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Gas sensors based on zinc oxide nanorods with colloid quantum dots

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Abstract. A design and technological solution for increasing the temporal stability of gas sensors based on the nanorods-colloidal quantum dots structure is presented. For this purpose, zinc oxide nanorods oriented predominantly to the surface normal were grown by the hydrothermal method. Silicon nitride, followed by etching to the level of zinc oxide colloidal dots in an inductively coupled plasma using a gas mixture based on sulfur hexafluoride, was deposited onto the resulting structure by RF magnetron sputtering. Through accelerated aging testing, it has been found that silicon carbide protected zinc oxide nanorods exhibit greater temporal stability due to less surface oxidation resulting in a reduction in specific surface area. Silver nanoparticles with a plasmon effect were deposited onto the resulting structure by centrifugation.

Keywords: gas-sensitive material, nanorods, optical radiation, silver nanoparticles

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Газовые сенсоры на основе наностержней оксида цинка с коллоидными квантовыми точками

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Аннотация. Представлено конструкторско-технологическое решение повышения временной стабильности газовых сенсоров на основе структуры наностержни-коллоидные квантовые точки. Для этого выращены наностержни оксида цинка, ориентированные преимущественно к нормали поверхности. На полученную структуру ВЧ-магнетронным распылением осаждался нитрид кремния, с последующим травлением до уровня коллоидных точек оксида цинка. Благодаря ускоренным испытаниям на старение установлено, что наностержни оксида цинка, защищенные карбидом кремния, демонстрируют большую временную стабильность засчет меньшего окисления поверхности, приводящего к снижению удельной площади поверхности. На полученную структуру методом центрифугирования наносились наночастицы серебра, обладающие плазмонным эффектом.

Ключевые слова: газочувствительный материал, наностержни, оптическое излучение, наночастицы серебра

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Introduction

The functionalized light-sensitive material is able to enter the excitation stage by means of radiation, which allows it to transfer electrons to the gas-sensitive material [1]. This role is played by colloidal quantum dots with silver nanoparticles, which have a plasmonic effect. This effect is due to the intense interaction of metal nanoparticles with electromagnetic radiation and consists in the resonant absorption of incident electromagnetic radiation by the nanocluster, accompanied by the presence of an intense absorption band (localized surface plasmon resonance) [11]. The mechanism of detected gases sensitivity by metal oxide materials is the conversion of optical radiation into charge carriers through the use of colloidal quantum dots. Illumination leads to an increase in the number of silver charge carriers. This solution makes it possible to circumvent the problem of replacing the thermal pump. Optical pumping of the system in the visible radiation range reduces the recovery time of the sensor layer.

The use of nanoscale structures as a sensitive element made it possible to achieve a significant increase in the surface to volume ratio [6]. For example, nanorods, demonstrating sensitivity to detected gases at the sub ppm level and a response time of up to 5 seconds are a promising structure [7]. However, low temporal stability due to oxidation and the formation of new compounds on the surface of the sensing element remains a common problem, for which a passivating layer of silicon carbide was applied in the presented work.

Materials and Methods

Zinc oxide, with specified dimensions, structure, porosity and morphology, has become widely used as the main material for a gas sensitive element [2, 3]. To form the nucleation layer of zinc oxide nanorods, $Zn(CH_3CO)_2$ was dissolved in ethanol to obtain a 5 mM zinc acetate solution. It, in turn, was applied to the substrate by centrifugation. Next, annealing was carried out at 350 °C. At the next stage, the substrate with the resulting seed layer was placed in an aqueous solution of 10 mM $Zn(CH_3CO_2)_2$, 10 mM $(CH_2)_6N_4$, and 1 mM $[(C_{16}H_{33})N(CH_3)_3]Br$. Exposure took place at a temperature of 85 °C for 1 hour. In this way, nanorods, oriented mainly along the normal to the substrate surface, shown in Figure 1 were obtained.

Zinc oxide nanorods grown by the hydrothermal method were coated with a passivating film of silicon carbide, which has a high chemical resistance to acids and alkalis [4], after which it

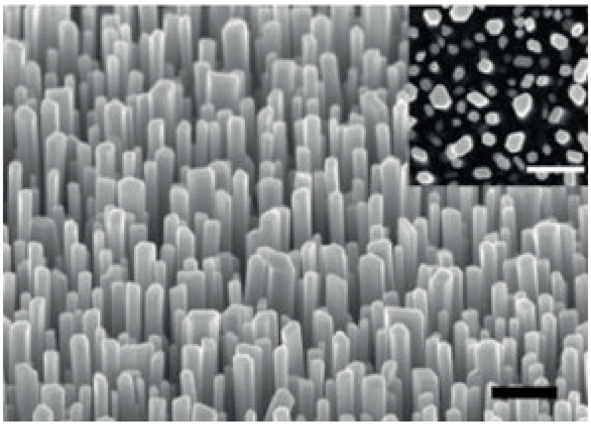

Fig. 1. ZnO nanorods

was etched to the level of zinc oxide colloidal dots in an inductively coupled plasma of sulfur hexafluoride and oxygen, which provides the best results from defect-free morphology point of view [5].

In addition, due to the high thermal conductivity of SiC (490 W/m·K), it is possible to achieve a more even distribution of heat generated on the heating element. The technology for obtaining SiC dielectric films is implemented by RF magnetron sputtering, according to the technological modes given in Table 1.

Table 1

Technological modes of silicon carbide deposition

Working gas	Target	Working gas pressure, Pa	Substrate temperature, °C	Sputtering time, min	Voltage, V
Ar	SiC	$1\cdot10^{-1}$	150	30	600

The SiC deposition using the magnetron method makes it possible not only to obtain denser films, but also to preserve the stoichiometric composition with the exclusion of the impurities influence. At the same time, silicon carbide films deposited at low temperatures have an amorphous structure, which does not contain recrystallization processes during operation at elevated temperatures [8].

Special requirements for the applied etching processes and equipment are due to the use of silicon carbide [9]. The best results, in terms of achieving a defect-free surface morphology, were obtained using plasma-chemical etching at reduced pressure in gas mixtures based on sulfur hexafluoride with oxygen dioxide additives [10]. Etching was carried out in inductively coupled plasma on an SI 500 insstallation according to the modes presented in Table 2.

Table 2

Technological modes of etching SiC

Gas mixture	Percentage of gases	Pressure, Pa	Power, W	Etching time, min	Bias voltage, V
SF_6/O_2	75/25	0.75	500	1	–50

To convert optical radiation into charge carriers, at the final stage of the technological cycle, silver nanoparticles with a diameter of about 50 nm were deposited by centrifugation. The nanoparticles themselves were obtained by the boron hydride method.

For subsequent measurements of gas-sensitive parameters, the chip shown in Figure 2 was used. The presented chip consists of a ceramic substrate with Ti/Ni contacts deposited on it. The width of one electrode, as well as the distance between them, was 50 µm.

The response time was calculated as the time interval during which the sensitive element reaches 90% of the readings corresponding to its being in a given environment (detectable gas or clean air).

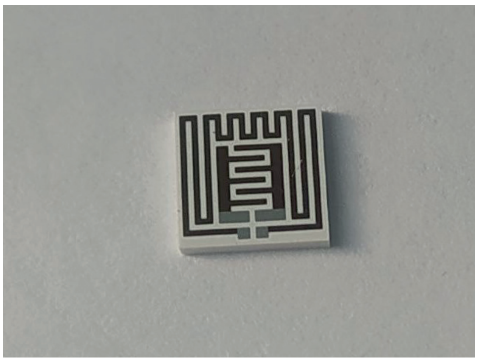

Fig. 2. Chip for measuring gas-sensitive parameters

Results and Discussion

The gas-sensitive characteristics of the obtained sensor with a passivating layer of silicon carbide and deposited silver nanoparticles were tested under the influence of isopropanol vapor and activation due to illumination (Fig. 3). For illumination, a LED with a wavelength of 365 nm was used constantly during gas detection.

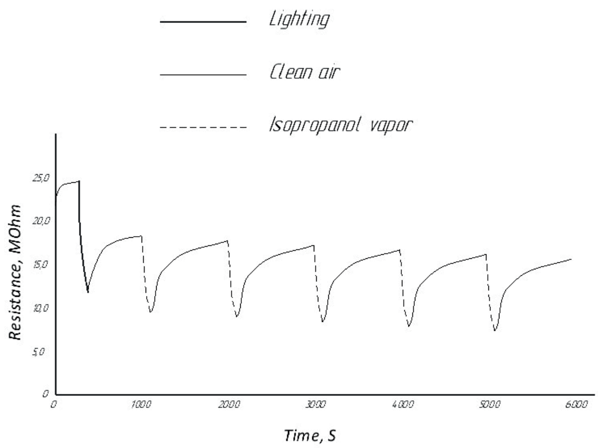

Fig. 3. Gas- sensitive characteristics

An analysis of the obtained results showed that the structure with silver nanoparticles and a protective SiC film made it possible to replace the heating of the sensor to operating temperatures by light pumping. Illumination led to a decrease in the resistance of the sample, which indicates that the resulting structures are photosensitive. It is also worth noting the positive effect of silver nanoparticles as high efficiency oxidation catalysts, which leads to accelerated decomposition of the detected gas and, as a result, an increase in the sensor sensitivity.

To assess the effect of the passivation layer on stability, gas sensors were subjected to accelerated aging tests in an isopropanol atmosphere at 400 °C for 20 days, after which the sensor was retested for gas sensitive characteristics. As a result of testing, the response time increased by 2 seconds to 32 seconds, which indicates a high stability of electrical parameters due to a decrease in oxygen vacancies and surface poisoning.

Conclusion

Measurements have shown that the presented structure has a high sensitivity due to silver nanoparticles adsorbed on the surface, as well as the stability of electrical parameters. Currently available analogues FECS45-10 (Alphasense, UK), MH-Z19C NDIR CO_2 Sensor for HVAC and IAQ (Winsen, China), MICS-4514 NO_2 SGX (SGX, Switzerland) do not have selective sensitivity to concentrations of detected gases less than 1 ppm.

The low resistance to poisoning of gas sensitive elements based on semiconductor metal oxides leads to a decrease in temporal stability. To solve this problem, silicon carbide, followed by etching to the level of colloidal dots, on which quantum nanorods dots of silver nanoparticles were deposited was deposited on the surface of a gas sensor based on zinc oxide. Measurements showed that the presented structure has a high stability of electrical parameters, as well as high sensitivity due to silver nanoparticles adsorbed on the surface.

REFERENCES

1. **Islam Md., Ashraful Khan I.,** ZnO/Ag Composite Nanoparticles for Surface Plasmon Resonance Based Sensor Application in UV-Vis Region. International Journal of Advancements in Research & Technology (IJOART), ISSN: (2012) 2278–7763.

2. **Theerthagiri J., Salla S., Senthil R.A., Nithyadharseni P., Madankumar A., Arunachalam P., Maiyalagan T., Kim H.S.,** A review on ZnO nanostructured materials: Energy, environmental and biological applications. Nanotechnology (2019) (30) 392001.

3. **Meng F., et al.,** Detection of four alcohol homologue gases by ZnO gas sensor in dynamic interval temperature modulation mode, Sensors and Actuators B: Chemical. 350 (2022) 130867.

4. **Volokhov I.V., Gurin S.A., Vergazov I.R.,** Study of the Properties of High-Sensitivity Thermally-Stable Thin-Film Resistance Strain Gauges for Integral Pressure Sensors, Measurement Techniques. 59 (1) (2016) 80–86.

5. **Okamoto N., Ohki T., Masuda S., Kanamura M., Inoue Y., Makiyama K., Imanishi K., Shigematsu H., Kikkawa T., Joshin K., Hara N.,** SiC backside via-hole process for GaN HEMT MMICs using high etch rate ICP etching//Proc. Int. CS MANTECH Conference. May 18th-21st. 2009. Tampa, Florida, USA.

6. **Bobkov A., Moshnikov V., Varezhnikov A., et al.,** The multisensor array based on grown-on-chip zinc oxide nanorod network for selective discrimination of alcohol vapors at sub-ppm range, Sensors. 19 (19) (2019) 4265.

7. **Jia Q., et al.,** Rapid and selective detection of acetone using hierarchical ZnO gas sensor for hazardous odor markers application, Journal of hazardous materials. 276 (2014) 262–270.

8. **Pecherskaya R.M., Volokhov I.V., Gurin S.A., Abdullin F.A.,** SiC as an insulating layer of a sensitive element of a strain gauge pressure sensor for especially harsh operating conditions, Nano- and Microsystems Techology. 18 (12) (2016) 767–772.

9. **Osipov A.A., Aleksandrov S.E., Soloviev Yu.V., et al.,** Etching of silicon carbide in inductively coupled plasma at low power, Microelectronics. 48 (1) (2019) 31–37.

10. **Okamoto N., Ohki T., Masuda S., Kanamura M., Inoue Y., Makiyama K., Imanishi K., Shigematsu H., Kikkawa T., Joshin K., Hara N.,** SiC backside via-hole process for GaN HEMT MMICs using high etch rate ICP etching, Proc. Int. CS MANTECH Conference. May 18th-21st. 2009. Tampa, Florida, USA.

11. **Mock J.J., Barbic M., Smith D.R., Schultz D.A., Schultz S.,** Shape effects in plasmon resonance of individual colloidal silver nanoparticles, J. Chem. Phys., 116 (15) (2002) 6755.

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