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Photosensitive nanostructures based on gallium phosphide nanowires and carbon dots

I.A Kozko [1, 2] ✉, E.P. Karaseva [2], Z.F. Sosnovitskaia [2], M.S. Istomina [4, 5],
V.V. Fedorov [1, 2], S.V. Shmakov [2], V.M. Kondratev [2, 3], A.D. Bolshakov [2, 3, 6, 7]

[1] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;
[2] Alferov University, St. Petersburg, Russia;
[3] Moscow Institute of Physics and Technology (State University), Dolgoprudny, Moscow Region, Russia;
[4] Almazov National Medical Research Centre, St. Petersburg, Russia;
[5] St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia
[6] Yerevan State University, Yerevan, Armenia
[7] St. Petersburg State University, St. Petersburg, Russia
✉ ivkozko@gmail.com

Abstract. This research is devoted to study of the photosensitive properties of gallium phosphide epitaxial nanowires (NWs) decorated with carbon dots (CDs). The deposition of CDs facilitates the development of a new functional GaP/CDs material with electronic and optical characteristics distinct from those of the original pristine NWs. The photosensitivity of GaP NWs, both before and after the decoration, was assessed by analyzing their I-V characteristics and impedance spectra when subjected to light irradiation of ultraviolet (UV), visible, and infrared (IR) ranges. The findings reveal a significant photoresistive response of pristine GaP NWs when exposed to UV and blue light (390 nm and 470 nm wavelengths, correspondingly). In contrast, GaP NWs / CDs heterostructures exhibit a spectrally broader photoresistive response to light irradiation within the wavelength range of 390 to 850 nm. The results of this study highlight the potential use of the developed functional nanomaterial for fabricating photodetectors capable of operating across a wide spectral range, utilizing a relatively simple fabrication protocol.

Keywords: GaP, nanowires, carbon dots, photodetector

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Фоточувствительные наноструктуры на основе нитевидных нанокристаллов фосфида галлия и углеродных точек

И.А. Козко [1, 2] ✉, Е.П. Карасева [2], З.Ф. Сосновицкая [2], М.С. Истомина [4, 5],
В.В. Фёдоров [1, 2], С.В. Шмаков [2], В.М. Кондратьев [2, 3], А.Д. Большаков [2, 3, 6, 7]

[1] Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;
[2] Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия;
[3] Московский физико-технический институт (государственный университет), г. Долгопрудный, Московская обл., Россия;
[4] Национальный медицинский исследовательский центр им. В. А. Алмазова, Санкт-Петербург, Россия
[5] Санкт-Петербургский государственный электротехнический университет «ЛЭТИ», Санкт-Петербург, Россия;
[6] Ереванский государственный университет, Ереван, Армения
[7] Санкт-Петербургский государственный университет, Санкт-Петербург, Россия
✉ ivkozko@gmail.com

Аннотация. В данной работе исследуются фоточувствительные свойства эпитаксиальных нитевидных нанокристаллов (ННК) фосфида галлия, а также пути их модификации углеродными точками (УТ). ННК GaP демонстрируют выраженный фоторезистивный отклик при облучении светом УФ и синего диапазона (390 нм и 470 нм, соответственно). Гибридные стурктуры GaP/УТ демонстрируют спектрально широкий фоторезистивный отклик к световому излучению в диапазоне от 390 до 850 нм. Результаты данной работы интересны, в первую очередь, с точки зрения возможности использования разработанного функционального наноматериала для создания фотодетекторов широкого спектрального диапазона согласно простому и технологичному протоколу.

Ключевые слова: фосфид галлия, нитевидный нанокристалл, углеродные точки, фотодетектор, детектор видимого света

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Introduction

The advancement of nanophotonics and quantum nanotechnologies has sparked significant demand for a new elemental and component base within quantum devices, encompassing light sources [1], waveguides [2], resonators [3], photodetectors [4], and sensors [5, 6]. Notably, semiconductor nanowires (NWs) obtained with molecular beam epitaxy, exhibiting a typical cross-sectional size of 50–300 nm and lengths ranging from hundreds of nanometers to several millimeters, present a promising avenue for leveraging their unique light absorption properties. Owing to their nanometer-scale cross-section, NWs manifest discernible differences in electronic and optical properties relative to bulk materials, while retaining a certain ease of post-growth processing due to their micrometer length. Additionally, NWs boast a substantial surface area to volume ratio, making it feasible to modify their surface with a range of nanostructures [7, 8]. These attributes render NWs highly versatile for fabricating memory elements, photodiodes, and photodetectors spanning various optical ranges, alongside their application in solar cells [9].

Semiconductor materials like gallium phosphide (GaP) can be synthesized in a NW geometry, offering both feasibility and efficient integration of III-V materials on silicon [10]. GaP NWs exhibit significant photoabsorption in the UV and blue light spectral ranges. However, their photosensitive characteristics can be effectively altered by applying coatings with altered absorption spectra. Such hybrid functional nanomaterials can be actively used to fabricate efficient detectors for visible light [11] and UV radiation [12].

This study introduces a novel approach for decoration of GaP NWs with carbon dots (CDs). Carbon dots (CDs) represent an advanced and distinctive class of modern nanomaterials that were initially derived by purifying single-walled carbon nanotubes in 2004 [13]. Since their inception, CDs have garnered considerable interest owing to their promising optoelectronic features properties, including adjustable absorption and emission. The photoluminescent characteristics of CDs present new opportunities for the processing of photosensitive nanomaterials, such as the hybrid nanostructure we are developing in this study.

Materials and Methods

The GaP NWs used in this work were synthesized with molecular beam epitaxy through a self-catalytic mechanism on a Si substrate with (111) orientation [10] using Veeco Gen-III machine (Veeco, St. Paul, USA). The morphology of the vertical arrays of GaP NWs was examined by scanning electron microscopy (SEM) (Zeiss Supra25, Carl Zeiss, Germany). The grown NWs exhibited a length of 25–30 μm and a typical cross-sectional size of approximately 200 nm (Fig. 1, *a*).

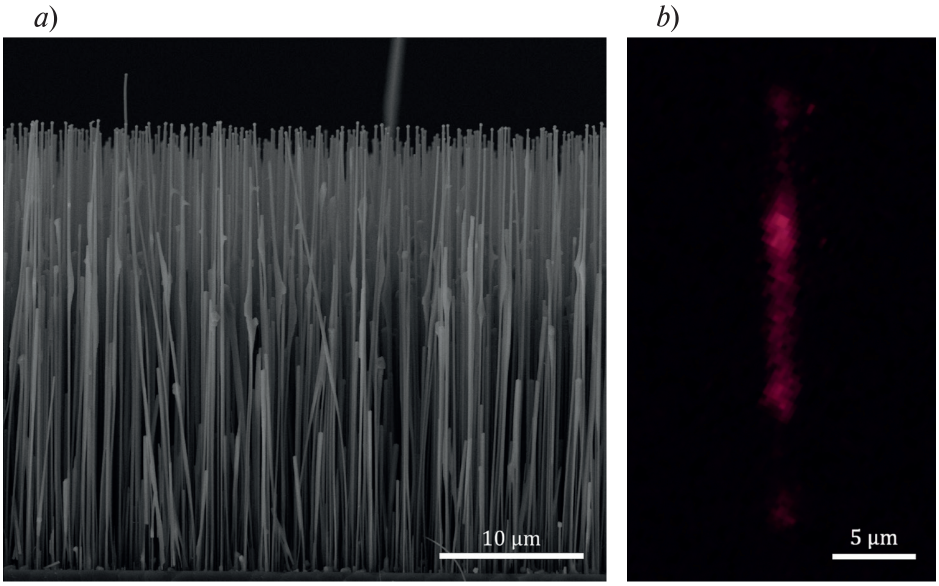

Fig. 1. SEM image of the as-synthesized vertical GaP NWs (*a*) and confocal image of the GaP NW /CDs on the measuring platform with interdigital gold contacts (laser wavelength: 561 nm; optical filter used for obtained image was set for central wavelength at 629 nm and a bandwidth of 62 nm) (*b*)

Carbon dots were derived from L-Lysine using a microwave-assisted technique [7]. The carbon precursors were diluted in water to achieve a homogeneous solution. Subsequently, the solution was transferred to a round bottom flask. Porous silicon plates were then added, initiating the microwave pyrolysis process. As the synthesis progressed, the color of the solution changed from colorless to dark brown, that indicated the carbonization reaction. Afterwards, the flask was cooled down to room temperature, and the silicon wafers were then removed.

To alter the photoresistive properties of the NWs, the synthesized vertical GaP NW array was transferred from a growth silicon substrate into an aqueous solution of CDs using an ultrasonic bath.

The photoresistive properties of the synthesized nanostructures were analyzed by examining their I-V characteristics using the SMU Keithley 2401 (Keithley Instruments, Solon, USA) and by performing electrical impedance spectroscopy using the impedancemeter TETRON-RLC501 (TETRON, Moscow, Russia). To fabricate the sensitive device, the GaP NWs, both pristine and modified, were placed on auxiliary platforms with interdigital gold contacts. The distribution of the NWs on the platform surface was studied using confocal microscopy with an AxioObserver Z1 microscope (Carl Zeiss, Oberkochen, Germany), as depicted in Fig. 1, *b*.

The photosensitive properties of GaP NWs before and after the modification were examined through the analysis of the I-V curves and impedance spectra under light irradiation with wavelengths of 390 nm, 470 nm, 570 nm, 622 nm, and 850 nm.

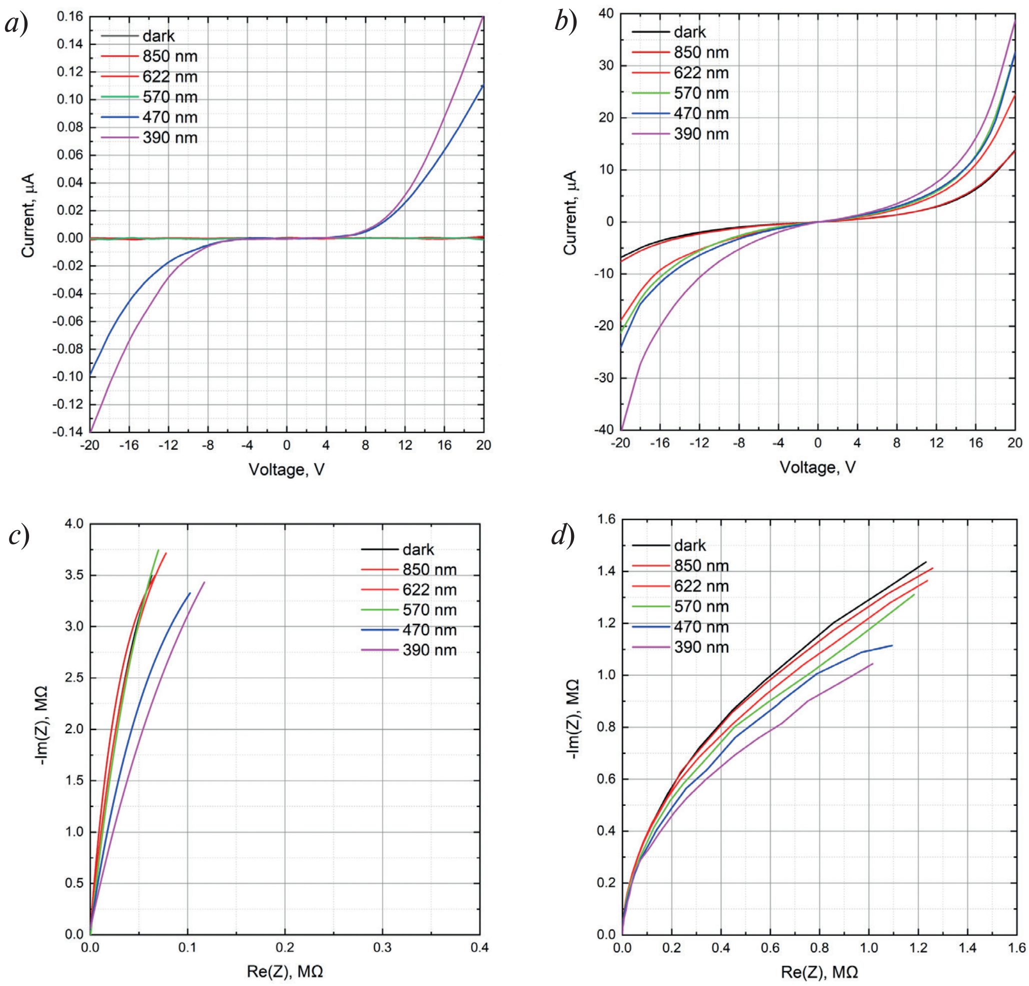

Fig. 2. Current–voltage characteristic demonstrating photoresponses of the non-modified GaP NWs (*a*) and GaP NWs/CDs (*b*), electrochemical impedance (Z) spectroscopy curves demonstrating photoresponses of the non-modified GaP NWs (*c*) and GaP NWs+CDs (*d*)

Results and Discussion

The confocal microscopy images revealed the fluorescence of GaP/CDs NWs under 561 nm laser illumination, and the spectral position of the observed fluorescence was estimated using an optical filter with a bandwidth of 598–660 nm (Fig. 1, *b*). Given the indirect GaP band structure, the observed fluorescence can be attributed solely to the CDs coating on the NW surface.

The CDs used in our study exhibit significant absorption in the visible range when in an aqueous solution [7]. Nonetheless, their photoabsorption undergoes considerable change after deposition, attributed to the agglomeration of the dots on the surface of the NWs. This effect is evident from the results of the performed electrophysical measurements (Fig. 2, *b*, Fig. 2, *d*).

The results depicted in Fig. 2, *b* and Fig. 2, *d* can be attributed to the effective transfer of charge carriers generated under light irradiation in the carbon coating into the conductive channel of the NWs. This process alters the electrical resistance of the NWs. Measurements of such resistance in both a DC and AC circuit can be used for detecting blue and UV light by unmodified NWs (Fig. 2, *a*, Fig. 2, *c*), and for detecting UV, visible, and near-IR light by GaP/CDs (Fig. 2, *b*, Fig. 2, *d*). Analysis of the I-V curves reveals the presence of a Schottky-type potential barrier at the NW-gold interface, which is responsive to changes in external conditions, akin to other semiconductor sensors and photodiodes featuring a Schottky barrier [5, 6].

The unmodified GaP NWs exhibited notable photoresponse exclusively under the blue and UV illumination (Fig. 2, *a*), in agreement with the optical absorption spectra of GaP [14]. Following modification with the CDs, the photosensitivity range of GaP extended to the visible optical range up to specific wavelengths (470, 570, 622, and 850 nm), accompanied by a significant increase in photocurrents, reaching tens of microamperes (Fig. 2, *b*).

Conclusion

In this study, we explore the photosensitive properties of GaP NWs modified by CD coating. Electrophysical measurements reveal a substantial extension of the photoabsorption range of GaP, that was optically transparent for visible light detection prior to the described modification. Our findings highlight the potential use of the synthesized GaP/CDs nanostructures for developing photodetectors with a broad spectral range. The obtained functional nanomaterial is of significant interest for advancing the nanophotonics and quantum nanodevices based on GaP [15-17].

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THE AUTHORS

KOZKO Ivan A.
ivkozko@gmail.com
ORCID: 0009-0006-0923-1501

KARASEVA Elizaveta P.
liza.karaseva@gmail.com
ORCID: 0009-0005-0777-6746

SOSNOVITSKAIA Zlata F.
sosnozlat@yandex.ru
ORCID: 0009-0006-2988-5027

ISTOMINA Maria S.
istomina_ms@almazovcentre.ru
ORCID: 0000-0002-2497-653X

FEDOROV Vladimir V.
burunduk.uk@gmail.com
ORCID: 0000-0001-5547-9387

SHMAKOV Stanislav V.
stas-svs@list.ru
ORCID: 0000-0002-9658-5036

KONDRATEV Valeriy M.
kvm_96@mail.ru
ORCID: 0000-0002-3469-5897

BOLSHAKOV Alexey D.
acr1235@mail.ru
ORCID: 0000-0001-7223-7232

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