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PROPERTIES OF RESISTIVE HYDROGEN SENSORS AS A FUNCTION OF ADDITIVES OF 3*D*-METALS INTRODUCED IN THE VOLUME OF THIN NANOCRYSTALLINE SnO_2 FILMS

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Analysis of the results of studying electrical and gas sensitive characteristics of the molecular hydrogen sensors based on thin nanocrystalline SnO_2 *films coated with dispersed* Au *layers and containing* Au+Ni *and* Au+Co *impurities in the bulk showed that the characteristics of these sensors are more stable under the prolonged exposure to hydrogen in comparison with* Au/SnO_2:Sb, Au *films modified only with gold. It has been found that introduction of the nickel and cobalt additives increases the band bending at the grain boundaries of tin dioxide already in freshly prepared samples, which indicates an increase in the density* N_i *of the chemisorbed oxygen. It is important that during testing, the band bending* $e\varphi_s$ *at the grain boundaries of tin dioxide additionally slightly increases. It can be assumed that during crystallization of films under thermal annealing, the 3d-metal atoms in the* SnO_2 *volume partially segregate on the surface of microcrystals and form bonds with lattice oxygen, the superstoichiometric tin atoms are formed, and the density* N_i *increases. If the bonds of oxygen with nickel and cobalt are stronger than those with tin, then, under the prolonged tests, atomic hydrogen will be oxidized not by lattice oxygen, but mainly by the chemisorbed one. In this case, stability of the sensors' characteristics increases.*

Keywords: sensors, tin dioxide, additives, hydrogen, thermo-cyclic mode, stability.

INTRODUCTION

Creation of highly sensitive and high-speed molecular hydrogen sensors is an important problem in the development of hydrogen power engineering. To solve this problem, semiconductor resistive sensors based on metal oxide semiconductors with various catalytic additives in the bulk and on the surface can be used. Most often, noble metals Pt, Pd, and Au are applied. It was established [1–3] that the maximum possible response values to the influence of hydrogen are observed for thin nanocrystalline films of tin dioxide doped with antimony impurity with dispersed layers of palladium and platinum deposited on the surface. In case of the gold-modified films, the responses to molecular hydrogen are much lower. We note that the peculiarity of sensors based on $Pt/Pd/SnO_2$:Sb and Au/SnO_2:Sb, Au films is instability of their parameters during prolonged exposure to hydrogen: during the tests, the resistance of films and the response to molecular hydrogen increase [3, 4]. To overcome these difficulties and stabilize the characteristics of the sensors, training for 30 or more days is required. It should be noted that under prolonged exposure

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to other reducing gases and vapors (CO, H_2S, acetone, ethanol, etc.), a decrease in the sensitivity of sensors is observed [5–7].

In a number of works (for example, [8-13]), it has been found that when additives of 3*d*-transition metal oxides (Cu, Ni, Co) are introduced into the bulk of tin dioxide films prepared using thick-film technology, the resistance and the response to hydrogen and a number of other gases increase. Optimum values of Ni and Co concentrations, at which the responses have maximum values, differed by 0.2 to 4 mass%, depending on the specific technology of the film production. It was suggested that the additives contribute to the increase of density of the chemisorbed oxygen. At the same time, the mechanisms of the influence of 3*d*-metals remain controversial, degradation of the film properties under the long-term tests practically has not been studied, and thin films of tin dioxide with similar impurities obtained by magnetron sputtering have not been studied.

The purpose of this work is to study the effect of additives of cobalt and nickel, introduced into the bulk of the gold-modified SnO_2 films in the process of the direct current magnetron sputtering, on the electrophysical and gas sensitive properties, as well as on the stability of the parameters of hydrogen sensors.

EXPERIMENTAL TECHNIQUE

The sensors based on thin (about 100 nm) Au/SnO_2:Sb, Au, Ni (series 1) and Au/SnO_2:Sb, Au, Co (series 2) films with the size of 0.7×0.7 mm and with an area of the sensitive layer of 0.3×0.3 mm^2 were studied. The contacts to the SnO_2 layers and heater on the back side of the substrate were formed by spraying of platinum with subsequent photolithographic engraving prior to the deposition of tin dioxide films. Peculiarities of the technology for the production of the antimony doped tin dioxide films using magnetron sputtering of a target from the Sn+Sb alloy are described in [1, 3]. For the introduction of gold and cobalt into the bulk of the films, pieces of these metals were placed on the surface of the target. The content of the additives was controlled by the ratio of the areas of the sputtered part of the target S_{Sn} and the pieces of the metals S_m. For the samples with nickel impurity, $S_{Au}/S_{Sn} = S_{Ni}/S_{Sn} = 3\cdot10^{-3}$. In case of films of series 2, two cobalt contents were used: $S_{Co}/S_{Sn} = 3\times10^{-3}$ (series 2-1) and $S_{Co}/S_{Sn} = 9\cdot10^{-3}$ (series 2-2). Dispersed layers of Au were deposited on the surface of the films using the same method of the direct current magnetron sputtering. The finished samples were annealed in the air at a temperature of 450° C for 24 hours. On one sapphire substrate, 150 μm thick and 30 mm in diameter, up to 500 sensors were prepared. Then, the plates were cut into the separate elements and the gold wire with the diameter of 50 μm was welded (by thermocompression) to the contact pads of the sensors. Samples were collected in the body of the type TO-8.

Time dependences of the conductivity of sensors in pure air $G_0(t)$ and under the action of hydrogen $G_1(t)$ were measured with the help of a specially designed stand that made it possible to easily adjust and stabilize the working temperature of the sample, to measure the relative humidity in the chamber, and to provide the operation of sensors in the constant heating and thermo-cyclic modes. The ratio $G_1(t)/G_0(t)$ was used as the adsorption response. The time, in which conductivity reached 0.9 of the stationary value G_{st}, was considered as the response time t_r.

For measuring the characteristics under the action of molecular hydrogen H_2, four sensors were simultaneously placed in a 1-liter quartz chamber, the experimental procedure was similar to [3, 4]. The properties of sensors were studied in the constant heating mode as a function of the operating temperature and hydrogen concentration, and also in the thermo-cyclic mode. To study the stability of parameters during long-term operation of the sensors under the influence of hydrogen, the concentration dependences of the response to the molecular hydrogen in the concentration range of 50–1000 ppm were measured every 2–4 or more (up to 30–60) days. On the basis of the time dependences of the conductivity in the thermo-cyclic mode in pure air, the band bending $e\varphi_s(T_2)$ at the grain boundaries of tin dioxide was estimated in accordance with the method [1, 3] by the following formula:

$$e\varphi_s(T_2) = \frac{kT_1T_2}{T_2 - T_1}\ln\left[\frac{G_0(T_2)}{G_0(T_1)}\left(\frac{T_2}{T_1}\right)^{0.75}\right], \quad (1)$$

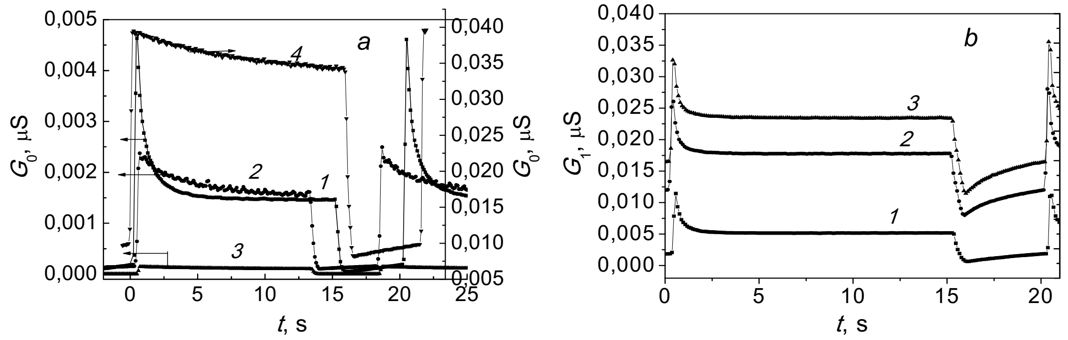

Fig. 1. Time dependences of the conductivity in pure air for the sensors from series: 1 (*1*), 2-1 (*2*), 2-2 (*3*), and 3 (*4*) (*a*). CTP of the sensors from series 1 under the influence of different concentrations of hydrogen, ppm: 100 (*1*), 600 (*2*), and 1000 (*3*) (*b*).

where T_2 and T_1 are the temperatures in the heating and cooling cycles, respectively and k is the Boltzmann constant. To determine $e\varphi_s(T_2)$, the temperature T_2 and the duration t_2 of the heating cycle were selected so that at the end of this cycle, the stationary values of the band bending $e\varphi_s(T_2)$ and $G_0(T_2)$ were established. In the cooling cycle, the temperature of the sensor T_1 must be significantly lower, so that during some time after the rapid temperature decrease from T_2 to T_1, the values of the oxygen ion density $N_i(T_2)$ on the surface and the band bending $e\varphi_s(T_2)$ of energy bands remained unchanged. At the same time, the condition $T_1 \geq 200°C$ must be satisfied, so that O^- ions are adsorbed on the SnO_2 surface. Based on the results of preliminary studies, the following thermo-cyclic modes were chosen: $T_2 = 410°C$ and $T_1 = 200°C$. The duration of the heating cycle t_2 was varied for the samples from different series to provide the above conditions [1, 3]. The obtained data were compared with the features of the characteristics of films modified only by gold Au/SnO_2:Sb, Au (series 3) [3].

RESULTS AND DISCUSSION

The studies have shown that introduction of the nickel and cobalt additives to the volume of tin dioxide films helps to reduce the conductivity of the freshly prepared sensors in pure air both in the constant heating mode and in the thermo-cyclic mode in comparison with the films of series 3 (Fig. 1*a*). These results agree with the data [8–13]. The times t_2 in the thermo-cyclic mode, necessary to establish the stationary values of $e\varphi_s(T_2)$ and $G_0(T_2)$, were 15, 13, and 16 s for the samples from series 1, 2, and 3, respectively. Changes in the conductivity-time profiles (CTP) under the introduction of different hydrogen concentrations are shown in Fig. 1*b* on the example of sensors from series 1: there is an increase of the conductivity in the heating cycle and it is most noticeable in the cooling cycle.

The values of the band bending $e\varphi_s(T_2)$ for the freshly prepared sensors calculated by formula (1) are significantly higher for the samples with the 3*d*-metal additives with higher values of $e\varphi_s(T_2) =$ 0.51–0.53 eV corresponding to the increased content of cobalt (series 2-2) (Fig. 2). Close values of 0.49–0.51 eV are observed in case of the addition of Ni (series 1). Low Co content slightly increases $e\varphi_s(T_2)$ up to 0.31–0.33 eV in comparison with $e\varphi_s(T_2) =$ 0.26–0.28 eV for the films from series 3 without Ni and Co additives. The maximum values of the response to H_2 are observed for the sensors from series 1 and 2-2.

Of considerable interest are the results of studies of changes in the properties of sensors during the tests. Obviously, for the Au/SnO_2:Sb, Au sensors, the most noticeable decrease of the conductivity in pure air and an increase of the values of the band bending and response to hydrogen are observed (Figs. 2 and 3). The changes in these parameters in case of films with additives of 3*d*-metals are much less pronounced that is, partial stabilization of the characteristics takes place.

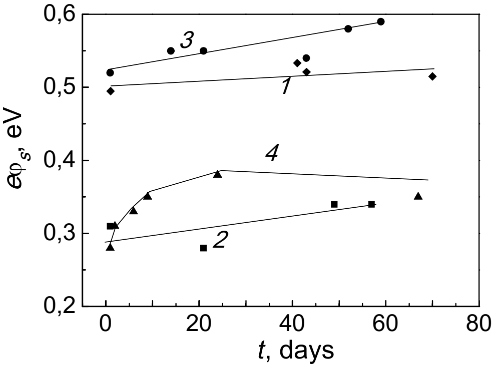

Fig. 2. Dependence of the band bending at the grain boundaries of SnO_2 on the duration of testing of sensors from series: 1 (*1*), 2-1 (*2*), 2-2 (*3*), and 3 (*4*).

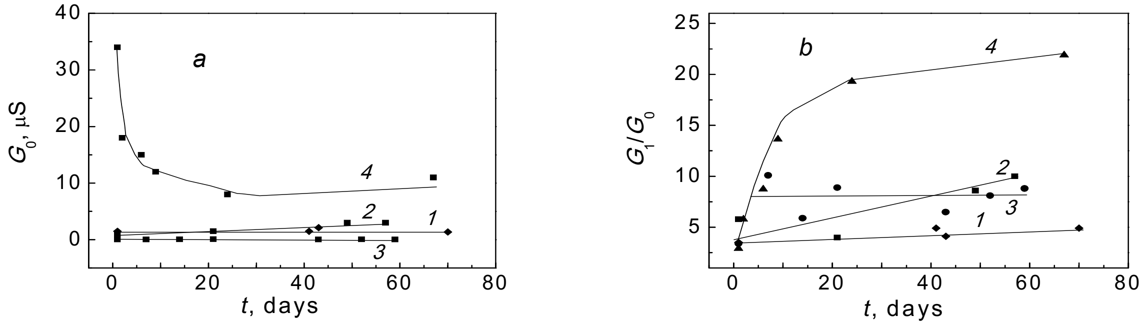

Fig. 3. Dependences of the conductivity in pure air and the response to 100 ppm of H_2 on the duration of testing of sensors from different series: 1 (*1*), 2-1 (*2*), 2-2 (*3*), and 3 (*4*).

The established regularities allow us to consider the processes that can be responsible for the instability of hydrogen sensors, and the role of additives. As suggested earlier [3], changes in the conductivities G_0, G_1 and the response of sensors to H_2 for the samples modified only with gold (series 3) are mainly due to the increase and the subsequent stabilization of $e\varphi_s$. Atomic hydrogen released during dissociative adsorption of H_2 can interact with the lattice oxygen and partially reduce the tin dioxide molecules appearing on the surface. There is an increase in the density of superstoichiometric tin atoms, which are the centers of oxygen adsorption.

Introduction of additives of nickel and cobalt promotes an increase in the band bending at the grain boundaries of tin dioxide already in freshly prepared samples, which indicates an increase in the density N_i of chemisorbed oxygen. It is important that during the tests, there is an additional slight increase in $e\varphi_s$ (Fig. 2). It can be assumed that during the crystallization of the sputtered films during the thermal annealing, the 3*d*-metal atoms in the SnO_2 bulk partially segregate on the surface of the microcrystals and form bonds with the lattice oxygen, the superstoichiometric tin atoms are formed, and the density N_i increases. If the bonds of Ni and Co with oxygen are stronger than those of Sn, then under the prolonged tests, atomic hydrogen will be oxidized not by the lattice oxygen, but mainly by the chemisorbed one and the stability of the sensors' characteristics increases.

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