Conference materials
UDC 538.9
DOI: https://doi.org/10.18721/JPM.163.128

Pressure sensing with ZnO structures in PDMS matrix via impedance spectroscopy

A.V. Nikolaeva [1] ✉, V.M. Kondratev [1, 2], S.A. Kadinskaya [1, 2], D.E. Markina [1, 4], F.M. Kochetkov [1], F.I. Zubov [1], A.O. Monastyrenko [1], A.D. Bolshakov [2, 3]

[1] Alferov University, St. Petersburg, Russia;
[2] Moscow Institute of Physics and Technology, Dolgoprudny, Russia;
[3] Laboratory of Advanced Functional Materials, Yerevan State University, Yerevan, Armenia;
[4] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;
✉ niklolaeva_alex@spbau.ru

Abstract. The work is devoted to fabrication of the mechanical pressure sensors based on zinc oxide microwires (ZnO MWs) synthesized via low-temperature hydrothermal method. The ZnO MWs were encapsulated in Poly(dimethylsiloxane) (PDMS) membrane by G-coating technique between two ceramic substrates with interdigital gold contacts. The correlation between the mechanical load applied to the sensor and its electrophysical characteristics is studied with electrical impedance spectroscopy. The results of the work are of interest for the development of pressure sensors, in particular for miniature portable flexible health monitoring systems.

Keywords: ZnO, PDMS, sensor

Funding: The Ministry of Science and Higher Education of the Russian Federation (Grant FSRM-2023-0009; agreement 075-03-2023-106, project FSMG-2021-0005; Grant FSRM 2023-0007, 075-03-2023-088; project FSRM-2023-0010).

Citation: Nikolaeva A. V., Kondratev V. M., Kadinskaya S. A., Markina D. E., Kochetkov F. M., Zubov F. I., Monastyrenko A. O., Bolshakov A. D., A ZnO-PDMS based pressure sensors, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 157–162. DOI: https://doi.org/10.18721/JPM.163.128

Материалы конференции
УДК 538.9
DOI: https://doi.org/10.18721/JPM.163.128

Детектирование давления со структурами ZnO в матрице ПДМС с помощью спектроскопии электрического импеданса

А.В. Николаева [1] ✉, В.М. Кондратьев [1, 2], С.А. Кадинская [1, 2], Д.Е. Маркина [1, 4], Ф.М. Кочетков [1], Ф.И. Зубов [1], А.О. Монастыренко [1], А.Д. Большаков [2, 3]

[1] Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия;
[2] Московский физико-технический институт (национальный исследовательский университет), г. Долгопрудный, Россия;
[3] Ереванский государственный университет, г. Ереван, Армения;
[4] Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия
✉ nikolaeva_alex@spbau.ru

Аннотация. Работа посвящена созданию и исследованию сенсоров механического давления на основе микрокристаллов оксида цинка, синтезированных низкотемпературным гидротермальным методом. Микрокристаллы ZnO были инкапсулированы в мембрану из полидиметилсилоксана (ПДМС) методом бакетного центрифугирования между двумя керамическими подложками со встречно-штырьевыми золотыми контактами. Корреляция между механической нагрузкой, приложенной к сенсору, и его электрофизическими характеристиками изучена с помощью спектроскопии электрического импеданса. Результаты работы представляют интерес для создания сенсоров давления, в частности для миниатюрных портативных гибких систем мониторинга состояния здоровья.

Ключевые слова: ZnO, ПДМС, сенсор

Финансирование: Министерство науки и высшего образования Российской Федерации (грант № FSRM-2023-0009); Соглашение 075-03-2023-106 от 13.01.2023, проект FSMG-2021-0005; грант № FSRM 2023-0007, 075-03-2023-088; проект FSRM-2023-0010).

Ссылка при цитировании: Николаева А.В., Кондратьев В.М., Кадинская С.А., Маркина Д.Е., Кочетков Ф.М., Зубов Ф.И., Монастыренко А.О., Большаков А.Д. Сенсоры давления на основе ZnO-ПДМС // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 157–162. DOI: https://doi.org/10.18721/JPM.163.128

Introduction

Nanostructures of various compounds, in particular quasi-1-D [1] and 0-D [2] are widely used for photonic [3], sensor [4] and electronic applications [5]. Zinc oxide (ZnO) is a chemically stable, easy to synthesize and non-toxic large bandgap semiconductor material (E_g = 3.36 eV at room temperature) with a wurtzite crystal structure [3–4, 6]. In particular, zinc oxide micro- and nanowires (ZnO MWs and NWs) have received an incredible amount of attention due to its eminent semiconducting and piezoelectric properties. The addition of zinc oxide (ZnO) into a flexible polymer matrix has emerged as potential piezocomposite materials that can be used for applications such as energy harvesters and pressure sensors [7]. Poly(dimethylsiloxane) (PDMS) as a material for polymer matrix has attracted immense interest in a wide range of fields including electronics, medical devices, adhesives, robotics and coatings due to its interesting properties such as flexibility, hydrophobicity, chemical stability, biocompatibility and high resistance to thermal and thermo-oxidative degradation in a wide temperature range [8, 9].

This work is devoted to the synthesis of ZnO microstructures via low-temperature hydrothermal method, fabrication and study of mechanical pressure sensors based on them.

Materials and Methods

The MWs were synthesized via low-temperature hydrothermal method on the surface of the ceramic substrate with applied interdigital gold contacts. For ZnO surface nucleation, we spin-coated the substrates with 3 seed layers of zinc acetate aqueous solution at a concentration of 5 mmol·L^{-1}. The growth solution consists of equimolar aqueous solutions of $Zn(NO_3)_2$ and hexamethylenetetramine (HMTA). Here $Zn(NO_3)_2$ serves as a source of Zn^{2+} ions, HMTA is a slowly decomposing weak base that provides an alkaline environment in solution and the desired amount of OH^- ions [10].

During the growth process, the following reactions take place:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn(NO_3)_2 \leftrightarrow Zn^{2+} + 2NO_3 \quad (3)$$

$$2OH^- + Zn^{2+} \leftrightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad (5)$$

These reactions can be deviated from this equilibrium by changing growth parameters such as temperature, precursor concentration, pH, and growth time. These parameters affect the synthesis results such as morphology and crystalline perfection of the obtained microcrystals.

Fig. 1, *a* shows the step-by-step protocol of the pressure sensor and Fig. 1, *b* – reference sample fabrication. The ZnO MWs were encapsulated in PDMS membrane by G-coating technique followed by application of the top electrode formed by the same platform with interdigital contacts and PDMS polymerization. The resulting structure represents a mechanical pressure sensor.

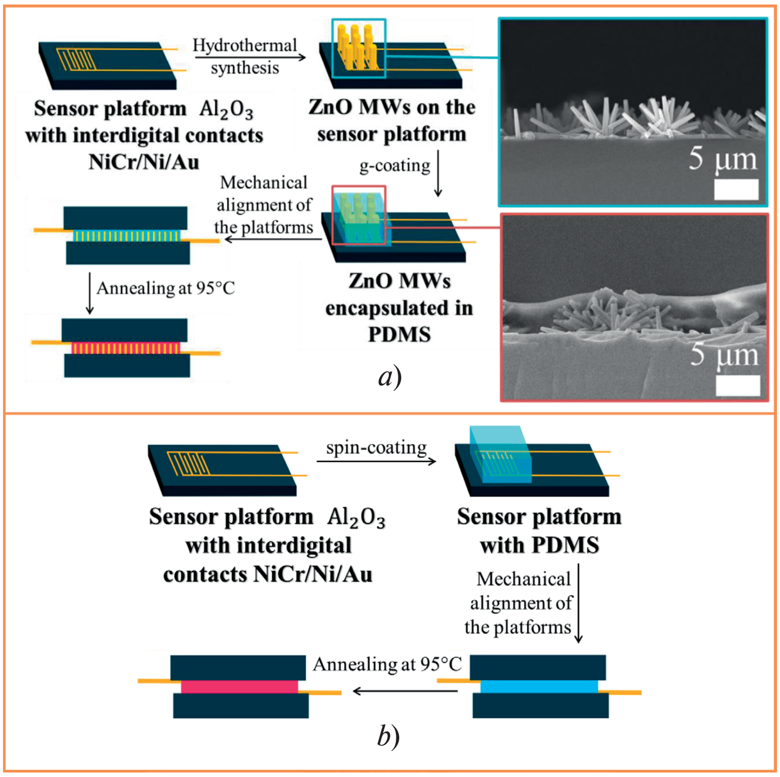

Fig. 1. Schematic diagram showing fabrication of pressure sensor (*a*) (inserts demonstrate corresponding cross section SEM images of the structures before and after PDMS encapsulation) and reference sample (*b*)

The reference sample was fabricated by a spin-coating technique instead of G-coating technique to apply PDMS to the ceramic substrate without ZnO MWs followed by application of the top electrode and PDMS polymerization.

Results and Discussion

The pressure sensor and the reference sample were studied with the use of precision TETRON-RLC meter (OOO TETRON, Russia) in terms of change in the resistance at various mechanical loads via electric impedance spectroscopy upon application of 100mV AC probe voltage. Impedance spectra for both sensors represented in Nyquist's plots – in the form of a dependence of the imaginary part (X) of the sensor impedance on the real one (R) are shown in Fig. 2.

An impedance spectrum of a typical RC circuit can be approximated by a semicircle with diameter corresponding to the resistance of a sample. Impedance spectra for different masses of weight loads varied from 0 to 4512 g have been obtained. For the pressure sensor, a decrease in the diameter of the semicircle with increasing mass of weight load has been documented.

The imaginary (X) part of impedance is determined by the capacitance (C) of the system.

The characteristics of both sensors are predominantly capacitive and its description in the flat capacitor approximation works more accurate at high frequencies measurements. Therefore, in the next step we investigated temporal behavior of the imaginary part of the sensor impedance (X) at the limiting frequency for our RLC meter, 500 kHz upon application of the weight load varied from 0 to 4512 g shown in Fig. 3. The dependence of the imaginary part of the impedance

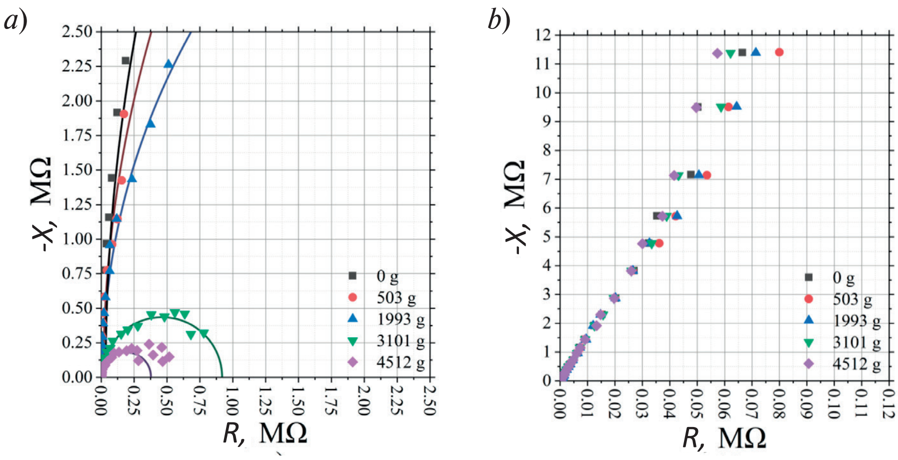

Fig. 2. Impedance spectra of the pressure sensor (*a*) and reference sample (*b*) under various weight loads varied from 0 to 4512 g

on the mass of the weight load is well defined in the range of 3 kg for the reference sample and over the whole mass range for the pressure sensor. The maximum amplitude of the imaginary part of the impedance change is 0.13% for the reference sensor and 0.68% for the pressure sensor. Therefore, the sensitivity of the device was significantly improved by almost 6 orders of magnitude after addition of zinc oxide to the PDMS membrane.

The real resistance of the pressure sensor at a single measurement current frequency not analyzed because it may deviate from the ohmic resistance obtained by approximating the impedance spectrum of such a sensor by a semicircle. This difference can be related to the non-linear dependence of zinc oxide dielectric constant on frequency [11], as well as to specific phenomena: inertial accumulation and dissipation of charge carriers in the sensors.

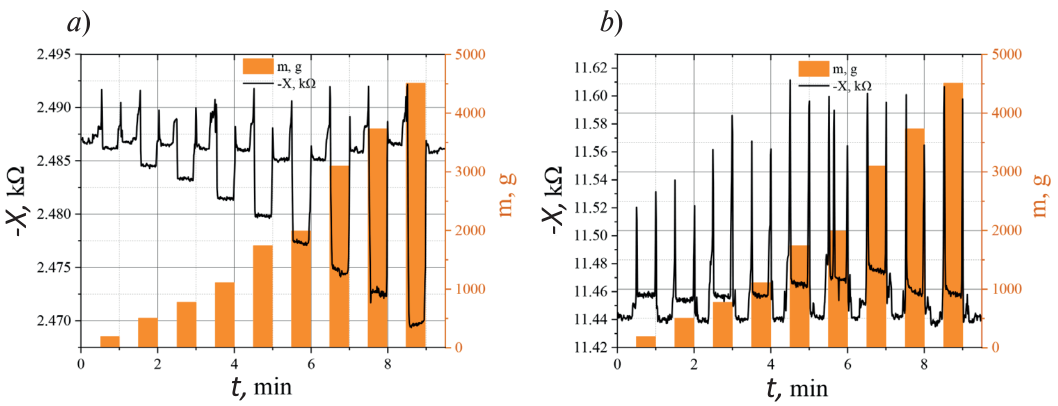

Fig. 3. Change in the imaginary part of the impedance of the pressure sensor (*a*) and reference sample (*b*): step response under various weight loads varied from 0 to 4512 g

Conclusion

In this work, we presented the mechanical pressure sensors based on zinc oxide microwires (ZnO MWs) synthesized via low-temperature hydrothermal method and investigated their resistance characteristics via electric impedance spectroscopy.

The dependence of the imaginary part of the impedance on the weight load is well defined in the range from 0 to 3 kg for the reference sample and from 0 to 4512 g for the pressure sensor. The amplitude of the change in the imaginary part of the pressure sensor impedance is almost 6 times greater than that of the reference sample.

The results of the work are of interest for the fabrication of pressure sensors, in particular for miniature portable flexible health monitoring systems such as heart rate monitors.

Acknowledgments

A.D.B. thanks Ministry of Science and Higher Education of the Russian Federation (agreement 075-03-2023-106, project FSMG-2021-0005) for support of the experiments.

V.M.K. and A.V.N. thanks Ministry of Science and Higher Education of the Russian Federation (Grant FSRM-2023-0009) for support of analysis of the experimental data.

K.F.M. and M.D.E. thanks the Ministry of Science and Higher Education of the Russian Federation (Grant FSRM 2023-0007, 075-03-2023-088).

F.I. gratefully acknowledges the financial support from Ministry of Science and Higher Education of the Russian Federation under project FSRM-2023-0010.

REFERENCES

1. **Dubrovskii V.G., Timofeeva M.A., Tchernycheva M., Bolshakov A.D.,** (2013). Lateral growth and shape of semiconductor nanowires. Semiconductors, 47 (1) 50–57.

2. **Sapunov G.A., Fedorov V.V., Koval O.Y., Sharov V.A., Dvoretckaia L.N., Mukhin I.S., Bolshakov A.D.,** Synthesis and optical characterization of GaAs epitaxial nanoparticles on silicon. Crystal Growth & Design, 2019.

3. **Kuznetsov A., Roy P., Kondratev V.M., Fedorov V.V., Kotlyar K.P., Reznik R.R., Vorobyev A.A., Mukhin I.S., Cirlin G.E., Bolshakov A.D.,** Anisotropic Radiation in Heterostructured “Emitter in a Cavity” Nanowire, Nanomaterials, 12 (2) (2022) 241.

4. **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 Appl. Nano Mater, 5 (2022) 9940–9949.

5. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Kuznetsov A., Punegova K.N.,** Hydrothermal ZnO-based Nanostructures: Geometry Control and Narrow Band UV Emission, Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus), 2022, pp. 958–961.

6. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Koval O.Y., Yakubovsky D.I., Kusnetsov A., Lihachev A.I., Nashchekin A.V., Akopyan I.K., Serov A.Y., Labzovskaya M.E., Mikushev S.V., Novikov B.V., Shtrom I.V., Bolshakov A.D.,** Deep-Level Emission Tailoring in ZnO Nanostructures Grown via Hydrothermal Synthesis, Nanomaterials, 13 (2023) 58.

7. **Koval O.Y., Fedorov V.V., Bolshakov A.D., Fedina S.V., Kochetkov F.M., Neplokh, V., Mukhin I.S.,** Structural and Optical Properties of Self-Catalyzed Axially Heterostructured GaPN/GaP Nanowires Embedded into a Flexible Silicone Membrane. Nanomaterials, 10 (11) (2020) 2110.

8. **Mata A., Fleischman A.J., Roy S.,** Characterization of Polydimethylsiloxane (PDMS) Properties for Biomedical Micro/Nanosystems. Biomed. Microdevices, 7 (2005) 281–293.

9. **Jin X., Deng M., Kaps S., Zhu X., Holken I., Mess K., Adelung R., Mishra Y.K.,** Study of Tetrapodal Zno-Pdms Composites: A Comparison of Fillers Shapes in Stiffness and Hydrophobicity Improvements. PLoS ONE, 9 (2014) e106991.

10. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Labzovskaya M.E., Novikov B.V., Shtrom I.V., Lihachev A.I., Nashchekin A.V., Bolshakov A.D.,** Hydrothermal zinc oxide nanostructures: geometry control and narrow band UV emission 2022 J. Phys.: Conf. Ser. 2227 012007.

11. **Dang Z.-M., Fan L.-Z., Zhao S.-J., Nan C.-W.,** Preparation of nanosized ZnO and dielectric properties of composites filled with nanosized ZnO. Materials Science and Engineering: B, 99 (1-3) (2003) 386–389.

THE AUTHORS

NIKOLAEVA Aleksandra V.
nikolaeva_alex@spbau.ru
ORCID: 0009-0008-4344-4863

KADINSKAYA Svetlana A.
skadinskaya@bk.ru
ORCID: 0000-0003-2508-2244

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

MARKINA Diana E.
diana666167@gmail.com
ORCID: 0009-0007-9013-7973

KOCHETKOV Fedor M.
azemerat@rambler.ru
ORCID: 0000-0002-2209-6483

ZUBOV Fyodor I.
fedyazu@mail.ru
ORCID: 0000-0002-3926-8675

MONASTYRENKO Anatoliy O.
monas@spbau.ru
ORCID: 0009-0009-7051-8458

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

Received 20.07.2023. Approved after reviewing 25.09.2023. Accepted 25.09.2023.