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Zinc stannate nanostructures for low-temperature gas sensors with improved response and performance

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Abstract. Nowadays, the development of approaches to increase the sensitivity and reduce the operating temperature of gas sensors based on metal oxides is the important task. In this paper, these problems are solved by forming zinc stannate nanostructures during hydrothermal treatment of zinc oxide nanowires. The microstructure and chemical composition of the synthesized nanostructures were studied by SEM, EDS and XPS. Sensor responses to isopropyl alcohol vapors (1000 ppm) at 120 °C, 180 °C and 250 °C were measured. It was found that the sensor response values of zinc stannate nanostructures significantly exceed the responses of zinc oxide. Moreover, zinc stannate demonstrates the response of 6.3 at 120 °C. Thus, the developed structures can be used to create sensors of reducing gases with low operating temperatures.

Keywords: nanostructures, sensitivity, hydrothermal treatment

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Наноструктуры станната цинка для низкотемпературных газовых сенсоров с улучшенным откликом и быстродействием

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Аннотация. В настоящее время важной задачей является разработка подходов к повышению чувствительности и снижению рабочей температуры газовых датчиков на основе оксидов металлов. В данной работе эти проблемы решаются путем формирования наноструктур станната цинка при гидротермальной обработке оксида цинка. Было обнаружено, что значения отклика сенсора наноструктур станната цинка значительно превышают отклики оксида цинка. Таким образом, разработанные конструкции могут быть использованы для создания датчиков восстанавливающих газов с низкими рабочими температурами.

Ключевые слова: наноструктуры, чувствительность, гидротермальный синтез

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Introduction

Metal oxide semiconductors are of great interest for chemoresistive gas sensors due to their high sensitivity, ease of manufacture and low cost [1–4]. The approaches for increasing the gas sensitivity of adsorption semiconductor sensors have been developing. The formation of nano-structured materials with a large surface-to-volume ratio, such as hollow nanostructures [5] and one-dimensional nanostructures [6], is among the most promising ones. Hierarchical flower-like ZnO have been demonstrated enhanced ethanol gas-sensing properties [7]. Selective ppb-level ozone gas sensor was developed based on hierarchical branch-like In_2O_3 nanostructures [8]. Another approach is the use of multicomponent or composite materials. For example, uniform CuO nanoflakes modified with rGO nanosheets showed ultrahigh response towards NO_2 at room temperature [9]. Mesoporous $CdS/PbS/SnO_2$ composites showed high-selective response towards H_2. Enhanced properties were explained by a great number of active sites to gas adsorption and diffusion in surface redox reaction. Numerous heterojunctions of the $CdS/PbS/SnO_2$ composites may serve as highly conductive channels to accelerate carrier transfer, thus further leading to an improved performance of the sensors [10].

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In recent years, triple oxides attract a lot of attention as a new type of sensor materials, since they have a stable and excellent sensing response when detecting various gases [11]. However, the sensitivity of many ternary metal oxides is too low for commercial application due to the small area of interaction with gas and, consequently, poor electron exchange [12]. Among tin-based ternary metal oxides, $ZnSnO_3$ is a typical multifunctional n-type semiconductor oxide with a perovskite structure. Due to its chemical activity and excellent electronic properties, $ZnSnO_3$ is widely used as gas sensing materials [13–15]. A range of $ZnSnO_3$ nanostructures in the form of nanoparticles [16], hollow spheres [17], cubic nanostructures [18], nanofibers [19] with large surface-to-volume ratio have been hollow spheres synthesized.

The aim of the work is the development of zinc stannate nanostructures with excellent and fast sensor response at lower working temperatures. Hydrothermal treatment of preliminary prepared zinc oxide nanowires was chosen to change their composition and to form zinc stannate nanostructures. The microstructure and element composition were studied. The sensor response was analyzed towards isopropyl alcohol vapors.

Materials and Methods

Gas-sensitive layers of zinc oxide nanowires were synthesized on substrates with interdigitated gold electrodes by hydrothermal method described in details in [20–22]. The resulting layers were further processed to partially replace zinc atoms in the crystal structure of the nanowires with tin atoms and form a triple oxide. A substrate with zinc oxide nanowires were placed in an aqueous alcohol solution of potassium stannate trihydrate and urea. The synthesis was carried out in stainless steel autoclave with Teflon liner at 170 °C for 30 minutes. After that, the samples were washed with distilled water, dried in air and annealed at 500 °C for 15 minutes.

The microstructure was studied by scanning electron microscopy, elemental composition was analyzed by energy dispersive spectroscopy (Zeiss Supra25, Carl Zeiss, Germany). X-ray photoelectron spectroscopy (K-Alpha, Thermo Scientific, USA) using a monochromatized Al Kα X-ray source (hν = 1486.6 eV) was used to acquire the chemical composition and bonding states.

The gas sensor responses of zinc oxide and zinc stannate towards isopropyl alcohol vapors (1000 ppm) were investigated at 120 °C, 180 °C, 250 °C. The current was recorded using a Keithley 6485 picoammeter. The bias voltage was 5 V. The sensor response was calculated using the following equation:

$$S = \frac{R_{air}}{R_{gas}},$$

where R_{air} and R_{gas} are the sample resistances in the air and when exposed to the detected gas (isopropyl alcohol).

a) *b*)

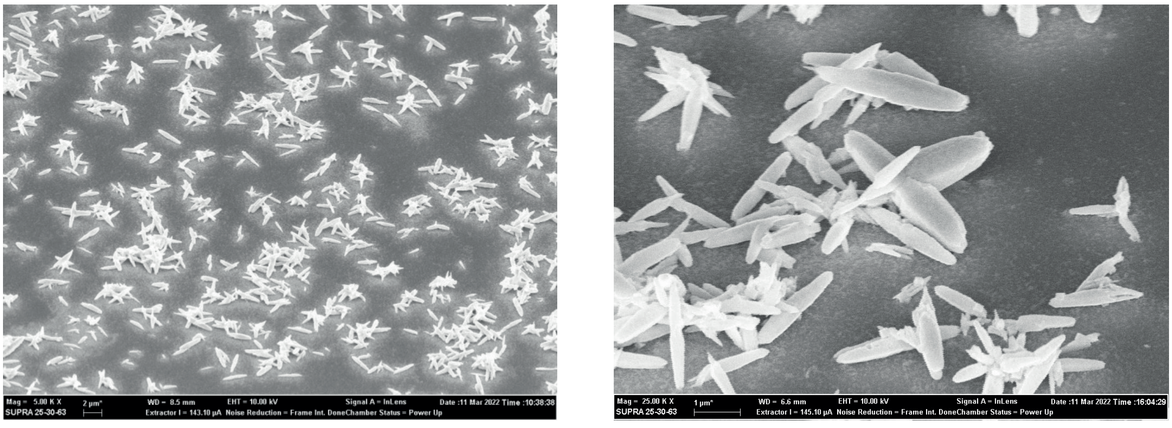

Fig. 1. Scanning electron microscopy images of zinc stannate

Results and discussion

The surface morphology and elements of the samples were characterized by SEM and EDS. As shown in Fig. 1, *a*, *b*, initial size and shape of zinc oxide nanowires remain the same as a result of hydrothermal treatment and zinc stannate formation. The EDS elemental distribution maps of zinc stannate are presented in Fig. 2, *a*, *b*, *c*, which show the presence of Zn and O elements in nanowires and uniform distribution of Sn on substrate surface.

The chemical composition and valence of zinc stannate nanostructures were analyzed by XPS (Fig. 3). The high-resolution spectrum of Zn 2p was divided into two photoelectron peaks: Zn 2p3/2 (located at 1022.5 eV) and Zn 2p1/2 (located at 1045.6 eV). The spin-orbit split is 23.1 eV, indicating the normal chemical state of Zn^{2+} in $ZnSnO_3$ [23]. The high-resolution spectrum of Sn 3d was divided into two photoelectron peaks: the peaks at 487.3 eV and 495.7 eV were attributed to Sn 3d5/2 and Sn 3d3/2, respectively. The split value of the bimodal spin orbit is about 8.4 eV, indicating the presence of Sn^{4+} cations [24]. The O 1s spectrum was divided into two fitting peaks corresponding to O^{2-} species in the lattice (530.7 eV) and chemically adsorbed hydroxyl groups (532 eV) [25].

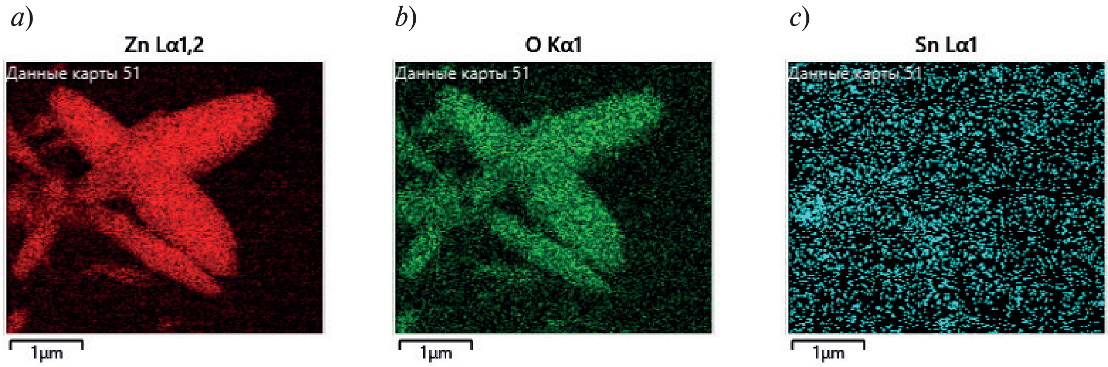

Fig. 2. EDS elemental mapping images of Zn (*a*), O (*b*) and Sn (*c*)

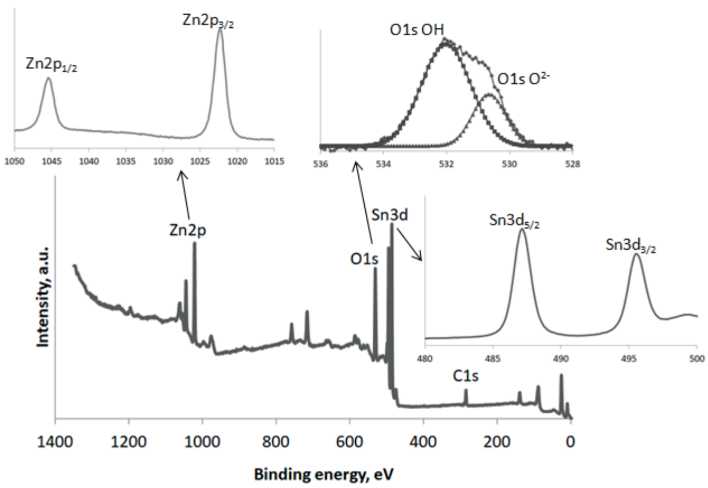

Fig. 3. X-ray photoelectron spectra of zinc stannate

The sensor responses of the layer consisting of zinc oxide nanowires are 1.4, 1.9 and 2.5, while for the zinc stannate layer they are 6.3, 6.7 and 15.6 (at 120 °C, 180 °C and 250 °C, respectively). The study of the interaction of samples with isopropyl alcohol vapors showed that at all temperatures the sensor responses of zinc stannate are much higher than the ones of zinc oxide (Fig. 4).

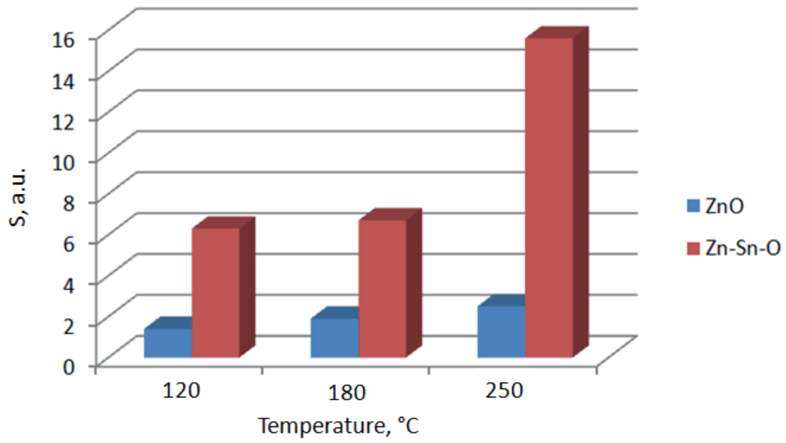

Fig. 4. Sensor responses of zinc oxide and zinc stannate layers

The changes in the sensor responses of zinc stannate sample during the exposure of isopropyl alcohol vapor are shown in Fig. 5. The exposure of isopropyl alcohol starts at 0 s and finished at 600 s. When isopropyl alcohol vapor is supplied, we can observe a decrease in resistance, and when air is supplied, an increase, which corresponds to the processes in the interaction of *n*-type semiconductors with reducing gases. It was found that an increase in temperature from 180 °C to 250 °C leads to a sharp increase in sensitivity. At the same time, the sensitivity values of the sample at measurement temperatures of 120 °C and 180 °C differ slightly. The response values of zinc stannate show that the developed sensor layers can be used at low operating temperatures less than 150 °C.

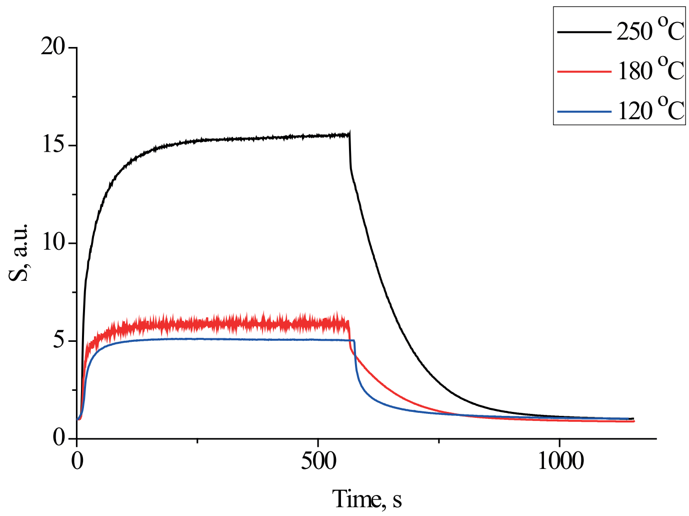

Fig. 5. Time dependences of the sensor responses of zinc stannate sample to isopropyl alcohol vapors at different temperatures

The improvement of the gas-sensitive properties of zinc stannate sample in comparison with ZnO can be explained as follows. The process of metal oxide interaction with the target gas is a complex process including both redox and acid-base catalytic reactions [26, 27]. Therefore, the improvement of the gas-sensitive properties is achieved by the development of materials containing adsorption centers with different redox and acid-base properties. When such sites are situated nearby a new effect of the nanosystem appears providing separate acceleration of the processes of adsorption and oxidation of gas molecules.

Conclusion

The improvement of the gas-sensitive properties of zinc oxide nanowires when treated in an aqueous alcohol solution of potassium stannate and urea is shown. The surface of resulting zinc stannate nanostructures contains sites of various types participated in the adsorption and oxidation of isopropyl alcohol vapors. Zinc stannate at 120 °C exhibits a response of 6.3, which indicates the prospects of the obtained layers for use in low-temperature gas sensors.

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REFERENCES

1. **Korotcenkov G.,** Nanomaterials 10 (2020) 1392.
2. **Moshnikov V.A., Gracheva I.E., Kuznezov V.V., Maximov A.I., Karpova S.S., Ponomareva A.A.,** Journal of Non-Crystalline Solids 356 (2010) 2020.
3. **Staerz A., Weimar U., Barsan N.,** 2022 Sensors and Actuators B 358 131531.
4. **Nalimova S.S., Moshnikov V.A., Myakin S.V.,** 2016 Glass Physics and Chemistry 4 597.
5. **Zhao R., Wang Z., Yang Y., Xing X., Zou T., Wang Z., Wang Y.,** Journal of Physics and Chemistry of Solids 120 (2018) 173.
6. **Kaur N, Singh M and Comini E.,** Langmuir 36 (2020) 6326.
7. **Zhu L., Li Y., Zeng W.,** Applied Surface Science 427 (2018) 281.
8. **Sui N., Zhang P., Zhou T., Zhang T.,** Sensors and Actuators B 336 (2021) 129612.
9. **Bai H., Guo H., Wang J., Dong Y., Liu B., Xie Z., Guo F., Chen D., Zhang R., Zheng Y.,** Sensors and Actuators B 337 (2021) 129783.
10. **Bai H., Guo H., Tan Y., Wang J., Dong Y., Liu B., Xie Z., Guo F., Chen D., Zhang R., Zheng Y.,** Sensors and Actuators B 340 (2021) 129924.
11. **Mongwaketsi N., Khamlich S., Kaviyarasu K., Matinise N., Maaza M.,** Applied Surface Science 446 (2018) 250.
12. **Wang B. S., Yu J. B., Li X. H., Yin J., Chen M.,** RSC Advances 9 (2019) 14809.
13. **Yin Y., Shen Y., Zhou P., Lu R., Li A., Zhao S., Liu W., Wei D., Wei K.,** Applied Surface Science 509 (2020) 145335.
14. **Levkevich E. A., Maksimov A. I., Kirillova S. A., Nalimova S. S., Kondrat'ev V. M**., IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus) (2020) 984.
15. **Levkevich E.A., Semenova A.A., Maximov A.I., Nalimova S.S., Kirillova S.A., Moshnikov V.A., Zhukov M.V.,** AIP Conference Proceedings (2020) 0018936.
16. **Feng G., Che Y., Song C., Xiao J., Fan X., Sun S., Huang G., Ma Y.,** Ceramics International 47 (2021) 2471.
17. **Bing Y., Zeng Y., Liu C., Qiao L., Sui Y., Zou B., Zheng W., Zou G.,** Sensors and Actuators B 190 (2014) 370.
18. **Guo W.W., Zhao B.Y., Fu M., Wang C.J., Peng R.,** Results in Physics 15 (2019) 102606.
19. **Chen Q., Wang Y.H., Wang M.X., Ma S.Y., Wang P.Y., Zhang G.H., Chen W.J., Jiao H.Y., Liu L.W., Xu X.L.,** Journal of Colloid and Interface Science **543** (2019) 285.
20. **Ryabko A.A., Maximov A.I., Moshnikov V.A., Terukov E.I., Verbitskii V.N., Levitskii V.S.,** Semiconductors 54 (2020) 1496.
21. **Nalimova S.S., Ryabko A.A., Maximov A.I., Moshnikov V.A.,** Journal of Physics: Conference Series 1697 (2020) 012128.
22. **Bobkov A., Moshnikov V., Varezhnikov A., Plugin I., Fedorov F. S., Goffman V., Sysoev V., Trouillet V., Geckle U., Sommer M.,** Sensors 19 (2019) 4265.
23. **Zhao S., Shen Y., Yan X., Zhou P., Yin Y., Lu R., Han C., Cui B., Wei D.,** Sensors and Actuators B 286 (2019) 501.
24. **Kim R., Jang J.-S., Kim D.-H., Kang J.-Y., Cho H.-J., Jeong Y. J., Kim I.-D.,** Advanced Functional Materials 29 (2019) 1903128.

25. **Jia X., Yu S., Yang J., Wang S., Li Y., Shao D., Song H.,** IEEE Sensors Journal 22 (2022) 1916.
26. **Karpova S.S., Moshnikov V.A., Mjakin S.V., Kolovangina E.S.,** Semiconductors 47 (2013) 392.
27. **Karpova S.S., Moshnikov V.A., Maksimov A.I., Mjakin S.V., Kazantseva N.E.,** Semiconductors 47 (2013) 2016.

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