Optoelectronic and nanoelectronic devices

Conference paper
UDC 538.9
DOI: https://doi.org/10.18721/JPM.171.122

Potentially flexible sensor based on the ZnO-PDMS matrix for measuring mechanical load

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

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

Abstract. This study presents zinc oxide (ZnO) microstructures encapsulated in a poly(dimethylsiloxane) (PDMS) polymer matrix for the fabrication of a flexible mechanical load sensor. The resistance and capacitance properties of the ZnO-PDMS membrane in the presence of mechanical load in the range of 0–500 g have been studied using electrochemical impedance spectroscopy. The obtained impedance spectra reveal a decrease in active resistance (*R*) with increasing load mass. This decrease is attributed to an increase in contact area between the ZnO crystals and the upper electrode, leading to enhanced conductivity of the ZnO-PDMS membrane. Apart from the resistive response, the sensor exhibits capacitive response. The volume fraction of ZnO and PDMS in the membrane has been estimated, and the electrical capacity of the sensor has been determined. The obtained results are found promising for fabrication of various applications in sensing, human health diagnostics, and wearable electronics.

Keywords: ZnO, PDMS, sensor

Funding: The Ministry of Science and Higher Education of the Russian Federation (Grant FSRM-2023-0009; Grant FSRM 2023-0007, 075-03-2023-088); agreement 075-03-2023-106, project FSMG-2021-0005, state order no. 0791-2023-0004. The Russian Science Foundation (Grant 23-72-01133).

Citation: Nikolaeva A.V., Kondratev V.M., Kadinskaya S.A., Markina D.E., Lendyashova V.V., Dvoretckaia L.N., Monastyrenko A.O., Kochetkov F.M., Bolshakov A.D., Potentially flexible sensor based on the ZnO-PDMS matrix for measuring mechanical load, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (1.1) (2024) 137–142. DOI: https://doi.org/10.18721/JPM.171.122

Материалы конференции
УДК 538.9
DOI: https://doi.org/10.18721/JPM.171.122

Потенциально гибкий сенсор на основе матрицы ZnO-ПДМС для измерения механической нагрузки

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

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

Аннотация. Работа посвящена созданию сенсора механического давления на основе микроструктур оксида цинка (ZnO), синтезированных низкотемпературным гидротермальным методом и инкапсулированных в полимерную матрицу полидиметилсилоксана (ПДМС). Зависимости электрофизических характеристик сенсора от величины приложенной механической нагрузки в диапазоне масс 0 г - 500 г были исследованы с помощью метода спектроскопии электрического импеданса. Полученные спектры импеданса свидетельствуют о снижении активного сопротивления (R) с увеличением массы нагрузки. Это уменьшение объясняется увеличением площади контакта между кристаллами ZnO и верхним электродом, что приводит к повышению проводимости мембраны ZnO-PDMS. Помимо резистивного отклика, датчик также демонстрирует емкостной отклик. Была оценена объемная доля ZnO и PDMS в мембране и определена электрическая емкость датчика. Полученные результаты представляют интерес в области сенсорики, диагностики здоровья человека и носимой электроники.

Ключевые слова: ZnO, ПДМС, сенсор

Финансирование: Министерство науки и высшего образования Российской Федерации (грант № FSRM-2023-0009, грант № FSRM 2023-0007, 075-03-2023-088); Соглашение 075-03-2023-106 от 13.01.2023, проект FSMG-2021-0005, государственное задание № 0791-2023-0004. Российский Научный Фонд (грант 23-72-01133).

Ссылка при цитировании: Николаева А.В., Кондратьев В.М., Кадинская С.А., Маркина Д.Е., Лендяшова В.В., Дворецкая Л.Н., Монастыренко А.О., Кочетков Ф.М., Большаков А.Д. Потенциально гибкий сенсор на основе матрицы ZnO-ПДМС для измерения механической нагрузки // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 1.1. С. 137–142. DOI: https://doi.org/10.18721/JPM.171.122

Introduction

Micro- and nanoscale structures of various materials [1] found broad applications in sensorics [2] and electronics [3]. Furthermore, the combination of semiconductor structures with polymer matrices enables the fabrication of flexible and wearable electronics devices [4].

Zinc oxide (ZnO) is a chemically stable, non-toxic, wide bandgap semiconductor material (E_g = 3.36 eV at room temperature) with a wurtzite-type crystal structure [5]. Due to its unique optical and electronic properties, as well as its versatility in synthesis methods, zinc oxide is an appealing material for the development of photosensitive sensors [6], piezoelectric elements, and mechanical pressure sensors [7]. Despite several approaches on ZnO-based mechanical pressure sensors [8–10], they suffer from low feasibility, high cost, and a limited range of detectable masses.

This study focuses on the hydrothermal synthesis of ZnO in the shape of vertical microwires, followed by encapsulation in a polymer matrix and processing into a mechanical load sensor. The aim is to address challenges in sensorics, human health diagnostics, and wearable electronics.

Materials and Methods

In this study, we utilised equimolar (100 mmol/L) aqueous solutions of zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine (HMTA–$C_6H_{12}N_4$) for the hydrothermal synthesis of zinc oxide (ZnO) nanostructures. $Zn(NO_3)_2$ serves as the source of Zn^{2+} ions, while HMTA acts as a slightly soluble base, providing an alkaline environment and the necessary amount of OH^- ions in the solution.

The equilibrium state of the reactions can be altered by adjusting growth parameters, such as temperature, precursor concentration, and pH of the growth medium. These parameters have an impact on the morphology and crystalline quality of the obtained structures [11].

However, a major drawback of the hydrothermal synthesis method is the lack of control over the size and density of the synthesised structures. To overcome this, a photolithography technique [12] was employed using spherical quartz lenses with a diameter of 1.5 μm. Subsequently, the growth Si substrate was etched to fabricate an array of holes in the silicon oxide layer (SiO_2), which served as nucleation centres for ZnO microcrystals. The result of the substrate preparation is depicted in Fig. 1, *a* as scanning electron microscopy (SEM) images obtained using ZEISS Supra 25 (Zeiss, Germany). On the next step, ZnO microstructures were successfully synthesised on the surface of the prepared substrate, as depicted in Figure 1, *b*.

Using the g-coating method [13], the synthesised array of ZnO 5 μm long microwires was encapsulated in poly(dimethylsiloxane) (PDMS). This method allows the polymer to cover the space between the crystals, resulting in their encapsulation within the polymer matrix [13]. To expose the tops of the ZnO crystals, the PDMS layer was etched in KOH, the top view of the final structure as shown in Fig. 1, *c*. The top and bottom electrodes were carbon nanotubes (CNTs) and a thermal-sprayed aluminium layer, respectively (see the schematic in Fig. 1, *d*).

To study the resistive and capacitive properties of the ZnO-PDMS membrane electrical impedance spectroscopy was employed. This method allows to evaluate resistive and capacitive characteristics by measuring the electrical impedance of the object over a wide range of frequencies of the applied voltage. Impedance is a complex number or vector rotating in the complex polar ohmic plane: $Z = R - iX$. In Nyquist coordinates, the real part of impedance (R) is plotted on the x-axis, while the frequency-dependent imaginary part (X) is plotted on the y-axis.

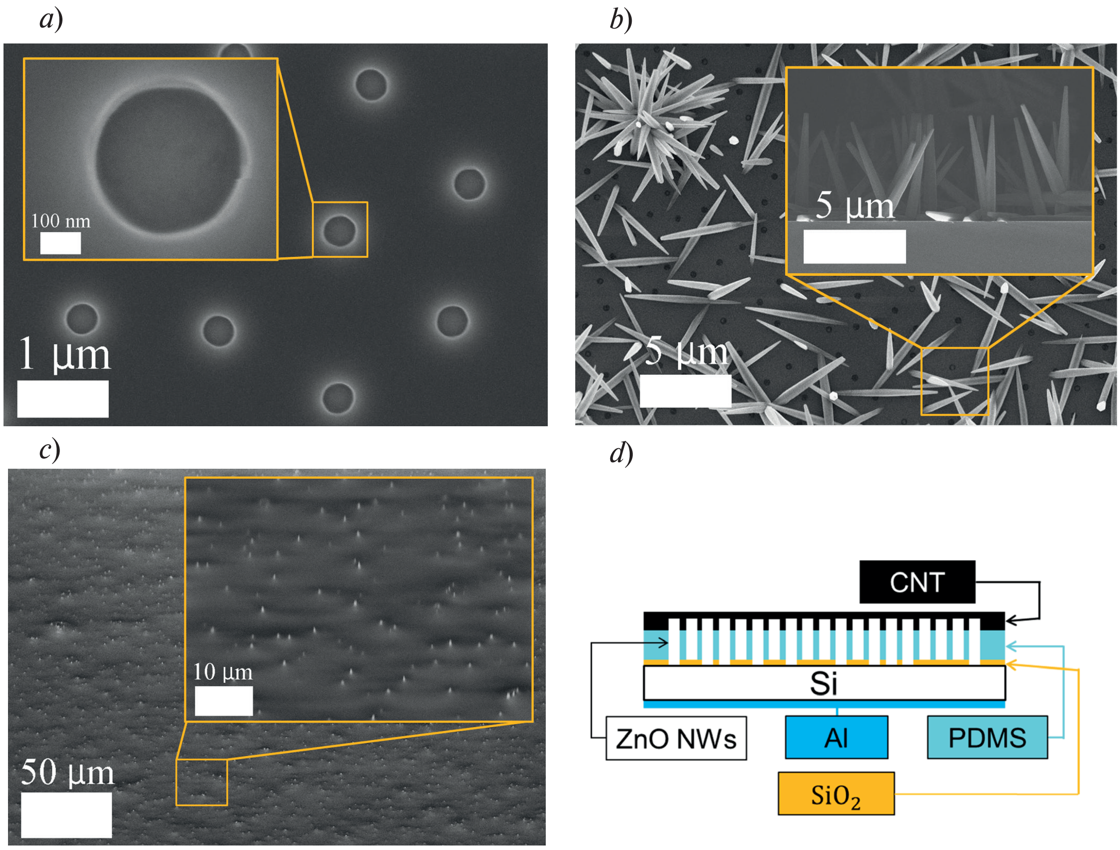

Fig. 1. Studied structure. SEM image of the array of holes formed in the SiO_2 layer on the surface of the growth Si substrate (*a*). SEM image of ZnO hydrothermal structures synthesised on the growth substrate (*b*). Top-view SEM image of ZnO hydrothermal structures encapsulated in PDMS (*c*). Circuit diagram illustrating the pressure sensor (*d*)

Results and Discussion

To assess its performance of the fabricated sensor structure, it was tested using a Z500P impedance metre (Elins Ltd., Russia) in a frequency range of 500 Hz to 500 kHz while being mechanically loaded with a 100 g to 500 g masses. The impedance spectra obtained under these conditions are presented in Fig. 2, *a*. The projection of the spectrum on the *x*-axis indicates the active resistance of the sensor (*R*) under different loads. To determine the specific value of *R* for each load mass, the projections of the impedance spectrum on the *x*-axis were determined and used to plot the graph shown in Fig. 2, *b*.

We interpret the change in impedance spectra as a decrease in the sensor's active resistance *R* when the load mass is increased. The encapsulated ZnO crystals within the polymer matrix vary in size and protrude from the PDMS layer at different heights. When a mechanical load is applied, the upper flexible electrode adheres more tightly to the ZnO-PDMS membrane, increasing conductance between the crystals and the CNTs. Consequently, as the load increases, more crystals come into contact with the upper electrode. These crystals serve as conduction channels, thus increasing the conductivity of the ZnO-PDMS membrane and decreasing the system's resistance.

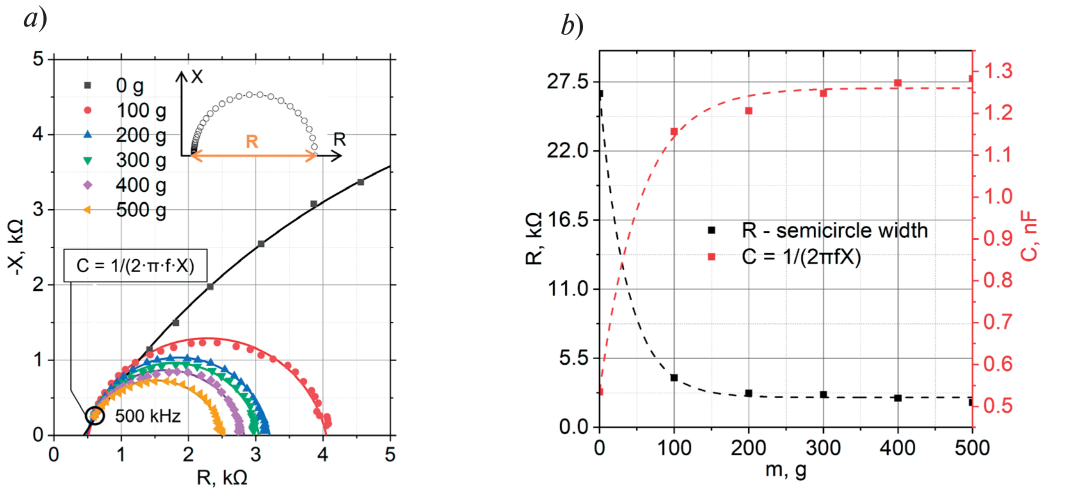

Fig. 2. Spectra showing the impedance of the sensor under mechanical load in the mass range from 0 g to 500 g (*a*). Correlation between the real part of the resistance and electrical capacitance of the sensor and the mass represented as *R*, *C* (*m*) (*b*)

The parameter *C*, representing the sensor response to different loads, was estimated as inversely related to the imaginary part of impedance *X* at a maximum frequency of 500 kHz. The sensor can be approximated as a planar capacitor:

$$C = \frac{\varepsilon_0 \cdot \varepsilon_k \cdot S}{d}, \quad (1)$$

where ε_0 is the dielectric constant ($8.854\cdot10^{-12}$ F/m), ε_k represents the relative permittivity of the medium (ZnO-PDMS), *S* denotes the area of the shells ($1.360\cdot10^{-3}$m^2), and *d* refers to the distance between the shells (microcrystal length, 5 μm).

In the case of heterogeneous systems, there exists an analytical model known as Lichtenecker's equation, which establishes a relation between the relative permittivity of the composition and the relative permittivities of its components [14]:

$$\ln \varepsilon_k = \theta_1 \cdot \ln \varepsilon_{k1} + \theta_2 \cdot \ln \varepsilon_{k2}, \quad (2)$$

where ε_k is the relative permittivity of the composite material, ε_{k1} and ε_{k2} are the relative permittivities of the components (ε_{ZnO} = 8.500, ε_{PDMS} = 3.150), and θ_1 and θ_2 are the volume fractions of the first and second components, respectively. The relative dielectric constant of the ZnO-PDMS membrane was determined using Lichtenecker's equation (2):

$$\ln \varepsilon_{ZnO+PDMS} = 0.095 \cdot \ln \varepsilon_{ZnO} + 0.905 \cdot \ln \varepsilon_{PDMS}; \quad (3)$$

$$\varepsilon_{ZnO+PDMS} = 3.448. \quad (4)$$

Using these data, the electrical capacity of the ZnO - PDMS membrane, based on the flat capacitor approximation, was determined to be 8.3 nF, which is in accordance with the experimental data (0.5 nF) shown in Fig. 2, *b* (0 g). It is worth mentioning that the calculation error may be attributed to variations in the surface density of crystals as well as deviations in their cross section and length.

Furthermore, based on the flat capacitor approximation (1), the distance between the contacts, denoted as '*d*', can be estimated. For 0 g, this distance corresponds to the length of the microcrystal, which is 5 μm. Conversely, for a weight load of 500 g, taking into account the experimental values of the electrical capacity, the estimated distance was found to be 3.89 μm. Thus, at the maximum weight load on the sensor, the membrane thickness experiences a 22% change. Consequently, a decrease in the thickness of the ZnO-PDMS membrane layer between the electrodes results in an increase in the electrical capacity of the sensor, supporting the findings of the flat capacitor approximation (1) and the dependence depicted in Fig. 2, *b*.

Conclusion

We demonstrate the potential use of hydrothermal ZnO microstructures encapsulated in a PDMS polymer matrix for the fabrication of a flexible mechanical load sensor. The sensor exhibits both resistive and capacitive characteristics, allowing it to effectively respond to varying mechanical loads. With a wide sensitivity range, this sensor holds promise for applications such as sensing, human health diagnostics, and wearable electronics.

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).

V.V.L. thanks Ministry of Science and Higher Education of the Russian Federation as part of state order no. 0791-2023-0004 for support of the substrate preparation.

D.L.N. thanks Russian Science Foundation (Grant 23-72-01133) for financial support.

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THE AUTHORS

NIKOLAEVA Aleksandra V.
nikalex2000@bk.ru
ORCID: 0009-0008-4344-4863

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

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

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

LENDYASHOVA Vera V.
erilerican@gmail.com
ORCID: 0000-0001-8192-7614

DVORETCKAIA Liliia N.
Liliyabutler@gmail.com
ORCID: 0000-0002-4172-940X

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

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

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

Received 01.12.2023. Approved after reviewing 23.01.2024. Accepted 15.04.2024.