Synthesis and study of zinc oxide nanorods for semiconductor adsorption gas sensors

M A Anikina, A A Ryabko, S S Nalimova and A I Maximov
St. Petersburg Electrotechnical University "LETI", 5 Prof. Popova st., St. Petersburg 197376, Russia
E-mail: marusianik@mail.ru

Abstract. Gas-sensitive coatings based on zinc oxide nanorods were synthesized by a low-temperature hydrothermal method. It was shown that the synthesis of nanorods significantly increases the sensitivity of the samples to isopropyl alcohol vapor. Zinc oxide nanorods are promising for practical application in semiconductor adsorption gas sensors.

1. Introduction
Zinc oxide, a wide-gap n-type semiconductor ($E_g \approx 3.3$ eV), in the form of nanorods has recently attracted considerable interest for use in optoelectronics [1], photocatalysis [2-4], gas sensors [5,6], energy converters such as photovoltaic cells [7,8], and piezoelectric nanogenerators [9,10]. Zinc oxide nanorods are promising for adsorption gas sensors, since the use of one-dimensional nanostructures can lead to an improvement in sensitivity, an increase in the rates of reaction and reduction, as well as to a decrease in the limit of detection. These improvements are associated with a high surface-to-volume ratio, a high specific surface area, a comparable scale between the diameter of ZnO nanorods and the width of the depletion layer, a fast electron transfer path, and good crystallinity [11]. The attractiveness of ZnO nanorods for practical use in semiconductor adsorption sensors is also due to the low cost of synthesizing ZnO nanorods by the low-temperature hydrothermal method.

2. Experiment
The ZnO nanorods were synthesized by the low-temperature hydrothermal method with suppression of nucleation in the bulk of the solution using seed layers, which is described in detail in [12]. The ZnO seed layer was deposited by centrifugation of an aqueous solution of zinc acetate with a concentration of 5 mM on ceramic substrates with interdigitated NiCr/Ni/Au electrodes (Sensor Platform, Tesla Blatna, figure 1). The seed layer deposition process consisted of one and three cycles of centrifugation (3000 rpm, 30 seconds) and annealing (500 °C, 5 minutes).

Figure 1. Ceramic substrate with interdigitated electrodes. The width and distance between the electrode strips are 25 µm.
ZnO nanorods synthesized on quartz glass substrates were examined using a spectrophotometer to determine the optical band gap by the Tauc method. Raman spectroscopy (LabRamHR800, Horiba Jobin Yvon) with sample irradiation with a solid-state Nd: YAG laser (Torus SLM) with a wavelength of 532 nm was used to confirm the crystal structure.

The gas sensitivity of the samples was studied at the typical operating temperature of adsorption gas sensors $T \approx 300$ °C. Since semiconductor adsorption gas sensors generally have low selectivity, isopropyl alcohol vapors have been used as a target gas for analyzing the sensitivity of sensor layers to reducing gases due to commercial availability. The isopropyl alcohol vapor concentration was maintained at 1500 ppm by adjusting the diluent air flow and the air flow through the isopropyl alcohol bubbler. The vapor concentration of isopropyl alcohol was calculated from the formula:

$$ C = \frac{P_{\text{gas}} F_{\text{gas}}}{P_{\text{atm}} (F_{\text{gas}} + F_{\text{air}})} $$

where $P_{\text{gas}}$, $F_{\text{gas}}$ are the pressure of saturated vapors of the bubbling liquid and the air flow rate through the bubbler; $P_{\text{atm}}$ is the atmospheric pressure (taken as 760 mm Hg), $F_{\text{air}}$ is the flow rate of the diluent air. The vapor pressure is calculated from the Antoine equation:

$$ P_{\text{gas}} = 10^{A - \frac{B}{C + T}}, $$

where $A$, $B$, $C$ are the tabular approximation parameters, $T$ is the solution temperature. The bias voltage was 5 V. The current was recorded using a Keithley 6485 picoammeter. The sensitivity of the samples was determined by the formula:

$$ S = \frac{R_a - R_g}{R_g}, $$

where $R_a$ and $R_g$ are the resistances of the sensor layer in air and under the exposure to a reducing gas.

3. Results and discussion

The band gap of ZnO nanorods, obtained by extrapolating the linear part of the optical density dependence in Tauc coordinates to the energy axis was $E_g \approx 3.29$ eV, which is a typical value for ZnO nanorods (figure 2). From the Raman spectrum, $E_2$(low), $E_2$(high)-$E_3$(low), $E_1$(TO), $E_2$(high), and $A_1$(LO) modes are observed, which correspond to zinc oxide nanocrystals with a wurtzite structure [13].

![Figure 2](image1.png)  
**Figure 2.** Optical density spectrum of ZnO nanorods on a quartz glass substrate in Tauc coordinates.

![Figure 3](image2.png)  
**Figure 3.** Raman spectrum of ZnO nanorods.
The change in the resistance of the ZnO seed layers, obtained during one and three centrifugation cycles under the exposure of isopropyl alcohol vapors with a concentration of 1500 ppm is shown in figure 4. It can be seen that isopropyl alcohol vapors act as a typical reducing gas leading to a decrease in the resistance of the layers. Oxygen ions $O^-$ and $O^{2-}$ adsorbed on the surface are removed from it as a result of interaction with gas molecules, which leads to a decrease in the surface charge and the width of the surface depletion layer. An increase in the number of deposition cycles from 1 to 3 leads to a decrease in resistance due to an increase in the thickness of the gas sensitive layer, as well as to an increase in sensitivity, which may be associated with an increase in the seed layer specific surface area, and therefore in the number of adsorption sites for gas molecules.

![Figure 4. Change in the resistance of the seed layers of ZnO deposited by 1 and 3 cycles of centrifugation, when exposed to isopropyl alcohol vapors with a concentration of 1500 ppm. The temperature of the substrates was maintained at ~ 300 °C.](image1)

![Figure 5. Change in the resistance of coatings based on ZnO nanorods synthesized on seed layers with 1 and 3 deposition cycles, when exposed to isopropyl alcohol vapors with a concentration of 1500 ppm. The temperature of the substrates was maintained at ~ 300 °C.](image2)

The hydrothermal synthesis of ZnO nanorods on seed layers leads to an increase in the sensitivity of samples to isopropyl alcohol vapor (figure 5). In the case of a seed layer obtained in one cycle of deposition, the sensitivity increases by more than 10 times, which is certainly associated with an increase in the surface-to-volume ratio and specific surface area. It is important to note that after the hydrothermal synthesis of ZnO nanorods, the samples demonstrate not only an increase in the conductivity in an atmosphere of isopropyl alcohol vapor, which is explained by an increase in the thickness of gas sensitive layer, but also a decrease in the conductivity in an air atmosphere compared to the seed layers. This can be explained by etching the seed ZnO layer during the low-temperature hydrothermal synthesis of ZnO nanorods. The lower sensitivity to isopropyl alcohol vapors of the sample obtained on the seed layer with 3 deposition cycles can be explained by the higher density of nanorods on the substrate, which is usually accompanied by splicing of the bases of nanorods near the substrate, i.e., the formation of a dense polycrystalline layer at the bases of nanorods with a thickness greater than the diameter of the nanorods.

4. Conclusion
The low-temperature hydrothermal method was used to synthesize coatings of zinc oxide nanorods with a wurtzite structure. The synthesis of ZnO nanorods on seed layers leads to a significant increase in the sensitivity of the samples to isopropyl alcohol vapors due to an increase in the specific surface area.
Coatings of ZnO nanorods are suitable for practical use in semiconductor adsorption gas sensors with high sensitivity due to commercially available equipment and low cost of the resulting sensing elements.

References
[1] Djurisić A B, Ng A M C and Chen X Y 2010 *Prog. Quant. Electron.* 34 191
[2] Pronin I A, Kaneva N V, Bozhinova A S, Averin I A, Papazova K I, Dimitrov D T and Moshnikov V A 2014 *Kinetics and Catalysis* 55(2) 166
[3] Yukhnovets O, Semenova A A, Levkevich E A, Maximov A I and Moshnikov V A 2018 *Journal of Physics: Conference Series* 2018 993(1) 012009
[4] Pronin I A, Donkova B V, Dimitrov D T, Averin I A, Pencheva J A and Moshnikov V A 2014 *Semiconductors* 48(7) 842
[5] Bobkov A, Varezhnikov A, Plugin I, Fedorov F S, Trouillet V, Geckle U, Sommer M, Goffman V, Moshnikov V A and Sysoev V 2019 *Sensors* 19 4265
[6] Bobkov A A, Mazing D S, Ryabko A A, Nalimova S S, Semenova A A, Maximov A I, Levkevich E A and Moshnikov V A 2018 *IEEE International Conference on Electrical Engineering and Photonics (EExPolytech)* 8564407 219
[7] Lashkova N A, Maximov A I, Ryabko A A, Bobkov A A, Moshnikov V A and Terukov E I *Semiconductors* 2016 50(9) 1254
[8] Vittal R and Ho K C 2017 *Renewable and Sustainable Energy Reviews* 70 920
[9] Wang Z L and Song J 2006 *J.Science* 312 242
[10] Semenova A A, Lashkova N A, Maximov A I and Moshnikov V A 2018 *Journal of Physics: Conference Series* 1038(1) 012044
[11] Comini E, Baratto C, Faglia G, Ferroni M, Vomiero A and Sberveglieri G 2009 *Prog. Mater. Sci.* 54 1
[12] Ryabko A A, Maximov A I, Verbitskii V N, Levitskii V S, Moshnikov V A and Terukov E I 2020 *Semiconductors* 54(11) 1496
[13] Schumm M 2009 *ZnO-based semiconductors studied by Raman spectroscopy. Semimagnetic alloying, doping, and nanostructures* (Würzburg: Südwestdeutscher Verlag für Hochschulschriften)