Study of the electrophysical and gas-sensitive properties of thin ZnO-SnO$_2$ films formed by the sol-gel method

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Abstract Thin films of ZnO-SnO$_2$, with a molar ratio of Zn: Sn = 0:100, 1:99, and 5:95, were synthesized by the sol-gel method. As a result of a study of the electrophysical and gas-sensitive properties of thin ZnO-SnO$_2$ films, the effect of a decrease in the working temperature at low concentrations of zinc oxide was found. The value of the coefficient of gas sensitivity of ZnO-SnO$_2$ films correlates with the activation energy of conduction. For sensor structures based on films with a composition of: 5:95 at a working temperature of 200 °C, a higher gas sensitivity coefficient and the fastest response among all the samples under study are observed.

1. Introduction
Recently, the most widespread materials for gas sensors are nanocomposites based on semiconducting metal oxides. Thin nanocomposite films based on tin and zinc oxides (ZnO-SnO$_2$) have several advantages due to their high sensitivity [1]. The aim of this work was to study and analyze the electrophysical and gas-sensitive properties of thin ZnO-SnO$_2$ films obtained by the sol-gel method with specified Zn: Sn molar ratios.

2. Experiment
In this work, ZnO-SnO$_2$ thin films were synthesized by the sol-gel method in Zn: Sn molar ratios of 0:100, 1:99, and 5:95. Tin (IV) chloride pentahydrate, zinc nitrate hexahydrate, and isopropanol were used as precursors. The required amount of salts was dissolved in isopropanol, after which they were applied three times onto pre-cleaned polycor substrates. Temperature treatment was carried out at 550 °C for two hours. After heat treatment, V-Ni contact metallization was applied over the films by vacuum thermal evaporation.

The study of the electrophysical properties of the film samples was carried out on a setup for studying the electrophysical properties of gas sensors [2]. The temperature dependence of the resistance $R$ of the obtained sensor structures based on thin nanocomposite ZnO-SnO$_2$ films was measured. The measurements were carried out in the temperature range from room temperature to 300 °C. Subsequently, the activation energy of conduction ($E_a$) was estimated according to the Arrhenius equation [3].
\[ G = G_0 \cdot \exp\left(\frac{-E_a}{k \cdot T}\right) \]  

(1)

where \( G \) - conductivity of the films \( (G=1/R) \), \( E_a \) is the activation energy of conduction, \( k \) is the Boltzmann constant, and \( G_0 \) - coefficient taking into account the bulk material conductivity, barrier value.

The gas-sensitive properties of ZnO-SnO\(_2\) films were studied under the action of NO\(_2\) with a concentration of 5-50 ppm on a dynamic setup designed for the preparation of calibration gas mixtures "Mikrogaz-FM" (Russia) at working temperatures of 150, 200, and 250 °C. [4]. The NO\(_2\) concentration was formed by mixing with synthetic air, which was purged after the formation of the response. A mixture of air and NO\(_2\) was introduced at a flow rate of 0.4 dm\(^3\)/min. The coefficient of gas sensitivity of sensor elements based on ZnO-SnO\(_2\) films was calculated by the formula:

\[ S = \frac{R_g}{R_0}, \]  

(2)

where \( R_g \), \( R_0 \) - resistance of the sensor upon exposure to and before exposure to gas, respectively. The correlations of \( S \) versus \( E_a \) were also investigated.

3. Results and discussion

Figure 1 shows the temperature dependence of the resistance of the test samples. The analysis of the presented dependences shows that the generation of charge carriers as a result of thermal excitation is of an activation nature.

![Figure 1. Temperature dependence of the resistance of samples with Zn: Sn ratios in them equal to 0: 100 (1), 1: 99 (2), and 5: 95 (3).](image)

The \( E_a \) values calculated in the temperature range 40-300 °C were 0.21; 0.43 and 0.64 eV for films with Zn: Sn ratios in them equal to 0:100; 1:99 and 5:95, respectively. Studies have shown that the resistance of the samples increases by 2.5-4.5 orders of magnitude with an increase in zinc oxide in the mixture from one to five mole percent.

The study of the gas-sensitive properties showed that the sol-gel SnO\(_2\) films without the addition of zinc oxide at a temperature of 250 °C have the maximum response to the effect of nitrogen dioxide with a concentration of 50 ppm - (figure 2, a). The gas sensitivity coefficient was 97.0. But the response time of this sample was the longest among all the others, equal to 1303 s. - (table 1).

However, already at a temperature of 200 °C, the coefficient of gas sensitivity of the sample without the addition of zinc oxide dropped sharply to 10.9. At the same time, for samples based on thin films with Zn: Sn ratios equal to 5: 95 and 1: 99, the gas sensitivity coefficient was 64.8 and 68.0, respectively - (figure 2). The sample with the Zn: Sn ratio of 5: 95 has the smallest response time and is 138 s.
In addition, it can be seen from Table 1 that at a temperature of 250 °C all three samples have the longest response times compared to lower temperatures under the same measurement conditions. At a lower working temperature (150 °C), the gas sensitivity coefficient for all samples was low.

Thus, it can be seen from figure 2 and table 1 that small additions of zinc oxide in the ZnO-SnO$_2$ nanoscale film formed by the sol-gel method make it possible to reduce the working temperature of the film samples to 200 °C and reduce the response time by 1.5-3 times.

**Figure 2.** Temperature dependence of the gas sensitivity coefficient at 150, 200, and 250 °C for film samples with Zn: Sn ratios equal to (1) 5:95, (2) 1:99, and (3) 0:100 on exposure to 50 ppm NO$_2$.

Figure 2 shows that samples with a Zn: Sn ratio of 1:99 and 5:95 exhibit the highest values of the gas sensitivity coefficient $S$ at $T = 200$ °C and the lowest values of the coefficient at 250 °C. This can be explained by the fact that the gas-sensitive properties of tin and zinc oxides primarily depend on the concentration of oxygen vacancies in the oxides [5].

We have shown [6] that for ZnO-SnO$_2$ films obtained by solid-phase pyrolysis, a higher sensitivity at 200 °C is observed just for a film with a Zn: Sn ratio of 0.5:99.5, which had a higher concentration oxygen vacancy in the crystal lattice. Apparently, a similar picture is observed in the ZnO-SnO$_2$ films obtained by the sol-gel method. However, at a working temperature of 250 °C, a higher concentration of oxygen vacancies can be observed in the pure tin oxide SnO$_2$ film. This may be due to a decrease in the concentration of water molecules adsorbed on the surface, which are desorbed at higher temperatures [7].

**Table 1.** Indicators of the response time of samples with the ratio Zn: Sn in them equal to 0:100; 1:99 and 5:95 at 150, 200 and 250 °C.

| ZnO: SnO | $t_{\text{resp}}$ (s), at a temperature (°C) |
|----------|---------------------------------------------|
|          | 150 | 200 | 250 |
| 0:100    | 941 | 430 | 1303|
| 1:99     | 916 | 184 | 868 |
| 5:95     | 253 | 138 | 318 |
Figure 3 shows typical responses of the obtained ZnO-SnO$_2$ films with a Zn: Sn molar ratio of 5:95 to exposure to 50 ppm NO$_2$ at 150, 200 and 250 °C.

![Figure 3](image)

**Figure 3.** Gas-sensitive responses of samples of a Zn: Sn molar ratio of 5:95 film at 150 °C (1), 200 °C (2), and 250 °C (3) to the effect of 50 ppm NO$_2$.

Analysis of the behavior of the quantities $S$ and $E_a$ showed their correlation. Figure 4 shows the dependence of the gas sensitivity coefficient when exposed to NO$_2$ with a concentration of 50 ppm and a temperature of 250 °C on the activation energy.

![Figure 4](image)

**Figure 4.** Dependence of the gas sensitivity coefficient ($S$) on the values of the activation energy ($E_a$) for ZnO-SnO$_2$ films with the Zn: Sn molar ratio of 0:100 (1), 1:99 (2), and 5:95 (3) to the effect of NO$_2$ with a concentration of 50 ppm at 250 °C.

From figure 4 it can be seen that the values of the gas sensitivity coefficient are the higher, the lower the values of the activation energy of conduction. The found constraint equation has a linear character with a correlation coefficient equal to 0.94:

$$S = 126.74\cdot E_a + 120.85$$ (3)
Thus, research have shown that for nanocomposite ZnO-SnO$_2$ films formed by the sol-gel method, due to small additions of zinc oxide, the working temperature decreases to 200 °C. In this case, films with the lowest activation energy of conduction have high values of the coefficient of gas sensitivity in. For sensor structures based on films with a composition of 5:95 at a working temperature of 200 °C, a higher gas sensitivity coefficient and the fastest response among all the samples under study are observed.

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