engineering proceedings

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Proceeding Paper

Binary and Ternary Oxide Nanostructured Multisystems for Gas Sensors †

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† Presented at the 2nd International Electronic Conference on Chemical Sensors and Analytical Chemistry, 16–30 September 2023; Available online: https://csac2023.sciforum.net/.

Abstract: Currently, semiconductor gas sensors are among the most common types of sensing devices for detecting dangerous and toxic gases in the atmosphere. However, their characteristics should be improved in order to use them in practical applications. In this study, 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 surfaces. 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 samples with a high content of oxygen vacancies exceeded the sensor responses of the samplewithinitial zinc oxide nanowires. The results are analyzed in terms of the interaction involving reducing gases with metal oxides.

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

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Citation: Nalimova, S.; Shomakhov, Z.; Moshnikov, V. Binary and Ternary Oxide Nanostructured Multisystems for Gas Sensors. *Eng. Proc.* **2023**, *48*, 47. https://doi.org/10.3390/CSAC2023-14880

Academic Editor: Marco Frasconi

Published: 18 September 2023

1. Introduction

The ongoing increase in exhaust, explosive and toxic gas emissions requires the widespread use of devices for environmental monitoring. This will help to avoid explosions and minimize the harmful effects of hazardous gases on nature and on human health. Among the variety of available sensors, adsorption semiconductor gas sensors are considered to be promising devices for use in practical applications [1]. Their working principle is based on conductivity changes as a result of the chemisorption of gases. The main advantages of such sensors are their simple construction, high reliability and low cost of manufacturing. 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 an autonomous power supply for a long time. A lot of semiconducting metal oxides have been studied for gas sensor applications;for example, SnO_2 [3], TiO_2 [4], ZnO [5], Fe_2O_3 [6], In_2O_3 [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 the widespread application of semiconductor gas sensors [9]. Therefore, improving the characteristics of zinc oxide gas sensors is an important task. There are two common approaches that can 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 doping with 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], MoO_3-WO_3 [20], $SnO_2/ZnSnO_3$ [21], $ZnO/ZnFe_2O_4$ [22] et al.

The aim of this research 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

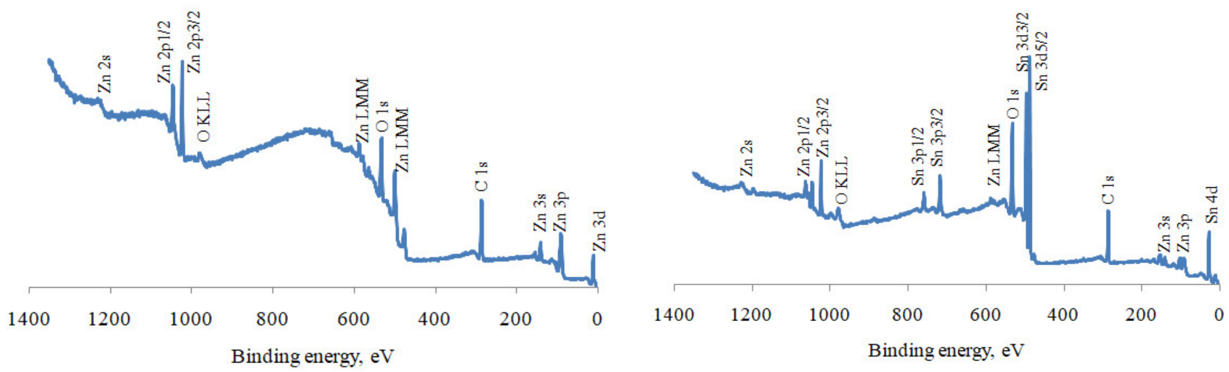
Two-stage methods are proposed to produce ternary oxide nanostructures of various composition and morphology [23,24]. At the first stage, zinc oxide nanowires were synthesized [25–27]. At the second stage, the chemical composition of the nanowires was modified as a result of post-treatment in a solution 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 $K_2SnO_3 \cdot 2H_2O$ and $(NH_2)_2CO$. Zn-Fe-O layers were synthesized by immersing zinc oxide nanowires in an $FeSO_4$ 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, Waltham, MA, USA) with an Al Kα 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 $S = R_{air}/R_{gas}$, where R_{air} is the resistance in the air atmosphere and R_{gas} is the resistance in the presence of the target gas.

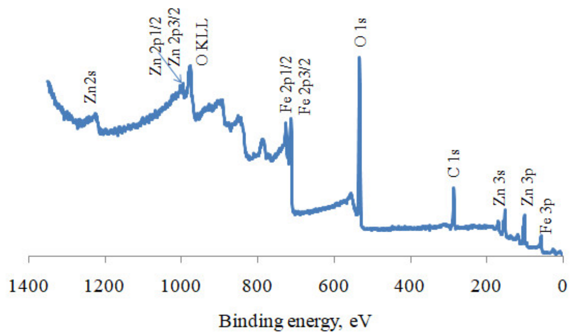
3. Results and Discussion

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



(**a**) (**b**)

Figure 1. *Cont.*



(**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 Figure 2. In these experiments, the 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.

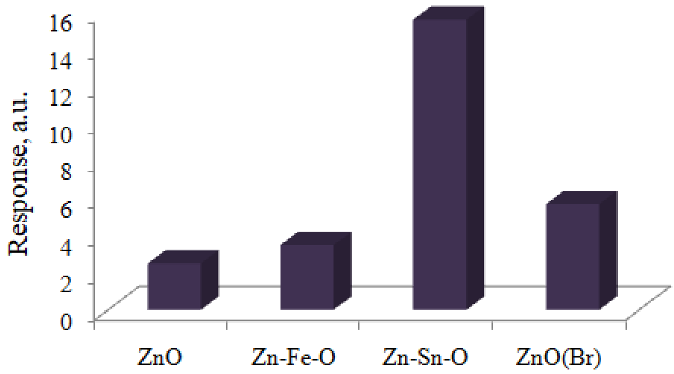


Figure 2. The responses of binary and ternary oxide samples to isopropanol vapors.

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 Figure 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.

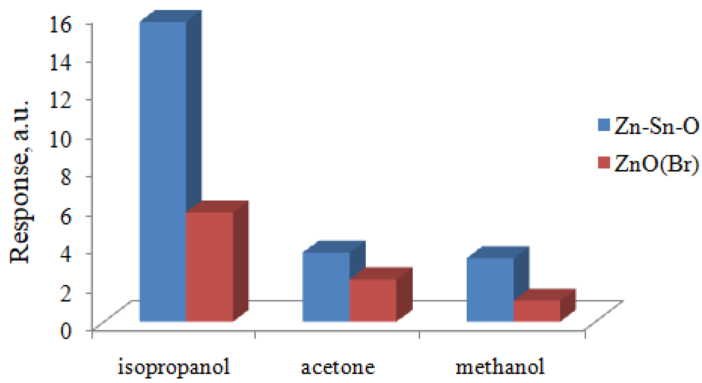


Figure 3. The responses of Zn-Sn-O and ZnO(Br) to vapors of volatile organic compounds.

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 modeling the interaction between metal oxides and reducing gases. The studied samples consist of randomly arranged one-dimensional nano-objects. Their morphology depends on the synthesis conditions of zinc oxide nanowire layers. The results correspond to the model, and the type of chemisorbed oxygen on the surface of metal oxide depends on the temperature (O^- at a temperature below 100 °C, O^- at a temperature between 100 °C and 300 °C, O^- at a temperature higher than 300 °C). In addition, since the oxidation of reducing gas requires activation energy, the rate of reaction increases with the temperature. Finally, all processes involved in the gas detection mechanism are temperature dependent [31]. Thus, with increasing temperature, there is an increase in the 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, which have been 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 in OH groups are close to that of oxygen vacancies. The same effect is observed in zinc oxide nanowires produced by the 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 and, therefore, to a higher thickness of the depleted layer. This 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 work function 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 the zinc stannate layer near the interface. The width of this layer will also decrease when the material interacts with the reducing gases.

Thus, this research shows the possibility of increasing the sensor response of zinc oxide nanowires due to 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.

Author Contributions: Conceptualization, V.M.; methodology, S.N., V.M. and Z.S.; validation, S.N. and Z.S.; formal analysis, S.N. and Z.S.; investigation, S.N. and Z.S.; writing—original draft preparation, S.N.; writing—review and editing, Z.S. and V.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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