Study of sensor properties of zinc oxide based nanostructures

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Abstract. Nanostructures based on zinc oxide were synthesized on ceramic substrate with interdigitated electrodes by spin-coating and low-temperature hydrothermal method. The sensor response to CO, CO₂ and O₂ was studied at room temperature under near UV light illumination. Gas exposure was supplied using metrological certified equipment. All samples showed no response to CO₂. Layers based on zinc oxide nanowires are most sensitive to CO because of complex morphology and more effective adsorption of gas molecules. The obtained dependencies allow us to characterize the interaction of nanostructure based on zinc oxide with the main oxidizing and reducing atmosphere gases.

1. Introduction
The detection of undesirable gas components in the atmosphere is an urgent task of modern electronics in the conditions of intensive urban growth. Sensors that change their electrophysical properties (electrical resistance) in the presence of oxidizing or reducing gases are the most popular [1, 2]. Solid-state adsorption gas sensors based on metal oxides that work at elevated temperatures have been widely studied [3–5]. Recently gas sensor of percolation type with extremely high gas sensitivity values were proposed [6].

Among metal oxides, ZnO with a wide band gap of 3.37 eV is one of the most studied sensing materials because of its good optical properties, electron mobility and high sensitivity to a variety of gases [7–9]. Zinc oxide has been considered as one of the promising materials in the field of gas sensors for CO [10, 11], CO₂ [12] and O₂ [13]. Our research team developed layers based on zinc oxide nanowires synthesized by hydrothermal method sensitive to acetone and alcohol vapors [14, 15]. It was shown that relation between adsorption sites of different types on the surface of ZnO nanowires depend on the concentration of added to growth solution surfactant (cysteine) [16].

The thermal activation of gas sensor leads to several disadvantages. A heating element increasing device complexity should be added to gas sensor. High working temperatures also reduce device lifetime and long-term stability of sensing performance as this will result in regrowth of nanomaterials. It will also limit the sensor’s application in the detection of flammable or explosive analytes because of safety issues [17]. Therefore, it is important to develop ZnO based sensors that could work at room temperature. Over the last years, there have been a number of publications concerning light activated metal oxide semiconductor gas sensors [18, 19]. It is well-known that when semiconductors are illuminated under light with photon energy higher than its band-gap energy electron-hole pairs will generate [20]. It was shown that the nonintrinsic photo-absorption induced by native defects of ZnO may be the primary reason for the photo-responded behavior under visible-light irradiation [21]. The modification with narrow band gap materials such as CdS [22], CdSe [23], PbS [24] is another method to extend the photo-response of ZnO from UV region into visible light region. In our recent work,
AgInS₂ nanoparticles were successively used for modification of ZnO nanowires [2]. It was found that synthesized composite samples showed sensor response to isopropyl alcohol vapors at room temperature under visible light illumination.

The aim of this work was the development of sensor layers based of zinc oxide nanostructures for monitoring air pollution. In our experiments, gas sensitivity to target gases was activated by near UV light.

2. Experiment

2.1. Synthesis of seed layers by spin-coating
Layers based on zinc oxide nanoparticles were synthesized by spin-coating. The sensor platform is a ceramic chip with NiCr/Ni/Au interdigitated electrodes. The width of electrodes and distance between them are 25 micrometers. The dimensions and image of the sensor platform are shown in figure 1.

First, an aqueous solution of zinc acetate dehydrate with a concentration of 5 mM was prepared. The prepared solution was spin coated on sensor platform at 3000 rpm for 30 s. The coated chip was annealed at 500 °C for 5 min after each coating cycle to remove the organic residuals. Samples after 1, 2 and 3 coating cycles were synthesized.

2.2. Synthesis of zinc oxide nanostructures by low-temperature hydrothermal method
An aqueous solution of hexamethylenetetramine and zinc nitrate with equimolar concentrations was used for the ZnO nanowires synthesis by a low-temperature hydrothermal method [25]. The resulting solution was placed in an ultrasonic bath until the precursors were completely dissolved. Ammonium hydroxide and polyethylenimine were also added to the volume of the solution to suppress bulk nucleation [26]. The samples were synthesized at 85 °C for 1 hour.

2.3. Study of sensitivity of zinc oxide nanostructures to oxidizing and reducing gases
The gas sensitivity of all the samples to CO (100 ppm) was investigated. The gas sensitivity of the sample synthesized by hydrothermal method to O₂ (209000 ppm (or 20.9 percent by volume)) and CO₂ (1300-7280 ppm) was investigated. The test bench consisted of a gas cabinet with zero gases (synthetic air and nitrogen) and target gases (carbon monoxide and carbon dioxide). Zero gases and target gases were mixed in the specified proportions using a certified gas mixing station and supplied to the test module using the gas interface. All measurements were made when exposed to light. In this work, an LED with center wavelength \( \lambda = 405 \) nm was used as a source of ultraviolet radiation.

3. Results and discussions
The dependence of the sensor resistance on time (figure 2) when exposed to carbon monoxide can be divided into three sections: in the presence of synthetic air, the samples had a constant resistance; gas
exposure was accompanied by a decrease in resistance; then the resistance was restored to its initial value in the presence of synthetic air.

Three samples of spin-coated seed layers showed close sensitivity to carbon monoxide. An increase in the number of coating cycles led to an increase in the gas adsorption time and a decrease in the slope of the time dependence of the resistance change.

It was found that the change in the resistance of a sample synthesized by hydrothermal method reached 5kOhm in 2 minutes.

![Figure 2](image)

Figure 2. Change in resistance of ZnO samples when exposed to CO (100 ppm).

It was found that all samples are insensitive to carbon dioxide. This experimental fact may be explained as follow. At room temperature most of the adsorption sites are occupied by oxygen, thus preliminary desorption of oxygen and activation of the CO$_2$ adsorption process are required. Lack of sensitivity to CO$_2$ at room temperature in some cases can be considered as an advantage, since such sensors can remain functional in excess of this gas that constantly present in the atmosphere.

The time dependence of the sensor resistance when exposed to oxygen (figure 3) is also divided into three sections: in the presence of nitrogen, the samples had a constant resistance; exposure to synthetic air was accompanied by an increase in resistance; then the resistance was restored to its initial value in the presence of nitrogen. In the first 15 seconds of the experiment, the resistance of the sample changed by more than 1 kOhm.

Thus, nanostructures based on zinc oxide synthesized by spin-coating and hydrothermal method showed sensitivity to reducing and oxidizing gases presented in the atmosphere such as carbon monoxide and oxygen.

The sensitivity to CO was studied in a wide time interval allowing us to observe the adsorption saturation and to fix the recovery time. Adsorption saturation was considered as a change in the sample resistance at the level minimally registered by the electronics unit for at least 1 min under gas exposure.
The recovery time was defined as the time needed to recover 90% of the original baseline resistance. An increase in the number of coating cycles led to an increase in the CO adsorption time and a decrease in slope of resistance time dependence upon gas exposure. This effect may be caused by an increase in the effective area of interaction between zinc oxide nanostructures and gas, as well as an increase in the number of surface adsorption sites with an increase in the number of coating cycles. Also, new grain boundaries may occur, so it should take more time to reduce the depleted region and field strength at the crystallite boundaries during the adsorption of CO molecules. At the same time, the recovery time of the samples’ resistance is decreased, what may be explained by an increase in the number of surface adsorption sites and the occurrence of new grain boundaries. With the exception of the previously described features, samples synthesized by spin-coating showed a close sensitivity to CO, the change in the resistance of all samples when exposed to CO was in the range of 30-40 kOhm.

![Figure 3. Change in resistance of ZnO sample synthesized by hydrothermal method when exposed to O_2 (209000 ppm).](image)

Zinc oxide nanowires synthesized by low-temperature hydrothermal method showed gas sensitivity to CO (100 ppm) and O_2 (209000 ppm). The change in the resistance of the sample when exposed to CO reached 92 kOhm, and when exposed to O_2 - 50 kOhm. The increased gas sensitivity of layers based on zinc oxide nanowires may be explained by the complex morphology of such nanostructures. Polycrystalline structuring arrays of nanowires form a complex system interacting with adsorbed gas molecules by a donor-acceptor mechanism. The resistance of such sensors depends on seed layers structure, electrode configuration, zinc oxide grain boundaries and current flow paths. The large effective area of nanowires also allows more surface adsorption sites to be opened for gas molecules interaction that leads to enhanced gas sensitivity.

4. Conclusion
Zinc oxide nanostructures showed sensor response to carbon monoxide (100 ppm) and oxygen (200900 ppm) at room temperature under illumination with near UV light. The results showed that light activation is an effective method for increasing the sensitivity of semiconductor gas sensors based on zinc oxide nanostructures. The most promising structures are zinc oxide nanowires fabricated by low-temperature hydrothermal synthesis.

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