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EFFECT OF LONG – TERM OPERATION ON ENERGY BAND BENDING AT THE SnO_2 MICROCRYSTALS INTERFACES IN THIN TIN DIOXIDE FILMS WITH VARIOUS CATALYSTS [1]

This work presents the results of investigation of stability of energy band bending at the SnO_2 microcrystals interfaces in thin films of tin dioxide with deposited Pt and Pd dispersed layers (Pt/Pd/SnO_2:Sb) and with the additions of gold in the bulk and on the surface (Au/SnO_2:Sb, Au) in long – term operation. Measurements of energy band bending were showed that the significantly variation of this value is observed in first month of the sensor using. Perhaps this phenomenon is caused by the surface reconstruction during operation of sensors and consequently by the increase of density of oxygen ions chemisorbed on the surface of tin dioxide.

Keywords: *tin dioxide; stability; energy band banding; hydrogen.*

In connection with the development of hydrogen energetic and other application areas are developing highly sensitive and high – speed hydrogen semiconductor sensors. The operating principle for these sensors is based on the fact that the reversible chemisorption 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.

The goal of this study was to investigate the stability in long – term operation of the characteristics of semiconductor hydrogen sensors based on thin films of Pt/Pd/SnO_2:Sb (series 1) and Au/SnO_2:Sb, Au (series 2). 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.

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. For introduction the additions of gold in the bulk of tin dioxide films were used mosaic targets with gold particles fixed on them. For both series ultra dispersed layers of noble metal (palladium, platinum and gold) were deposited on the surface of tin dioxide. The fabrication process of sensors is described in detail in [1].

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 [1, 2]. Moreover the stability of characteristics at long – term operation sensors depends on the type of additives [3]. The antimony acts as shallow donor impurity, the impregnation of Sb lets to decrease working resistance of sensors [2].

In this study is discussed the stability of value of the energy band bending $e\varphi_s$ at the SnO_2 microcrystals interfaces in polycrystalline thin tin dioxide films and the sensor response to hydrogen at long – term operation. There e is electron charge, φ_s is the surface potential. In order to determine the value of energy band bending was used the original method described in the paper [4]. This method is based on the analysis of the time dependence of the conductivity $G(t)$ of sensors operating in the thermo-cyclic operation modes.

In order to determine the value of energy band bending of series 1 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 [4]. In the case of modification SnO_2 films by gold the operation temperatures were the same, however the duration of heating cycle is 17 s and the duration of cooling cycle – 6 s. The introduction the additions of gold in the bulk and on the surface of tin dioxide films increases the time of reduction of the surface density of adsorbed neutral hydroxyl groups.

Figure 1 shows the variations of energy band bending between the SnO_2 microcrystals of the sensor based on thin films of Pt/Pd/SnO_2:Sb 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

[1] This work was performed under the RF Ministry for Education and Science, task no. 2014/223 of project 1368.

measurement of parameters of sensors were performed at the same level of absolute humidity A = = 5.62 g/m^3.

During operation, sensors of series 1 repeatedly were exposed to impact of hydrogen and high levels of humidity of gas mixture. For an objective interpretation of the results, it was decided to investigate the dependence $e\varphi_s$ from the time of long – term operation for the new sensor series 1 for 30 days. Thus, after determining $e\varphi_s$ each time the sensors were exposed to impact of 100 ppm of H_2 for 5 min. The results of this experiment are shown in Fig. 2.

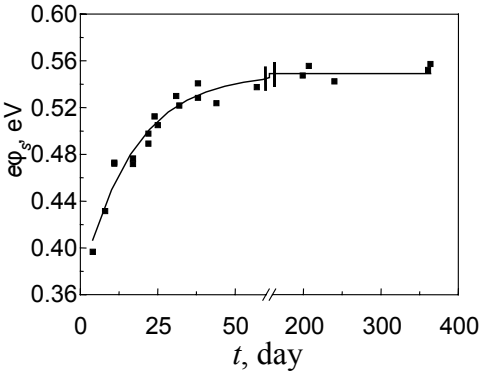

Fig. 1. Variations of the energy band bending after one year of the operation of the sensor Pt/Pd/SnO_2:Sb.

During the first 30 days of the value $e\varphi_s$ is increased and tends to steady-state value. It is worth noting that this behavior of the characteristics of the sensor is caused by the interaction of surface of the SnO_2 film with hydrogen. To verify this fact, an additional experiment was conducted. The value $e\varphi_s$ of new sensors series 1, which are never exposed to any gas and stored in a desiccator, was measured for 5 hours at a value of A = 6.9 g/m^3. The measurements $e\varphi_s$ are carried out only in an atmosphere of clean air. In these experimental conditions, the reduction of $e\varphi_s$ was showed on 0.5 eV. $e\varphi_s$ increased more than on 0.5 eV after the three-time exposure to 500 ppm of hydrogen on sensors.

The energy band bending is described by the following equation [4]:

$$e\varphi_s = \frac{(eN_i)^2}{2\varepsilon_r\varepsilon_0 N_d} + kT\,, \tag{1}$$

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, k is the Boltzmann constant.

According to the works [5] the N_d is constant. From expression (1) follows that the increase of energy band bending is caused by the increase of density oxygen ions chemisorbed on the surface of tin dioxide for during long – term operation of sensors. Perhaps because of its high reactivity atomic hydrogen cleans the surface of the semiconductor from the previously adsorbed undesired compounds which have been formed on the surface of SnO_2 during the manufacture, installation, storage sensors.

The characteristics of hydrogen sensors series 2 in the long – term operation behave similarly to the characteristics of sensors based on Pt/Pd/SnO_2: Sb. The most significant changes $e\varphi_s$ occur in the operation of the sensors in the first 30 days (Fig. 3). Over this period, the value of $e\varphi_s$ was increased by 1.3 – 1.4 times.

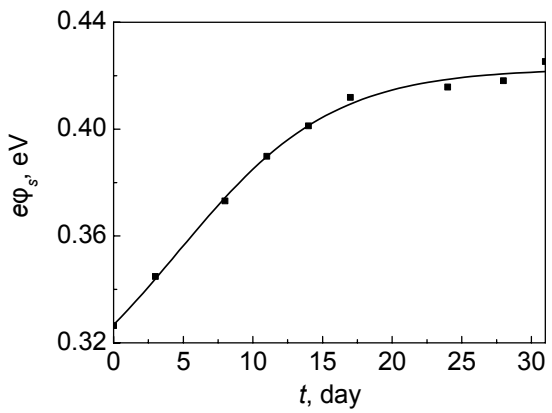

Fig. 2. Variations of the energy band bending of the new sensor Pt/Pd/SnO_2:Sb for 30 days.

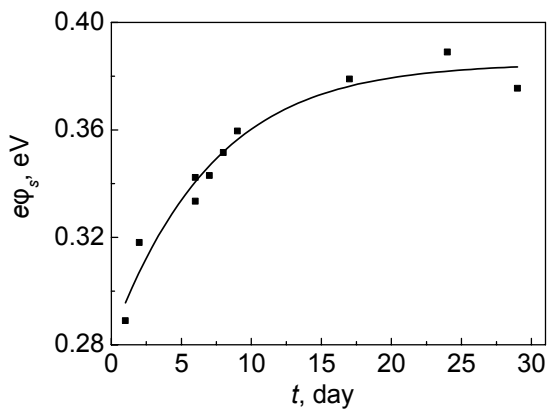

Fig. 3. Variations of the energy band bending of the sensor Au/SnO_2:Sb, Au for 30 days.

In long – term operation the value of $e\varphi_s$ of hydrogen sensor is increases in the first 30 days after the start of operation and stabilized under increase of operation time of sensors independently of the type of additives in the SnO_2 films. The increase of energy band bending is caused by the increase of density oxygen ions chemisorbed on the surface of tin dioxide for during long – term operation of sensors.

REFERENCES

1. Sevastyanov E.Yu., Maksimova N.K., Novikov V.A., et al. // Semiconductors. – 2012. – V. 46. – No. 6. – P. 801–809.
2. Cabot A., Die'guez A., Barzan N., et al. // Sensors and Actuators. – 2001. – V. 79. – P. 98–106.
3. Oleksenko L.P., Maksymovych N.P., Sokovykh E.V., et al. // Russian Journal of Physical Chemistry A. – 2014. – V. 88. – No. 5. – P. 831–835.
4. Gaman V.I., Almaev A.V., Sevastyanov E.Yu., et al. // Russian Physics Journal. – 2014. – V. 56. – No. 12. – P. 1427–1434.
5. Krivetskiy V.V., Rumyantseva M.N., Gaskov A.M. // Russian Chemical Reviews. – 2013. – V. 82. – No. 10. – P. 917–941.

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