Stability of Characteristics of Resistive Hydrogen Sensors Based on Thin Tin Dioxide Films with Deposited Catalysts Pt and Pd

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***Abstract*— This work presents the results of investigation of stability of gas sensitive and electrical characteristics of resistive hydrogen sensors based on thin films of tin dioxide with deposited Pt and Pd dispersed layers. Measurements of the sensor response and energy band bending $e\varphi_s$ at the SnO_2 microcrystals interfaces at long – term operation of sensors were showed that the significantly variation of these values are observed in first month of the sensor using. Perhaps these phenomena are caused by the surface reconstruction during operation of sensors and consequently the increase of density oxygen ions chemisorbed on the surface of tin dioxide. The stability of the sensors parameters depends heavily on level of absolute humidity. The changes of the energy band bending $e\varphi_s$ and the sensor response are caused by process of dissociative chemisorption of water molecules on the semiconductor surface.**

Keywords—tin dioxide; stability; sensor response; energy band banding; hydrogen; humidity

I. INTRODUCTION

At present, detectors for determining concentration of toxic and explosive gases in the air find wide application in different branches of industry. In connection with the development of hydrogen energetic an important task is develop highly sensitive and high – speed sensors of molecular hydrogen. The conductivity of thin films of tin dioxide depends on state of the gas environment. This ability of tin dioxide thin films widely used to create sensors of various gases. The sensors based on thin films of tin dioxide have high sensitivity and low power consumption.

The operating principle for these sensors is based on the fact that the reversible chemisorptions of active gases (H_2, CO, CH_4, etc.) on their surfaces is accompanied by reversible changes in the conductivity of the SnO_2 film.

Nevertheless there are same problems which related to widely introduction of these devices in manufacture. One of these problems is the stability of characteristics at long – term operation of the sensors [1, 2].

The goal of this study was to investigate the stability of the characteristics of semiconductor hydrogen sensors based on thin films of Pt/Pd/SnO_2:Sb. The existing studies of the stability of parameters of hydrogen sensors are mainly devoted to the devices based on thick films of tin dioxide. The physical – chemical processes which occur to aging of sensors depend heavily on manufacturing technology of the devices.

II. EXPERIMENT

The sensitive material of sensor obtained by magnetron sputtering of tin – antimony alloy target (0.49 at.% of Sb) at the direct current. The film thickness was about 100 nm. Ultra dispersed layers of noble metal (palladium and platinum) were deposited on the surface of tin dioxide. The fabrication process of sensors is described in detail in [3].

The working temperature of sensors was set by the platinum heaters deposited on the back side of the 150 μm thick sapphire substrate. The sample size is 0,7x0,7 mm^2 with an area of the sensitive element 0,3x0,3 mm^2. The structure of sensors is showed on figures 1 and 2. After all technological operation the films of tin dioxide represent the pollycrystalline structure.

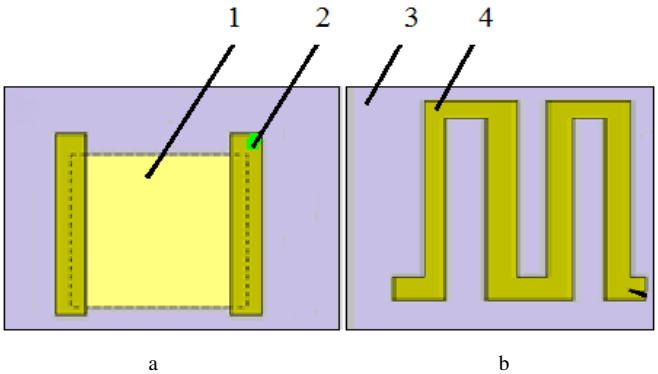

Fig. 1. The scheme of sensitive element (a) and heater (b): 1 is sensitive layer of SnO_2, 2 is platinum contacts, 3 is sapphire substrate, 4 is platinum heaters.

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The role of the additives of noble metals is catalysts of reactions on the surface of semiconductors. The mechanisms of catalysts effect on sensor properties are described in the investigations [3, 4]. Moreover the stability of characteristics at lond – term operation sensors depends on the type of additives [5]. The antimony acts as shallow donor impurity, the impregnation of Sb lets to decrease working resistance of sensors [3].

The gas sensitive characteristics of samples were studied in a chamber equipped with a fan. To control the level of humidity, two air flows were directed through the chamber at controlled rates. One flow was dried with a zeolite, and the other was damped by bubbling. Next, the chamber was sealed. Humidity was controlled by an HIH-4000 sensor placed in the chamber. For realization of diferent regimes of sensor operation (the thermo-cyclic mode and a stationary regime), an automated test stand that allowed to register conductivity at a time interval of Δt = 0,01 s and retune the duration of the heating and cooling cycles in a wide temperature range was used.The principle of operation of automated test stend is described in detail in [6].

Fig. 2. Photo of the semiconductor gas sensor

III. Results and discusstion

In this study is discussed the stability of value of the energy band behding between the SnO_2 microcrystals in polycrystalline thin tin dioxide films and the sensor response to hydrogen at long – term operation. In order to determine the value of energy band bending was used the original method desribed in the paper [7]. This method is based on the analysis of the time dependence of the conductivity G(t) of sensors operating in a gas mixture containing hydrogen (air + H_2) in the isothermal and thermo-cyclic operation modes.

The semiconductor sensors are sensitive to the gases adsorption at high temperatures. In order to determine the value of energy band bending used the following thermo – cyclic operation mode: the temperature in heating cycle T_2=673 *K*, the duration of heating cycle is 8 *s*, in the cooling cycle, the temperature T_1=473 *K*, the duration of cooling cycle 6 *s*. The reasons for which a selected such operation mode are discussed in paper [7].

In the sensors based on thin films Pt/Pd/SnO_2:Sb exposed to hydrogen, the over – barrier component of conductivity plays a decisive role [8, 9]. The over – barrier mechanism of conductivity of polycrystalline films is due to the fact that in the presence of oxygen in a gas mixture the tin dioxide film contains SnO_2 microcrystals separated by two space charge regions depleted of electrons (Fig. 3). The interaction between hydrogen and oxygen on the film surface helps to the decrease of the space charge region width.

The response of such devices can be described by following expression [8, 9]:

$$\frac{G_{\mathrm{H}}(A,T)}{G_0(A,T)} = \exp\left[\frac{e\varphi_s(A,T)\eta_{\mathrm{H}}n_{\mathrm{H}_2}}{kT(1+\eta_{\mathrm{H}}n_{\mathrm{H}_2})}\left(2-\frac{\eta_{\mathrm{H}}n_{\mathrm{H}_2}}{1+\eta_{\mathrm{H}}n_{\mathrm{H}_2}}\right)\right], \quad (1)$$

where G_{H} is conductivity of sensor in the air + hydrogen mixture, G_0 is conductivity of sensor in the clean air, $e\varphi_s$ is the energy band bending between the SnO_2 microcrystals in thin tin dioxide films, e is electron charge, φ_s is the surface potential, η_{H} is the coefficient proportional to the ratio of the probability of adsorption of hydrogen atom on the surface of the semiconductor to the probability of its desorption, n_{H_2} is hydrogen concentration, k is the Boltzmann constant, A is the level of absolute humidity.

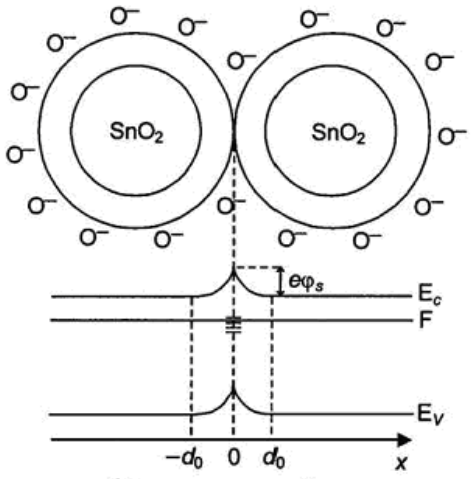

Fig. 3. Model for SnO_2 microcrystals contacting in the presence of a spece charge region depleted of electrons and energy diagram of contact for the this case (E_c, E_v and F are the conductivity band bottom, valence band top, and Fermi level, respectively, d_0 is space charge regions width) [8]

The process of hydrogen adsorption on the surface of SnO_2 film is characterized by the value of η_{H}, which does not depend on the sensor temperature, concentration of hydrogen, the level of absolute humidity [8, 9]. The energy band bending depends on the oxygen concentration and humidity of the gas mixture.

Figure 4 shows the variations of energy band bending between the SnO_2 microcrystals of the sensor that have

occurred within one year of their work. Value of $e\varphi_s$ rises and stabilizes with increase of time of use the sensor. The significantly variation are observed in first month of the sensor operation. In order to exclude the influence of the humidity on value of $e\varphi_s$, the measurement of parameters of sensors were performed at the same level of absolute humidity A = 5,62 g/m^3.

The energy band bending is described by the following equation [8, 9]:

$$e\varphi_s(A,T) = \frac{(eN_i(A,T))^2}{2N_d\varepsilon_r\varepsilon_0} + kT\,, \qquad (2)$$

where N_i is surface density of oxygen ions (O^-) adsorbed on the surface of the SnO_2 microcrystals, N_d is concentration of donor impurity, ε_r is the relative permittivity, ε_0 is the dielectric constant.

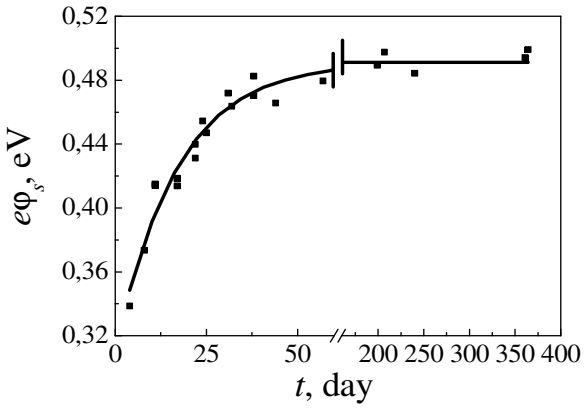

Fig. 4. Variations of the energy band bending after one year of the operation of the sensor Pt/Pd/SnO_2:Sb.

The expression (2) shows that variation of energy band bending is caused by changes of N_i and N_d. The concentration of donor impurity is described by the following equation [7, 8, 9]

$$N_d = n_0 + n_v\,, \qquad (3)$$

where n_0 is the equilibrium electron concentration in the microcrystals, equel to the concentration of ions of shallow donor impurity (Sb), n_V is concentration of electrons generated by ionization of oxygen vacancies.

The value of n_0 at temperatures which used to determine of energy band bending is constant. In paper [10] reported that change of oxygen vacancies concentration with increase the level of humidity is small compared to variation of N_i. Perhaps such situation is observed at long – term operation of sensors. Based on the above it can be concluded that the increase of energy band bending is caused by the increase of density oxygen ions chemisorbed on the surface of tin dioxide by the effect surface reconstruction during operation of sensors.

The variations of the energy band bending determine the response increase at long – term operation of sensors. In the table 1 and 2 are showed such changes of value of response of sensors.

The response of sensor in the isothermal operation is measure at two different concentration 300 and 1000 ppm. Table 1 show that value of the response sensors in the air + hydrogen mixture rises and stabilizes with increase of time of use the device. The analogy situation is observed to changes of energy band bending with the increase of the operation time of sensor (Fig. 4).

TABLE I. THE CHANGES OF VALUE OF RESPONSE IN THE ISOTHERMAL OPERATION OF THE SENSORS WITH PROLONGED USE

Day	$G_H(A,T)/G_0(A,T)$ (n_{H2}= 300 ppm)	$G_H(A,T)/G_0(A,T)$ (n_{H2}=1000 ppm)
04.03.14	80,41	170,39
05.03.14	70,95	179,93
07.03.14	127,89	263,70
21.03.14	184,67	573,75
03.09.14	133,28	857,57
04.09.14	161,20	848,79
05.09.14	153,54	811,02
05.09.14	149,09	712,73
09.09.14	187,71	910,68

The response of sensor in thermo – cyclic operation mode is measured at 300 ppm of hydrogen concentration, the results are presented at table 2.

TABLE II. THE CHANGES OF VALUE OF THE RESPONSE SENSORS WITH PROLONGED USE IN THE THERMO – CYCLIC OPERATION MODE.

Day	$G_H(A,T)/G_0(A,T)$ (n_{H2}=300 ppm)
07.03.14	61,21
11.03.14	64,54
12.03.14	85,60
13.03.14	106,62
22.03.14	135,75
13.05.14	91,83
15.09.14	135,14
29.10.14	126,47

Table 2 as well as Table 1 show that value of sensors response in the air + hydrogen mixture rises and stabilize with increase of the time of the device using. The significant variation of the sensor response was observed in first month of the operation sensor. The deviations of value $G_H(A,T)/G_0(A,T)$

are caused by variations of the level of absolute humidity in measuring chamber.

The stability of sensors parameters depends heavily on the humidity level. The changes of sensor response with the increase the level of absolute humidity are presented in figure 5.

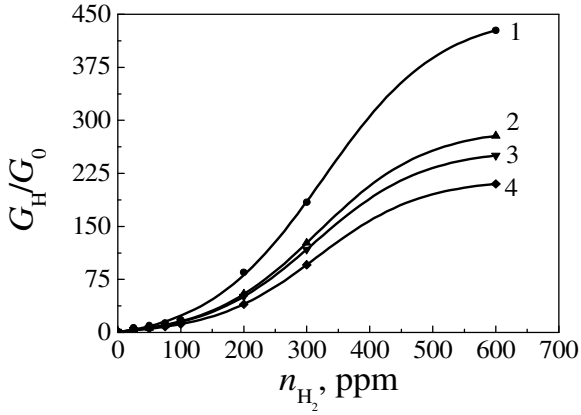

Fig. 5. The dependence of the response of the sensor on the hydrogen concentration at different levels of absolute humidity A, g/m^3: 1 – 2,84, 2 – 6,04, 3 – 8,17, 4 – 10,33.

The results of experiment are shown that response of sensors decreases with increasing of the humidity level. This phenomenon is caused by a decrease of the energy band bending at the interface of the SnO_2 microcrystals with an increase of humidity (Fig. 6).

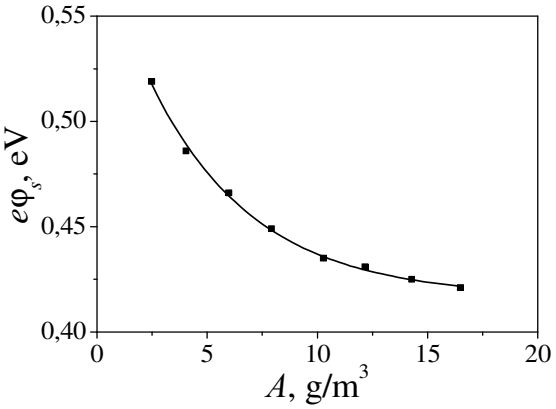

Fig. 6. The dependence of the energy band bending on the level of absolute humidity.

The decrease of the energy band bending at the SnO_2 microcrystals interfaces is caused by process of dissociative chemisorption of water molecules, and as a result the decrease N_i and increase of $G_0(A,T)$ [11].

The received results of investigation are very important especially when using hydrogen sensors in the real conditions.

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