

Binary and Ternary Oxide Nanostructured Multisystems for Gas Sensors [†]

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Abstract: Currently, semiconductor gas sensors are among the most common types of sensing devices for detecting dangerous and toxic gases in the atmosphere. However, the problem of improving their characteristics should be solved for practical application. In this work, techniques have been developed to improve the response of sensors based on zinc oxide nanowires. The first technique is to modify the chemical composition of the nanowires by forming a shell of ternary Zn-Sn-O and Zn-Fe-O systems on their surface. Another approach is to control the surface concentration of oxygen vacancies by adding sodium bromide during the synthesis of zinc oxide nanowires. The surface chemical composition and the sensor properties of the samples were studied. It was found that the sensor responses of samples of ternary oxide systems and zinc oxide sample with a high content of oxygen vacancies exceed the one of the initial zinc oxide nanowires. The results are analyzed in the terms of the interaction of reducing gases with metal oxides.

Keywords: zinc oxide; gas sensor; ternary oxide; hydrothermal synthesis; oxygen vacancies; adsorption sites

1. Introduction

The ongoing increase in exhaust, explosive and toxic gas emissions requires the widespread use of devices for environmental monitoring. They will help to avoid explosions and minimize the harmful effects of hazardous gases on nature and human health. Among all the variety of available sensors, adsorption semiconductor gas sensors are considered as promising devices for practical application [1]. Their working principle is based on conductivity changes as a result of the chemisorption of gases. The main advantages of such sensors are a simple construction, high reliability, low cost of manufacture. The possibility of miniaturization ensures their use in portable devices and micro-electromechanical systems (MEMS) [2]. Relatively low power consumption allows these sensors to operate with autonomous power supply for a long time. A lot of semiconducting metal oxides have been studied for gas sensor applications, for example SnO₂ [3], TiO₂ [4], ZnO [5], Fe₂O₃ [6], In₂O₃ [7]. Among them, zinc oxide is one of the most prominent semiconductor sensing materials. It is a typical *n*-type wide-gap (3.3 eV) semiconductor [8].

However, the relatively low sensor signal and slow response and recovery rate limit widespread application of semiconductor gas sensors [9]. Therefore, improving the characteristics of zinc oxide gas sensors is an important task. There are two most common approaches to enhance sensor properties. The first one is the synthesis of nanostructured materials with different shapes and sizes: nanowires [10], nanoparticles [11], hollow nanoparticles [12], nanosheets [13] and hierarchical structures [14]. Another approach to improve sensor characteristics of metal oxides is to control their chemical composition, for example, by decoration with metals [15], doping with metals [16] and

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non-metals [17] as well as the formation of heterostructures [18]. Mixed semiconducting oxides have enhanced sensor properties compared to their constituent binary oxides. Multicomponent oxide systems with improved sensor properties have been successfully synthesized, for example ZnO-CdO [19], MoO₃-WO₃ [20], SnO₂/ZnSnO₃ [21], ZnO/ZnFe₂O₄ [22] et al.

The aim of this work is to develop approaches to enhance the response of gas sensors based on zinc oxide nanowires. Ternary Zn-Sn-O and Zn-Fe-O oxide nanostructures as well as zinc oxide nanowires with high surface content of oxygen vacancies were synthesized. It was shown that these structures have higher sensor response to volatile organic compounds compared with initial zinc oxide nanowires.

2. Experiment

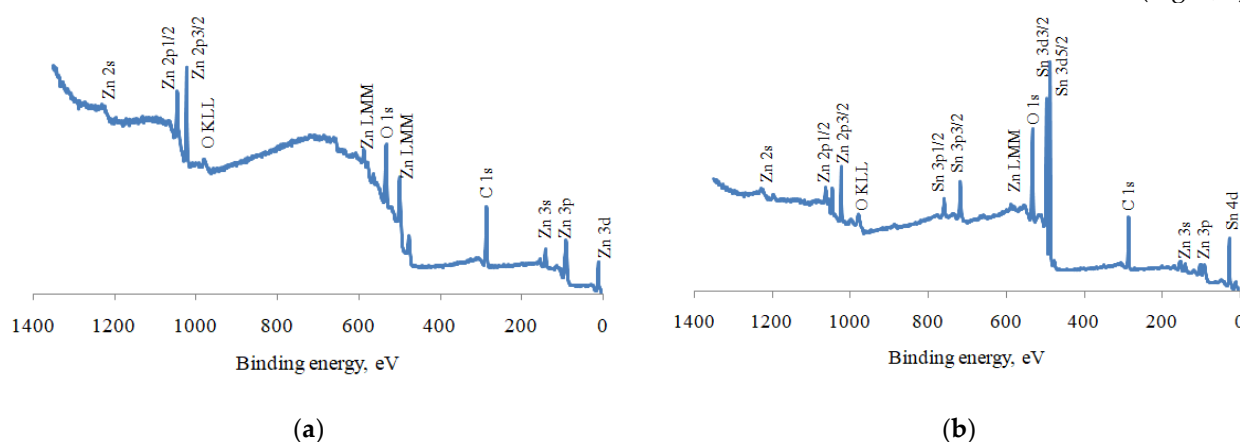
Two-stage methods are proposed to produce ternary oxide nanostructures of various composition and morphology [23, 24]. At the first stage zinc oxide nanowires were synthesized [25-27]. At the second stage, the chemical composition of the nanowires was modified as a result of post-treatment in a solution containing tin or iron ions to produce ternary oxides of Zn-Sn-O and Zn-Fe-O systems, respectively. Zn-Sn-O sensor layers were synthesized by hydrothermal treatment of zinc oxide nanowires in a solution of K₂SnO₃·2H₂O and (NH₂)₂CO. Zn-Fe-O layers were synthesized by immersing zinc oxide nanowires in FeSO₄ solution. Optimal synthesis conditions were chosen for each system [28, 29]. Gas-sensitive layers were synthesized on the surface of BI2 sensor platforms (Tesla Blatna, Czech Republic).

Binary zinc oxide nanostructures were also fabricated. Sodium bromide was added to the solution used for hydrothermal synthesis [30] and ZnO-Br samples were synthesized. The formation of binary and ternary oxide systems was studied using X-ray photoelectron spectroscopy (K-Alpha, Thermo Scientific, USA) with an Al K α X-ray source.

Sensor properties of zinc oxide nanowires and ternary Zn-Sn-O and Zn-Fe-O systems based on them were studied when detecting vapors of isopropanol, acetone and methanol. The response was determined as $S = R_{\text{air}} / R_{\text{gas}}$, where R_{air} is the resistance in the air atmosphere, R_{gas} is the resistance in the presence of target gas.

3. Results and Discussion

X-ray photoelectron spectroscopy has shown that tin (Fig. 1, a) and iron (Fig. 1, b) are observed on the surface of samples synthesized as a result of post-treatment of zinc oxide nanowires. At the same time, samples synthesized in the presence of sodium bromide in initial solution do not contain additional elements on the surface (Fig. 1, c).



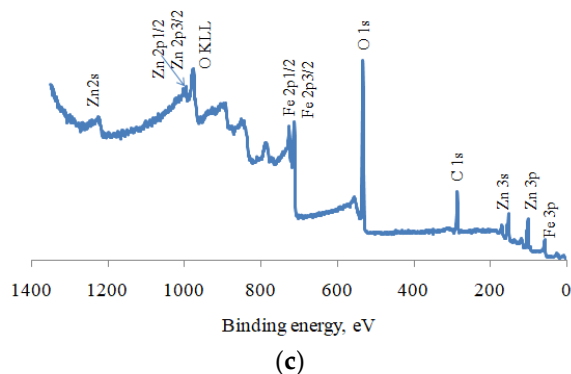


Figure 1. Survey XPS spectra of Zn-Sn-O (a), Zn-Fe-O (b) and ZnO-Br (c).

A comparison of the sensor properties when detecting isopropanol vapors is shown in Fig. 2. In these experiments temperature was 250 °C, and the target gas concentration was 1000 ppm. The sensor response of all the modified samples exceeds that of zinc oxide. At the same time, ternary Zn-Sn-O sample has the highest response.

Samples that showed high response when detecting isopropanol vapors (Zn-Sn-O and ZnO(Br)) were studied when exposed to acetone vapors with a concentration of 1500 ppm and methanol vapors with a concentration of 1000 ppm. The results are summarized in Fig. 3. The samples of both types show the maximum response to isopropanol vapors. Also, the resistance of ZnO(Br) is almost unchanged when interacting with methanol vapors.

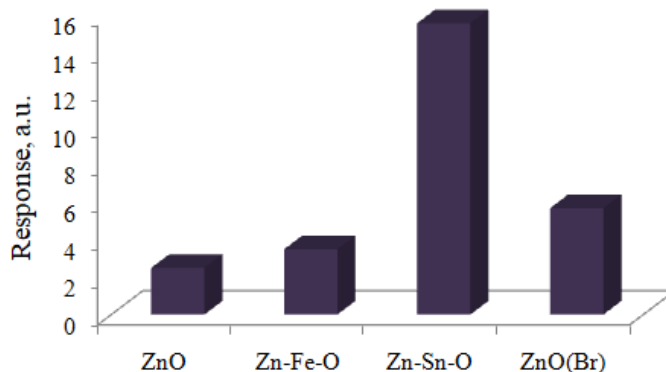


Figure 2. The responses of binary and ternary oxide samples to isopropanol vapors.

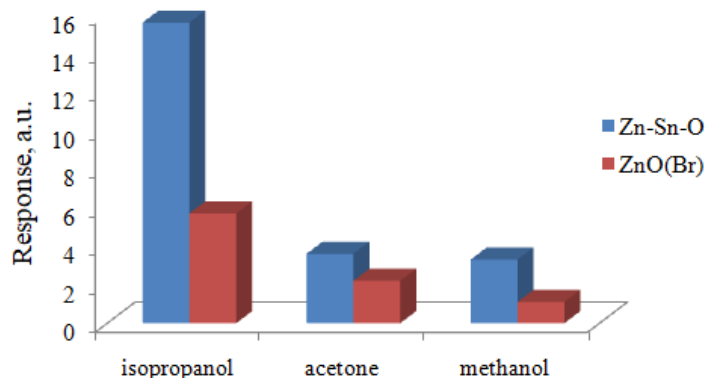


Figure 3. The responses of Zn-Sn-O and ZnO(Br) to vapors of volatile organic compounds.

The response of Zn-Sn-O to isopropanol vapors (1000 ppm) was analyzed at lower temperatures. At 120 °C, its value was 5.1, and at 180 °C it was 6.8. The sensor properties of zinc oxide nanowires and ternary oxide nanostructures were analyzed in terms of a model of interaction between metal oxides and reducing gases. The studied samples consist of randomly arranged one-dimensional nanoobjects. Their morphology depends on the synthesis conditions of zinc oxide nanowire layers. The results correspond to the model, according to which type of chemisorbed oxygen on the surface of metal oxide depends on temperature (O_2^- at a temperature below 100 °C, O^- at a temperature between 100 °C and 300 °C, O^{2-} at a temperature higher than 300 °C). Besides, since the oxidation of reducing gas requires activation energy, the rate of reaction increases with temperature. At last, all processes involved in gas detection mechanism are temperature dependent [31]. Thus, with increasing temperature, there is an increase in sensor response due to the formation of more electrons as a result of the interaction of gas with metal oxide. At the same time, an increase in the operating temperature leads to an increase in the power consumption of the sensor, which limits its practical application. Therefore, methods are currently being developed to achieve a high response at lower operating temperatures.

Previous studies have shown that in ternary oxide systems, fabricated as a result of modification with both iron and tin, there is a significant change in the oxygen content in different charged states. The proportion of oxygen in the form of adsorbed hydroxyl groups increases [32, 33]. The binding energies of oxygen of OH-groups are close to that of oxygen vacancies. The same effect is observed in zinc oxide nanowires produced by hydrothermal method in the presence of sodium bromide in the initial solution [30]. Oxygen vacancies are local defect sites, where oxygen can be chemisorbed. Thus, an increase in the concentration of these defects leads to a higher concentration of O^- on the surface, therefore, to a higher thickness of the depleted layer. It results in a higher modulation of resistance during the oxidation of reducing gaseous species on the surface of the sensor layer.

Ternary oxide structures are formed to increase the reactivity with molecules of isopropanol. The surface of such structures contains zinc ions, as well as metal ions of another type. In our experiments, such structures exhibit a higher response to reducing gases, since the properties of the active sites complement each other, and the adsorption capacity and catalytic activity of the surface increase [34, 35].

When modifying zinc oxide nanowires with tin and iron, the formation of heterojunctions is possible. As a result of post-treatment in a solution containing tin ions, a shell of ternary Zn-Sn-O oxide is formed on the surface of the nanowires. By electron backscatter diffraction, it is shown that under the selected synthesis conditions, inverse spinel Zn_2SnO_4 [36] is formed. Consequently, ZnO/ Zn_2SnO_4 heterojunction contributes to the sensor response. The work function of zinc oxide is 5.3 eV, and the one of Zn_2SnO_4 is 4.9 eV [37]. The electrons will move from zinc stannate to the conduction band of zinc oxide to reach thermal equilibrium. Thus, an electron-depleted layer is formed in zinc stannate layer near the interface. The width of this layer will also decrease when the material interacts with the reducing gases.

Thus, this work shows the possibility of increasing the sensor response of zinc oxide nanowires by the formation of ternary oxide systems, as well as by an increase in the concentration of oxygen vacancies on the surface of a binary oxide system.

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