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Humidity Sensor Element Based on Porous Silicon–Graphene Nanosystem

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In this study, the hybrid porous silicon (PS)–reduced graphene oxide (*r*GO) nanosystems are suggested as sensitive elements to the humidity sensor creation. The electrical characteristics of the PS–*r*GO nanosystems are studied in the frequency range of 25 Hz–1 MHz. As shown, the electrical resistance and capacitance of sensory elements strongly depend not only on the ratio between the contents of the PS and *r*GO nanoparticles but also on the surrounding atmosphere. An essential increase in the electrical capacitance and decrease in resistance by about three orders of magnitude due to increasing relative humidity from 40 to 90% is detected. Dependences of sensing ability of resistive and capacitive sensor elements based on the PS–*r*GO nanosystems on relative humidity are analysed. The obtained results demonstrate high potential of applications of the PS–*r*GO nanosystems in humidity sensors.

Створено вологочутливі сенсорні елементи на основі гібридних наносистем поруватий кремній (PS)–відновлений графенів оксид (*r*GO). Електричні характеристики наносистем PS–*r*GO досліджено у частотному діапазоні 25 Гц–1 МГц. Встановлено, що електричний опір та ємність сенсорних елементів істотно залежать не тільки від співвідношення між вмістами наночастинок PS і *r*GO, а й від навколишньої атмосфери. Виявлено збільшення електричної ємності та зменшення електроопору приблизно на три порядки внаслідок збільшення відносної вологості

повітря від 40 до 90%. Проаналізовано залежність адсорбційної чутливості резистивних та ємнісних сенсорних елементів на основі наносистем PS-rGO від відносної вологості. Одержані результати демонструють високий потенціал застосування наносистем PS-rGO у сенсорах вологості.

Key words: nanosystem, graphene, porous silicon, humidity sensor, sensing ability.

Ключові слова: наносистема, графен, поруватий кремній, сенсор вологості, адсорбційна чутливість.

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1. INTRODUCTION

The creation of semi-conductor gas sensors is important for the monitoring of the environment, control of food quality, as well as in medicine and industry. Special attention is focused on the development of cheap and reliable humidity sensors for scientific, industrial, and medical applications [1]. Nanostructured materials with an ultrahigh specific surface are extremely promising in the field of sensor electronics [2–4]. In particular, porous silicon (PS) nanostructures are widely used as sensitive elements of gas sensors [5, 6]. The PS layers can be obtained by a simple method of electrochemical etching of silicon wafers [7, 8]. As a result, small cavities are formed, which are directed inside the single crystal. Both the pores and the walls between them can be nanometer in size. The large area of the branched PS surface provides a high sensitivity of the material to the effect of adsorbed particles including polar molecules of water. Due to the field-effect related to the adsorption of gas molecules, redistribution of charge carriers and changes in the PS electrical characteristics are found [9]. These effects underlie the operation of gas sensors of resistive and capacitive types [6, 10, 11].

Catalysts or a combination of several nanomaterials are often used to increase the sensitivity and selectivity of sensors. One of the most promising technologies for obtaining nanocomposites for gas sensors is the infiltration of 2D carbon materials into the PS layer [12]. It should be noted that the extremely high sensitivity of the electrical conductivity of graphene nanosheets to the adsorption of molecules is promising for the creation of gas-sensing devices [13, 14]. Besides, the low electrical noise of graphene makes it possible to register the absorption of individual molecules. Therefore, the synergistic combination of useful properties of nanoparticles of the PS and graphene can increase the sensitivity and selectivity of

gas sensors based on the formed nanosystems. In addition, graphene nanosheets can be used as electrode material for the PS nanostructures [15, 16].

In this work, the silicon–graphene nanosystems are prepared in order to study their potential for application in humidity sensors. Freestanding nanostructures of the PS coated with particles of reduced graphene oxide (*rGO*) are used to ensure the maximum working surface area and to eliminate the undesirable effects of the silicon substrate or other host medium. The obtained nanosystems can also be deposited on a flexible substrate, which expands the application area of humidity sensors.

2. METHODS

Hybrid nanosystems for humidity sensors are manufactured by combining two promising sensory materials, namely, the PS nanostructures and graphene nanosheets. Single-crystalline silicon wafers with the electronic type of conductivity (*n*-Si) and the specific resistance of 4.5 Ohm·cm are used to obtain the PS nanostructures. The PS layers are prepared by the photoelectrochemical method in an ethanol solution of hydrofluoric acid with a volume ratio HF:C₂H₅OH = 1:1. The anodic current density is 25–30 mA/cm², while the duration of the etching process is of about 10 min. The working surface of a silicon wafer is additionally irradiated by a 500 W filament lamp for the efficient course of electrochemical reactions and the formation of the porous layer on the *n*-Si [17]. After etching, the PS samples are cleaned with distilled water and dried in the air. Finely dispersed PS particles are obtained by mechanical separation of the porous layer from the silicon substrate.

The second component of the hybrid nanosystem is graphene prepared by the chemical reduction of graphene oxide method with the use of reducing agents [18, 19]. Aqueous suspension with a graphene oxide concentration of 2 mg/ml produced by Biotool (Germany) is used. The graphene oxide suspension is dispersed by ultrasonic treatment for 20 min under the action of hydrazine monohydrate. As a result, *rGO* nanosheets are obtained. Besides, the 0.2 M solution of sodium dodecylbenzene sulfonate in water is used to prevent the aggregation of graphene nanoparticles. The finely dispersed PS powder is mixed with graphene suspension in proportions PS:*rGO* = 1:1 and 2:1. The obtained mixtures are deposited to prepared substrates with electrical contacts, the distance between which is of about 1 mm. After drying suspensions at room temperature, the sensory elements based on hybrid PS–*rGO* nanosystem are formed for humidity sensing.

The samples of the PS-*r*GO nanosystem are characterized by a scanning electron microscope (SEM) 'Selmi' in secondary electron mode. The electrical resistance and capacitance of the obtained sensory elements are measured in the AC regime at room temperature, using device E7-20 'Kalibr' in the frequency range of 25 Hz–1 MHz. The study of sensory properties of experimental samples is performed at 1 kHz frequency in an airtight chamber with a controllable gas medium. The concentration of water vapour in the air is determined by means of the 'Honeywell' HHH-4000-004 humidity sensor.

3. RESULTS AND DISCUSSION

The study of the surface morphology of the sensory elements based on the PS-*r*GO nanosystem is carried out, using the SEM method. As one can see in Fig. 1, the mix of the PS and *r*GO nanoparticles forms a nonmonolithic film on the substrate after drying the deposited suspension. The SEM images show silicon nanostructures ranging in size from several tens to hundreds of nanometers. Individual PS and *r*GO nanoparticles are aggregated into clusters, the size of which can reach several micrometers. In turn, the connection of these clusters forms a conductive path between the electrodes of the sensor element. It should be noted that *r*GO nanosheets surrounding PS nanoparticles could not only increase the sensitivity of gas sensors but also decrease the resistance of sensory elements due to percolation processes. Sensory films based on the PS-*r*GO nanosystems show greater porosity than nanocomposite films based on conjugated polymers [20]. This causes increasing the working surface of the sensitive elements.

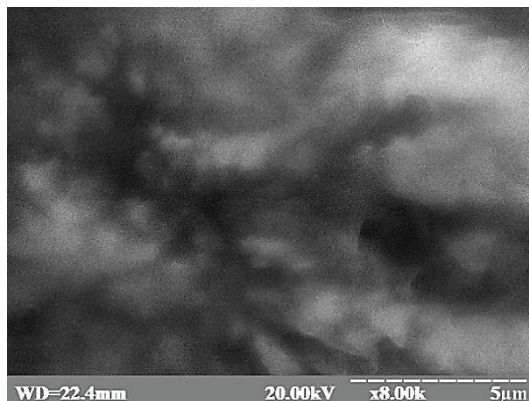


Fig. 1. SEM image of the PS-*r*GO nanosystem.

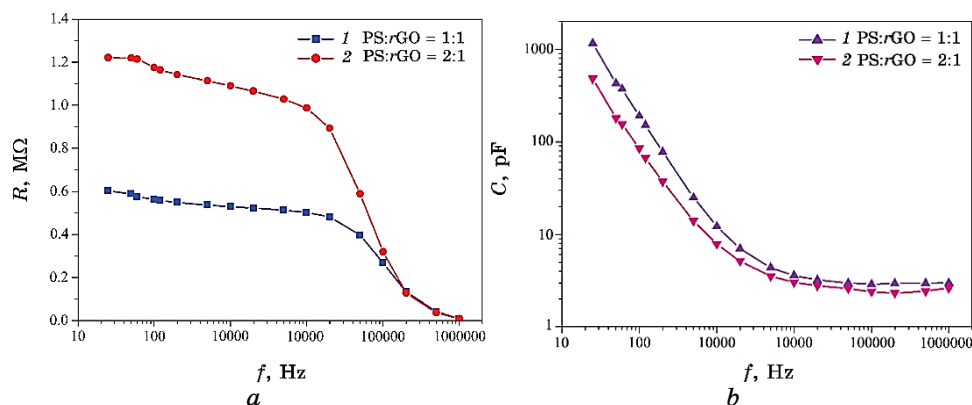


Fig. 2. Frequency dependences of electrical resistance (a) and capacitance (b) of the PS-*r*GO nanosystems with different components' ratio.

Based on experimental studies, it is found that the electrical characteristics of the PS-*r*GO nanosystems are strongly dependent on both the composition of the material and the surrounding atmosphere. In particular, the increase in the content of reduced graphene-oxide nanoparticles causes a decrease in electrical resistance and an increase in the capacitance of the nanocomposite (see Fig. 2).

The detected increase in conductivity may be due to the percolation clusters' formation in the system of low-resistance graphene nanosheets. A decrease in internal resistance and electrical capacitance with increasing frequency from 25 Hz to 1 MHz is established, based on the measurement of frequency dependences of the impedance. Besides, different capacitance dispersion of the PS-*r*GO nanosystems in different frequency ranges is found. It can be related to both the hopping mechanism of the conductivity and the complex processes of transfer and relaxation of charge in PS nanostructures [21, 22]. Usually, low-frequency dispersion is associated with the transport of charge carriers through barriers between nanoparticles and high frequency with the electron or hole processes in the bulk of the PS nanocrystals.

The adsorption of polar water molecules shows a significant effect on the electrical characteristics of the PS-*r*GO nanosystems. As shown in Fig. 3, an increase in relative humidity causes a decrease in electrical resistance and an increase in the capacitance of sensitive elements based on the investigated nanomaterials in the AC mode. It should be noted that the capacitance change range due to moisture adsorption is larger for nanosystems with a higher content of *r*GO nanosheets. The resistive sensor elements with components ratio PS:*r*GO = 1:1 and 2:1 show almost the same decrease in re-

sistance by about three orders of magnitude with an increase in relative humidity from 40 to 90%.

The observed dependences are likely caused by the interaction of water molecules with the surface of the PS and *r*GO nanoparticles. In particular, the adsorption of water molecules with donor properties causes an increase in the concentration of free electrons in *n*-Si nanostructures due to the field effect [9]. Graphene-based materials also demonstrate a significant dependence of impedance on humidity [23]. Besides, the effective dielectric permittivity of the PS-*r*GO nanosystems increases due to the water adsorption, which has a

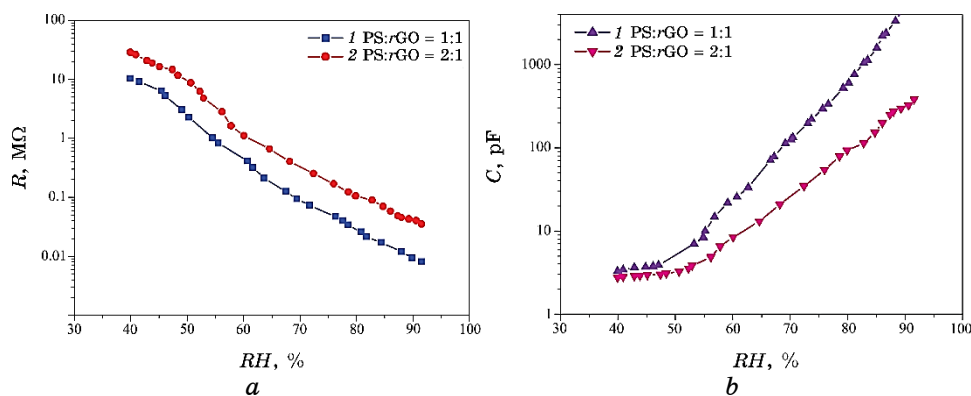


Fig. 3. Dependences of resistance (*a*) and capacitance (*b*) of sensor elements based on the PS-*r*GO nanosystems on relative humidity.

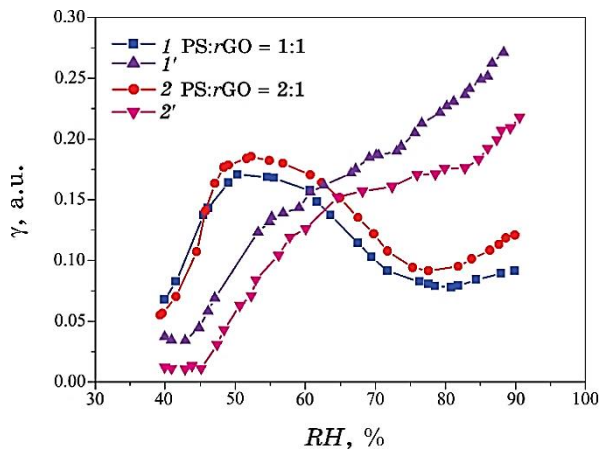


Fig. 4. Dependences of sensing ability of resistive (*1*, *2*) and capacitive (*1'*, *2'*) sensor elements based on the PS-*r*GO nanosystems on relative humidity.

large dielectric constant ($\epsilon = 81$) as compared to silicon. The combination of these effects forms the resulting electrical response of the PS-*r*GO-based sensor elements to changes in relative humidity.

An important characteristic of sensory materials is the determination of their sensing ability to adsorption of gas molecules. The sensing ability γ of the PS-*r*GO nanosystems to the action of moisture is calculated, using the equation

$$\gamma = \frac{\Delta S/S}{\Delta p/p_0},$$

where $\Delta S/S$ denotes the relative change in the electrical characteristics (namely, resistance or capacitance) of sensor elements, and $\Delta p/p_0$ is the change in the relative humidity of the air. The sensing ability of the resistive and capacitive sensor elements based on the PS-*r*GO nanosystems with the various ratios of the components as a function of relative humidity is shown in Fig. 4.

Analysis of the calculated dependences indicates that the resistive and capacitive sensor elements have maximum sensitivity in different ranges of relative humidity (see Fig. 4). Resistive humidity sensors are characterized by slightly higher sensitivity in the range of 45–60%, which is promising for environmental monitoring. Instead, the maximum values of sensitivity of capacitive sensors based on the PS-*r*GO nanosystems are observed in the 70–90% range of relative humidity. Moreover, capacitive sensor elements with a higher content of the *r*GO nanoparticles demonstrate greater sensing ability to the adsorption of water molecules. An increase in the sensor sensitivity at relative humidity above 80% is probably due to the condensation of water in the pores of the PS nanoparticles and the formation of additional charge-transfer channels. A similar increase in sensitivity at high air humidity was registered for the sensory PS structures on a silicon substrate [6].

Similarly to adsorption–desorption processes in PS structures, the interaction of the water molecules with the PS-*r*GO nanosystem surface has a character of physical adsorption because the initial resistance and capacitance of the sensor elements are restored after elimination of the moisture from the experimental chamber.

4. CONCLUSIONS

The PS-*r*GO nanosystems are obtained by the PS electrochemical etching technique and further mixing separated nanostructures from silicon substrate with *r*GO nanosheets. The SEM study has found that the PS and graphene nanoparticles are aggregated into micrometer clusters and formed nonmonolithic high-porosity film.

The ultrahigh specific area of the working surface of sensitive elements based on the PS-*r*GO nanosystems expands prospects for their application in sensory electronics.

Impedance spectroscopy of the PS-*r*GO nanosystems in the 25 Hz–1 MHz frequency range reveals a decrease in both resistance and capacitance with increasing frequency. Nanosystems with a higher content of graphene nanosheets are characterized by lower resistance and greater capacitance. Water adsorption causes a decrease in resistance and an increase in capacitance of studied sensor elements. Based on the analysis of the dependences of sensing ability on the water concentration, it has been established that resistive and capacitive sensor elements have maximum sensitivity in different ranges of relative humidity. Besides, an increase in sensitivity of humidity sensors based on the PS-*r*GO nanosystems at relative humidity above 80% is found. The obtained results can be used to create sensitive elements of humidity sensors.

REFERENCES

1. Z. Chen and C. Lu, *Sensor Letters*, **3**: 274 (2005); <https://doi.org/10.1166/sl.2005.045>
2. A. Cao, E. J. R. Sudhölter, L. C. P. M. de Smet, *Sensors*, **14**: 245 (2014); <https://doi.org/10.3390/s140100245>
3. C. J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, *Nano Lett.*, **3**: 929 (2003); <https://doi.org/10.1021/nl034220x>
4. E. Singh, M. Meyyappan, and H. S. Nalwa, *ACS Appl. Mater. Interfaces*, **9**: 34544 (2017); <https://doi.org/10.1021/acsami.7b07063>
5. S. Ozdemir and J. Gole, *Curr. Opin. Solid St. Mater. Sci.*, **11**: 92 (2007); <https://doi.org/10.1016/j.cossms.2008.06.003>
6. I. B. Olenych, L. S. Monastyrskii, O. I. Aksimentyeva, and B. S. Sokolovskii, *Ukr. J. Phys.*, **56**: 1198 (2011).
7. H. Föll, M. Christophersen, J. Carstensen, and G. Hasse, *Mater. Sci. Eng. R*, **39**: 93 (2002); [https://doi.org/10.1016/S0927-796X\(02\)00090-6](https://doi.org/10.1016/S0927-796X(02)00090-6)
8. O. Bisi, S. Ossicini, and L. Pavesi, *Surf. Sci. Rep.*, **38**: 1 (2000); [https://doi.org/10.1016/S0167-5729\(99\)00012-6](https://doi.org/10.1016/S0167-5729(99)00012-6)
9. L. S. Monastyrskii, I. B. Olenych, and B. S. Sokolovski, *Appl. Nanosci.*, **10**: 4645 (2020); <https://doi.org/10.1007/s13204-020-01321-1>
10. F. A. Harraz, *Sensor. Actuat. B Chem.*, **202**: 897 (2014); <https://doi.org/10.1016/j.snb.2014.06.048>
11. Y. Wang, S. Park, J. T. W. Yeow, A. Langner, and F. Müller, *Sensor. Actuat. B Chem.*, **149**: 136 (2010); <https://doi.org/10.1016/j.snb.2010.06.010>
12. N. S. A. Eom, H. B. Cho, Y. Song, W. Lee, T. Sekino, and Y. H. Choa, *Sensors*, **17**: 2750 (2017); <https://doi.org/10.3390/s17122750>
13. I. Karaduman, E. Er, H. Çelikkan, and S. Acar, *Sensor. Actuat. B Chem.*, **221**: 1188 (2015); <https://doi.org/10.1016/j.snb.2015.07.063>
14. H. J. Yoon, D. H. Jun, J. H. Yang, Z. Zhou, S. S. Yang, and M. M. C. Cheng, *Sensor. Actuat. B Chem.*, **157**: 310 (2011);

- <https://doi.org/10.1016/j.snb.2011.03.035>
15. L. Oakes, A. Westover, J. W. Mares, S. Chatterjee, W. R. Erwin, R. Bardhan, S. M. Weiss, and C. L. Pint, *Sci. Rep.*, **3**: 3020 (2013); <https://doi.org/10.1038/srep03020>
 16. J. Kim, S. S. Joo, K. W. Lee, J. H. Kim, D. H. Shin, S. Kim, and S. H. Choi, *ACS Appl. Mater. Interfaces*, **6**: 20880 (2014); <https://doi.org/10.1021/am5053812>
 17. A. G. Cullis, L. T. Canham, and P. D. J. Calcott, *J. Appl. Phys.*, **82**: 909 (1997); <https://doi.org/10.1063/1.366536>
 18. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, *Carbon*, **45**: 1558 (2007); <https://doi.org/10.1016/j.carbon.2007.02.034>
 19. D. Li, M. B. Müller, S. Gilje, R. B. Kaner, and G. G. Wallace, *Nat. Nanotechnol.*, **3**: 101 (2008); <https://doi.org/10.1038/nnano.2007.451>
 20. I. B. Olenych, O. I. Aksimentyeva, B. R. Tsizh, Y. Y. Horbenko, Y. I. Olenych, and I. D. Karbovnyk, *Molec. Cryst. Liq. Cryst.*, **701**: 98 (2020); <https://doi.org/10.1080/15421406.2020.1732567>
 21. S. J. Rezvani, N. Pinto, E. Enrico, L. D. Ortenzi, A. Chiodoni, and L. Boarino, *J. Phys. D Appl. Phys.*, **49**: 105104 (2016); <https://doi.org/10.1088/0022-3727/49/10/105104>
 22. I. Olenych, B. Tsizh, L. Monastyrskii, O. Aksimentyeva, and B. Sokolovskii, *Solid State Phenom.*, **230**: 127 (2015); <https://doi.org/10.4028/www.scientific.net/SSP.230.127>
 23. C. Lv, C. Hu, J. Luo, S. Liu, Y. Qiao, Z. Zhang, J. Song, Y. Shi, J. Cai, and A. Watanabe, *Nanomaterials*, **9**: 422 (2019); <https://doi.org/10.3390/nano9030422>