3 as well as the spectrum of the lamp after filter.



Fig. 3. Absorption spectra for Tb 1 mol.% and with or without 0,007 mol.% Ce^{3+} samples, after UV irradiation (UV) and subsequent heat treatment (520C10H) (*a*) and spectrum of the mercury lamp after using the cut-off filter (*b*)

It can be seen from the absorption spectra absence of any plasmon resonance absorption peak. It means that irradiation to the mercury lamp after the cut-off filter does not lead to the release any electron. However, the crystal formation can be noticed from the absorption spectra for samples with Tb 1 mol.% and 0.007 mol.% Ce^{3+} .

Observed effect can be explained from the fact that the most preferable irradiation wavelength intensity was decreased by the filter and electrons from the ground state of Tb^{3+} ions did not excite to the ${}^{5}D_{3}$ level and further also the dosage of needed wavelength for exciting electron from the ${}^{5}D_{4}$ level was not enough. But at the first part of the study when samples without Ce³⁺ were irradiated by mercury lamp there is a plasmon resonance absorption peak. That can be explained by the high intensity of UV irradiation wavelengths at around 300nm in the spectrum of not filtered lamp. It means that partly electrons were excited to the 5d4f⁷ level by these photons and energy of around 4.1 eV is enough for that process.

Conclusion

The absorption spectra of two types of PTR glass doped with Tb^{3+} ions and codoped with Ce^{3+} were measured before, after UV irradiation with a mercury lamp, and after heat treatment of irradiated glasses. In samples without Ce^{3+} there was a plasmon resonance absorption peak at the absorption spectra located at 430 nm which corresponds to the presence of silver nanoparticles in the studied PTR glass. At the same time in samples codoped with Ce^{3+} and Tb^{3+} and containing only Tb^{3+} after irradiation to the filtered spectrum of the mercury lamp and heat treatment did not appear any silver nanoparticles. It can be explained by the fact that only wavelengths shorter than 350 nm were influential in formation of nanoparticles in case of samples with Tb^{3+} ions irradiated by the mercury lamp without filter.

REFERENCES

1. **Glebov** Alexei L., et al., Volume Bragg gratings as ultra-narrow and multiband optical filters. Micro-Optics 2012. Vol. 8428. SPIE, 2012.

2. Andrusyak O., et al., Spectral combining and coherent coupling of lasers by volume Bragg gratings. IEEE journal of selected topics in quantum electronics 15.2, 2009.

3. Kompan Fedor, et al., Photo-thermo-refractive glass with sensitivity to visible and near IR radiation. Optical Materials Express 6.12 (2016): 3881–3891.

4. **Dubrovin Victor, Nikolay Nikonorov, Alexander Ignatiev**, Bromide photo-thermo-refractive glass for volume Bragg gratings and waveguide structure recording. Optical Materials Express 7.7 (2017) 2280–92.

5. Nikonorov N.V., Sidorov A.I., Tsekhomskii V.A., Silver nanoparticles in oxide glasses: technologies and properties. Vol. 177. Vukovar (Croatia): In-Tech, 2010.

THE AUTHORS

PESNIAKOV Vladislav V. v.pesnyackoff@yandex.ru NIKONOROV Nikolay V. nvnikonorov@corp.ifmo.ru

IGNATIEV Alexander I. alexander151957@yandex.ru

Received 01.08.2023. Approved after reviewing 05.09.2023. Accepted 06.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 620.3 DOI: https://doi.org/10.18721/JPM.163.249

Technology of manufacturing thin-film aluminum nanostructures by dry aerosol printing

E.I. Kameneva¹⊠, A.A. Lizunova¹, E.M. Filalova¹, D. Malo^{1,2}, D.V. Kornyushin¹, V.V. Ivanov¹

¹Moscow Institute of Physics and Technology (National Research University), Moscow, Russia;

² Damascus University, Damascus, Syria

[™] katerinakamenev@yandex.ru

Abstract. The article under discussion is about technology of creating film structures from aluminum nanoparticles synthesized in spark discharge that can be used for plasmon amplification of the electromagnetic field in the ultraviolet range. Nanostructures of various patterns were applied by dry aerosol printing on a substrate of polished quartz glass. The dependences of the line width on the printing parameters such as focus, speed of sample movement and gas flow were studied. The optimal printing parameters were defined to produce thin-films with different patterns: grids, arrays of lines and uniform distribution of nanoparticles over the surface (films).

Keywords: nanoparticles, aluminum, plasmonic nanostructures, dry aerosol printing

Funding: This work was funded by the Russian Science Foundation as part of the research on the technology for fabrication of plasmonic nanostructures by aerosol dry printing (project 22-19-00311, https://rscf.ru/project/22-19-00311 /). Denis Kornyushin thanks the Ministry of Science and Higher Education of the Russian Federation (state contract 075-03-2023-106, project identifier 0714- 2020-0007) for supporting the research with an optical 3D profilometer.

Citation: Kameneva E.I., Lizunova A.A., Filalova E.M., Malo D., Kornyushin D.V., Ivanov V.V., Technology of manufacturing thin-film aluminum nanostructures by dry aerosol printing, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 282–287. DOI: https://doi.org/10.18721/JPM.163.249

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 620.3 DOI: https://doi.org/10.18721/JPM.163.249

Технология изготовления тонкопленочных алюминиевых наноструктур методом сухой аэрозольной печати

Е.И. Каменева¹⊠, А.А. Лизунова¹, Э.М. Филалова¹, Д. Мало^{1,2}, Д.В. Корнюшин¹, В. В. Иванов¹

¹ Московский физико-технический институт (национальный исследовательский университет), Москва, Россия;

² Дамасский университет, Дамаск, Сирия

^{III} katerinakamenev@yandex.ru

Аннотация. Обсуждаемая статья посвящена технологии создания пленочных структур из наночастиц алюминия, синтезированных в искровом разряде, которые могут быть использованы для плазмонного усиления электромагнитного поля в ультрафиолетовом диапазоне. Наноструктуры различных рисунков наносились методом сухой аэрозольной печати на подложку из полированного кварцевого стекла. Были исследованы зависимости ширины линии от параметров печати, таких как фокусное расстояние,

© Kameneva E.I., Lizunova A.A., Filalova E.M., Malo D., Kornyushin D.V., Ivanov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

скорость перемещения подложки и расход газа. Были определены оптимальные параметры печати для получения пленок с различными рисунками: сетками, линиями и равномерным распределением наночастиц по поверхности.

Ключевые слова: наночастицы, алюминий, плазмонные наноструктуры, сухая аэрозольная печать

Финансирование: Работа профинансирована Российским научным фондом в рамках исследования технологии изготовления плазмонных наноструктур методом аэрозольной сухой печати (проект № 00311-19-22, https://rscf.ru/project/22-19-00311 /). Денис Корнюшин благодарит Министерство науки и высшего образования Российской Федерации (государственный контракт № 106-2023-03-075, идентификатор проекта 0007-2020 -0714) за поддержку исследований с помощью оптического 3D профилометра.

Ссылка при цитировании: Каменева Е.И., Лизунова А.А., Филалова Э.М., Мало Д., Корнюшин Д.В., Иванов В.В. Технология изготовления тонкопленочных алюминиевых наноструктур методом сухой аэрозольной печати // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 282–287. DOI: https:// doi.org/10.18721/JPM.163.249

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Recently, the efforts of researchers have focused on obtaining nanoparticles that are widely used in nanoelectronics, sensor technology, nonlinear optics and other fields [1]. The dry aerosol printing method has many advantages over other methods, such as electron lithography, vapor deposition [3], photochemical deposition [4]. The most valuable advantage is the ability to control the process of nanoparticles synthesis in real time due to a wide range of parameters of the spark discharge. It is also possible to use various nanomaterials for the synthesis in spark discharge generator, such as metals (Au, Ag, Cu, Al, Ge, etc.) and alloys, such as Ag-Cu and Cu-W [6]. Metal oxides can also be obtained due to the possibility of synthesis in an atmosphere of air [7]. The morphology of the plasmonic nanostructure has a great influence on the SERS signal amplification and luminescence due to the ability to influence the localization of the electromagnetic field. To demonstrate this influence, the authors carefully selected the pyramidal surface configuration and the thickness of the Au-Ag plasmonic layer [8]. Studies [9] reported on the enhancement of the luminescence of zinc oxide several times, depending on the configuration of the plasmonic aluminum layer. Aluminum nanoparticles are of particular interest in nonlinear optical spectroscopies [10]. The extinction peak of this nanoparticles is in the range of 200–500 nm, depending on the size and morphology of the nanoparticles [11]. Thus, the shift of peaks position on the extinction spectrum in the region to a longer wavelength with increasing diameter was demonstrated in this work [11]. It is known, that the packing density of metal nanoparticles, their size, shape and pattern on the surface can significantly affect the ability to amplify electromagnetic radiation due to surface plasmons [12]. In this article, we demonstrate the application of the dry aerosol printing method to create thin-film aluminum nanostructures. We also developed printing technology for the fabrication of various patterns of nanostructures for further study.

Materials and Methods

Printing of film nanostructures from Al nanoparticles was carried out at a spark discharge synthesis facility (Fig. 1) in the atmosphere of Ar gas (6.0) according to the principle described earlier [13]. First, the air was removed from the system, after that Ar gas was introduced. Ar gas passes through the anode and carries out with the flow the nanoparticles synthesized in the gas discharge chamber. Next, the synthesized nanoparticles are carried out through the nozzle. During the work, the following parameters varied: the focal length (S), the rate of the substrate relative to the nozzle (V), the flow of the carrier gas (Qa) and a distance between the lines (h). By varying the printing parameters it is possible to influence the line width and the surface concentration of particles. Polished quartz glasses of the KU-1 brand were used as substrates for printing.

© Каменева Е.И., Лизунова А.А., Филалова Э.М., Мало Д., Корнюшин Д.В., Иванов В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. The constant installation parameters were as follows: the pressure in the nanoparticle generation chamber was 1.2 atm, the pressure of the cooling gas flow was 1.6 atm, a capacitor with a capacity of 107 nF was used, the pulse period was 2 ms, the focusing gas flow was 20 ml/min, the temperature was 25 °C. The width and height of the obtained nanostructures were determined from images taken using an optical 3D profilometer (S neox, Sensofar, Terrassa, Spain, Nikon EPI 10X lens, capture area 1689, 12×1413, 12 um). The surface morphology of the nanostructures of the samples was studied using scanning electron microscopy (JSM 7001F, JEOL) at an accelerating voltage of 3 kV. The optical density of aluminum nanostructures on quartz glass was studied using a JASCO V-770 spectrophotometer (Japan).





Results and Discussion

Studies have shown that an increase in the rate from 10 to 200 um/s leads to a decrease in the line width of the nanostructure from 470 ± 10 nm to 240 ± 50 nm (Fig. 2,*a*). By increasing the focal length from 1 to 2,5 mm, it is possible to reduce the line width by 19 ± 7 nm. With an increase in the gas flow from 50 to 600 ml/min at fixed parameters *S* and *V*, an increase in the line width from 170 ± 23 um to 500 ± 43 um is observed (Fig. 2,*b*). At the first stage, the dependences of the surface concentration of particles and the line width on the printing parameters were studied. Next, we selected the optimal printing parameters (Q_a , *V* and *S*) to create identical lines of aluminum nanoparticles: $Q_a = 200$ ml/min, V = 250 um/s, S = 1.5 mm. Aluminum nanostructures of various patterns (films, arrays of lines, grids) (Fig. 1) were applied on the surface of the quartz glass. During the experiments, 6 types of nanostructures were manufactured: grids (h = 1050 um, h = 2100 um), arrays of lines (h = 1050 um, h = 2100 um), films (h = 250 um, h = 350 um). Also, the roughness (R_a) was determined for the films, it was 0.16 ± 0.003 um.



Fig. 2. Dependency graphs: line width from rate of the substrate movement (a), line width from the gas flow (b), area of nanoparticles from the rate of the substrate relative to the nozzle (c), absorption spectrum of nanostructures of various patterns (arrays of lines, grids, films) (d)



Fig. 3. Line profile from 3D profilometer (*a*); optical microscopy of various nanostructures: array of lines (*b*), film (*e*), grid (*f*) with printing parameters: $Q_a = 200 \text{ ml/min}$, S = 1,5 mm, V = 250 um/s; SEM-image of the microstructure surface (*c*), (*d*); inset: TEM images of Al nanoparticles

We observed a peak in the optical density spectrum in middle ultraviolet range for each nanostructure. However, the morphology of the surface of the nanostructures and the pattern affect the location of the peak ambiguously. We observed a shift of peaks' maximums to a longer wavelength in films (h = 250 um) and grids (h = 2100 um) relative to other nanostructures (Fig. 2,d). The clearest peaks in the structures such as array of lines and grids (206 nm and 204 nm respectively) with h = 1050 um.

Conclusion

Thus, during the experiments, the technology of manufacturing thin-film nanostructures from aluminum nanoparticles was developed. Nanostructures of various patterns were obtained and the optical density of each nanostructure was investigated. It was found that regardless the pattern the obtained films had an extinction peak in the middle ultraviolet region in the wavelength range of 200–220 nm. At the same time, we have shown that the method of dry aerosol printing is a new clean way to create nanostructures of various configurations and morphologies.

Acknowledgments

This work was funded by the Russian Science Foundation as part of the investigation into the fabrication technology of plasmon nanostructures by aerosol dry printing (project 22-19-00311, https://rscf.ru/project/22-19-00311/). Denis Kornyushin acknowledges the Ministry of Science and Higher Education of the Russian Federation (state contract 075-03-2023-106, project identifier 0714-2020-0007) for support for optical 3D profilometer studies.

REFERENCES

1. Vaughn D. D., Schaak R. E., Chem. Soc. Rev. 42 2861, 2013.

2. Wilkinson N. J., Smith M.A.A., Kay R.W., Harris R.A., A review of aerosol jet printing – a non-traditional hybrid process for micro-manufacturing. The International Journal of Advanced Manufacturing Technology, (105) (2019) 4599–4619.

3. Jarvis R. M., Goodacre R., Analytical Chemistry, 2004 76(1), 40-47.

4. Keating C.D., Kovaleski K.K., Natan M.J., The Journal of Physical Chemistry B, (102) (1998) 9414.

5. Tabrizi N.S., Ullmann M., Vons V.A., Lafont U., Schmidt-Ott A. Generation of nanoparticles by spark discharge. J. Nanoparticle Res. (11) (2009) 315–332.

6. Tabrizi N. S., Xu Q., Van Der Pers N. M., Schmidt-Ott A., Generation of mixed metallic nanoparticles from immiscible metals by spark discharge. J. Nanopart. Res., (12) (2010) 247–259.

7. Ivanov V. V., Efimov A. A., Myl'nikov D. A., Lizunova A.A., Synthesis of Nanoparticles in a Pulsed-Periodic Gas Discharge and Their Potential Applications. Russ. J. Phys. Chem. A, (92) (2018) 607–612.

8. Shinki M., Shreya J., Subhendu S., Role of Au–Ag alloy plasmonic layer thickness over pyramidal silicon in controlling SERS activity // The European Physical Journal Special Topics volume (231) (2022) 791–797.

9. Muravitskaya A., Gokarna A., Movsesyan A., Kostcheev S., Rumyantseva A., Couteau C., Lerondel G., Baudrion A.-L., Gaponenko S., Adam P.-M., Refractive index mediated plasmon hybridization in an array of aluminium nanoparticles. Nanoscale, (12) (2020) 6394–6402.

10. **Castro-Lopez M., Brinks D., Sapienza R., van Hulst N. F.,** Aluminum for Nonlinear Plasmonics: Resonance-Driven Polarized Luminescence of Al, Ag, and Au Nanoantennas. Nano Lett. (11) (2011) 4674–4678.

11. Ekinci Y., Solak H.H., Luffler J.F., Plasmon resonances of aluminum nanoparticles and nanorods. Journal of Applied Physics, 104 (8) (2008) 83107.

12. **Maidecchi G., et al.,** Deep ultraviolet plasmon resonance in aluminum nanoparticle arrays, Acs Nano, 7 (7) (2013) 5834–5841.

13. Efimov A.A., et al., URL: https://doi.org/10.3390/nano11010234, Nanomaterials.

THE AUTHORS

KAMENEVA Ekaterina I. katerinakamenev@yandex.ru ORCID: 0009-0001-7234-8730

LIZUNOVA Anna A. lizunova.aa@mipt.ru ORCID: 0000-0002-2895-4696

FILALOVA Emiliia M. filalova.em@phystech.edu ORCID: 0000-0002-3391-4576 MALO Dana malo.d@mipt.ru ORCID: 0000-0001-6310-9183

KORNYUSHIN Denis V. kornyushin.d@phystech.edu ORCID: 0000-0003-4164-178X

IVANOV Victor V. ivanov.vv@mipt.ru ORCID: 0000-0002-9149-0468

Received 25.08.2023. Approved after reviewing 08.09.2023. Accepted 12.09.2023.

BIOPHYSICS AND MEDICAL PHYSICS

Conference materials UDC 616-71 DOI: https://doi.org/10.18721/JPM.163.250

Implementation of electrical impedance tomography

A.I. Levin¹, E.A. Pecherskaya¹, Yu.A. Varenik², J.V. Shepeleva¹

¹ Penza State University, Penza, Russia;

² Penza State University of Architecture and Construction, Penza, Russia

^{III} Ievin.alescha2013@yandex.ru

Abstract. The method of electrical impedance tomography, which calculates images of the electrical conductivity inside the body based on surface measurements is considered. The basis of the method is an alternating electric current, which is supplied to various configurations of injecting and detecting electrodes located on the body surface and the potential field that arises in its volume is measured. It is shown that each link of the hardware that implements the electrical impedance tomography method has an impact on the final visualization. The implementation essence of the software part of the method based on the Laplace equation is stated. It is advisable to use the results of the work when monitoring the respiratory and cardiovascular systems using a chest belt with electrodes.

Keywords: EIT, ADC, biological object, impedance

Citation: Levin A.I., Pecherskaya E.A., Varenik Yu.A., Shepeleva J.V., Implementation of electrical impedance tomography, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 288–293. DOI: https://doi.org/10.18721/JPM.163.250

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 616-71 DOI: https://doi.org/10.18721/JPM.163.250

Реализация электроимпедансной томографии

А.И. Левин¹[™], Е.А. Печерская¹, Ю.А. Вареник², Ю.В. Шепелева¹

¹ Пензенский государственный университет, г. Пенза, Россия;

² Пензенский государственный университет архитектуры и строительства, г. Пенза, Россия

^{III} levin.alescha2013@yandex.ru

Аннотация. Электроимпедансная томография (ЭИТ) — это метод томографической визуализации, который рассчитывает изображения электропроводности внутри тела на основе измерений поверхности, который нашел свое применение в различных сферах, в частности, в неинвазивном мониторинге биологических функций в режиме реального времени. Основой медицинской ЭИТ является переменный электрический ток, который подается на различные конфигурации инжектирующих и детектирующих электродов, расположенных на поверхности тела и измеряемое возникающее в его объеме потенциальное поле. Однако для медицинских приложений ЭИТ все еще находится на экспериментальной стадии; она еще не использовалась для регулярного ухода за пациентами.

Ключевые слова: ЭИТ, АЦП, биологический объект, импеданс

© Levin A.I., Pecherskaya E.A., Varenik Yu.A., Shepeleva J.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.
Ссылка при цитировании: Левин А.И., Печерская Е.А., Вареник Ю.А., Шепелева Ю.В. Реализация электроимпедансной томографии // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 288–293. DOI: https:// doi.org/10.18721/JPM.163.250

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Implementation of the EIT hardware

The hardware implementation of electrical impedance tomography (EIT) is as important as the image reconstruction algorithm. It plays a decisive role in the excitation of a part of the body and, accordingly, is in direct contact with the tested biological object (patient). When receiving and transmitting data, due to nonlinearity and extremely incorrect formulation of the inverse problem, the image reconstruction quality is sensitive to the error measured by an analog-to-digital converter (ADC) in this case. In the last decade, a variety of high-precision automatic measuring devices and advanced measurement methods have been proposed to reduce measurement noise, but with inherent systematic errors. Meanwhile, data transfer mode and speed, convenience, power consumption and cost are also key indicators in EIT medical imaging, where this medical imaging method is required to monitor changes in the impedance of physiological and patholog-ical conditions in real time [1].

It is shown that each link of the hardware has an impact on the final EIT visualization. For example, electrodes located at the front end of a highly sensitive detection system. The electrodes are in direct contact with the human body, thus, any signals on them, including useful information, noise, artifacts, contact resistance, polarization voltage, etc., will be amplified and processed in the subsequent circuit and ultimately affect image reconstruction results. Therefore, the calculation of the electrode parameters, its dimensions, quantity and sensory ability is especially important. A small number of electrodes (< 16) in the EIT will reduce the measurement sensitivity, and too many electrodes will reduce the measurement speed (> 16). The Standard EIT configuration uses 16 electrodes.

Electrodes in direct contact with the human body can detect noise, contact transient resistance, polarization voltage, etc. These interferences will be amplified and processed in the subsequent circuit and ultimately affect the results of calculating the electrical conductivity of biological tissues. In addition, different contact force of the working electrodes surface with the human body also leads to different readings of bioimpedance measurements. Therefore, the calculation of the electrode parameters, its dimensions, quantity and noise immunity is especially important. A small number of electrodes (less than 16) in the EIT reduces the measurement sensitivity, since the maximum display matrix is built by dividing the plane into 256 segments [2], and an increase in the number of electrodes to 32 reduces the measurement speed [3], but the display matrix is already built by the plane into 1024 segments. At the same time, 16 electrodes are used in the standard EIT configuration.

The main method for implementing EIT is to supply a stable probing current to the object and evaluate the impedance distribution by measuring the potential difference between two active electrodes. Methods for measuring the potential difference can be based on two-electrode and four-electrode methods. Current injection and voltage measurement are performed from the same pair of electrodes in the first method, and the measurement values are always inaccurate due to the contact impedance. In comparison, the four-electrode measurement method can effectively reduce the effect of contact impedance [4].

Implementation of the EIT software

A number of scientists have proved the presence of a significant capacitive component in the final complex bioimpedance [5], therefore, a sinusoidal probing current signal will have a phase shift, which leads to an additional measurement error.

Thus, the results of bioimpedance measurements contain measurement errors due to the voltage between the electrodes on the body surface, random capacitances and impedances of the

© Левин А. И., Печерская Е. А., Вареник Ю. А., Шепелева Ю.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

contacts themselves and the supply cables, as well as the presence of polarization in the measured tissues. The measurement error increases significantly with frequency, cable length and the number of used electrodes and multiplexers, if the circuit is built on their basis. Therefore, it is required to carry out a thorough calibration of measuring instruments in the EIT system [6].

Undoubtedly, EIT has always been and remains a rather controversial topic of study, of importance for both scientific and clinical applications. The main reason for it is directly related to the fundamental problem of the low-energy electromagnetic field when applied to complex biological systems: low contrast and spatial resolution due to the mechanisms underlying the interaction of EMF with biological tissues. This problem was recognized over 40 years ago and remains a major drawback of low energy electromagnetic imaging techniques. Recently, there have been many reports about approaches to overcome the shortcomings or at least reduce their impact [7].

To solve this problem, the authors propose new circuit solutions that allow EIT to be carried out in a wide frequency range from 1 kHz to 100 kHz, which will improve the accuracy of measuring the electrical conductivity of biological tissues of human internal organs. It is proposed to use three sets of electrodes arranged parallel to each other instead of one set of electrodes arranged along the circumference (Fig. 1). It makes it possible to increase the number of planes for measuring the distribution of electrical conductivity (up to 9) through the applied electrodes. Software analysis of the obtained distributions of electrical conductivity will reduce the methodological error of measurements, and, accordingly, the display of electrical conductivity in the measured planes. Fig. 1 illustrates the new methodology for conducting EIT [8].



Fig. 1. Proposed scheme for applying electrodes for EIT

Their location on the patient is also important. It is a competent arrangement that determines the amount of high-quality information contained in the measurement processes, the conditionality of the inverse EIT problem and the EIT measurements reliability. The electrodes position affects the reconstruction quality of the resulting image. Typically, electrodes are placed in the intercostal space between the 4th and 6th ribs. A number of researchers in their works claim that the most favorable angles between the injecting and detecting electrodes are in the range from 60 to 150 degrees [9].

The EIT essence is the inverse problem of determining the impedance, where the relationship between the electric field and the electric current is determined. There are two methods for obtaining electrical impedance. The first method is to establish a stable voltage across the object's surface and then evaluate the impedance distribution over the current flowing through the object. The main EIT method is to apply a stable current to the object and evaluate the impedance distribution by measuring the boundary voltage, which is discussed in this summary. Measurement methods are usually divided into two-electrode and four-electrode approaches. Current injection and voltage measurement are performed from the same pair of electrodes in the first approach, where the strategy can be easily implemented, but the measurement values are always inaccurate due to the contact impedance [10]. Usually, a number of mathematical methods: Newton-Gauss, the method of finding a unique solution of the Laplace equation under the Newman boundary condition are used to construct the EIT image.

In particular, based on Maxwell's equation, Ohm's law and the law of charge conservation, Laplace's equation can be obtained as follows:

$$\nabla \left[\sigma(r) \nabla \varphi(r) \right] = 0, \ r \in \Omega, \tag{1}$$

where φ is the electric potential, Ω is the measured area.

In this case, the boundary condition on the electrodes will be as follows:

$$\sigma(r)\frac{\partial \varphi(r)}{\partial n} = j, \ r \in \Omega, \tag{2}$$

where *j* is the current density at the electrodes, Ω is the boundary of the body.

The relationship between excitation, system response and measurement can be easily represented as follows:

$$\overline{V} = F(\sigma(r))|_{i}, \qquad (3)$$

where $\sigma(r)$ is the conductivity distribution, V is the theoretical boundary stress, and F is a nonlinear function representing the conductivity distribution space in the measurements space [11].

As a result of the application of the new proposed scheme for applying electrodes, the number of matrices for the distribution of the electrical conductivity of the human body increases (up to 9 pieces).



Fig. 2. Calculation grid: (a) thickening on the electrodes (1256 cells);(b) thickening to the entire boundary of the region (2804 cells)

Table 1

Deviation	of i	numerical	results	from	the	analytical
------------------	------	-----------	---------	------	-----	------------

Net	Deviation
No thickening	0.03017
Condensation on the electrodes	0.01435
Condensation at the border with air	0.01681
Condensation on the entire border	0.02062

Step-by-step processing of these matrices in comparison with the electrical conductivity distribution of the human body (as shown in Fig. 2) will allow, using mathematical processing methods, to build a more adequate model of the electrical conductivity distribution and determine the foci of blood clots and edema in the vessels and internal organs at the site of electrode application much more accurately [12].

In order to obtain high-quality solutions in places with large gradients of changes in the parameters of the distribution of electrical conductivity of tissues of various kinds, grids (unstructured and structured) for mathematical calculation need to be thickened.

A number of researchers [13-14], having carried out work on the construction and calculation of grids with different grid density (at the electrodes, at the boundary with air and along the entire boundary of the volume), came to the conclusion that the smallest deviation of the numerical results from the analytical one occurs when the grid is thickened precisely at the electrodes (Table 1).

Thus, based on these results, we came to the conclusion that in order to increase the speed and quality of mathematical calculations of the electrical conductivity of tissues during EIT, it is required to implement in an applied way this grid thickening on the electrodes by applying them in three rows around a circle with a displacement angle $\varphi = 30$ degrees. In this work, studies were carried out between two electrodes located diametrically along the circumference. The use of three rows of electrodes with an offset by an angle φ makes it possible to implement two variants of thickening: both on the electrodes and along the entire boundary. This improves the efficiency of the control program by eliminating time and technical resources for mesh modeling and subsequent calculations.

Conclusions

The EIT ability to detect conductivity changes finds application in the monitoring of the respiratory and cardiovascular systems using a chest belt with electrodes.

The conductivity changes are caused by the lung's expansion with each breath and the blood movement with each heartbeat. Continuous monitoring of vital physiological parameters of ventilated patients in the intensive care units or operating rooms will provide healthcare professionals with additional information about the patient's health status or the therapy effectiveness, which can improve patient outcomes. According to the business plan of startup company Swisstom, 3.8 million people are ventilated annually in developed countries, about 15% of them receive acute lung injury, and about 5% (190,000 patients) of ventilated patients eventually die from acute lungs injury.

REFERENCES

1. Aleksanyan G.K., Shcherbakov I.D., Sulyz A.V., Tetelev M.V. Problems of implementation of algorithms for the reconstruction of multi-angle electrical impedance tomography // Modern science-intensive technologies. 12 (2) (2019) 243–248.

2. Uhlmann G., Electrical impedance tomography and Calderyn's problem, Inverse Problems, (25) (2009).

3. Korzhenevsky A.V., Research electrical impedance tomograph, available for manufacturing in non-standard conditions, Journal of radio electronics [electronic journal], (in Russian), (9) (2021).

4. **K. Knudsen, A. Kaastrup Rasmussen**. "Direct regularized reconstruction for the three-dimensional Calderyn problem," Inverse Problems and Imaging, 871 (16) (2022) 1930–8337.

5. Cao L., Li H., Xu C., et al., A novel time-difference electrical impedance tomography algorithm using multi-frequency information, BioMed Eng OnLine 18 (84) (2019).

6. Liu D., Wang J., Shan Q., Smyl D., Deng J., Du J., DeepEIT: Deep Image Prior Enabled Electrical Impedance Tomography, in IEEE Transactions on Pattern Analysis and Machine Intelligence.

7. Tushar Kanti Bera, Applications of Electrical Impedance Tomography (EIT): A Short Review, IOP Conf. Ser.: Mater. Sci. Eng., (331) (012004) (2018).

8. Prins S., Weller D., Labout J., Corstiaan U., Electrical Impedance Tomography As a Bedside Diagnostic Tool for Pulmonary Embolism, Critical Care Explorations, 5 (1) (2023) 0843.

9. Hamilton S. J., Isaacson D., Kolehmainen V., Muller P.A., Toivanen J., Bray P.F., 3D Electrical Impedance Tomography reconstructions from simulated electrode data using direct inversion and Calderyn methods, Inverse Problems and Imaging, 15 (5) (2021) 1135–1169.

10. H. Garde, K. Knudsen. "3D reconstruction for partial data electrical impedance tomography using a sparsity prior," Conference Publications, 2015(special), pp. 495–495. doi: 10.3934/proc.2015.0495.

11. Goren N., Avery J., Dowrick T., et al., Multi-frequency electrical impedance tomography and neuroimaging data in stroke patients, Sci Data (5) (180112) (2018).

12. Ferreira J., Seoane F., Lindecrantz K., AD5933-based electrical bioimpedance spectrometer. Towards textile-enabled applications, Annual International Conference of the IEEE Engineering in Medicine and Biology Society, (2011) 3282–3285.

13. Gao Z., Darma P.N., Kawashima D., Takei M.A., High Accuracy Voltage Approximation Model Based on Object-oriented Sensitivity Matrix Estimation (OO-SME Model) in Electrical Impedance Tomography, J Electr Bioimpedance, 13 (1) (2023) 106–115.

14. Afanas'eva A.A., Starchenko A.V., Numerical solution of the direct problem of electroimpedance tomography in a complete electrode formulation. Vestnik Tomskogo gosudarstvennogo universiteta. Matematika i mekhanika – Tomsk State University Journal of Mathematics and Mechanics. (78) (2022) 5–21.

THE AUTHORS

LEVIN Alexis I. levin.alescha2013@yandex.ru ORCID: 0000-0003-0428-2319()

PECHERSKAYA Ekaterina A. pea1@list.ru ORCID: 0000-0001-5657-9128 **VARENIK Yuriy A.** yurik_ru@mail.ru 0009-0009-6455-3011

SHEPELEVA Juliya V. eduard.shepelev.67@mail.ru ORCID: 0000-0001-5075-2727

Received 03.07.2023. Approved after reviewing 06.09.2023. Accepted 07.09.2023.

Conference materials UDC 615.47 DOI: https://doi.org/10.18721/JPM.163.251

Development of an automated system for measuring bioimpedance for the study of body composition

V.V. Antipenko¹⊠, E.A. Pecherskaya¹, D.E. Tuzova¹, D.V. Yakushov¹, D.V. Artamonov¹

¹ Penza State University, Penza, Russia

[™] v.antipenko7@yandex.ru

Abstract. Bioimpedance analyzers are non-invasive instruments that practitioners use to measure physiological parameters of body composition. The existing technology for measuring bioimpedance is constantly being improved, and more and more commercially available analyzers that do not solve the problems with measurement errors and the information content of the obtained data appear on the market. This article proposes an automated bioimpedance measurement system for studying body composition with a reduced impedance measurement error up to 1% and an increase in the information content of the human body composition due to the expansion of the impedance frequency measurement from 0.3 kHz to 2000 kHz.

Keywords: bioimpedance, current source, circuit, model, object

Citation: Antipenko V.V., Pecherskaya E.A., Tuzova D.E., Yakushov D.V., Artamonov D.V., Development of an automated system for measuring bioimpedance for the study of body composition, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 294–300. DOI: https://doi.org/10.18721/JPM.163.251

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 615.47 DOI: https://doi.org/10.18721/JPM.163.251

Разработка автоматизированной системы измерения биоимпеданса для изучения состава тела

В.В. Антипенко¹[™], Е.А. Печерская¹, Д.Е. Тузова¹, Д.В. Якушов¹, Д.В. Артамонов¹

¹ Пензенский государственный университет, г. Пенза, Россия

[™] v.antipenko7@yandex.ru

Аннотация. Биоимпедансные анализаторы относятся к неинвазивным инструментам, которые практикующие врачи используют для измерения физиологических параметров состава тела. Существующая технология измерения биоимпеданса постоянно совершенствуется и на рынке появляется все больше коммерческих доступных анализаторов, которые не решают проблемы с погрешностью измерений и информативностью полученныхданных. Вданнойстатье предлагается автоматизированная система измерения биоимпеданса для исследования состава тела с уменьшенной погрешностью измерений импеданса до 1% и повышением информативности состава тела человека, благодаря расширению измерения частотного диапазона импеданса от 0,3 кГц до 2000 кГц.

Ключевые слова: биоимпеданс, источник тока, схема, модель, объект

© Antipenko V.V., Pecherskaya E.A., Tuzova D.E., Yakushov D.V., Artamonov D.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Антипенко В.В., Печерская Е.А., Тузова Д.Е., Якушов Д.В., Артамонов Д.В. Разработка автоматизированной системы измерения биоимпеданса для изучения состава тела // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 294–300. DOI: https://doi.org/10.18721/ JPM.163.251

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The development of new approaches to both hardware and software for bioimpedance analysis in recent years has significantly increased its capabilities and expanded the list of both already implemented and promising applications [1]. In the modern world, the introduction of diagnostic devices is receiving great development, which makes it possible to save money and effectively influence the patient [2]. Although the technology has been improved, it is currently difficult to obtain high-quality measurements of physiological parameters with most commercially available bioimpedance analyzers because they do not detect large amounts of fat under the skin [3].

The creation of an automated system is based on the idea of measuring human bioimpedance, with improved measurement accuracy (impedance measurement error up to 1%) and an increase in the information content of the human body composition, due to the expansion of the measurement of the impedance frequency range from 0.3 kHz to 2000 kHz [3].

When measuring the impedance of biological objects, there are instrumental and methodological errors. Instrumental errors are caused by the presence of errors of electronic components that are part of the developed automated system. A detailed analysis of methodological measurement errors is presented by the authors in [4]. Thanks to the calibration of the digital automated bioimpedance meter, it was established that the total methodological and instrumental accuracy of bioimpedance measurement in relative form does not exceed 1%.

Structural diagram of the automated bioimpedance measurement system

The automated bioimpedance measurement system includes a measurement object, a measuring unit (highlighted by a dotted line in Fig. 1) and a personal computer. The object of measurement can be either a person or a calibration device. In the case of measuring human parameters, the measuring unit is connected to the object through measuring electrodes (not shown in the diagram). The calibration device is connected to the measuring unit through a connector and it is necessary for calibrating the measuring unit before operation.



Fig. 1. Structural diagram of an automated system for measuring bioimpedance

© Антипенко В.В., Печерская Е.А., Тузова Д.Е., Якушов Д.В., Артамонов Д.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The calibration device imitates the parameters of the electrode-human cell transition. The personal computer is intended for processing, displaying and storing the measurement results. The measuring unit operates under the control of a microcontroller, to which a ROM (read-only memory) is connected to store calibration coefficients, the number of the measuring unit, and other service information. The voltage reference source generates the voltage with high accuracy and temperature stability for the ADC (analog-to-digital converter) operation. The microcontroller is connected to a personal computer through a digital isolator and an interface converter. The digital isolator prevents leakage current from flowing into the personal computer, and also additionally protects a person from electric shock (in the grounding absence of the personal computer case).

To form a sinusoidal signal, a generator, which is controlled via the SPI interface (serial peripheral interface) is provided. The current source generates a sinusoidal current on the measurement object. The voltage drop across the object is measured by a differential amplifier with an input ESD protection (electrostatic discharge protection) circuit. The matching and gain control device is controlled by a digital potentiometer, which makes it possible to change the gain of the entire receiving path. From the output of the matching and gain control device, the signal is fed to the input of the ADC3 of the microcontroller, as well as to the detector, which extracts the signal amplitude and feeds it to the input of the ADC2 of the microcontroller. To assess the shape of the flowing current, a current sensor is provided, the voltage from which is measured by a second differential amplifier, after which the signal is fed to the matching device and to the input of the ADC1 of the microcontroller.

The microcontroller is designed to implement the control of all nodes of the bioimpedance meter, measurement, digitization and output of values on a personal computer. The micro-controller contains two ADCs, the signals to the inputs of which are received through internal demultiplexers. The ADC1 channel in the block diagram is connected to the first ADC inside the microcontroller. The ADC2 and ADC3 channels are connected to the second ADC of the microcontroller through a demultiplexer. The range of voltages applied to the ADC inputs is from 0 V to 3.3 V. The reference voltage value is 3.3 V. The microcontroller has two SPI interfaces to control peripherals. The first SPI interface controls the oscillator, the other one controls the digital potentiometer and ROM. The digital potentiometer and ROM have different signals for selecting slave devices (chip select) [5, 6].

The generator is designed to form a sinusoidal signal at the output with a constant amplitude. The microcontroller, via the SPI interface, sets only the signal frequency from the generator output. To synchronize the signal from the generator output, from the microcontroller output, a pulse signal sync 'sync.' with the frequency of 2 MHz, with a duty cycle of 2 is provided. The frequency of 2 MHz corresponds to the maximum operating frequency of the sinusoidal signal on the sample. The rest of the output frequencies are set by dividing the frequency 2 MHz.

The current source is designed to form a sinusoidal current in the range from -1 mA to +1 mA with a frequency set by the generator. The current source is controlled by voltage. The signal from the generator output through the matching device is fed to the input of the current source. The matching device removes the DC (direct current) component of the signal, and also amplifies it. The output stage of the current source is made according to the bridge circuit.

The differential amplifier is designed to measure the voltage on the sample. It has a high input impedance to eliminate the influence on measurements. An ESD protection device, which 'drains' excess voltage in the power circuit is provided at the input of the differential amplifier.

Before starting the measurement, the microcontroller must set the measurement limit to 1000 ohms and send a command to the generator to generate a signal with a frequency of 1 MHz. Depending on the resistance of the object, the voltage amplitude on it will change, and its value will be fixed by the detector for a period of 10 ms. Depending on the voltage level at the output of the detector, the microcontroller decides how to set the measurement limit.

The measurement limit is set by a digital potentiometer, which is controlled via the SPI interface by a microcontroller. In total, the digital potentiometer has 256 positions, the resistance ratio is given by the number Dn (position) placed in the register.

At the time of measurements, two channels ADC1 and ADC3 are involved (Fig. 1). The signal to ADC1 is proportional to the current flowing through the sample, and the signal to ADC3 is proportional to the voltage across the sample. According to the voltage on the sample, one can judge the resistance according to Ohm's law. The dependence of the voltage on ADC1 on the current flowing through the sample is shown in Table 1.

Table 1

Dependence of voltage on ADC1 of	n
current flowing through sample	

Current, mA	Voltage at ADC1, V
+1	+3
0	+1.65
-1	+0.3

The dependence of the voltage on the ADC3 on the resistance at a constant current through a sample of 1 mA is shown in Table 2.

At all measurement limits, zero voltage on the sample corresponds to 1.65 V at ADC3 (middle point). The dependence of the voltage on the ADC3 on the resistance at a constant current through the 1mA sample is shown in Table 3.

Table 2

Dependence of voltage on ADC3 on resistance at constant current voltage through 1mA sample

Measurement limit, Ohm	Sample resistance, Ohm	ADC3 voltage, V
50	50	2.96
100	100	2.97
200	200	3
500	500	3
1000	1000	3

Table 3

Dependence of voltage on ADC3 on resistance at constant current through -1mA sample

Measurement limit, Ohm	Sample resistance, Ohm	ADC3 voltage, V
50	50	0.34
100	100	0.33
200	200	0.3
500	500	0.3
1000	1000	0.3

As it can be seen from the tables, the measurements do not use the full range of voltage measurements at the ADC input (from zero to 3.3 V). Such a voltage margin is necessary in order to increase the overload capacity, as well as to carry out correct operation at all measurement limits. On some samples, more frequency response drops, which, if the limit is chosen erroneously, can lead to saturation of the ADC input can be observed. A sufficient voltage margin eliminates this disadvantage. It is not necessary to programmatically limit the measured resistance to the value of the selected limit, if the system measures, for example, at the limit of 1000 ohms a value of more than 1000 ohms, then these values must be reflected in the frequency response.

Automated Bioimpedance Measurement System

The automated bioimpedance measurement system (Fig. 2) in its design has a device and measuring electrodes. The device is connected to a personal computer.

The input action is created on the patient's body in the form of a weak electric current of a given frequency using electrodes. A reaction to an impact in the form of a potential difference in a certain part of the body is perceived. The following patient data are used to perform calculations: measured data (active and reactance), sex, height, weight, age.



Fig. 2. Automated Bioimpedance Measurement System

Based on bioimpedance measurements and input data, a set of physiological parameters of the body is determined. Measurement data, calculations and experimental conditions are stored in the database. The report can be displayed on a PC (personal computer) screen, saved as a file and printed (Fig. 3). The dynamics of changes in indicators is recorded and visualized and a preliminary medical report is formed.



Fig. 3. Main application menu of the automated bioimpedance measurement system

A circuitry part of the measuring apparatus, which will allow measurements of bioimpedance in a wide frequency range from 300 Hz to 2 MHz has been developed. Thanks to the obtained frequency response, the selectivity of measurements, which allows increasing the influence of some tissues or organs on the measuring signal and at the same time reducing the influence of others will become possible.

The accuracy of body composition data has been improved by developing a current source that measures both currents flowing into the object and currents flowing out of the object. It will allow hardware to minimize the influence of leakage currents inside the measuring apparatus on the final result.

Calibration is performed using a 910 ohm resistor. As a result of calibration, a table of complex coefficients is formed at each of the thirteen frequencies in the range from 300 Hz to 2 MHz (Fig. 3). Then, using the correction coefficients obtained, the resistance of the resistor with a nominal value of 910 ohms is measured. The resulting frequency response is shown in Fig. 3.

The ordinate axis on the left shows the module of the complex resistance, measured in ohms. The tangent of the phase angle $tg\varphi$, expressed as a percentage, is displayed on the ordinate axis on the right. The frequency in Hz is deposited along the abscissa axis. The abscissa axis has a logarithmic scale. Bright colors of red, blue and green (in the upper part of Fig. 3) the module of the complex resistance Z is indicated, and the tangent of the phase angle $tg\varphi$ is indicated in pale colors (in the lower part of Fig. 3)

It can be seen from the graph that the maximum absolute deviation of the resistance:

$$\Delta R = 918 \text{ ohms} - 910 \text{ ohms} = 8 \text{ ohms}. \tag{1}$$

The maximum relative deviation is determined as follows:

$$\delta_{\Delta Z} = \frac{918 \text{ ohms} - 910 \text{ ohms}}{910 \text{ ohms}} \cdot 100\% \approx 0.87\%.$$
 (2)

In turn, the maximum absolute deviation:

$$\Delta R = -0.9 - 0 = -0.9\%. \tag{3}$$

As a result, the relative error of the impedance measurements will not exceed 1%.

Conclusion

An automated bioimpedance measurement system has been developed, in which the total instrumental and methodological error of bioimpedance measurements has been reduced to 1%, which is confirmed by the calibration results. The proposed bioimpedance meter has an extended frequency range from 0.3 kHz to 2000 kHz. A distinctive feature of the proposed automated system is the use of a current source in the system for bioimpedance measurements, which minimizes the influence of a parasitic leakage current from the measuring object to the ground, which positively affects the accuracy of measurements.

REFERENCES

1. Tronstad C., Strand-Amundsen R., Possibilities in the application of machine learning on bioimpedance time-series, J Electr Bioimp, (10) (2019) 24–33.

2. Anamika P., Mukesh R., Bioimpedance analysis of vascular tissue and fluid flow in human and plant body: A review. Biosystems engineering, (197) (2020) 170–178.

3. Freeborn T.J., Crircher S., Artifacts in Localized Multi-Frequency Bioimpedance Measurements, IFAC PapersOnLine 54-15 (2021) 55-60.

4. Antipenko V.V., Pecherskaya E.A., Zinchenko T.O., Melnikov O.A., Fimin A.V., Zaryvahina S.A., Analysis of methodological errors in measuring a digital automated bio-impedance meter J. Phys.: Conf. Ser. 1695 0120510, 2020.

5. Antipenko V.V., Pecherskaya E.A., Zinchenko T.O., Artamonov D.V., Spitsina K.Yu., Pecherskiy A.V., Development of an automated bioimpendance analyzer for monitoring the clinical condition and diagnosis of human body diseases, J. Phys. Conf. Ser. 1515 (5), 2020.

6. Levin A. I., et al., Application of an automated complex resistance and phase difference measuring method for rheographic studies of human cardiovascular system,". Journal of Physics: Conference Series, 2086 (1), 012113, 2021.

THE AUTHORS

ANTIPENKO Vladimir V. v.antipenko7@yandex.ru ORCID: 0000-0003-0274-7004

PECHERSKAYA Ekaterina A. pea1@list.ru ORCID: 0000-0001-5657-9128

TUZOVA Diana E. diana.tuzova.02@bk.ru ORCID: 0000-0002-7352-3932 YAKUSHOV Dmitriy V. hammer.fate@yandex.ru ORCID: 0009-0005-0892-312X

ARTAMONOV Dmitriy V. dmitrartamon@yandex.ru ORCID: 0000-0002-3240-7222

Received 30.06.2023. Approved after reviewing 24.07.2023. Accepted 26.07.2023.

Conference materials UDC 547.458:535.56 DOI: https://doi.org/10.18721/JPM.163.252

Optical activity anisotropy in thin films of chitosan L- and D-ascorbate

A.B. Shipovskaya¹[∞], D.A. Rudenko¹, S.L. Shmakov¹, N.O. Gegel¹

¹ Saratov State Univercity, Saratov, Russia

□ Shipovskayaab@yandex.ru

Abstract. The specific optical rotation $[\alpha]$ of thin films of chitosan L- and D-ascorbate was studied. It was found that optical activity anisotropy occurs in the systems analyzed and $[\alpha]$ depends on the orientation angle θ of the film sample relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. The angular dependences $[\alpha] = f(\theta)$ (indicatrices) were processed to extract the constant term $[\alpha]_0$ and four harmonics ($[\alpha]_i$, Fourier's series) determined by structure elements with the corresponding symmetry, namely: the amorphous (isotropic) chitosan phase ($[\alpha]_0$), irregular-shaped structures ($[\alpha]_1$), rod-shaped ones in the film plane ($[\alpha]_2$), helical ones located perpendicular to the film surface ($[\alpha]_3$), and crystalline structures ($[\alpha]_4$).

Keywords: chitosan, L- and D-ascorbic acid, films, optical activity, anisotropy

Funding: The study was supported by a grant from the Russian Science Foundation 22-23-00320, https://rscf.ru/project/22-23-00320/.

Citation: Shipovskaya A.B., Rudenko D.A., Shmakov S.L., Gegel N.O., Optical activity anisotropy in thin films of chitosan L- and D-ascorbate, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 301–306. DOI: https://doi.org/10.18721/JPM.163.252

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 547.458:535.56 DOI: https://doi.org/10.18721/JPM.163.252

Анизотропия оптической активности тонких пленок L- и D-аскорбата хитозана

А.Б. Шиповская¹⊠, Д.А. Руденко¹, С.Л. Шмаков¹, Н.О. Гегель¹

¹Саратовский национальный исследовательский государственный университет

им. Н.Г. Чернышевского, г. Саратов, Россия

[⊠] Shipovskayaab@yandex.ru

Аннотация. Исследовано удельное оптическое вращение [α] тонких пленок хитозана L- и D-аскорбата. Установлено, что в анализируемых системах меет место анизотропия оптической активности и [α] зависит от угла ориентации θ образца пленки относительно направления вектора поляризации падающего пучка света в плоскости, перпендикулярной этому пучку. Угловые зависимости [α] = $f(\theta)$ (индикатрисы) были обработаны для извлечения постоянного члена [α]₀ и четырех гармоник ([α]₁, ряд Фурье), определяемых элементами структуры с соответствующей симметрией, а именно: аморфная (изотропная) фаза хитозана ([α]₀), структуры неправильной формы ([α]₁), стержнеобразные в плоскости пленки ([α]₂), и кристаллические структуры ([α]₄).

Ключевые слова: хитозан, L- и D-аскорбиновая кислота, пленки, оптическая активность, анизотропия

© Shipovskaya A.B., Rudenko D.A., Shmakov S.L., Gegel N.O., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Финансирование: Исследование выполнено при поддержке гранта Российского научного фонда № 00320-23-22, https://rscf.ru/project/00320-23-22/.

Ссылка при цитировании: Шиповская А.Б., Руденко Д.А., Шмаков С.Л., Гегель Н.О. Анизотропия оптической активности тонких пленок L- и D-аскорбата хитозана // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 301–306. DOI: https://doi.org/10.18721/JPM.163.252

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Optical activity anisotropy is a vivid example of self-organization in chiral polymer systems. This property was first discovered for lyotropic LC phases of acetic cellulose esters [1] and subsequently found in oriented films of both acetic and basic chitosan [2]. This phenomenon consists in the manifestation of a clear functional dependence of the specific optical rotation [α] on the samples orientation angle θ relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. Decomposition of the indicatrices [α] = $f(\theta)$ into individual sinusoids (harmonics) allows drawing some conclusions about the supramolecular optically active structures formed in the polymer material during its preparation.

For example, by comparing the harmonic components $[\alpha]_i$ with the axisymmetric elements, the contribution of individual supramolecular structures (anisotropic subsystems) to the total optical activity of chitosan was estimated: crystalline and rod-shaped (in the film plane) structures predominate for freshly formed films of the salt form, while crystalline ones predominate for the basic form [2]. The conditioning of chitosan films of both chemical forms is accompanied by spontaneous water removal, increases the absolute value of $[\alpha]$ and enhances the harmonics corresponding to crystallites. At the same time, the results of our numerical decomposition of the $[\alpha]$ indicatrices are in satisfactory agreement with the X-ray diffractometry data of chitosan films.

Nonlinear optical activity effects have also been found for biological macromolecules and biological microstructures built therefrom, in particular, collagen fibers and multilayer vesicles, considered from the standpoint of complex anisotropic 3D media [3]. It was noted that studying of optical anisotropy and optical activity is very promising for assessing the orientation of protein macromolecules and their supramolecular aggregates in anisotropic collagen membranes used in tissue engineering [4]. These optical quantities play an important role in the comparative analysis of the complex degree of mutual anisotropy of birefringent structures in biological tissues with benign and malignant changes [5].

The optical activity of chitosan predetermines the possibility of obtaining smart materials based thereon, performing the function of a "chemical plug" or "chemical corkscrew", a depot of genetic material or biologically significant compounds with their subsequent release after volume reduction in the planned localization zone [6]. Recent publications have reported on chitosan-containing chiro-optic switches responding to the acid—base properties of a liquid medium [7], imprinted materials for the enantioselective separation of racemic drug mixtures [8], hydrogels with supramolecular chiral architecture [9], as well as non-invasive measuring instruments based on linear and non-linear optical effects [10].

The aim of this work was to study the chiro-optic properties of chitosan salt films obtained from solutions in L- and D-ascorbic acid in order to reveal and quantitatively describe optical activity anisotropy.

Materials and Methods

Powdered chitosan (CS) with an average-viscosity molecular weight of 200 kDa and a deacetyl(ation degree of $82\pm 2 \mod \%$ (Bioprogress LLC, RF); L-ascorbic acid (L-AscA) with 99% of the main substance (Glenvitol LLC, RF) and D-ascorbic acid (D-AscA) with 98% of the main substance (CJSC Khimreaktiv, RF) were used. Films were cast by pouring a 2 g/dL CS solution, prepared at an equimolar CS : AscA ratio, onto a polyethylene terephthalate substrate, followed by drying in the absence of natural light at room temperature and under atmospheric pressure for 3-4 days. The film thickness was 802 µm.

© Шиповская А.Б., Руденко Д.А., Шмаков С.Л., Гегель Н.О., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Optical activity was recorded on a PolAAr 3001 automatic spectropolarimeter (Optical Activity Ltd, England) in the wavelength range $\lambda = 405-589$ nm at 25 ± 0.5 °C. A 20 W tungsten-halogen lamp was the light source. The experimental conditions were standard, the measurement error of rotation angles did not exceed ± 0.001 deg. Spectra [α] = $f(\theta)$ (where θ is the rotation angle of the sample in the plane perpendicular to the direction of the incident light beam, with respect to an arbitrarily chosen initial position) were recorded using a specially designed cuvette with a thermal chamber and a cell rotating around its horizontal axis and having a circular scale calibrated from 0 to 360° with a 5° step relative to an arbitrarily chosen reading direction. At least 10 film samples were used for each measurement. Three replicate experiments were carried out at each orientation angle.

The specific optical rotation $[\alpha]$ (deg mL dm⁻¹ g⁻¹) of films was calculated by the formula:

$$\left[\alpha\right]_{\lambda, nm}^{20^{\circ}C} = \frac{\alpha}{\ell \cdot \rho},$$

where α is the measured angle of optical rotation of the film sample, deg; ℓ the length of the optical path, dm; and ρ the density of the film material, g·cm⁻³. Graphic dependences $[\alpha] = f(\theta)$ in polar and Cartesian coordinates were plotted in the Microcal Origin Pro software.

The algorithm for processing indicatrices consisted of extracting the constant term and several harmonics (Fourier's series) from the $[\alpha] = f(\theta)$ dependence, which were given a certain physical meaning. It is described in detail elsewhere [2]. The general approximating formula was:

$$[\alpha] = [\alpha]_0 + \sum_{i=1}^4 [\alpha]_i \cos[i(\theta - \Delta_i)],$$

where $[\alpha]_0$ and $[\alpha]_i$ are the components of specific optical rotation corresponding to the isotropic and anisotropic subsystems; Δ_i is the phase shift (specific for each harmonic). Since the average cosine over an integer number of periods is zero, $[\alpha]_0$ is actually the average value of $[\alpha]$ over all orientation angles, i.e., the angle-average specific optical rotation.

Results and Discussion

The optical rotary dispersion curves (ORD) of thin films of CS L- and D-ascorbate were established to be of the normal type and characterized by [α] values close in absolute value, but opposite in sign, namely: negative for CS·L-AscA and positive for CS·D-AscA. It was found that [α] depended on the orientation angle θ of the film sample relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. The indicatrices, as can be seen, have a complex, irregular shape. For CS·L-AscA films, the values of specific optical rotation range from +18 to -62 deg·mL·dm⁻¹·g⁻¹ (Fig. 1, *a*, *b*). CS·D-AscA film samples are characterized by more positive [α] values: from +40 to -5 deg·mL·dm⁻¹·g⁻¹ (Fig. 1, *c*, *d*).

To process the angular dependences $[\alpha] = f(\theta)$, an algorithm was used with the isolation of a constant term $([\alpha]_0)$ and four harmonics $([\alpha]_i)$. Fourier's series) determined by the structure elements with the corresponding symmetry, namely: $[\alpha]_1$ corresponds to irregular shaped structures, $[\alpha]_2$ to rod-shaped ones in the plane of the film, $[\alpha]_3$ to helical ones, located perpendicular to the surface of the film, and $[\alpha]_4$ to crystalline ones. The results of the numerical decomposition of the $[\alpha] = f(\theta)$ indicatrices into harmonics are given in Table. The graphic dependences $[\alpha]_i = f(\theta)$ at $\lambda = 436$ nm are shown in Fig. 2. For clarity, the origin of coordinates is chosen so that the value of the specific optical rotation is $[\alpha]_0$ at the point $\theta = 0$ deg. The value of the argument of the function $[\alpha] = f(\theta)$ was chosen so that it coincided with the beginning of the period of the corresponding sinusoid.

It is shown that the mean-angle specific optical rotation $[\alpha]_0$ reflects the optical activity of the amorphous phase of the sample, is characterized by simple dispersion and satisfactory agreement with the experimental ORD curves. For CS·L-AscA films, the fourth harmonic $[\alpha]_4$ had the highest amplitude, followed by $[\alpha]_2$ and $[\alpha]_3$. For CS·D-AscA film samples, $[\alpha]_4$ and $[\alpha]_2$ predominated, followed by $[\alpha]_1$ as the intensity decreases. The intensity of these harmonics for CS·L-AscA films was significantly higher compared to CS·D-AscA ones.



Fig. 1. Dependence of the specific optical rotation [α] of CS·L-AscA (a, b) and CS·D-AscA (c, d) films on the sample rotation angle θ in polar (a, c) and Cartesian (b, d) coordinates; $\lambda = 405$ (I), 436 (2), 546 (3), and 589 nm (4)

Thus, the numerical processing of the indicatrices $[\alpha] = f(\theta)$ showed that the optical activity of the films analyzed is due not only to the molecular chirality of the elementary macromolecular chains, but also to the supramolecular chirality of the supramolecular structures of CS L-and D-ascorbates.

Table

Film	Wavelength	Harmonics (Fourier's series) $[\alpha]_{i}$, deg·mL·dm ⁻¹ ·g ⁻¹							
	λ, nm	i = 0	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 4			
	405	-17.5	7.03	6.51	5.48	13.9			
CS·L-AscA	436	-7.62	3.15	12.9	4.99	7.89			
	546	-1.96	1.26	6.93	3.11	5.64			
	589	-2.07	1.87	5.77	2.71	4.94			
CS·D-AscA	405	42.9	3.42	6.06	2.25	7.21			
	436	41.9	3.70	2.22	1.30	4.42			
	546	21.7	1.57	1.34	0.94	2.74			
	589	16.4	2.4	1.47	0.93	2.38			

Harmonic amplitudes at several wavelengths for CS·L-AscA and CS·D-AscA films



Fig. 2. Angular dependence of the specific optical rotation $[\alpha]$ at $\lambda = 436$ nm and its decomposition into harmonics for CS·L-AscA (*a*) and CS·D-AscA (*b*) films; 1-4 are the numbers of harmonics $[\alpha]_1 - [\alpha]_4$, 5 the total curve. The horizontal line corresponds to the constant term $[\alpha]_0$

Conclusion

As a result of our studies, it was found that CS L- and D-ascorbate films selectively rotate the polarization plane of polarized light passing through them, depending on the sample orientation angle relative to the direction of the polarization vector of the incident light beam in the plane perpendicular to this beam. The discovered regularities predetermine the prospects for obtaining film thermal indicators, optical filters, chiral planar waveguides, and chiro-optic sensors with novel functional properties based on these systems.

REFERENCES

1. Shipovskaya A.B., Shmakov S.L., Kazmicheva O.F., Shchyogolev S.Yu., Optical activity of the anisotropic solutions of cellulose acetates in mesophasogenic solvents, Liquid Crystal. 38 (3) (2011) 361–369.

2. Shipovskaya A.B., Shmakov S L., Gegel N.O., Optical activity anisotropy of chitosan-based films, Carbohydrate Polymers, 206 (2019) 476–486.

3. Huttunen M.J., Partanen M., Bautista G., Chu S.-W., Kauranen M., Nonlinear optical activity effects in complex anisotropic three-dimensional media, Optical Materials Express. 5 (1) (2015) 11–21.

4. Nakagawa K., Harper-Lovelady H., Tanaka Y., Tanaka M., Yamato M., Asahi T., A highaccuracy universal polarimeter study of optical anisotropy and optical activity in laminated collagen membranes, Chemical Communications. 50 (95) (2014) 15086–15089.

5. Ushenko V.A., Gorsky, M.P., Complex degree of mutual anisotropy of linear birefringence and optical activity of biological tissues in diagnostics of prostate cancer, Optics and Spectroscopy, 115 (2) (2013) 290–297.

6. Schneider H.J., Chemomechanical gels-actuators and sensors, In: Chemoresponsive Materials, RSC Publishing, Cambridge, 2015.

7. Liu C., Dong C., Liu S., Yang Y., Zhang Z., Multiple chiroptical switches and logic circuit based on salicyl-imine-chitosan hydrogel, Carbohydrate Polymers. 257 (2021) ID 117534.

8. Mokhtar M., Sherin F. Hammad, Aya A. Abdella, Fotouh R., Mansour Enantioselective chitosanbased racemic ketoprofen imprinted polymer: Chiral recognition and resolution study, International Journal of Biological Macromolecules. 200 (2022) 327–334.

9. Manuela M.I., Luminita M., Chiral betulin-imino-chitosan hydrogels by dynamic covalent sonochemistry, Ultrasonics Sonochemistry. 45 (2018) 238–247.

10. Gogoi A., Konwer S., Zhuo G.-Y., Polarimetric measurements of surface chirality based on linear and nonlinear light scattering, Frontiers in Chemistry. 8 (2021) ID 611833.

THE AUTHORS

SHIPOVSKAYA Anna B. Shipovskayaab@yandex.ru ORCID: 0000-0003-1916-4067

RUDENKO Daria A. darudenko@mail.ru ORCID: 0000-0002-6741-7746 SHMAKOV Sergei L. shmakovsl@info.sgu.ru ORCID: 0000-0001-8019-0083

GEGEL Natalia O. gegelno@yandex.ru ORCID: 0000-0001-5724-7571

Received 04.07.2023. Approved after reviewing 09.08.2023. Accepted 09.08.2023.

Conference materials UDC 004.622 DOI: https://doi.org/10.18721/JPM.163.253

Development of an algorithm for preprocessing ultra-high resolution electrocardiosignals

K.V. Zaichenko¹, A.S. Afanasenko¹,², A.A. Kordyukova¹ E.A. Denisova¹¹[∞], D.O. Sevakov¹,²

¹Institute for Analytical Instrumentation RAS, St. Petersburg, Russia;

² Saint-Petersburg State University of Aerospace Instrumentation, St. Petersburg, Russia

□ Tiranderel@yandex.ru

Abstract. The necessity of developing an algorithm for preprocessing ultra-high resolution electrocardiosignals (UHR ECS) is substantiated. The causes of distortion of the useful signal are analyzed, two filtering methods have been developed for cardiac signals obtained from high-frequency (HF) and low-frequency (LF) channels for recording electrocardiograms (ECG). An algorithm for identifying the characteristic points of the ECS, denoted by the Latin letters P, Q, R, S, T, necessary for synchronization has been developed. The efficiency of the presented algorithm is estimated using the processing time of one signal record, as well as using the error matrix and calculating the Recall and Precision parameters.

Keywords: UHR ECS, UHR ECG, cardiogram, algorithm, characteristic points, signal processing, filtering, release

Funding: State Order No. 075-01157-23-00, Project FZZM-2022-0011.

Citation: Zaichenko K.V., Afanasenko A.S., Kordyukova A.A., Denisova E.A., Sevakov D.O., Development of an algorithm for preprocessing ultra-high resolution electrocardiosignals, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 307–311. DOI: https://doi.org/10.18721/JPM.163.253

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 004.622 DOI: https://doi.org/10.18721/JPM.163.253

Разработка алгоритма предварительной обработки электрокардиосигналов сверхвысокого разрешения

К.В. Зайченко¹, А.С. Афанасенко¹,², А.А. Кордюкова¹ Е.А. Денисова¹[⊠], Д.О. Шевяков¹,²

¹Институт аналитического приборостроения РАН, Санкт-Петербург, Россия;

² Санкт-Петербургский государственный университет аэрокосмического приборостроения, Санкт-Петербург, Россия

^{III} Tiranderel@yandex.ru

Аннотация. Обоснована необходимость разработки алгоритма предварительной обработки электрокардиосигналов сверхвысокого разрешения (ЭКС СВР). Проанализированы причины искажения полезного сигнала, разработаны два метода фильтрации для кардиосигналов, полученных из высокочастотного (ВЧ) и низкочастотного (НЧ) каналов регистрации электрокардиосигналов (ЭКС). Разработан алгоритм выделения характерных точек ЭКС, обозначаемых латинскими буквами P, Q, R, S, T, необходимых для синхронизации. Эффективность представленного алгоритма

© Zaichenko K.V., Afanasenko A.S., Kordyukova A.A., Denisova E.A., Sevakov D.O., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

оценена с помощью времени обработки одной записи сигнала, а также с помощью матрицы ошибок и вычисления параметров Recall и Precision.

Ключевые слова: ЭКС СВР, ЭКГ СВР, кардиограмма, алгоритм, характерные точки, обработка сигналов, фильтрация, ишемия

Финансирование: Государственный заказ № 075-01157-23-00, проект № FZZM-2022-0011.

Ссылка при цитировании: Зайченко К.В., Афанасенко А.С., Кордюкова А.А., Денисова Е.А., Шевяков Д.О. Разработка Алгоритма Предварительной Обработки Электрокардиосигналов Сверхвысокого Разрешения // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 307–311. DOI: https:// doi.org/10.18721/JPM.163.253

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Every year there are more and more people suffering from diseases of the cardiovascular system (CVS), in particular, coronary heart disease. To obtain more complete information about the stages of its development, the staff of the laboratory Radio and Optoelectronic Devices for Early Diagnosis of Pathologies of Living Systems of the Institute of Analytical Instrumentation of the Russian Academy of Sciences performs studies on modeling this disease in experimental animals based on the use of a new author's method of ultra-high resolution electrocardiography (UHR ECG) [1–4]. However, the recorded electrocardiosignals (ECS) are influenced by various factors. The purpose of this work is to develop an algorithm for preprocessing the ECS obtained by the UHR ECG method. To do this, it is necessary to solve the following tasks: development of an algorithm for filtering ECS obtained from low-frequency (LF) and high-frequency (HF) channels of their registration; selection of characteristic points of ECS from LF-channels, which are analogous to the information obtained using a standard ECG [5].

Algorithm for filtering ECS from the low-frequency and high-frequency channels of ECG registration

To detect samples on the cardiogram that are outliers that occur on the curve with accidental exposure to the device for registering the ECS, an algorithm was developed based on the assumption that the number of outliers is many times less than the number of working points. This can also be seen from the distribution of signal values. The values of all samples declared as outliers are replaced by the value of the nearest useful sample on the left.

As is known, a useful ECS for a standard ECG method is recorded in the frequency range from 1 to 100 Hz. The next stage of preprocessing the ECS from the LF-channel is the use of a bandpass filter with the appropriate bandwidth. In addition, the use of a notch filter reduces the impact of network interference (50 Hz).



Fig. 1. UHR ECS from the HF-channel before and after filtration (*a*), UHR ECS spectra from the HF-channel before and after filtration (*b*)

© Зайченко К.В., Афанасенко А.С., Кордюкова А.А., Денисова Е.А., Шевяков Д.О., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. The useful UHR ECS received from the high frequency (HF) channel is recorded in the frequency range from 100 to 2000 Hz [5]. Therefore, the further stage of signal preprocessing is the use of a bandpass filter with the appropriate bandwidth. The signal spectrum contains harmonics with frequencies that are multiples of 156 Hz, the amplitude of which significantly exceeds the amplitudes of neighboring spectral components. These harmonics are interference, so it must be removed from the signal. Fig. 1a shows the superimposed unfiltered and filtered UHR ECS obtained from the HF-channel of ECG registration, Fig. 1, b shows their spectra.

Algorithm for the selection of characteristic points of the ECS from LF-channel

To selecting the characteristic points of the ECG, that are traditionally designated by Latin letters P, Q, R, S, T, the standard command from the native Python waveform-database (WFDB) package for ECG processing is used - wfdb.processing [6]. This function identifies two groups of points: suspicious for R-peaks and suspicious for P, Q, S, T-peaks. If one of the found points is higher by 3 standard deviations from the base line, then it is a P, T or R-peak [7]. A point above the base line is followed by a point below (Q or S-peaks).

A fragment of the ECS with selected P, Q, R, S, T-peaks is shown in Fig. 2.



Fig. 2. UHR ECS with selected characteristic points

Results and discussion

To evaluate the effectiveness of the developed algorithm, an error matrix was constructed for the algorithm for selecting characteristic points of the ECS from the LF-channel, and the values were obtained for filtered and unfiltered signals during the comparison of the coordinates of the selected characteristic points with the reference markup. Due to the lack of evidence, the True Negative parameter is not calculated. The error matrix is presented in the form of Table 1.

The data presented in Table 2 confirm the validity of the application of the developed UHR ECS filtering algorithm, since during the processing of the filtered signal, 2 times fewer points that are not P, Q, R, S, T-peaks were allocated. Using the error matrix, you can get the values of the *Recall* and *Precision* parameters, which are calculated using formulas (1) and (2), respectively.

Table 1

EITOI MAUIX							
Signal before filtration			Signal after filtration				
	True	False		True	False		
Positive	22638	160	Positive	22795	77		
Negative	_	812	Negative	_	648		

$$Recall = \frac{\mathrm{TP}}{\mathrm{TP} + \mathrm{FN}};\tag{1}$$

$$Precision = \frac{\text{TP}}{\text{TP} + \text{FP}}.$$
(2)

The values of the parameters for evaluating the efficiency of the preprocessing algorithm are presented in Table 2.

Based on the data obtained, it can be concluded that the developed algorithm for preprocessing UHR ECG allows to improve the quality of *Recall* and *Precision*.

Table 2

Parameters for evaluating the efficiency of the algorithm of preprocessing ECS

	Signal	Signal
	before filtration	after filtration
Recall	0.7646	0.9966
Precision	0.9723	0.9929

Conclusion

The results obtained show the validity of the application of the developed algorithm for the preprocessing of the UHR ECS. The developed algorithm makes it possible to filter the signal with minimal distortion of useful information, as well as to identify characteristic points on the ECS from the LF-recording channel. This will facilitate the task of identifying new diagnostically significant markers of coronary heart disease in the signal obtained by the UHR ECG method. On the other hand, studies conducted on experimental animals with artificially induced myocardial ischemia have revealed certain limitations in the use of the developed algorithm. The main one is related to the need to adjust the parameters of the function when changing the living object of study. In this regard, the work on further improvement of the developed application software and the development of new methods of filtering UHR ECS are relevant.

REFERENCES

1. Grevtseva A.S., Smirnov K.J., Rud V.Yu., Development of methods for results reliability raise during the diagnosis of a person's condition by pulse oximeter. Journal of Physics: Conference Series. 1135(1) (2018) 12056.

2. Davydov R.V., Yushkova V.V., Stirmanov A.V., Rud V.Yu., A new method for monitoring the health condition based on nondestructive signals of laser radiation absorption and scattering. Journal of Physics: Conference Series. 1410 (1) (2019) 012–067.

3. Davydov V.V., Davydova T. I., A nondestructive method for express testing of condensed media in ecological monitoring, Russian Journal of Nondestructive Testing. 53 (7) (2017) 520–529.

4. Davydov V.V., Porfir'eva E.V., Davydov R.V., Nondestructive Method for Testing Elasticity of Walls of Human Veins and Arteries. Russian Journal of Nondestructive Testing. 58 (9) (2022) 847–857.

5. Zaichenko K.V., Kordyukova A.A., Logachev E.P., Luchkova M.N., Application of Radar Techniques of Signal Processing for Ultra-High Resolution Electrocardiography. Biomedical Engineering. 55 (1) (2019) 31–35.

6. Aalbers J., Bell P., Bowhay J., Signal processing (scipy.signal). Numpy and Scipy Documentation. 1.9.3. (2022).

7. Dor D., Zwick U., Finding percentile elements. Proceedings Third Israel Symposium on the Theory of Computing and Systems. vol. 4881271 (2002).

THE AUTHORS

ZAICHENKO Kirill V. kvz235@mail.ru ORCID: 0000-0002-2881-4386

AFANASENKO Arseniy S. ar.afanasenko@gmail.com ORCID: 0009-0001-0859-9252

KORDYUKOVA Anna A. annygm00@mail.ru ORCID: 0000-0002-6099-4276 DENISOVA Elena A. Tiranderel@yandex.ru ORCID: 0000-0003-0329-2881

SEVAKOV Daniil O. sevakovdaniil@gmail.com ORCID: 0000-0001-5609-4091

Received 05.07.2023. Approved after reviewing 31.07.2023. Accepted 31.07.2023.

Conference materials UDC 543.9, 546.06 DOI: https://doi.org/10.18721/JPM.163.254

Coating of hydrophilic chalcogenide quantum dots with carboxymethyl chitosan for lateral flow immunoassay applications

E.A. Sidorov¹[⊠], N.N Troshkina¹, E.D. Gribova¹, P.P. Gladyshev¹, N.A. Polotnyanko¹

¹ Dubna State University, Dubna, Russia

⊠ siea.18@uni-dubna.ru

Abstract. Quantum dots (QDs) is a class of fluorescent label widely using for biological and biomedical applications. The unique optical properties of QDs make them promising tool as fluorescent markers and analytical labels of proteins. To apply them in biological fluids it is essential to coat QDs with biocompatible polymers. In this research CdTe/CdS/ZnS QDs with mercaptopropionic acid as stabilizer was coated with carboxymethyl chitosan (CMC) by electrostatic interactions. The physicochemical properties of resulting QDs-CMC were studied by absorption and fluorescence spectroscopy, dynamic light scattering and capillary zone electrophoresis.

Keywords: quantum dots, chitosan, immunoassay

Funding: The work was carried out with the financial support of the Foundation for Assistance to Small Innovative Enterprises in Science and Technology under the contract 17262GU/2022 from 05.04.2022.

Citation: Sidorov E.A., Troshkina N.N, Gribova E.D., Gladyshev P.P., Polotnyanko N.A., Coating of hydrophilic chalcogenide quantum dots with carboxymethyl chitosan for lateral flow immunoassay applications, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 312–317. DOI: https://doi.org/10.18721/JPM.163.254

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 543.9, 546.06 DOI: https://doi.org/10.18721/JPM.163.254

Покрытие гидрофильных халькогенидных квантовых точек карбоксиметилхитозаном для применения в иммунохроматографическом анализе

Е.А. Сидоров¹⊠, Н.Н. Трошкина¹, Е.Д. Грибова¹, П.П. Гладышев¹, Н.А. Полотнянко¹

¹ Федеральное государственное бюджетное образовательное учреждение высшего образования «Университет «Дубна», г. Дубна, Россия

⊠ siea.18@uni-dubna.ru

Аннотация. Одним из бурно развивающихся направлений в мире науке является использование квантовых точек (КТ) в различных приложениях биоанализа в качестве флуоресцентных маркеров и аналитических меток белковых молекул. Для применения КТ в биоанализе, их поверхность покрывают биосовместимыми полимерами. В данной работе покрытие КТ состава CdTe/CdS/ZnS-MПК карбоксиметилхитозаном (KMX) осуществляли электростатической адсорбцией. Физико-химические свойства полученных КТ-КМХ исследованы методами капиллярного зонного электрофореза, динамического рассеяния света, методами спектроскопии поглощения и флуоресцентной спектроскопии.

© Sidorov E.A., Troshkina N.N, Gribova E.D., Gladyshev P.P., Polotnyanko N.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: квантовые точки, хитозан, иммуноанализ

Финансирование: Работа выполнена при финансовой поддержке Фонда содействия развитию малых форм предприятий в сфере науки и техники по договору 17262ГУ/2022 от 05.04.2022.

Ссылка при цитировании: Сидоров Е.А., Трошкина Н.Н., Грибова Е.Д., Гладышев П.П., Полотнянко Н.А. Покрытие гидрофильных халькогенидных квантовых точек карбоксиметилхитозаном для применения в иммунохроматографическом анализе // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 312–317. DOI: https://doi.org/10.18721/JPM.163.254

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Currently, colloidal quantum dots (QDs) have drawn tremendous attention as promising tool for in vivo imaging and biosensoric applications. The unique optical properties make them exciting alternative for conventional analytical labels in lateral flow immunoassay (LFIA). To apply QDs in bioanalysis their surface usually coating with biocompatible polymers with different functional groups for attachment of biological molecules. The most commonly used polymeric coating is chitosan. Chitosan is a natural, glucosamine polysaccharide which display good biocompatibility. However, chitosan is insoluble in neutral and alkaline media. As a result, the coating is conduct in an acetic acid medium. Low pH values lead to protonation of anionic stabilizers of QDs (for example: thioglycolic acid, mercaptopropionic acid (MPA), 2-mercaptoethanol, etc) and decrease of quantum yield. In addition, chitosan does not have carboxyl groups required for protein conjugation by the carbodiimide-succinimide method.

Materials and Methods

CdTe/CdS/ZnS-MPA QDs, chitosan (deacetylation degree: \geq 80%, molecular weight \leq 50 kDa, National Research Centre, Egypt), monochloroacetic acid (for synthesis, VEKTON, Russia), sodium hydroxide (98%, VEKTON, Russia), isopropyl alcohol (99.9%, Sigma-Aldrich), deionized water.

Microcentrifuge Eppendorf 5425 (Eppendorf, Germany), magnetic stirrer IKA C-MAG HS 7 (IKA-Werke, Germany), analytical balance CAUX-120 (CAS Corporation, Republic of Korea), polyethersulfone syringe filters with 0.22 µm pores, Amicon ultra-0.5 mL centrifugal filters (Merck, Germany), spectrophotometer UNICO-2100 (United Products & Instruments, USA), spectro-fluorometer FluoroLog 3 model FL3–21 (Horiba Jobin Yvon SAS, France), Zetasizer Nano S Size Analyzer (Malvern, Germany), Agilent Capillary Electrophoresis System 7100 (Agilent Technologies, USA), Elix Advantage 5 Water Purification System (Millipore, USA).

Preparation of carboxymethyl chitosan

Analyzing a number of articles [1-6], usually chitosan is dissolved in acetic acid and mix with solution of negative charged nanoparticles (NPs). Since chitosan does not have carboxylic groups which required to protein conjugation by carbodiimide-succinimide method and negatively charged QDs degrade in acid solutions it is necessary to modify chitosan.



Scheme 1. Carboxymethylation of chitosan

© Сидоров Е.А., Трошкина Н.Н., Грибова Е.Д., Гладышев П.П., Полотнянко Н.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. In this study, to ensure solubility in water and the introduction of carboxyl groups into the structure, chitosan was modified with monochloroacetic acid in a sodium hydroxide medium. Chitosan is dispersed in isopropyl alcohol for 20 minutes. 40% sodium hydroxide solution and monochloroacetic acid are added to the reaction mixture with constant stirring at a temperature of 45 °C. The resulting CMC was washed with anhydrous isopropyl alcohol and dried.

Carboxymethylation of chitosan is conducted by alkylation of chitosan with monochloroacetic acid in sodium hydroxide medium according to [7] (Scheme 1).

Further, the resulting CMC was used for coating CdTe/CdS/ZnS-MPA QDs by electrostatic interaction according to Scheme 2.



Scheme 2. Coating of CdTe/CdS/ZnS-MPA QDs with CMC

The obtained QDs-CMC were studied by absorption and fluorescence spectroscopy, dynamic light scattering and capillary zone electrophoresis.

Results and Discussion

To determine the presence of carboxyl groups, the obtained CMC was studied by IR spectroscopy with a frustrated total internal reflection attachment (Fig. 1).

Analyzing the obtained CMC IR spectrum, it can be noted that after carboxymethylation, chitosan retains its native structure, as evidenced by the presence of vibrations in the region of $1024-877 \text{ cm}^{-1}$. Vibrations in the region of 1668 and 1409 cm⁻¹ points the successful introduction of carboxyl groups into the structure of chitosan.



Fig. 1. IR spectra of chitosan (blue) and CMC (violet)

Table 1

Frequency, cm ⁻¹	Characteristic frequencies
3455–3445	O-H, N-H
2860-2850	C-H
1668	C=O
1409	-CH ₂ COONa
1024-877	C-0, C-0-C

Characteristic	frequencies	in	the	IR	spectra	of	chitosan	and	CMC
						~ -	• · · · · · · · · · · · · · · ·		



Fig. 2. Overlay of electrophoregrams of CdTe/CdS/ZnS-MPA (blue) and CdTe/CdS/ZnS-MPA-CMC (red) QDs. Analysis conditions: detection wavelength 220 nm, voltage +30 kV, supporting electrolyte 25 mM borate buffer solution pH = 9.2

To define the physicochemical properties and the possibility of application in bioanalysis, the obtained QDs-CMC were studied by absorption and fluorescence spectroscopy, dynamic light scattering and capillary zone electrophoresis.

The migration time of CdTe/CdS/ZnS-MPA QDs is 12.9 minutes, and that of the CdTe/CdS/ZnS-MPA-CMC one is 6.5 minutes, which is associated with a change in the surface charge of QDs as a result of the addition of CMCs to the surface of QDs. It can be noted that the peak has a narrow symmetrical shape, which indicates the monodispersity of QDs-CMC.

Fig. 3 shows the normalized absorption spectra of CdTe/CdS/ZnS-MPA and CdTe/CdS/ ZnS-MPA-CMC QDs, and their fluorescence spectra (excitation wavelength: 350 nm).

The peak in the absorption spectrum of QDs of the composition CdTe/CdS/ZnS-MPA in the region of 569 nm corresponds to the formation energy of an electron-hole pair (exciton). After QDs coating, the position of the exciton peak slightly shifts to the red region of the spectrum due to CMC coating absorption. The maximum fluorescence peaks are at a wavelength of 621 nm. The luminescence wavelength does not change after coating since CMC does not participate in emission processes. The QDs quantum yield decreases. The relative quantum yield of CdTe/CdS/ZnS-MPA and CdTe/CdS/ZnS-MPA-CMC are 27% and 25%, respectively. The decrease in the quantum yield is due to the fact that the CMC immobilized on the QD surface shields the secondary emission.

The hydrodynamic diameters of QDs and QDs-CMC determined by the dynamic light scattering method are presented in Table 2.

Thus, after CMC coating of QDs, the hydrodynamic diameter of QDs increased by 96 nm, which is associated with the capture of a single CMC fragment of several QDs.



Fig. 3. Overlay of the absorption (dotted lines, left axis) and fluorescence (solid lines, right axis) spectra of the CdTe/CdS/ZnS-MPA and CdTe/CdS/ZnS-MPA-CMC QDs

Table 2

Tryurouynamic manieters of QDS and QDS-CNIC						
Sample	Hydrodynamic diameter, nm					
CdTe/CdS/ZnS-MPA	46 ± 2					
CdTe/CdS/ZnS-MPA-CMC	137 ± 5					

Hydrodynamic diameters of QDs and QDs-CMC

Conclusion

Modification of QDs with CMC makes it possible to introduce functional groups required for conjugation with proteins. The functionalization of QDs based on electrostatic interactions leads to increase in the hydrodynamic size of QDs as a result of the capture of several QDs by a single polymer fragment. As a result, the CMC coating preserve the optical properties of QDs. The immobilization of CMC leads to a slight decrease in the quantum yield.

The biocompatibility of chitosan makes it a promising polymer coating for the conjugation of QDs with proteins. In further studies, it is planned to immobilize antibodies on the surface of QDs-CMC for lateral flow immunoassay applications.

REFERENCES

1. Ghormade V., Gholap H., Kale S., Kulkarni V., Bhat S., Paknikar K., Fluorescent cadmium telluride quantum dots embedded chitosan nanoparticles: a stable, biocompatible preparation for bioimaging, Journal of Biomaterials Science, Polymer Edition. 26 (1) (2015) 42–56.

2. Qi P., Zhang T., Shao J., Yang B., Fei T., Wang R., A QCM humidity sensor constructed by graphene quantum dots and chitosan composites, Sensors and Actuators A: Physical. 287 (2019) 93–101.

3. Dogan Ü., Kasap E., Cetin D., Suludere Z., Boyaci I. H., Türkyılmaz C., Ertas N., Tamer, U., Rapid detection of bacteria based on homogenous immunoassay using chitosan modified quantum dots, Sensors and Actuators B: Chemical. 233 (2016) 369–378.

4. Nie Q., Tan W. B., Zhang Y., Synthesis and characterization of monodisperse chitosan nanoparticles with embedded quantum dots, Nanotechnology. 17 (1) (2005) 140.

5. Korolev D.V., Shulmeyster G.A., Evreinova N.V., Syrovatkina M.S., Istomina M.S., Postnov V.N., Aleksandrov I.V., Krasichkov A.S., Galagudza, M.M., Theranostic Platforms Based on Silica and Magnetic Nanoparticles Containing Quinacrine, Chitosan, Fluorophores, and Quantum Dots, International Journal of Molecular Sciences. 23 (2) (2022) 932.

6. Sarkar T., Bohidar H.B., Solanki P.R., Carbon dots-modified chitosan based electrochemical biosensing platform for detection of vitamin D, International journal of biological macromolecules. 109 (2018) 687–697.

7. Siahaan P., Mentari N.C., Wiedyanto U.O., Hudiyanti D., Hildayani S.Z., Laksitorini, M.D., The optimum conditions of carboxymethyl chitosan synthesis on drug delivery application and its release of kinetics study, Indonesian Journal of Chemistry. 17 (2) (2017) 291–300.

THE AUTHORS

SIDOROV Evgeniy A. siea.18@uni-dubna.ru ORCID: 0000-0003-0326-3554 GLADYSHEV Pavel P. pglad@yandex.ru

POLOTNYANKO Natalia A. polot.nat@gmail.com

TROSHKINA Natalia N. tnn.18@uni-dubna.ru

GRIBOVA Elena D. elena_g67@mail.ru

Received 07.07.2023. Approved after reviewing 27.07.2023. Accepted 28.07.2023.

Conference materials UDC: 57.084.1 DOI: https://doi.org/10.18721/JPM.163.255

Fabrication of porous hydrogels containing hyaluronic acid by photoinduced crosslinking

V.I. Kuzyaeva¹, A.V. Sochilina^{1,2,3}, A.G. Savelyev¹, R.A. Akasov^{1,2,3}, A.N. Generalova^{1,2}

¹FSRC Crystallography and Photonics RAS, Moscow, Russia;

² M.M. Shemyakin and Yu.A. Ovchinnikov Institute of bioorganic chemistry of the RAS, Moscow, Russia;

³ Moscow Pedagogical State University, Moscow, Russia

⊠ kuzyaeva.valeriya@mail.ru

Abstract. Biocompatible hydrogels have gained much attention in tissue engineering, preferably as scaffolds providing the cell attachment and viability in the hydrogel bulk. This requires fabrication of the hydrogels with pores, the sizes of which are in the range of 100-300 μ m, most optimal for cell growth. The composition of hydrogels or method of fabrication may affect the formation of porous structure. We prepared hydrogels via photoinduced crosslinking of hyaluronic acid modified with glycidyl methacrylate under irradiation at different wavelengths using two photoinitiators. The hydrogel structure was varied by blending hyaluronic acid derivative with other modified polymers of natural origin (gelatin and pullulan) with grafted vinyl moieties or using filler (sucrose). The most optimal pore sizes for cell growth were obtained for hydrogels derived from modified hyaluronic acid, with the addition of sucrose or processed with the single freeze-thaw cycle. The produced hydrogels demonstrated lack of cytotoxicity with HaCaT cells incorporated inside gel bulk.

Keywords: pores, scaffolds, photoinduced crosslinking, biopolymers, bioink

Funding: This study was supported by Russian Science Foundation under grant 21-79-10384 in part of photocrosslinking in red light and was prepared under the state order of the Ministry of Education of the Russian Federation 122122600055-2 in part of photocrosslinking in blue light.

Citation: Kuzyaeva V.I., Sochilina A.V., Savelyev A.G., Akasov R.A., Generalova A.N., Fabrication of porous hydrogels containing hyaluronic acid by photoinduced crosslinking, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 318–322. DOI: https://doi.org/10.18721/JPM.163.255

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Kuzyaeva V.I., Sochilina A.V., Savelyev A.G., Akasov R.A., Generalova A.N., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК: 57.084.1 DOI: https://doi.org/10.18721/JPM.163.255

Формирование пористых гидрогелей, содержащих гиалуроновую кислоту, методом фотоиндуцируемой сшивки

В.И. Кузяева¹[⊠], А.В. Сочилина^{1,2,3}, А.Г. Савельев¹, Р.А. Акасов^{1,2,3}, А.Н. Генералова^{1,2}

¹ ФНИЦ «Кристаллография и фотоника» РАН, Москва, Россия;

² Институт биоорганической химии им. академиков М.М. Шемякина и Ю.А. Овчинникова РАН, Москва, Россия;

³Московский Педагогический государственный университет, Москва, Россия

⊠ kuzyaeva.valeriya@mail.ru

Аннотация. Биосовместимые пористые гидрогели привлекают большое внимание в тканевой инженерии, преимущественно в качестве скаффолдов, обеспечивающих прикрепление клеток и их жизнеспособность в объеме гидрогеля. В данной работе была исследована структура гидрогелей, полученных разными способами на основе модифицированных полимеров природного происхождения методом фотоиндуцированной сшивки. Наиболее оптимальные размеры пор для роста клеток были у гидрогелей, сформированных из модифицированной гиалуроновой кислоты с добавлением сахарозы или обработанных с помощью однократного цикла замораживания-оттаивания. Полученные гидрогели продемонстрировали отсутствие цитотоксичности на примере культуры клеток НаСаТ, включенным в объем геля.

Ключевые слова: поры, скаффолды, фотоиндуцируемая сшивка, биополимеры, биочернила

Финансирование: Работа выполнена при финансовой поддержке Российского научного фонда, грант № 21-79-10384, в части фотосшивки красным светом и в рамках Государственного задания Министерства просвещения Российской Федерации № 122122600055-2 в части фотосшивки синим светом.

Ссылка при цитировании: Кузяева В.И., Сочилина А.В., Савельев А.Г., Акасов Р.А., Генералова А.Н. Формирование пористых гидрогелей, содержащих гиалуроновую кислоту, методом фотоиндуцируемой сшивки // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 318–322. DOI: https:// doi.org/10.18721/JPM.163.255

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Biocompatible hydrogel scaffolds have recently gained increasing interest in tissue engineering, while manufacturing suitable scaffolds for cell culture and tissue regeneration remains an intensive area of development [1]. Cell attachment and viability are strongly correlated with pore sizes. The average size of animal cells is $\sim 10-30 \mu m$, therefore the most optimal sizes of hydrogel pores for their growth and development are within 100 to 300 μm [2]. Porous matrix can be produced by various methods such as fiber bonding, salt leaching, foaming and 3D printing. Moreover, the various components of hydrogel can exert influence on the formation of pore sizes during gelation [3]. In our study, the emphasis was made on the evaluation of the factors which can tune pore sizes.

Materials and methods

Photocompositions (inks). All inks for the formation of hydrogels were made on the basis of modified polymers of natural origin – hyaluronic acid (mHA), pullulan (mPul) and gelatin (mGel) – prepared by using the method of grafting moieties with double bonds through

© Кузяева В.И., Сочилина А.В., Савельев А.Г., Акасов Р.А., Генералова А.Н., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

polymer-analogous reaction with glycidyl methacrylate [4]. Sucrose (20%) was added to the composition of some inks to study the effect on the pore formation. In order to activate the process of crosslinking by irradiation upon wavelengths of 450 and 660 nm, two photoinitiators of the type II were used: flavin mononucleotide (FMN) and pyridine-substituted phthalocyanine (Pht). Co-initiators chosen from compounds with amino groups (for FMN) and with thiol groups (for Pht) provide the efficiency of photoinitiators.

Photo crosslinking. In order to form hydrogels of the equal volume, silicone molds opened on both sides (height 1 mm, diameter 6 mm) were used. The ink was placed in a mold clamped between two slides and exposed with laser radiation at wavelength of 450 nm (600 MW power) for 15 min for each side of the mold if FMN was contained [5], or 660 nm (2500 MW power) for 15 min on one side of the mold if Pht was contained. Different power and time were used to ensure efficient crosslinking and formation of stable hydrogels.

Pore size measurement. The gel pore images were acquired using a scanning electron microscope (Phenom ProX, Thermo Fisher Scientific) after hydrogel shock freezing in liquid nitrogen and lyophilic drying.

In vitro study. The human keratinocytes (HaCaT cell line) were entrapped into the ink during fabrication, and their growth within the gel bulk was demonstrated with fluorescent dye Calcein-AM using fluorescent microscopy.

Results and Discussion

The pore sizes of formed gels varied approximately from 5 to 100 μ m depending on the cone stituents. The pore sizes of hydrogels based on only mHA (Fig. 1,*a*) containing either FMN or Pht almost did not differ and were in the range of 30–50 μ m, at the same time Pht gels posr sessed slightly larger pores with ragged edges. The smallest pores (2–20 μ m) were evaluated in the hydrogels based on mGel and mPul, as well as in their mixtures with mHA (Fig. 1, *b*, *c*). Insignificant changes in pore size during the treatment of mixtures of mHA with mGel and mPul with the enzyme hyaluronidase, as well as their more prominent enzymatic degradation compared to hydrogels based on pure mHA, suggested that mGel and mPul make the main contribution to the formation of the structure. Limited mHA crosslinking was likely due to the high level of affinity for water compared to other biopolymers.



Fig. 1. SEM images of gels containing: mHA 20% (*a*); mHA 10% and mGel 10% (*b*); mHA 10% and mPul 10% (*c*). Scale bar 50 μ m

It was found that scaffolds contained from mHA 20% after treatment with hyaluronidase resulted to substantial increase in pore sizes (from 100 μ m) (Fig. 2,*a*). Moreover it was discovered that utilization of sucrose, which can be removed after irradiation by swelling in aqueous solutions, led to the formation of larger pores (50–100 μ m) in hydrogels (Fig. 2,*b*). The same effect can be achieved by using the freezing-thawing technique for polymer compositions in the range of temperatures from -30 to -5 °C, when even more significant increase in pore size (100–150 μ m) was observed (Fig. 2,*c*).

The in vitro study of HaCaT cells embedded in hydrogel bulk demonstrated fluorescence of Calcein-AM (Fig. 3), indicating living cells in both FMN and Pht gels (mHA 20%) during 3 days of experiment, which confirms good cell viability in such environment.



Fig. 2. SEM images of gels containing: mHA 20% after treatment with hyaluronidase (scale bar 50 μm) (a); mHA 20% and sucrose 20% (scale bar 50 μm) (b); mHA 20%, after freeze-thawing cycle treatment (scale bar 100 μm) (c)



Fig. 3. Fluorescence of HaCaT cells inside of hydrogels containing: FMN (*a*); Pht (*b*). Scale bar 100 μ m

Conclusion

Hence, the most auspicious hydrogel scaffolds are produced from mHA with the addition of sucrose or treated with a single freeze-thaw cycle, since they have the most optimal pore size for cell growth. Furthermore, the developed compositions can be used as bioinks with incorporated cells.

Acknowledgments

The authors thank Alexander Efimov and Lijo George from Tampere University for the synthesis of water-soluble phthalocyanine.

REFERENCES

1. Drury J.L., Mooney D.J., Hydrogels for tissue engineering: scaffold design variables and applications //Biomaterials. 24 (24) (2003) 4337–4351.

2. Han Y., et al., Effect of pore size on cell behavior using melt electrowritten scaffolds //Frontiers in Bioengineering and Biotechnology. 9 (2021) 629270.

3. Cao H., et al., Current hydrogel advances in physicochemical and biological response-driven biomedical application diversity //Signal transduction and targeted therapy. 6 (1) (2021) 426.

4. Sochilina A.V. et al., Preparing Modified Hyaluronic Acid with Tunable Content of Vinyl Groups for Use in Fabrication of Scaffolds by Photoinduced Crosslinking //Russian Journal of Bioorganic Chemistry. 47 (2021) 828–836.

5. **Savelyev A.G. et al.,** Flavin mononucleotide photoinitiated cross-linking of hydrogels: Polymer concentration threshold of strengthening //Journal of Photochemistry and Photobiology A: Chemistry. 341 (2017) 108–114.

THE AUTHORS

KUZYAEVA Valeriia I. kuzyaeva.valeriya@mail.ru ORCID: 0009-0008-5419-5217

SOCHILINA Anastasia V. ddraig@yandex.ru ORCID: 0000-0002-2399-316X

SAVELYEV Alexander G. a.g.savelyev@gmail.com ORCID: 0000-0001-7616-3285 AKASOV Roman A. roman.akasov@gmail.com ORCID: 0000-0001-6486-8114

GENERALOVA Alla N. angeneralova@gmail.com ORCID: 0000-0001-9646-1693

Received 10.07.2023. Approved after reviewing 17.07.2023. Accepted 19.07.2023.

Conference materials UDC 544.018.2 DOI: https://doi.org/10.18721/JPM.163.256

Miniature potentiometric system for determination of H^+ , K^+ , Na⁺, Cl⁻, NO⁻, - and Ca²⁺ ions in liquid biological environment

V.V. Romanova¹, V.S. Sibirtsev^{2,1}, A.Yu. Zaitceva¹

¹Institute for Analytical Instrumentation RAS, St. Petersburg, Russia;

² St. Petersburg State Chemical and Pharmaceutical University, St. Petersburg, Russia

⊠ venjo@mail.ru

Abstract. An intelligent potentiometric system for the analysis of liquid biological environments has been developed and researched. The system consists of a set of 6 miniature measuring cells, including polyvinylchloride-membrane electrodes, selective to the presence of H^+ , K^+ , Na^+ , Ca^{2+} , Cl^- , NO_3^- ions in the analyzed solutions, and one central 'reference' cell with a chlorosilver reference electrode. For potentiometric measurements of the voltages of our system, an eight-channel analog-to-digital converter was used, which receives a signal from the down conductor of each of the measuring cells and the central 'reference' cell. This system was tested with aqueous solutions of HCl, KCl, NaCl, NaNO₃ and CaCl₂ at concentrations from 10^{-1} to 10^{-5} M. This confirmed the usefulness of the developed potentiometric multisensor system for the analysis of the ionic composition of biological environment.

Keywords: potentiometry, potentiometric sensor, ionic composition, miniature system, biological environment, plasticized membranes, multisensor system

Funding: The work was supported by the Ministry of Science and Higher Education of the Russian Federation (project 075-15-2021-1057).

Citation: Romanova V.V., Sibirtsev V.S., Zaitceva A.Yu., Miniature potentiometric system for determination of H⁺, K⁺, Na⁺, Cl⁻, NO₃⁻ - and Ca²⁺ ions in liquid biological environment, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 323–327. DOI: https://doi.org/10.18721/JPM.163.256

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 544.018.2 DOI: https://doi.org/10.18721/JPM.163.256

Миниатюрная потенциометрическая система для определения в жидких биологических средах содержания H⁺, K⁺, Na⁺, Cl⁻, NO₃⁻ и Ca²⁺ ионов

В.В. Романова¹⊠, В.С. Сибирцев^{2,1}, А.Ю. Зайцева¹

¹Институт аналитического приборостроения РАН, Санкт-Петербург, Россия;

² Санкт-Петербургский государственный Химико-Фармацевтический Университет,

Санкт-Петербург, Россия

⊠ venjo@mail.ru

Аннотация. Разработана и исследована интеллектуальная потенциометрическая система анализа жидких биологических сред. Система состоит из набора из 6 миниатюрных измерительных ячеек, включающих мембранные поливинилхлоридные электроды, селективные к присутствию ионов H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻, NO₃⁻ в анализируемых растворах, и одной центральной «эталонной» ячейки с хлорсеребряным электродом сравнения. Для потенциометрических измерений напряжений нашей

© Romanova V.V., Sibirtsev V.S., Zaitceva A.Yu., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

системы использовался восьмиканальный аналого-цифровой преобразователь, на который поступает сигнал с токоотвода каждой из измерительных ячеек и центральной «эталонной» ячейки. Данная система была протестирована с водными растворами HCl, KCl, NaCl, NaNO₃ и CaCl₂ в концентрациях от 10^{-1} до 10^{-5} М. Это подтвердило пригодность разработанной потенциометрической мультисенсорной системы для анализа ионного состава биологической среды.

Ключевые слова: потенциометрия, потенциометрический датчик, ионный состав, миниатюрная система, биологическая среда, пластифицированные мембраны, мультисенсорная система

Финансирование: Работа выполнена при поддержке Министерства науки и высшего образования Российской Федерации (проект 1057-2021-15-075).

Ссылка при цитировании: Романова В.В., Сибирцев В., Зайцева А.Ю. Миниатюрная потенциометрическая система для определения в жидких биологических средах содержания H⁺, K⁺, Na⁺, Cl⁻, NO₃⁻ и Ca²⁺ ионов // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 323–327. DOI: https:// doi.org/10.18721/JPM.163.256

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Ion-selective electrodes are an attractive tool for analyzing the ionic composition of various multicomponent aqueous solutions (which include most biological environment) due to their simplicity of operation, low cost, short analysis time, and the possibility of miniaturizing the sensors and automating the analysis process [1-6].

Ion selective electrodes have been widely used for more than 30 years in a wide range of applications for determining the concentration of certain ions in aqueous solution. The most commonly used ion-selective electrode is the pH electrode [7]. The first pH sensing glass electrode was introduced by Cremer in 1906. Since then wide range of ion-selective electrodes has been developed for the analysis of samples containing many different ions. A chemical sensor is a device which responds to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative and quantitative determination of the analyte [8].

Recently ion-sensors are taking place of various analytical techniques, as they provide a convenient and fast method of electroanalysis. Hence efforts are being made to develop a good sensor for ion sensing which should permit estimation of ion at a very low concentration and have good selectivity and low response time [9]. Advantages of using ion-selective electrodes include their very short measurement time, continuous monitoring ability, measurement of the activity rather than the concentration, and their usefulness in turbid and coloured samples [10, 11].

In this connection, the aim of our work was to develop and test the potentiometric system consisting of a set of 6 miniature measuring cells (MC) including PVC-membrane electrodes selective to the presence of H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻, NO₃⁻ ions (the most common in biological environment) in the analyzed solutions and one central 'reference' cell with chlorosilver reference electrode.

Materials and Methods

Our system was based on the method of direct potentiometry, based on transformation of activity of target ions (H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻ or NO₃⁻, respectively) into electromotive force (EMF), described by the Nernst equation.

Each of the 6 MC included in the developed potentiometric multisensor system and located around the central 'reference' cell (CRC) was a case made on a 3D-printer from PETG filament (see Fig. 1).

This housing was divided inside by a horizontal partition (HP). The lower (next to the HP) section of the case of MC has a volume of 1 ml and three side fittings. One of them (the central one filled with agar-agar with KCl) served as a 'salt bridge' connecting the MC with the CRC. Whereas the other two fittings served to input and output the analyzed solution from the MC and connect the MC to each other.

© Романова В.В., Сибирцев В.С, Зайцева А.Ю., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.


Fig. 1. Scheme of the potentiometric multisensor system developed by us. The device of the measuring cell (MC) is shown on the left; on the right, a diagram of a possible connection of the MC and the central 'reference' cell into a single system (in which two additional MCs are provided for the future expansion of the system with additional sensors)

In the middle of the HP there was a hole, which was sealed with an ion-selective membrane made of polyvinyl chloride plasticized with di-2-ethylhexylsebacinate (DOS), o-nitrophenyloctyl ether (oNPOE), or 2-fluorophenyl-2-nitrophenyl ether (2F2N) with an organic ionophore added during the assembly of the measuring cell.

Then, the upper (with respect to the HP) part of the MC also having a volume of 1 ml was filled with a solution of 2 M KCl - while the lower with respect to the HP part of the MC was filled either with the solution to be analyzed or (between the measurements) with a solution with a given concentration of the ion measured by this MC.



Fig. 2. Graphs obtained during testing of the potentiometric multisensor system developed by us: (*a*) calibration graph for the pH electrode for buffer solutions with pH 1.65, 4.01, 6.86 and 9.18 (calibration equation: $pH = 5 - 19 \cdot E_{H}$); (*b*) calibration graph for the pCa electrode for aqueous solutions CaCl₂ (calibration equation: $pCa = -4.64 - 42 \cdot E_{Ca}$); (*c*) calibration graph for the pK electrode for aqueous solutions KCl (calibration equation: $pK = 4.54 - 21 \cdot E_{K}$); (*d*) calibration graph for the pNa electrode for aqueous solutions NaCl (calibration equation: $pNa = 2.3 - 20 \cdot E_{Na}$); (*e*) calibration graph for the pCl electrode for aqueous solutions HCl (calibration equation: $pCl = -1.4 - 20 \cdot ECl$); (*f*) calibration graph for the pNO₃ electrode for aqueous solutions NaNO₃ (calibration equation: $pNO_3 = -2.86 + 20 \cdot E_{NO3}$)

After that, the top of the MC was closed with a cover in which a silver wire, galvanically coated with AgCl and slightly short of the HP, connected to the screened current collector was installed. The CRC of the developed potentiometric multisensor system had the same case and lid as the MC considered above - only completely filled with 2 M KCl solution, without a HP.

Results and Discussion

At approbation of our developed potentiometric multisensor system, we filled it in turn as the analyzed media with aqueous solutions of HCl, KCl, NaCl, NaNO₃ and CaCl₂ with concentrations 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} and 10^{-5} mol/l and also buffer solutions with pH 1.65, 4.01, 6.86 and 9.18. The data obtained in measurements of these solutions confirmed a high sensitivity of the developed MC to the target ions (H⁺, K⁺, Na⁺, Ca²⁺, Cl⁻ or NO⁻₃, respectively) at the absence of such sensitivity to non-target ions, as well as high reproducibility and linearity between values of potential differences between measuring cell and CRC and negative decimal logarithms of molar concentrations of target ions in the whole range of investigated concentrations of these ions from 10^{-5} to 10^{-1} M.

In this case, the resulting calibration equations between the indicated values for the EMF values measured in volts had the form: $pH = 5 - 19 \cdot E_{H}$, $pK = 4.54 - 21 \cdot E_{K}$, $pNa = 2.3 - 20 \cdot E_{Na}$, $pCa = -4.64 - 42 \cdot E_{Ca}$, $pCl = -1.4 - 20 \cdot E_{Cl}$ and $pNO_3 = -2.86 + 20 \cdot E_{NO3}$, and the original graphs used to calculate the above calibration equations are shown in Fig. 2.

For potentiometric measurements of voltages in our system, an eight-channel analog-to- digital converter (ADC) is used, which receives a signal from the down conductor of each of the measuring cells and the central 'reference' cell. The result of signal processing from the ADC is transferred to a personal computer for further processing.

Conclusion

At approbation of our developed potentiometric multisensor system, having carried out researches of solutions with known concentrations H^+ , K^+ , Na^+ , Ca^{2+} , Cl^- and NO_3^- ions, we have made sure of high enough stability, selectivity and sensitivity of our system in relation to ionic composition of researched solutions. These results confirmed the suitability of our developed potentiometric multisensor system for the analysis of the ionic composition of biological environment.

REFERENCES

1. Guzenko M.M., Zaitceva A.Yu., Intelligent sensory system for ranking the ionic composition of breast milk. Scientific instrumentation. 32 (4) (2022) 58–67.

2. Kokina M.S., Friui M., Shamtsyan M., Sibirtsev V.S., Krasnikova L.V., Konusova V.G., Simbirtsev A.S., Influence of pleurotus ostreatus beta-glucans on the growth and activity of some lactic acid bacteria. // Scientific research and research: chemistry and chemical technology, biotechnology, food industry. 19 (4) (2018) 465–471.

3. Vlasov Yu.G., Chemical sensors. Problems of analytical chemistry. M.: Nauka, (14) (2011) 399.

4. Sibirtsev V.S., Olekhnovich R.O., Samuylova E.O., Assessment of integral toxicity of water resources by instrumental methods of analysis. // SGEM Conference Proceedings. 17 (61) (2017) 507–514.

5. Vlasov Yu.G., Ermolenko Yu.E., Legin A.V., Rudnitskaya A.M., Kolodnikov V.V., Chemical sensors and their systems. Journal of Analytical Chemistry. 65 (9) (2010) 900–919.

6. Mikhelson K.N., Electrochemical sensors based on ionophores: current state, trends, prospects. Russian Chemical Journal. (2) (2008) 30–36.

7. Frant M.S., History of early commercialization of Ion-selective electrodes. Analyst (199) (1994) 2293.

8. Cattrall R.W., Chemical Sensors. New York: Oxford Chemistry Primers 1997.

9. Smyth M.R., Vos J.G., Electrochemistry, Sensors & Analysis. Amsterdam: Elsevier Science Publisher B. V. 1986.

10. Bakker E., Meyerhoff M.E., Anal Chim Acta (416) (2000) 121.

11. Bakker E., Buhlmann P., Pretsch E., Chem Rev (97) (1997) 3083.

THE AUTHORS

ROMANOVA Veronika V. venjo@mail.ru ORCID: 0009-0001-6587-787X

SIBIRTSEV Vladimir S. sibircev.vladimir@pharminnotech.com ORCID: 0000-0003-0829-5213 anna@da-24.ru ORCID: 0000-0003-0334-2770

ZAITCEVA Anna Yu.

Received 18.07.2023. Approved after reviewing 31.07.2023. Accepted 06.08.2023.

Conference materials UDC 612.16 DOI: https://doi.org/10.18721/JPM.163.257

New opportunities for studying the oxygen saturation of blood hemoglobin in capillaries and tissues

S. Msokar¹, R.V. Davydov^{1,2⊠}, M.S. Mazing³, D.D. Isakova⁴, M.A. Yakusheva¹

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² Alferov University, St. Petersburg, Russia;

³Institute for Analytical Instrumentation of the RAS, St. Petersburg, Russia;

⁴ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

^{III} davydovrv@spbstu.ru

Abstract. A new method of express diagnostics of the health state based on the results of non-invasive measurements of the pulse waveform, pulse values, blood pressure, and oxygen saturation of blood vessels and tissues is considered. The feature of these measurements is that they can be carried out both in the hospital and at home (a person can implement them independently). To measure tissue oxygen saturation, a new optical hardware-software complex has been developed, which is compact and portable. The results of experimental studies of various people are presented.

Keywords: oxygen saturation, pulse wave, blood, tissues

Citation: Msokar S., Davydov R.V., Mazing M.S., Isakova D.D., Yakusheva M.A., New opportunities for studying the oxygen saturation of blood hemoglobin in capillaries and tissues, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 328–332. DOI: https://doi.org/10.18721/JPM.163.257

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 612.16 DOI: https://doi.org/10.18721/JPM.163.257

Новые возможности изучения насыщения кислородом гемоглобина крови в капиллярах и тканях

С. Мсукар¹, Р.В. Давыдов^{1,2⊠}, М.С. Мазинг³, Д.Д. Исакова⁴, М.А. Якушева¹

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;

² Алфёровский университет, Санкт-Петербург, Россия;

³ Институт аналитического приборостроения РАН, Санкт-Петербург, Россия;

⁴ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия;

^{III} davydovrv@spbstu.ru

Аннотация. Рассмотрен новый метод экспресс-диагностики состояния здоровья, основанный на результатах неинвазивных измерений формы пульсовой волны, значений пульса, артериального давления, насыщения кислородом сосудов и тканей. Особенность этих измерений в том, что их можно проводить как в стационаре, так и дома (человек

© Msokar S., Davydov R.V., Mazing M.S., Isakova D.D., Yakusheva M.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

может осуществить их самостоятельно). Для измерения насыщения тканей кислородом разработан новый оптический программно-аппаратный комплекс, отличающийся компактностью и портативностью. Представлены результаты экспериментальных исследований различных людей.

Ключевые слова: насыщение кислородом, пульсовая волна, кровь, ткани

Ссылка при цитировании: Мсукар С., Давыдов Р.В., Мазинг М.С., Исакова Д.Д., Якушева М.А. Новые возможности изучения насыщения кислородом гемоглобина крови в капиллярах и тканях // Научно-технические ведомости СПбГПУ. Физикоматематические науки. 2023. Т. 16. № 3.2. С. 328-332. DOI: https://doi.org/10.18721/ JPM.163.257

Статья открытого доступа, распространяемая по лицензии СС ВУ-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In recent years, for many reasons, the issues of express diagnostics of the functional state of human health in various situations have received increased attention [1, 2]. In contrast to the many methods of express diagnostics, pulse oximetry has not exhausted its possibilities for obtaining additional information about the state of human health in various situations, the potential of which has yet to be fully explored [3-7].

One of the new solutions for obtaining additional information about human health is using new optical systems we developed [8] to register pulse wave signals and tissue oximetry simultaneously. We process them with the combination of diagnostic information into a database and compare them with data obtained earlier by other methods [8, 9]. It allows obtaining additional health information in a short time, using new equipment and techniques, both for measuring and processing the recorded signals to interpret the integral signal.

Materials and Methods

The main goal of all work in this area is to increase the reliability of data on the state of the human body, which are obtained after processing the results of measuring pulse waves and changes in tissue oxygen saturation. To successfully achieve the primary target, we have developed a combined system for express diagnostics of the state of human health. Its block diagram is shown in Fig. 1.



Doctor's computer

Fig. 1. Scheme for monitoring the state of human health in express mode

© Мсукар С., Давыдов Р.В., Мазинг М.С., Исакова Д.Д., Якушева М.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

An optical sensor developed by us for registering a pulse wave and an optical system for studying tissue oximetry, and a standard device for measuring pressure are placed at three points on the hands to carry out measurements. For breath control, a CO_2 sensor is used. It should be noted that, unlike many previous studies, all measurements are carried out synchronously.

We have developed the following technique to identify additional information in the pulse wave signal, dividing it into six intervals (2 correspond to the rising front, 2 to the falling front, and 2 to the locality of the maxima). One dependence is used to describe the rising fronts of the pulse wave, and another is used for the falling front. In addition, unlike previous studies, we propose to use a separate function to study the neighborhoods of two maxima [9]. A separate function for studying the maxima is necessary because the change in the nature of the pulse waveform and the parameters of the steps in the presence of some diseases in a person, for example, angina pectoris or arrhythmia, requires a more detailed consideration of this part of the pulse wave (in the locality of both maxima).

To obtain additional information about the oxygen state of tissues and the processes occurring in the microcirculatory bed under study, we developed a multichannel system that operates in a wide range of optical radiation from 410 to 940 nm. A multichannel integrated optic spectrum analyzer registers and processes the reflected laser radiation. We used 18 channels with laser radiation of different wavelengths. Each channel has a spectral bandwidth of 20 nm. As radiation sources in the developed layout of the optical system, 3 SMD LEDs of varying glow colors were used: cold white, red, and infrared. SMD-type LEDs have some advantages: the small size of the LED, low cost, and long service life. Although the white LED is not a source of a broadband emission spectrum (as, for example, incandescent lamps), the white SMD LED emits a fairly wide region of the visible range from blue to red light (range from 450 to 660 nm) with a pronounced dip in the blue-green color (approximately 500 nm).

In the developed hardware-information complex, a novelty is the possibility of simultaneous registration of radiation backscattered in tissues at once at eighteen wavelengths of the visible and near-infrared ranges of optical radiation in real-time with a wireless connection to a computer, which allows recording measurements both at rest and when the patient performs functional and physical activity.

Results and Discussion

Patients of different age groups are studied, and their pulse waves are analyzed using improved previously developed formulas [9]. The improvement consists in considering several local maxima in the pulse wave (from 1 to 3), which occurred in patients and some empirical corrections in coefficients. Fig. 2, as an example, presents the results of the registration of pulse waves from people of different age groups.

During the study, patients held their breath for a minute, and after that observed for about 2 minutes. An example of the received results is presented in Fig. 3.



Fig. 2. One period of the pulse wave of patients. Age of male patients: 20 years old (a), 30 years old (b), 56 years old (c). Age of female patients: 22 years (d), 28 years (e), 40 years (f)



Fig. 3. Results of oxygen saturation for one of the patients

The results are collected and analyzed for 30 patients. Analysis showed that the new system makes it possible to detect minor deviations in pulse waveforms and tissue oxygen saturation problems, which were sometimes hard to do on the previously used equipment. After that, the results were compared with the patient's history and clinical study. In most cases, problems were confirmed.

Conclusion

Comparing data on human health obtained using the new methods and devices with examination data on certified clinical equipment showed a high degree of agreement. It confirms the validity of the methods and optical devices we developed for the integrated monitoring of the work of the human cardiovascular system. Some further investigations are needed to connect deviations with worse health states for different reasons.

The advantage of the developed system over those previously used for express diagnostics is the ability to detect progressive destructive changes in the blood supply in real-time. And also to compare these results with the dynamics of changes in the pulse wave. Previously, similar studies using other methods were carried out at different points in time (a person's condition could change, especially if the interval between measurements was long). As a result, the information was difficult to compare, which led to errors. In our case, all measurements are carried out simultaneously, making it possible to help determine the onset of vascular disease and pathological changes in the human body. It is needed to provide early medical intervention and prevent the transition of diseases to the chronic stage. In addition, rapid monitoring of the state of microcirculation and basic hemodynamic parameters will help control the treatment process and, in the future, may increase the number of cases of timely seeking qualified medical care, which will reduce the number of complications after the disease, as well as reduce the time of patients' stay in hospitals.

REFERENCES

1. Nascimento L. M. S.d., Bonfati L. V., Freitas M. L. B., Junior J. J. A., Siqueira H. V. and Stevan S.L., Sensors and Systems for Physical Rehabilitation and Health Monitoring-A Review, Sensors. 20(15) (2020) 4063.

2. Allen J., Photoplethysmography and its application in clinical physiological measurement, Physiological Measurement. 28(3) (2007) R1-39.

3. Fine J., McShane M.J., Coté G. L., Scully C.G., A Computational Modeling and Simulation Workflow to Investigate the Impact of Patient-Specific and Device Factors on Hemodynamic Measurements from Non-Invasive Photoplethysmography, Biosensors. 12(8) (2022) 598.

4. Luks A.M., Swenson E.R., Pulse Oximetry for Monitoring Patients with COVID-19 at Home. Potential Pitfalls and Practical Guidance, Annals of the American Thoracic Society. 17 (2020) 1040–1046.

5. Nitzan M., Nitzan I., Arieli Y., The Various Oximetric Techniques Used for the Evaluation of Blood Oxygenation. Sensors 20(17) (2020) 4844.

6. Grevtseva A.S., Smirnov K.J., Greshnevikov K.V., Davydov V.V., Rud V.Yu., Glinushkin A.P., Method of assessment the degree of reliability of the pulse wave image in the rapid diagnosis of the human condition, Journal of Physics: Conference Series. 1368(2) (2019) 022072.

7. Grevtseva A.S., Smirnov K.J., Davydov V.V., Rud V.Yu., Development of methods for results reliability raise during the diagnosis of a person's condition by pulse oximeter. Journal of Physics: Conference Series. 1135 (1) (2018) 012056.

8. Davydov R., Zaitceva A., Davydov V., Isakova D., Mazing M., New Methodology of Human Health Express Diagnostics Based on Pulse Wave Measurements and Occlusion Test, Journal of Personalized Medicine. 13(3) (2023), 443.

9. Yakusheva M.A., Davydov R.V., Isakova D. D., Features of signal absorption fronts of laser radiation in rapid diagnosis of human health, Proceedings of 8th International Conference on Information Technology and Nanotechnology (2022), 1–5.

THE AUTHORS

MSOKAR Souhair souhair.msokar@gmail.com ORCID: 0009-0004-1809-484X

DAVYDOV Roman V. davydovroman@outlook.com ORCID: 0000-0003-1958-4221

MAZING Maria S. mazmari@mail.ru ORCID: 0000-0003-1739-9671 ISAKOVA Darya D. isakova.dd@yandex.ru ORCID: 0000-0003-1958-4221

YAKUSHEVA Maria A. yakusheva.ma@edu.spbstu.ru ORCID: 0000-0002-0198-6209

Received 09.07.2023. Approved after reviewing 19.07.2023. Accepted 19.07.2023.

Conference materials UDC 539.192 DOI: https://doi.org/10.18721/JPM.163.258

Mathematical modeling of determination of "Premeltons" sites in DNA by ultra short laser pulses

A.A. Kharlamova¹⊠

¹ Northern (Arctic) Federal University named after M.V. Lomonosov, Arkhangelsk, Russia

[⊠] Kharlamova.anastasya2015@yandex.ru

Abstract. The article discusses a method for analyzing the structure of a molecule using ultrashort laser pulses (USP). A premelton or elongation in the structure of a molecule was chosen as a sample for theoretical modeling of the interaction of a laser pulse with a substance. A premelton is a region of a molecule in which the distance between two adjacent nitrogenous bases is increased. The study of such structures is interesting for limiting the parameters of DNA denaturation, since the process of separation of the molecule begins with the elongation region. At the moment, the study of such features of the DNA structure is difficult, electrophoresis and staining methods cannot always give an accurate result, especially on short sections of the molecule. In this paper, we theoretically model the results of the interaction of USP with a molecule in two cases, when elongation takes place and when the molecule is ideal. The results obtained show the expediency of using laser pulses as a method for determining the structure of a complex polyatomic object. _

Keywords: ultrashort laser pulses, premelton, molecule elongation, denaturation, DNA, RNA

Funding: The study was supported by a grant from the Russian Science Foundation, 23-12-20014; State assignment of the Russian Federation, FSRU-2021-0008.

Citation: Kharlamova A.A. Mathematical modeling of determination of "Premeltons" sites in DNA by ultra short laser pulses, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 333–337. DOI: https://doi.org/10.18721/JPM.163.258

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 539.192 DOI: https://doi.org/10.18721/JPM.163.258

Математическое моделирование определения премельтонных участков в ДНК ультракороткими лазерными импульсами

А.А. Харламова 🖂

¹Северный (Арктический) федеральный университет им. М.В. Ломоносова, Архангельск, Россия

[™] Kharlamova.anastasya2015@yandex.ru

Аннотация. В статье рассматривается метод анализа структуры молекулы с использованием ультракоротких лазерных импульсов (УКИ). Премельтон или удлинение в структуре молекулы было выбрано в качестве объекта для теоретического моделирования взаимодействия лазерного импульса с веществом. Премельтон - это участок молекулы, в котором расстояние между двумя соседними азотистыми основаниями увеличено. Изучение таких структур интересно для определения параметров денатурации ДНК, поскольку процесс разделения молекулы начинается с области удлинения. На данный момент исследование таких участков ДНК затруднено, методы электрофореза и окрашивания не всегда могут дать точный результат, особенно на коротких участках молекулы. В этой статье теоретически смоделированы результаты взаимодействия УКИ с молекулой для двух случаев: когда в молекуле есть удлинение и когда молекула идеальна. Полученные результаты показывают целесообразность использования лазерных импульсов в качестве метода определения структуры сложного многоатомного объекта.

© Kharlamova A.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: ультракороткие лазерные импульсы, премельтон, удлинение молекул, денатурация, ДНК, РНК

Финансирование: Работа выполнена при поддержке гранта Российского научного фонда № 23-12-20014; Государственного задания Российской Федерации № ФСРУ-2021-0008.

Ссылка при цитировании: Харламова А.А. Математическое моделирование взаимодействия ультракоротких лазерных импульсов с участками премельтонов в ДНК // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 333–337. DOI: https://doi.org/10.18721/JPM.163.258

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Of great interest are the various states of DNA. The presence of elongations in the DNA structure affects the stacking interaction in the molecule, the probability of bubble birth, the rate and time of its denaturation. Elongations were first described in 1983 [1] as a discontinuity of the stacking interaction. At the same time, the H-bonds remain intact, which complicates the theoretical and experimental modeling of an object of such a conformation. There are some calculated data linking elongations with the peculiarities of the dynamics of DNA opening. Also, the presence of elongations is indirectly confirmed by the inability to exchange H with solution molecules, but at the same time by the presence of a high activation barrier [2].

The statistics of experimental data describing such states are small. A different approach is required in modeling and studying molecules with a violation of the stacking interaction. DNA elongation is the trigger for its transition to an open state. This structure of the molecule has a great influence on a number of biochemical processes, including the transfer of the electric charge of DNA. Elongated areas may be sensitive to temperature, pH, ionic strength and other thermo-dynamic factors. Some studies indicate the importance of DNA elongation in the recognition of the DNA polymerase promoter [3, 4, 5].

To determine the spatial structure of a molecule with elongations, a dye is intercalated into the molecule, which stands in the place of elongation Fig. 1, b [3, 4]. They also use the method of X-ray diffraction analysis Fig. 1, a. Both methods do not accurately determine the location of the presence of elongation. The intercalation graph is blurry and approximately indicates the presence of elongation. The X-ray diffraction analysis image also does not display the elongation structure because it does not have the physical ability to work at the level of one or two nitrogenous bases of the molecule.

Today, scientists have turned to the use of ultrashort laser pulses instead of X-rays, as a tool capable of seeing the structure of a molecule at the atomic level. In this paper, we mathematically simulate the process of interaction of an ultrashort pulse with a DNA molecule having elongation in the structure and show the sensitivity of such a method to similar DNA configurations.



Fig. 1. Result of X-ray structural analysis of a DNA molecule whose structure contains elongations between nitrogenous bases: X-ray structural analysis of the molecule (*a*); result of analysis of the molecule by staining (*b*)

© Харламова А.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Materials and Methods

The article proposes to consider the DNA molecule as a polyatomic system on which an ultrashort laser pulse falls. The modeling of the scattering spectrum is based on the Dirac-Hartree-Fock-Slater model [6,7].

Consider a molecule with a complex polyatomic structure [8]. An ultrashort laser pulse falls on this molecule in the direction of \mathbf{n}_0 . We assume that the duration of such a pulse τ is many times less than the characteristic atomic time τ_a . It is well known that this condition applies in the approximation of a sudden disturbance. In the approximation of a sudden perturbation of the system's own Hamiltonian, it can be neglected, since the electron in the atom does not have time to evolve under the action of the ultrashort laser pulse field. Next, we will use the electromagnetic field strength USP in a general way, $\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 h(t - \mathbf{n}_0 \mathbf{r}/c)$, that is, we will consider it spatially inhomogeneous, where \mathbf{E}_0 is the field amplitude, $h(t - \mathbf{n}_0 \mathbf{r}/c)$ is an arbitrary function defining the USP form, *c* is the speed of light. In the case of such pulses, in particular [9], when solving the Dirac equation, the electron wave function in the USC field with the intensity was found $\mathbf{E}(\mathbf{r},t)$.

$$\Psi(t) = \varphi_0(\{\mathbf{r}_a\}) e^{-\sum_{a} i \int_{-\infty}^{\infty} \mathbf{E}(\mathbf{r}_a, t') \mathbf{r}_a dt'},$$
(1)

where \sum is the summation over all electrons in complex polyatomic structures, $\varphi_0({\mathbf{r}_a})$ is the initial wave function of all electrons in such a system.

To calculate the main scattering characteristics, we will use the quantum theory of USP scattering, in which there are no restrictions on the number of atoms in the system [10]. In this theory, general expressions for calculations of the main scattering characteristics are obtained. As a result, using equation ((1) and theory in [10], we obtain an expression for calculating the scattering energy ε per unit solid angle Ω_k ($\mathbf{k} = (\omega/c)\mathbf{n}$, where \mathbf{n} is the direction of the scattered pulse) in a single frequency interval ω (next – spectrum)

$$\frac{d^{2}\varepsilon}{d\Omega_{k}d\omega} = \frac{\left[\mathbf{E}_{0}\mathbf{n}\right]^{2}}{\left(2\pi\right)^{2}} \frac{\left|\tilde{h}(\omega)\right|^{2}}{c^{3}} \left\langle \varphi_{0} \left| \sum_{a,a'} e^{-i\mathbf{p}(\mathbf{r}_{a}-\mathbf{r}_{a'})} \right| \varphi_{0} \right\rangle, \tag{2}$$

where $\tilde{h}(\omega) = \int_{-\infty}^{+\infty} h(\eta) e^{i\omega\eta} d\eta$ and $\mathbf{p} = (\omega/c)(\mathbf{n} - \mathbf{n}_0)\mathbf{n}$ has the value of the recoil pulse when the

USP is scattered on the bound electron. Next, we use the well-known model of independent atoms, see, for example [11]. In this case, the problem can be solved by switching to the electron density of individual isolated atoms that make up a complex polyatomic structure. Dividing equation ((2) into two, where the first term corresponds to the summation a = a', and the second term $a \neq a'$, we obtain

$$\frac{d^{2}\varepsilon}{d\Omega_{\mathbf{k}}d\omega} = \frac{\left[\mathbf{E}_{0}\mathbf{n}\right]^{2}}{\left(2\pi\right)^{2}} \frac{\left|\tilde{h}(\omega)\right|^{2}}{c^{3}} \left\langle \sum_{i=1}^{s} N_{e,i}N_{A,i}\left(1-\left|F_{i}\right|^{2}\right) + \sum_{i,j=1}^{s} \delta_{i,j}N_{e,i}N_{e,j}F_{i}F_{j}^{*}\right\rangle,\tag{3}$$

where $N_{e^{i}}$ is the number of electrons in the atom of the *i*-variety; $N_{A^{i}}$ is the number of atoms of the *I*-variety; $F_{i} = \frac{1}{N_{e,i}} \int \rho_{e,i}(\mathbf{r}) e^{-i\mathbf{p}\mathbf{r}} d^{3}\mathbf{r} = 1$ is a form factor of the atom of the *i*-variety with an electron density $\rho_{e,i}(\mathbf{r})$. Coefficient $\delta_{i,j} = \sum_{Ai,A^{i}j} e^{-i\mathbf{p}(\mathbf{R}_{Ai}-\mathbf{R}_{Aj})}$ depends only on the coordinates of atoms of the *i*-variety (a) atoms of the *i*-variety (a) atoms of the *i*-variety (b) atoms of the *i*-variety) depends only on the coordinates of atoms of the *i*-variety (b) atoms of the *i*-variety) atoms of the *i*-variety (b) atoms of the *i*-variety) atoms of the *i*-variety (b) atoms of the *i*-variety) atoms of the *i*-variety (b) atoms of the *i*-variety) atoms of the *i*-variety (b) atoms of the *i*-variety) atoms of the *i*-variety (b) atoms of *i*-variety) atoms of *i*-variety (b) atoms of *i*-variety (b) atoms of *i*-variety) atoms of *i*-variety (b) atoms of *i*-variety (b) atoms of *i*-variety) atoms of *i*-variety (b) atoms of *i*-variet

i-variety (with A_i number), the position of which is determined by the radius vector \mathbf{R}_{A_i} . Eq. (3) is analytical, which contributes to a fairly simple calculation of spectra. The calculation of the electron density is difficult here. To find it, we use the method described in [12].

Results and Discussion

As an object of research, we take a small fragment of DNA with the bases cytosine, cytosine, guanine, cytosine between which there was an elongation (Fig. 2,b).



Fig. 2. Perfect DNA fragment (a) DNA fragment with elongation or 'premelton' (b)

We compare it with the same DNA fragment, but of an ideal shape, without elongation (Fig. 2,a).

As a result of mathematical modeling of the interaction of USP with elongated DNA, a radiation spectrum was obtained, which we can compare with the spectrum of interaction from ideal DNA in Fig. 2 where θ the angle between the spiral axis and the scattering direction **n**, φ is the angle between the *x*-axis and the projection **n** on a plane perpendicular to the axis of the spiral.

Conclusion

As can be seen from the obtained contour graph, a change in the distance between the nitrogenous bases leads to a change in the scattering angle, which is reflected in the form of elongated spots. This suggests that the resulting theory is able to respond to changes in the spatial position of atoms in the object of study.

Acknowledgments

The author expresses gratitude to her supervisor Makarov Dmitry Nikolaevich for significant comments and important advice during the research and the design of this work.

REFERENCES

1. Shigaev A.S., Ponomarev O.A., Lakhno V.D., Theoretical and experimental studies of open states of DNA, Mathematical Biology and Bioinformatics: Physics and Mathematics. 8 (2) (2013) 553–664.

2. Suryanarayana C., Norton M., X-Ray Diffraction: Springer Science & Business Media (2013).

Sobell H., Stereochemistry of Actinomycin-DNA Binding: Nature New Biology. 231(24) (1971).
 Sobell H., How Actinomycin Binds to DNA: Scientific American. 231(2) (1974) 82–91.

5. Sobell H., Organization of DNA in chromatin: Proc. Natl. Acad. Sci. 73(2) (1974) 32–91.

6. Makarov D.N., Kharlamova A.A., Scattering of X-ray Ultrashort Pulses by Complex Polyatomic

Structures: J. Mol. Sci 23 (1) (2022) 163.

7. Makarov D.N., Kharlamova A. A., Peculiarities of Scattering of Ultrashort Laser Pulses on DNA and RNA Trinucleotides: J. Mol. Sci 23(23), (2022) 15417.

8. Makarov D.N., Makarova K.A., Kharlamova A.A., Specificity of scattering of ultrashort laser pulses by molecules with polyatomic structure: Scientific Reports, 12(1), (2022) 4976.

9. Makarov D.N., Eseev M.K., Makarova K.A., Analytical wave function of an atomic electron under the action of a powerful ultrashort electromagnetic field pulse: Opt. Lett. 44(12), (2019) 3042–3045.

10. Makarov D.N., Quantum theory of scattering of ultrashort electromagnetic field pulses by polyatomic structures. Opt. Express 27(22), (2019) 31989–32008.

11. Eseev M.K., Goshev A.A., Makarova K.A., Makarov D.N., X-ray diffraction analysis of matter taking into account the second harmonic in the scattering of powerful ultrashort pulses of an electromagnetic field: Sci. Rep. 11, (2021) 3571.

12. Kharlamova A.A., Makarov D.N., Peculiarity of electron density calculation during interaction of ultrashort laser pulse with nitrogenous base of DNA molecule adenine: St. Petersburg Polytechnic University Journal: Physics and Mathematics, 15 (3.2), (2022).

THE AUTHOR

KHARLAMOVA Anastasya A. kharlamova.anastasya2015@yandex.ru ORCID: 0000-0002-8192-615X

Received 09.07.2023. Approved after reviewing 07.08.2023. Accepted 26.09.2023.

Conference materials UDC 004.852 DOI: https://doi.org/10.18721/JPM.163.259

Development of an algorithm for predicting the strength of laser reconstruction of biological tissue

D.I. Ryabkin^{1,2}, V.V. Suchkova^{1,2}, A.Yu. Gerasimenko^{1,2}

¹I.M. Sechenov First Moscow State Medical University, Moscow, Russia;

² National Research University of Electronic Technology MIET, Zelenograd, Moscow, Russia

□ ryabkin@bms.zone

Abstract. Laser reconstruction of biological tissue is a fast and minimally invasive method of wound closure without the risk of stenosis, foreign body reaction or inflammation. However, the strength of the welds is inferior to the traditional suture method in the first few days after surgery. This limitation can be overcome by optimizing the laser beam and solder component composition using machine learning methods. The aim of the study was to develop and experimentally verify an algorithm for predicting the strength of laser reconstruction of biological tissues. The best prediction models were based on an extreme gradient boosting algorithm and random forest. To train the algorithms, a dataset consisting of experiments described in published research papers was used. The dataset contains a total of 394 samples and 39 features on which training was performed. The effectiveness of the model was tested experimentally in two stages. Bovine ex vivo vascular repair was the first step. The second stage was in vivo testing of the algorithm on laboratory animals. The average percentage error of the strength prediction was 19%. This error is due to the large scatter in the strength values obtained experimentally. The strength obtained is sufficient to analyses the laser radiation characteristics and the component composition of the solder prior to laser reconstruction.

Keywords: machine learning, laser soldering, tissue reconstruction

Funding: The study was supported by the Russian Science Foundation grant 22-75-00089, https://rscf.ru/project/22-75-00089/.

Citation: Ryabkin D.I., Suchkova V.V., Gerasimenko A.Yu., Development of an algorithm for predicting the strength of laser reconstruction of biological tissue, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 338–343. DOI: https://doi.org/10.18721/JPM.163.259

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 004.852 DOI: https://doi.org/10.18721/JPM.163.259

Разработка алгоритма прогнозирования прочности лазерного восстановления биологических тканей

Д.И. Рябкин^{1,2}, В.В. Сучкова^{1,2}, А.Ю. Герасименко^{1,2}

¹ Первый Московский государственный медицинский университет имени И.М. Сеченова, Москва, Россия

² Национальный исследовательский университет «Московский институт электронной техники», Зеленоград, Москва, Россия

[™] molodykh1999@gmail.com

Аннотация. Цель исследования заключалась в разработке и экспериментальной проверке алгоритма прогнозирования прочности лазерного восстановления биологических тканей. Лучшие модели прогнозирования были основаны на алгоритме

© Ryabkin D.I., Suchkova V.V., Gerasimenko A.Yu., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

экстремального градиентного бустинга и случайном лесе. Для обучения алгоритмов использовался набор данных, состоящий из экспериментальных данных, описанных в опубликованных научных работах по лазерному восстановлению биологических тканей. Средняя процентная ошибка прогноза прочности составила %19. Эта ошибка обусловлена большим разбросом значений прочности, полученных экспериментально. Достигнутая точность значений прочности является достаточной для анализа характеристик лазерного излучения и компонентного состава припоя до операции по лазерному восстановлению биотканей.

Ключевые слова: машинное обучение, лазерная пайка, реконструкция тканей

Финансирование: Работа выполнена в рамках гранта Российского научного фонда № 00089-75-22, https://rscf.ru/project/00089-75-22/.

Ссылка при цитировании: Рябкин Д.И., Сучкова В.В., Герасименко А.Ю. Разработка алгоритма прогнозирования прочности лазерного восстановления биологических тканей // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 338–343. DOI: https://doi.org/10.18721/JPM.163.259

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Laser reconstruction of biological tissues, is a seamless method of wound closure that uses the application of an absorbent bioorganic solder to tissue and the subsequent absorption of laser radiation by the tissue and produces a thermal effect by interaction to achieve the goal of tissue fusion [1-3]. However, despite the speed and painlessness of the procedure, laser reconstruction has not become widespread clinically. As the structure of biological tissue is complex, its thermal and optical characteristics are different, and different laser radiation parameters and solder component compositions will cause different thermal effects, which may result in insufficient tensile strength, especially in the first days after surgery [2].

At the moment, the selection of laser reconstruction parameters is realized by performing numerous tests on laboratory animals, which is a low-efficient and resource-intensive strategy [4, 5]. This paper investigated the possibility of predicting the results of laser reconstruction of biological tissues using machine learning methods.

Machine learning is one of the most important and effective tools for analyzing complex medical data. Machine learning techniques have been shown to be effective in predicting the progression of diseases such as dementia [6], lung cancer, liver disease, etc. [7,8].

The use of machine learning methods for predicting laser reconstruction results will accelerate and automate the process of selecting laser irradiation characteristics and solder component compositions. In this paper, machine learning regression models have been trained, optimized and experimentally tested.

Materials and Methods

The prediction algorithm for all regression models is based on learning from the data set. The accuracy of the prediction depends on the correctness, completeness and homogeneity of the input data. A data set of 400 unique objects based on 45 published scientific sources was generated to train an algorithm for predicting the strength of laser repair of biological tissues. The dataset was generated using the python programming language. Using a library for processing and analysis of structured data pandas. All categorical were converted linear using the one hot encoding method. In one hot coding, each categorical feature value is represented as a separate binary feature column. In this case, the categorical value corresponding to the object received a value of 1, all others 0 [9]. Thus, after conversion, the dataset has 54 features on which the prediction was based. The data provided information on laser restoration of biological tissues including tissue type and type of operation, laser irradiation parameters, component composition of laser solders, and methodology for measuring the strength of welds. The target variable in the data set was the tensile strength of the laser welds expressed in kPa. The minimum strength value in the data set

© Рябкин Д.И., Сучкова В.В., Герасименко А.Ю., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

is 2.07 kPa. The maximum strength in the data set is 6000 kPa. The average strength value in the data set is 657 kPa. This scatter of values indicates a heterogeneity in the data. To minimize the role of outliers in prediction, values between the 5th and 95th percentile of the data distribution were used to train the models.

Two strategies were used to fill in the missing values in the data set: filling in the mean value for a feature and filling in the median value for a feature [10]. Normalization (1) and standardization (2) functions were used to bring the values into the same range [11]. For each machine learning regression model, the most efficient combination of data processing was selected.

The normalization of the data is presented in Equation 1:

$$\overline{x} = \frac{x - x_{\min}}{x_{\max} - x_{\min}},\tag{1}$$

where x is the initial value of the feature, x_{min} is the minimum value of the feature, x_{max} is the maximum value of the feature, \bar{x} is the value of the feature after normalization.

The standardization of the data is presented in Eq. 2:

$$\overline{x} = \frac{x - x_{mean}}{\sigma},\tag{2}$$

where x_{mean} is the arithmetic average value of the feature, σ is the standard deviation of the feature values.

Seven different models were trained to predict the strength of laser reconstruction of biological tissues: linear regression, k-nearest neighbors, decision tree, random forest, gradient boosting, and variations of gradient boosting (XGBoost, LightGBM). All models based on the sklearn library of the python programming language. A preprocessing strategy was chosen for each model.

The coefficient of determination and the mean absolute percentage error were used to assess performance. The mean absolute percentage error (MAPE) has a dimensionless value and allows the relative error of the prediction to be determined:

$$MAPE = \frac{100\%}{N} \sum_{i=1}^{N} \frac{|y_{i(pred)} - y_i|}{y_i},$$
(3)

where $y_{i(pred)}$ is the predicted strength value, y_i is the actual strength value, N is the number of data objects.

The coefficient of determination (R^2) is defined as the ratio of the variance of the target variable explained by the predictive model with a given set of inputs:

$$R^{2} = 1 - \frac{\frac{1}{N} \sum_{i=1}^{N} (y_{i} - y_{i(pred)})^{2}}{\frac{1}{N} \sum_{i=1}^{N} (y_{i} - y_{mean})^{2}},$$
(4)

where y_{mean} is the average strength value. A 5-block cross-validation was used to assess the stability of the performance. The 5-block cross-validation was also used to determine the best combination of preprocessing data. The models that performed the best were also optimized manually by parameter enumeration, using grid-based parameter search, and random search. The training hyper-parameters chosen were: tree depth, the maximum number of features that the model is allowed to sample at each partitioning, the number of decision trees.

To experimentally validate the strength algorithm, a series of *ex vivo* and *in vivo* experiments were conducted on laser reconstruction of biological tissues (skin) using the most commonly used bioorganic solders and a laser complex with the ability to maintain a set temperature in the weld formation zone.

The laser system for biological tissue reconstruction consists of an optical module, a temperature module, and a surgical pencil-tip. To recover the integrity of biological tissues, a diode laser generating continuous infrared radiation with a wavelength of $\lambda = 810 \pm 3$ nm was used.

In order to experimentally test the algorithm for predicting the strength of laser solder, a bioorganic solder consisting of bovine serum albumin (BSA), green indocyanine (ICG) and water was fabricated. The solder was an aqueous solution of 25 wt% BSA and 0.1 wt% ICG.

Ex vivo experiments were performed using bovine aortic tissue and pig skin. 50 μ l of solder was applied to the area of the joint. The laser irradiation was performed using the spot method. Each spot was irradiated for 1 minute. A total of approximately 5 dots were placed per weld. Maximum temperature in the laser exposure area was T = 55 °C. The laser power was varied from 1.1 to 2.5 W. The diameter of the laser spot was 2 mm.

Chinchilla rabbits were used for the *in vivo* experiment. The skin was dissected with a surgical scalpel, forming a 1 cm linear incision. The reconstructed area was irradiated with laser at 42 °C for 1 minute. Tensile strength was recorded on days 1, 3, 7 and 10 postoperatively.

Results and Discussion

Fig. 1,*a* and 1,*b* shows the cross-validation results of all trained models. Cross-validation results revealed that the worst model for predicting laser reconstruction results is linear regression (average values: MAPE = 75%, $R^2 = 0.7$) this is due to non-linear relationships between laser reconstruction features and strength, as well as non-uniformity of feature distribution. Models based on ensembles of decision trees showed the best results. These models were also optimized manually by parameter oversampling, grid search, and random search for the best result (Fig. 1,*c*). The highest accuracy in strength prediction is achieved by the extreme gradient boosting model XGBoost, optimized using random search with ridge regularization of the decision trees.

A preprocessing strategy was chosen for each model. The best preprocessing strategy in all cases was to fill in the missing values with the median value for the relevant feature and then standardize all values (Table 1).



Fig. 1. Results of training and cross-validation of weld strength prediction models after laser reconstruction: MAPE of all models (*a*), determination coefficient of all models (*b*), comparison of MAPE tree-based models after optimization (*c*)

Table 1

Bringing values	Filling in the skip patterns	
into the same range	Average value	Median
MinMaxScaler	$R^2 = 0.80 \pm 0.12$	$R^2 = 0.92 \pm 0.13$
StandardScaler	$R^2 = 0.90 \pm 0.12$	$R^2 = 0.93 \pm 0.14$

Choosing the best data preprocessing strategy

Based on the results of training and cross-validation on the dataset, an extreme gradient boost based XGBoost model was selected for experimental validation of the predictive strength of laser reconstruction of biotissues. For this purpose, laser repair of bovine and porcine skin vessels was performed. A total of 80 specimens were used, which were divided into 4 groups and reconstructed with different types of solder (Fig. 2). The mean value of the coefficient of determination was 0.82, indicating the high accuracy of the predictive model.

After ex vivo validation, an in vivo study of laser tissue repair in rabbits was conducted jointly. The rabbits were divided into 2 groups. The groups differed in the presence or absence of ICG in the component composition of the solders. A comparison of actual strength and predicted strength is shown in Fig. 3. A coefficient of determination of 0.84 and an average absolute percentage error of 19% were obtained.

The error is caused by the large dispersion of strength values obtained experimentally. The achieved strength is sufficient for analyzing the laser radiation characteristics and the component composition of the solder prior to the laser reduction procedure.



Fig. 2. *Ex vivo* validation of the prediction algorithm: laser vascular reconstruction (*a*), laser skin reconstruction (*b*)



Fig. 3. In vivo validation of the prediction algorithm: solder based on BSA 25 wt.% (a), solder based on BSA 25 wt% and ICG 0.1 wt% (b)

Conclusion

Laser reconstruction of biological tissues is a promising minimally invasive technique, however, in order to achieve maximum recovery strength, each operation requires individual selection of laser irradiation characteristics and solder component compositions. The results of the research confirm the possibility of using trained machine learning models to predict the results of laser reconstruction of biological tissues. The use of predictive models will significantly increase the efficiency of the process of selecting optimal parameters for laser tissue reconstruction, reducing the time and cost of the experimental study.

REFERENCES

1. Li C., Wang K., Huang J., Effect of scanning modes on the tensile strength and stability in laser skin welding in vitro, Optik. 179 (2019) 408–412.

2. Gomes D.F., Galvana I, Ramos Loja M.A., Overview on the Evolution of Laser Welding of Vascular and Nervous Tissues, Applied sciences. 9 (2019) 9102157.

3. Li C., Wang K., Effect of welding temperature and protein denaturation on strength of laser biological tissues welding, Optics and Laser Technology. 138 (2021) 106862.

4. Fekrazad R., Mortezai O., Pedram M., Kalhori K.A., Joharchi K., Mansoori K., Mashhadiabbas F., Transected sciatic nerve repair by diode laser protein soldering, Journal of Photochemistry and Photobiology B: Biology. 173 (2017) 441–447.

5. Schiavon M., Experimental evaluation of a new system for laser tissue welding applied on damaged lungs, Interactive cardiovascular and thoracic surgery. 16 (5) (2017) 441–447.

6. Kumar S., Oh I., Schindler S., Lai A. M., Payne P.R., Gupta A. Machine learning for modeling the progression of Alzheimer disease dementia using clinical data: a systematic literature review, Journal of the American Medical Informatics Association: JAMIA open. 4 (3) (2021) 00ab052.

7. Le T.L., Fuzzy C-means clustering interval type-2 cerebellar model articulation neural network for medical data classification, IEEE Access. 7 (2019) 20967–20973.

8. Garg A., Mago V., Role of machine learning in medical research: A survey, Computer science review. 40 (2021) 100370.

9. Potdar K., Pardawala T.S., Pai C.D., A comparative study of categorical variable encoding techniques for neural network classifiers, International journal of computer applications. 175 (4) (2017) 7–9.

10. Wang S., Celebi M.E., Zhang Y.D., Yu X., Lu S., Yao X., Advances in data preprocessing for biomedical data fusion: An overview of the methods, challenges, and prospects, Information Fusion. 76 (2021) 376–421.

11. Ali P. J. M., Faraj R. H., Koya E., Ali P. J. M., Faraj R. H., Data normalization and standardization: a technical report, Machine Learning: Science and Technology. 1 (1) (2014) 1–6.

THE AUTHORS

RYABKIN Dmitry I. ryabkin@bms.zone ORCID: 0000-0002-1327-5690 GERASIMENKO Alexander Yu. gerasimenko@bms.zone ORCID: 0000-0001-6514-2411

SUCHKOVA Victoria V. molodykh1999@gmail.com ORCID: 0000-0002-3207-7622

Received 10.07.2023. Approved after reviewing 27.07.2023. Accepted 01.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 004.94 DOI: https://doi.org/10.18721/JPM.163.260

Modelling of laser welding of biological tissues using focused radiation

D.I. Ryabkin^{1,2}, V.V. Suchkova^{1,2}, A.Yu. Gerasimenko^{1,2}

¹ I.M. Sechenov First Moscow State Medical University, Moscow, Russia;

² National Research University of Electronic Technology MIET, Zelenograd, Moscow, Russia

□ ryabkin@bms.zone

Abstract. Laser welding is an alternative technology for biological tissue reconstruction. The laser weld is small, liquid-tight and does not cause mechanical stress. However, thermal necrosis of the joined living tissue occurs during suture formation, and the depth of suture formation may be much less than required. This paper proposes the use of laser radiation with dynamically varying focusing parameters to reduce the area of thermal necrosis of the attached living biological tissue and increase the depth of suture formation. The influence of laser focusing parameters was evaluated by simulation. Absorption by biological tissue and braze was calculated according to the Beer-Lambert law. The degree of protein conversion in biological tissue and solder was determined using chemical kinetic methods and the Arrhenius equation. Heat transfer was calculated using the thermal conductivity equation.

Keywords: mathematical modeling, laser soldering, tissue reconstruction

Funding: The study was supported by the Russian Science Foundation grant 22-75-00089, https://rscf.ru/project/22-75-00089/.

Citation: Ryabkin D.I., Suchkova V.V., Gerasimenko A.Yu., Modelling of laser welding of biological tissues using focused radiation, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 344–348. DOI: https://doi.org/10.18721/JPM.163.260

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 004.94 DOI: https://doi.org/10.18721/JPM.163.260

Моделирование лазерной сварки биологических тканей с использованием сфокусированного излучения

Д.И. Рябкин^{1,2}, В.В. Сучкова^{1,2}, А.Ю. Герасименко^{1,2}

¹ Первый Московский государственный медицинский университет имени И.М. Сеченова, Москва, Россия;

² Национальный исследовательский университет «Московский институт электронной техники», Зеленоград, Москва, Россия

^{III} ryabkin@bms.zone

Аннотация. Лазерное сваривание — это альтернативная технология реконструкции биологических тканей. Лазерный шов имеет небольшие размеры, герметичен и не вызывает механического напряжения. Однако, во время формирования шва происходит термический некроз соединяемы живых тканей, а глубина формирования шва может быть гораздо меньше, чем требуется. В данной работе предлагается использовать лазерное излучение с динамически изменяемыми параметрами фокусировки для уменьшения площади термического некроза присоединенной живой биологической ткани и увеличения глубины формирования шва. Влияние параметров фокусировки лазерного излучения оценивалось путем моделирования. Поглощение биологической тканью и пайкой

© Ryabkin D.I., Suchkova V.V., Gerasimenko A.Yu., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

рассчитывалось по закону Бера-Ламберта. Степень превращения белка в биологической ткани и припое определялась с помощью химико-кинетических методов и уравнения Аррениуса. Теплопередача рассчитывалась с помощью уравнения теплопроводности.

Ключевые слова: математическое, моделирование, лазерное сваривание, реконструкция тканей

Финансирование: Работа выполнена в рамках гранта Российского научного фонда № 00089-75-22, https://rscf.ru/project/00089-75-22/.

Ссылка при цитировании: Рябкин Д.И., Сучкова В.В., Герасименко А.Ю. Моделирование лазерной сварки биологических тканей с использованием сфокусированного излучения // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 344–348. DOI: https://doi.org/10.18721/JPM.163.260

Статья открытого доступа, распространяемая по лицензии СС ВУ-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Laser welding provides an alternative method of joining biological tissues. Laser welding provides advantages over traditional joining techniques by creating small sutures that are impermeable to fluids and cause no mechanical stress.

Laser suture formation involves heating the joining area and adjacent tissues. The heat generated results in thermal necrosis of the fused living tissue. This study aims to minimize the area of thermal necrosis of biological tissues during welding by modelling and optimizing the process.

Materials and Methods

The absorbed energy of the laser radiation was determined according to the Beer–Lambert law [1]:

$$I = I_0 e^{-\int_0^L \mu(\vec{r}) dl},$$
 (1)

where I is the intensity of laser radiation after the beam passes through a layer with a thickness L, I_0 is the power of the incident laser radiation, $\mu(r)$ is the absorption coefficient.

The degree of suture formation and thermal necrosis of the living tissue was determined by the conversion α at time *t* [2]:

$$\alpha(\tau) = \frac{C_{\tau}}{C_0},\tag{2}$$

where C_{τ} is the concentration of denatured protein at time *t*, C_0 is the initial concentration of native protein. The degree of weld formation and thermal necrosis was taken into account $\alpha = 0.63$.

The conversion was calculated according to the Arrhenius equation:

$$\alpha(\tau) = 1 - e^{-\int_{0}^{\tau} A e^{-\frac{E_{a}}{RT(t)}dt}},$$
(3)

where A is the dimensionless pre-exponential factor of the Arrhenius equation E_a is the activation energy, R is the universal gas constant, T is the temperature, and t is the time [3–5].

Heat transfer has been calculated using the heat transfer equation:

$$\frac{\partial T(r,t)}{\partial t} - \nabla(\vec{a(r,t)}) \nabla T(\vec{r},t)) = f(\vec{r},t), \tag{4}$$

where T is the temperature, a is the thermal diffusivity, f is the function of heat sources, t is the time.

©Рябкин Д.И., Сучкова В.В., Герасименко А.Ю., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Results and Discussion

A simulation of the effects of laser radiation on the skin was performed. An area of $1 \cdot 1 \cdot 1$ mm was simulated. Diameter of laser radiation beam area in the area of contact with tissue was $d_{laser_{beam}} = 1 \text{ mm}$. Spatial discretization of the simulation area was $d = 2 \cdot 10^{-5} \text{ m}$.

Laser weld formation occurs as a consequence of thermal denaturation of proteins. Bovine serum albumin was used as a protein in this work. Thermal denaturation is initiated by heating the proteins in the laser solder. The denaturation rate is defined as the derivative of the concentration of the denatured albumin by time. An acceptable albumin denaturation rate is achieved at temperatures above 55 °C. At lower temperatures, the rate will be so low that it will take more than 1 minute to form a 1 mm long suture. Such a long formation time is not acceptable for surgical applications.

When irradiating biological tissue and laser braze, the laser intensity decreases according to the Beer-Lambert law. This leads to uneven heating of the solder. In this case, overheating will occur in the upper layers, while in the deeper layers the solder temperature will not be sufficient to form a suture. The solution to this problem can be the use of focused laser radiation. A simulation of the heating process of solder and biological tissue using focused laser irradiation was carried out (Fig. 1).



Fig. 1. Dependence of solder temperature along the optical axis of laser radiation at focal lengths of 0.2, 0.4 mm (a) and 0.1, 0.3, 0.5 mm (b)

The curves in Fig. 1 clearly show the general nature of the temperature distribution, which is inversely proportional to the exponent. However, local maxima corresponding to the depth of focus of the laser radiation can be distinguished. The presence of local maxima indicates the possibility of heating the solder deeper than the surface layers. In this simulation, the heating temperature of the solder in the focal area was not significantly higher than in the case of heating with collimated radiation. However, this limitation can be overcome by using laser radiation with a large cross-sectional radius in the area of contact with the surface of the biological tissue.

Fig. 2 shows temperature distributions in the biological tissue and suture when exposed to laser radiation with a focusing depth from 0.2 to 0.8 mm.

Fig. 2 clearly shows that the main heating takes place in the upper layers of the solder. In the deeper layers the heating temperature decreases. However, there is an increase in temperature in the focal zone. It can be seen that the area of biological tissue exposed to the laser radiation is not significantly heated. The increase in temperature of the biological tissue is mainly due to heat exchange with the hotter solder. The area of contact between the biological tissue and the solder is the riskiest in terms of thermal necrosis formation. Biological tissue necrosis occurs at a lower temperature than laser weld necrosis. This is an additional negative factor that increases the risk of significant thermal necrosis formation. The use of focused laser radiation can partially neutralize this effect. In this case, the heating is localized rather than along the entire length of the weld.

Fig. 2 shows that the solder areas around the perimeter of the weld are heated more than the solder areas inside the weld. The energy is delivered to the braze by photons passing through the biological tissue at an angle to the surface of the braze. In this way, the outer walls of the future weld and the top of the braze exposed to direct irradiation are formed first. Then, as the inner parts of the braze are heated by heat exchange, the inner part of the braze is formed. The rate of weld formation is therefore inversely proportional to the width of the weld.



Fig. 2. Temperature distribution in biological tissue and solder in the area exposed to laser radiation with depth of focus 0.2 (*a*), 0.4 (*b*), 0.6 (*c*), 0.8 mm (*d*)

The overheating of the weld in the area of direct radiation exposure and the formation of a zone of thermal necrosis of the biological tissue can be reduced by cutting off the part of the laser radiation that falls on the weld and does not pass through the biological tissue.

Reducing overheating of the suture in the area of direct exposure to radiation and the formation of a zone of thermal necrosis of biological tissue is possible by cutting off the part of the laser radiation that falls on the solder, not passing through the biological tissue.

Conclusion

Studies have shown that the use of focused laser radiation allows more energy to be delivered deep into biological tissue. In the future, it will be possible to use laser radiation with a variable focal length. With this approach, the suture is formed only in the area where the laser radiation is focused. Increasing the diameter of the laser beam reduces the intensity of the irradiation.

REFERENCES

1. Ryabkin D., Meglinsk I., Gerasimenko A., Amendments of weld formation in human skin laser soldering, Journal of Biophotonicsthis, Article in press (2023).

2. **Pearce J.A.**, Comparative analysis of mathematical models of cell death and thermal damage processes, International Journal of Hyperthermia. 29(4) (2013) 262–280.

3. Kampmeier J., Radt B., Birngruber R., Thermal and biomechanical parameters of porcine cornea, Cornea. 19(3) (2000) 355–363.

4. Rossi F., Pini R., Menabuoni L., Experimental and model analysis on the temperature dynamics during diode laser welding of the cornea, Journal of Biomedical Optics. 12(1) (2007) 14031.

5. Gosalia K., Weiland J., Humayun M., Thermal elevation in the human eye and head due to the operation of a retinal prosthesis, IEEE Transactions on Biomedical Engineering. 51(8) (2004) 1469–1477.

THE AUTHORS

RYABKIN DMITRY I. ryabkin@bms.zone ORCID: 0000-0002-1327-5690 GERASIMENKO Alexander Yu. gerasimenko@bms.zone ORCID: 0000-0001-6514-2411

SUCHKOVA Victoria V. molodykh1999@gmail.com ORCID: 0000-0002-3207-7622

Received 10.07.2023. Approved after reviewing 27.07.2023. Accepted 01.08.2023.

Conference materials UDC 637.073 DOI: https://doi.org/10.18721/JPM.163.261

Application of optical methods for quality control of dairy products using data mining

M.Yu. Zanevskaya¹^{III}, M.S. Mazing², A.Yu. Zaitceva², V.V. Romanova²

¹St. Petersburg State University of Aerospace Instrumentation, St. Petersburg, Russia;

² Institute for Analytical Instrumentation RAS, St. Petersburg, Russia

^{III} mnevskaya1@gmail.com

Abstract. A method has been developed for express-assessment of the quality of dairy products according to the indicators of optical sensors in the visible and near-IR wavelength range. The use of modern machine learning methods, in particular the principal component method, made it possible to identify groups of samples similar in their properties and determine whether products belong to an industrial or piece manufacturing method. The technique allows you to designate a group of 'references', deviations from it, and is an inexpensive express method for controlling the quality of food products.

Keywords: IR spectroscopy, spectrum analyzer, dairy products

Citation: Zanevskaya M.Yu., Mazing M.S., Zaitceva A.Yu., Romanova V.V., Application of optical methods for quality control of dairy products using data mining, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 349–353. DOI: https://doi.org/10.18721/JPM.163.261

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 637.073 DOI: https://doi.org/10.18721/JPM.163.261

Применение оптических методов для контроля качества молочной продукции с использованием интеллектуального анализа данных

М.Ю. Заневская¹[™], М.С. Мазинг², А.Ю. Зайцева², В.В. Романова²

¹ Санкт-Петербургский государственный университет аэрокосмического приборостроения, Санкт-Петербург, Россия;

² Институт аналитического приборостроения РАН, Санкт-Петербург, Россия

^{III} mnevskaya1@gmail.com

Аннотация. Разработана методика экспресс-оценки качества молочной продукции по показателям оптических датчиков видимого и ближнего ИК диапазона длин волн. Применение современных методов машинного обучения, в частости метода главных компонент, позволило выделить группы схожих по своим свойствам образцов и определить принадлежность продукции к промышленному или штучному методу изготовления. Методика позволяет обозначить группу «эталонов», отклонения от нее и является недорогим и мгновенным методом контроля качества пищевой продукции.

Ключевые слова: ИК-спектроскопия, анализатор спектров, молочная продукция

© Zanevskaya M.Yu., Mazing M.S., Zaitceva A.Yu., Romanova V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Заневская М.Ю., Мазинг М.С., Зайцева А.Ю., Романова В.В. Применение оптических методов для контроля качества молочной продукции с использованием интеллектуального анализа данных // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 3.2 № .16. С. 349–353. DOI: https://doi.org/10.18721/JPM.163.261

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Dairy products are the basis of the food basket of the typical consumer not only in the Russian Federation, but around the world. Modern food production requires accurate and rapid methods of controlling the properties and composition indicators of the products [1]. At present, there is a growing tendency in the world to accurately determine the quality of dairy products, since one of the most common practices is the addition of some substance to increase the volume of raw materials [2]. Due to the intensive development of instrumental analysis methods, including infrared spectroscopy, it is increasingly becoming a question not only of determining the main components, such as lactose, fat, protein, dry matter, but also of simultaneously identifying various adulterants [3, 4]. Due to the large volumes of processed dairy raw materials in production, fast and effective methods of monitoring its composition are required [4, 5]. The following methods are used for qualitative and quantitative evaluation of individual components of the composition: photometric, ultrasonic, conductometric, infrared spectroscopy and others [5]. IR-spectroscopy is widespread due to the fact that for a short period of time allows to register the spectrum of most significant chemical compounds in the composition of the studied sample [6, 7].

Thus, the aim of the work was to create a technique for express quality control of dairy products and detection of adulteration in them on the basis of infrared spectroscopy methods with the possibility of training and recognition of images of the studied raw materials.

Materials and Methods

The study of dairy products samples was carried out using the developed hardware and equipment complex consisting of two modules: an optoelectronic module and a computer-information module. Scheme of work and process of research of dairy products are shown in Fig.1. The opto-electronic module is a modern multichannel analyzer of spectra which has an array of 18 fast photosensitive elements, working at wavelengths from 410 to 940 nm, and 3 sources of radiation. These technical characteristics allow the device to obtain spectral data of a product sample in less than 10 seconds [8]. A 500 mA/h battery is built into the system, allowing 5 hours of operation without recharging. There are operating modes of both pulse illumination of the sample and continuous. The data are transmitted via wireless personal networks to a PC. Computation and information module is represented by a complex of statistical algorithms of multidimensional data processing and analysis with the use of machine learning methods (method of main components). The result of the analysis is the assignment of the sample to one of the established similarity groups. Fig. 1 shows schematic diagram of the hardware-software complex and the process of dairy products research.

Two groups of samples of dairy products were studied. The first group included 10 samples of milk of industrial production, the second group included 8 samples of milk from individual farms. The milk samples were produced and purchased at the same time. The samples were stored under the same conditions. Each of them was poured into a specially made black container. Measurements were taken at room temperature.

Results and Discussion

The experimental data obtained during the study were an array of numerical values of each of the 18 elements of the optoelectronic unit. In order to qualitatively analyze the composition of dairy product samples and determine the presence of impurities and adulterations, the spectra of reflected and backscattered radiation in the visible and near-infrared wavelength range were examined (Fig.2).

© Заневская М.Ю., Мазинг М.С., Зайцева А.Ю., Романова В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



b)



Fig. 1. Schematic diagram of the hardware-software complex (*a*) and the process of dairy products research (*b*)





During the analysis of the experimental data the following trends are traced: the peaks of the radiation intensity of industrial milk samples are noticeable in the visible range of the spectrum, at wavelengths of 460–535 nm. In contrast, the maximum intensities of milk samples from individual farms are located in the near-infrared wavelength range, at wavelengths of 900–940 nm. This indicates different composition of samples, the presence of higher intensity peaks among industrial dairy products may indicate the presence of impurities in the samples. Intelligent multivariate data processing methods were used to examine the structure of the data and to find relationships between samples and variables, in particular, the principal component method (PCA). PCA is a multivariate statistical analysis aimed at reducing the dimensionality of the data set. It allows us to

identify new variables (principal components) that most accurately reflect the correlation between the original variables and explain the largest proportion of variance in the data [9, 10]. The result of the analysis is a graph, which allows you to represent the relationship between the data. In the Cartesian coordinate system, each point is one of the samples. To determine the optimal number of principal components, a scree plot (Kettel's method) was used, according to which it was necessary and sufficient to leave three components [11]. The following trends are traced: the formation of a cluster of points - samples of industrial milk, which indicates their similarity to each other and a large scatter on the graph of points - samples of farm milk (Fig. 3.).



Fig. 3. Result of visualization of multivariate data obtained using optical sensors in the space of the three principal components, where samples marked in blue are dairy products of individual farms; in red - industrial dairy products

The result of intellectual processing of the data obtained with the help of optical sensors were formed groups of product samples. According to the belonging of a particular sample to one of the groups, it is possible to judge about the difference in the composition of the samples, adulteration and the possible presence of impurities. It has been established that the composition and quality of dairy product samples can be assessed using optical spectroscopy methods with subsequent intelligent mathematical processing of the data obtained (including the use of methods of multivariate statistical analysis of data).

Conclusion

Thus, the results obtained testify to the effectiveness of the developed technique based on the optical device - multi-channel spectra analyzer. The presented technique can be used as one of the highly effective methods of controlling the composition and quality of dairy products, which has such advantages as availability for wide application, sufficiently high expressiveness and efficiency, low requirements for the qualification of the operator, etc.

Acknowledgments

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (project 075-15-2021-1057).

REFERENCES

1. Gastélum-Barrios A., et al., Optical methods based on ultraviolet, visible, and nearinfrared spectra to estimate fat and protein in raw milk: A review, Sensors. 20 (12) (2020) 3356.

2. Taterka H., Zamora A., Castillo M., Developing an optical backscatter method for determining casein micelle particle size in heated milk. Food Research International. (161) (2022) 111745.

3. Rojas Lypez M., Analysis of milk adultered with whey powder and liquid by infrared infrared spectroscopy. (2012).

4. Lypez H., Oropeza I., Betancourt C., Determination of calcium, magnesium and potassium concentration in liquid milk of three commercial brands using the atomic spectroscopy technique. Research Journal. (2017).

5. Calderyn de la Barca A.M., et al., Evaluation of human milk consumption by dilution with deuterium and detection by infrared spectroscopy //Perinatol. reprod. hum. (1998).

6. Holroyd S.E., The use of near infrared spectroscopy on milk and milk products. Journal of Near Infrared Spectroscopy. (2013).

7. Pu Y., et al., Recent advances in portable and handheld NIR spectrometers and applications in milk, cheese and dairy powders. Foods. 10 (10) 2021 2377.

8. Zaitceva A.Y., Sensor Intelligent Systems for Monitoring the Oxygen Status of Human Tissues Under Functional Loads //Journal of Pharmaceutical Negative Results. 13 (1) (2022) 6–13.

9. **Pearson K.,** LIII. On lines and planes of closest fit to systems of points in space. The London, Edinburgh, and Dublin philosophical magazine and journal of science. 2 (11) (1901) 559–572.

10. Hasan B.M.S., Abdulazeez A.M., A review of principal component analysis algorithm for dimensionality reduction. Journal of Soft Computing and Data Mining. 2 (1) (2021) 20–30.

11. Del Giudice M., The Square-Root Scree Plot: A Simple Improvement to a Classic Display. (2022).

THE AUTHORS

ZANEVSKAYA Maria Yu. mnevskaya1@gmail.com ZAITCEVA Anna Yu. anna@da-24.ru ORCID: 0000-0003-0334-2770

MAZING Mariia S. mazmari@mail.ru ROMANOVA Veronika V.

venjo@mail.ru ORCID: 0009-0001-6587-787X

Received 24.07.2023. Approved after reviewing 16.08.2023. Accepted 17.08.2023.

Conference materials UDC 615.45 DOI: https://doi.org/10.18721/JPM.163.262

In vivo visualization of albumin nanoparticles loaded with cyanine dyes

M.E. Stepanov¹⊠, P.A. Demina^{1,2,3}, R.A. Akasov^{1,2,3}, G. Babayeva⁴, T.V. Egorova¹, A.N. Generalova^{1,2,3}, A. Parodi⁵, E. V. Khaydukov^{1,2,3}

¹ Moscow State Pedagogical University, Moscow, Russia;

² FSRC Crystallography and Photonics RAS, Moscow, Russia;

³ Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry RAS, Moscow, Russia;

⁴ Research Institute of Molecular and Cellular Medicine, RUDN University, Moscow, Russia;

⁵ Division of Biotechnology, Sirius University of Science and Technology, Sochi, Russia

^{III} stepanov_me@mail.ru

Abstract. Protein nanoparticles (NPs) based on endogenous biopolymers are promising platform for bioimaging and advanced therapy since they are biocompatible, biodegradable and have low systematic toxicity with high loading capacity. In this work we studied albumin NPs loaded with three cyanine dyes: ICG, IR-806 and IR-820 for colloidal and optical properties. We demonstrated that cross-linked albumin nanoparticles functionalized with IR dyes were promising for optical bioimaging in biotissue transparency window (700-1700 nm). The proposed dye-loaded NPs were of low toxicity *in vitro* and could be promising for *in vivo* applications.

Keywords: bioimaging, albumin nanoparticles, cyanine dyes, IR-806 dye

Funding: The study was prepared as part of the work on the topic "Laser technologies for biomedical applications" (122122600055-2) under the state order of the Ministry of Education of the Russian Federation. R. Akasov, T. Egorova, M. Stepanov and E. Khaydukov are members of leading scientific school of Russian Federation "Optical spectroscopic nanoscopy of quantum objects and diagnostics of perspective materials" (grant of the President of the Russian Federation 776.2022.1.2).

Citation: Stepanov M.E., Demina P.A., Akasov R.A., Babayeva G., Egorova T.V., Generalova A.N., Parodi A., Khaydukov E.V., In vivo visualization of albumin nanoparticles loaded with cyanine dyes, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 354–359. DOI: https://doi.org/10.18721/JPM.163.262

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Stepanov M.E., Demina P.A., Akasov R.A., Babayeva G., Egorova T.V., Generalova A.N., Parodi A., Khaydukov E.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 615.45 DOI: https://doi.org/10.18721/JPM.163.262

In vivo визуализация альбуминовых наночастиц, загруженных цианиновыми красителями

М.Е. Степанов¹⊠, П.А. Демина^{1,2,3}, Р.А. Акасов^{1,2,3}, Г. Бабаева⁴, Т.В. Егорова¹, А.Н. Генералова^{1,2,3}, А. Пароди⁵, Е.В. Хайдуков^{1,2,3}

¹ Московский государственный педагогический университет, Москва, Россия;

² ФНИЦ «Кристаллография и фотоника» РАН, Москва, Россия;

³ Институт биоорганической химии им. академиков М.М. Шемякина и Ю.А. Овчинникова РАН, Москва, Россия;

⁴ НИИ молекулярной и клеточной медицины РУДН, Москва, Россия;

⁵ Отделение биотехнологии, Научно-технический университет «Сириус», г. Сочи, Россия

□ stepanov_me@mail.ru

Аннотация: Белковые наночастицы (НЧ) на основе эндогенных биополимеров являются перспективной платформой для развития тераностики, поскольку они характеризуются биосовместимостью, биоразлагаемостью и низкой системной токсичностью при высокой загрузочной емкости. В данной работе мы исследовали коллоидные и люминесцентные свойства НЧ на основе альбумина, загруженных тремя цианиновыми красителями - ICG, IR-806 и IR-820. Мы показали, что сшитые наночастицы альбумина, функционализированные ИК-красителями, перспективны для оптического биоимиджинга в окне прозрачности биоткани (700-1700 нм). Предлагаемые нагруженные красителем НЧ не демонстрировали in vitro токсичность и могут быть использованы в условиях *in vivo*.

Ключевые слова: биовизуализация, альбуминовые наночастицы, цианиновые красители, краситель IR 806

Финансирование: Исследование подготовлено в рамках выполнения работ по теме «Лазерные технологии для биомедицинских приложений» (№ 2-122122600055) по государственному заказу Министерства образования Российской Федерации. Р.А. Акасов, Т.В. Егорова, М.Е. Степанов и Е.В. Хайдуков являются членами ведущей научной школы Российской Федерации «Оптико-спектральная наноскопия квантовых объектов и диагностика перспективных материалов» (грант Президента РФ НШ776.2022.1.2-).

Ссылка при цитировании: Степанов М.Е., Демина П.А., Акасов Р.А., Бабаева Г., Егорова Т.В., Генералова А.Н., Пароди А., Хайдуков Е.В. In vivo визуализация альбуминовых наночастиц, загруженных цианиновыми красителями // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 354–359. DOI: https:// doi.org/10.18721/JPM.163.262

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Protein nanoparticles based on endogenous biopolymers are promising platform for bioimaging and advanced therapy since they are biocompatible, biodegradable and have low systematic toxicity with high loading capacity [1]. In particular, albumin nanoparticles (ANs) represent one of the most promising carriers due to the cost-effectiveness of fabrication and versatility for delivering both hydrophilic and hydrophobic therapeutics and diagnostic agents. Moreover, albumin-based nanoparticles inherite most of the useful properties of albumins themselves. Being the main protein component of the blood (\sim 40%), albumins are non-toxic, biodegradable, easy-to-functionalize, water-soluble and long-circulating molecules [2], so they perfectly fit as binding agents. Still, one of the main challenges of ANs based theranostics is precise luminescent control of

© Степанов М.Е., Демина П.А., Акасов Р.А., Бабаева Г., Егорова Т.В., Генералова А.Н., Пароди А., Хайдуков Е.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

nanoparticles in vitro and in vivo. The desired degree of control can be achieved by using optical methods, namely techniques of optical bioimaging.

Of particular interest today is the optical bioimaging based on near infrared (NIR) light, because light from this spectral region can penetrate deep into the biotissue [3, 4] matching the so-called biological tissue transparency window (~750–1700 nm). The approach with excitation and luminesce detection in biological transparency window provides visualization up to several centimeters deep in the tissue, which is in many cases sufficient for in vivo control purposes.

At this point the idea is to join carrier properties of albumin nanoparticles and imaging properties of NIR dyes by noticing that they can be easily mixed together giving nanocomplexes both friendly to the organism and able to be controlled by NIR light emitted by loaded fluorescent dyes. The problem is then to obtain the brightest nanocomplexes with stable fluorescence, which are still hydrophilic for high solubility in blood plasma and can effectively hide dye molecules from environment and provide their transport to a target area.

In present work we have used two different types of bovine serum albumin (BSA) nanoparticles, loaded with three different cyanine dyes (ICG, IR-806, IR-820) aiming to evaluate visualization ability. Indocyanine green (ICG) dye approved to use in clinical practice [5] was used as a reference dye. Physicochemical and photoluminescent properties of BSA nanocomplexes of all cross-variants were studied. The proposed dye-loaded NPs were found to be of low toxicity *in vitro* and could be promising biovisualizing agents for *in vivo* applications.



Fig. 1. Scheme illustrating BSA protein molecule, its cross-linking to HBSA and LBSA nanoparticles, size analysis, dye loading and NIR *in vivo* bioimaging.
LP filter – long-pass filter used to cut off excitation light, CCD detector is charge-coupled device used to detect the fluorescence emission signal from nanocomplexes *in vivo*

Materials and Methods

The BSA nanoparticles were obtained by precipitation in a non-solvent followed by cross-linking using glutaraldehyde (cross-linking agent binding separate BSA molecules togehter) of high and low concentration, resulting in two types of organic nanoparticles called HBSA (letter "H" stands for high degree of cross-linking) and LBSA ("L" means low degree), correspondingly. The IR dye were incorporated into BSA NPs due to non-covalent interactions.

The scheme illustrating nanoparticles preparation is presented in Fig. 1. The loading capacity and optical properties were studied by spectrometric methods. The luminescence spectra were studied with Fluorolog 3 (HJY, France). The size distribution was measured with dynamic light scattering (DLS) and cryo-TEM microscopy (Tecnai G212 SPIRIT, FEI, USA). *In vivo* studies were done on home-build bioimaging system [6]. The resulting *post mortem* images of mice organs were analyzed with ImageJ software to obtain background-corrected pharmacokinetics data according to brightness of captured NIR fluorescence.

Results and Discussion

HBSA and LBSA had the same size distribution with maximum at 200 nm. Based on DLS study and TEM analysis we found that albumin NPs loading with IR dye dramatically changed the size distribution in the case of LBSA, but not int the case of HBSA. Dye loading capacities were the same for both types of NPs, and were $\sim 85\%$.

Nanoparticles loaded with three different cyanine dyes ICG, IR-806, IR-820 were synthesized, and among them the BSA@IR-806 nanocomplex was the most stable and had the brightest fluorescence, which was substantially greater than in the case of the clinically approved ICG dye. The phenomenon of fluorescence change under entrapment in albumin was reported earlier [5] and confirmed in our experiments for IR-806 and IR 820 dyes (see Fig. 2).



Fig. 2. Fluorescence of free ICG, IR 806 and IR 820 dyes under 750 nm excitation in solution (*a*); fluorescence of BSA@IR-820 nanocomplexes (*b*) and BSA@IR-806 nanocomplexes (*c*). Red arrows show the red shifts. Data corresponding to the free dye in solution is shown here to demonstrate the effect of interaction with albumin nanoparticles on the luminescent properties of the dyes

Additionally, we determined correlation between cross-linking degree and luminescent properties of nanocomplexes (Fig. 2, *b* and 2, *c*). In particular IR 806 and IR 820 demonstrate red shift of luminescence after intercalation in HBSA complexes. At the same time, red shift after intercalation in LBSA nanocomplex is demonstrated only by IR 820 dye. The highest quantum efficiency was observed for BSA@IR-806 (Fig. 2, *a*). The BSA@IR-806 nanocomplex solution was also found to be colloidally stable. Considering all the results, BSA@IR-806 was chosen for subsequent *in vitro* and *in vivo* experiments (as shown at Fig. 1).

The *in vitro* studies demonstrated the absence of cytotoxicity in MTT assay at the concentrations up to 0.05 mg/ml in MCF-7 breast adenocarcinoma and fibroblasts cell culture.

In vivo pharmacokinetics study of BSA@IR806 was made in comparison with free IR 806 dye (Fig. 3) to determine the effect of albumin nanoparticles. We can conclude that 5 min after intravenous injection the similar distribution for free and albumin encapsulated dye was observed. The most intensive signal was observed in liver, gall-bladder and intestines, which makes gall duct the main excretion pathway for the IR 806 dye. It can be attributed to cyanine dyes in general [2] (sulfur-containing groups being responsible). Their appearance can in principle be modified to switch the excretion pathway to renal. In 24 hours the biodistribution was dramatically changed and nanocomplexes were accumulated in liver and spleen in contrary to free dye.







HBSA-IR 806 5 min



IR 806 24 h

HBSA-IR 806 24 h

Fig. 3. *In vivo* pharmacokinetics study (5 min and 24 hours after injection) of free IR 806 in comparison with HBSA@IR806 nanocomplexes based on *post mortem*NIR photoluminescent imaging. Each image is an overlap of reference image of mouse and NIR image of dye emission (pictured with light red)

Conclusion

In present work the synthesis of BSA nanoparticles loaded with cyanine dyes (ICG, IR 806, IR 820) was performed for *in vivo* bioimaging. BSA@IR806 dye nanocomplexes were found to demonstrate high colloidal stability and flexible spectral behavior. The *in vitro* studies demonstrated the absence of cytotoxicity in MTT assay at the concentrations up to 0.05 mg/ml in cell cultures. *In vivo* studies showed pronounced time-stable accumulation of BSA@IR806 nanocomplexes mainly in gastrointestinal tract in contrary to free IR 806.

REFERENCES

1. **Parodi A., et. al.,** Albumin nanovectors in cancer therapy and imaging, Jr. Biomolecules, 9 (6) (2019).

2. Tian R., et al., Albumin-chaperoned cyanine dye yields superbright NIR-II fluorophore with enhanced pharmacokinetics. Sci Adv, 5 (9) (2019) 0672.

3. Wallyn J., et al., Biomedical Imaging: Principles, Technologies, Clinical Aspects, Contrast Agents, Limitations and Future Trends in Nanomedicines. Pharm Res, 36 (6) (2019) 78.

4. Hong G., A.L. Antaris, and H. Dai, Near-infrared fluorophores for biomedical imaging. Nature Biomedical Engineering, 2017. 1(1).

5. Xu L., et al., Multifunctional Albumin-Based Delivery System Generated by Programmed Assembly for Tumor-Targeted Multimodal Therapy and Imaging. ACS Appl Mater Interfaces, 11 (42) (2019) 38385–38394.

6. Generalova A.N., et al., Submicron polyacrolein particles in situ embedded with upconversion nanoparticles for bioassay. Nanoscale, 7 (5) (2015) 1709–17.

THE AUTHORS

STEPANOV Maxim E. stepanov_me@mail.ru ORCID: 0000-0002-0332-1235

DEMINA Polina A. polidemina1207@yandex.ru ORCID: 0000-0001-6349-2979

AKASOV Roman A. roman.akasov@gmail.com ORCID: 0000-0001-6486-8114

BABAYEVA Gulyalek babaevagulyalek@gmail.com ORCID: 0000-0001-5781-7925 EGOROVA Tatiyana V. tv.egorova@mpgu.su ORCID: 0000-0002-3346-3242

GENERALOVA Alla N. a-generalova@yandex.ru ORCID: 0000-0001-9646-1693

PARODI Alessandro aparodi.sechenovuniversity@gmail.com ORCID: 0000-0002-5086-8233

KHAYDUKOV Evgenii V.

khaydukov@mail.ru ORCID: 0000-0002-3900-2949

Received 07.08.2023. Approved after reviewing 16.08.2023. Accepted 25.08.2023.

PHYSICS OF MOLECULES

Conference materials UDC 547.96: 54.03 DOI: https://doi.org/10.18721/JPM.163.263

Determination of the isoelectric point of the antibody to SARS-CoV-2 by molecular modeling for conjugation with quantum dots

S.K. Rudnykh¹[⊠], E.D. Gribova¹, K.T. Kholmurodov^{1,2},

P.P. Gladyshev¹, N.A. Polotnyanko¹

¹ Dubna State University, Moscow region, Dubna, Russia;

² Joint Institute for Nuclear Research, Moscow region, Dubna, Russia

[™] rudnih@yandex.ru

Abstract. Rapid and effective diagnosis is an integral part of the infectious disease control system. One of the promising directions for achieving this goal is the creation of a biosensor device consisting of a biologically active component (antibody) and a fluorescent label that produces an analytical signal. A necessary condition for the conjugation of proteins with a label is the preservation of their specific activity, since this factor determines the reliability of the analysis result. Violation of the ability of antibodies to form a complex with the antigen directly affects the result of the analysis. A fundamental property of antibodies and other proteins is the isoelectric point, which is defined as the pH at which the macromolecule carries no net electrical charge. Knowing the surface charge distribution and the total pI, it is possible to predict the behavior of the antibody-substrate complex. The isoelectric antibodies to Sars-Cov-2 CA521 FALA (PDB code 7e23) equal to 7.4 were calculated using the molecular modeling method using the Amber complex. Based on the results obtained, the covalent conjugation of this antibody with multilayer chalcogenide quantum dots was carried out by carbodiimide binding in combination with sulfo-N-Hydroxysuccinimide. The quantum dot-antibody complex was tested in an immunochromatographic assay and showed a 200% increase in fluorescence in the test and control zones, indicating successful conjugation under pH conditions below the isoelectric point.

Keywords: antibodies, isoelectric point, molecular modeling, quantum dots.

Citation: Rudnykh S.K., Gribova E.D., Kholmurodov K.T., Gladyshev P.P., Polotnyanko N.A., Determination of the isoelectric point of the antibody to Sars-Cov-2 by molecular modeling for conjugation with quantum dots, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 360–365. DOI: https://doi.org/10.18721/JPM.163.263

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

[©] Rudnykh S.K., Gribova E.D., Kholmurodov K.T., Gladyshev P.P., Polotnyanko N.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.
Материалы конференции УДК 547.96: 54.03 DOI: https://doi.org/10.18721/JPM.163.263

Расчёт изоэлектрической точки антитела к SARS-CoV-2 методом молекулярного моделирования и его применение в конъюгации с квантовыми точками

С.К. Рудных¹, Е.Д. Грибова¹, Х.Т. Холмуродов^{1,2},

П.П. Гладышев¹, Н.А. Полотнянко¹

¹ Федеральное государственное бюджетное образовательное учреждение высшего образования «Университет «Дубна», Дубна, Россия;

² Международная межправительственная организация Объединенный институт ядерных исследований, Дубна,

⊠ rudnih@yandex.ru

Аннотация. Фундаментальным свойством антител и других белков является изоэлектрическая точка, которая определяется как pH, при котором макромолекула не несет суммарного электрического заряда. Зная распределение поверхностного заряда и общую изоэлектрическую точку белка возможно предсказать поведение комплекса антитело-субстрат. В работе методом молекулярного моделирования рассчитана изоэлектрическая точка антитела к Sars-Cov2- CA521 FALA (код PDB 7e23) и по полученным результатам была проведена конъюгация данного антитела с многослойными халькогенидными квантовыми точками.

Ключевые слова: антитела, изоэлектрическая точка, молекулярное моделирование, квантовые точки

Ссылка при цитировании: Рудных С.К., Грибова Е.Д., Холмуродов Х.Т., Гладышев П.П., Полотнянко Н.А. Расчет изоэлектрической точки антитела к Sars-Cov-2 методом молекулярного моделирования и его применение в конъюгации с квантовыми точками // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 360–365. DOI: https://doi.org/10.18721/JPM.163.263

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Various analytical labels are used to visualize complexes of biomolecules. It should be noted that test systems that use fluorescent labels, which include quantum dots (QDs) are the most sensitive [1]. They have a number of unique properties, including a narrow symmetrical fluorescence peak, high fluorescence brightness, a wide excitation band, and high photostability. Due to these properties, it is possible to reduce the limits of detection and increase the sensitivity of test systems created on their basis. The isoelectric point (pI) is one of the most important characteristics of antibodies (Abs) that affect the interactions of the Abs-QDs system [2]. Currently, there is no physicochemical method for determining the local charge on the AT surface; the influence of various factors on the surface charge can be calculated using molecular modeling [3]. Information about the surface charge of Abs is necessary for the conjugation of antibodies with QDs and obtaining a complex with high analytical characteristics (Fig. 1).

Fig. 1 shows one of the most popular ways of attaching Abs to nanoparticles through amines. Amino groups of Abs are located over their entire surface, and are reactive without any chemical modification with various groups of QDs. In turn, the surface carboxyl groups of QDs must be activated using carbodiimide (EDC) and N-hydroxysuccinimide (NHS) before binding to Abs. The adsorption of Abs on the carboxyactivated surface of QDs is the most acceptable strategy that uses the force of ionic interaction [4]. By controlling the immobilization conditions, the

© Рудных С.К., Грибова Е.Д., Холмуродов Х.Т., Гладышев П.П., Полотнянко Н.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Carbodiimide binding activating reagents that provide the carboxyl-functionalized QD matrix with a distinct surface charge that can attract AT

carboxyl-activated matrix has fast reversible electrostatic adsorption and covalent binding, and the activating reagent has a significant effect on the orientation of bound biomolecules. As can be seen from Fig. 1, for oriented conjugation, it is necessary to create a pH below the isoelectric point of the protein, since in this case the crystallizing fragment of the antibody acquires a positive charge and, due to electrostatic interaction, is covalently bound by the lower part of the antibody, leaving the antigen-binding pocket open.

Materials and Methods

For molecular dynamics (MD) modeling and calculation of molecular energy minimization within the framework of general mechanics, the Amber complex was used. The electrostatic surface potential of the antibody surface was calculated at different solvent pH. The calculation was performed in PyMol 3.3 (PDB code: 7e23) using the APBS Electrostatics plugin with a range of ± 5 kbT/e on the Govorun supercomputer at JINR, Dubna. The calculations are based on the following potentials.

The Lennard–Jones potential models Van der Waals interactions:

$$U(r) = 4E_i \left[\left(\frac{\sigma_i}{r + \delta_i} \right)^{12} - \left(\frac{\sigma_X}{r + \delta_i} \right)^6 \right], \tag{1}$$

where *r* is the smallest distance between the side and the surface, E_i is the energy at minimum value, σ_i is the equivalent Van der Waals radius for each residue, δ_i is the dimension parameter.

Electrostatic interaction can be represented through Goui-Chapman potential:

$$U(r) = \frac{\sigma_s q_i e^{-kr}}{k E_r E_0} , \qquad (2)$$

where q_i is the smallest distance between the side and the surface, σ_s is the surface charge density, k is the reciprocal Debye length calculated from ionic strength.

The net charges of both Ab fragments at different pH values in accordance with the Henderson-Hasselbalch equation:

$$pH = pKa + lg(A^{-}/[HA]), \qquad (3)$$

Results and Discussion

The CA521 antibody (PDB code 7e23) was chosen as a model antibody, since it simultaneously effectively binds all three fragments of the receptor-binding domain of one trimer of the SARS-CoV-2 spike [5]. The structure of this antibody was analyzed according to its charge distribution (Fig. 2, a), due to the presence of acidic and alkaline amino acids, as well as carboxyl and amino groups at the ends of both the heavy and light chains, positive and negative charges were unevenly distributed throughout the antibody, which determines the pI of the entire antibody, antigen-binding (Fab)2 and crystallizing (Fb) fragments. The antibody under test consists of 420 amino acid residues formed by 14 amino acids (Fig. 2,a). Among which there are acidic amino acids (Arg, His and Lys), basic amino acids (Asp and Glu) and neutral amino acids. The charge of amino acids depends on the pH value of the medium and on the structure of their radical. When the pH decreases, then the H^+ ions present in the solution are attached to the amino and carboxy groups - the charge of the amino acid becomes positive. In the (Fab)2 fragment, the amount of alkaline amino acids was much higher than that of acidic amino acids, while in the Fc fragment they were almost the same (Fig. 2,b). According to equation, the total charges of the (Fab)2 and Fc fragments were calculated at different pH values (Fig. 2,c). The calculation results showed that the amount of all positively charged residues (basic): 158 (Lys, Arg, etc.) and all negatively charged residues (acidic): 128 (Asp, Glu, etc.) compensate each other at pH 7.4. Thus, the isoelectric point of the CA521 FALA antibody is (pH = 7.4). However, from pH 5.8 to 7.8, the absolute net charge of the Fab fragment was greater than that of the Fc fragment. Even when the net charge of the entire antibody was negative in alkaline environment, the Fab fragment was positively charged and affected the adsorption of the antibody. Thus, electrostatic attraction played a dominant role in the interaction of the positively charged fragment Fab with the negatively charged carboxyl QDs. In contrast, the Fc fragment was less charged, so its hydration shell was thinner and its hydrophobicity stronger. At pH 7.8, both adsorption and covalent



Fig. 2. Results of molecular modeling calculations. Three-dimensional crystal structure of the anti-SARS-CoV-2 antibody CA521 (PDB code 7e23) (*a*). Alkaline and acidic amino acid groups are marked in red and yellow, respectively. The number of alkaline and acidic amino acids on fragments (Fab) 2 and Fc (*b*). Total charge of (Fab)2 and Fc fragments at different pH (*c*).

attachment were unfavorable for tail orientation of the antibody. First, the Fab fragment was positively charged, while the Fc fragment was negatively charged, so that Fab was preferentially adsorbed on the QDs. Secondly, the deprotonation of the primary amino groups of the Fab ends was much more complete than the deprotonation of the side chains of lysine (located in the Fc fragment), and these primary amino groups more easily reacted with carboxyl groups.

At pH 5.8, both the (Fab)2 and Fc fragments were positively charged. In addition, most of the amino groups of the Fab ends were also protonated and thus their cross-linking priority was reduced. In addition, the hydrophobicity of the Fc region was enhanced due to their relatively small net charge, which favors binding to the carboxyl groups of QDs through hydrophobic interaction. Finally, the reduced crosslinking rate gave the adsorbed antibodies time to fully adapt their orientation before forming covalent bonds.



Fig. 3. Images obtained with a fluorescent reader, QDs conjugates at pH 7.8 (*a*), QDs conjugates at pH 5.8 (*b*)

Conclusion

The results obtained were tested in practice, when conjugating AT with multilayer chalcogenide QDs by the carbodiimide binding method. Chalcogenide QDs were obtained by the following procedure [6]. Conjugation was carried out at a value below pI (pH = 5.5) and at a value above pI (pH 7.8), according to the following procedure [7]. The success of the conjugation was assessed by the fluorescence intensity of the AT-CT complex on an immunochromatographic test strip. Fluorescence intensity was measured using a fluorescent reader.

As a result, conjugation at pH 7.8 (Fig. 3,a) showed a fluorescence intensity 200% higher than at pH 5.8. The final results can be used in the development of test systems for the identification of pathogenic biological agents with improved analytical characteristics.

REFERENCES

1. Farias P. M. A., Fontes A., Galembeck A., Figueiredo R., Santos B.S., Fluorescent II-VI semiconductor quantum dots: Potential tools for biolabeling and diagnostic. Journal of the Brazilian Chemical Society. 19 (2) (2008) 352–356.

2. Matsuda Y., Mendelsohn B.A., An overview of process development for antibody-drug conjugates produced by chemical conjugation technology. Expert Opinion on Biological Therapy. (7) (2021) 963–975.

3. Gao S.P., Rojas-Vega F., Rocha-Martin J., Guisan J.M., Oriented immobilization of antibodies through different surface regions containing amino groups: Selective immobilization through the bottom of the Fc region. International Journal of Biological Macromolecules. (177) (2021) 19–28.

4. Akinshina Y.A., Mardanly S.S., Kiseleva V.A., Immunochromatographic test for differentiation detection of IgM and IgG to SARS-CoV-2. Klinicheskaia laboratornaia diagnostika. 65 (11) (2020) 688–692.

5. Cerofolinia L., Fragaia M., Luchinata C., Raveraa E., Orientation of immobilized antigens on common surfaces by a simple computational model: Exposition of SARS-CoV-2 Spike protein RBD epitopes. Biophysical Chemistry. 64 (3) (2020) 559–567.

6. Troshkina N., Novikova S., Nasirov P., Volobueva M., Mukhina I., Popova A., Gribova E., Investigation of the properties of quantum dots depending on the nature and number of additional semiconductor layers, St. Petersburg Polytechnic University Journal: Physics and Mathematics. 15 (3.2) (2022) 106–110.

7. Nasirov P., Sidorov E., Kryger V., Novikova S., Gribova E., Gladyshev P., Mukhina I., Study of quantum dots conjugation with antibodies to be used in a lateral flow immunochromatographic assay, St. Petersburg Polytechnic University Journal: Physics and Mathematics. 15 (3.2) (2022) 331–335.

THE AUTHORS

RUDNYKH SERGEY K. rudnih@yandex.ru GLADYSHEV PAVEL P. pglad@yandex.ru

GRIBOVA ELENA D. elena_g67@mail.ru **POLOTNYANKO Natalya.** A. polot.nat@gmail.com

KHOLMURODOV Kholmirzo. T. mirzo@jinr.ru

Received 18.07.2023. Approved after reviewing 19.07.2023. Accepted 20.07.2023.

MATHEMATICAL PHYSICS

Conference materials UDC 535.8 DOI: https://doi.org/10.18721/JPM.163.264

Experimental evaluation of imperfections of quantum states for time-bin encoding

I.S. Gerasin^{1,2,3,4}⊠, N.V. Rudavin^{1,3,4,5}, P.A. Kupriyanov^{1,2,3,4}, A.A. Dvurechenskiy^{1,2,3,4}, R.A. Shakhovoy^{1,2,3,4}

¹QRate, Moscow, Russia;

² Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, Russia;

³ NTI Center for Quantum Communications, National University of Science and Technology MISiS, Moscow, Russia;

⁴ Russian Quantum Center, Skolkovo, Moscow, Russia;

⁵ HSE University, Moscow, Russia

^I i.gerasin@goqrate.com

Abstract. We propose here a simple method to estimate quality of quantum states for quantum key distribution (QKD) protocols with phase-time encoding. The parameters proposed to estimate the quality of states can be easily measured experimentally and will be useful in setting up and debugging the QKD system.

Keywords: quantum key distribution, state preparation, time-bin encoding

Funding: The study was commissioned by JSCo RZD.

Citation: Gerasin I.S., Rudavin N.V., Kupriyanov P.A., Dvurechenskiy A.A., Shakhovoy R.A., Experimental evaluation of imperfections of quantum states for time-bin encoding, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 366–371. DOI: https://doi.org/10.18721/JPM.163.264

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.8 DOI: https://doi.org/10.18721/JPM.163.264

Экспериментальная оценка неидеальностей квантовых состояний в пространственно-временном кодировании

И.С. Герасин^{1,2,3,4}, Н.В. Рудавин^{1,3,4,5}, П.А. Куприянов^{1,2,3,4}, А.П. Двуреченский^{1,2,3,4}, Р.А. Шаховой^{1,2,3,4}

¹ QRate, Москва, Россия;

² Московский физико-технический институт, Московская область, г. Долгопрудный, Россия;

³ НТИ Центр квантовых коммуникаций, Национальный исследовательский технологический университет «МИСиС», Москва, Россия;

⁴ Российский Квантовый центр, Сколково, Москва, Россия;

⁵ Национальный исследовательский университет «Высшая школа экономики», Москва, Россия

^{III} i.gerasin@goqrate.com

Аннотация. В данной работе предлагается простой метод оценки качества приготовления квантовых состояний, использующихся в системах квантового распределения ключей

© Gerasin I.S., Rudavin N.V., Kupriyanov P.A., Dvurechenskiy A.A., Shakhovoy R.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

(КРК), с фазово-временным кодированием. Параметры для оценки, предложенные в данной работе, могут быть легко измерены экспериментально и будут полезны при настройке и отлаживании систем КРК.

Ключевые слова: квантовое распределение ключей, приготовление состояний, пространственно-временное кодирование

Финансирование: Исследовательская работа выполнена по заказу ОАО «РЖД».

Ссылка при цитировании: Герасин И.С., Рудавин Н.В., Куприянов П.А., Двуреченский А.П., Шаховой Р.А. Экспериментальная оценка неидеальностей квантовых состояний в пространственно временном-кодировании // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 366–371. DOI: https://doi. org/10.18721/JPM.163.264

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Nowadays, a lot of efforts are aimed at improving the security of transmitted data. In this regard, quantum key distribution (QKD) is a promising technology towards unconditional security [1]. However, despite the theoretical possibility of achieving unconditional security, real QKD systems are not at all information-theoretic secure. The reason is that practical implementations of QKD systems have imperfections, due to which many of the assumptions used in the theoretical construction of quantum protocols are violated. For instance, instead of ideal single photons, one generally uses weak coherent pulses, which, with some probability, can contain more than one photon. Instead of an ideal quantum channel standard fiber optic communication lines having significant losses are usually employed. Real single photon detectors are characterized by an efficiency different from 100%; moreover, they have a finite dead time and a non-zero probability of dark counts. Finally, phase modulators have a finite bandwidth, intensity modulators have finite extinction, and the high-frequency drivers used to drive them have non-zero jitter and can distort the shape of electrical signals. All these imperfections make the real QKD system vulnerable to various attacks that Eve can implement without being noticed.

In this article, we will focus on the study of imperfections associated with phase and intensity modulators, namely, on the non-ideality of quantum state preparation. This type of imperfection leads to the distinguishability of quantum states in non-orthogonal bases, which can be used by Eve to obtain partial information about the quantum key. Therefore, it is always important to know the accuracy with which quantum states are prepared to properly deal with possible information leakage. The quantum bit error rate (QBER) is usually used to estimate the non-ideality of quantum states; however, QBER is an integral parameter [2] and does not allow separating various effects that lead to imperfections. So, it would be useful to have additional criteria for assessing the quality of quantum states that would allow, e.g., finer tuning of laser drivers, phase modulators, intensity modulators, etc.

In this paper, we introduce simple criteria for estimating the quality of quantum states for QKD protocols with phase-time encoding. These criteria can help assess the leakage of information in the implementation of such protocols. In addition, they will be useful in setting up and debugging the QKD system.

Materials and Methods

There are two widespread approaches to encode quantum states in QKD: polarization and time-bin encoding [3]. The former approach employs light polarization to encode quantum information and is preferred for free-space communication since air environment does not significantly disturb the polarization state of light. In the latter approach, information is encoded in the time of appearance of the optical signal from the source. The times used for encoding can be very short and have an order of magnitude corresponding to the period of oscillation of the electromagnetic field in a pulse. In this case, one usually speaks of optical phase encoding, where

© Герасин И.С., Рудавин Н.В., Куприянов П.А., Двуреченский А.П., Шаховой Р.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. interferometric methods or homodyne detection are used for decoding. If the times are comparable with the pulse width, then one speaks of time-bin coding, where a detector that can distinguish between the arrival times of the pulses is used for decoding. Roughly speaking, with phase encoding, the transmitter shifts in time (using a phase modulator) the carrier wave in the pulse, whereas with time-bin encoding, the transmitter manipulates (using an intensity modulator) the pulse envelope. Since polarization of light is not maintained in optical fiber during propagation, polarization encoding requires additional polarization control system [4]; therefore, time-bin encoding is widely used in fiber-optic systems.

Similar to BB84 protocol with polarization encoding, one can introduce two non-orthogonal bases with time-bin encoding (let us denote them as X- and Z-basis). In the X-basis, a bit can be encoded by a pair of laser pulses separated in time by ΔT and having a given phase difference. In the Z-basis, a single pulse is prepared either in an early (*E*-pulse) or late (*L*-pulse) time slot within the frame corresponding to a given quantum state (Fig. 1). A general quantum state prepared within time-bin encoding can be represented by a tensor product of consecutive weak coherent pulses: $|\psi\rangle = |\alpha\rangle \otimes |\beta\rangle \equiv |\alpha,\beta\rangle$, where α , β are complex amplitudes of coherent states in the neighboring bins (time slots), i.e., in *E*- and *L*-pulses, respectively.



Fig. 1. Schematic of time-bin encoding

Quantum states prepared via real optical modulators inevitably differ from ideal qubits. For instance, intensity modulators employed for cutting pulses from continuous light have finite extinction; therefore, some light remains in the "empty" time slot of the Z-basis. In addition, an electrical signal driving the modulator deviates from an ideal rectangular function already due to finite duration of rising and falling edges or even because of the impedance mismatch, which leads to a distortion of the shape of the optical pulse. Non-ideal electrical signals driving the phase modulator may lead, in turn, to inaccuracies in the preparation of the phase difference between pulses.

To characterize the quality of a quantum state, one generally uses *fidelity F*, which is a measure of similarity of quantum states. For pure states $|\psi\rangle$ and $|\phi\rangle$, it is defined via the scalar product as $F = |\langle \psi | \phi \rangle|^2$. Thus, for one of the states in the Z-basis, we may define fidelity as

$$F_{Z} = \left| \left\langle vac, \sqrt{s} \left| \sqrt{\zeta}, \sqrt{s} \right\rangle \right|^{2} = e^{-\zeta}, \tag{1}$$

where $|vac\rangle$ is the signal in the absence of a pulse (vacuum), s is a mean photon number in the 'non-empty' bin, and ζ is the intensity of the signal, which is prepared instead of a vacuum state due to modulator imperfections. Experimentally, it is easier to measure mean photon number per quantum state $S_z = s + \zeta$, so, introducing the ratio of intensities in the early and late time bins, $r_z = s/\zeta$, we may write for the residual intensity:

$$\zeta = \frac{S_Z}{r_Z + 1}.\tag{2}$$

It easy to see form (1) that fidelity higher than 0.99 is achieved when the ratio of intensities, r_{z} is greater than 20 dB (in assumption that $S_z < 1$).

For the states in the X-basis, we assume that intensity of laser pulses in the early and late time bins may differ by the value $\delta\gamma$, whereas the phase difference can be prepared with an error $\delta\theta$. In this case, fidelity is written as follows:

$$F_{X} = \left| \left\langle \sqrt{\gamma}, \sqrt{\gamma} \middle| \sqrt{\gamma}, e^{\delta \theta} \sqrt{\gamma + \delta \gamma} \right\rangle \right|^{2} =$$

$$= e^{-2\zeta - \delta \gamma + 2\sqrt{\gamma(\gamma + \delta \gamma)} \cos(\delta \theta)} = e^{-\gamma(1 + r_{X} - 2\sqrt{r_{X}} \cos(\delta \theta))}$$
(3)

where $r_{\chi} = (\gamma + \delta \gamma)/\gamma$. Such a fidelity depends on the two parameters, $\delta \gamma$ and $\delta \theta$; therefore, it is convenient to define additional fidelities:

$$F_Z^{\theta} = F_X |_{\delta \gamma = 0} = e^{-2\gamma (1 - \cos(\delta \theta))}, \tag{4}$$

$$F_X^r = F_X|_{\delta\theta=0} = e^{-\gamma(1+r_X - 2\sqrt{r_X})},$$
(5)

which can be easily measured separately. Using numerical calculations, it is easy to show that $F_{\chi}^{0} > 0.99$ if $\delta \theta < 10^{\circ}$ and $F_{\chi}^{\prime} > 0.99$ if $r_{\chi} < 1.4$.

Results

Now, we turn to the experimental estimation of the above parameters and corresponding fidelity values. Let us first consider the imperfections associated with the intensity modulator. For this, we will use three states in the *X*-basis, $|vac\rangle \otimes |vac\rangle$, $|\sqrt{v}\rangle \otimes |\sqrt{v}\rangle$, $|\sqrt{\mu}\rangle \otimes |\sqrt{\mu}\rangle$ (they can be used as decoy states in a real-world QKD system) and one state in the *Z*-basis, $|vac\rangle \otimes |\sqrt{s}\rangle$, where s = 0.6, $\mu = 0.3$, and v = 0.06 are corresponding intensities (mean photon numbers) of coherent states.

To prepare the states and measure their fidelities, we used the experimental setup schematically shown in Fig. 2. Note that it can be used for measuring non-idealities in QKD systems with point-to-point connection as well as for QKD with untrusted central note (MDI QKD [5]). The setup consists of two transceivers (TX1 and TX2), each including a CW laser, a phase modulator (PM), and an intensity modulator (IM). To measure IM-related non-idealities, we used the first transceiver (TX1), whose output was connected to both single-photon detector (SPD) and classical photodetector (PD). PM was disabled during these measurements. Light pulses were cut from the beam of the CW laser; pulse repetition rate was 312.5 MHz. The pulses were then split by the 50:50 beam splitter: half of the power were then measured with PD, and the second half was attenuated by variable optical attenuator and then measured with gated SPD. Pulse shapes measured with PD and acquired with an oscilloscope are presented in Fig. 3,*a*. Pulse shapes recovered with SPD by scanning the phase of the gate (with the step 25 ps) are shown in Fig. 3,*b*.

To calculate r_{z} , we measured the ratio between areas of the early and late pulses of the state $|Z_0\rangle$ (see Fig. 3, *a* and 3, *b*). Similarly, we calculated the parameter r_x for $|X_{\mu}\rangle$ - and $|X_{\nu}\rangle$ -state. Obtained values are listed in Table 1.



Fig. 2. Experimental setup



Fig. 3. Experiment results.

Table 1

Experimental and bound values of introduced criteria

Parameter	r _z	r_X^{μ}	r_X^{ν}	δθ	s/v
'Classical' value	85±45 dB	1.03±0.01	1.23±0.2	5±1°	11.3±0.2
'Quantum' value	14±1 dB	1.06 ± 0.01	1.01±0.2	—	2.5±0.2

To measure the phase error, $\delta\theta$, we prepared a continuous sequence of states $|X_{\pi}\rangle$ with the first transceiver (TX1) and a continuous sequence of states $|X_{0}\rangle$ with the second transceiver (TX2). The sequences from TX1 and TX2 interfered at the beam splitter (precise overlapping of pulses was achieved with an optical delay line in TX2, whereas alignment of pulse intensities was carried out by varying the bias voltage of the IM in TX1). In this configuration, odd pulses of the sequence from TX1 should interfere constructively with odd pulses of the sequence from TX2, whereas corresponding even pulses should interfere destructively. However, since the lasers in TX1 and TX2 have not been locked to each other, we observed beats: a sinusoidal intensity variation of odd pulses and another sinusoidal variation of even pulses shifted by phase of approximately π . Beats from even and odd pulses were fitted by the function $f(t,a,b,\omega,\theta) = a + b\sin(\omega t + \theta)$ (the data and their fits are presented in Fig. 3, c and 3, d). The difference between the values of the fitting parameter θ provide the phase error $\delta\theta$. (The measured value of $\delta\theta$.)

Discussion

Pulse shapes measured 'classically' (with PD) and 'quantum-mechanically' (with SPD) look similar, although some differences should be noted. First, high non-linearity of SPD and the influence of the dead time led to the fact that relative intensities of the pulses in different bases measured with PD and SPD significantly differ (this is clearly seen from the comparison of $|X_{\lambda}\rangle$ states in Fig. 3 and 4). In fact, when the number of clicks increases, dead time of the SPD plays a more significant role and an effective time of the detection is decreased, such that the measured amplitude of the signal becomes less than the real one. Thus, the ratio s/v (which nominally should be equal to 10) measured with PD is close to nominal value (see Table 1), whereas in quantum case it is four times smaller due to the non-linearity. This also partially explains the difference in the values of r_z obtained with PD and SPD. Note that the non-linearity of the SPD can be easily taken into account by pre-calibration, after which both quantum and classical values should be quite close.

As for the measurement of the phase error, the method described here is more suitable for MDI QKD and determines the relative phase error between transmitters. However, it can be easily extended to point-to-point protocols if the phase difference between the pulses in one of the TX is fixed.

Conclusion

We have introduced a simple method to estimate quality of quantum states for QKD protocols with phase-time encoding. Proposed parameters can be easily measured experimentally and can help assess the leakage of information in the implementation of such protocols. In addition, they will be useful when setting up and debugging the QKD system, particularly when tuning intensity and phase modulators.

REFERENCES

1. Scarani V., et al., The security of practical quantum key distribution, Reviews of modern physics 81 (3) (2009) 1301.

2. Bennett C.H., Gilles B., Quantum cryptography: Public key distribution and coin tossing, arXiv preprint arXiv: 2003. (2020) 06557.

3. Gisin N., et al., Quantum cryptography, Reviews of modern physics 74 (1) (2002) 145.

4. Mekhtiev E.E., et al., Polarization control algorithm for QKD systems, Journal of Physics: Conference Series. IOP Publishing, 2086 (1) (2021).

5. Grosshans F., et al., Quantum key distribution using gaussian-modulated coherent states, Nature 421 (6920) (2003) 238–241.

6. Woodward R.I., et al., Gigahertz measurement-device-independent quantum key distribution using directly modulated lasers, npj Quantum Information 7.1 (2021): 58.

7. Hiskett P.A., et al., Long-distance quantum key distribution in optical fibre, New Journal of Physics 8 (9) (2006) 193.

THE AUTHORS

GERASIN Ilya S. i.gerasin@goqrate.com ORCID: 0000-0001-5084-7056

RUDAVIN Nikita V. n.rudavin@goqrate.com ORCID: 0000-0003-0264-5710

KUPRIYANOV Pavel A. p.kupriyanov@goqrate.com ORCID: 0009-0006-1663-6806 **DVURECHENSKIY Alexander A.** a. dvurechenskiy@goqrate.com ORCID: 0009-0008-7391-0079

SHAKHOVOY Roman A.

r.shakhovoy@goqrate.com ORCID: 0000-0003-2750-0518

Received 11.07.2023. Approved after reviewing 12.09.2023. Accepted 12.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

RADIOPHYSICS

Conference materials UDC 621.396.42 DOI: https://doi.org/10.18721/JPM.163.265

Reconfigurable reflectarrays for 5/6G wireless systems with linear polarization

A.V. Lvov¹, A.N. Prikhodko^{1,2}, A.S. Shurakov^{1,2}, G.N. Goltsman^{1,2}

¹ Moscow Pedagogical State University, Moscow, Russia;

² National Research University Higher School of Economics, Moscow, Russia

^{III} andrei.lvov1707@yandex.ru

Abstract. Numerous studies on wireless technologies for the fifth and sixth generation networks are widely conducted at the moment. They are driven by potential opportunities of digitalization in the information society era. Further enlargement of data transfer rates is required to enhance virtual interactions in various public areas via appearance of new services and applications. In this work, we report on the development of a reconfigurable reflectarray for 5/6G wireless communication systems with linear polarization. The proposed reflectarray utilizes current controlling diodes in a metallic screen inserted in between of front and rear metallizations of a planar patch antenna array. This makes it capable of a digital beam steering on a microsecond scale. Performance of the reflectarray designed for operation at 15 GHz is described in terms of numerical simulations and prototyping. We also discuss prospects and technological challenges of fabricating a scaled-down version of the reflectarray for 150 GHz operation.

Keywords: reconfigurable reflectarray, 5/6G network, wireless channel, sub-terahertz communication

Funding: This study was funded by the Russian Science Foundation grant number 22-79-10279, https://rscf.ru/project/22-79-10279/.

Citation Lvov A.V., Prikhodko A.N., Shurakov A.S., Goltsman G.N., Reconfigurable reflectarrays for 5/6G wireless systems with linear polarization, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 372–376. DOI: https://doi.org/10.18721/JPM.163.265

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 621.396.42 DOI: https://doi.org/10.18721/JPM.163.265

Реконфигурируемые антенные решетки отражательного типа для беспроводных систем 6/5G с линейной поляризацией

А.В. Львов¹, А.Н. Приходько^{1,2}, А.С. Шураков^{1,2}, Г.Н. Гольцман^{1,2}

¹ Московский Педагогический Государственный Университет, Москва, Россия;

² Национальный исследовательский университет «Высшая школа экономики», Москва, Россия

^{III} andrei.lvov1707@yandex.ru

Аннотация. В настоящее время активно проводятся многочисленные исследования беспроводных технологий для сетей связи пятого и шестого поколений. Они обусловлены возрастающим потенциалом цифровизации в эпоху информационного общества. Для улучшения виртуального взаимодействия в различных общественных

© Lvov A.V., Prikhodko A.N., Shurakov A.S., Goltsman G.N., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

сферах за счет появления новых сервисов и приложений требуется дальнейшее увеличение скоростей передачи данных. В данной работе мы сообщаем о разработке реконфигурируемой антенной решетки отражательного типа для беспроводных систем 6/5G с линейной поляризацией. Предлагаемая конструкция антенной решетки основана на использовании управляющих током диодов в металлическом экране между лицевой и тыльной металлизацией двумерной решетки патч-антенн. Это обеспечивает дискретное диаграммообразование в отраженном свете с микросекундным быстродействием. Представленные в работе характеристики антенной решетки с рабочей частотой 15 ГГц получены как в рамках численного моделирования, так и прототипирования. Обсуждение перспектив и технологических сложностей изготовления масштабированной версии антенной решетки с рабочей частотой 150 ГГц также представлено в работе

Ключевые слова: реконфигурируемая антенная решетка отражательного типа, сеть 6/5G, беспроводной канал, суб-терагерцовая связь

Финансирование: Исследование выполнено за счет гранта Российского научного фонда № 22-79-10279, https://rscf.ru/project/22-79-10279/.

Ссылка при цитировании: Львов А.В., Приходько А.Н., Шураков А.С., Гольцман Г.Н. Реконфигурируемые антенные решетки отражательного типа для беспроводных систем 6/5G с линейной поляризацией // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 372–376. DOI: https://doi.org/10.18721/ JPM.163.265

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

The studies on wireless technologies for the fifth and sixth generation (5/6G) networks are of current interest. They are driven not only by a potential enlargement of data transfer rates, but by the prospects of appearance of new services and applications as well [1]. Ultra-directional transceivers are proposed to improve connection quality in sub-terahertz (sub-THz) communication channels. This makes them less vulnerable to propagation losses and fading, but more vulnerable to blockages [2]. The issue can be resolved if reconfigurable reflectarrays are used for beam routing in sub-THz data links. The reflectarrays together with a transmitter and receiver in a wireless channel should utilize optics capable of fast beam steering [3]. In this work, we report on the development of a reconfigurable reflectarray for 5/6G networks. It makes use of a diode-based design of each cell ensuring a sub-THz beam steering on a microsecond scale or faster.

Materials and Methods

Fig. 1 illustrates schematic of a 15 GHz reconfigurable reflectarray (RRA). RRA utilizes current controlling diode switches (DSs) in a metallic screen (MS) inserted in between of front and rear metallizations of a planar patch antenna array. The latter is based on a 0.338 mm thick low-loss dielectric substrate with relative permittivity $\varepsilon_r = 3.5$ [4]. This makes the design compatible with the use of a fused quartz if operation at sub-THz frequencies is considered.

Referring to Fig. 1, Gaussian beam (GB) of a linearly polarized light incident along normal to the RRA surface is reflected at angle θ determined by the configuration of up to 3 DSs. Quantities **k** and **E**₀ denote wavevector and electric field strength of incident GB. The design ensures a multidirectional beam steering by rearranging currents in MS. For turned on DSs 2–3 all over RRA and tuned on/off DS 1 in even/odd rows (or vice versa) oriented along **E**₀, in-reflection phase shift between neighboring rows is approximately 180°. Thus, bidirectional beam steering is implemented. Calculated θ swings from -15° to $+15^{\circ}$ if DSs act as ideal switches. These findings are further experimentally justified.

To measure reflective properties of the developed RRA, we designed transmitting (Tx) and receiving (Rx) planar patch antenna arrays. Using classic literature [5–7] as guidelines, we developed a first-run geometry of the antenna arrays comprising 8×8 elements. Given that desired operating frequency was in the range of 13–16 GHz, we chose a relatively thin substrate with low

© Львов А.В., Приходько А.Н., Шураков А.С., Гольцман Г.Н., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Schematic of a 15 GHz RRA in action

permittivity and small loss tangent (namely, FSD255G series PCB laminate with a thickness of 1 mm [8]). This allowed us to implement a feeding network with a microstrip line significantly narrower than the patch and to achieve efficient distribution of a microwave power in the array. In accordance with equations (14–6) and (14–7) from [5], linear dimensions of patch antennas were calculated in the computer algebra system (CAS) Maxima. The distance between them of $3\lambda_0/4$ was chosen with λ_0 denoting a free space wavelength. For an 8×8 elements patch antenna array, we calculated beam profiles in E- and H-planes with the aid of CAS Maxima.

The developed pattern of patch antennas was further equipped with a feeding network. Due to the pattern compactness, we decided not to rely on regular quarter-wave matching impedance transformers, but to implement a constant width microstrip line with multiple T-junctions. Such a geometry potentially suffers from excessive input return losses but lacks noticeable distortion of beam parameters as compared to classic patch antenna array designs. Electrical lengths of the microstrip lines from each antenna in the array to the common microwave input port were kept identical.

Results and Discussion

Fig. 2,*a* provides resulting drawing of the developed pattern of a ready-to-use Tx/Rx antenna array. This drawing was used as an input for a computer numeric control (CNC) machining with the aid of a MITS Eleven Lab milling machine.

To measure beam profiles of the fabricated antenna array prototypes, we developed an experimental setup including a microwave vector network analyzer (VNA) and 3D-printed holders. Two prototypes of the antenna array under study were connected to the VNA ports 1 and 2 through coax cables. The array planes were set parallel such that their optical axes were coaligned. Sweeping the scan angle of the receiving antenna array from -90° to $+90^{\circ}$, we measured the magnitude of S21-parameter at carrier frequency of 15 GHz. The developed antenna arrays demonstrated consistent performance in both simulations and performance tests. Moreover, the achieved beamwidths of 10° were suitable for using the arrays as remote probes in evaluation of RRA prototypes developed by us.

When prototyping RRA, all DSs 2–3 were replaced by bridges and DS 1 was replaced by a bridge/gap in even/odd rows oriented along \mathbf{E}_0 in the dendriform slots of MS (see Fig. 1). Fabrication tolerances for the slot width, w, and the spacing between the top substrate of RRA and MS, s, were found to be the most crucial. We measured relative fabrication errors $\delta w = 7.2\%$ and $\delta s = 9.5\%$, and used these values to predict margins for parameters of reflected GB. We numerically observed relative errors $\delta \theta = 5.9\%$ and $\delta I = 7.6\%$ for the angle of reflection and the intensity of the reflected beam, respectively. In the numerical simulations, the spacing between the substrate with MS and the ground plane was fixed to $\lambda_0/4$. This was consistent with our experimental findings.



Fig. 2. Developed pattern of a ready-to-use Tx/Rx antenna array (*a*). Experimental setup for measuring H-plane profiles of Tx beam after reflection from tilted mirror or RRA (*b*)

Fig. 3 demonstrates measured H-plane profile of Tx beam after reflection from RRA. The profile was compared with that reflected from tilted mirror replacing RRA, when rays in the beam obey the geometrical-optics law of reflection. The beam profiles were measured at 15 GHz in accordance with experimental setup presented in Fig. 2,*b*. As one can clearly see, behavior of main and side lobes in the beam profiles agree well. We also observed identical main lobe levels within the measurement uncertainty of 0.5 dB. The profiles of the main lobes are quantitively consistent down to -12 dB. It is also worth noting that RRA outperforms tilted mirror in terms of side lobe levels, whose peak values are correspondingly equal to -10.5 dB and -6 dB. Angle θ was fixed to 15° in all the measurements.

We believe that obtained experimental results are quite promising for further development of a miniaturized version of RRA. Thus, we expect reduction of δw and δs down to 1–2% leading to significant decrease in $\delta \theta$ and δI , when fabricating a 150 GHz RRA with the chosen form factor. This is to be achieved upon use of photo-, e-beam lithographies for deposition and patterning of thin-film metallic surfaces and precise computer-aided machining for packaging. Additionally, our simulations of RRA with different impedances of DSs in on/off states confirm usability of Schottky diodes with feasible parasitic parameters. We believe that all together proves technological robustness and suitability of the developed RRA for 5/6G wireless communication systems.



Fig. 3. H-plane profiles of Tx beam after reflection from tilted mirror or RRA

Conclusion

We developed and prototyped RRA operational at 15 GHz. The RRA design relies on a lowloss PCB substrate with relative permittivity of 3.5. This makes it a quartz-compatible and easily scalable for operation in the sub-THz band. The proposed design utilizes current controlling diodes in a metallic screen inserted in between of front and rear metallizations of a planar patch antenna array. To simplify prototyping, the fabricated RRA has 1-bit elements, the pattern of phase shift upon reflection from them is fixed such that the deflection angle equals 15°. We observe agreement between calculated and experimentally measured profiles of reflected from RRA beams. The profiles are also compared with that reflected from tilted mirror replacing RRA in position, when rays in the routed beam obey the geometrical-optics law of reflection. Behavior of main and side lobes in the beam profiles agree well. We also observed identical main lobe levels within the measurement uncertainty of 0.5 dB. The profiles of the main lobes are quantitively consistent down to -12 dB. It is also worth mentioning that RRA outperforms tilted mirror in terms of side lobe levels, whose peak values are correspondingly equal to -10.5 dB and -6 dB. The developed RRA design potentially ensures up to a 3-bit resolution of the elements. This, in turn, significantly increases number of available states upon digital beamforming in reflected light. Use of Schottky diodes for in-reflection phase shift in the RRA elements enables sweep time on a microsecond scale. We believe that all together suggests suitability of the proposed RRA for beam routing in 5/6G wireless communication systems.

REFERENCES

1. Yeh C., Do Jo G., Ko Y.J., Chung H.K., Perspectives on 6G wireless communications, ICT Express. 9 (1) (2023) 82–91.

2. Shurakov A., Moltchanov D., Prikhodko A., Khakimov A., Mokrov E., Begishev V., Belikov I., Koucheryavy Y., Gol'tsman G., Empirical blockage characterization and detection in indoor sub-THz communications, Computer Communications. 201 (2023) 48–58.

3. Chen Z., Ning B., Han C., Tian Z., Li S., Intelligent reflecting surface assisted terahertz communications toward 6G, IEEE Wireless Communications. 6 (28) (2021) 110–117.

4. FSD888T PCB laminate. URL: http://www.eltm.ru/svch-materialy-fsd.html/nid/2087. Accessed Mar. 31, 2023.

5. Balanis C.A., Antenna theory: analysis and design. – John Wiley & sons, 2016.

6. Volakis J.L., Antenna engineering handbook. - McGraw-Hill Education, 2007.

7. Levine. E., A study of microstrip array antennas with the feed network, IEEE Transactions on antennas and propagation, 31 (4) (1989) 426.

8. FSD255G PCB laminate. URL: http://www.eltm.ru/svch-materialy-fsd.html/nid/2106. Accessed Jun. 07, 2023.

THE AUTHORS

LVOV Andrey V. andrei.lvov1707@yandex.ru ORCID: 0000-0002-2969-7695

PRIKHODKO Anatoliy N. anatprikh1995@yandex.ru ORCID: 0000-0002-4859-8975 SHURAKOV Alexander S. alexander@rplab.ru ORCID: 0000-0002-4671-7731

GOLTSMAN Gregory N. goltsman@rplab.ru

ORCID: 0000-0002-1960-9161

Received 20.07.2023. Approved after reviewing 05.09.2023. Accepted 05.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535 DOI: https://doi.org/10.18721/JPM.163.266

Creation of an automated system for adjusting the position of the laser radiation axis for the air communication channel

K.S. Nazarova¹[™], V.V. Davydov^{1,2}

¹Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia

[™] knazarova0@ya.ru

Abstract. A model of an optical system for adjusting the axis of laser radiation on a photodetector module in a plane perpendicular to laser radiation has been developed. The operation of the optical system for controlling the position of the laser radiation axis on the photosensitive layer of the photodetector is simulated. Experimental studies are presented on correcting the position of the plates relative to the direction of the laser radiation axis and the value of stresses to change their refractive indices. The technique for determining the optimal parameters of the plates in the developed optical system for various tasks has been confirmed. The laser axis is automatically corrected and the displacement can be observed in real time. This allows data from other devices to be analyzed to identify the cause of the displacement and take the necessary action. Obtaining information on changes in displacement is a new principle not available in previously developed systems.

Keywords: Optical system, semiconductor laser, laser radiation axis, quartz plates, refractive index, linear and quadratic approximations

Citation: Nazarova K. S., Davydov V.V., Creation of an automated system for adjusting the position of the laser radiation axis for the air communication channel, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 377–382. DOI: https://doi.org/10.18721/JPM.163.266

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535 DOI: https://doi.org/10.18721/JPM.163.266

Разработка автоматической системы подстройки положения оси лазерного излучения для воздушного канала связи

К.С. Назарова^{1,⊠}, В.В. Давыдов^{1,2}

¹ Санкт-Петербургский Политехнический университет Петра Великого

Санкт-Петербург, Россия;

² Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия

[™] knazarova0@ya.ru

Аннотация. Разработана модель оптической системы для юстировки оси лазерного излучения на модуле фотодетектора в плоскости, перпендикулярной лазерному излучению. Смоделирована работа оптической системы управления положением оси лазерного излучения на фоточувствительном слое фотодетектора. Представлены экспериментальные исследования по коррекции положения пластин относительно направления оси лазерного излучения и величины напряжений для изменения

© Nazarova K.S., Davydov V.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

их показателей преломления. Подтверждена методика определения оптимальных параметров пластин в разработанной оптической системе для различных задач. Ось лазерного излучения автоматически корректируется, и можно наблюдать смещение в реальном времени. Это позволяет анализировать данные других устройств для выявления причин смещения и принятия необходимых мер. Получение информации об изменениях в смещении - новый принцип, недоступный в ранее разработанных системах.

Ключевые слова: оптическая система, полупроводниковый лазер, ось лазерного излучения, кварцевые пластины, показатель преломления, линейная и квадратичная аппроксимации

Ссылка при цитировании: Назарова К.С., Давыдов В.В. Разработка автоматической системы подстройки положения оси лазерного излучения для воздушного канала связи // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 377–382. DOI: https://doi.org/10.18721/JPM.163.266

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Currently, the volume of information that is transmitted via different communication lines is constantly increasing [1-6]. The optical network, especially in large cities, operates with high overload [7-9]. The use of various methods of transmitting information with an increase in traffic volumes does not solve this problem. It is required to lay new lines that can damage existing communications. If you lay new communication channels in underground utilities, then you need to change everything, which is very expensive and takes a lot of time. The laying of overhead communication lines with optical fiber between buildings is prohibited, as this creates many problems when the cable breaks, for example from strong wind, etc. One of the solutions to the problem is the use of aerial optical communication channels (laser radiation spreads between modules through the air at distances of no more than 200 meters in the city, in mountainous areas and the sea, these distances increase to 2,000 m or more). The use of radio communication systems when transmitting large amounts of information in the city between buildings is impractical (low transmission speed and a large amount of electromagnetic interference) [2, 3, 9, 10]. In the other two cases, radio communication competes with the aerial optical communication channel (AOCC).

One of the problems of such systems is the displacement of the axis of the laser radiation, which contains information, relative to the plane of the photodetector. A shift from the center of the photosensitive layer of the photodetector module leads to a decrease in the amplitude of the recorded signal, which can lead to loss of information. Some AOCC designs use a focusing lens [11-13]. This allows to focus the laser radiation on photosensitive layer. These systems are often used in digital fiber optic communication lines (FOCL) [14-16]. Due to the reflections of the laser beam, information is distorted, especially when the axis of the laser radiation is shifted to the edge of the lens. The laser beam has a size. When it collides with the edge of the plate, diffraction occurs. Bit errors occur and the information cannot be recovered. Therefore, the development of an automatic system for the position of the laser radiation axis without the use of additional focusing elements in the receiving module is extremely relevant for the developing direction of aerial optical communication channels. Our goal is to develop a new automatic system to control the position of the laser axis.

Design of the aerial optical communication channel and the system of automatic adjustment of the axis of laser radiation

An analysis of the methods used to construct the position of the axis of laser radiation and the photodetector module in AOCC using the movement of a laser or photodetector, or mirrors, or lenses, allowed us to offer a new optical system of automatic adjustment. Fig. 1 shows the design of an aerial optical communication channel developed by us with a new auto-tuning module.

The adjustment of the position of the laser radiation axis is carried out according to the maximum amplitude of the current of the recorded optical signal on the photodetector module 6. In the case of a laser radiation axis from the center of the photodetector module 6, an error signal is

[©] Назарова К.С., Давыдов В.В. 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Block diagram of an aerial optical communication channel: server *1*, laser transmitting module with electrooptical modulator *2*, automatic system for adjusting the position of the laser radiation axis *3*, laser radiation *4*, multifunctional power supply *5*, photodetector module *6*, photodetector power supply *7*, analog-digital converter (ADC) *8*, processing device *9*, current meter *10*, data processing and transmission device *11*, radio receiving device *12*, information processing and control device *13*, airspace *14*, *L* is the airspace length, U_{treg} is the applied voltage

generated in the device 13, which is transmitted using a radio channel to the building where the transmitting laser module 2 is located. A fundamentally new element in this design is an automatic optical system developed by me to adjust the position of the laser beam axis. Fig. 2 shows the design developed by us, one of two parts of the automatic system for aligning the position of the laser axis 3 for the AOCC under study (Fig. 1).

Fig. 2 shows the geometric position of the variation of the laser axis in the oX plane. To change the position of the laser radiation axis in the oY plane, such a part of the optical system design as shown in Fig. 2 is used, Only the quartz plates 2 (Fig. 2) will be oriented to the plane of incidence of laser radiation along the oZ axis at a different angle.

In order to implement the process of controlling the position of the laser radiation axis using the optical structure 3 we developed (Fig. 1), it is necessary that radiation with a plane-parallel front should arrive at the end of the plates. For this, the laser transmitting module 2 uses built-in optics (a macro lens with a short focal length). The macro lens is placed at the end of the laser resonator, so that the laser beam is placed in its focus.

The position of the laser beam axis is controlled by applying voltage to the ends of the plates *I*. Under the action of voltage, the refractive index *n* of quartz or other material from which the plate is made changes. The position of the laser radiation axis is shifted by the separation of Δl_x .



Fig. 2. Block diagram of part of automatic system for adjusting the position of the laser radiation axis along the X coordinate in a plane perpendicular to oZ: quartz plate I, laser radiation 2, copper plate 3

and Δl_y in a given plane. To determine the values of Δl_x and Δl_y it is necessary to derive mathematical relations from the change of *n*. Taking into account the semetricality of the arrangement of the plates relative to each other, the formula for calculating Δl_x or Δl_y will be the same (the difference will be only in the angles of inclination of the plates α .

Calculation of the displacement of the laser radiation axis and investigation of the operation of the automatic adjustment scheme

Based on the presented design of the optical system (Fig. 2), a calculation was performed to determine the offset of the radiation axis Δl_x in the *oX* plane.

$$\Delta l_x = l_1 - l_2,\tag{1}$$

$$l_{1} = d(\sin(\alpha_{1}) - \frac{\frac{\sin(\alpha_{1}) * n}{n_{0}} * \cos(\alpha_{1})}{\sqrt{1 - (\frac{\sin(\alpha_{1}) * n}{n_{0}})^{2}}}),$$
(2)

$$l_{2} = d(\sin(\alpha_{2}) - \frac{\frac{\sin(\alpha_{2}) * n}{n_{0}} * \cos(\alpha_{2})}{\sqrt{1 - (\frac{\sin(\alpha_{2}) * n}{n_{0}})^{2}}}).$$
(3)

Eqs. (2) and (3) with angles α_3 and $\alpha 4$ only will be used to calculate Δl_y . The main parameter that is used to control the value of Δl_x is *n*. As an example, Fig. 3 shows the results of these studies with a detailed emphasis on the value of $\lambda = 1550$ nm at a temperature of $T \approx 294$ K.



Fig. 3. Experimental dependence of the change in the refractive index *n* on λ . Graphs (*a*), (*b*) and (*c*) correspond to the following material: sapphire, quartz, and KU-1 glass

To determine the optimal position of the plates to the optical axis of the laser transmitting module, the optimal value of the angle α was determined for three materials that are supposed to be used for the manufacture of plates (quartz, glass KU-1 and sapphire). The dependences of ΔI_x or ΔI_y were differentiated by the angles of an and equated to zero. For all three materials (the refractive index was used for $\lambda = 1550$ nm at a temperature $T \approx 294$ K), the value of the optimal angles was about 52 degrees. This angle is at the point with the maximum steepness of the graph slope. Here the system's sensitivity to displacement is higher. Determination of the optimal angle is necessary to ensure high sensitivity of the system to changes in the position of the axis of laser radiation relative to the center of the photosensitive layer of the receiving module 6 (Fig. 1). Fig. 4 shows as an example the results of a study of the effect of changes in the angle of inclination α on the displacement ΔI_y .

The analysis of the obtained results showed that the most optimal is the placement of deflecting plates I (Fig. 2) at an angle $\alpha \approx 52^{\circ}$. This optimal value of the angle α within ± 30 minutes corresponds to all three materials (quartz, glass KU-1 and sapphire). Plates with d = 4 cm were used in the studies.



Fig. 4. Calculation of change in displacement of laser radiation axis from inclination angle of plates for various refractive indices of quartz (measured using a refractometer (*a*), linear approximation from tabular values when determining *n* for $\lambda = 1550$ nm (*b*))

To determine the possibility of adjusting the position of the laser radiation axis, the change in Δl_x from the change in the value of the refractive indices n of three materials was investigated. Fig. 5 shows the results of these studies for the case $\alpha = 52^\circ$, d = 4 cm.



Fig. 5. Dependence of change in Δl_x on the index of refraction. Graphs (a), (b) and (c) correspond to sapphire, quartz and glass KU-1

The studies have shown that there is no big difference between quartz and sapphire in the characteristics of laser radiation position adjustment. In some cases of increasing the value of d and changing the optimum angle α , it is more appropriate to make plates from KU-1 glass. Advantages will be sapphire in the cost of plates, as well as this material is easier to process and polish. Sapphire should be preferred for use in different regions of the world. Quartz is a glass with a crystal lattice in the far zone. A pattern forms on its surface, especially after polishing, in wet and frosty weather conditions. Laser radiation is scattered and information is lost. It is possible to make a protective system with temperature stabilization (this will increase the cost and size of the structure). But it is more reasonable to use sapphire for all three reasons discussed, as well as a slight advantage in characteristics (Fig. 2). The conducted studies allowed us to establish that the range of variation of the optimal values of the angle α is from 35 to 65 degrees for different values of *d*. It is more appropriate to use a plate up to 100 mm thick. It should also be noted that an increase in the value of d leads to a slight increase in the constant voltage U_{gov} , which must be applied to the plates to change *n*. In experiments, the U_{gov} values changed to 42.8 V.

Conclusion

The results obtained confirm the possibility of using an automatic system developed by me to adjust the position of the laser radiation axis on the plane of the photodetector module in FOCL. Depending on the limitations on the size of the optical system (the *d* value is no more than 15 cm), it is possible to provide a maximum range of adjustment of the position of the laser axis in the range ± 13.5 mm. With an increase in the size of the deflecting plates and, accordingly, the U_{gov} values, the values of Δl_x or Δl_y change.

Due to the reflection, which does not follow from mathematical calculations. This fact must be taken into account when developing such systems in the case of transmitting an optical signal over FOCL over long distances. With an increase in L, in order to ensure stable FOCL operation, it is necessary to increase the setting range of Δl_{x} .

REFERENCES

1. **Petrov A.A.**, Improvement frequency stability of caesium atomic clock for satellite communication system, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). Vol. 9247 (2015) 739–744.

2. Mihov E.D., Nepomnyashchiy O.V., Selecting informative variables in the identification problem Journal of Siberian Federal University - Mathematics and Physics. 9(4) (2016) 473–480.

3. **Ryzhenko I.N., Lutsenko A.E., Varygin O.G., Nepomnyashchiy O.V.,** Carrier compensation mode implementation in satellite communication channels. In: Proceedings of 2019 International Siberian Conference on Control and Communications, SIBCON 2019, Vol. 8729665 (2019) 23–29.

4. Lukashev N.A., Davydov V.V., Glinushkin A.P., Rud' V.Yu., Improving characteristics of microwave frequency standard on Hg-199 ions for telecommunication systems, Journal of Physics: Conference Series. Vol. 1)1326) (2019) 012046.

5. **Petrov A.A., Grebenikova N.M.,** Some Directions of Quantum Frequency Standard Modernization for Telecommunication Systems, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). Vol. 11118 LNCS (2018) 641–648.

6. Lukashev N.A., Glinushkin A.P., Rud V.Yu., Lukyantsev V.S., Microwave low mass-dimensional frequency standard on Hg- 199 ions, Journal of Physics: Conference Series. Vol. 1410(1) (2019) 012211.

7. Davydov V.V., Dudkin V.I., Velichko E.N., Karseev A.Yu., Fiber-optic system for simulating accidents in the cooling circuits of a nuclear power plant, Journal of Optical Technology (A Translation of Opticheskii Zhurnal). Vol. 82(3) (2015) 132–135.

8. Davydov V.V., Dudkin V.I., Karseev A.Yu., Nuclear magnetic flowmeter - Spectrometer with fiber -optical communication line in cooling systems of atomic energy plants, Optical Memory and Neural Networks (Information Optics). Vol. 22(2) (2013) 112–117.

9. Ermolaev A.N., Krishpents G.P., Vysoczkiy M.G., Compensation of chromatic and polarization mode dispersion in fiber-optic communication lines in microwave signals transmittion, Journal of Physics: Conference Series. Vol. 741(1) (2016) 012171.

10. Tarasenko M.Y., Lenets V.A., Akulich N.V., Yalunina T.R., Features of use direct and external modulation in fiber optical simulators of a false target for testing radar station, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), Vol. 10531 LNCS (2017) 227–232.

11. Kozlova T.I., Konovoltzev M.I., Lebedev P.S., Techko O.L., Method for correcting the laser beam position of laser beam, Foton express. Vol. 6 (2021) 201-205.

12. Aliev A.A., Two-coordinate optoelectronic system for determining the position of a ring laser, Radiooptic. Vol. 2 (2016) 11–25.

13. Isaenko D., Reznikov B., Rodin S., Vakorina D., Development of Communication Channel for data Transmission Over Single-Mode Optical Fiber in Environmental Monitoring System from Remote Multifunctional Complexes, Proceedings of the 2022 International Conference on Electrical Engineering and Photonics, EExPolytech-2022, (2022) 315–319.

14. Şerbănescu M., Pandelea M., Achim A., Iliescu M., Command and control system for laser beam position within transmission line at CETAL-PW, U.P.B. Sci. Bull., Series A. Vol. 80(3) (2018) 207–216.

15. Franczek E., Franczek W., Popiolek-Masajada A., Laser Beam Positioning by Using a Broken-Down Optical Vortex Marker, Applied Sciiences. Vol. 11(16), (2021) 7677–7682.

16. **Popovskiy N.I., Valiullin L.R.,** Features of the construction of fiber-optic communication lines with code division multiplexing, Journal of Physics: Conference Series. Vol. 1695(1) (2020) 012120.

THE AUTHORS

NAZAROVA Kseniya S. Knazarova0@ya.ru ORCID: 0009-0004-4496-1505 DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: 0000-0001-9530-4805

Received 09.07.2023. Approved after reviewing 14.09.2023. Accepted 14.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 537.86 DOI: https://doi.org/10.18721/JPM.163.267

Magneto-electric dipole antenna as a transceive element in a phased array

V.D. Burtsev¹[™], N.O. Bulatov¹, A.V. Nikulin¹, P.V. Semkin², S.A. Kuznetsov², D.S. Filonov¹

¹ Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russia;

² Joint-Stock Company Information Satellite Systems Reshetnev, Zheleznogorsk, Russia.

[™] burtsev.vd@phystech.edu

Abstract. We propose a transceive element of a phased array antenna for satellite communications systems operating in K_u frequency band. The proposed element based on a magneto-electric dipole antenna. A substrate-integrated waveguide and a cruciform slit of a special shape are used as a feeding element. We aim to drive the circular polarization at two subbands simultaneously. We performed electromagnetic simulations and optimization of the single element and applied array factor to evaluate beam steering, directivity and cross-polarization. The antenna elements were optimized using 8 criteria to obtain acceptable *S*-parameters and ellipticity. As a results, we obtain satisfactory cross-polarization for R_x -band of <-20 dB. For T_x -band we obtained value <-14.2 dB for oblique beam position and of -20.1 dB for normal beam position. The results obtained indicate the prospects of using such broadband transceive elements in phased arrays.

Keywords: Magneto-electric dipole, Antenna, Phased Array, Sequential Feeding, SIW waveguide_

Funding: The research was supported in part by the Federal Academic Leadership Program Priority 2030 (mathematics) and the Ministry of Science and Higher Education of the Russian Federation under the project 075-11-2022-011 (numerical part).

Citation: Burtsev V.D., Bulatov N.O., Nikulin A.V., Semkin P.V., Kuznetsov S.A., Filonov D.S., Magneto-electric dipole antenna as a transceive element in a phased array, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 383–388. DOI: https://doi.org/10.18721/JPM.163.267

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Burtsev V.D., Bulatov N.O., Nikulin A.V., Semkin P.V., Kuznetsov S.A., Filonov D.S., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 537.86 DOI: https://doi.org/10.18721/JPM.163.267

Магнитоэлектрический диполь в качестве приемопередающего элемента в фазированной антенной решетке

В.Д. Бурцев¹[∞], Н.О. Булатов¹, А.В. Никулин¹, П.В. Семкин², С.А. Кузнецов², Д.С. Филонов¹

¹ Московский физико-технический институт (национальный исследовательский университет), Долгопрудный, Россия;

² АО НПП «Информационно-спутниковые системы Решетнёв», г. Железногорск, Россия

[™] burtsev.vd@phystech.edu

В данной работе рассматривается приемопередающий элемент Аннотация. фазированной антенной решетки для систем спутниковой связи, работающих в Ки диапазоне частот. Предлагаемый элемент основан на магнитоэлектрической дипольной антенне. В качестве питающего элемента используются встроенный в подложку волновод и крестообразная щель специальной формы. Целью работы является управление круговой поляризацией в двух поддиапазонах одновременно. Были проведены электромагнитное моделирование и оптимизация одиночного элемента, а также применен фактор массива для оценки направления луча, направленности и кроссполяризации. Элементы антенны были оптимизированы по 8 критериям для получения приемлемых S-параметров и коэффициента эллиптичности. В результате была получена достаточно хорошая кроссполяризация для R_x -диапазона <-20 дБ. Для T_x -диапазона мы получили значение <-14,2 дБ для наклонного положения луча и -0,1 дБ для нормального положения луча. Разработанная топология на печатной плате соответствует производственным требованиям. Полученные результаты указывают на перспективность использования таких широкополосных приемопередающих элементов в фазированных решетках.

Ключевые слова: магнитоэлекрический диполь, антенна, фазированная антенная решетка, последовательная запитка, SIW-волновод

Финансирование: данная работа поддержана частично Программой стратегического академического лидерства «Приоритет 2030» (математическое описание) и Министерством науки и высшего образования Российской Федерации по проекту -075 011-2022-11 (численное моделирование).

Ссылка при цитировании: Бурцев В.Д., Булатов Н.О., Никулин А.В., Семкин П.В., Кузнецов С.А., Филонов Д.С. Магнитоэлектрический диполь в качестве приемопередающего элемента в фазированной антенной решетке // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 383–388. DOI: https://doi.org/10.18721/JPM.163.267

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Modern satellite communications systems require developing compact and planar phased array antennas operating in K_u band. Such an antenna should have possibilities of fast electronical beam steering in azimuthal or/and elevations planes. Such an array can be implemented as two dual-polarized sub-arrays for R_x and T_x bands [1–3] or one combined linear polarized transceive array [4]. Combined transmit-receive phased arrays antennas for K_u are challenging to implement because an antenna element should work in a broad band. To implement an array with the desired properties one can, use magneto-electric dipole (MED) [5–7]. Such a MED has been known for some time and has managed to gain popularity due to its wide operating band (up to ~30% [8]),

© Бурцев В.Д., Булатов Н.О., Никулин А.В., Семкин П.В., Кузнецов С.А., Филонов Д.С., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого. high directivity [9] and relatively simple geometry [10]. Its performance is based on constructive interference of near electromagnetic fields of a magnetic dipole (effective current frame) and an electric dipole (two poles with different potentials) [11].

We have allocated the R_x (left-handed circular polarization (CP): 10.95-11.7 GHz) and T_x (right-handed CP: 14–14.25 GHz) bands and designed MED geometry in order for both of these bands to be covered. Since the original Γ -shaped feeding element is extremely difficult to implement for modern mass production, such a phased array would greatly lose in performance. This is why we decided to use sequential laminated waveguide or substrate integrated waveguide (SIW) feeding [12]. Although sequential feeding causes frequency beam steering, it is quite stable when operating at the single frequency.

Another challenge is to develop a broadband array element operating in circular polarization at both band simultaneously [13]. In such arrays it is difficult to maintain acceptable level of ellipticity and cross-polarization for R_x and T_x bands. In this work we propose and perform electromagnetic simulation and optimization of such a broad-band MED element for phased arrays in K_x band.

It is noticeable that such an element, with the proper manufacture of feeding SIW and cruciform slits, provides circular polarizations depending on the direction of the feeding, and the suggested array is capable of electrical beam steering in the presence of phase shifters.

Methods

Full-wave electromagnetic simulation was performed using finite-element method (FEM)-based solver and far field approximation to compute S-parameters and radiation patterns. The geometry of MED and its geometrical parameters are shown in Fig. 1. The MED was implemented on Rogers RO3003 substrate ($\varepsilon_r = 3$, tg $\delta = 0.001$) from embedded material library. All traces were modeled using lossy copper of 36 µm in thickness. Arms of MED were connected to the upper ground plate using vias. In this upper ground plate, we modeled a slot in the SIW to feed the MED. This SIW waveguide was implemented between upper and lower ground planes that are interconnected using vias. The space between these planes was filed also by Rogers RO3003 substrate. The structure was driven by two emitting waveguide ports 1 and 2, whereas 3 and 4 are receiving ports.

The parameters of the MED, SIW and feeding slot were optimized using trust region algorithm. We used 8 optimization criteria such as minimization of reflection coefficient S_{11} and transmission coefficient S_{21} . In addition, we computed axial ratio and minimized ellipticity at six frequency points that are the borders and the middle of R_x and T_x bands. After this minimization,



Fig. 1. Suggested geometry of MED and its parameters

the array factor was employed to obtain the far field lattice sum. The array period was 13mm in both x/y directions. This period was optimized to avoid strong sidelobes at T_x band for oblique beam positions. The number of elements was set to 32 in both directions to obtain desired directivity and beam width. We show the results for three beam positions: 0°, +15°, +30° at the central frequency for each band (11.325 and 14.125 GHz). For each beam position we estimated directivity, ellipticity, cross-polarization, -3dB beam width and sidelobe level.

Results

S-parameters computed in EM simulations are shown in Fig. 2. In this plot we also denote R_x and T_x bands as blue and pink zones. Here S_{11} and S_{22} are the reflection coefficients, S_{21} and S_{41} are the port isolation coefficients, and S_{31} is the directional coupling or SIW waveguide characteristics [12]. Such parameters as S_{12} , S_{32} and S_{42} are not shown because they are identical to S_{21} , S_{41} and S_{31} . As it can be observed, we obtained the worst value of S_{11} coefficient in in the lower R_x band of -17.9 dB whereas worst value S_{22} coefficient in the upper T_x band of -16.8 dB. The port isolation S_{21} and S_{41} are -16.3 dB and -13.7 dB respectively for the R_x band, whereas -17.4 dB and -25.2 dB for the T_x band. The directional coupling S_{31} is -0.61 dB and -0.68 dB for the R_x and T_x band respectively. It is important to note that this directional coupling has to be toughly optimized depending on the number of elements in the full array to maintain desired magnitude distribution.



Fig. 2. Simulated S-parameters (dB) in the range from 10.7 GHz to 14.5 GHz



Fig. 3. Directivity patterns of the suggested MED at frequencies of 11.325 GHz and 14.125 GHz for three beam positions: normal, 15° and 30°

The directivity patterns and antenna array evaluation are shown in Fig. 3. In this figure we show left-handed CP for R_x band, and right-handed CP for T_x band. It is important to note that we succeeded to optimize the ellipticity for the central frequency, where it equals to 1.17 dB for the 0°, 1.15 dB for 15° and 1.59 dB for 30°. It is observed that optimized antenna provided low level of ellipticity in R_x band that lead to cross polarization level below -20 dB for all beam positions. For T_x band the ellipticity becomes to 1.72 dB for the 0°, 2.05 dB for 15° and 3.3 dB for 30°, and therefore cross polarization comes to -20.1 dB for 0°, whereas it drops to -18.2 and -14.2 dB for oblique beams. Nevertheless, minimization of cross polarization is a common problem [13, and requires thorough optimization of the array [14].

Conclusion

We performed EM simulations and optimization of magneto-electric dipoles for combined circular polarized transceiver phased array antenna operating in K_u -band. We obtain acceptable level of cross-polarization for R_x -band of <-20 dB. For T_x -band we obtained value <-14.2 dB for oblique beam position and of -20.1 dB for normal beam position. Proposed and designed MED can be employed in a phased array, which can be used for beam steering in a presence of the phase shifters However, to construct the array period and directional coupling coefficient has to be further optimized.

Acknowledgments

The research was supported in part by the Federal Academic Leadership Program Priority 2030 (mathematics) and the Ministry of Science and Higher Education of the Russian Federation under the project 075-11-2022-011 (numerical part).

REFERENCES

1. Aljuhani A.H., Kanar T., Zihir S., Rebeiz G.M., A Scalable Dual-Polarized 256-Element Ku-Band Phased-Array SATCOM Receiver with $\pm 70^{\circ}$ Beam Scanning, IEEE MTT-S Int. Microw. Symp. Dig., (2018) 1203–1206.

2. Gultepe G., Kanar T., Zihir S., Rebeiz G.M., A 1024-Element Ku-Band SATCOM Phased-Array Transmitter with 45-dBW Single-Polarization EIRP, IEEE Trans. Microw. Theory Tech., 69 (9) (2021) 4157–4168.

3. Aljuhani A.H., Kanar T., Zihir S., Rebeiz G.M., A Scalable Dual-Polarized 256-Element Ku-Band SATCOM Phased-Array Transmitter with 36.5 dBW EIRP per Polarization, 2018 48th Eur. Microw. Conf. EuMC. (2018) 938–941.

4. **Kapusuz K.Y., Sen Y., Bulut M., Karadede I., Oguz U.,** Low-profile scalable phased array antenna at Ku-band for mobile satellite communications, IEEE Int. Symp. Phased Array Syst. Technol., Jul. (2016).

5. Ge L., Luk K.M., A wideband magneto-electric dipole antenna, IEEE Trans. Antennas Propag., 60 (11) (2012) 4987–4991.

6. Ketham R., Althuwayb A.A., Kumar A., Low-profile Magneto-electric Dipole Antenna, (2021).

7. Guo J., Chu Q. X., A Dual-Band Nested Ku/Ka Magneto-Electric Dipole Antenna Array with High Isolation, 2022 Int. Conf. Microw. Millim. Wave Technol. ICMMT 2022 - Proc., (2022).

8. Causse A., Rodriguez K., Bernard L., Sharaiha A., Collardey S., Compact Bandwidth Enhanced Cavity-Backed Magneto-Electric Dipole Antenna with Outer Γ -Shaped Probe for GNSS Bands, Sensors. 21 (11) (2021) 3599.

9. Kakhki M.B., Dadgarpour A., Antoniades M.A., Sebak A.R., Denidni T.A., Dual Complementary Source Magneto-Electric Dipole Antenna Loaded with Split Ring Resonators, IEEE Access, 8 (2020) 59351–59361.

10. Limpiti T., Chantaveerod A., Petchakit, W., Design of a magneto-electric dipole antenna for FM radio broadcasting base station antenna implementation, Prog. Electromagn. Res. M, 60 (2017) 75–84.

11. Li M., Luk K.-M., Wideband Magneto-electric Dipole Antennas, Handb. Antenna Technol., (2015) 1–43.

12. Uchimura H., Takenoshita T., Fujii M., Development of a 'laminated waveguide, IEEE Trans. Microw. Theory Tech., 46 (12) (1998) 2438–2443.

Zeng Q., Xue Z., Ren W., Li W., Yang S., A high-gain circular polarization beam scanning transmit array antenna, IET Microwaves, Antennas Propag., 15 (11) (2021) 1519–1528.
 Hussain S., Qu S. W., Bu D., Wang X.H., Sharif A.B., A meta-surface loaded, low profile 28

GHz phased array antenna," Int. J. RF Microw. Comput. Eng., 32 (1) (2022).

THE AUTHORS

BURTSEV Vladmir D. burtsev.vd@phystech.edu ORCID: 0000-0000-0000-0000 SEMKIN Petr V. semkin@iss-reshetnev.ru

BULATOV Nikita O. vosheva.ts@mipt.ru ORCID: 0000-0003-1145-3075 **KUZNETSOV Stanislav A.** ksa@iss-reshetnev.ru

NIKULIN Anton V. vosheva.ts@mipt.ru ORCID: 0000-0002-5786-4972

FILONOV Dmitry S. filonov.ds@mipt.ru ORCID: 0000-0002-5394-8677

Received 04.07.2023. Approved after reviewing 24.07.2023. Accepted 28.07.2023.

Conference materials UDC 537.86 DOI: https://doi.org/10.18721/JPM.163.268

Using mobile phone as a ripeness sensor

I.I. Mikheev¹[™], V.D. Burtsev¹, T.S. Vosheva¹, I.M. Yusupov², D.S. Filonov¹

¹ Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russia;

² ITMO University, St. Petersburg, Russia

[™] mikheev.ii@phystech.edu

Abstract. In this paper, the possibility of using a mobile phone as a ripeness sensor is considered. The concept of differentiation based on changes in the dielectric constant of the product as it matures (increase in sugar content) is proposed. A scheme is considered in which one device plays the role of a base station and transmits a Wi-Fi signal at a frequency of 2.4 GHz, and another device uses a specially developed mobile application to analyze this signal and determine by its changes whether a fruit located in the near field of a telephone antenna is edible. The results of the distinctness of different types of products, as well as different degrees of ripeness (unripe/ripe) for one product (avocado) are presented. The sensitivity of the method is also evaluated based on comparison with laboratory measurements using high-quality patch antennas.

Keywords: product ripeness, smartphone sensor, agriculture, smartphone application

Funding: The research was supported in part by the Federal Academic Leadership Program Priority 2030 (manufacturing and measuring) and by the Russian Science Foundation Project 19-79-10232 (numerical part).

Citation: Mikheev I.I., Burtsev V.D., Vosheva T.S., Yusupov I.M., Filonov D.S., Using mobile phone as a ripeness sensor, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 389–393. DOI: https://doi.org/10.18721/JPM.163.268

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 537.86 DOI: https://doi.org/10.18721/JPM.163.268

Использование мобильного телефона в качестве сенсора спелости

И.И. Михеев¹, В.Д. Бурцев¹, Т.С. Вошева¹, И.М. Юсупов², Д.С. Филонов¹

¹ Московский физико-технический институт (национальный

исследовательский университет), Долгопрудный, Россия;

² Университет ИТМО, Санкт-Петербург, Россия

[™] mikheev.ii@phystech.edu

Аннотация. В данной работе рассматривается возможность использования мобильного телефона в качестве сенсора спелости. Предлагается концепция различения на основе изменения диэлектрической проницаемости продукта по мере его поспевания (увеличение содержания сахара). Рассматривается схема, в которой один аппарат играет роль базовой станции и передает вай-фай сигнал на частоте 2,4 ГГц, а другой аппарат при помощи специально разработанного мобильного приложения анализирует данный сигнал и по его изменениям определяет, съедобен ли фрукт, находящийся в ближнем поле телефонной антенны. Приводятся результаты различимости различных видов продуктов, а также различных степеней спелости (неспелый/спелый) для одного продукта (авокадо). Также оценивается чувствительность метода, исходя из сравнения с лабораторными измерениями при помощи добротных патч-антенн.

© Mikheev I.I., Burtsev V.D., Vosheva T.S., Yusupov I.M., Filonov D.S., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: зрелость продукта, сенсор, сельское хозяйство, приложение для смартфона

Финансирование: Данная работа была поддержана частично Программой стратегического академического лидерства «Приоритет-2030» (изготовление и измерения) и Российским научным фондом по проекту 10232-79-19 (численное моделирование).

Ссылка при цитировании: Михеев И.И., Бурцев В.Д., Вошева Т.С., Юсупов И.М., Филонов Д.С. Использование мобильного телефона в качестве сенсора спелости // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 389–393. DOI: https://doi.org/10.18721/JPM.163.268

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Smartphones have firmly entered human activity and, with the help of many imperceptible changes, significantly improve the quality of life. Various nuances associated with the growth of the world's population force the agrotechnical sector of the market to grow proportionally, throwing new challenges to sensorics. It is required to provide many agricultural enterprises with accessible, but at the same time reliable device. In this paper we propose to use an antenna inside smartphones as sensors for the ripeness of products. There are nearly 7 billon people using smartphones in their daily routine that make this idea easily accessible. In contrast, many sensors for the ripeness of products have been known, for example, non-invasive nitrate sensors [1], external sensors connected to the phone [2], optical systems [3] and others. However, a rather big disadvantage of all these systems is that they are, in essence, separate devices. Smartphone antennas [4] themselves are rather sensible resonators, which allows them to accurately react on changes in such parameters of the immediate environment, such as dielectric permittivity. Thus, we already have a compact spectral analyzer, for the full functioning of which it is necessary to develop software. Such a solution will also allow analyzing all products right on the spot in a non-invasive way and in real time, reducing the logistical costs of laboratory research.

Methods

To measure the incoming signal, a Wi-Fi antenna operating in the range from 2.412 GHz to 2.472 GHz was selected. By default, the Android system can provide periodic information about the signal from this antenna (in dBm), however, such a series is highly discrete in time, since one measurement occurs approximately once every 15 seconds to reduce overall power consumption. However, it is possible to neglect this protection and disable the built-in smartphone throttling in the application for the duration of its operation, customizing it to the required needs. In the following experiments, we settled on two measurements per second. The WifiManager [5] service was used to obtain the relevant data (RSSI signal strength). The graphical interface was implemented in the Kotlin language.

It was found that an external signal (from a base station at the nearest cell tower) is not enough to determine nearby fruits: the random noise of the incoming signal played a more significant role than the change in the environment. Therefore, we decided to put the experiment as follows. Two smartphones are located close to each other, and access point mode is enabled on one of them. This mode is autonomous and even in the absence of an external network creates a local signal picked up by a second mobile device on which the developed application is running.

To assess the possibility of measuring the signal in such a system, numerical modeling was carried out using the finite element method in electrodynamics in the CST Studio Suite software package. Due to the uncertainty of the exact topology of the antenna, as well as the differences in it for different brands of phones, we are further operating only with relative values, and we assume the geometry as IFA [4], as a common version of a telephone antenna. We placed two antennas at a fixed distance from each other (Fig. 1,*a*). There were various dielectric samples between them, simulating real products. In addition, the antenna was surrounded by battery packs, which are simple metal screens at these frequencies, as well as an effective phone frame consisting of various plastics and composites, whose permittivity was assumed to be equal to 2. The dielectric constant and the loss tangent of the products were taken from the article [6]. In full-wave modeling, 3 cases were considered: free space, a cucumber ($\varepsilon = 56+14i$) and an avocado ($\varepsilon = 77+9i$). The results of



Fig. 1. Numerical experiment to distinguish different types of products: general setup (*a*); results (*b*)

the calculations can be seen in Fig. 1,*b*. It is noticeable that the transmitted signal (S_{21}) strongly depends on the object under test. In free space, the antennas exchange energy well, and when a dielectric is placed between them with losses, part of the electromagnetic energy, depending on the size of the sample and the magnitude of losses in the dielectric, goes into thermal.

Thus, the numerical experiment predicted that using an internal smartphone antenna to distinguish the types of products based on the electrodynamic response. To verify this statement, two modern smartphones (Doogee S40Pro and Redmi Note 8 Pro), driven by Android system, were used. Since the position of the antenna in them was unknown in advance, and the information in the manuals is a trade secret, it was decided to find the direction of the best communication of the antennas, i.e. the relative location of the phones, in which the signal received by the second device from the first would be maximized. This direction is equivalent to the lobes of the antenna pattern pointing at each other.

We found that the maximum communication between the phones was carried out by turning them to each other with touchscreens (Fig. 2,*a*). The graphical interface of the application (Fig. 2,*b*) in the measurement mode plotted the dependence of the signal strength on time and saved data, as well as showed the instantaneous magnitude of the signal and the width of the band used. In this experiment, only one 20 MHz wide band was used at a frequency of 2412 MHz. The results of measurements distributed over time are shown in Fig. 2,*c*. The colored line shows the median, the box contains 50% of the sample, and also each of the whiskers extends another 24.65% to the side. The punctured dots on the graph indicate single outliers. It is clearly noticeable



Fig. 2. Measurements of different types of products: general setup (*a*); application user interface (*b*); results of the measurements (*c*)

that, although the absolute values of the energy received in a real experiment do not coincide with the predictions of numerical modeling, however, monotony is quite preserved, which suggests that with proper calibration and collection of a database of various responses, the proposed method is fully suitable for determining the type of product based on its dielectric properties.

However, in addition to the goal of identifying the type of product, the idea was also to find out whether this product is ripe or unripe. To do this, we found a statistical difference in the readings of the received smartphone antenna power next to the corresponding products. An avocado was chosen for this experiment because it can ripen while in a warm illuminated place. Thus, it is possible to dynamically monitor the electrical response from our system for several days, and then evaluate the points of ripeness and rotting according to the data.

In this experiment, the signal level coming to the smartphone antenna remained the same, around -30 dBm, while the difference in signals between start (unripe fruit) and finish (ripe fruit) was lesser than 1 dBm, which is about 0.3%. To make sure that there is a difference in the dielectric constant of this fruit at various stages of ripeness, a laboratory experiment was conducted. For this purpose, two patch antennas were manufactured (Fig. 3,*b*), impedance matched (Fig. 3,*a*). To carry out the experiment, P9374A Keysight Streamline USB Vector Network Analyzer was used. During these measurements, it was found that, indeed, there is a statistically significant difference between ripe and unripe avocados, however, even with antennas matched at -15 dB, this difference is only 2 dB at -30 dB (Fig. 3,*c*). This, in particular, explains the fact that with the help of ordinary smartphone antennas, we were not able to get noticeable differences.

In fact, this can be a predictable result since smartphone antennas are created by engineers in such a way as to be able to receive a signal in a very different dielectric environment.



Fig. 3. Measurements of differences between ripe and unripe avocados: return loss graphs (*a*) of manufactured patch antennas (*b*); energy exchange between patch-antennas through the tested objects (*c*)

Conclusion

Thus, it can be concluded that at this stage it is impossible to obtain accurate results by the proposed method on the ripeness of medium-sized fruits. The intended field for study is the determination of the efficiency of the method on large berries (such as watermelon or melon). In addition, these methods are still working to determine the type of product located near the phone, respectively, the second area of development will be the collection of a database of various responses and analysis of the results obtained, depending on the brand of the phone (antenna model) and the size of the product.

Acknowledgments

The research was supported in part by the Federal Academic Leadership Program Priority 2030 (manufacturing and measuring) and by the Russian Science Foundation Project 19-79-10232 (numerical part).

REFERENCES

 Alahi M.E. E., Li X., Mukhopadhyay S., Burkitt L., A Temperature Compensated Smart Nitrate-Sensor for Agricultural Industry. IEEE Transactions on Industrial Electronics, (2017) 1–1.
 Marić A., Scherf K.A., A Portable Gluten Sensor for Celiac Disease Patients May Not

Always Be Reliable Depending on the Food and the User. Front Nutr. (8) (2021) 712992.

3. O'Farrell M., Lewis E., Flanagan C., Lyons W., Jackman N., Comparison of k-NN and neural network methods in the classification of spectral data from an optical fibre-based sensor system used for quality control in the food industry. Sensors and Actuators B: Chemical, 111–112, (2005) 354–362.

4. Zhan Li, Rahmat-Samii Y., Optimization of PIFA-IFA Combination in Handset Antenna Designs. IEEE Transactions on antennas and propagation, 53 (5) (2005).

5. WifiManager reference in Android documentation URL: https://developer.android.com/ reference/android/net/wifi/WifiManager Accessed: March 2023

6. Nelson S.O., IEEE Instrumentationand Measurement Technology Conference Proceedings - Dielectric Spectroscopy of Fresh Fruits and Vegetables, (1) (2005) 360–364.

THE AUTHORS

MIKHEEV Ilya I. mikheev.ii@phystech.edu YUSUPOV Ildar M. ildar.yusupov@metalab.ifmo.ru ORCID: 0000-0002-4878-7039

BURTSEV Vladmir D. burtsev.vd@phystech.edu ORCID: 0000-0000-0000-0000 **FILONOV Dmitry S.** filonov.ds@mipt.ru

ORCID: 0000-0002-5394-8677

VOSHEVA Tatyana S.

vosheva.ts@mipt.ru ORCID: 0000-0002-5786-4972

Received 04.07.2023. Approved after reviewing 24.07.2023. Accepted 28.07.2023.

Conference materials UDC 53.06. DOI: https://doi.org/10.18721/JPM.163.269

Improvement of the thermoregulator of the quantum frequency standard on rubidium-87 atoms

E.V. Isupova¹[™], S.Yu. Shvetsov², V.V. Davydov^{1,3}

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² Russian Institute of Radionavigation and Time, St. Petersburg, Russia;

³ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia

□ isupova.e24@mail.ru

Abstract. The necessity of increasing the metrological characteristics of the quantum frequency standard on rubidium-87 atoms is substantiated. It is noted that the main destabilizing factor that reduces the accuracy of frequency determination is temperature. To control it, the quantum standard uses thermostating and thermoregulation. It is established that the systems currently used for laser and optical components cannot provide the necessary temperature stability, which is required to improve the metrological characteristics of the quantum standard. A new circuit of a quantum frequency standard temperature controller with a rubidium gas cell using a PID controller and an instrument amplifier has been developed, and its operation in the LTspice environment has been simulated. Transient processes in the circuit of the thermostat are analyzed. A decrease in the influence of temperature on the optical components and characteristics of the laser in the quantum frequency standard has been established (the signal-to-noise ratio in the recorded optical signal has increased), which, in turn, improves the short-term stability of the QFS frequency by 7-10%, synchronization of time scales in the object.

Keywords: thermoregulation, thermostating, quantum frequency standard with rubidium gas cell, feedback, power amplifier, stability, differential amplifier, PID controller

Citation: Isupova E.V., Shvetsov S.Yu., Davydov V.V., Improvement of the thermoregulator of the quantum frequency standard on rubidium-87 atoms, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 394–399. DOI: https://doi.org/10.18721/JPM.163.269

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.06. DOI: https://doi.org/10.18721/JPM.163.269

Усовершенствование терморегулятора квантового стандарта частоты на атомах рубидия-87

Е.В. Исупова¹[™], С.Ю. Швецов², В.В. Давыдов^{1,3}

¹ Санкт-Петербургский Политехнический университет Петра Великого, Санкт-Петербург, Россия;

² Российский институт навигации и времени, Санкт-Петербург, Россия;

³ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М. А. Бонч-Бруевича, Санкт-Петербург, Россия

[™] isupova.e24@mail.ru

Аннотация. Представлена улучшенная схема терморегулятора квантового стандарта частоты с рубидиевой газовой ячейкой. Данный стандарт частоты является важной

© Isupova E.V., Shvetsov S.Yu., Davydov V.V.,2023. Published by Peter the Great St. Petersburg Polytechnic University.

частью в спутниковых навигационных системах, так как обеспечивают точность и стабильность и определяют положение и скорость спутника. Для борьбы с основным дестабилизирующим фактором — температурой — в мерах частоты применяют термостатирование и терморегуляцию. Рассмотрена структурная схема терморегулятора, а также проведено моделирование принципиальной схемы в среде LTspice. Проанализированы переходные процессы в схеме и подобраны необходимые номинальные значения емкостей и сопротивлений.

Ключевые слова: терморегуляция, термостатирование, квантовый стандарт частоты с рубидиевой газовой ячейкой, обратная связь, усилитель мощности, стабильность, дифференциальный усилитель, ПИД-регулятор_

Ссылка при цитировании: Исупова Е.В., Швецов С.Ю., Давыдов В.В. Усовершенствование терморегулятора квантового стандарта частоты на атомах рубидия-87 // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 394–399. DOI: https://doi.org/10.18721/JPM.163.269

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Space navigation systems largely depend on the generation of accurate time and frequency signals [1-3]. Global satellite navigation systems are the Russian Global Navigation Satellite System (GLONASS), the US Global Positioning System (GPS), the European System (Galileo) and the Chinese Navigation Satellite System (BeiDou). The widespread use of satellite navigation systems, which are used to determine the location of air, water and ground objects, would be difficult without the simultaneous development of frequency standards and synchronization methods [4, 5].

On board the satellites are atomic clocks that provide accuracy and stability and determine the position and speed of the satellite. The most widely used type of atomic clock is the quantum frequency standard with a rubidium gas cell [6].

One of the main factors impairing the frequency stability of the rubidium quantum frequency standard (QFS) is temperature. A change in temperature leads to a change in the values of the parameters of all elements. To combat the influence of temperature and its changes, QFS parts are made of heat-resistant materials with possibly small temperature coefficients [7–11]. In a wide range of ambient temperature determined by the operating conditions, this measure is not enough, so there is a need for the use of thermostating and thermoregulation.

The essence of thermostating is to provide for the entire circuit such a mode in which the average value and the change in temperature of the medium surrounding the thermostated object, as well as the change in heat flows in this medium are so small that they lead to changes in the generated frequency, significantly less than permissible [6].

These conditions are created with the help of special devices, thermostats, which ensure the constancy of temperature in a closed volume with a certain degree of accuracy of its maintenance.

Table 1 shows the main characteristics of the maximum deviations in temperature stability for different temperatures in the blocks of the quantum frequency standard.

Analysis of the developments has shown that it is quite difficult to solve the problem of thermal stabilization in various blocks of QFS on rubidium 87 atoms using these devices. This is due to the fact that quantum standards used on mobile objects have strict limitations both in mass and size. In addition, there are restrictions on the possible increase in electrical energy consumption during the modernization of the structure.

All these restrictions cannot be met when using the design of the thermoregulators presented in Table 1. Therefore, based on the analysis of modern developments, it is necessary to modernize the current design of the thermostat while maintaining the size of the unit in which it is installed, the characteristics of weight and energy consumption. One of the possible solutions to this problem is presented in the work.

© Исупова Е.В., Швецов С.Ю., Давыдов В.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

Table 1

Developers of thermoregulators	T_{max} , K	Obtained stability, uK	Scope of use	
Bonetti	348	±500	communication base stations, guidance systems, precision measurements	
Dratler	308	±10	radars, satellites	
Esman	300	±100	precision measurements, radars, satellites, atomic clocks	
Lee	296	±60	global positioning, telemetry, guidance systems	
Sarid	333	±15	atomic clocks, communication base stations, telemetry	
Grubic	320	±40	precision measurements, radars, satellites	
Larsen	301	±25	global positioning, atomic clocks, telemetry	
Harvey	301	±25	global positioning, atomic clocks, telemetry	

Comparative analysis of various developments of thermoregulators to compensate for temperature surges

Method of constructing and modeling the operation of the thermostat

In most cases, thermistor temperature sensors are used in the rubidium QFS thermostat in operation, since they are sensitive, small and have fairly good stability. To ensure good performance, the sensors must have good thermal contact with the thermostat, as well as avoid any mechanical influences.

The classical design of the thermoregulator used in the rubidium QFS is shown in Fig. 1.



Fig. 1. Block diagram of the thermostat: temperature sensor R_{∂} , Wheatstone Bridge WB, differential amplifier DA, amplifier A, power amplifier PA, heater H, stabilizing circuit SC

One of the schemes suitable for temperature measurement is the Wheatstone Bridge with a temperature sensor used as one of the branches of the bridge. This sensor generates a signal proportional to the temperature value. Fig. 2 shows a diagram of the Wheatstone bridge, and the place where the sensor is switched on is marked.

Then the signal goes to the amplifiers, which are necessary to increase the sensitivity of the temperature control system and provide the power required for the operation of the executive bodies. In this case, the signal passes through the feedback – the stabilizing circuit. The output of the power amplifier is controlled by the currents that flow to the heater. It, in turn, is connected by temperature feedback to the sensor.

The main disadvantages of this scheme are the large error in reading temperature data, the slow reaction of the bridge to unbalance with fast flow effects, which often occur in outer space.


Fig. 2. Wheatstone bridge with temperature sensor

Therefore, we have developed a new design of the thermostat. In this scheme, instead of an amplifier block, a proportional-integral-differentiating (PID) regulator block will be used, which allows for a higher level of regulation. A control signal is generated in this device to obtain the necessary accuracy and quality of the transient process. The scheme of the developed PID controller is shown in Fig. 3.



Fig. 3. Scheme of the developed PID controller

Also, an instrumental amplifier built on three operational amplifiers is introduced into the new circuit of the thermostat. The instrumental amplifier is a high-precision device for amplifying differential voltages, which is suitable for operation in conditions of high noise and strong temperature fluctuations. This device has a high input impedance, which allows to work with sensors with a large output impedance.

Results and Discussion

In the new design of the thermostat, in order to improve the stability of the entire QFS, the cascade of the power amplifier with a feedback chain was upgraded. In the LTspice environment, the schematic diagram of the new and old temperature controller is assembled. Transient processes at the output of the power amplifier are simulated. Fig. 4 shows its results.

Capacitances and resistances are selected in such a way that the output voltage located in the power amplifier unit instantly reacts to a single voltage surge at the input of the circuit, and the oscillatory processes after this surge are minimal.

Fig. 5, *a* shows the results of a study of changes in the resistance of a temperature sensor depending on the temperature of the air in the heat chamber for the old circuit of the thermostat in the discriminator. The temperature in the thermal chamber changed every 4 hours. The change in the resistance of the thermistor was about 3 ohms, which is unacceptable for a thermostat in the QFS. Fig. 5, *b* shows the simulated results of the same experiment for the new circuit of the thermostat.



Fig. 4. Simulation results: transients in the old scheme (a); transients in the new scheme (b)

In the newly developed design, the sensitivity of the resistance to temperature changes is ≈ 1 ohm. The scheme works out the temperature change more quickly. The use of a PID controller in the design of the thermostat allows you to increase the speed in the thermal stabilization system by 65% compared to the previously used design.



Fig. 5. Changing the resistance of the thermistor in the thermal chamber (a); simulation of changes in the resistance of the thermistor in the new circuit of the thermostat (b)

Conclusion

Analysis of data on the operation of temperature control systems in various models of QFS on rubidium-87 atoms with an optical gas cell and the results of modeling the thermostat circuit showed that the new implementation scheme works correctly, the introduction of a PID controller and an instrument amplifier instead of the previously used transistor power amplifier stage improves the operation of the thermostat. The threshold for changing the resistance of the thermistor in the Wheatstone bridge ≈ 1 Ohm allows to improve the signal-to-noise ratio of the recorded optical signal at least twice. This improves the short-term stability of the QFS frequency by 7–10%, synchronizes the time scales in the satellite navigation system and increases the accuracy of determining the coordinates of the object. The conducted experiments have shown the effectiveness of using a new circuit of the thermostat.

REFERENCES

1. Petrov A., Davydov V. and Grebenikova N., Journal of Communications Technology and Electronics 63(11) (2018) 1159–1164.

2. Lukashev N.A., Davydov R.V., Glinushkin A.P., Rud' V.Y., Improving characteristics of microwave frequency standard on Hg-199 ions for telecommunication systems Journal of Physics: Conference Series. 1326(1) (2019) 012046.

3. Riehle F., Frequency standard. Basic and applications, WILEY-VCH Verlag CmbH Co. KGaA: New-York (2008).

4. Riley W.J., Rubidium Frequency Standard Primer, W.J. Riley –Hamilton Technical Services Beaufort (2011) 149.

5. Riley W.J., A Modern Militarized Rubidium Frequency Standard, Microwave Journal (2002).

6. Daniel A. Steck., Rubidium-87 D Line Data, Los Alamos National Laboratory Technical report LA-UR-03-8638 (2001).

7. **Dupuis R.F., Lynch T.J., Vaccaro J.R.,** Rubidium Frequency Standard for the GPS IIF Program and Modifications for the RAFSMOD Program, Proceedings of the 2008 IEEE International Frequency Control Symposium, Honolulu, HI (2008) 655–660.

8. Lutwak R., Emmons D., English T., Riley W., Duwel A., Varghese M., Serkland D. K., Peake G.M., The Chip-Scale Atomic Clock - Recent Development Progress, Proceedings of the 35th Annual Precise Time and Time Interval (PTTI) Applications and Planning Meeting, San Diego, CA (2003).

9. Arinushkina K., Valov A., Isupova E., Improvement of the frequency standard on cesium atoms used in spacecraft for remote sensing of the Earth, in. Proceedings of 8th International Conference on Information Technology and Nanotechnology (ITNT), Samara, Russian Federation. (21992028) (2022) 20302.

10. Huang X., Xia B., Zhong D., An S., Zhu X., Mei G., A Microwave Cavity with Low Temperature Coefficient for Passive Rubidium Frequency Standards, Proceedings of the 2001 IEEE International Frequency Control Symposium (2001) 105–107.

11. Zhu H.B., Wu Z.B., Liu G.Q., Study of quartz temperature characteristics for precise oscillator applicationsr, Acta. Phys. SinCh Ed, (62 014205) (1) (2013).

THE AUTHORS

ISUPOVA Ekaterina V. isupova.e24@mail.ru ORCID: 0000-0002-0963-5497 SHVETSOV Sergey Yu. shvetsov0000@gmail.com ORCID: 0000-0001-6849-1481

DAVYDOV Vadim V. davydov_vadim66@mail.ru ORCID: 0000-0001-9530-4805

Received 10.07.2023. Approved after reviewing 09.08.2023. Accepted 11.08.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 535.8 DOI: https://doi.org/10.18721/JPM.163.270

Two-channel fiber-optic communication line for measuring the parameters of active phased antenna arrays in the far zone a landfill conditions

E.M. Gryaznova^{1™}, E.D. Semicheva²

¹ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

² Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

[™] katya.gryaznova@mail.ru

Abstract. The necessity of using fiber-optic communication lines (FOCL) for testing active phased antenna arrays (APAA) in landfill conditions in a complex electromagnetic environment is substantiated. The advantages of FOCL application for working with microwave signals during testing of various antennas especially in the far zone are noted. The developed two-channel FOCL for measuring APAA parameters in the far zone is presented. The choice of the components of the optical system for transmitting microwave signals is justified. The results of the study of the characteristics of the fiber optic and directional patterns of antenna arrays are presented

Keywords: fiber-optic communication line, laser radiation, active phased array antenna, microwave signal, far range, dynamic range, radiation pattern.

Citation: Gryaznova E.M., Semicheva E.D., Two-channel fiber-optic communication line for measuring the parameters of active phased antenna arrays in the far zone a landfill conditions, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 400–405. DOI: https://doi.org/10.18721/JPM.163.270

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535.8 DOI: https://doi.org/10.18721/JPM.163.270

Двухканальная волоконно-оптическая линия связи для измерения параметров активных фазированных антенных решеток в дальней зоне в условиях полигона

Е.М. Грязнова¹[™], Е.Д. Семичева²

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия;

² Санкт-Петербургский 193232Политехнический университет Петра Великого

Санкт-Петербург, Россия,

katya.gryaznova@mail.ru

Аннотация. Обоснована необходимость использования волоконно-оптических линий связи (ВОЛС) для тестирования активных фазированных антенных решеток (АФАР) в условиях полигона в сложной электромагнитной обстановке. Отмечены преимущества применения ВОЛС для работы с СВЧ сигналами при тестировании различных антенн, особенно в дальней зоне. Представлена разработанная двухканальная ВОЛС для измерения параметров АФАР в дальней зоне. Обоснован выбор компонентов оптической системы для передачи СВЧ сигналов. Представлены результаты исследования характеристик волоконно-оптической системы и диаграмм направленности антенных решеток.

© Gryaznova E.M., Semicheva E.D., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: волоконно-оптическая линия связи, лазерное излучение, активная фазированная антенная решетка, СВЧ сигнал, дальняя зона, динамический диапазон, диаграмма направленности

Ссылка при цитировании: Грязнова Е.М., Семичева Е.Д. Двухканальная волоконнооптическая линия связи для измерения параметров активных фазированных антенных решеток в дальней зоне в условиях полигона // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 400–405. DOI: https:// doi.org/10.18721/JPM.163.270

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In the modern world much attention is paid to the development of systems for transmitting information and determining the position of object coordinates using microwave signals [1-6]. In these systems development is done mainly in three directions: radio navigation, radio bearing in various applications and radar. Among radars a large segment is occupied by stations with active phased array antennas. The use of optoelectronic and optical methods [12-15] for transmitting, generating and processing microwave signals makes it possible to create devices and systems of the microwave range with parameters unattainable by traditional electronic means due to the properties of optical fiber: ultra-low losses and dispersion (for a microwave signal), wide transmission bandwidth, immunity to electromagnetic interference, complete galvanic isolation, mechanical flexibility, low weight and dimensions [9-18].

One of the difficult tasks that developers of antenna arrays solve is related to their testing and configuration [6–8]. Especially the greatest difficulties arise with APAA due to the fact that it is necessary to suppress the side lobes in the APAA directional pattern, and this requires tests in the far zone [19]. This will clearly determine the side lobes of the radiation pattern and the nature of their changes from various parameters as well as other characteristics of the antenna. This is only possible in landfill conditions. In this case it is necessary to solve the problem of transmitting information without distortion in the area of high-power electromagnetic interference. The most appropriate solution for the transmission of information in such conditions is the use of FOCL. The development of a FOCL design for APAA tests in the far zone in landfill conditions is the goal of this work.

Design of fiber-optic system and principle of its operation

To measure the APAA parameters in the far zone in the landfill conditions we have developed the following system the block diagram of which is shown in Fig. 1.



Fig. 1. Developed measuring system for testing APAA with FOCL

© Грязнова Е.М., Семичева Е.Д. 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The system consists of two antenna posts, the distance between which is 1 km. Antenna post 1 (AP1) includes the investigated APAA, microwave signal generators, spectrum analyzers, as well as PC placed in the operator's post to analyze the results. Antenna post 2 (AP2) contains an auxiliary horn. The signal between the antenna posts is transmitted via a fiber-optic communication line.

This system allows measuring APAA parameters in two modes: transmission mode and reception mode. The system also allows to work in two bands: 1-2 GHz and 8-12 GHz. In the transmission mode the APAA unit connected to a generator and PC which control the APAA with computer simulator installed in it, emits a signal in one of two frequency ranges, which is received by the receiving horn. The signal from the horn goes to a low—noise amplifier (LNA), and then to an optical transmitter. The optical signal is sent via fiber to the receiver in AP1. Then the signal is sent via the switch to the PC at the operator's post. A signal is transmitted from the spectrum analyzer through the switch to the PC, which is emitted by the APAA.

During tests of the APAA in reception mode the signal of one of the ranges from the generator located in AP1 goes to the receiver through second channel of the FOCL, then to the LNA and the horn, which acts as an element of the microwave signal emission. The received APAA signal is sent to the spectrum analyzer, the information from which is displayed on the PC.

Results of experimental investigation and discussion

The main characteristic of any fiber optic cable for transmitting analog microwave signals is the dynamic range. For a stable transmission of information it is necessary to work on a linear section of the amplitude characteristic of the FOCL. The source of the microwave signal was a frequency generator, and the output power was recorded using a spectrum analyzer. In Fig. 2 the obtained amplitude characteristic of the developed FOCL for various frequencies of microwave signal emission is presented.



Fig. 2. Amplitude characteristic of the developed FOCL



Fig. 3. Frequency response of the developed FOCL at different temperatures

Analysis of the data obtained allows us to establish that the dynamic range of the microwave signal transmission is 60 dBm. This value is sufficient for stable transmission of the microwave signal during APAA tests in various modes.

The frequency response of the FOCL was also measured at various temperatures because of the fact that in the landfill conditions the temperature may be different, and the conditions for temperature stabilization cannot always be fully realized. The measurements were carried out using a vector analyzer of circuits and a thermal camera. Fig. 3 shows obtained amplitude-frequency characteristic of the developed FOCL.

As results show the frequency response of the developed FOCL practically does not change in the operating frequency range of APAA. The unevenness of the transfer characteristic at frequencies of 1-12 GHz is \pm 3 dB. At frequencies above 12 GHz, there is a significant decrease in the signal amplitude.

The results obtained also show that the developed FOCL allows transmitting stable microwave signals in the frequency range from 1 to 12 GHz. This conclusion made it possible to conduct studies of changes in the APAA radiation pattern in the landfill conditions with high accuracy and determine the APAA parameters at which the suppression of the side lobes of the directional pattern is the lowest. Fig. 4 shows an example of the APAA radiation patterns obtained in landfill conditions using a coaxial cable and a fiber optic cable.

The analysis of the results obtained (Fig. 4) shows that the use of a fiber optic cable allows to obtain a correct radiation pattern that corresponds to the calculated one for the antenna (Fig. 5). In the directional pattern there is no distortion and broadening along the main lobe and side lobes due to noise and interference. The result obtained allows to adjust the headlights to the desired scanning mode.



Fig. 4. APAA radiation pattern obtained using a coaxial cable (left) and using the developed FOCL (right) for transmitting microwave signals



Fig. 5. Calculated radiation pattern for the developed FOCL

Conclusion

The analysis of the data obtained shows that the design we have developed, which includes a two-channel fiber-optic line for transmitting information, can be used to configure and test APAA in a landfill conditions in the frequency range from 1 to 12 GHz.

The results obtained show that the developed design of the fiber optic cable is resistant to temperature fluctuations in a wide range of its changes. This means that the element base used and the principle of building the FOCL can be used for radar with APAA at various facilities (sea and land-based). In addition the temperature drop along its length L, which is possible in landfill conditions, is not substantial for the design of the FOCL (one part of the FOCL can be placed in the air, another part is laid in an aqueous medium). For these reasons the distance L between two antenna posts in the case of high—power APAA studies can be increased up to 10-15 km if necessary.

REFERENCES

1. Davydov V., Fokin G., Moroz A., Lazarev V., Instantaneous Interference Evaluation Model for Smart Antennas in 5G Ultra-Dense Networks, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 13158 LNCS (2022) 365–376.

2. Nhan N.T., Podstrigaev A.S., Likhachev V.P., Myazin N.S., Makeev S.S., Study of detection characteristics in recognition of simple radio pulses and signals with lfm and psk in the autocorrelation receiver, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 12525 LNCS (2020) 415–423.

3. Lukashev N.A., Davydov R.V., Glinushkin A.P., Rud' V.Yu., Improving characteristics of microwave frequency standard on Hg-199 ions for telecommunication systems, Journal of Physics: Conference Series. 1326 (1) (2019) 012046.

4. Fokin G., Vehicles Tracking in 5G-V2X UDN Using Range and Bearing Measurements, IEEE Vehicular Networking Conference, VNC-2021. (2021) 103–106.

5. Likhachev V.P., Podstrigaev A.S., Trong Nhan N., Study of the accuracy of determining the location of radio emission sources with complex signals when using autocorrelation and matrix receivers in broadband tools for analyzing the electronic environment, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 12525 LNCS (2020) 326–333.

6. Nikolaev D., Chetiy V., Dudkin V., Determining the location of an object during environmental monitoring in conditions of limited possibilities for the use of satellite positioning, IOP Conference Series: Earth and Environmental Science. 578 (1) (2020) 012052.

7. Sviatkina V., Kuptsov V., Davydov V., Rud V., On possibility of using of spectral analysis for control the energy distribution of electromagnetic waves in radar channels. Proceedings of ITNT 2020 - 6th IEEE International Conference on Information Technology and Nanotechnology. 9253166 (2020) 45–49.

8. Davydov V., Reznikov B., Dudkin V., New Optical System for Long Distance Control of Electrical Energy Flows, Energies. 16 (2023) 1040–1052.

9. Smirnova S.M., Nikolaev D.I., The research of temperature instability influence of optic communication line on the phase difference a deep-sea direction finder, Journal of Physics: Conference Series. 1695 (1) (2020) 012136.

10. Pchelkin G.A., Rud V.Yu., Multifunctional fiber optic system for microwave signals transmitting in frequency range from 0.135 to 40 GHz, Journal of Physics: Conference Series. 1745(1) (2021) 012014.

11. Pchelkin G.A., Fadeenko V.B., Davydov V.V., Features of the transmission of microwave signals at offshore facilities, Journal of Physics: Conference Series. 1368 (2) (2019) 022045.

12. Podstrigaev A.S., Lukiyanov A.S., Smolyakov A.V., Nikitina M.I., The expediency of fiber-optical communication line used in different schemes of receiver tract of the radio-monitoring complex, Journal of Physics: Conference Series. 1368 (2) (2019) 022027.

13. Jianping Y., Microwave photonics IEEE/OSA, Journal of Lightwave Technology. 27 (3) (2009) 314–335.

14. Clark T.R., Waterhouse R., Photonics for RF front ends, IEEE Microwave magazine. 12 (3) (2011) 87–95.

15. Ridgway R. W., Dohrman C.L., Conway J.A., Microwave Photonics Programs at DARPA, IEEE/OSA Journal of Lightwave Technology. 32 (20) (2014) 3428–3439.

16. Fadeenko V.B., Pchelkin G.A., Rud V.Yu., Features of the transmission of microwave signals in the range of 8-12 GHz in the maritime radar station over fiber-optic communication line, Journal of Physics: Conference Series. 1400 (4) (2019) 044010.

17. Sinicyna E.A., Galichina A.A., Lukiyanov A.S., Podstrigaev A.S., A study of temperature dependence of phase shift in optoelectronic path of direction finder channels, Journal of Physics: Conference Series. 1236 (1) (2019) 012075.

18. Moroz A.V., Gubareva D.V., Rud V.Yu., Development of a fiber-optic microwave signal transmission system for an X-band receiving module with dual frequency conversion, Journal of Physics: Conference Series. 2086 (1) (2021) 012061.

19. Filatov D.I., Galichina A.A., Vysoczky M.G., Yalunina T.R., Rud' V.Yu., Features of transmission at analog intermediate frequency signals on fiber – optical communication lines in radar station, Journal of Physics: Conference Series. 917 (8) (2017) 082005.

THE AUTHORS

GRYAZNOVA Ekaterina M. katya.gryaznova@mail.ru ORCID: 0000-0001-6761-251X SEMICHEVA Ekaterina D. semicheva.ed@edu.spbstu.ru ORCID: 0009-0006-9883-1647

Received 11.07.2023. Approved after reviewing 10.08.2023. Accepted 14.08.2023.

Conference materials UDC 537.876 DOI: https://doi.org/10.18721/JPM.163.271

Optimization of a prism coupler for a THz photonic integrated metamaterial Si waveguide: simulation and experiment

S.V. Seliverstov¹[™], S.S. Svyatodukh^{1,2}, A.N. Prikhodko^{1,2}, A.S. Shurakov^{1,2}, E.D. Sheveleva¹, G.N. Goltsman^{1,2}

¹ Moscow State Pedagogical University, Moscow, Russia;

² National Research University Higher School of Economics, Moscow, Russia

[™] sv.seliverstov@mpgu.su

Abstract. The use of terahertz radiation to create data transmission systems with ultra-high transfer rate still remains a kind of *terra incognita* of our time. The main difficulty in using terahertz radiation for these purposes is associated with high losses in standard metal waveguides at these frequencies. One of the possible solutions is the use of all-dielectric waveguides. So, the coupling waveguides of this type with other devices is an actual and scientifically significant task. In this paper we present the results of simulating and measuring the insertion loss of a coupling prism interface for a terahertz waveguide based on metamaterial high resistive silicon platform. The obtained S₂₁ parameter value of -0.5 dB for a coupler apex width of 90 µm and a coupler length of 3500 µm at frequency of 0.15 THz is in good agreement with the experimentally measured one. These devises will be a part of the future next-generation terahertz data communication system with a high data transfer rate.

Keywords: terahertz photonics, waveguide coupling, photonic integrated circuit, metamaterial waveguide

Funding: The study was supported by a grant from the Russian Science Foundation 21-72-10119, https://rscf.ru/project/21-72-10119/.

Citation Seliverstov S.V., Svyatodukh S.S., Prikhodko A.N., Shurakov A.S., Sheveleva E.D., Goltsman G.N., Optimization of a prism coupler for a THz photonic integrated metamaterial Si waveguide: simulation and experiment, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 406–410. DOI: https://doi.org/10.18721/JPM.163.271

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 537.876 DOI: https://doi.org/10.18721/JPM.163.271

Оптимизация согласующей призмы для ТГц фотонного интегрального метаматериального кремниевого волновода: моделирование и эксперимент

С.В. Селиверстов¹, С.С. Святодух^{1,2}, А.Н. Приходько^{1,2}, А.С. Шураков^{1,2}, Е.Д. Шевелёва¹, Г.Н. Гольцман^{1,2}

¹ Московский педагогический государственный университет, Москва, Россия;

² Национальный исследовательский университет «Высшая школа экономики», Москва, Россия

[™] sv.seliverstov@mpgu.su

Аннотация. Использование терагерцового излучения для создания систем связи со сверхвысокой скоростью передачи данных до сих пор остается своего рода *terra incognita* нашего времени. Основная трудность использования терагерцового излучения для

© Seliverstov S.V., Svyatodukh S.S., Prikhodko A.N., Shurakov A.S., Sheveleva E.D., Goltsman G.N., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

этих целей связана с большими потерями в стандартных металлических волноводах на этих частотах. Одним из возможных решений является использование полностью диэлектрических волноводов. Таким образом, согласование волноводов данного типа с другими устройствами является актуальной и научно значимой задачей. В этой статье мы представляем результаты моделирования и измерения вносимых потерь согласующего интерфейса на основе призмы для интегрированного терагерцового волновода на платформе метаматериального высокоомного кремния. Полученное значение S21-параметра в -0.5 дБ для ширины острия призмы в 90 мкм и длины призмы в 3500 мкм на частоте 0.15 ТГц хорошо согласуется с экспериментальными данными. Эти устройства станут частью будущей терагерцовой системы передачи данных нового поколения с высокой скоростью передачи данных.

Ключевые слова: терагерцовая фотоника, согласование волноводов, фотонная интегральная схема, метаматериальный волновод

Финансирование: Работа выполнена при поддержке гранта РНФ № 10119-72-21, https://rscf.ru/project/10119-72-21/.

Ссылка при цитировании: Селиверстов С.В., Святодух С.С., Приходько А.Н., Шураков А.С., Шевелёва Е.Д., Гольцман Г.Н. Оптимизация согласующей призмы для ТГц фотонного интегрального метаматериального кремниевого волновода: моделирование и эксперимент // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 406–410. DOI: https://doi.org/10.18721/JPM.163.271

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Latest advances in such modern fields as internet of things [1] or big data processing [2] have led to the need to dramatically increase the rate of wireless data transmission. The solution to this problem is possible by transfer to higher frequencies of the carrier signal. In particular, the use of terahertz (THz) range of the electromagnetic radiation spectrum looks promising. For the effective use of radiation in this range, it is necessary to solve a number of problems related primarily to the fact that THz radiation is strongly absorbed by water vapor contained in the atmosphere. There are some transparency windows in the THz water vapor absorption spectrum, but their use makes it possible to create a THz data transfer system that operates only at short distances (about the size of a room) [3]. These systems will operate like Wi-Fi, but will have a much higher data transfer rate. For example, a such system with data transfer rate reaches of up to 1 Tbit/s has been previously demonstrated [4].

Such systems should be equipped with compact receiving and transmitting devices, the basic element of which is a THz waveguide. The main challenge here is that standard waveguides (including coplanar waveguides, metallic microstrip lines, hollow metallic waveguides) used for similar tasks today are not acceptable in THz range, because they demonstrate a rather high insertion loss in this range [5–7]. An obvious solution under such conditions is the use of all-dielectric waveguides [8]. In this regard, matching waveguides of this type with other devices is an actual and scientifically significant task.

Materials and Methods

In this paper we present the results of simulating and measuring the insertion loss of a coupling interface based on a prism geometry for a THz waveguide formed on metamaterial high resistive silicon (HRSi) platform. Waveguide structures designed for a frequency of 0.15 THz were fabricated on the HRSi substrate of 400 μ m thick. The spread in thickness at different points of the substrate does not exceed 12.5%. To create an effective medium, a square grid of through openings was created on both sides of the waveguide core. The grid period was 165 μ m. The hole radius was 36.5 μ m. The waveguide width was taken equal to the wavelength in the material, which was 585 μ m. The width is the distance between the tangents to the holes in the upper part of the substrate on both sides of the waveguide core. Details can be found in our previous articles [9, 10]. The parameters of the

© Селиверстов С.В., Святодух С.С., Приходько А.Н., Шураков А.С., Шевелёва Е.Д., Гольцман Г.Н., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

waveguide and the effective medium around it were chosen in such a way that a single TE_1 radiation mode could propagate inside it. We used the finite element method in the simulation.

The process of manufacturing of the experimental samples consisted of applying a Cr mask, plasma-chemical etching of Si unprotected by the mask (so called Bosch Process [11]), and subsequent separation of the substrate into individual chips. A photograph of the fabricated sample obtained with an electron microscope is shown in Fig. 1,*b*. In the experiment, the fabricated waveguide sample with prism couplers on both sides of the waveguide was installed in a metal holder, which made it possible to place the coupler exactly in the center of a rectangular hollow metal waveguide. A backward wave oscillator was used as a radiation source. A THz calibrated calorimeter-style power meter was used as a detector.

Results and Discussion

We fabricated a set of waveguide samples of various lengths l_i to estimate the insertion loss for energy leakage into free space, characterized by the corresponding loss per unit length α and the insertion loss of input and output of radiation into the waveguide through the coupling prism L_m . The total insertion loss, expressed in decibels, was $L_{tot,i} = 2L_m + \alpha l_i$. For two samples of the waveguide of length l_1 and l_2 with the corresponding measured losses $L_{tot,1}$ and $L_{tot,2}$, the value of α can be calculated by the formula: $\alpha = (L_{tot,2} - L_{tot,1})/(l_2 - l_1)$. At the same time, the value of L_m can be calculated by the formula: $L_m = (L_{tot,1}l_2 - L_{tot,2}l_1)/(2(l_2 - l_1))$.



Fig. 1. Dependencies of the S_{21} parameter on the coupler apex width at different values of the prism length (*a*) and SEM photos of the fabricated structures (*b*)



Fig. 2. Simulated electric-field distribution inside the transition from the metal rectangular waveguide (on the right) to the prism coupled dielectric waveguide (on the left)

At the frequency of 0.15 THz, the dependences of the S_{21} parameter on the width of the coupler apex for various values of its length were simulated. The measurements were carried out with a sample in which the width of the coupler apex was 90 µm and the coupler length was 3500 µm. The results of the simulation and experiment are shown on Fig. 1,*a*.

One can see that the insertion loss decreases when the coupler apex width goes down. This can be explained by a smoother change in the average value of the permittivity in the direction along the waveguide at small values of the coupler apex width. This results in a better match between two waveguides. The measured S_{21} parameter value of -0.5 dB for the waveguide sample under study is in good agreement with the simulation.

The electric-field distribution inside the transition from a metal rectangular waveguide to a prism coupled dielectric waveguide is presented on Fig. 2. The boundaries of the metal waveguide are indicated in the figure by white horizontal lines. The boundaries of the substrate, the coupling prism, and the core of the dielectric waveguide are marked with red dotted lines.

Conclusion

The proposed prismatic coupling interface has demonstrated low insertion loss at THz band. The developed structures will become the basic elements of an array of THz emitters with active adjustment of its radiation pattern. These devises will be a part of a future next-generation THz data communication system with a high data transfer rate.

REFERENCES

1. Khalid N., Abbasi N.A., Akan O.B., Statistical characterization and analysis of low-THz communication channel for 5G Internet of Things, Nano Communication Networks. 22 (2019) 100258.

2. Zhang C., Ota K., Jia J., Dong M., Breaking the blockage for big data transmission: Gigabit road communication in autonomous vehicles, IEEE Communications Magazine. 55 (6) (2018) 152–157.

3. Boronin P., Petrov V. Moltchanov D., Koucheryavy Y., Jornet J.M., Capacity and throughput analysis of nanoscale machine communication through transparency windows in the terahertz band, Nano Communication Networks. 5 (3) (2014) 72–82.

4. Corre Y., Gougeon G., Doré J.B., Bicans S., Miscopein B., Faussurier E., Saad M., Palicot J., Bader F., Sub-THz spectrum as enabler for 6G wireless communications up to 1 Tbit/s, 6G Wireless Summit (2019).

5. Frankel M.Y., Gupta S., Valdmanis J.A., Mourou G.A., Terahertz attenuation and dispersion characteristics of coplanar transmission lines, IEEE Transactions on microwave theory and techniques. 39 (6) (1991) 910–916.

6. Murano K., Watanabe I., Kasamatsu A., Suzuki S., Asada M., Withayachumnankul W., Tanaka T., Monnai Y., Low-profile terahertz radar based on broadband leaky-wave beam steering, IEEE Transactions on Terahertz Science and Technology. 7 (1) (2016) 60–69.

7. Virginia Diodes Inc., Waveguide Band Designations, Diodes Inc. (2010).

8. Gao W., Yu X., Fujita M., Nagatsuma T., Fumeaux C., Withayachumnankul W., Effective-mediumcladded dielectric waveguides for terahertz waves, Optics express. 27 (26) (2019) 38721–38734.

9. Seliverstov S.V., Svyatodukh S.S., Prokhodtsov A.I., Goltsman G.N., Simulation of terahertz photonic integrated antenna, St. Petersburg State Polytechnical University Journal: Physics and Mathematics. 15 (3.2) (2022) 370–374.

10. Seliverstov S., Svyatodukh S., Prokhodtsov A., Prikhodko A., Shurakov A., Sheveleva E., Chulkova G., Goltsman G., Transmission and reflection spectra of Si wave-guiding structures for THz integrated photonics, Infrared, Millimeter-Wave, and Terahertz Technologies IX, SPIE, 12324 (2022) 229–234.

11. Manning M.P., An investigation of the Bosch process: doctoral dissertation, Massachusetts Institute of Technology. (1976).

THE AUTHORS

SELIVERSTOV Sergey V. sv.seliverstov@mpgu.su ORCID: 0000-0001-9624-5325

SVYATODUKH Sergey S. sergey.svetodux@gmail.com ORCID: 0000-0001-9436-6641

PRIKHODKO Anatoliy N. anprihodko@hse.ru ORCID: 0000-0002-4859-8975 SHURAKOV Alexander S. alexander@rplab.ru ORCID: 0000-0002-4671-7731

SHEVELEVA Evgeniya D. sheveleva@phystech.edu ORCID: 0000-0000-0000-0000

GOLTSMAN Grigory N. goltsman10@mail.ru ORCID: 0000-0002-1960-9161

Received 18.07.2023. Approved after reviewing 19.07.2023. Accepted 21.07.2023.

Conference materials UDC 537 DOI: https://doi.org/10.18721/JPM.163.272

Hardware- and user-induced micromobility effects in in-door radio access at 140 GHz

T.A. Yaropolov¹[⊠], A.N. Prikhodko^{1,2}, P.V. Rozhkova¹, A.S. Shurakov^{1,2}, G.N. Goltsman^{1,2}

¹ Moscow Pedagogical State University, Moscow, Russia;

² National Research University Higher School of Economics, Moscow, Russia

[™] yaropolov.26012001@yandex.ru

Abstract. Sub-terahertz frequency band is beneficial for radio access networks of the sixth generation. Due to rather limited power capacity, there appears a necessity to equip transmitters and receivers in sub-terahertz wireless channels with high directivity antennas. This, however, leads to a potential connection failure in response to even a minor linear or angular displacement of a user equipment. This article is focused on a hardware- and user-induced micromobility effects for different scenarios of in-door radio access at carrier frequency of 140 GHz. The developed measurement setup enables fast simultaneous logging of linear and angular displacements of a user equipment with respect to radio access point and the corresponding received signal strength. Experimental data is processed by Allan variance analysis, statistics is acquired for a large number of samples. We believe that our findings should be of use in the development of beam steering solutions for reliable sub-terahertz wireless communications.

Keywords: user micromobility, 6G wireless system, sub-terahertz communication

Funding: Hardware development was conducted as a part of strategic project "Digital Transformation: Technologies, Effectiveness, Efficiency" of Higher School of Economics development programme granted by Ministry of science and higher education of Russia "Priority-2030" grant as a part of "Science and Universities" national project. Data processing was partly funded by the Russian Science Foundation grant 22-79-10279, https://rscf.ru/project/22-79-10279/.

Citation: Yaropolov T.A., Prikhodko A.N., Rozhkova P.V., Shurakov A.S., Goltsman G.N., Hardware- and User-Induced Micromobility Effects in In-Door Radio Access at 140 GHz, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 411–416. DOI: https://doi.org/10.18721/JPM.163.272

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

© Yaropolov T.A., Prikhodko A.N., Rozhkova P.V., Shurakov A.S., Goltsman G.N., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Материалы конференции УДК 537 DOI: https://doi.org/10.18721/JPM.163.272

Аппаратный и пользовательский вклад в эффект микромобильности при радиодоступе на 140 ГГц внутри помещений

Т.А. Ярополов^{1⊠,} А.Н. Приходько^{1,2}, П.В. Рожкова¹, А.С. Шураков^{1,2}, Г.Н. Гольцман^{1,2}

¹ Московский Педагогический Государственный Университет, Москва, Россия;

² Национальный исследовательский университет «Высшая школа экономики», Москва, Россия

[™] yaropolov.26012001@yandex.ru

Аннотация. Суб-терагерцовый диапазон частот привлекателен для сетей радиодоступа шестого поколения. Ограниченность уровня доступной мощности приводит к необходимости оснащения передатчиков и приемников в суб-терагерцовых беспроводных каналах связи сверхузконаправленными антеннами. Это, в свою очередь, способно приводить к разрыву соединения даже при незначительных линейных или угловых смещениях пользовательского устройства. Данная статья посвящена исследованию аппаратного и пользовательского вклада в эффект микромобильности при радиодоступе на несущей частоте 140 ГГц внутри помещений. Разработанная измерительная установка обеспечивает возможность быстрой записи линейных и угловых перемещений пользовательского устройства относительно точки радиодоступа и соответствующего уровня принимаемого сигнала. Статистический анализ экспериментальных данных осуществляется с использованием кривой дисперсии Аллана для большой выборки измерений. Мы полагаем, что наши результаты могут быть использованы при разработке устройств управления пучком в суб-терагерцовой беспроводной связи повышенной надежности.

Ключевые слова: микромобильность пользователя, беспроводная система 6G, субтерагерцовая связь

Финансирование: Разработка аппаратного обеспечения подготовлена в ходе реализации стратегического проекта «Цифровая трансформация: технологии, эффекты, эффективность» программы развития национального исследовательского университета «Высшая школа экономики» в рамках участия в программе Минобрнауки России «Приоритет-2030» национального проекта «Наука и университеты». Обработка данных частично выполнена за счет гранта Российского научного фонда № 22-79-10279, https:// rscf.ru/project/22-79-10279/.

Ссылка при цитировании: Ярополов Т.А., Приходько А.Н., Рожкова П.В., Шураков А.С., Гольцман Г.Н. Аппаратный и пользовательский вклад в эффект микромобильности при радиодоступе на 140 ГГц внутри помещений // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 411–416. DOI: https:// doi.org/10.18721/JPM.163.272

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Sub-terahertz frequency (sub-THz) band is beneficial for wireless radio access networks of the sixth generation (6G). It is conventionally proposed to use highly directive antennas in transmitters (T_x) of access points and receivers (R_x) of user equipment (UE) in 6G networks. In this case, reliability of wireless channel can be notably compromised if UE is mobile. User micromobility is one of the main issues in the implementation of 6G wireless communication systems [1, 2]. In this work, we study hardware- and user-induced micromobility effects for different scenarios

© Ярополов Т.А., Приходько А.Н., Рожкова П.В., Шураков А.С., Гольцман Г.Н., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

of in-door radio access at carrier frequency of 140 GHz. The considered scenarios are mainly related to web searching and online gaming characterized by low-deterministic misalignment between sub-THz beams of T_x and R_x . We develop measurement setup for fast simultaneous log-ging of time-dependent position of UE with respect to T_x and the corresponding signal strength at R_x . Time related metrics are statistically acquired by Allan variance analysis. In addition, our measurements enable profiling of the R_x signal strength in different T_x beam planes. This should find use in the development of beamforming solutions for 6G wireless communication systems.

Materials and Methods

We fabricate UE with linear dimensions similar to a typical large-screen smartphone to insure its realistic mechanics in user hands. UE is equipped with a motion sensor and R_x and is placed far behind a Fraunhofer distance in front of T_x . The sensor makes use of microelectromechanical system (MEMS) accelerometers and gyroscopes and measures linear accelerations and angular velocities with respect to 3-dimensional intrinsic reference frame (IRF). Referring to Fig. 1,*a*, the angles φ and θ are restored in the spherical coordinate system fixed to UE. They are defined as the angles between the corresponding axes of IRF at the initial moment of time t = 0 (x(0) and z(0)) and during current measurement (x(t) and z(t)). The measurements are carried out with T_x providing a constant waveform signal at carrier frequency of 140 GHz and an amplitude modulation at 25 kHz. R_x is based on a waveguide Schottky diode envelope detector [2]. The readout is maintained by a selective nanovoltmeter. The detector response voltage, i.e., signal strength at R_x , is recorded simultaneously with the readings of accelerometers and gyroscopes by a data acquisition system. This ensures an exact correspondence of the changes in the received signal strength with the UE angular coordinates.

As shown in Fig. 1,b, antennas of T_x and R_x have far-field beamwidths of 6–17°. We subsequently use a pair of diagonal horn antennas with bigger (Horn 1) and less directivity (Horn 2) to distinguish between the beamwidth and polarization impacts on signal attenuation upon user micromobility. Schematic diagram of the measurement setup developed for the empirical studies is presented in Fig. 2. The R_x unit utilizes a membrane-integrated Schottky diode detector [3] and a 16-bit motion sensor [4] enabling simultaneous logging of 3 linear accelerations (a_x , a_y , a_z) and 3 angular velocities (ω_x , ω_y , ω_z). Quaternion math and Mahony complementary filter are used for fast (on a millisecond scale) and precise position measurements of the motion sensor.

To ensure reliability and reproducibility of the position measurement of R_x with respect to the T_x beam, we perform a series of calibrations for different initial orientations of R_x (i.e., for different initial orientations of the motion sensor IRF). Tables 1 and 2 contain statistics on the triplets of linear accelerations and angular velocities measured for static R_x , when its different planes (see Fig. 1,*a*) are set parallel to the horizon.

After achieving the appropriate performance of the measurement setup, we further decide to conduct a series of independent measurements of a signal strength at R_x as a function of its angular position with respect to the T_x beam for different radio access scenarios in 6G networks.



Fig. 1. Wireless channel with static sub-THz access point and mobile UE (*a*). *E*- and *H*- plane beam profiles of 2 alternatively employed T_y/R_y horn antennas (*b*)



Fig. 2. Measurement setup developed for empirical studies of user micromobility at 140 GHz

Table 1

Statistics on linear accelerations for a set of 10 time series with up to 45000 readings logged for a static R_y with different orientations of the motion sensor IRF

IRF orientation	Statistics on linear accelerations			
	$\langle a_x \rangle_{avg} \pm \Delta a_x, \mathrm{m/s^2}$	$\langle a_{y} \rangle_{avg} \pm \Delta a_{y}, \mathrm{m/s^{2}}$	$< a_z >_{avg} \pm \Delta a_z, \mathrm{m/s^2}$	
ХОҮ	$0.002{\pm}0.002$	-0.002 ± 0.001	-0.001 ± 0.009	
XOZ	0.02±0.17	-0.01 ± 0.04	-0.08 ± 0.19	
YOZ	-0.03 ± 0.15	$0.06{\pm}0.08$	$-0.17{\pm}0.05$	

Notations: Here $\langle a_x \rangle_{avg}$, $\langle a_y \rangle_{avg}$, $\langle a_z \rangle_{avg}$ are the average values of mean linear accelerations along the x-, y-, z-axes of the motion sensor IRF and Δa_x , Δa_y , Δa_z are the corresponding confidence intervals.

Table 2

Statistics on angular velocities for a set of 10 time series with up to 45000 readings logged for a static R_y with different orientations of the motion sensor IRF

IRF orientation	Statistics on angular velocities			
	$<\omega_x>_{avg}\pm\Delta\omega_x$, rad/s	$<\omega_{y}>_{avg}\pm\Delta\omega_{y}, rad/s$	$<\omega_z>_{avg}\pm\Delta\omega_z$, rad/s	
ХОҮ	-6.5e-5±3.6e-5	-6.3e-5±3.0e-5	-5.4e-5±4.5e-5	
XOZ	-6.4e-5±3.4e-5	-5.8e-5±1.0e-5	-5.8e-5±2.8e-5	
YOZ	-6.3e-5±1.1e-5	-5.9e-5±1.5e-5	-6.3e-5±1.7e-5	

Notations: Here $\langle \omega_x \rangle_{avg}$, $\langle \omega_y \rangle_{avg}$, $\langle \omega_z \rangle_{avg}$ are the average values of mean angular velocities along the *x*-, *y*-, *z*-axes of the motion sensor IRF and $\Delta \omega_x$, $\Delta \omega_y$, $\Delta \omega_z$ are the corresponding confidence intervals.

Results and Discussion

As a first measurement of interest, we choose the scenario of an incoming phone call to a person working at the office desk. In this scenario, UE (i.e., R_x) is initially put on the desk, optical axis of R_x horn antenna is coaligned with that of T_x placed 1.5 m away. Polarization planes of the antennas are also coaligned. UE is in the hand of a user moving it from the desk to his ear, the elbow does not leave the desk surface upon the move. Thus, 2 key effects are presented: gradual change of the angle between the polarization planes of the T_x and R_x horn antennas from 0 to 90° and spontaneous changes in the orientation of the R_x horn antenna optical axis induced by the human mechanics. We carry out 2 series of 10 independent measurements for the considered scenario. Statistically processed results of the measurements for 2 pairs of T_x/R_x pyramidal horn antennas with bigger (Horn 1) and less directivity (Horn 2) are provided in Fig. 3,*a*. The figure contains smoothed mean signal strengths at R_x with 68% confidence intervals for different values of angle θ . We employ a moving average with a window size of 178 samples to get a 3° resolution upon smoothing. Using this empirical data together with Malus's law, one can distinguish between the beamwidth and polarization impacts on signal attenuation upon user micromobility in a phone call scenario.

We further employ the developed measurement setup to study stability of the received signal upon a short distance transmission for online gaming and web searching scenarios. During the online gaming scenario, the user pretends to play an arcade racing game on a UE tilted forward at 45° with respect to the vertical in his hands. The wide side of the UE is oriented horizontally. The web searching scenario focuses on the user mechanics in the process of using the search engine in the UE browser. The orientation of the UE in the hands of the user is the same as during the online gaming scenario. In both scenarios, the user stands still and taps on the UE screen inducing its angular displacements followed by changes in the signal strength at R_{y} . To analyze the signature of application-dependent mechanics, a series of up to 100 independent measurements with a duration of 60 s each is conducted. At the beginning of each measurement, optical axis and polarization plane of R_{y} horn antenna are coaligned with those of T_{y} placed 1.5 m away. The experimental data is statistically processed by Allan variance analysis [5]. Fig. 3,b summarizes results of the processing, stability of the received signal for a static position of UE at the initial moment of time t = 0 is provided as a reference. The latter obeys a radiometer equation for integration times, τ , from 2 ms to 2 s. This ensures reliable extraction of the micromobility-induced instabilities in the received signal. For online gaming scenario, we observe white noise and drift signatures for τ of below and above 4 ms, respectively. No 1/*F*-noise signature is recognized. Furthermore, confidence intervals for the Allan variance values widen with increase in τ . And they are notably wider as compared to the web searching curve at any given τ . For web searching scenario, we observe 1/F-noise and drift signatures for τ of below and above 4 ms, respectively. No pronounced white noise signature is recognized. The acquired Allan variance curves also reveal high repeatability in numerous independent measurements. Moreover, the developed measurement setup enables stability profiling for a number of planes with respect to the T_{y} beam. This aids to analyze contribution of UE optics design and user activity to the received signal stability. Further detailed studies of the mutual impact of user micromobility and dynamic blockages [6] on connection quality in sub-terahertz communications are in our future plans. However, we believe that the reported results should find use in the development of efficient beam steering solutions for reliable sub-terahertz wireless communication systems.



Fig. 3. Signal strength at UE measured for user micromobility during a phone call (a). Experimental Allan variance curves for signal strength at UE in various application scenarios (b)

Conclusion

To study user micromobility for different radio access scenarios in 6G networks, we fabricate UE with linear dimensions similar to a typical large-screen smartphone to insure its realistic mechanics in user hands. UE is equipped with a motion sensor and R_x and is placed far behind a Fraunhofer distance in front of T_x . The motion sensor is a MEMS-based multi-channel logging device combined with quaternion math and Mahony complementary filter for fast (on a millisecond scale) and precise position measurements. Antennas of T_x and R_x have far-field beamwidths of 6–17° similar to those expected for first-run wireless 6G systems. The measurements of a signal strength at R_x in user hands are carried out with T_x providing a constant waveform signal at carrier frequency of 140 GHz and an amplitude modulation at 25 kHz. The experimental data is statistically processed by Allan variance analysis for the considered gaming and web searching scenarios. The developed measurement setup enables stability profiling for a number of planes with respect to the T_x beam. This aids to analyze contribution of UE optics design and user activity to the received signal stability. We believe that the reported results should find use in the development of efficient beam steering solutions for reliable sub-terahertz wireless communication systems.

REFERENCES

1. Petrov V., Moltchanov D., Koucheryavy Y., Jornet J.M., Capacity and outage of terahertz communications with user micro-mobility and beam misalignment, IEEE Transactions on Vehicular Technology. 69 (4) (2020) 6822–6827.

2. Stepanov N., Moltchanov D., Begishev V., Turlikov A., Koucheryavy Y., Statistical analysis and modeling of user micromobility for THz cellular communications, IEEE Transactions on Vehicular Technology. 71 (1) (2021) 725–738.

3. Shurakov A., Belikov I., Prikhodko A., Mikhailov D., Gol'tsman G., Membrane-integrated planar Schottky diodes for waveguide mm-Wave detectors, Microwave & Telecommunication Technology. 3 (2021) 34.

4. TDK InvenSense. URL: https://invensense.tdk.com/products/motion-tracking/6-axis/ mpu-6500/.

5. Allan D. W., Statistics of atomic frequency standards, Proceedings of the IEEE. 54 (2) (1966) 221–230.

6. Shurakov A., Moltchanov D., Prikhodko A., Khakimov A., Mokrov E., Begishev V., Belikov I., Koucheryavy Y., Gol'tsman G., Empirical blockage characterization and detection in indoor sub-THz communications, Computer Communications. 201 (2023) 48–58.

THE AUTHORS

YAROPOLOV Terentiy A. yaropolov.26012001@yandex.ru ORCID: 0000-0001-9521-9651

PRIKHODKO Anatoliy N. anatprikh1995@yandex.ru ORCID: 0000-0002-4859-8975

ROZHKOVA Polina V. pv_rozhkova2@student.mpgu.edu ORCID: 0009-0005-6258-9353 SHURAKOV Alexander S. alexander@rplab.ru ORCID: 0000-0002-4671-7731

GOLTSMAN Grigory N. goltsman@rplab.ru

ORCID: 0000-0002-1960-9161

Received 21.07.2023. Approved after reviewing 06.09.2023. Accepted 07.09.2023.

© Peter the Great St. Petersburg Polytechnic University, 2023

Conference materials UDC 53.081.1 DOI: https://doi.org/10.18721/JPM.163.273

Modernization of quantum frequency standard with optical pumping

D.A. Boldarev¹, K.G. Arinushkina², A.P. Valov², R.A. Dmitriev²

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia

⊠ k-arinushkina@mail.ru

Abstract. The development of information transmission systems, satellite navigation systems, metrological service systems lead to the need for constant modernization of the currently used quantum frequency standards (QFS). In radar systems, frequency standards determine the synchronism of work on moving objects. A small frequency deviation from the nominal value leads to large errors, especially when transmitting large data streams. The article presents a method for upgrading QFS in order to improve short-term stability. Experimental studies of the metrological characteristics of QFS with laser optical pumping have shown the effectiveness of the new development. The practical significance of the work lies in the development of an assembly device and the substantiation of new methods for improving the metrological characteristics, such as daily frequency standards. It also found an improvement in metrological characteristics, such as daily frequency stability of the output signal of the frequency standard, by 25%.

Keywords: time scale, stabilization, automatic frequency control, frequency stabilizer, cesium frequency standard, operational amplifier, remote sensing spacecraft, atomic beam tube

Citation: Boldarev D.A., Arinushkina K.G., Valov A.P., Dmitriev R.A., Modernization of quantum frequency standard with optical pumping, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 417–422. DOI: https://doi. org/10.18721/JPM.163.273

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.081.1 DOI: https://doi.org/10.18721/JPM.163.273

Модернизация квантового стандарта частоты с оптической накачкой

Д.А. Болдарев¹, К.Г. Аринушкина^{2™}, А.П. Валов², Р.А. Дмитриев²

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;

² Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия

^{III} k-arinushkina@mail.ru

Аннотация. Развитие систем передачи информации, систем спутниковой навигации, систем метрологического обслуживания приводит к необходимости постоянной модернизации используемых в настоящее время квантовых стандартов частоты (КСЧ). В радиолокационных системах стандарты частоты определяют синхронность работы по движущимся объектам. Небольшое отклонение частоты от номинального значения

© Boldarev D.A., Arinushkina K.G., Valov A.P., Dmitriev R.A., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

приводит к большим ошибкам, особенно при передаче больших потоков данных. В статье представлен метод модернизации КСЧ с целью повышения кратковременной стабильности. Экспериментальные исследования метрологических характеристик КСЧ лазерной оптической накачкой показали эффективность новой разработки. Практическая значимость работы заключается в разработке нового устройства и обосновании методов улучшения метрологических характеристик КСЧ. Предлагаемый метод усовершенствования стандарта частоты может быть использован для дальнейших исследований в области стандартов частоты. Также установлено улучшение метрологических характеристик, таких как суточная стабильность частоты выходного сигнала стандарта частоты на 25%.

Ключевые слова: шкала времени, стабилизация, автоматическая подстройка частоты, стабилизатор частоты, цезиевый эталон частоты, операционный усилитель, космический аппарат дистанционного зондирования Земли, атомно-лучевая трубка

Ссылка при цитировании: Болдарев Д.А., Аринушкина К.Г., Валов А.П., Дмитриев Р.А. Модернизация квантового стандарта частоты с оптической накачкой // Научнотехнические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 417–422. DOI: https://doi.org/10.18721/JPM.163.273

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Various academic studies of the last decades have made it possible to make quantum frequencies standard the basis of highly stable, precise, spectrally purest electrical signals [1–7]. The obtained accuracy, as well as frequency stability, made it possible to effectively use QFS as synchronizing generators in communication technology, as well as data transmission devices, and, in addition, to use them as signal sources in radio measuring equipment [6–11].

At present, the world does not stop improving the use of satellite navigation systems (SNS) in various fields of human activity [1-3, 6, 10-13].

Over the past 10 years, the GLONASS SNS has been rapidly developing in the Russian Federation, and as practice shows, it has a high location accuracy and is highly competitive compared to American, European and Chinese systems [1-3, 10-17]. The continuous expansion of the range of tasks, the solution of which should be provided by the SNS, requires both the development of new systems and the modification of existing ones. Also, with the development of technology, the composition of the radio-electronic means used is changing. All this requires constant modernization of the QFS [3, 6, 10, 11, 13-20].

Solving the problem of precision synchronization of reboarded time scales required the installation of highly stable synchronization devices on satellites. To improve the accuracy characteristics of the navigation system, in particular, when determining the position on a real scale, time, with an error of no more than 1 m, in addition to increasing the degree of reliability of its operation, it significantly depends on increasing the accuracy of the metrological characteristics of the QFS.

In order to solve this problem, the work of atomic clocks is being improved. The procedure for studying the newest type of QFS based on basic academic studies and putting them into practice is a rather lengthy process [13-17, 19-22]. Research and implementation require large financial resources, for this reason, in a number of cases, studies are being carried out to solve specific navigation problems in order to modernize single structures and blocks. This paper considers the modernization of the block of the automatic frequency control system using the input of a thermal compensation device.

Materials and Methods

In laser frequency standards, a suitable atomic, ionic or molecular transition is selected, in which a laser with a tunable wavelength is used to excite it. This helps to achieve the highest possible accuracy of the standard. The frequency standard with laser pumping on cesium-133 atoms works on the principle of adjusting the frequency of a quartz oscillator to the frequency of

© Болдарев Д.А., Аринушкина К.Г., Валов А.П., Дмитриев Р.А., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

the cesium-133 atomic transition. To implement the noted frequency adjustment of the quartz oscillator, a microwave signal is applied to an atomic beam tube (ABT) filled with cesium-133 atoms [2, 3, 11, 17, 22].

The output signal of an atomic ray tube contains a stable part, as well as an unstable part, which characterizes the discrepancy between the signal and the average value of the error signal component. The frequency auto-tuning system creates a control voltage of magnitude, as well as polarity, which make it possible to compensate for the deviation of the actual (real) value of the frequency of the quartz oscillator relative to the value that corresponds to the frequency of the atomic transition of the ABT (5 MHz). Fig. 1 shows a QFS device with laser pumping.



Fig. 1. QFS with laser pumping

After receiving the "Search" command, the (control device) CD begins to change from 0 to 255 the upper eight bits of the code transmitted via the serial interface to the CD crystal oscillator (CDXO). The output voltage of the CDXO is supplied to the varicap of the crystal oscillator (XO) frequency adjustment. Changing the voltage on the XO leads to a change in the frequency of the XO and, consequently, to a change in the frequency of the microwave signal at the input of the ABT, which in turn leads to a change in the voltage at the output of the ABT in accordance with the resonance curve. The voltage from the ABT output goes to the amplifier, where it is filtered and fed into the output circuit. The signal from the output of the amplifier goes to the input of the CD. In the process of rebuilding the code between the extreme values in the CD, the code value at which the signal voltage has the highest value is stored, and at the end of the code rebuilding cycle between the extreme values, the integrator automatically sets the stored code value.

After that, the CD switches to the auto frequency system ("AFS" mode), which is the main mode of operation of the product. The output voltage of the CD by a quartz oscillator is supplied to the varactor of the frequency adjustment of the crystal oscillator (XO). Changing the voltage on the varactor XO leads to a change in the frequency of the XO and also to a change in the frequency of the microwave signal at the ABT input. Further, this leads to a change in the voltage at the output of the ABT in accordance with the resonant curve.

The voltage supplied to the control unit in the automatic frequency control circuit, as well as the voltage supplied to the crystal oscillator, depends on the ambient temperature. These dependences lead to a mismatch in the frequencies of the microwave signal and the atomic transition, which leads to miscalculations in the matching of satellite time scales. Moreover, this process occurs regardless of whether the QFS uses highly stable laser radiation or a magnetic field to create a population inversion in ABT [2, 3, 11, 17, 22].

The modernization of this device allows improving the metrological characteristics of the entire QFS system, since the signal from this block is used in other functional devices, including frequency converters and frequency synthesizers that form microwave signals for the quantum discriminator. The properties of these signals directly affect the metrological properties of the QFS system.

The ambient temperature determines the voltage supplied to the control device in the automatic frequency control circuit, and, consequently, the voltage supplied to the crystal oscillator. This leads to a mismatch between the frequencies of the microwave signal and the atomic transition, which leads to errors in the matching of satellite time scales. Moreover, this process occurs regardless of whether the QFS uses highly stable laser radiation or a magnetic field to create a population inversion in ABT.

The following principle is implemented in the system developed by us. The ambient temperature directly affects the resistance of the thermistor and the output signal of the operational amplifier (op-amp), which is located in the automatic frequency control system. Depending on the design of the resistor, there is a different change in voltage with temperature.

The temperature control device is designed to generate a voltage range from 0.01 to 5.00 V at the output, proportional to the ambient temperature range from 0 °C to +50 °C. Due to the change in the resistance of the thermistor as part of the temperature control device due to temperature changes, the output voltage will depend on the ambient temperature.

The output voltage of the amplifier at a temperature of 0 °C is from 0.01 to 1.00 V, and at a temperature of +50 °C from 4 to 5 V.

Results and Discussion

According to the data obtained, the graph of the dependence of RMSD on time was recalculated. After ten days of testing, the value of the daily instability of the QFS decreased by $0.8 \cdot 10^{-14}$, that is, it improved by 25%. One of the main characteristics of the QFS is the Allan deviation.

Graphs 1 and 2 in Fig. 2 correspond to the AFS system previously used in QFS and developed by us. The results obtained show an improvement in the Allan deviation at a measurement time of 1-day $\sigma_y(t)$ by 25%. Studies of the work of the laboratory model of the QFS were carried out for 10 days in a temperature chamber. The experiments performed have shown the efficiency of using automatic frequency control systems with a thermal compensation device.

As a result, it can be seen that if the U(T) dependence goes into a non-linear form, auxiliary errors arise. In the new studied concept of auto-tuning of frequency, this error is eliminated.

The modernization of this device allows improving the metrological characteristics of the entire QFS system, since the signal from this block is used in other functional devices, including frequency converters and frequency synthesizers that form microwave signals for the quantum discriminator. The properties of these signals directly affect the metrological properties of the QFS system.



Fig. 2. Plot of Allan deviation σ_v versus time t

Conclusion

As a result of the development of a device for compensating the temperature coefficient of frequency, the temperature sensitivity has decreased by 6 times, which can improve the synchronization of the satellite time scale of the navigation system, while reducing the time scale matching error, which can reduce the geolocation error to meet new requirements.

The results obtained indicate an enhancement in the Allan deviation $\sigma_y(t)$ by 25%. The conducted experiments have shown the efficiency of using automatic frequency control systems with the thermal compensation device developed by us.

In addition, an improvement in metrological properties was determined in the role of daily frequency stability of the output signal of the frequency standard by 25%. The conducted studies demonstrate the effectiveness of the application of an automatic frequency control system with a thermal compensation device.

REFERENCES

1. Hudson A., Camparo J., Quantum System Dynamics and the Quasistatic Approximation, Physical Review Applied. 13(6) (2021) 064007.

2. **Riehle F.,** Frequency standard. Basic and applications, WILEY-VCH Verlag CmbH Co. KGaA: New-York, September 2008.

3. **Petrov A. A.,** Improvement frequency stability of caesium atomic clock for satellite communication system, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 9247 (2015) 739–744.

4. Myazin N. S., Dudkin V. I., Grebenikova N. M., Davydov R. V., Podstrigaev A. S., Fiber - optical system for governance and control of work for nuclear power stations of low power, Lecture Notes in Computer Science. 11660 (2019) 744–756.

5. Kuzmin M.S., Rogov S.A., On the use of a multi-raster input of one-dimensional signals in twodimensional optical correlators, Computer Optics. 43 (3) (2019) 391–396.

6. **Petrov A. A., Zaletov D. V., Shapovalov D. V.,** Peculiarities of Constructing a Scheme for Formation of a Microwave Excitation Signal in a Cesium Atomic Clock, Journal of Communications Technology and Electronics. 66 (3) (2021) 295–299.

7. Davydov V. V., Davydova T. I., A nondestructive method for express testing of condensed media in ecological monitoring, Russian Journal of Nondestructive Testing. 53 (7) (2017) 520–529.

8. Dudkin V.I., Myazin N.S., Davydov R.V., On the Possibility of Studying Ferrofluids by a Nuclear Magnetic Magnetometer with a Flowing Sample, Journal of Communications Technology and Electronics. 65 (5) (2020) 558–564.

9. Mihov E.D., Nepomnyashchiy O.V., Selecting informative variables in the identification problem Journal of Siberian Federal University - Mathematics and Physics. 9 (4) (2016) 473–480.

10. Ryzhenko I.N., Lutsenko A.E., Varygin O.G., Nepomnyashchiy O.V., Carrier compensation mode implementation in satellite communication channels. In: Proceedings of 2019 International Siberian Conference on Control and Communications, SIBCON. (8729665) (2019) 23–29.

11. **Petrov A. A., Grebenikova N. M.,** Some Directions of Quantum Frequency Standard Modernization for Telecommunication Systems, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 11118 LNCS (2018) 641–648.

12. Davydov R., Antonov V., Moroz A., Parameter Control System for a Nuclear Power Plant Based on Fiber-Optic Sensors and Communication Lines, In: IEEE International Conference on Electrical Engineering and Photonics (EExPolytech), Saint-Petersburg, Russia, (8906791) (2019) 295–297.

13. Petrov A.A., Shabanov V.E., Zalyotov D.V., Bulyanitsa A.L., Shapovalov D.V., Modernization of the frequency synthesizer of cesium atomic clock, IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2018, Saint-Petersburg, (8564389) (2018) 52–55.

14. Lukashev N.A., Moroz A.V., Compact microwave frequency standard on Hg-199 ions for navigation systems, Journal of Physics: Conference Series. 1236 (1) (2019) 012068.

15. **Tarasov A.D., Milder O.B.,** Gradation tracetories as an analog of gradation curves in the metric cie lab space discrete approache, Computer Optics. 43 (1) (2018) 104–110.

16. Lukashev N.A., Petrov A.A., Grebenikova N.M., Improving performance of quantum frequency standard with laser pumping, Proceedings of 18th International conference of Laser Optics ICLO-2018 Saint-Petersburg, (8435889) (2018) 271.

17. **Petrov A.A.**, Digital Frequency Synthesizer for 133Cs-Vapor Atomic Clock, Journal of Communications Technology and Electronics. 62 (3) (2017) 289 – 293.

18. Davydov V.V., Kruzhalov S.V., Vologdin V.A., Concerning some features of studying the flow of liquid media by a Doppler method: Journal of Optical Technology (A Translation of Opticheskii Zhurnal). 84 (8) (2017) 568–573.

19. Almat N., Pellaton M., Moreno W., et al., Rb vapor-cell clock demonstration with a frequencydoubled telecom laser, Appl. Opt. 57 (2008) 4707.

20. Valov A.P., Arinushkina K.G., The use of digital data processing to improve the metrological characteristics of the rubidium frequency standard, Journal of Physics: Conference Series. 2086 (1) (2021) 012070.

21. Lukashev N.A., Glinushkin A.P., Rud V.Yu., Lukyantsev V.S., Microwave low mass-dimensional frequency standard on Hg- 199 ions, Journal of Physics: Conference Series. 1410 (1) (2019) 012211.

22. Bandi T., Affolderbach C., Calosso C.E., et al., High-performance aser-pumped rubidium frequency standard for satellite navigation, Electron. Lett. 47 (2001) 698–699.

23. Shavshin A.V., Development of automatic control of optical signal gain in a atomic frequency standard based on rubidium-87 atoms, IEEE 2022 VIII International Conference on Information Technology and Nanotechnology (ITNT), (21991987) (2022) 126–131.

THE AUTHORS

BOLDAREV Dmitriy A. boldarev2001@inbox.ru ORCID: 0009-0001-7899-6843

ORCID: 0000-0002-1156-2071

ARINUSHKINA Kseniya G. k-arinushkina@mail.ru

DMITRIEV Roman A. rusher.official@gmail.c

rusher.official@gmail.com ORCID: 0000-0002-2964-1165

ORCID: 0000-0001-9276-1736

tony.valov2015@yandex.ru

VALOV Anton P.

Received 26.07.2023. Approved after reviewing 24.08.2023. Accepted 26.08.2023.

Conference materials UDC 537.867 DOI: https://doi.org/10.18721/JPM.163.274

Fiber-optic system development for the output frequency setting of a voltage-controlled oscillator at the radar station antenna complex

V.B. Fadeenko¹[™], D.A. Ryzhova¹, A.P. Valov², A.V. Shavshin¹

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;

² The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia

⊠ v21.07.96@mail.ru

Abstract. The necessity of introducing fiber-optic communication lines for the frequency tuning codes transmission and frequency regulation is substantiated. A new scheme is presented for constructing the radar station radiation path in the range from 1 to 18 GHz. A functional expansion of the radar station capabilities is presented through the introduction of a modernized radiation path and the study of radiation formations. Fiber-optic lines investigations have been carried out in terms of launching frequency codes and a control channel. The corresponding characteristics have been given.

Keywords: Fiber optic communication line, microwave signal, radar station, radiation monitoring, voltage controlled oscillator

Citation: Fadeenko V.B., Ryzhova D.A., Valov A.P., Shavshin A.V., Fiber-optic system development for the output frequency setting of a voltage-controlled oscillator at the radar station antenna complex, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 423–427. DOI: https://doi.org/10.18721/JPM.163.274

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 537.867 DOI: https://doi.org/10.18721/JPM.163.274

Разработка волоконно-оптической системы для управления и контроля частоты генератора, управляемого напряжением в антенном комплексе радиолокационной станции

В.Б. Фадеенко¹[™], Д.А. Рыжова¹, А.П. Валов², А.В. Шавшин¹

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;

² Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия

⊠ v21.07.96@mail.ru

Аннотация. Обоснована необходимость внедрения волоконно-оптических линий связи для передачи частотных кодов настройки и частотного регулирования. Представлена новая схема построения тракта излучения радиолокационной станции в диапазоне от 1 до 18 ГГц. Представлено функциональное расширение возможностей радиолокационной станции за счет внедрения модернизированного тракта излучения и исследования радиационных образований. Проведены исследования волоконно-оптических линий в части запуска кодов частоты и канала контроля, приведены соответствующие характеристики.

© Fadeenko V.B., Ryzhova D.A., Valov A.P., Shavshin A.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ключевые слова: волоконно-оптическая линия связи, СВЧ сигнал, радиолокационная станция, радиационный контроль, генератор управляемый напряжением

Ссылка при цитировании: Фадеенко В.Б., Рыжова Д.А., Валов А.П., Шавшин А.В., Разработка волоконно-оптической системы для управления и контроля частоты генератора, управляемого напряжением в антенном комплексе радиолокационной станции // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 423–427. DOI: https://doi.org/10.18721/JPM.163.274

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Much attention is paid to monitoring the airspace and environment state in the modern world [1-3]. A large number of different instruments and devices have been developed to solve these problems [3-6]. Most of these devices have a number of disadvantages that are associated with weather factors, detection range, and others, especially for the airspace state monitoring [6-9]. The radar station usage eliminates many of these shortcomings. Therefore, increased attention is paid to the radar station development and modernization [6, 7, 9-13]. One of the radar development areas is the expansion of its functionality to the airspace state control [6, 10, 11, 13-15].

The operation of any nuclear power plant results in the release of radioactive isotopes through ventilation systems into the air [3, 6, 8]. The reflected microwave signal is associated with the natural radionuclide isotopes resonant frequencies (for example, ¹³¹I, ¹⁶N, ¹³³Xe, ⁸⁸Kr and others). It is required to ensure a change in the microwave frequency f_{SHF} of the radar microwave signal radiation in the range of all radionuclide natural frequencies. The microwave radiation frequency f_{SHF} varies in the range from 1 to 18 GHz, providing the same power level over the entire frequency range for plasmoid research. Therefore, the article goal is new fiber-optic communication line (FOCL) design development for controlling and monitoring voltage-controlled oscillator (VCO) frequency changes in the range from 1 to 18 GHz.

Materials and Methods

The stationary post includes equipment for processing and generating commands. A microwave signal is transmitted from it to the antenna. The distance between them is from 50 to 2000 meters. The FOCL can be placed in various temperature conditions, areas of increased electromagnetic activity, areas with γ -radiation, etc. Fig. 1 shows a block diagram of the two-channel FOCL developed by us for solving problems of controlling f_{SHF} in the VCO and controlling its nominal value.



Fig. 1. Block diagram of the two-channel FOCL for VCO frequency monitoring and control: Read Only Memory (ROM) 1; digital-to-analog converter (DAC) 2; laser module with direct modulation 3; photodetector module 4; low-noise amplifier 5 based on an operational amplifier (LNA); voltage controlled analog oscillator 6; 1:4 power divider 7; electro-optical modulator 8; analog-to-digital converter (ADC) 9; indication and control device 10; amplifier 11; bandpass filter 12 in the feedback circuit of the amplifier; short emitter-dipole 13 of a parabolic antenna; single-mode optical fiber *14*

© Фадеенко В.Б., Рыжова Д.А., Валов А.П., Шавшин А.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

The designer loads special codes into the memory device (1) during the development and manufacture of the radar transmitting path in this work. The launch codes are applied to VCO to generate a signal of a certain frequency $f_{\rm SHF}$ in the range from 1 to 18 GHz with a given step. These frequency codes are unique for the developed FOCL, are loaded on a permanent basis and remain unchanged during the FOCL operation. The frequency codes usage makes it possible to set a master signal stable frequency. The launch codes are sent in turn to the DAC (2). An analog signal is formed for a given frequency at the output (2). It is necessary to transmit the signal to the antenna complex. This construction is located at a distance of 50 to 2000 meters from the premises with the installed equipment. The trajectory of the line and the features of its laying are taken into account on development stage. It is possible to increase the distance. Typical construction length of solid fiber is 2, 3, 4 and 10 km. There is no big problem to have such path length. A single-mode fiber of the G.652 standard is used with a core doped with 2% germanium oxide GeO₂ to microwave signal transmit. The power loss is 0.32 dB/km at $\lambda = 1310$ nm. Therefore, the margin is more than sufficient to signal transmit. The analog signal is fed to the laser module 3 with direct modulation of the pump current. The optical signal is fed through the fiber 14 to the antenna complex (to the input of the photodetector module 4).

Results and Discussion

The studies were carried out for two channels of the developed FOCL under laboratory conditions with different characteristics. Fig. 2 shows the FOCL frequency response.



Fig. 2. Frequency response of the FOCL for the frequency code transmission channel (*a*) and the radiation frequency f_{SHF} control channel (*b*)

Analysis of the obtained results shows that the frequency code transmission channel characteristic unevenness is 3-6 dB at a radiation frequency f_{SHF} up to 18 GHz (Fig. 2,*b*). This fact confirms the high degree of the reliability of signal transmission over FOCL. The uneven characteristics of the code transmission channel is less than 1 dB, which ensures high information transmission stability (Fig. 2,*a*).



Fig. 3. Frequency response of the FOCL frequency control channel f_{SHF} for various temperatures *T*. Graphs *1*, *2* and *3* correspond to the following temperature values *T* in °C: -23; -5; 27

An analysis was made of the temperature factor influence on the channel for controlling the radiation frequency f_{SHF} in the research course. Fig. 3 shows the amplitude-frequency characteristics of the FOCL at three temperatures.

The obtained data analysis showed that the temperature factor has practically no effect on signal transmission over FOCL. Temperature shift is about 0.5 dB. Stable operation of the frequency control channel is maintained in the operating range of the FOCL. A similar situation applies to the code transmission channel.

Conclusion

The obtained results show the reliability of the developed two-channel FOCL to provide the necessary operating mode of the radiating antenna in each frequency range and to conduct research on radioactive formations.

The introduction of an additional control channel on the FOCL makes it possible to control the radar transmitting path operability, serviceability of the frequency generation system by means of the VCO, and to determine the exact value of the steady-state radiation frequency $f_{\rm SHF}$ for atmospheric research. It becomes possible to localize weak reflected signals from supposed ionization radiations formed as a result of the ingress of radioactive elements into the atmosphere, and to establish a possible type of particles, since the microwave signal reflected at different frequencies $f_{\rm SHF}$ is closely related to the natural frequencies of radionuclide isotopes that have entered the atmosphere.

The obtained results show that the FOCL developed design allows to control the operation of the antenna complex radiator at distances of the order of 100 km. It is especially important for work in the areas of the far north.

REFERENCES

1. Davydov V. V., Fokin G., Lazarev A., Instantaneous Interference Evaluation Model for Smart Antennas in 5G Ultra-Dense Networks, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 13158 LNCS (2022) 365–376.

2. Nhan N.T., Podstrigaev A.S., Likhachev V.P., Myazin N.S., Makeev S.S., Study of detection characteristics in recognition of simple radio pulses and signals with lfm and psk in the autocorrelation receiver, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 12525 LNCS (2020) 415–423.

3. Davydov R.V., Dudkin V.I., Nikolaev D.I., Makeev S.S., Moroz A.V., Structure of a Nuclear Magnetic Resonance Signal in a Small Relaxometer, Journal of Communications Technology and Electronics. 66 (5) (2021) 632–636.

4. Likhachev V.P., Podstrigaev A.S., Nhan N.T., Study of the accuracy of determining the location of radio emission sources with complex signals when using autocorrelation and matrix receivers in broadband tools for analyzing the electronic environment, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 12525 LNCS (2020) 326–333.

5. **Petrov A.A., Grebenikova A.A.,** Some Directions of Quantum Frequency Standard Modernization for Telecommunication Systems, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 11118 LNCS (2018) 641–648.

6. Fadeenko V.B., Fadeenko I.V., Vasiliev D.A., Rud V.Yu., Multifunctional radar system for remote control of environment and the Earth's surface, Journal of Physics: Conference Series. 1745 (1) (2021) 012023.

7. Tarasenko M.Y., Lenets V.A., Akulich N.V., Yalunina T.R., Features of use direct and external modulation in fiber optical simulators of a false target for testing radar station, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 10531 LNCS (2017) 227–232.

8. Elokhin A.P., Ran D.F., Berkovich V.M., Vinogradov A.P., Zhilina M.V., Estimate of the emission rate of radioactive rare gases during an unanticipated accident at a VVЙR-1500 reactor, Atomic Energy. 104 (1) (2008) 62–76.

9. Podstrigaev A.S., Lukiyanov A.S., Smolyakov A.V., Nikitina M.I., The expediency of fiber-optical communication line used in different schemes of receiver tract of the radio-monitoring complex, Journal of Physics: Conference Series. 1368 (2) (2019) 022027.

10. Moroz A.V., Davydov V.V., Malanin K. Y., Krasnov A. A., Development of a Compensation System Based on Horn Antennas for an Active Phased Antenna Array, Proceedings of the 2019 Antennas Design and Measurement International Conference, ADMInC 2019. 8969090 (2018) 114–116.

11. Moroz A.V., Malanin K.Y., Krasnov A.A., Rud V.Yu., Features of the construction of the noise compensation circuit of a small-sized active phased antenna array, Journal of Physics: Conference Series. 1400 (4) (2019) 044009.

12. Davydov R.V., Saveleiv I.K., Lenets V.A., Rud' V.Yu., Fiber-optic transmission system for the testing of active phased antenna arrays in an anechoic chamber, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 10531 LNCS (2017) 177–183.

13. Sviatkina V., Kuptsov V., Rud V., On possibility of using of spectral analysis for control the energy distribution of electromagnetic waves in radar channels, Proceedings of ITNT-2020 – 6th IEEE International Conference on Information Technology and Nanotechnology. 9253166 (2020) 232–237.

14. **Gryaznova E.M., Malanin K.Y.,** A system with a fiber-optic communication line for measuring the parameters of active phased antenna arrays in the far zone in landfill conditions, Proceeding 8th International Conference on Information Technology and Nanotechnology, (ITNT-2022) (2022) 234–258.

15. Fadeenko V.B., Pchelkin G.A., Beloshapkina O.O., Rud V.Y., Features of construction of the scheme of fiber-optic communication system for transmission of analog signals in the frequency range from 0.135 to 40 GHz, Journal of Physics: Conference Series. 1410 (1) (2019) 012238.

THE AUTHORS

FADEENKO Varvara B. v21.07.96@mail.ru

VALOV Anton P. tony.valov2015@yandex.ru

RYZHOVA Daria A. qwdarya1234@gmail.com ORCID: 0000-0002-7155-1892 SHAVSHIN Artyom V. shavshin2107@gmail.com ORCID: 0000-0002-3597-8901

Received 28.07.2023. Approved after reviewing 18.09.2023. Accepted 22.09.2023.

Conference materials UDC 53.06 DOI: https://doi.org/10.18721/JPM.163.275

Improving microwave output in rubidium-87 atomic frequency standard with new automatic gain control

A.V. Shavshin¹

¹ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

^{III} shavshin2107@gmail.com

Abstract. It's necessary to upgrade the existing scheme automatic control of the optical signal. The presented design was created to maintain the output power of an atomic frequency standard (AFS) based on rubidium-87 atoms at a given level, correcting changes in its operation introduced by external conditions. An improved circuit for automatic gain control with an additional link in the form of a proportional-integral-derivative (PID) controller and an improved circuit for extracting the 'error' signal are presented. A separate contribution of the subtractor and PID controller to the final gain control is considered, and mathematical modeling of microwave devices included in the microwave path is carried out.

Keywords: optical signal, atomic frequency standard, automatic gain control, optical pumping, stimulated emission, error signal, PID controller, Allan deviation

Citation: Shavshin A.V., Improving microwave output in rubidium-87 atomic frequency standard with new automatic gain control, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 428–433. DOI: https://doi.org/10.18721/JPM.163.275

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.06 DOI: https://doi.org/10.18721/JPM.163.275

Улучшение выходной мощности квантового стандарта частоты на атомах рубидия-87 с помощью новой автоматической регулировки усиления

А.В. Шавшин¹⊠

¹ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

^{III} shavshin2107@gmail.com

Аннотация. Обоснована необходимость модернизации существующей схемы автоматической регулировки оптического сигнала. Представленная конструкция создана для поддержания выходной мощности квантового стандарта частоты (КСЧ) на атомах рубидия87- на заранее заданном уровне, корректируя изменения в его работе, вносимые внешними условиями. Представлены усовершенствованные схемы автоматической регулировки усиления (АРУ) с дополнительным звеном в видео пропорционально-интегрального-дифференциального (ПИД) регулятора, и схема выделения «сигнала ошибки». Рассмотрен отдельный вклад системы выделения «сигнала ошибки» и ПИД-регулятора на конечную регулировку усиления, а также выполнен математических расчет СВЧ-компонент, входящих в СВЧ-тракт.

Ключевые слова: оптический сигнал, квантовый стандарт частоты, автоматическая регулировка усиления, оптическая накачка, вынужденная эмиссия, сигнал ошибки, ПИД-регулятор, девиация Аллана

© Shavshin A.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Шавшин А.В. Улучшение выходной мощности квантового стандарта частоты на атомах рубидия87- с помощью новой автоматической регулировки усиления // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 428–433. DOI: https://doi.org/10.18721/JPM.163.275

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In the modern world, quantum frequency standards are indispensable sources of highly stable, spectrally pure electrical signals to consider more in-depth topics in the scientific and technical fields [1-6]. There are areas in which they cannot be dispensed with [7-11]. Special requirements are imposed on atomic frequency standards (AFS), which are used in navigation systems, and common time systems [2, 8, 10, 12–14]. One of such AFSs are standards based on rubidium-87 atoms [1, 2, 8]. Considering more stringent conditions for accuracy and stability of the output optical signal formation, it becomes necessary to modernize the AFS or develop new types of AFS based on other physical principles of operation. To carry out work to improve the accuracy characteristics of the AFS, in some cases it is sufficient to upgrade the functional units that directly affect total output values of the AFS. Thus, this paper presents the modernization of the path for the formation of the microwave signal of the excitation of rubidium-87 atoms, aimed at the formation of both the microwave signal itself and the parameters of the AFS output signal. Similar situations arise for other types of standards.

Updated atomic frequency standard circuit and system of automatic gain control with additional adjustment elements

During the analysis of the block diagram of the quantum frequency standard based on rubidium-87 atoms, it was decided to make a number of adjustments to its general form. The modified scheme of the atomic frequency standard is shown on Fig. 1.



Fig. 1. Updated block diagram for the rubidium frequency standard: quartz oscillator *I*; phase locked loop (PLL) rings 2 and 3; mixer 4; frequency synthesizer 5; automatic gain control 6; attenuator 7; quantum discriminator 8; automatic frequency control system (AFC) 9; frequency converter 10

The block diagram shows the operation of AFS, based on the principle of stabilization of the frequency of a quartz oscillator by the transition frequency of rubidium-87 atoms. CFS on rubidium atoms is a passive type frequency standard. The output signal of a 5 MHz quartz oscillator is used in the microwave frequency generation path as follows [1, 2, 8]. Frequency of 5 MHz to signal is fed from a crystal oscillator to a phase locked loop (PLL), which consists of two subsystems. From the output of the first subsystem, a wave with a frequency of 100 MHz is generated, which is a reference for the second PLL subsystem. The output signal of the second system is a signal with a frequency of 6.8 GHz. At the same time, another signal comes from the quartz oscillator to the frequency synthesizer. The output signal of the frequency synthesizer is a frequency modulated signal with a frequency of 34.5 MHz. After that, both signals enter the mixer, at the output of which the exact

frequency of the transition of the rubidium atom from one sublevel to another, equal to 6.834 GHz, is already formed. Next, the signal enters the automatic gain control (AGC) scheme, created to equalization the power level of the microwave signal with the same values. After the signal has stabilized thanks to the AGC system, it goes further to the attenuator. In our scheme, the final attenuator needed for the ending correction of the output microwave signal, which is then fed to the quantum discriminator.

© Шавшин А. В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 2. Upgraded automatic gain control circuit, with the addition of a PID controller section; attenuator 2; directional coupler 3; low-pass filter 4; detector diode 5, 'error' signal amplifier 6 connected as a subtractor; PID controller 7

As can be seen from the presented description of the operation of the AFS, the AGC system is one of the most important functional units of the microwave generation path and the entire structure of the AFS. Fig. 2 shows a modernized circuit diagram of the AGC system.

Since the input of the system receives a signal of insufficient power. The initial task is to strengthen it so that its power is captured for the work of combating discrimination. To fulfill this condition, an amplifier was integrated (1). Then attenuator (2) will be used as a controlled element, due to the adjustment of which the output power of the signal will be adjusted. To create an 'error' control signal, a portion of the original

signal is applied to the AGC circuit using a directional coupler set to -3dB. (3) and the rest of the signal passes at the output of the system. Next, the 'error' control signal must be straightened for the AGC system to work. Therefore, the signal passed through the directional coupler will then pass through the detector diode. (4). After detection, the signal, depending on the external operating conditions of the AFS, can have a different amplitude, based on which there is a need to be able to set the level yourself. For this, an 'error' signal enhancer is used on the operational amplifier (5), connected according to the subtractor circuit. Further, the generated 'error' signal is fed to the input of the PID controller (7). Depending on the values coming to the proportion-al-integral-derivative (PID) controller, the necessary corrective gain is analyzed, which will be applied to the attenuator.

Modeling and calculation of individual parts of automatic gain control

Initially, a directional coupler can be described as two pairs of parallel microstrip lines, representing an eight-terminal network. It is important to note that the electrical length of such microstrip lines must be equal to 1/4 of the wavelength to which the coupler must be tuned, Fig. 3. In the diagram, the numbers 1–4 indicate the inputs and outputs of the microstrip directional coupler.



Fig. 3. Microstrip stub bridge

The calculation of such a microstrip directional coupler will look like this:

$$\frac{1}{Z_{A2}^2} - \frac{1}{Z_{A1}^2} = 1, \ s_{ii} = 0, \ s_{14} = s_{32} = 0,$$

$$s_{21} = -jZ_{B2}, \ s_{31} = -Z_{B2} / Z_{B1}.$$

Using the following well-known formulas [15], where in the calculations the unit wave impedance of a microstrip line Z_0 is taken as 1 Ohm, in our case we will take it as 50 Ohm. Next, we find the unknown parameters of the stub bridge.

The modular values of S_{21} and S_{31} will only be equal if Z_{B1} is equal to unit impedance. In our case, let us take it equal to 50 Ohms.

$$Z_{B1} = 50$$
 Ohm,

$$Z_{Bi} = \frac{Z_{Bi}}{Z_0}; 1/Z_{B2}^2 - 1/Z_{B1}^2 = 1 \Longrightarrow 1/Z_{B2}^2 = 2.$$

In our case, the resistance Z_{B2} will take a value equal to 35.5 Ohms. Having completed all the calculated for a directional coupler, we obtain its final scattering matrix.

$$S = \frac{1}{\sqrt{2}} * \begin{pmatrix} 0 & 1 & -j & 0 \\ 1 & 0 & 0 & -j \\ -j & 0 & 0 & 1 \\ 0 & -j & 1 & 0 \end{pmatrix}.$$

To model a directional coupler for a specific frequency, it is necessary to calculate it in Microwave Office with the given substrate parameters. In our case, the calculation will be performed for the Rogers RO4003C substrate at a frequency of 6.834 GHz. In the program to draw the model, using the MLIN element, a microstrip line was simulated, and the element MTEE was simulated the implementation of the separation of microstrip lines in two directions. Figs. 4 and 5 show calculated parameters and circuit of a new microstrip directional coupler.



Fig. 4. Schematic view of a directional coupler in Microwave Office



Fig. 5. Spectral power distribution in a new microstrip directional coupler design. Decibels are plotted on the vertical axis

On the final characteristics of the spectral power distribution in the directional coupler, one can observe an improvement in performance by 10 dB, which is due to the correct choice of substrate and more precise tuning.

Analysis of experimental data

For illustration, in the work of this study, the results of the values of the QFS in the temperature range from -20 °C to 35 °C are given. Allan variance measurements $\sigma^2(\tau)$ are presented for three different AFS configurations: the first characteristic was taken without AGC, the second characteristic was taken using the old version of AGC, the third characteristic was taken using the new AGC configuration using a PID controller Fig. 6.



Fig. 6. Diagram of Allan variance versus time with an upgraded AGC system (graph 3), previously used (graph 2) and without the AGC system (graph 1) in AFS

Thanks to dispersion, it is possible to estimate the level of stability of the frequency of atomic clocks and generators. Analyzing the obtained results, we can make sure that the addition of the AGC system in the first case improved the Allan variance values $\sigma^2(\tau)$ by 12%, and with an additional link in the form of a PID controller, it showed an improvement by 16%.

Conclusion

Through a series of improvements, a new AGC system was implemented for the microwave path of the ASC based on rubidium-87 atoms using a PID controller. An improved directional coupler for a frequency of 6.834 GHz was configured on a new substrate, removed its characteristics, which turned out to be better than the previous model necessary for use in AFS.

After analyzing all the obtained results of the prototype AGC system, it can be seen that the output characteristics of the frequency converter have been improved. Thanks to the new AGC system, it was possible to achieve a decrease in the values of the Allan variance by 16%.

REFERENCES

1. Hudson A., Camparo J., Quantum System Dynamics and the Quasistatic Approximation, Physical Review Applied. V. 13 (6) 064007.

2. **Riehle F.,** Frequency standard. Basic and applications, WILEY-VCH Verlag CmbH Co. KGaA: New-York, September 2008.

3. **Petrov A.A.**, Improvement frequency stability of caesium atomic clock for satellite communication system, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 9247 (2015) 739–744.

4. Myazin N.S., Dudkin V.I., Grebenikova N.M., Davydov R.V., Podstrigaev A.S., Fiber - optical system for governance and control of work for nuclear power stations of low power, Lecture Notes in Computer Science. 11660 (2019) 744–756.

5. Kuzmin M.S., Rogov S.A., On the use of a multi-raster input of one-dimensional signals in twodimensional optical correlators, Computer Optics. 43 (3) (2019) 391–396.

6. **Petrov A.A., Zaletov D.V., Shapovalov D.V.,** Peculiarities of Constructing a Scheme for Formation of a Microwave Excitation Signal in a Cesium Atomic Clock, Journal of Communications Technology and Electronics. 66 (3) (2021) 295–299.

7. Davydov V.V., Davydova T.I., A nondestructive method for express testing of condensed media in ecological monitoring, Russian Journal of Nondestructive Testing. 53 (7) (2017) 520–529.

8. Dudkin V.I., Myazin N.S., Davydov R.V., On the Possibility of Studying Ferrofluids by a Nuclear Magnetic Magnetometer with a Flowing Sample, Journal of Communications Technology and Electronics. 65 (5) (2020) 558–564.

9. Mihov E.D., Nepomnyashchiy O.V., Selecting informative variables in the identification problem Journal of Siberian Federal University - Mathematics and Physics. 9 (4) (2016) 473–480.

10. **Ryzhenko I.N., Lutsenko A.E., Varygin O.G., Nepomnyashchiy O.V.,** Carrier compensation mode implementation in satellite communication channels. In: Proceedings of 2019 International Siberian Conference on Control and Communications, SIBCON, 8729665 (2019) 23–29.

11. **Petrov A.A., Grebenikova N M.,** Some Directions of Quantum Frequency Standard Modernization for Telecommunication Systems, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 11118 LNCS (2018) 641–648.

12. Davydov R., Antonov V., Moroz A., Parameter Control System for a Nuclear Power Plant Based on Fiber-Optic Sensors and Communication Lines, In: IEEE International Conference on Electrical Engineering and Photonics (EExPolytech), Saint-Petersburg, Russia, 8906791 (2019) 295–297.
13. Petrov A.A., Shabanov V.E., Zalyotov D.V., Bulyanitsa A.L., Shapovalov D.V., Modernization of the frequency synthesizer of cesium atomic clock, IEEE International Conference on Electrical Engineering and Photonics, EExPolytech 2018, Saint-Petersburg, 8564389 (2018) 52–55.

14. Lukashev N.A., Moroz A.V., Compact microwave frequency standard on Hg-199 ions for navigation systems, Journal of Physics: Conference Series. 1236 (1) (2019) 012068.

15. Shavshin A.V., Development of automatic control of optical signal gain in a atomic frequency standard based on rubidium-87 atoms, IEEE 2022 VIII International Conference on Information Technology and Nanotechnology (ITNT), (21991987) 126–131.

THE AUTHOR

SHAVSHIN Artyom V. shavshin2107@gmail.com ORCID: 0000-0002-3597-8901

Received 04.08.2023. Approved after reviewing 29.08.2023. Accepted 29.08.2023.

Conference materials UDC 53.081.1 DOI: https://doi.org/10.18721/JPM.163.276

Investigation of a method for improving phase noise in the frequency standard generator block

A.P. Valov¹[™], R.A. Dmitriev², V.V. Davydov³, A.V. Shavshin³

¹ The Bonch-Bruevich St. Petersburg State University of Telecommunications, St. Petersburg, Russia;

² The Russian Institute of Radionavigation and Time, St. Petersburg, Russia;

³ Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

[™] tony.valov2015@yandex.ru

Abstract. In the modern world, information transmission systems, telecommunication and satellite navigation systems, as well as metrological services play an important role in our lives. However, the development of these systems leads to the constant need to upgrade the currently used quantum frequency standards. To improve the short-term stability of the frequency standard, a new method has been developed to upgrade the oscillator unit and the frequency standard output amplifiers. In the course of experimental studies of the metrological characteristics of the quantum frequency standard based on rubidium-87 atoms, the effectiveness of the new development was shown.

Keywords: atomic clock, frequency standard, phase noise, metrology, stabilization

Citation: Valov A.P., Dmitriev R.A., Davydov V.V., Shavshin A.V., Investigation of a method for improving phase noise in the frequency standard generator block, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 434–438. DOI: https://doi.org/10.18721/JPM.163.276

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 53.081.1 DOI: https://doi.org/10.18721/JPM.163.276

Исследование метода снижения фазового шума в блоке генератора стандарта частоты

А.П. Валов¹[™], Р.А. Дмитриев², В.В. Давыдов³, А.В. Шавшин³

¹ Санкт-Петербургский государственный университет телекоммуникаций им. проф. М.А. Бонч-Бруевича, Санкт-Петербург, Россия;

² Российский институт радионавигации и времени, Санкт-Петербург, Россия;

³ Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

[™] tony.valov2015@yandex.ru

Аннотация. В современном мире важную роль в нашей жизни играют информационные системы, телекоммуникационные и спутниковые навигационные системы, а также службы метрологических передач. Однако развитие этих систем приводит к постоянной необходимости модернизации используемых в настоящее время квантовых стандартов частоты. Для повышения кратковременной стабильности эталона частоты был разработан новый метод модернизации блока генератора и выходных усилителей эталона частоты. В ходе экспериментальных исследований метрологических характеристик квантового стандарта частоты на основе атомов рубидия-87 была показана эффективность новой разработки.

Ключевые слова: атомные часы, стандарт частоты, фазовый шум, метрология, стабилизация

© Valov A.P., Dmitriev R.A., Davydov V.V., Shavshin A.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Валов А.П., Дмитриев Р.А., Давыдов В.В., Шавшин А.В. Исследование метода снижения фазового шума в блоке генератора стандарта частоты // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 434–438. DOI: https://doi.org/10.18721/JPM.163.276

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

In today's world, accurate measurement of time and frequency is necessary for conducting various experiments in many fields of science, for example, atomic physics (atomic-photon interactions, atomic collisions and atomic interactions with static and dynamic electromagnetic fields), the study of the earth's surface (geodesy) or outer space radio astronomy and pulsar astronomy [1–6]. Without highly stable sources of frequency and time, the operation of communication equipment and metrological services is impossible [2–4, 7–11].

A special place among devices for determining frequency and time is occupied by quantum frequency standards (QFS). The main advantage of QFS over other devices is the use of laser radiation frequency stabilization systems and optical elements for stable operation [7, 10, 12–15].

A slight deviation of the frequency from the nominal value leads to large errors, especially when transmitting large data streams. One of the main problems of the satellite system is the mutual synchronization of time scales of space vehicles up to ns or less [3]. For example, the error of navigation signals emitted by different satellites with a time mismatch of 10 ns causes an additional error in determining the location of an object at 10-15 m.

The expansion of the range of tasks for which satellite navigation systems are used required an increase in the accuracy of determining the position of an object up to 0.5 m. On the other hand, with the development of scientific and technological progress, the composition of the used electronic equipment changes. All this requires constant modernization of QFS [3, 10, 12, 15–17].

The development and commissioning of new QFS models is a very long and expensive process. In most cases, there is no time and sufficient funds for its implementation. Therefore, in most cases, to solve specific problems, modernization is carried out: changing the weight and dimensions, reducing energy consumption, improving the metrological characteristics of QFSs that are in operation on rubidium-87 and cesium-133 atoms. The QFS is characterized by the fact that modernization can be carried out not of its entire structure, but only of individual units or blocks [3, 10, 12, 15-17].

One of the important functional devices is the unit of the generator and output signal amplifiers (generator block), which is also a source of the QFS reference signal. The modernization of this device allows improving the metrological characteristics of the entire QFS, since the signal coming from this block is used in other QFS functional devices, including a frequency converter and a frequency synthesizer that generates a microwave signal for a quantum discriminator. The characteristics of this signal directly affect the metrological characteristics of the QFS.

Materials and Methods

The main function of the generator block in the operation of the frequency standard is the formation, reproduction and characterization of a certain level of the frequency amplitude of 5 MHz by regulating the voltage of the crystal oscillator (XO).

The signal from the XO is consumed at the pre-amplifier, where it is overtaken and divided into three channels. The next signal is consumed from the amplifier-filter, where the presence and filtering of the side components of the XO are manifested. The signal is turned off at the output of the amplifier, where there is a complete loss of the output signal.

Signal detection consumes higher frequencies in the frequency converter and frequency synthesizer, which generates high frequency signals of 60 MHz and 5.313 MHz used to observe the transition frequency of the rubidium-87 atoms in the discrimination measurement. Because of this, high demands are placed on the characteristics of the output signals of the blocking of the results of the increase in productivity.

© Валов А.П., Дмитриев Р.А., Давыдов В.В., Шавшин А.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.



Fig. 1. Structural diagram of the generator and output signal amplifiers

It is important that the generator block provides high accuracy of the output frequency, has a high suppression of side amplitude components in the signal spectrum with a frequency of 5 MHz, a low dependence of the change in the frequency and amplitude of the output signal on temperature, a low level of phase noise of the spectral characteristic of the signal, and was also implemented on the domestic electronic component base.

Taking into account all these requirements necessary to improve the metrological characteristics of the QFS, the authors upgraded the generator block and output signal amplifiers.

The new design of the generator block and frequency output amplifiers was developed based on bipolar type transistors with low phase noise characteristics.



Fig. 2 Power spectral density of phase noises: signal of old generator block design (a); low-noise quartz oscillator (b)



Fig. 3. Power spectral density of phase noises: signal of modified generator block design (*a*); low-noise quartz oscillator (*b*)

Results and Discussion

According to the research results, it has been established that the new design is capable of reducing the spectral density of phase noise to a level comparable to that of a crystal oscillator with the best characteristics. Such a reduction in the spectral density of phase noise also allows for a reduction in their influence on subsequent devices in the frequency standard, which in turn improves short-term frequency stability.

Measurements of the old generator block design and the modified design are shown in Fig. 2 and Fig. 3.

Reducing the phase noise spectral density also reduces the effect of phase noise on further devices in the frequency standard, which improves short-term frequency stability.

Measurement of the root mean square deviation with a measurement time of 1 second using a sliding window over a 3-hour observation period of the output signal of the QFS with a modernized generator block and output amplifiers showed a decrease in this value compared to the old design. The mean of the old design was $1.9-10^{-12}$ arb. units, while the mean of the modified design is $1.7-10^{-12}$ arb. units.

Conclusion

The results of the research on the new design of the generator block and output signal amplifiers showed the feasibility of using this solution as part of a quantum frequency standard. As a result of the tests conducted on the generator block and output signal amplifiers in the QFS, a 6% reduction in the level of spectral phase noise was recorded at tuning frequencies of 10–100 Hz and allowed to improve the short-term frequency stability by 10%.

REFERENCES

1. **Riehle F.**, Frequency standard. Basic and applications, WILEY-VCH Verlag CmbH Co. KGaA: New-York, 2008.

2. Arinushkina K., Grevsteva A., Valov A., Lukashev N., Development of the Controllable C-field Current Stabilizer for the Atomic Beam Tube of the Cesium Atom Clock. Springer Proceedings in Physics. 268 (2022) 589–596.

3. Petrov A. A., Shabanov V. E, Zalyotov D. V., Bulyanitsa A. L., Shapovalov D. V., Modernization of the frequency synthesizer of cesium atomic clock, In IEEE International Conference on Electrical Engineering and Photonics, (EExPolytech - 2018), Saint-Petersburg, Russia, 8564389 (2018) 52–55.

4. Almat N., Pellaton M., Moreno W., et al. Rb vapor-cell clock demonstration with a frequencydoubled telecom laser, Appl. Opt. 57 (2008) 4707.

5. Mihov E.D., Nepomnyashchiy O.V., Selecting informative variables in the identification problem Journal of Siberian Federal University - Mathematics and Physics. 9(4) (2016) 473–480.

6. **Ryzhenko I.N., Lutsenko A.E., Varygin O.G., Nepomnyashchiy O.V.,** Carrier compensation mode implementation in satellite communication channels. In: Proceedings of 2019 International Siberian Conference on Control and Communications, SIBCON. 8729665 (2019) 23–29.

7. **Petrov A.A.**, Improvement frequency stability of caesium atomic clock for satellite communication system, Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics). 9247 (2015) 739-744.

8. Myazin N.S., Dudkin V.I., Grebenikova N.M., Davydov R.V., Podstrigaev A.S., Fiber - optical system for governance and control of work for nuclear power stations of low power, Lecture Notes in Computer Science. 11660 (2019) 744–756.

9. Kuzmin M.S., Rogov S.A., On the use of a multi-raster input of one-dimensional signals in twodimensional optical correlators, Computer Optics. 43(3) (2019) 391–396.

10. **Petrov A.A., Zaletov D.V., Shapovalov D.V.,** Peculiarities of Constructing a Scheme for Formation of a Microwave Excitation Signal in a Cesium Atomic Clock, Journal of Communications Technology and Electronics. 66(3) (2021) 295–299.

11. Davydov R., Antonov V., Moroz A., Parameter Control System for a Nuclear Power Plant Based on Fiber-Optic Sensors and Communication Lines, In: IEEE International Conference on Electrical Engineering and Photonics (EExPolytech), Saint-Petersburg, Russia, 8906791 (2019) 295–297.

12. Lukashev N.A., Moroz A.V., Compact microwave frequency standard on Hg-199 ions for navigation systems, Journal of Physics: Conference Series. 1236 (1) (2019) 012068.

13. **Tarasov A.D., Milder O.B.**, Gradation traectories as an analog of gradation curves in the metric cie lab space discrete approache, Computer Optics. 43 (1) (2018) 104–110.

14. Lukashev N.A., Petrov A.A., Grebenikova N.M., Improving performance of quantum frequency standard with laser pumping, Proceedings of 18th International conference of Laser Optics ICLO-2018 Saint-Petersburg, 8435889, (2018) 271.

15. **Petrov A.A.**, Digital Frequency Synthesizer for ¹³³Cs-Vapor Atomic Clock, Journal of Communications Technology and Electronics. 62 (3) (2017) 289–293.

16. Shavshin A.V., Development of automatic control of optical signal gain in a atomic frequency standard based on rubidium-87 atoms, IEEE 2022 VIII International Conference on Information Technology and Nanotechnology (ITNT), 21991987 (2022) 126–131.

17. Valov A.P., Arinushkina K.G., The use of digital data processing to improve the metrological characteristics of the rubidium frequency standard, Journal of Physics: Conference Series. 2086 (1) (2021) 012070.

THE AUTHORS

VALOV Anton P. tony.valov2015@yandex.ru DAVYDOV Vadim V. davydov_vadim66@mail.ru

DMITRIEV Roman A. Rusher.official@gmail.com ORCID: 0000-0002-2964-1165 SHAVSHIN Artyom V. shavshin2107@gmail.com ORCID: 0000-0002-3597-8901

Received 07.08.2023. Approved after reviewing 21.09.2023. Accepted 27.09.2023.

THEORETICAL PHYSICS

Conference materials UDC 535 DOI: https://doi.org/10.18721/JPM.163.277

Excess leakage of information in quantum key distribution with passive side channels

D.V. Babukhin¹[™], D.V. Sych²

¹Limited Liability Company QRate, Moscow, Russia;

² P.N. Lebedev Physical Institute of the RAS, Moscow, Russia

[™] dv.babukhin@gmail.com

Abstract. Passive side channels of the photon source make quantum key distribution (QKD) protocols insecure. To restore security, we need to incorporate the leakage through the side channel into the secret key estimate, but there is no definitive way to do that. In this work, we compare several practical methods of secret key rate estimating in QKD protocols with photon distinguishability side channel. We calculate upper bounds on secret key generation rates, using two reinterpretations of eavesdropper excess information – the effective error method and the a-priori loss method. We demonstrate that the effective error method provides tighter upper bound on the secret key rate than a-priori loss. Our results refine the toolbox of estimating security of QKD protocols with passive source side channels.

Keywords: quantum key distribution, source side channels, BB84 with decoy states

Citation: Babukhin D.V., Sych D.V., Excess leakage of information in quantum key distribution with passive side channels, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 439–442. DOI: https://doi.org/10.18721/JPM.163.277

This is an open access article under the CC BY-NC 4.0 license (https://creativecommons. org/licenses/by-nc/4.0/)

Материалы конференции УДК 535 DOI: https://doi.org/10.18721/JPM.163.277

Избыточная утечка информации в системах квантового распределения ключей с пассивными побочными каналами

Д.В. Бабухин¹[™], Д.В. Сыч²

¹ООО «КуРэйт», Москва, Россия;

² Физический институт имени П. Н. Лебедева РАН, Москва, Россия

[™] dv.babukhin@gmail.com

Аннотация. Пассивные побочные каналы источника фотонов делают протоколы квантового распределения ключей (КРК) небезопасными. Чтобы восстановить безопасность, необходимо включить утечку через побочный канал в оценку секретного ключа, но не существует определенного способа сделать это. В этой работе мы сравниваем несколько практических методов оценки скорости секретного ключа в протоколах КРК с побочным каналом, возникающим от частичной различимости фотонов, и демонстрируем, что метод эффективной ошибки обеспечивает более жесткую верхнюю границу для скорости генерации секретных ключей, чем метод априорных потерь.

Ключевые слова: квантовое распределение ключей, побочные каналы источников информации, протокол ББ84 с состояниями-ловушками

[©] Babukhin D.V., Sych D.V., 2023. Published by Peter the Great St. Petersburg Polytechnic University.

Ссылка при цитировании: Бабухин Д.В., Сыч Д.В. Избыточная утечка информации в системах квантового распределения ключей с пассивными побочными каналами // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.2. С. 439–442. DOI: https://doi.org/10.18721/JPM.163.277

Статья открытого доступа, распространяемая по лицензии СС BY-NC 4.0 (https:// creativecommons.org/licenses/by-nc/4.0/)

Introduction

Theoretical QKD protocols, which promise unconditional security, are based on idealistic model of optical hardware. These models often differ from real devices performance. The gap between practice and theory leads to excess leakage of information about secret key towards an eavesdropper through side channels. There are many reasons why such leakage can occur, and the problem of estimating and/or eliminating unwanted leakages of information is an active research topic [1, 2].

Photon distinguishability side channel is one of such side channels, which provide the eavesdropper with additional information. This kind of such channel does not require any active interaction between the eavesdropper and hardware of legitimate users, so this side channel is passive. One of the prospective ways to solve the problem of passive source side channels is the development of methods to estimate information leakage. The standard method, used in the field, is a GLLP approach [3], which incorporates side channel eavesdropping from the general perspective. Although being general, this approach provides pessimistic rates of secret key generation, thus guaranteeing QKD systems to be secure only on very short distances. Taking into account specific structure and nature of a particular side channel, as well as considering explicit eavesdropping strategies on QKD systems with such a side channel can provide more optimistic security estimates [4].

In recent paper [5], there was introduced a practical method to estimate excess leakage of information through the photon distinguishability side channel in a BB84 decoy state protocol. This method uses reinterpretation of additional information of the eavesdropper to calculate a so-called effective error, a cumulative parameter, which incorporates both eavesdropping on the protocol and on the passive side channel. This method is aimed to be a convenient practical tool to estimate security of QKD. Here we further refine the idea of this method. In particular, we consider another possible reinterpretation of additional information, dubbed a-priori loss method, and investigate the security of the QKD protocol, estimated using both of described methods. We show that the effective error method provides more tight security estimate than the a-priori loss method.

Materials and Methods

When the eavesdropper (Eve) attacks the QKD protocol without side channels, she obtains information about secret key bit at the cost of introducing errors in legitimate sides communication, Alice (sender) and Bob(receiver), of the value Q. If a side channel is available, Eve obtains excess information Δh about the secret key without introducing communication error. This excess information formally incorporated to the loss of mutual information between legitimate sides and interpreted as an information leaked to the eavesdropper. The secret key rate of the QKD protocol then is calculated from information relations between three main actors:

$$R^{\Delta} = 1 - h(Q) - (h(Q) + \Delta h), \tag{1}$$

Formally, the excess information term can be moved across the secret key rate, and the meaning of this term changes. In particular, the secret key rate (1) contains three terms. The first term (the a-priori term) corresponds to initial entropy of the Alice source and bounds the amount of information to be send through a communication channel (it is 1 bit in most QKD protocols with discrete variables). The second term (the a-posteriori term) is the conditional entropy of the Bob after measurement of the physical carrier (a photon or another light pulse) at the end of the communication channel. Finally, the third term corresponds to information leakage towards Eve as a result of her eavesdropping actions. Moving the excess information from side channels to one

[©] Бабухин Д.В., Сыч Д.В., 2023. Издатель: Санкт-Петербургский политехнический университет Петра Великого.

of the two first terms, we reinterpret excess information of the eavesdropper such that this amount of information influences legitimate sides instead of the adversary. This transforms the equation for the secret key rate to the following:

$$R^{\Delta} = 1 - h(Q) - (h(Q) + \Delta h) = 1 - h(Q^{\Delta}) - h(Q) = 1 - \Delta h - 2h(Q).$$
⁽²⁾

Moving excess information to the a-priori term corresponds to Bob knowledge about Alice before measurement or, alternatively, to the randomness of Alice source; this interpretation constitutes the *a-priori loss method* of estimating QKD security. Contrary, moving excess information to the a-posteriori term corresponds to information gain about Alice photon state after Bob's measurement; this interpretation constitutes *the effective error method*.

The proposed two methods provide novel points of view on the effect of the source side channel on the communication process. The first point is the decrease of the randomness of the Alice source, and the other point is the reduced quality of Bobs measurement devices, leading to equivalent theoretic information relations between communication sides. It is interesting to compare these interpretations in application to a particular QKD protocol. To do so, we calculate secret key rates in the BB84 protocols with decoy states in two ways: using the effective error method

$$R_{\rm l}^{\Delta} = Q_{\rm l} \left(1 - h \left(e_{\rm l}^{\Delta} \right) \right) - f Q_{\mu} h \left(E_{\mu}^{\Delta} \right), \tag{3}$$

and using the a-priori loss method

$$R_{2}^{\Delta} = Q_{1} \left(1 - \Delta h - h(e_{1}) \right) - f Q_{\mu} h(E_{\mu}).$$
(4)

To model the eavesdropping on the signal degree of freedom – the photon physical quantity, used to distribute a secret key bit – we use a phase-covariant cloning attack, which is the most powerful attack on the ideal BB84 protocol (without side channels and with single photons as a bit carrier) [6]. This operation then is followed by a collective attack on the signal and side channel system: Eve measures the state of composite system with a collective measurement, which gives her the Holevo value amount of information [7] about secret bits. The main purpose of this work is to compare these two methods and to define which one provides a tighter upper bound on the secret key rate for the BB84 decoy state protocol with a passive source side channel.

Results and Discussion

Fig. 1 shows secret key rates for two estimation approaches described above. We use standard parameters of QKD setups – optical fiber attenuation $\alpha = 0.2$, average photon number per pulse $\mu = 0.5$, optical error rate 1%, dark count probability $Y_0 = 10^{-5}$, and error correction efficiency f = 1.1.



Fig. 1. Secret key rates, calculated with two methods, the effective error method and a-priori loss method, for different values of side channel leakage parameter Δ

From the figure we can see the difference between resulting secret key rates, calculated with two approaches. In particular, the effective error method provides tighter upper bound on the secret key generation rate than the a-priori loss method. This result illustrates imbalance in interpreting excess eavesdropper information as an information change of legitimate sides.

Conclusion

In this work we provided an extended analysis of the method to estimate QKD security with passive source side channels, proposed in [2]. We show that assigning the loss of excessive error to a-posteriori outcome of legitimate receiver, the basis of the effective error method, provides tighter estimate of the secret key upper bound than in the case of a-priori information loss. This finding allows us to definitely use the effective error method as a practical way to estimate security of QKD with passive side channels, compared to a-priori information loss interpretation. Development tools of estimating security in real-world QKD systems, which inevitably contain side channels, allow faster engagement of these systems into practice.

REFERENCES

1. Scarani V., Kurtsiefer C., The black paper of quantum cryptography: real implementation problems, Rev. Mod. Phys. 1 (560) (2014) 27–32.

2. Sych D.V., Duplinskiy A.V., Babukhin D.V., Practical security of quantum key distribution in the presence of side channels, J. Phys.: Conf. Ser. (1984) 012001.

3. Gottesman D., Lo H.-K., Lütkenhaus N., Preskill J., Security of quantum key distribution with imperfect devices, Quant. Inf. Comput. 5 (2004) 325–360.

4. **Babukhin D., Kronberg D., Sych D.,** Explicit attacks on the Bennett-Brassard 1984 protocol with partially distinguishable photons, Phys. Rev. A 106, 042403 (2023).

5. **Babukhin D.V., Sych D.V.,** Joint eavesdropping on the BB84 decoy state protocol with an arbitrary passive light-source side channel, arXiv2211.13669.

6. Bruß D., DiVincenzo D.P., Ekert A., Fuchs C.A., Macchiavello C., Smolin J.A., Optimal universal and state dependent quantum cloning, Phys. Rev. A 57, 2368 (1998).

7. Holevo A.S., Bounds for the Quantity of Information Transmitted by a Quantum Communication Channel, Problems Inform. Transmission 9 (1973) 177–183.

THE AUTHORS

BABUKHIN Danila V. dv.babukhin@gmail.com SYCH Denis V. denis.sych@gmail.com

Received 07.07.2023. Approved after reviewing 13.07.2023. Accepted 26.09.2023.

Journal

ST. PETERSBURG STATE POLYTECHNICAL UNIVERSITY JOURNAL: PHYSICS AND MATHEMATICS

Vol. 16, No. 3.2, 2023

Founder and publisher: Peter the Great St. Petersburg Polytechnic University

The journal is registered with the Federal Service for Supervision of Communications, Information Technology and Mass Media (Roskomnadzor). Certificate $\Pi M \Phi C77$ -51457 issued 19.10.2012.

Editorial Office

Dr. Prof. V.K. Ivanov, Editor-in-Chief Dr. Prof. A.E. Fotiadi, Deputy Editor-in-Chief Dr. Prof. V.V. Dubov Dr. Prof. P.A. Karaseov Dr. Assoc. Prof. V.M. Kapralova A.S. Kolgatina, translator N.A. Bushmanova, editorial manager

All papers presented are final author versions Peer review is under responsibility of the Organizing Committee

Phone 8 (812) 294-22-85

Website https://physmath.spbstu.ru/

E-mail: physics@spbstu.ru

Typesetting by A.S. Kolgatina

Published 30.10.2023. Format 60x84/8. Digital print. Printer's sheets Print circulation 1000. Order ID