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Effect of gold and nickel co-additives on gas-sensitive characteristics of SnO₂ thin-film on exposure to hydrogen and nitrogen dioxide

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Abstract. The results of investigation of the gas-sensitive properties of sensors based on the tin dioxide thin films with combined additives of gold and nickel obtained by the DC - magnetron sputtering are presented. The investigated sensors are characterized by a high response to low concentrations of NO_2 of 0.45 – 10.23 ppm at temperatures of 50 – 150 °C with response time of 10 s. The sensitivity of sensors to hydrogen appears at the temperature of 250 °C. The hydrogen sensors are characterized by high reproducibility of the measurement results. The obtained results are explained by the synergistic effect of gold and nickel additives, as well as the ability of the Ni to prevent the interaction of hydrogen with lattice oxygen atoms in the subsurface part of tin dioxide.

1. Introduction

The development of air monitoring systems and methods for monitoring the human exhaled mixture require the creation of sensors of low concentrations of gases characterized by high sensitivity, selectivity, stability of parameters and the low energy consumption. The most promising direction in this area is the development of sensors based on thin films of metal oxide semiconductors. This work is devoted to thin-film gas sensors with a sensitive layer based on polycrystalline tin dioxide with gold and nickel additives. Hydrogen and nitrogen dioxide were chosen as detected gases.

Hydrogen sensors based on SnO_2 thin films can replace H_2 leakage monitoring systems in nuclear power plant premises and become the basis of safety for hydrogen energy. For these purposes, it is sufficient to develop high-speed devices that are sensitive to the effects of a gas concentration equal to 0.1–0.2 of the lower explosive limit (LEL). According to the state standard for hydrogen LEL is 4 vol. %, so conversion into part per million equals $4 \cdot 10^4$ ppm. The more difficult task is the development of measuring instruments for low hydrogen concentration below 10^3 ppm. Such devices are of interest for laboratory and medical purposes. In particular testing of a mixture exhaled by a person for the presence of hydrogen at concentrations from 5 to 120 ppm is the "gold standard" for the diagnosis of lactose, fructose, sorbitol and xylitol intolerance [1,2]. The increased concentration of hydrogen in the exhaled mixture also indicates the presence of the syndrome of excessive growth of bacteria in the small intestine, cirrhosis of the liver, problems with the pancreas [2].

Interest in the development of sensors of low concentrations of nitrogen dioxide is due to the need for environmental monitoring of urban air. According to sanitary norms, the maximum permissible concentration of the working area of this gas is 1 ppm. In addition, the detection of nitrogen oxides at a level of 10 ppb permits to detect the traces of explosives in the air. Such sensitivity is achieved by an expensive and cumbersome system based on the lidar principle using the laser fragmentation/laser-induced fluorescence method [3]. Cheap and mobile nitrogen oxides sensors are needed for the broad introduction of such systems for monitoring and security.

The principle of operation of gas sensors is based on the phenomenon of reversible chemisorption of gases on the surface of SnO_2. Sensors based on "pure" SnO_2 are characterized by low gas responses and long response times [4, 5]. The sensor response to hydrogen is the ratio G_H/G_0, where G_H is the conductance of the sensor in the atmosphere containing hydrogen; G_0 is the conductance of the sensor in the atmosphere of clean air. Hydrogen is a reducing gas and its chemisorption on the surface of SnO_2 electrons receive to the conduction band of the semiconductor and the conductivity of the sensor increases. As a response of the sensor to the effect of nitrogen dioxide we take the ratio G_0/G_{ND}, where G_{ND} is the conductance of the sensor in an atmosphere containing nitrogen dioxide. Nitrogen dioxide is an oxidizing gas and when NO_2 is chemisorbed to the SnO_2 surface, electrons are captured from the conduction band of the semiconductor and the conductivity of the sensor decreases. The response time t_{res} is the time interval when the conductance of the sensor reaches $0.9G_{gst}$ on exposure to H_2 and $1.1G_{gst}$ on exposure to NO_2, where G_{gst} – stationary conductance on exposure to a certain gas concentration. A promising way to improve the characteristics of the sensors is the modification of the bulk and surface of the sensitive layers with gold and nickel additives.

There is not general consensus on the question of the effect of an addition of nickel on the properties of gas sensors. The authors [6-10] came to the conclusion that modification of films and other nanoscale structures of tin dioxide with nickel contributes to increasing of sensor resistance in clean air and response to a reducing gases, the displacement of the operating temperature in the low-temperature range. The high resistance of the films is caused by the formation of deeper impurity levels in the forbidden gap of SnO_2, as well as an increase in the surface density of chemisorbed oxygen. The addition of nickel is presented in the form of oxide and on the border with SnO_2 microcrystals can form a heterojunction that prevents the percolation of electrons. As a result of that the sensors have high resistance. The increase in nickel concentration contributes to the formation of fine-grained developed structure of tin dioxide films. The addition of nickel not only can be integrated into the crystal lattice of SnO_2, but is able to form clusters with its own crystal structure.

Gold due to its properties is not able to form compounds with oxygen and other gases, so the influence of Au on the characteristics of sensors is explained only by its catalytic properties [11,12]. It is noted that metal clusters of gold activate special forms of chemisorbed oxygen O^{2-} in the three-phase boundary Au-SnO_2-gas, that at operating temperatures are not the main on the surface, but are extremely reactive with atoms of reducing gases. It should be noted that the sensitivity to NO_2 tin dioxide shows only with the introduction of gold in its structure [11,12].

According to [13-18], sensors based on metal oxide films and nanostructures can be used for NO_2 detection. The most common sensing elements of NO_2 sensors are thin WO_3 films that demonstrate sensitivity to gas at the room temperatures. However, to increase the response to the gas and reduce the response time, the semiconductor must be heated to high temperatures. To improve the performance of the sensors, the WO_3 sensing element is modified with gold. This allows to increase the response and reduce the response time. Other materials (ZnO, SnO_2:In) demonstrate a short response time and a high response when exposed to a concentration of NO_2 in the range of 10 – 100 ppm, that is not suitable for solving the problems described above. In [16] presents research of thick films SnO_2 modified by joint additives Au and NiO. Such films were obtained by precipitation from the solution. It is shown that the combined introduction of Au and Ni additives significantly increases the response of sensors to NO_2 and reduces their operating temperature T. Mechanism of this synergistic effect of additives is unclear and requires further research. Study the system Au–Ni/SiO_2 by the method of x-ray photoelectron spectroscopy has shown [16] that joint presence of Au^0 and Ni^{2+} leads to a partial flow of the charge

from the oxidized surface of nickel atoms and the appearance of additional charge on the Au nanoparticles, that is manifested in the shift of position of the electronic Au *4f* level towards higher energies. Selective adsorption on charged centers can provide a significant effect in changing the electrical conductivity of materials. Most of the results are devoted to sensors made by thick-film technology that has a number of inconveniences, for example, does not allow combining sensitive elements with microelectronic technology.

Thus, the aim of this work is to research the gas-sensitive properties of SnO_2 thin films modified with joint additives Au and Ni under the influence of low concentrations of hydrogen and nitrogen dioxide.

2. Experiment

SnO_2 films were obtained by direct current magnetron sputtering of a target consisting of alloy Sn and Sb (Sb – 0.49 at.%). To introduce additives into the bulk of films pieces of the corresponding metal were placed on the surface of the target. On the basis of special studies, the optimal ratio S_m/S_{Sn} was estimated, where S_m is the area of metal pieces, S_{Sn} is the area of the sprayed part of the target. For the studied samples $S_{Au}/S_{Sn}=3\cdot10^{-3}$ and $S_{Ni}/S_{Sn}=3\cdot10^{-3}$. On the surface of the films by the same method of magnetron sputtering dispersed Au layers were sprayed for 30 s. The finished samples were annealed in air at the temperature of 723 K for 24 hours.

To research the electrophysical and gas-sensitive parameters of the samples the installation described in [19] was used. The conductivity of the sensors was measured using an automated stand with the temperature controller of the devices of the devices and the humidity of the gas-air mixture in the measuring chamber. The measuring stand provides measurement of conductivity with an error of 1 %, measurement of the level of relative humidity with an error of 3 %, the temperature of the sensors with an accuracy of 0.5 °C. In this work, all studies were carried out at a relative humidity of 30 – 35 %.

3. Results and discussions

The introduction of Ni additives into the bulk of SnO_2 films leads to a significant increase in the sensor resistance in the atmosphere of pure air R_0 compared to films only with gold additives in the bulk and on the surface. So for thin-films Au/SnO_2:Sb,Au R_0 at room temperature is 0.25 MΩ , and for Au/SnO_2:Sb,Au,Ni – 2.5 MΩ. The increase in film resistance is due to the formation of deeper levels localized in the band gap of the semiconductor. The $R_0(T)$=const·exp[$\Delta Ea/kT$] ratio is performed for partially compensated semiconductor in the sensor operating temperature range. Figure 1 shows the dependence of lnR_0 on the 1000/temperature for the samples. The dependence has a characteristic form of tin dioxide thin films. In the low temperature region there are two linear sections corresponding to donor levels in the forbidden zone of SnO_2. The activation energies of donor levels were calculated using linear approximation of these sections. For the studied sensors $\Delta Ea_1 = 0.23\pm0.01$ eV, $\Delta Ea_2 = 0.50\pm0.01$ eV. R_0 rises due to an increase in the surface density of chemisorbed oxygen in the form of O^- [10] with increasing the temperature from 210 °C. The growth of R_0 continues up to T=500 °C. The presence of such a large area of growth of R_0 due to an increase in the negative charge on the surface does not contradict the data of [20]. However, it can be concluded that the addition of nickel leads to growth of the surface density of oxygen ions due to the formation of high-temperature adsorption centers. According to many works [6-8], not only non-stoichiometric tin atoms, but also non-stoichiometric nickel atoms can act as adsorption centers.

Temperature dependences of sensor response at exposure to 100 ppm of H_2 and 10.23 ppm of NO_2 are shown in figure 2. Sensors demonstrate high sensitivity to NO_2 at low operating temperatures range from 50 to 150 °C. The sensitivity of the sensors to hydrogen appears at higher temperatures. The response to hydrogen rises with increasing T and reaches a maximum at 500 °C. Based on the analysis of temperature dependences of response and resistance of sensors it can be concluded that the interaction of SnO_2 films with H_2 occurs with the participation of previously chemisorbed O^- ions that surface density increases with the introduction of nickel additives. As a result of the reaction between H_2 and chemisorbed O^- ions the negative charge on the SnO_2 surface decreases and the conductivity of the sensors increases. The mechanism of interaction between NO_2 and the surface of SnO_2 films modified

with gold and nickel includes two processes: 1 – the formation of negatively charged nitrite ions by adsorption of NO_2 to the center and the capture of an electron from the conduction band of SnO_2; 2 – the interaction of NO_2 with chemisorbed molecular oxygen in the form of O^{2-}. In the first and in the second case NO_2^- appears on the surface, but as a result of the first process, a negative charge on the surface of the semiconductor increases and the conductivity of the sensors decreases.

It should be noted that the conductivity of the sensors after pumping of hydrogen at all operating temperatures is recovered to initial value. The heating of the sensor at $T = 400 – 500$ °C for 10 to 30 s is required to full recovering of sensor conductivity after exposure to NO_2. Strong links with the semiconductor surface are formed at chemisorption of the nitrogen dioxide molecules. So to clean the surface heating of the sensors is required. Water molecules and hydroxyl groups are formed on the surface at the hydrogen interacts with SnO_2, for desorption of these products of reactions temperatures above 200 °C are sufficient [21].
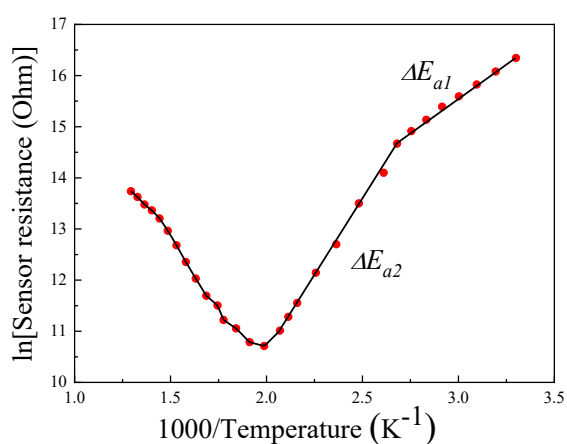

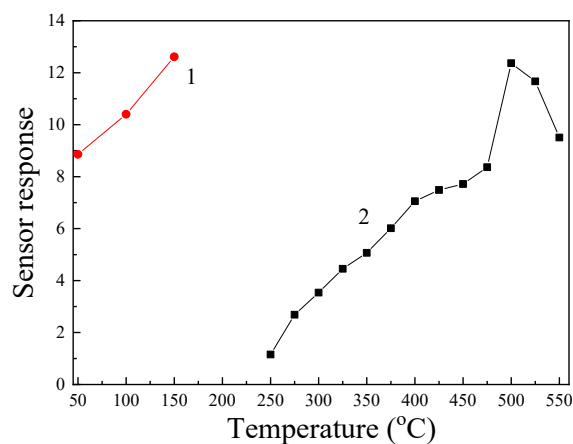**Figure1.** Temperature dependence of sensor resistance in clean air.

Figure 2. Temperature dependence of sensor response: 1 – at exposed to 10.23 ppm NO_2; cu. 2 – at exposed to 100 ppm H_2.

The dependences of the sensor response on the concentration of NO_2 at $T=50$ °C and the hydrogen concentration at $T=425$ °C are shown in figure 3. Analysis of the experimental data showed that G_0/G_{ND} with increasing NO_2 concentration rises exponentially with $G_0/G_{ND}=\exp(b_{ND}*n_{ND}+A_{ND})$, where A_{ND} and b_{ND} are constants; n_{ND} is the concentration of nitrogen dioxide. At $T=50$ °C $A_{ND} = 0.15\pm0.03$, $b_{ND} = (0.199 \pm 0.005)$ ppm^{-1}. The response of the sensor G_H/G_0 with increasing hydrogen concentration rises according to the power law $G_H/G_0=A_H*n_H^{bH}$, where A_H and b_H are constants, n_H is the concentration of hydrogen. At $T=425$ °C $A_H = (0.29 \pm 0.01)$ ppm^{-1}, $b_H = 0.70 \pm 0.01$. The power dependence of the sensor response on the hydrogen concentration is observed in many works. For the same films, the exponential dependence of response on n_{ND} is observed for the first time. By increasing the operating temperature of the sensors to $100 – 150$ °C, the dependence of G_0/G_{ND} on n_{ND} becomes linear that is observed in many works [13-15] in this area of T.

Analysis of the concentration dependence of the response under the influence of hydrogen concentrations up to 1.4 vol. % showed that in the atmosphere of pure air the ratio of the width of the space charge region due to the chemisorption of oxygen and the width of the conducting channel SnO_2 is 0.95 that is a known condition for a high response to reducing gases [11].

The estimates showed that at $T = 50$ °C and $n_{ND} = 0.45$ ppm the response time of the sensors is 10 s. it is worth noting that in [13] the response times at exposure to 0.9 ppm NO_2 on samples based on tungsten trioxide and $T = 230$ °C were $115 – 400$ s. For sensors based on thin films of SnO_2:In at $T = 230$ °C and $n_{ND} = 50$ ppm $t_{res} = 115$ s. [14], for sensors based on nanorods of ZnO at $T = 230$ °C and $n_{ND} = 7.5$ ppm $t_{res} = 120$ s. [15]. Also in the works response times – 55 and 26 s are specified at temperatures

140 and 160 °C for thin films SnO_2/C [17] and α-MnO_2 [18], respectively, but do not specify the gas concentration. It is known [21] that the response times are determined by two processes, the rapid adsorption of NO_2 molecules to the semiconductor surface and their long diffusion into the semiconductor bulk. At $T = 50$ °C diffusion is negligible. Given the large difference in t_{res}, it can be concluded that the introduction of Au and Ni additives compared to other modifiers is an effective way to improve the performance of sensors.

At exposure to 100 ppm hydrogen and $T = 425$ °C t_{res} of sensors studied was 23.8 s. This value is not outstanding in comparison with the literature data.

The results of the study of short-term reproducibility of sensor characteristics under the influence of 100 ppm H_2 and $T = 425$ ° C are shown in figure 4. The portion of the hydrogen was supplied to chamber after 20 minutes of the start of operation of the sensor. After establishing a stationary value of G_H clean air was pumped through the measuring chamber. G_0 and G_H values were measured every 20 minutes. From figure 4 it is seen that G_0 and G_H and the response of the sensors change slightly. As in [22], the stability of the characteristics is determined by nickel additives that prevent the interaction of hydrogen with lattice oxygen atoms on the surface of SnO_2.
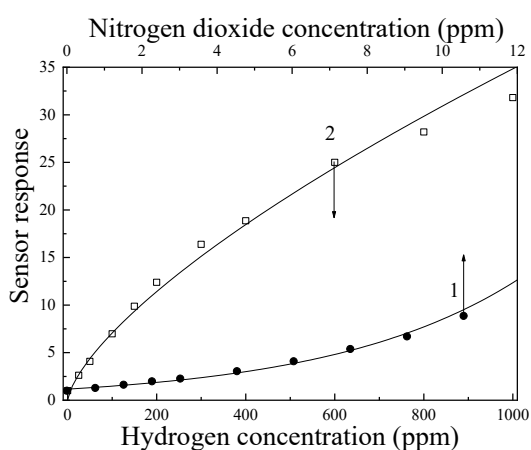

Figure 3. The concentration dependence of the sensor response: 1 – at $T = 50$ °C and exposure to NO_2; 2 – at $T = 425$ °C and exposure to H_2.
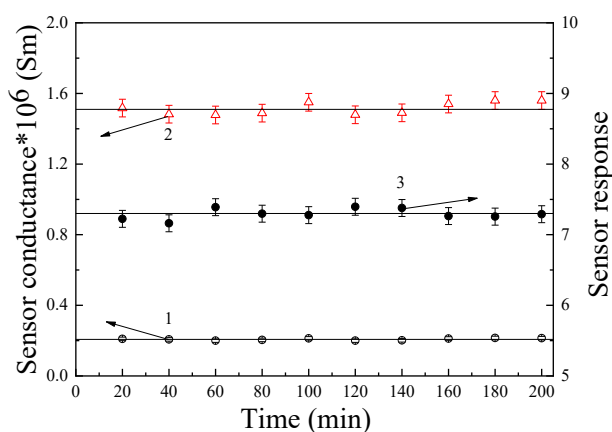
Figure 4. The reproducibility of the sensor characteristics at periodic exposure to 100 ppm H_2: $1 - G_0$; $2 - G_H$; $3 - G_H/G_0$.

Studies of the effect of long-term tests on the conductivity of the investigated sensors in clean air, at n_H=100 ppm and at n_H=1000 ppm have shown that G_0 and G_H do not have any tendency to change with increasing of service life.

4. Conclusion

The mechanism of interaction between NO_2 and the surface of SnO_2 films modified with gold and nickel includes two processes: 1 – the formation of negatively charged nitrite ions by adsorption of NO_2 to the center and the capture of an electron from the conduction band SnO_2; 2 – the interaction of NO_2 with chemisorbed molecular oxygen in the form of O_2^-.

The joint modification of SnO_2 thin films with gold and nickel additives results in the sensitivity of sensors to NO_2 at low temperatures of $50 - 150$ °C with response times at the level of 10 s. This behavior of sensors is due to the synergistic effect of additives. Gold, because of their catalytic properties increases the density of the adsorption centers on the surface of SnO_2 for NO_2, on the other hand super-stoichiometric nickel atoms are also the centers of adsorption for oxygen and NO_2.

The sensitivity of sensors to hydrogen appears at a temperature of 250 °C, the maximum response is observed at 500 °C. Hydrogen sensors based on SnO_2 thin films with gold and nickel additives

demonstrate high reproducibility of characteristics due to the ability of Ni additives to prevent the interaction of hydrogen and lattice oxygen atoms in the near-surface area of tin dioxide.

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