Study of the influence of the electrophysical properties of ZnO nanorods grown on glass on their gas-sensitive properties

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Abstract. The article discusses the sensory properties of an array of ZnO-based nanorods, which were used as sensitive elements of carbon (II) oxide sensors. By hydrothermal synthesis, arrays of ZnO nanorods were grown on glass, which had an average transverse size of up to 40 nm and a height of up to 660 nm. Formed rods had a predominantly vertical orientation. Metal contacts were formed over the array of nanorods. Studies of the electrophysical properties showed that the temperature dependence of the conductivity of the formed structure has a hysteresis at temperatures above 160 °C, and the current-voltage characteristic is close to linear. The gas sensitive properties of the ZnO array of nanorods were investigated to carbon monoxide (II) with a concentration of 20–100 ppm at operating temperatures from 20 to 270 °C. It has been shown that the sensor response is strongly influenced by the rate of blowing the array with nanorod air or the test gas.

1. Introduction
The properties of nanostructured materials based on oxide semiconductors are currently being intensively studied, since these materials have great potential for practical application. ZnO-based nanostructures are used to manufacture sensitive elements of gas sensors, piezo transducers and energy harvesters [1-4]. The principle of operation of gas sensors is based on the property of ZnO to change its electrical parameters during the adsorption of gas molecules.

2. Experiment
Arrays of ZnO nanorods were synthesized on p-type silicon and quartz glass by the hydrothermal method. Previously, a seed layer was applied to the surface of thoroughly cleaned substrates by the sol-gel method. Sol was obtained by dissolving zinc acetate in ethanol. A uniform distribution of the sol on the substrate surface was achieved by centrifuging at a rotational speed of about 2000 rpm, further drying at 130 °C and annealing at 350°C [1]. The hydrothermal synthesis of ZnO nanorods was carried out in an aqueous solution of zinc nitrate and hexamethylenetetramine (C₆H₁₂N₄) in a glass beaker, in which the substrate with the seed layer was placed in a vertical position on a fluoroplastic holder. Hydrothermal treatment was carried out in the temperature range 90-97 °C for 3 hours with vigorous stirring. Samples were washed with deionized water and dried. The formed ZnO nanorods are predominantly vertical in orientation with a height of 590–660 nm and have an average transverse size of about 30–40 nm — figure 1 (a.). Then, contact metallization of V-Cu-Ni 0.2-0.3 μm thick was applied on them. The resistance of the obtained samples of gas sensors ranged from hundreds of kOhms to several tens of MOhm.
Measurements of electrophysical and gas-sensitive properties were carried out on an automated bench for gas calibration of the collective use center “Microsystem Engineering and Integrated Sensors” — figure 2.

**Figure 1 (a, b, c).** (a) SEM images of the grown ZnO nanorod on glass; (b) CVC of the sensor structure at 200 °C; (c) Temperature dependence of the resistance of the sensor structure.
3. Results and discussion

Figure 2 (b) shows the current-voltage characteristic (VAC) of a formed structure heated to a temperature of 200 °C. It can be seen that it indicates the presence of a weak potential barrier arising from the contact of ZnO nanorods with each other. A similar view of the IVC was shown in [3]. It is known that the electrical conductivity of zinc oxide is determined by oxygen vacancies, which are electron donors [4], and, accordingly, the activation energy of conductivity is determined by donor levels formed by vacancies in the forbidden zone ZnO.

On the temperature dependence of the resistance of the sensor structure presented in Figure 1, there is a temperature hysteresis with a portion of the positive temperature coefficient in the range of 170 – 225 °C. This can be explained by the interaction of the surface of zinc oxide with atmospheric oxygen. Oxygen molecules in the atmosphere are adsorbed on the surface of zinc oxide and become negatively charged due to the capture of electrons from near-surface ZnO layers, which leads to the formation of a lunch layer in the near-surface region and a decrease in conductivity [5]:

\[ O_2(gas) \leftrightarrow O_2(ads) \]  
\[ O_2(ads) + e^- \leftrightarrow O_2^-(ads) \]  
\[ O_2^-(ads) + e^- \leftrightarrow 2O^-(ads) \]

Thus, the change in conductivity during heating and cooling is caused by two competing processes — thermal generation and recombination of electrons and their capture by oxygen adsorbed on the surface. Moreover, if in the first case, the equilibrium concentration is established almost instantly, then in the second it depends on the speed of the processes of adsorption and desorption. The presence of hysteresis in the temperature dependence of the conductivity indicates a low rate of these processes.

In addition, blowing air or gas ZnO nanorods can lead to a decrease in the temperature of their free ends, which can affect the kinetics of the response. Estimation of the temperature decrease of the free end of ZnO nanorod due to blowing with air or gas under isothermal heating / cooling conditions was carried out according to the formula [6]:

\[ T - T_0 = (T_1 - T_0) \frac{ch a(l-x)}{ch al} \]

where \( a = \sqrt{\frac{\mu p}{k \sigma}} \), \( T_0, T_1, T \), are the ambient temperature, the temperature of the fixed end of the ZnO nanorod and the temperature at any point \( x \) ZnO of the nanorod, respectively; \( l, \sigma, p \) are the length, area and perimeter of the cross section of a ZnO nanorod, respectively; \( k \) is the coefficient of thermal conductivity of the rod; \( \mu \) - coefficient of heat transfer from the rod to the environment, can take values of 5 ÷ 30 W / m · K.

Calculations according to equation (4) showed that the temperature of the free end of the nanorod can decrease by 20 - 40 °C, depending on the experimental conditions. All this, in the end, determines the magnitude of the potential barrier when ZnO contacts the nanorods, and also affects the type of response of the sensor structure to the effect of gas. The study of gas-sensitive properties was carried out at a concentration of carbon monoxide (CO) of 20-1000 ppm at operating temperatures of 100-270 °C. The air supply and the CO supply of the required concentration, obtained by dilution in air, was carried out several times according to the following cycle: gas supply for 2 minutes with a flow rate of 0.3 l / min - air blowing - 2 minutes with a flow rate of 0.03 l / min - Figure 2 (a) and at an air flow rate of 0.3 l / min - Figure 2 (b). As can be seen from Figure 2, when exposed to CO, the resistance does not decrease, as it should be when the n-semiconductor affects the reducing gas, but increases. A similar response when exposed to CO on a gas sensor based on ZnO nanorods was also observed in [7].
Figure 2 (a, b). Sensor response based on ZnO array of nanorods at 200 °C to CO exposure with a concentration of: (a) 20 ppm and a gas flow rate of 0.3 l/min and air of 0.03 l/min; (b) 50 ppm and gas and air feed rates of 0.3 l/min.

Apparently, the main reason for this response is an increase in the height of the potential barrier during the adsorption of CO molecules on the surface of ZnO nanorods. The dynamics of the sensor response in Figure 2 (a) and 2 (b) shows the effect of the velocity difference of the blower. When the gas is supplied at a higher rate by an order of magnitude than the air supply after the end of the CO supply, the resistance of the sensor abruptly increases due to an increase in the temperature of the free ends of ZnO nanorods. Upon further air blowing, the resistance of the sensor was restored to its original values. During the second gas supply cycle, the sensor resistance initially fell due to a decrease in the temperature of the free ends of ZnO nanorods, and then increased due to the influence of CO molecules. To avoid the effect of this effect, the rate of blowing gas and air in subsequent experiments was the same (0.3 l/min). So in Figure 2 (b) it can be seen that there is practically no jump in resistance after at the time of the end of the gas supply and the start of air blowing.

In addition, it is necessary to avoid the influence of the hysteresis of the temperature dependence of the resistance presented in Figure 1 (c). For this, the temperature of the gas sensitivity experiment needs to be increased to 250 °C or higher. In this case, the response of the sensory structure becomes 30–40%
higher than the response of a similar sensory structure based on an array of ZnO nanorods, but grown on silicon [8].

The maximum response of the sensory structure at 270 °C was 1.36, when exposed to CO from concentrations of 100 ppm, 1.28 and 1.19 at 50 and 20 ppm, respectively.

Thus, the results of the study of the electrophysical properties of the sensor structure based on an array of ZnO nanorods grown on glass made it possible to adjust the method for conducting a study of their gas-sensitive properties. Studies have shown that temperature hysteresis is observed on the temperature dependence of the resistance of the sensor structure. When heated to 225 °C, a temperature hysteresis is observed with a portion of the positive temperature coefficient in the range of 170 ÷ 225 °C. In addition, the flow rate of gas or air affects the appearance of the sensor structure. In this regard, the methodology for conducting experiments to study the gas-sensitive properties of sensory elements was adjusted. The effect of carbon monoxide (II) depends on the rate of purging the sensitive element, and after exposure to CO and sample heating temperature. You can also see that using gas sensors based on ZnO nanorods grown on glass, you can record the concentration of carbon monoxide at the level of 20-50 ppm.

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