

PHYSICS OF SEMICONDUCTORS AND DIELECTRICS

EFFECT OF ADDITIVES OF Pt, Pd, Ag, AND Y IN THIN NANOCRYSTALLINE SnO_2 FILMS ON THE CHARACTERISTICS OF RESISTIVE HYDROGEN SENSORS

E. Yu. Sevast'yanov,¹ N. K. Maksimova,¹ A. I. Potekaev,^{1,2} A. V. Almaev,²
E. V. Chernikov,¹ N. V. Sergeichenko,¹ and S. V. Kim²

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The results of studying electrical and gas sensitive characteristics of H_2 sensors based on thin nanocrystalline SnO_2 films with the Pt, Pd, and Ag dispersed layers deposited on the surface and Ag, Y, and Ag + Y additives in the volume are presented. It is shown that various combinations of catalysts on the surface and in the volume have a significant effect on the microstructure of films and density of oxygen adsorption sites on the surface of tin dioxide. As a result, the resistance values of sensors in clean air R_0 , activation energies of the temperature dependences of R_0 , responses to hydrogen in the concentration range of 50–2000 ppm are different. Studies performed by the method of UV-visible spectroscopy revealed in the absorption spectra of films with a silver addition in the volume a band of surface plasmon resonance of silver indicating that the additive is present in the form of metallic Ag nanoparticles. Particular attention was paid to the influence of long-term tests on the properties of sensors with the listed additives. It was established that the joint introduction of Ag+Y into the volume of films prevents the increase of the resistance and responses during prolonged exposure to hydrogen, which is observed during the operation of all other samples studied. Possible mechanisms for changing the sensors' properties during testing and the role of additives in their stabilization are considered.

Keywords: sensors, tin dioxide, additives, platinum, palladium, silver, yttrium, hydrogen, long-term tests, stability.

INTRODUCTION

The development of hydrogen power engineering and a number of other applied areas (monitoring of H_2 concentration in the premises of nuclear power plants, control of the H_2 leakages in the storage batteries of submarines and train cars) requires creating high-speed, highly sensitive, and selective hydrogen sensors with low energy consumption. To solve this problem, it is advisable to use sensing elements based on metal oxide semiconductors, whose properties can be controlled by introducing into the volume and depositing on the surface catalytic additives.

The most commonly used are noble metals: Pt, Pd, and Au. It was previously established [1–4] that the peculiarity of the sensors based on the Pt/ Pd/ SnO_2 :Sb and Au/ SnO_2 :Sb, Au films is the instability of their parameters during prolonged exposure to hydrogen: during the tests, the film resistance and response values to H_2 increase. These effects are due to the fact that atomic hydrogen released during dissociative adsorption of H_2 is able to interact with

¹V. D. Kuznetsov Siberian Physical-Technical Institute at Tomsk State University, Tomsk, Russia, e-mail: sese@ngs.ru; nkmax3@yandex.ru; kanc@spti.tsu.ru; ewch192184@gmail.com; Edelveisu@yandex.ru; ²National Research Tomsk State University, Tomsk, Russia, e-mail: almaev_alex@mail.ru; thestimas@mail.ru. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 5, pp. 155–163, May, 2018. Original article submitted March 14, 2018.

lattice oxygen and partially reduce the molecules of tin dioxide on the surface. There is an increase in the density of superstoichiometric tin atoms, which are the centers of oxygen adsorption. To stabilize the characteristics of the sensors, training for 30 or more days is required.

The effect of additions of 3d-transition metals Co and Ni, introduced into the volume of gold-modified SnO₂ films, on the electrophysical and gas sensitive properties, as well as on the stability of the parameters of hydrogen sensors, was investigated in [5]. For the freshly prepared Au/SnO₂:Sb, Au, Ni, and Au/SnO₂:Sb, Au, and Co samples, the resistance of the films and the response to H₂ increase compared to Au/SnO₂:Sb, Au films, since the additives contribute to an increase in the density of chemisorbed oxygen N_i and the band bending on the grain boundaries of tin dioxide in the process of the sensors manufacturing. It is shown that there is a slight additional increase in $e\varphi_s$ during the tests. It can be assumed that under the crystallization of deposited films during the thermal annealing, the 3d-metal atoms in the SnO₂ volume partially segregate on the surface of the microcrystals and form bonds with lattice oxygen, superstoichiometric tin atoms are formed, and the density N_i increases. During long-term tests, atomic hydrogen is oxidized predominantly by chemisorbed oxygen and the stability of the sensors' characteristics increases. However, complete stabilization of the response of the films, especially in the region of high concentrations (>100 ppm) of hydrogen, was not achieved.

It is of interest to study the effect of rare earth additives on the characteristics of chemical sensors. The published information on the properties of such structures is limited and usually refers to samples obtained by the methods of thick-film technology [6–9]. Data for thin films with additives of rare-earth elements fabricated by magnetron sputtering methods are not available in the literature known to us. Preliminary studies have shown that to stabilize the characteristics of thin-film hydrogen sensors, it is expedient to use films of tin dioxide with the joint addition of yttrium and silver into the volume. The catalytic properties of silver are known [10–14], but questions about the mechanisms of influence of Ag on the properties of gas sensors remain controversial.

This paper presents the results of a study of the microstructure, electrical and gas sensitivity characteristics of H₂ sensors based on thin nanocrystalline SnO₂ films with the disperse Pt, Pd, Ag layers deposited on the surface and Ag, Y, and Ag + Y additives introduced into the volume. The influence of long-term tests on the properties of sensors with various additives was studied. To clarify the phase state of silver (Ag, AgO, or Ag₂O) in tin dioxide, specially prepared SnO₂:Sb, Ag films were investigated by the UV-visible spectroscopy method.

EXPERIMENTAL TECHNIQUE

We studied sensors based on thin (about 100 nm) films 0.7×0.7 mm in size with the sensitive layer area of 0.3×0.3 mm². The features of the technology for making samples using magnetron sputtering of a Sn + Sb alloy target with pieces of metallic additives placed on the surface are similar to those described in [3-5]. The ratio of the areas of the metal pieces S_m and the sputtered part of the target S_{Sn} was $S_Y/S_{Sn} = S_{Ag}/S_{Sn} = 3 \cdot 10^{-3}$ for the samples under study. A film with two additives Ag + Y was obtained on one substrate in one technological cycle. Then, the plate was cut into two parts, and the dispersed layers of the Pt/Pd and Ag catalysts were deposited on the surface of each of them using the same method of magnetron sputtering at a constant current.

We introduce the following series numbering and notations for the films obtained with different surface catalysts and additives in the volume: 1) Pt/Pd/SnO₂:Sb, Ag; 2) Pt/Pd/SnO₂:Sb, Y; 3) Pt/Pd/SnO₂:Sb, Ag, Y; 4) Ag/SnO₂:Sb, Ag, Y. The experimental results are compared with the previously published data [2, 3] for the Pt/Pd/SnO₂:Sb films without volume additives, which are designated by series 5.

To study the thickness, microrelief, and grain size of thin films, the atomic force microscopy (AFM) method was used. Measurement of the absorption spectra by UV-visible spectroscopy using a CM2203 spectrophotometer was carried out on the SnO₂:Sb and SnO₂:Sb films with an area of 10×10 mm².

The resistance (conductivity) of sensors in clean air $R_0(G_0)$ and under the action of hydrogen $R_1(G_1)$ were studied as a function of the operating temperature T and concentration n of the gas in air. For the adsorption response, the ratio G_1/G_0 and for the response time t_r , the time of establishment of 0.9 G_{11} , where G_{11} is the stationary value of the conductivity, were taken, respectively. For the measurement of the characteristics, four sensors were simultaneously placed in a 1-liter quartz chamber. The experimental procedure did not differ from that described in [2, 3].

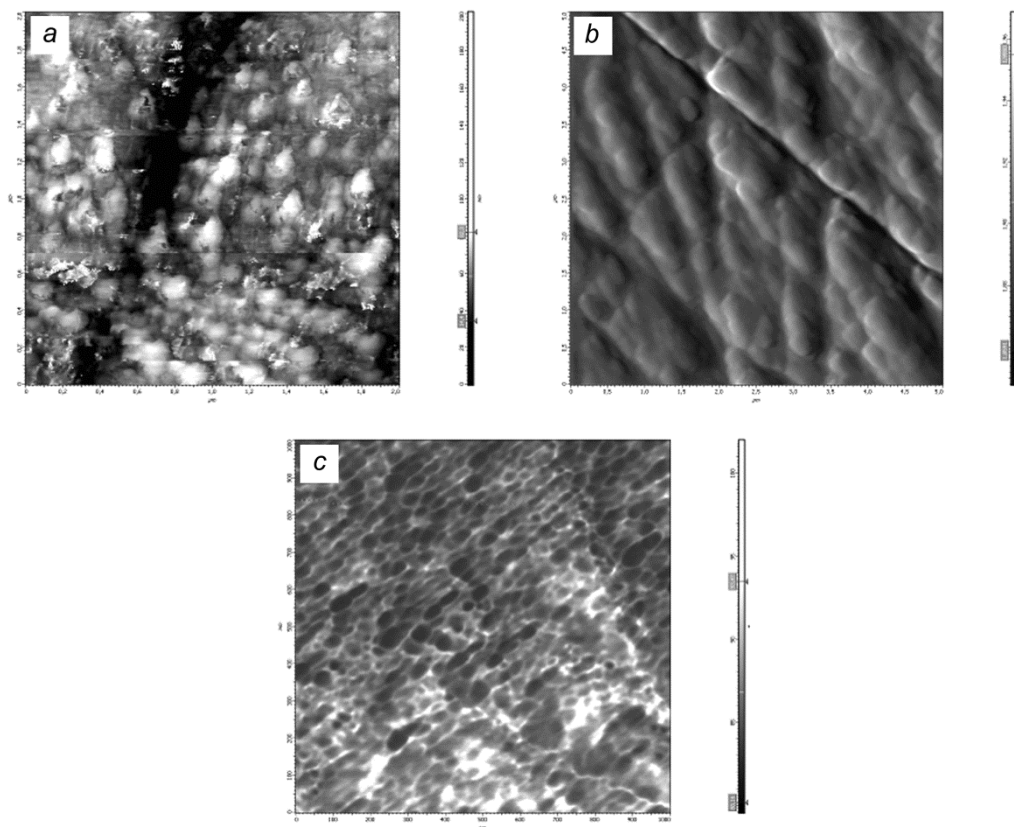


Fig. 1. Two-dimensional AFM images of the surface of tin dioxide films from series: 1 (a), 2 (b), and 3, 4 (c).

The measurements were carried out using a universal automated stand that made it possible to easily adjust and stabilize the operating temperature of sensors and measure the relative humidity in the chamber. The stand was controlled using a personal computer. The stand made it possible to measure the conductivity of the sensing element every 10 ms with an error of not more than 1%.

To study the stability of the parameters during long-term operation of the sensors under the action of hydrogen, the concentration dependences of the response were measured every 2–4 or more (up to 30–60) days in the concentration range 50–2000 ppm of H_2 . In the present work, experimental data obtained at an average relative humidity $RH = 30\text{--}35\%$ are presented.

EXPERIMENTAL RESULTS

According to the AFM data, the thicknesses of films from series 1 and 2 were about 140 nm. For the films of series 1 with the addition of Ag, the presence of microcrystals with the sizes of 30–60 nm is characteristic, in films with the addition of Y, larger crystallites of 200–350 nm in size are observed (Fig. 1, Table 1). In [6, 7], the introduction of rare-earth elements Ce, La, and Y or their oxides into the tin dioxide during the synthesis of films was used to control the crystallite size in the thermal annealing process in the temperature range 550–1100°C: in an amount of 5 at.%, the additives segregate on the surface of microcrystals and provide small (5–12 nm) grain sizes.

Apparently, in case of thin films obtained by magnetron sputtering and annealed at 730 K for 24 hours, the introduction of yttrium does not prevent the formation of large crystallites. The layers from series 3 and 4 with a thickness of 110 nm contain nanocrystallites of $d_1 \approx 8\text{--}30$ nm in size, some of the crystallites form agglomerates with

TABLE 1. Typical Dimensions of Grains d_1 and Agglomerates d_2 , the Values of the Resistance in Clean Air R_0 of Freshly Prepared Films Measured at 300 K, and the Activation Energies ΔE_1 and ΔE_2 of the Temperature Dependences of R_0

Series number and composition	1 Pt/Pd/SnO ₂ : Sb, Ag	2 Pt/Pd/SnO ₂ : Sb, Y	3 Pt/Pd/SnO ₂ : Sb, Ag, Y	4 Ag/SnO ₂ : Sb, Ag, Y	5 Pt/Pd/SnO ₂ : Sb
d_1 , nm	30–60	–	18–30	18–30	18–20
d_2 , nm	–	200–350	120–200	120–200	70–100
R_0 , M Ω	2.5–3.7	5–15	26–30	0.23–0.4	1.5–5
ΔE_1 , eV	0.31	0.34	0.30	0.10	0.11
ΔE_2 , eV	0.45	0.62	0.69	0.49	0.77

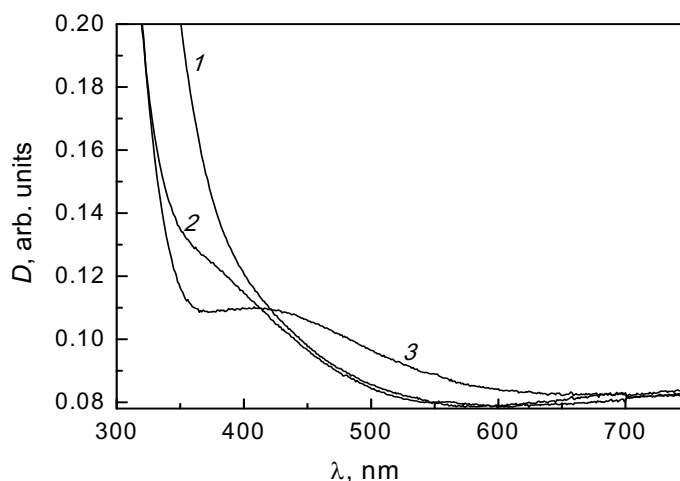


Fig. 2. Absorption spectra of the SnO₂:Sb (1) and SnO₂:Sb, Ag (2) thin films before thermal annealing and of a SnO₂:Sb, Ag sample after heat treatment at 720 K for 24 hours (3).

the sizes d_2 from 120 to 200 nm, i.e. the microstructure of these films is slightly different from that of films from series 5 with the thickness of 105 nm without additives (Table 1).

Figure 2 shows the absorption spectra in the spectral range 220–750 nm recorded with a step of 1 nm from plates placed in the holder for solid samples. The zero line corresponds to the sapphire substrate. Absorption spectra of non-heat-treated structures (Fig. 2, curves 1, 2) are characteristic for amorphous films. The surface plasmon resonance (SPR) band is weakly expressed and has a maximum at 375 nm. Apparently, silver is present in an ionic form of Ag⁺ corresponding to the Ag₂O oxide. In the process of thermal annealing, a polycrystalline tin dioxide film is formed, in the absorption spectrum of which, SPR of silver is clearly manifested at a maximum at 412 nm (Fig. 2, curve 3). The SPR band is broadened and “blurred”, indicating the presence of polydisperse metal Ag⁰ nanoparticles up to 10 nm in size and larger, which apparently segregate on the surface of tin dioxide microcrystals 30–60 nm in size and prevent the formation of large agglomerates commonly present in Pt/Pd/SnO₂:Sb samples (Table 1). It should be noted that the authors of [12] reported about the metallic state of silver based on the observation of the SPR band in the absorption spectra of thin (30–40 nm) films obtained by magnetron sputtering in an argon plasma of a target of Sn coated with Ag pieces followed by oxidation in O₂ at 450–800°C for 10–30 minutes.

Let us further consider the electrical and gas sensitive properties of freshly prepared films with various additives that have not been subjected to long-term tests under the action of hydrogen. The values of R_0 of the samples from series 1 with the addition of Ag practically did not change, the resistance of the sensors increased somewhat after

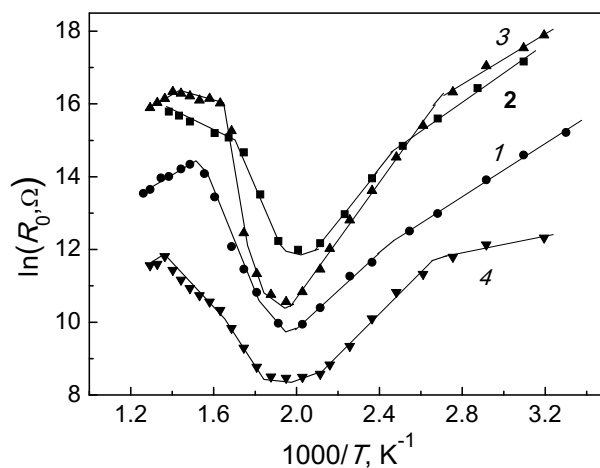


Fig. 3. Temperature dependences of the resistance R_0 in the coordinates $\ln R_0$, $1000/T$ for films from series: 1) Pt/Pd/SnO₂:Sb, Ag (1), 2) Pt/Pd/SnO₂:Sb, Y (2), 3) Pt/Pd/SnO₂:Sb, Ag, Y (3), and 4) Ag/SnO₂:Sb, Ag, Y (4).

the introduction of yttrium (series 2). After joint introduction of Y and Ag into the volume, the resistance in the clean air of the sensors from series 3 increased by almost an order of magnitude (up to 26–30 MΩ) in comparison with the samples from series 5 without additives (Table 1). The increase in the resistance of the sensors indicates an increase in the density of chemisorbed oxygen on the surface of tin dioxide and the width of space charge region (SCR). Interestingly, when a dispersed Ag layer was deposited on the surface of a film with Y and Ag additives instead of Pt/Pd catalysts, R_0 of sensors from series 4 decreased by two orders of magnitude compared to series 3, i.e. there is a decrease in the density of oxygen adsorption centers.

The studied sensors are characterized by the temperature dependences of the resistance R_0 of an N-shaped type, typical for thin films of tin dioxide [2, 3] (Fig. 3). When heated from room temperature up to 470–500 K, the resistance decreases mainly due to the ionization of shallow and deep centers in the volume of the films, the dependences of $\ln R_0$ on $1000/T$ can be approximated by Arrhenius curves, in which, two linear regions with activation energies ΔE_1 and ΔE_2 are observed. The values of these energies are the higher, the larger R_0 and the SCR width (Table 1).

The region of the resistance increase at $T > 470$ –500 K is due to an increase in the negative surface charge due to the desorption of OH groups from the surface and transfer of chemisorbed oxygen from the molecular form O_2^- to the atomic form O^- . As a result, the SCR width increases and, accordingly, the resistance of the film increases. The effects of changing the surface charge stop at high temperatures (≥ 700 K) and then, R_0 again decreases.

The type of additives in the volume and on the surface of thin films of tin dioxide has a significant effect on the gas sensitive properties of sensors. The dependences of the adsorption response on the operating temperature for all the studied tin dioxide films have the form of curves with a maximum at a temperature T_{\max} . The values of T_{\max} are on the average 670–700 K in case of sensors from series 2, 3, and 5 (Table 2, before the tests). The addition of Ag into the volume of tin dioxide (series 1) reduces T_{\max} to 570–600 K, but the deposition of this catalyst on the surface of the film in the Ag/SnO₂: Sb, Ag, Y samples (series 4) leads to an increase in T_{\max} to 730–750 K. Further measurements of R_0 and G_1/G_0 were performed at 670 K, since this operating temperature provides sufficiently high response values for all types of sensors and a low response time: t_r did not exceed 10–15 s.

Figure 4 shows the comparison of the dependences of the response on the concentration of hydrogen. Table 2 shows the values of G_1/G_0 at fixed concentrations of H₂ of 100 and 1000 ppm. The introduction of silver into the volume of films of series 1, and especially joint introduction of silver and yttrium (series 3), leads to an increase in the resistance R_0 measured at 600 K and the response to hydrogen in comparison with the samples from series 5 (Table 2). The concentration dependences of the response of these sensors (Fig. 4, curves 1) are characterized by the presence of

TABLE 2. Main Parameters of Sensors from Various Series Before and After the Completion of Tests with the Duration of t Days.

Series number	1	2	3	4	5
Before the tests					
T_{\max} , K	570–600	690–730	670–690	730–750	670–690
R_0 , M Ω	1.5–2.5	3.5–4.5	5.9–6.5	0.08–0.09	0.5–0.7
G_1/G_0 (100 ppm)	19–30	18–20	30–35	5–7	16–18
G_1/G_0 (1000 ppm)	290–330	42–45	580–590	12–14	170–180
After the tests					
t , days	67	50	70	70	600
T_{\max} , K	640–650	690–730	670–690	730–750	670–690
R_0 , M Ω	9.1–10	3.5–4.5	6.2–7.1	0.07–0.09	1.5–3.5
G_1/G_0 (100 ppm)	130–139	18–20	30–35	5–7	14–16
G_1/G_0 (1000 ppm)	2480–2490	100–110	590–597	18–20	840–860

Notation. The values of R_0 in clean air and the response G_1/G_0 are measured at an operating temperature of 670 K at hydrogen concentrations $n = 100$ and 1000 ppm.

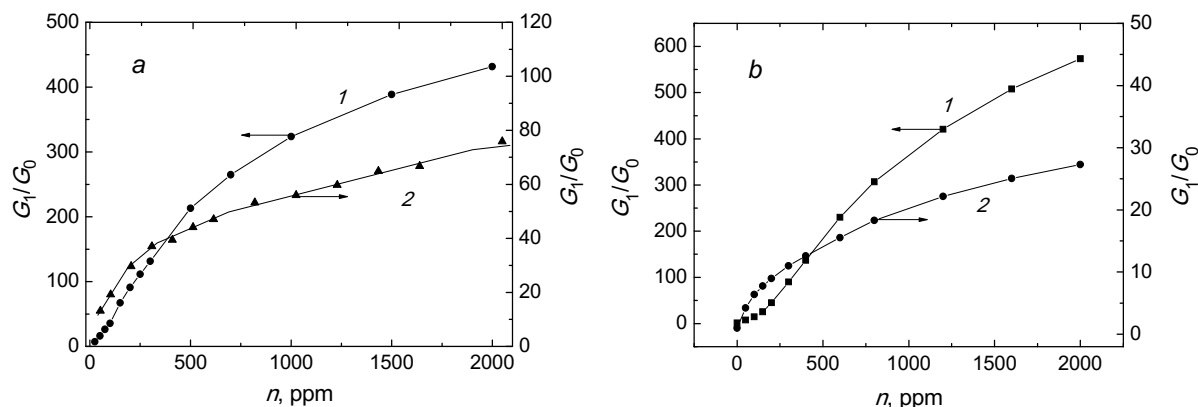


Fig. 4. Concentration dependences of the response measured at an operating temperature of 670 K before testing the sensors from different series: series 1, curve 1 and series 2, curve 2 (a), series 3, curve 1 and series 4, curve 2 (b).

a superlinear region in the range of low H_2 concentrations. Similar dependences were observed for the sensors from series 5 without additives [2, 3].

In case of introduction of an yttrium additive, the resistance R_0 of the films from series 2, measured at 670 K, increased (Table 2) with the concentration dependence G_1/G_0 being sublinear (Fig. 4a, curve 2) and the response to high hydrogen concentrations is lower compared to series 5. The properties of films with the Ag+Y additives significantly change, when a dispersed silver layer is deposited on their surface instead of the most active oxidation catalysts Pt/Pd (series 4): the values of R_0 and G_1/G_0 decrease (Table 2) and a sublinear concentration dependence of the response is observed (Fig. 4b, curve 2).

Of particular interest are the results of a study of the effect of additives in the volume and on the surface of tin dioxide on the change in the characteristics of sensors during long-term tests with the periodic exposure to hydrogen. The main parameters of the samples after the tests are given in Table 2. The dependences of the response to 1000 ppm H_2 on the duration of operation are shown in Fig. 5. Obviously, in case of films from series 1 with the silver addition in the volume, the increase in the resistance in clean air and the response to both low (100 ppm) and high (1000 ppm)

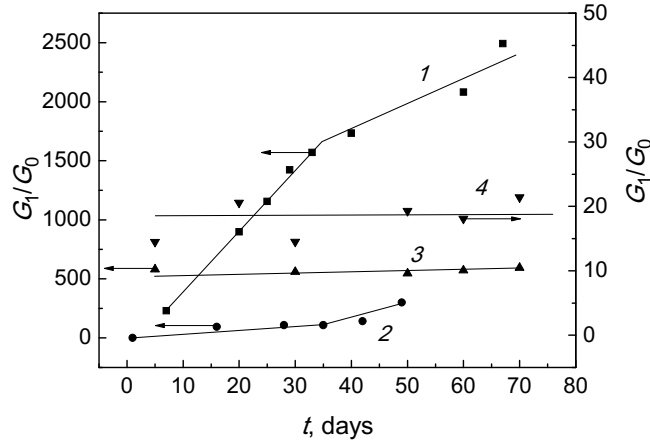


Fig. 5. Dependences of the response values to 1000 ppm of H₂ measured at 670 K on the test duration for sensors from different series: 1 – curve 1, 2 – curve 2, 3 – curve 3, and 4 – curve 4.

hydrogen concentrations is more sharp than for the samples from series 5. T_{\max} shifts to higher temperatures. In case of the addition of yttrium, the resistance R_0 and the response to 50–100 ppm of H₂ of films from series 2 are independent of the duration of tests, but in the region of high concentrations (1000 ppm) of hydrogen, the response values after the tests increased by 2–2.5 times (Fig. 5, curve 2, Table 2). Joint introduction of Ag+Y into the volume of films results in a significant stabilization of the sensor parameters over a wide range of hydrogen concentrations of 50–2000 ppm, this effect being independent of the type of deposited catalysts for the samples from series 3 and 4 (Fig. 5, curves 3 and 4, Table 2).

DISCUSSION OF EXPERIMENTAL RESULTS

Electrical and gas sensitive properties of thin films of metal oxide semiconductors are determined, on the one hand, by the adsorption processes and surface reactions, and on the other hand, an important role is played by the nanocrystalline structure and the ratio between the doubled width of the space-charge region $2d_0$ and the thickness of the film (or the conductivity bridges d_B) [3, 15]. In real polycrystalline samples, as a rule, different types of intergrain contacts are simultaneously present: a part of the crystallites are separated from each other by two space charge regions with a potential barrier between them, the other microcrystals are connected by narrow channels (bridges) of conductivity consisting of the same substance.

Depending on the density of negative charge on the semiconductor surface caused by the chemisorbed oxygen, bridges of open type in case of $2d_0 \leq d_B$ or bridges of closed type at $2d_0 = d_{br}$ can be realized. In general, the conductivity G_0 in clean air of a resistive sensor can be represented as a sum of the over-barrier G_{0b} and channel G_{0ch} components:

$$G_0 = G_{0b} + G_{0ch}. \quad (1)$$

According to the physical models of thin-film sensors developed and presented in [3, 15], the energy band bending in SCR is determined by the charge density of the oxygen ions eN_i and the donor impurity concentration N_d :

$$e\varphi_S = \frac{(eN_i)^2}{2\varepsilon_r\varepsilon_0N_d} + kT, \quad (2)$$

and the SCR width can be written in a form

$$d_0 = \sqrt{2\varepsilon_r\varepsilon_0(e\varphi_S - kT)/e^2N_d}, \quad (3)$$

where ε_r is the relative permittivity of SnO₂, ε_0 is the electrical constant, e is the electron charge, k is the Boltzmann constant, and T is the absolute temperature of the sensor.

In the air, there are usually water vapors that actively adsorb on the surface of the semiconductor. At operating temperatures, two hydroxyl groups form on the surface of SnO₂ under adsorption of an H₂O molecule and the negative charge of the O⁻ ion disappears. As a result of the interaction of protons with lattice oxygen atoms, oxygen vacancies can arise, which diffuse into the depths of the SnO₂ grains and play there the role of donors due to the ionization of which, electrons with a concentration n_v appear.

If the over-barrier conductivity component is the predominant one, the expression for the response at absolute humidity A can be written as follows:

$$G_{1b}/G_{0b} = \exp\left[\frac{e\varphi_S(A)}{kT} \frac{\eta n}{(1+\eta n)} \left(2 - \frac{\eta n}{(1+\eta n)}\right)\right], \quad (4)$$

Where the parameter $\eta = (\alpha/v)\exp(\Delta E/kT)$ is determined by the heat of adsorption $\Delta E = E_d - E_a$, E_d and E_a are the activation energies of desorption and adsorption of gas atoms, respectively, and α/v is proportional to the ratio of the probabilities of adsorption and desorption of gas molecules. In the region of low gas concentrations at $\eta n \ll 1$, a superlinear dependence of G_{1b}/G_{0b} on n is observed, while at $\eta n > 1$, this dependence is sublinear.

Analysis of the experimental data shows that the concentration dependences of sensors from series 1 and 3 (Fig. 4, curves 1) correspond to Eq. (4), i.e., in case of films containing microcrystals 18–30 and 30–60 nm in size with Pt/Pd dispersed catalysts deposited on the surface, the over-barrier component of conductivity plays a decisive role. Similar results were obtained for the samples from series 5 [1–3].

In case of the predominant role of the channel component of conductivity, the expression for the response can be written in the form

$$G_{1ch}/G_{0ch} = \left[1 - \frac{2d_0(A)}{d_B(1+\eta n)}\right] / \left[1 - \frac{2d_0(A)}{d_B}\right]. \quad (5)$$

According to Eq. (5), the dependence G_{1ch}/G_{0ch} on n is sublinear and the increase of the response with increasing hydrogen concentration is much weaker than for G_{1b}/G_{0b} . Such a character of the concentration dependences is observed for the sensors from series 2 and 4 (Fig. 4, curves 2). The predominant role of the channel component of conductivity in the films with an yttrium additive is due to the fact that in the presence of microcrystals with the dimensions of 200–350 nm, the condition $2d_0 < d_B$, corresponding to the open conductivity bridges, is realized. The fulfillment of this condition in case of sensors from series 4 can be explained on the assumption that in the dispersed layers deposited on the surface, silver is in the metallic state at 720 K [10] and during the annealing for 24 hours, it partially diffuses into the volume of tin dioxide. There is a sharp decrease in the density of the oxygen adsorption centers and the SCR width, as evidenced by lower values of R_0 and G_1/G_0 compared to the films of series 3 with the deposited Pt/Pd layers, which are particularly active in the oxidation of hydrogen.

Let us consider the possible mechanisms of the influence of the Ag and Y additives in the volume of SnO₂ on the change and stabilization of properties of the sensors studied under the long-term tests. The parameters of sensors with the addition of silver change most significantly in the process of long tests with periodic exposure to hydrogen. After operation for 60–70 days, the values of R_0 and G_1/G_0 increased practically by an order of magnitude (Table 2, Fig. 5, curve 1). It is important that, in contrast to the samples from series 5, for which the responses at low (50–

100 ppm) hydrogen concentrations practically do not change, the addition of silver leads to a sharp increase in G_1/G_0 over the entire range of $n = 100$ – 2000 ppm.

These facts allow to suggest that Ag in the volume contributes to a more intensive process of partial reduction of tin dioxide when exposed to H_2 , than in the samples from series 3–5. To explain the role of Ag, one can draw on the data of X-ray photoemission spectroscopy given in [14] about a 0.5–0.7 eV decrease in the binding energy of Sn3d and O1s in $SnO_2:Ag$ films compared to clean SnO_2 , which can facilitate the interaction of atomic hydrogen with lattice oxygen.

The addition of yttrium helps to increase the resistance of films. In [9], the acetone sensors based on hollow nanoscale tapes of tin dioxide with the addition of 0.2 to 0.7 wt.% of yttrium were studied by the method of electrospinning. After annealing in the air for 2 hours at $600^\circ C$, mesoporous polycrystalline samples with a rutile structure were formed. Using the photoelectron spectroscopy method, it was established that the Y-O bond length in SnO_2 does not correspond to the Y_2O_3 oxide, that is, yttrium oxide is absent and the Y^{3+} ions are embedded in the SnO_2 lattice. According to the reference data [16], the breaking energy of the Y-O bond $\Delta H_{298}^0 = 171$ kcal/mol is greater than that of Sn-O bond equal to $\Delta H_{298}^0 = 127$ kcal/mol. It can be assumed that in thin films during heat treatment, yttrium segregates on the surface of microcrystals and forms strong bonds with lattice oxygen, the density of superstoichiometric tin atoms and, consequently, of oxygen adsorption centers increases. Therefore, under long-term tests, the resistance and the response to low hydrogen concentrations do not change. However, the action of yttrium is not sufficient to prevent an increase in the response at high $n > 300$ ppm of H_2 .

For the films studied in this paper, the simultaneous introduction of yttrium and silver into the volume promotes the formation of fine-crystalline films (Table 1) and stabilization of R_0 and G_1/G_0 during long-term tests (Table 2). When the binding energy of Sn-O is reduced in the presence of nanodispersed particles of metallic Ag, the Y^{3+} cations penetrate (diffuse) from the surface into the volume and are distributed in the near-surface layers of SnO_2 crystallites, thereby preventing further reduction of tin cations. As a result, the resulting “barrier layer” of the Sn-Y-O composition provides a reaction between hydrogen and chemisorbed oxygen only on the SnO_2 surface.

CONCLUSIONS

Complex investigations of the microstructure, electrical and gas sensitive characteristics of H_2 sensors based on thin polycrystalline SnO_2 films obtained with the magnetron sputtering method with the dispersed layers of Pt, Pd, and Ag deposited on the surface and Ag, Y, and Ag + Y additives in the volume were performed. It is shown that various combinations of catalysts on the surface and in the volume of the films have a significant effect on the dimensions of the tin-dioxide nanocrystallites, the resistance of sensors in clean air, the activation energy of the temperature dependence of R_0 , and the responses to hydrogen in the concentration range of 50–2000 ppm. Particular attention was paid to the influence of long-term tests on the properties of sensors with the listed additives. Possible mechanisms for changing the properties of sensors during testing and the role of additives in their stabilization are considered.

In the Pt/Pd/ $SnO_2:Sb$, Ag films, there are polydisperse metallic Ag nanoparticles up to 10 nm in size and larger that segregate on the surface of microcrystals of tin dioxide 30–60 nm in size and do not significantly affect the characteristics of freshly prepared sensors. At the same time, in the process of testing, an increase in the resistance and response over the entire studied range of 50–2000 ppm of hydrogen concentrations is more significant than in case of Pt/Pd/ $SnO_2:Sb$. The nanoparticles of Ag (possibly due to the decrease in the binding energy of Sn3d and O1s) promote active interaction of H_2 with lattice oxygen and the formation of additional superstoichiometric tin atoms on the surface, which are the centers of oxygen adsorption.

The Pt/Pd/ $SnO_2:Sb$, Y films contain large crystallites 200–350 nm in size. During the thermal annealing of the deposited films, Y^{3+} ions form bonds with lattice oxygen stronger than those formed by Sn^{4+} ions. As a result, the density of the adsorption centers of chemisorbed oxygen increases, the resistance and the response of the sensors increase, and partial stabilization of the parameters occurs: during the tests, R_0 and G_1/G_0 do not change at low H_2 concentrations, the responses increase insignificantly only at $n > 300$ ppm.

Of greatest interest are the characteristics of sensors based on Pt/Pd/ $SnO_2:Sb$, Y, Ag films, into whose volume, both yttrium and silver additives are introduced. In this case, the films contain small crystallites 18–33 nm in size,

partially combined into agglomerates 120–200 nm in size. They are characterized by the increased resistances $R_0 = 26\text{--}30\text{ M}\Omega$, ultrahigh response values and stabilization of R_0 and G_1/G_0 at 50–2000 ppm H_2 during long-term tests. It can be assumed that there is a synergetic effect: in the presence of silver nanoparticles, Y^{3+} ions actively form strong bonds with lattice oxygen and the resulting Sn-Y-O “barrier layer” provides the reaction between hydrogen and chemisorbed oxygen only on the SnO_2 surface.

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