**Материалы Международной научно-технической конференции,
21 – 25 ноября 2016 г.**

МОСКВА **INTERMATIC – 2 0 1 6, часть 1** **МИРЭА**

EFFECT OF HUMIDITY ON CHARACTERISTICS OF HYDROGEN SENSORS BASED ON NANOCRYSTALLINE SnO_2 THIN FILMS WITH VARIOUS CATALYSTS

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National Research Tomsk State University, Tomsk
almaev_alex@mail.ru

Introduction

The mechanisms of water vapor adsorption on the surface and the effect of a mixture of reducing gas with moist air on the characteristics of SnO_2 sensors were studied in detail in the papers [1,2]. Based on a detailed analysis of time dependence of the sensor conductivity in the atmosphere of clean air when the sensor operates in a thermo-cyclic mode, a method for determining the energy band bending $e\varphi_s$ (e is the electron charge, φ_s is the surface potential) at the interface of the contacting SnO_2 microcrystals in the polycrystalline tin-dioxide film with deposited Pt/Pd catalysts is proposed in the paper [3]. Further studies [4] have shown that in the process of long-term tests of sensors based on thin films of Pt/Pd/SnO_2:Sb at periodic influence of hydrogen, the decrease in the conductivity in clean air and the increase in the response to H_2 sensors are observed. The most significant changes occur in the first month of testing, and then the parameters are stabilized. It has been shown that the increase in humidity helps to reduce $e\varphi_s$. For these samples the curves show the dependence of conductivity G_0 on humidity, there are two linear areas with various coefficients of proportionality γ_{01} (at $A<A_0$) and γ_{02} (at $A>A_0$), where A is an absolute humidity; A_0 corresponds to absolute humidity in point of inflection [2]. Two linear areas testify the existence of two types of the sites of adsorption of water molecules on SnO_2 surface. Presumably, the role of these centers can be performed by the surface defects occupied by O^{2-} and O^- ions.

Preliminary studies have shown that additives of silver and yttrium in the bulk of tin dioxide films promote stability of sensor's characteristics. In this research, we study the effect of humidity on electrical and gas sensitive characteristics of thin nanocrystalline films of tin dioxide modified by platinum, palladium, gold, silver and yttrium additives in the semiconductor bulk and on the surface.

Gas sensor fabrication

Tin dioxide films were produced by dc magnetron sputtering target in oxygen–argon plasma. The target represents an alloy of tin with 0,51 at % antimony. The antimony impurity forms donor centers in tin dioxide and promotes a decrease in the film resistance to 1–10 MΩ under operation conditions. 150 μm thick sapphire wafers were used as substrates. The dispersed layers of Pt, Pd, Au and Ag on the tin dioxide surface were sputtered by dc magnetron sputtering in the same conditions. To introduce additives into the film bulk, pieces of corresponding metals were placed onto the target surface. The additive content was estimated by the ratio of metal pieces areas S_m (m=Ag, Y, Au) and the sputtered target S_{Sn}. Based on special studies, the optimum ratios S_m/S_{Sn} allowing directional effect on the sensor properties were determined as $S_{Au}/S_{Sn}=S_{Ag}/S_{Sn}=S_Y/S_{Sn}=3\cdot10^{-3}$. The manufacturing process of the sensors is described in detail in the paper [5].

We introduce the following designations for films, which were grown with various bulk additives and deposited catalysts: (1) Pt/Pd/SnO_2:Sb; (2) Au/SnO_2:Sb, Au; (3) Pt/Pd/SnO_2:Sb, Ag, Y and (4) Ag/SnO_2:Sb, Ag, Y. Testing equipment, which was used in order to measure the sensor conductivity in the clean air and under exposure to hydrogen, at

different humidity levels of the gas mixture, in different operation modes are describe in the paper [4].The ratio G_1/G_0 was taken as the adsorption response to hydrogen, where G_1 is the conductivity of the sensor under exposure to hydrogen; G_0 is conductivity of sensor in air. The thickness of films based on Pt/Pd/SnO_2:Sb and Au/SnO_2: Sb, Au was approximately 100 nm and in the case of films with additives of silver and yttrium in the bulk – 120-150 nm.

Results and discussions

The analysis of the time dependency of the conductivity G_0 of sensors in the thermocyclic operation mode with the use of the original method described in the paper [3] allowed to determine the value of energy band bending at intergrain boundaries in SnO_2. It is assumed that in all types of samples in clean air the over–barrier conductivity component prevails. There are $e\varphi_s$ in SnO_2 films with different additives at the level of absolute humidity 6,8 g/m^3 in the table 1. It is known [2-4], that value of $e\varphi_s \sim N_i^2$, where N_i is the surface density of chemosorbed oxygen ions (O^-). The deposited two-layer dispersed Pt/Pd catalysts provide a high density of chemisorbed oxygen O^{2-} and a transition to the atomic form O^- during film heating. Therefore, sensors of series (1) have higher value of $e\varphi_s$ in comparison with sensors based on thin films of Au/SnO_2:Sb, Au since in the case of series (2) the negative charge density decreases. For the films Pt/Pd/SnO_2: Sb, Ag, Y the increase of $e\varphi_s$ to 0,70 eV is further evidence of the growth of the density of chemisorbed oxygen with the introduction of additives Ag and Y. These sensors demonstrate a high response whereas $G_1/G_0 \sim \exp[e\varphi_s]$ [2,3]. Elevated value of $e\varphi_s$=0,62 eV in the case of Ag/SnO_2: Sb, Ag, Y films (see Table 1) is contrary to low values of the resistivity and G_1/G_0. It is possible to suggest that the method of the evaluation of $e\varphi_s$ proposed in the work [3] for films of series (4) in the presence of silver oxide on the surface SnO_2 is not applicable.

Let us consider the effect of humidity on characteristics of the sensors with various additives. The curves show the dependence of conductivity G_0 on humidity (Fig. 1. a, b), there are two linear areas with various coefficients of proportionality γ_{01} (at $A<A_0$) and γ_{02} (at $A>A_0$). Results are similar to those obtained earlier [2]. Fig. 2 a, b, c and d show the concentration dependences of responses to H_2 for studied films at various levels of humidity. Parameters A_0, γ_{01} and γ_{02} for the sensors of researched series are presented in the table 2.

Table 1

Energy band bending eφs at intergrain boundaries in SnO_2 films with different additives

Series	$e\varphi_s$ (eV) at A=6,8 (g/m^3)
Pt/Pd/SnO_2:Sb (1)	0,514
Au/SnO_2: Sb, Au (2)	0,370
Pt/Pd/SnO_2: Sb, Ag, Y (3)	0,704
Ag/SnO2: Sb, Ag, Y (4)	0,619

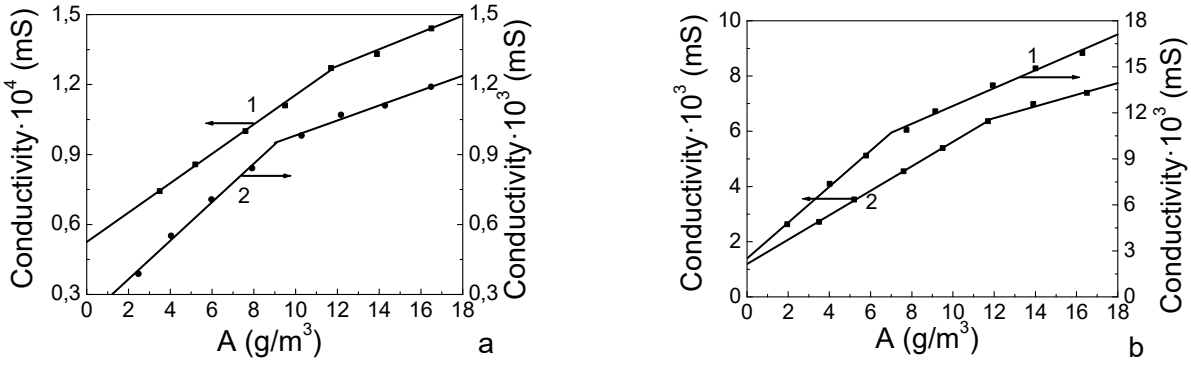

Fig. 1. (a) the dependences of the conductivity in clean air on the level of absolute humidity for the sensors of series (3) – curve 1 and series (1) – curve 2; (b) the same dependences for the sensors of series (2) – curve 1 and series (4) – curve 2.

Increase of the humidity level of the air-gas mixture leads to decrease of the sensors response to hydrogen. The surface density of chemisorbed ions of oxygen is decreased by

the dissociative adsorption of water molecules. Chemisorbed ions of oxygen, in turn, are the centers of adsorption for hydrogen. As shown in the Fig. 2 a, b, c and d the most significant influence of humidity on the sensor response occurs on condition of $A>A_0$. You can see that low values of γ_{01} and γ_{02} are caused by the introduction of additives of Ag and Y in the bulk of the film. The sensors based on these films have a weaker dependence of conductivity G_0 and the responses G_1/G_0 on humidity.

The sensor conductivity in gas-air mixture is $G=G_b+G_{ch}$, where G_b and G_{ch} are the over-barrier and channel components, respectively [6]. Upon exposure of sensors of series (1) to hydrogen in the region of low concentrations (<300 ppm), a superlinear portion is observed (Fig. 2 a), which suggests that the over–barrier component of conductivity prevails [6]. Introduction of additives of silver and yttrium in the bulk of films (3) promotes an increase in the region with superlinear dependence. It can be caused by a high value of $e\varphi_s$. In the case of films modified with gold (series (2)) and Ag/SnO_2:Sb, Ag, Y sublinear dependence (Fig. 2 c, d) corresponds to channel conductivity component [6].

Table 2

Special values A_0, γ_{01} and γ_{02} for the sensors of different series at different levels of humidity

Parameter	$Pt/Pd/SnO_2$:Sb	$Pt/Pd/SnO_2$:Sb, Ag, Y	Ag/SnO_2:Sb, Ag, Y	Au/SnO_2:Sb, Au
A_0 (g/m^3)	9,1	11,7	11,7	7,0
γ_{01} ($g^{-1}m^3$)	0,41	0,12	0,37	0,47
γ_{02} ($g^{-1}m^3$)	0,048	0,042	0,053	0,087

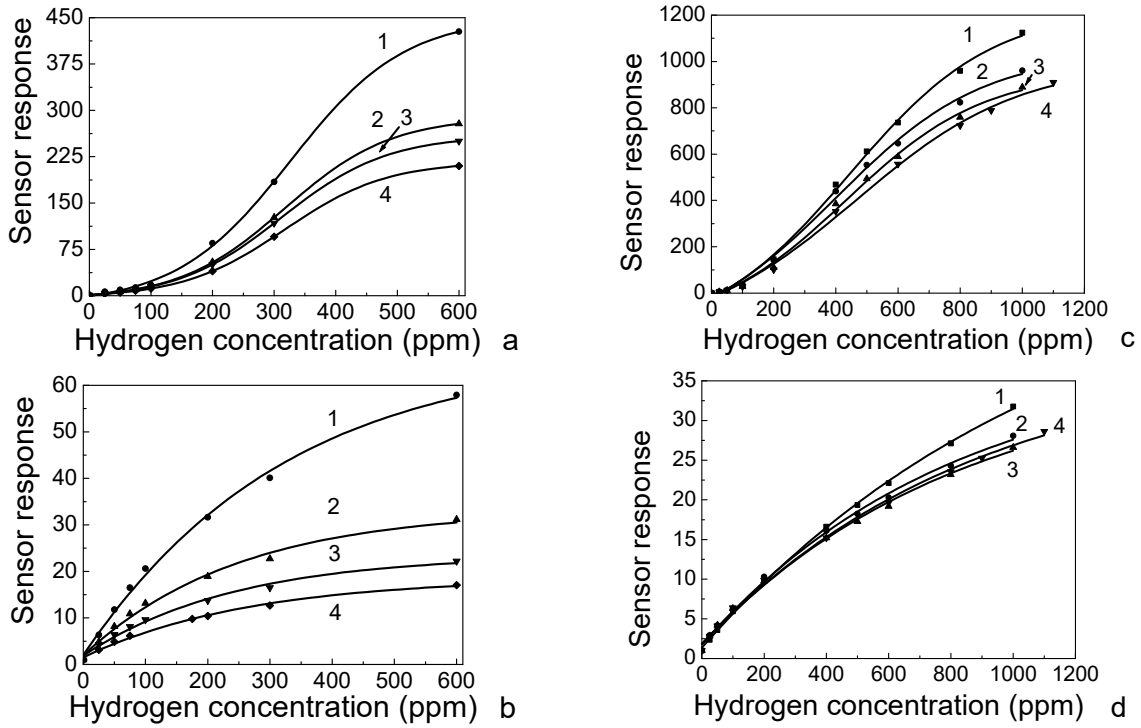

Fig. 2. The dependence of the sensor response on the hydrogen concentration at different levels of absolute humidity: 1 – 2,84; 2 – 6,04; 3 – 8,17; 4 – 10,33; a for series (1); b for series (2). The dependence of the response of the sensor of series (3) on the hydrogen concentration at different levels of absolute humidity: 1 – 4,1; 2 – 8,1; 3 – 12,5; 4 – 16,6; c for series (3); d for series (4)

Of great interest is the reduced sensitivity to humidity for the sensors based on films of the series (3), (4) containing the additives of Ag and Y in the bulk. Also these sensors are characterized by higher stability of parameters at long-term tests at periodic influence of H_2. We can make the following assumptions about the mechanisms of the effect of additives Ag, Y on the properties of the sensors similar to the effect of additives Pt and Pd in the bulk of thin films of tin dioxide [5]. Ag and Y introduced into the tin dioxide bulk in the course of stabilizing annealing during the crystallization of SnO_2 thin films in samples of series (3) and (4)

are mainly arranged on the surface of microcrystals [7,8]. As the result of interaction of additives with lattice oxygen, the density of superstoichiometric tin, which generates oxygen adsorption centers, increases. For the films of series (3) with deposited Pt/Pd the sensor's resistance and response to H_2 increase when the dissociative adsorption of H_2 molecules released atomic hydrogen interacts with lattice oxygen. As a result, the number of excess tin atoms and hence the density of the sites of oxygen adsorption increase. Unsaturated Sn atoms on the oxide surface and lattice oxygen can be stabilized by adding atoms, which have ability to associate with lattice oxygen. In this case, the possibility of interaction of protons H^+ with the lattice oxygen and formation of oxygen vacancies decreases.

Conclusions

The introduction of the additives of Ag+Y to the bulk of the SnO_2 films and the deposition ultrathin layers of Ag on the surface of SnO_2 thin films are effective methods for stabilization of sensor characteristics at fluctuations in the humidity level of the atmosphere. The stabilization of the characteristics of the films is based on the ability of additives to form a strong bond with the lattice oxygen. Thus, additives of Ag and Y allow to control the structure of the films when working in real conditions. High response of H_2 sensors based on thin films of Pt/Pd/SnO_2:Sb and Pt/Pd/SnO_2:Sb, Ag, Y is caused by the increase of the surface density of the chemisorbed oxygen due to the deposition disperse layers of the Pt/Pd on the surface of films and due to the introduction of additives of Ag+Y in the bulk of SnO_2 films. The addition of Au is not the active catalyst of reaction of the interaction between the H_2 and the chemisorbed oxygen, therefore, in the case of sensors based on thin films of Au/SnO_2:Sb, Au low resistance and the sensor response to hydrogen are observed.

Acknowledgements

This research was performed with the financial support of the program "UMNIK" of the Fund of assistance to development of small forms of enterprises in scientific-technical sphere (agreement no. 8039 GU2015).

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