

## PROPERTIES OF HYDROGEN SULFIDE SENSORS BASED ON THIN FILMS OF TIN DIOXIDE AND TUNGSTEN TRIOXIDE

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UDC 621.382

*The effect of hydrogen sulfide in the concentration range of 0–100 ppm on the characteristics of thin films of tin dioxide and tungsten trioxide obtained by the methods of magnetron deposition and modified with gold in the bulk and on the surface is studied. The impurities of antimony and nickel have been additionally introduced into the SnO<sub>2</sub> bulk. An optimal operating temperature of sensors 350°C was determined, at which there is a satisfactory correlation between the values of the response to H<sub>2</sub>S and the response time. Degradation of the sensor characteristics is investigated in the long-term (~0.5–1.5 years) tests at operating temperature and periodic exposure to hydrogen sulfide, as well as after conservation of samples in the laboratory air. It is shown that for the fabrication of H<sub>2</sub>S sensors, the most promising are thin nanocrystalline Au/WO<sub>3</sub>:Au films characterized by a linear concentration dependence of the response and high stability of parameters during exploitation.*

Keywords: tin dioxide, tungsten trioxide, catalytic gold, nickel additive, gas sensors, hydrogen sulfide

### INTRODUCTION

Hydrogen sulfide is one of the most toxic gases present in the emissions of a number of industrial enterprises in various industries. Maximum allowable concentration (MAC) of H<sub>2</sub>S in the air of operating zone is  $n = 7.05$  ppm. Therefore, it is necessary to develop miniature high-speed gas analyzers for selective detection of hydrogen sulfide in the air in a concentration range of  $n = 1–100$  ppm. In this regard, of greatest interest are the sensors based on thick and thin films of metal oxide semiconductors with the additions of a number of catalysts, including Pt, Pd, Au, and Ag, and oxides CuO, Ag<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO, and LaO<sub>2</sub> [1–7]. The published data are ambiguous, which is due, first of all, to the processes of rapid degradation of characteristics observed under exposure of films produced using various technological methods to H<sub>2</sub>S. It is shown in [8] that upon exposure for 10 h in the flux of a mixture of 2 ppm H<sub>2</sub>S+air, the most stable parameters are characteristic of thick porous (20 μm) films of WO<sub>3</sub> with the addition of 0.03 wt.% Au (as compared with samples based on SnO<sub>2</sub> and ZnO). However, there are no data on the stability of parameters during long-term (within a month or more) operation of sensors based on both thick and especially thin films of metal oxide semiconductors.

Earlier [9], by magnetron sputtering we obtained thin (~100 nm) films of tin dioxide with an addition of the antimony and gold dopants into the bulk and with the two-layer disperse catalytic layers of platinum and palladium deposited on the surface (Pt/Pd/SnO<sub>2</sub>:Sb,Au) as well as the Au/SnO<sub>2</sub>:Sb, Au films modified with gold. The

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investigations showed that these films are characterized by initially high values of response to hydrogen sulfide. When testing for 20–40 days, first, a sharp and then, a gradual decrease in the response value and time takes place. Therefore, the sensors require long ageing to stabilize their parameters.

In the present work, to ensure the possibility of detecting H<sub>2</sub>S in the range of 1–100 ppm and elimination of the phenomena of degradation, we studied the characteristics of thin nanocrystalline films of tungsten trioxide Au/WO<sub>3</sub>:Au modified with gold in the bulk and on the surface as well as of tin dioxide films Au/SnO<sub>2</sub>:Sb, Au, Ni modified with gold with an addition of nickel in the bulk.

## EXPERIMENTAL

The Au/SnO<sub>2</sub>:Sb, Au, Ni (a series i) and Au/WO<sub>3</sub>:Au (a series ii) films have been obtained by magnetron sputtering. The manufacturing technology of nanocrystalline thin films and sensors based on them is presented in detail in [9–12]. For the introduction of Ni impurity into the bulk of tin dioxide of the series i, in addition to the gold, the pieces of nickel have been deposited on the surface of the Sn+Sb alloy target. The ratio of areas of these metals was  $S_{Au}/S_{Ni} = 1$ . Disperse layers of catalytic gold were deposited on the film surface by magnetron sputtering at a constant current before the thermal annealing, which was carried out in the air at 450°C for 24 h in case of tin dioxide and at 500°C for 5 h in case of tungsten trioxide. The size of one sensor of both series was 0.7×0.7 mm, the area of the sensitive layer was 0.3×0.3 mm<sup>2</sup>, and the number of sensors manufactured in a single technological cycle on a sapphire substrate with the diameter of ~30 mm was about 500 instances.

For the measurements of characteristics, four sensors were simultaneously placed in a quartz chamber with a volume of 1 l. To control the level of humidity, two streams of air with controlled speeds – air dried with zeolite and humidified with a bubbler – were pumped through the camera, and then, the chamber was sealed. A sample of hydrogen sulfide was submitted with a syringe dispenser from the cylinder with the calibration mixture (0.0486% H<sub>2</sub>S and the rest was the air), which created in the chamber the required composition of the gas mixture. The gas mixture in the chamber was continuously mixed with a fan. During the measurements of the dependence of the sensor electric conductivity on the gas concentration in the air, an increase in  $n$  was provided by the addition of certain doses of calibration gas. After the measurements, the chamber was pumped by clean air with a given humidity level. The studies were performed at a relative humidity  $RH = 30\%$ .

Unlike the data of [1–9], thin-film sensors of series i and ii studied in this work are characterized by some spread in the characteristics in the first two days of testing. Visible degradation is absent. After the training of the freshly prepared samples by exposure in the measuring chamber at  $T = 350^\circ\text{C}$  and periodic supply of 50 and 100 ppm of H<sub>2</sub>S, the properties of the sensors have been stabilized, and from the third day, systematic research was carried out. To further increase the reproducibility of parameters, all sensors were heated at  $T = 450^\circ\text{C}$  for 10 s before each measurement.

The resistance (conductivity)  $R_0$  ( $G_0$ ) of films in pure air and these parameters when exposed to gas  $R_1$  ( $G_1$ ) were measured using a specially designed stand [13]. As the adsorption response, the ratio  $S = G_1/G_0$  was taken and as the response time  $t_r$ , the time of establishment of 0.9  $G_{st}$ , where  $G_{st}$  is the stationary value of conductivity, was taken.

## 1. DISCUSSION OF RESULTS

To optimize the operating temperatures of sensors, investigations were performed of the response to 5 ppm of hydrogen sulfide in the range of  $T$  from 230 to 450°C. It is shown that the dependence  $G_1/G_0$  on  $T$  of the samples based on tin dioxide has the form of a curve with a maximum at  $T = 330\text{--}350^\circ\text{C}$  (Fig. 1, curve 1). For the Au/WO<sub>3</sub>:Au films, the response has maximum values at low temperatures  $T = 200\text{--}250^\circ\text{C}$ , then it is decreased, and at  $T = 420\text{--}450^\circ\text{C}$ , the values of  $G_1/G_0$  increase again (Fig. 1, curve 2).

On the basis of the time dependences of the sample resistance after introduction of gas into the measuring chamber (Fig. 2), we evaluated the response time  $t_r$ . The values of  $t_r$  are substantially lower for the samples from series ii. In the region 200–250°C, they reach several minutes and decrease down to 12–15 s with increasing  $T$  up to 350–

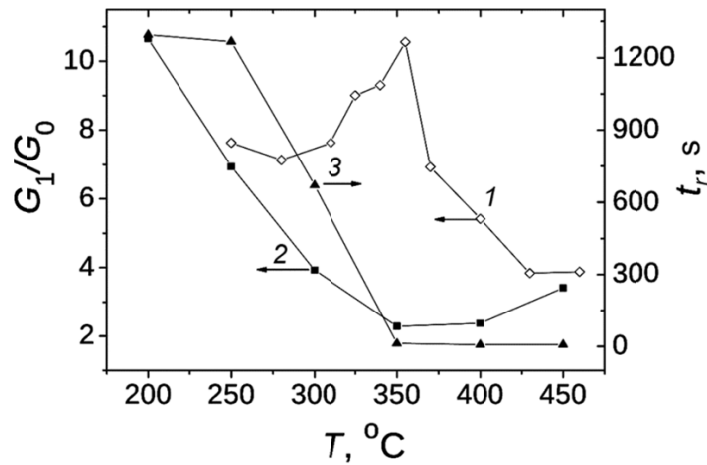


Fig. 1. Dependences of the response to 5 ppm of hydrogen sulfide for sensors based on tin dioxide (1) and tungsten trioxide (2) films and the response time of the samples from series ii (3) on the operating temperature  $T$ .

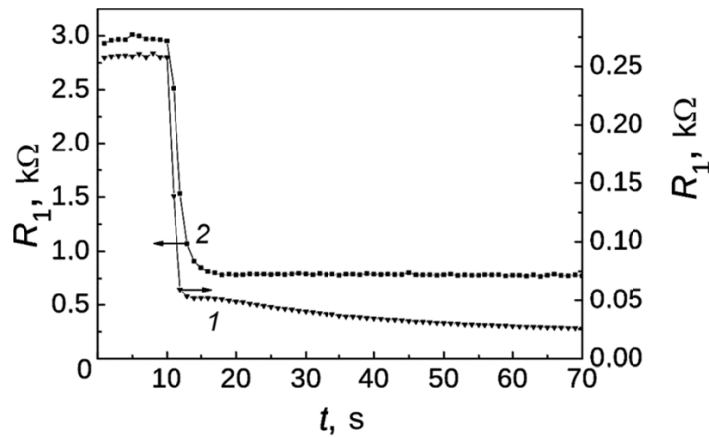


Fig. 2. Time dependences of the sensor resistance of series i (1) and ii (2) after the introduction of a sample of gas in the measuring chamber. The introduction time of the sample corresponds to  $t = 10$  s, the operating temperature of the sensors  $T = 350^\circ\text{C}$ .

450°C (Fig. 1, curve 3). In case of tin dioxide, the values of  $t_r$  are 130–140 s at these high temperatures. An analysis of these data showed that it is advisable to use  $T = 350^\circ\text{C}$  as the operating temperature, since at this temperature, there is an optimal relation between high values of  $G_1/G_0$  and low values of  $t_r$  for all sensors.

The concentration dependences of the Au/SnO<sub>2</sub>:Sb, Au, Ni sensor response are sub-linear in the whole temperature range (Fig. 3, curves 1 and 2) and at hydrogen sulfide concentrations up to 100–200 ppm. To discuss the role of the nickel dopant in the bulk of films, we compare the properties of samples from series i with the data [14], which relate to the sensors based on Au/SnO<sub>2</sub>:Sb, Au films containing no nickel (Fig. 3, curve 3).

Previously [9, 12], we have shown that in the presence of gold in the bulk and on the surface of the tin dioxide films, the probability of dissociative chemisorption of oxygen is lower than that in the presence of oxidation catalysts Pt/Pd. As a result, the density of negative charge and the width of the space charge region are decreased, the samples are characterized by low values of the resistance at room temperature  $R_0 = 0.1\text{--}0.3$  MΩ and response to the reducing gases (CO, H<sub>2</sub>). When exposed to hydrogen sulfide, low values of  $G_1/G_0$  for  $n > 20$  ppm and the saturation at  $n > 50$  ppm are observed (Fig. 3, curve 3). An addition of nickel in the bulk of thin films of tin dioxide increases the

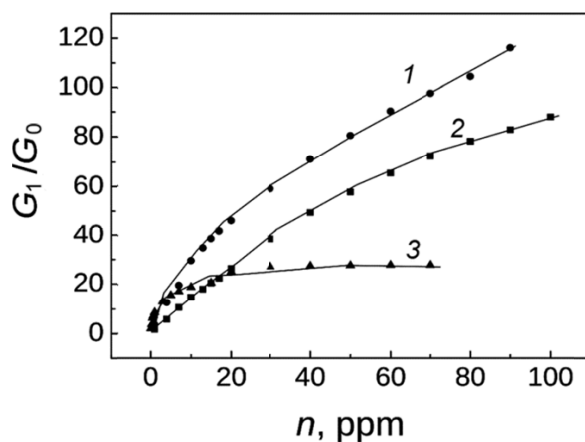


Fig. 3. Concentration dependences of the response to H<sub>2</sub>S of the sensors Au/SnO<sub>2</sub>:Sb, Au, Ni (1, 2) and Au/SnO<sub>2</sub>:Sb, Au (3) at the operating temperatures, °C: 330 (1), 350 (2), and 310 (3).

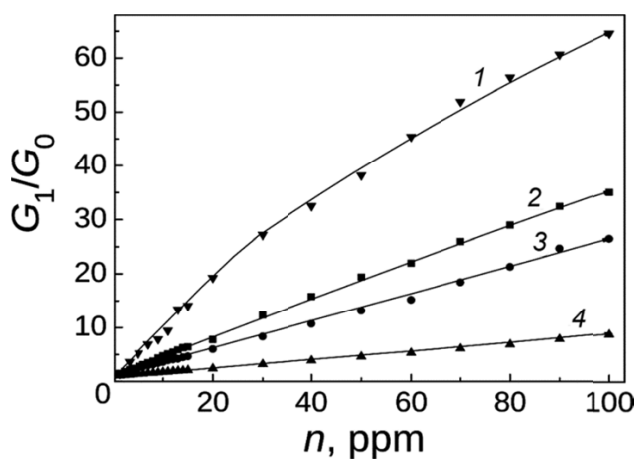


Fig. 4. Concentration dependences of the response to H<sub>2</sub>S of the Au/WO<sub>3</sub>:Au sensors at operating temperatures, °C: 310 (1), 330 (2), 350 (3), and 370 (4).

resistance of samples by 2 orders of magnitude ( $R_0 = 35\text{--}40\text{ M}\Omega$  in case of Au/SnO<sub>2</sub>:Sb, Au, Ni) and the response to H<sub>2</sub>S, as well as it expands the dynamic range of the detection up to  $n > 100\text{ ppm}$  (Fig. 3, curves 1 and 2).

In a number of works [12, 14], a significant increase in the resistance  $R_0$  was observed with the introduction of additives of platinum and palladium in the bulk of thick and thin SnO<sub>2</sub> films. It was established [14] that under the introduction of platinum, in the band-gap of the SnO<sub>2</sub> microcrystals, formation of surface states (SS) takes place, the density of which is uniquely related to the amount of platinum in the form of Pt<sup>2+</sup> associated with the interaction of the dopant with the lattice oxygen and formation of PtO on the grain surface. It can be assumed that during thermal annealing of sputtered thin Au/SnO<sub>2</sub>:Sb, Au, Ni films, when crystallization of tin dioxide occurs, nickel (as well as Pt and Pd) partially segregates on the surface of the microcrystals and forms the bonds with the lattice oxygen (perhaps, NiO). The formed super-stoichiometric tin atoms are the centers of oxygen adsorption. As a result, the density of chemisorbed oxygen is increased. The width of the space charge region and hence, the resistance of the sensors, are also increased. Apparently, the density of centers of the H<sub>2</sub>S adsorption is increased as well.

For the Au/WO<sub>3</sub>:Au films at  $T \leq 310^\circ\text{C}$ , sublinear concentration dependences of the response are observed (Fig. 4, curve 1). There is no saturation in the whole range of concentrations from 1 to 100 ppm, i.e., the density of the

TABLE 1. The Values of the Resistance in Clean Air  $R_0$ , the Response  $S$ , and Time  $t_r$  as a Function of Test Duration  $t$  for the Sensors of Series i and ii at the Operating Temperature 350°C.  $S$  and  $t_r$  are Mainly Measured under the Action of 5 ppm of Hydrogen Sulphide.

Au/SnO <sub>2</sub> :Sb, Au, Ni (i)				Au/WO <sub>3</sub> :Au (ii)			
$t$ , days	$R_0 \cdot 10^{-3}$ , kΩ	$S$	$t_r$ , s	$t$ , days	$R_0 \cdot 10^{-4}$ , kΩ	$S$	$t_r$ , s
3	3.3	12.2	35	3	12.1	2.3	12
36	1.8	12.2	129	4	12.3	2.4	12
50	2.4	11.8	132	9	12.2	2.4	19*
63	0.4	5.7	133*	10	11.7	2.5	18*
359	0.35	3.2	120	15	11.5	1.8	15
364	0.41	3.1	121*	23	16.7	1.8	12
366	0.45	3.9	115*	59	12.7	2.1	10*
392	0.45	4.1	14*	64	11.5	1.9	9*
546	0.23	1.5	12*	148	8.7	1.8	8*
556	0.22	1.5	12*	157	9.2	1.6	3*

\* Measurements are performed at  $n = 1$  ppm.

adsorption centers is sufficient to provide the required dynamic range of the gas concentration measurements. With increasing operating temperature, the values of the response are decreased and the dependences become linear (Fig. 4, curves 2–4). Peculiarities of the sensor characteristics of series ii are most probably due to the fact that the dopant of gold in the bulk of the tungsten trioxide has a significant influence on the phase composition [10, 11]:  $\beta$ -WO<sub>3</sub>, monoclinic phase  $\gamma$ -WO<sub>2.72</sub>, and the Au crystallites with the sizes of 9–15 nm are present in the films. The presence of a non-stoichiometric phase  $\gamma$ -WO<sub>2.72</sub> contributes to the increase in the concentration of oxygen vacancies, which are the donor centers in the tungsten trioxide, and to the decrease in the resistance of the sensor  $R_0$ . The density of super-stoichiometric tungsten that can play the role of adsorption centers for oxygen and H<sub>2</sub>S is increased.

Sublinear concentration dependences of the response under the adsorption of hydrogen sulfide observed in the present work (Figs. 3 and 4, curve 1) indicate the predominant role of a channel component of the conductivity. It can be assumed that the films contain micro-crystals of SnO<sub>2</sub> and WO<sub>3</sub>, which are interconnected between each other by narrow bridges of conductivity of the same substance [15]. The linear curves 2–4 in Fig. 4 serve as a further confirmation of the peculiarities of the reactions taking place at  $T > 330^\circ\text{C}$  on the surface of thin tungsten trioxide films modified with gold.

Stability of the sensor parameters was investigated under periodic measurements of the concentration dependences of the response to H<sub>2</sub>S in the process of continuous operation of sensors in the operating mode ( $T = 350^\circ\text{C}$ ) and after storage of the samples in the laboratory air. The test durations for the sensors of series i and ii were about 560 and 160 days, respectively. The values of  $R_0$ ,  $S = G_1/G_0$ , and the response time  $t_r$  are presented in Table 1 as a function of test duration.

In the process of testing during the first 60–64 days, when the sensors were continuously in the operating mode under the periodic exposure to H<sub>2</sub>S, all parameters did not change significantly. Then, the sensors were removed from the measurement chamber and placed in a Petri dish, where they were stored for ~60–130 days in the laboratory air. The resumption of tests showed that the values of the resistance  $R_0$  in the clean air of the sensors of series i decreased by almost an order of magnitude and the value of  $G_1/G_0$  decreased by almost 2 times. Then,  $R_0$  was not changed during operation and storage of samples for 130–400 days. The value of  $G_1/G_0$  decreased after storage from 140 to 360 days, and the last decrease in  $R_0$  down to 0.21–0.24 MΩ and in the response down to 1.2–1.7 occurred after storage of the samples from 400 to 540 days.

For the sensors of series ii, the values of the response, when exposed to 5 ppm of H<sub>2</sub>S, decreased slightly down to  $S = 1.8$ –1.9 after 14 days of testing and further, they practically did not change. The decrease in  $R_0$  by approximately 25–30% was observed after storage of sensors from 65 to 150 days. The response was also slightly decreased. The concentration dependences of the response remained linear. Overall, it seems that main changes of the sensor's

parameters (especially, of series i) were observed after prolonged storage at room temperature in the laboratory air of samples previously undergone to daily operation for 60 or more days. It is important to note that after the test, the response times are reduced for all samples (Table 1).

It is known [1, 9] that in the presence of hydrogen sulfide in the air, dissociative adsorption of  $\text{H}_2\text{S}$  molecules occurs on the surface of  $\text{SnO}_2$  with the release of two hydrogen atoms that interact with the pre-chemisorbed oxygen with the formation of  $\text{OH}^-$  groups. Sulfur atoms can also be oxidized with the participation of the previously chemisorbed oxygen. Different authors [1, 7–9] write the reactions occurring during the interaction of  $\text{H}_2\text{S}$  with the semiconductor surface in different ways. The numbers of electrons that can return to the conduction band significantly differ from each other: from three [1] to seven [7]. As a result of these reactions, the density of  $\text{O}^-$  ions on the surface is reduced, the width of the SCR decreases, and the film conductivity increases.

Similar reactions also take place on the surface of  $\text{WO}_3$  [2]. According to the data [2], as the basis for an additional mechanism of sensitivity of gas sensors based on  $\text{WO}_3$  to hydrogen sulfide, formation of tungsten sulfide  $\text{WS}_2$  can serve, because it is reported that the conductivity of tungsten trioxide is increased when exposed to  $\text{H}_2\text{S}$  in the absence of oxygen in the atmosphere. In [7], it is also supposed that tin sulfides can be formed in the surface region of  $\text{SnO}_2$  contributing to the irreversible degradation of thick-film sensors during the first two days of testing. Overall, to date in the literature, there is no unanimous point of view on the reactions responsible for the increase in the conductivity of sensors upon exposure to hydrogen sulfide and for the degradation of their characteristics. It is important to note that the processes occurring under adsorption of hydrogen sulfide on the surface of the  $\text{Au/SnO}_2\text{:Sb}$ ,  $\text{Au}$ ,  $\text{Ni}$  and  $\text{Au/WO}_3\text{:Au}$  films heated to  $350^\circ\text{C}$  are completely reversible, as there is a rapid decrease of the sensor resistance after the submission of a gas sample in the chamber (see Fig. 2) and a complete restoration of  $R_1$  after the pumping clean air through the camera.

To clarify the nature of interaction of hydrogen sulfide with the surface of the studied films, a comparison was made of the responses to  $\text{H}_2$  ( $S_{\text{H}_2}$ ) and  $\text{H}_2\text{S}$  ( $S_{\text{H}_2\text{S}}$ ) of sensors aged as a result of long-term tests. The measurements were performed in the gas concentration range from 15 to 100 ppm at the operating temperature of  $350^\circ\text{C}$  (Fig. 5). Evidently, in all cases,  $S_{\text{H}_2} < S_{\text{H}_2\text{S}}$ . For the films of series i, the ratio of responses is  $S_{\text{H}_2\text{S}}/S_{\text{H}_2} \approx 6$  at  $n = 15$  ppm, then, it increases up to  $\sim 7.3$  with increasing  $n$  to 30–40 ppm, and further, it practically does not change up to 100 ppm. For the films of series ii,  $S_{\text{H}_2\text{S}}/S_{\text{H}_2}$  is increased from about 2.5 to 5.7 with increasing  $n$  in the range 15–100 ppm.

It should be taken into account that at  $350^\circ\text{C}$ , on the surface of the studied films containing no catalytic Pt and Pd, the processes of molecular adsorption of  $\text{H}_2$  and dissociation in two atoms are possible. In the first case, one electron is returned in the conduction band and in the second case, two electrons are returned in the conduction band [15]. Apparently, for thin films of series i and ii, under adsorption of  $\text{H}_2\text{S}$ , reactions [7], in which seven electrons can arrive into the conduction band, are preferred. For the samples from series ii, an increase of the response in the region  $390\text{--}450^\circ\text{C}$  (see Fig. 1, curve 2) indicates an additional reaction (possible formation of tungsten sulfide) that takes place on the surface of  $\text{Au/WO}_3\text{:Au}$  under adsorption of  $\text{H}_2\text{S}$  at higher temperatures. It can be assumed that after long-term tests in the operating modes, the anions of sulfur remain in the thin films. These anions form an  $\text{SO}_2$  oxide during storage and are stabilized on the surface reducing the density of the oxygen adsorption centers. As a result, under the resumption of tests after storage of the samples, the measurements indicate a decrease in  $R_0$  and  $S_{\text{H}_2\text{S}}$ . These effects are less pronounced in the samples from series ii.

A decrease in the response time of the sensors (Table 1) after the tests also can be explained by the presence of adsorbed molecules of sulfur dioxide on the grain boundaries, which hamper the diffusion of the hydrogen sulfide molecules in the bulk of the films. Confirmation of this point of view can be the data [8], where after exposure to 2 ppm of  $\text{H}_2\text{S}$  for 10 h followed by ageing in a humid (80%) air for 10 h, in the S 2p spectra, the peaks corresponding to  $\text{SnSO}_3$  and  $\text{ZnSO}_4$  are detected on the surface of porous thick films of tin dioxide and zinc oxide by the method of XPS (x-ray photoelectron spectroscopy). In the spectra of  $\text{WO}_3$  films, similar peaks are absent.

Thus, the use of thin  $\text{Au/SnO}_2\text{:Sb}$ ,  $\text{Au}$ ,  $\text{Ni}$  and  $\text{Au/WO}_3\text{:Au}$  films investigated in the present work made it possible to eliminate the process of fast degradation of characteristics of  $\text{H}_2\text{S}$  sensors in the first days of operation and during the subsequent 60 days. Wide dynamic range (1–100 ppm) of the  $\text{H}_2\text{S}$  concentration measurements in the air is provided. Sensors based on  $\text{Au/WO}_3\text{:Au}$  thin films are characterized by high stability of parameters and after long-term tests, they have a linear concentration dependence of the response at the operating temperature of  $350^\circ\text{C}$  and low

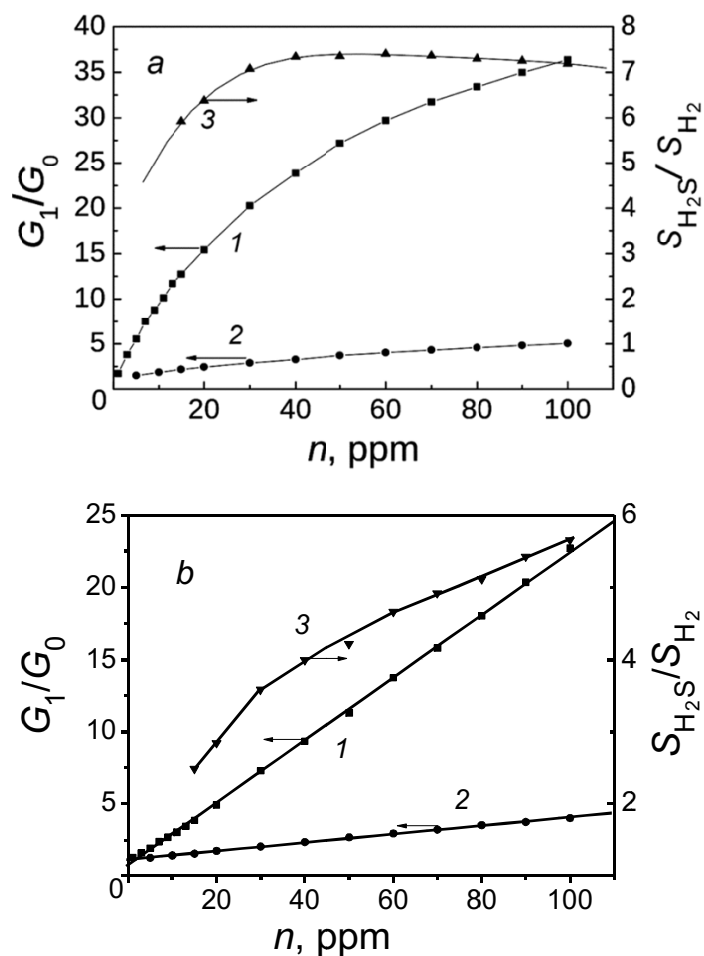


Fig. 5. Dependences of the responses of sensors of series i (a) and ii (b) on the concentrations of hydrogen sulphide (1) and hydrogen (2); curve 3 corresponds to the ratios of these responses  $S_{H_2S}/S_{H_2}$ . The measurements are performed at  $T = 350^\circ\text{C}$ .

response times. The lowest threshold of the confidently detected concentrations is 1 ppm of  $H_2S$  for the response value  $S_{H_2S} = 1.1\text{--}1.15$  and response time  $t_r = 3$  s.

The work was performed as a part of the State Task of the Ministry of Education and Science (the Task No. 2014/223, Project code: 1368) and by the financial support of the Russian Foundation for Basic Research, Grant No. 14-02-31015.

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