Gas sensitive properties of ZnO nanorods formed on silicon and glass substrates

V V Petrov¹, A P Starnikova¹, Y N Varzarev¹, K A Abdullin² and D P Makarenko³
¹ Southern Federal University, Research and Education and Centre “Microsystem technics and multisensor monitoring systems”, Taganrog, 347922, Russia
² Al Farabi Kazakh National University, National Nanotechnology Laboratory of Open Type, Almaty, 050040, Kazakhstan
³ JSC “VNIIHOLODMASH”, Moskow 127410, Russia

E-mail : vvp2005@inbox.ru

Abstract. Nanostructured materials based on zinc oxide are being intensively studied, since such materials are used to create energy harvesters, gas sensors, and solar cells. Arrays of nanoscale ZnO nanorods are synthesized on silicon and glass substrates by the hydrothermal method. The formed ZnO nanorods with predominantly vertical orientation have an average transverse size of about 30–40 nm and a length of 500–600 nm. For electrical contact, V-Cu-Ni metallization was deposited over ZnO nanorods. The work investigated the gas-sensitive and electrophysical properties of the formed sensitive elements with respect to carbon monoxide (CO). It is shown that the sensor element based on ZnO nanorods on glass has a 30% higher sensitivity and lower (10 ppm) sensitivity limit than similar structures, but formed on silicon. Peculiarities of the response of gas sensors based on ZnO arrays of nanorods were determined, including the effect of temperature, the rate of gas flow, and the effect of the substrate. A method for measuring gas-sensitive properties has been developed. It is shown that sensors based on such sensor structures can be used as energy-efficient gas sensors, as well as detectors in early fire detection systems, robotic sensor systems, and other modern technologies.

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.

The principle of operation of gas sensors is based on the property of ZnO to change its electrical parameters (for example, electrical conductivity) during adsorption of gas molecules. Resistive-type gas sensors based on ZnO nanorods formed by the method of pulsed laser deposition exhibit high sensitivity to carbon monoxide (II) [4]. However, research in this area is not enough. In particular, in [5, 6], the hydrothermal method formed arrays of ZnO nanorods on various substrates, but their gas sensitivity has not been sufficiently investigated. The purpose of this work was to study the gas...
sensitivity of gas sensors based on arrays of ZnO nanorods, to carbon monoxide (CO) at different temperatures.

2. Experiment
Arrays of ZnO nanorods were synthesized on p-type silicon and quartz glass by the hydrothermal method. A uniform distribution of the zinc acetate sol dissolved in ethanol on the substrate surface was achieved by centrifuging at a rotation speed of about 2000 rpm, further drying at 110-130 °C and annealing at 350-450°C [5, 6]. The hydrothermal synthesis of ZnO nanorods was carried out in an aqueous solution of zinc nitrate and hexamethylenetetramine (C₆H₁₂N₄) in a glass beaker. Hydrothermal treatment was carried out in the temperature range 90-97 °C for 1-3 hours. 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 structures ranged from hundreds of kOhms during the formation of ZnO nanorods on silicon and up to tens of MΩ during the formation of ZnO nanorods on glass.

![SEM image](image_url)

**Figure 1.** SEM images of the as-grown ZnO nanorod layer on a Si substrate.

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.

![Gas sensor calibration setup](image_url)

**Figure 2.** Automated gas sensor calibration stand: electronic control unit for the gas distribution system (1), solenoid valves (2), mixing chamber (3), receiver (4), unit for controlling the flow rate of the original gas components (5) unit for controlling the flow of gas
mixture (6); measuring chamber (7); cylinders with original gas components (8), personal computer (9), Keithly multimeter 2450 (10) heating control unit (11).

With the help of the stand, it is possible to automatically generate a mixture of gases up to three components of a given concentration with a lower concentration limit of 1 ppm or less, with a dilution factor of up to 100. The supply of the finished gas mixture is possible by controlling the speed of the gas flow is possible within 0.1–3.5 cm/min. The Study of the electrophysical and gas-sensitive properties of newly developed materials is possible by heating the samples to 400°C. The measuring unit provides double shielding and allows high-accuracy measurement of parameters such as resistance of test samples of sensors and conductivity of samples of gas-sensitive materials in the range 0-10¹⁰ Ohm·cm (S⁻¹·cm).

For this case, the CO concentration was set in the range of 20-1000 ppm in air at operating temperatures of 100-270°C. The air and CO mixture were introduced at a flow rate of 0.3 dm³/min.

The response of sensor elements based on ZnO nanorods on silicon was calculated using the formula $S=R/R_0$, and the response of sensor elements based on ZnO nanorods on glass was calculated using the formula $S=R_0/R$ (here $R_0$ is the resistance of the sensor element in the absence of gas; $R$ is resistance sensor element when exposed to gas).

### 3. Results and discussion

It was experimentally determined that the minimum sensitivity of sensor elements based on ZnO nanorods on silicon was 100 ppm, and that of sensor elements based on ZnO nanorods on glass was 10 ppm - figure 3 (a, b). The operating temperature of sensor elements based on ZnO nanorods on silicon was near 200°C (figure 3, a). At the same time, the operating temperature of the sensor elements based on ZnO nanorods on glass was in the range of 250-270°C (figure 3, b (curves 2 and 3)). At 200°C, the response was unstable (figure 3, b (curve 1)).

![Figure 3](image-url)
Figure 4 shows typical responses of sensor structures based on ZnO nanorods grown on p-type silicon (figure 4, a) [7] and on glass (figure 4, b). The comparison shows that the response of the sensor formed on the glass became 1.3 times higher, and the sensitivity limit can reach units of ppm. Such parameters could not be achieved on sensor elements based on ZnO nanorods grown on p-type silicon.

In addition, the response to CO exposure for sensor structures based on ZnO nanorods grown on p-type silicon was inverse. When exposed to CO, the resistance grew (figure 4, a), but did not decrease, as it was when exposed to CO on the sensor structure based on ZnO nanorods grown on glass (figure 4, b). The result obtained is explained by the fact that zinc oxide is an n-type semiconductor. In the case when ZnO nanorods are grown on p-type silicon and there is contact metallization on top of them, two p-n-junctions are formed, which are connected towards each other. When measuring the resistance in such a structure (figure 5, a), the measuring current proceeds in two ways.

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Figure 4. Normalized responses of sensor elements to CO 100 (1), 200 (2), 500 (3) ppm at 200 °C based on ZnO silicon nanorods (a) and response to CO (50 ppm) at 250 °C (ZnO on glass) (b).
The first path is from the first metal contact to the nanorods, on which it lies, and further, through numerous contacts of ZnO nanorods in contact with each other (Rk) to the second metal contact. The second way: from the first metal contact to ZnO nanorods, then through them to the silicon substrate, and through it to the second contact through ZnO nanorods. Since the resistance of the RSi silicon substrate is less than the resistance of Rk nanorods in contact with each other ZnO nanorods, the current will mainly flow through the silicon substrate. As a result, two p-n junctions are formed, connected towards each other - figure 5, a. In structure on the glass, it realizes only the first path of the passage of electric current - figure 5, b. These assumptions are confirmed by the current-voltage characteristics of the ZnO structures of nanorods grown on p-type silicon (figure 5, c), and on glass - (figure 5, d).

In the first case (figure 5, d), the current-voltage characteristic is non-linear and its form corresponds to the electrical equivalent circuit (figure 5, a). In the second case, the current-voltage characteristic is linear (figure 5, d), which corresponds to the electrical equivalent circuit (figure 5, b) and is consistent with the results presented in [8].

4. Conclusions
In this work, the sensitivity of sensory elements based on arrays of ZnO nanorods formed on p-type silicon and glass to carbon monoxide (CO) at temperatures of 200–270 °C was investigated. Studies have shown that the shunting effect of two p-n junctions involved in opposite directions leads to a decrease in the gas sensitivity coefficient and the inverse response of the sensor structure based on ZnO nanorods grown on p-type silicon. The obtained response of the formed sensors based on the ZnO array of nanorods grown on glass was 30–40% higher than the response of a similar sensor structure based on the array of nanorods but grown on silicon. The maximum response of the sensory structure at 270 °C was 1.36, when exposed to CO from concentrations of 100 ppm, and 1.28 and 1.19 at 50 and 20 ppm, respectively.

Thus, using gas sensors based on ZnO nanorods, one can measure the carbon monoxide concentration at a level of 10-50 ppm, which is necessary, for example, for the manufacture of gas fire detectors.

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