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CHARACTERISTICS OF HYDROGEN SENSORS BASED ON THIN TIN DIOXIDE FILMS MODIFIED WITH GOLD

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Effect of hydrogen in the concentration range from 10 to 2000 ppm on the characteristics of sensors based on thin films of tin dioxide modified with gold (Au/SnO₂:Sb, Au) is studied in the thermo-cyclic mode at temperatures from 623 to 773 K and absolute humidity from 2.5 to 20 g/m³. Experimental data are discussed using expressions obtained within the framework of a model that takes into account the presence of three types of adsorbed particles (O⁻, OH, and OH⁻) on the surface of SnO₂ nanocrystals. The characteristics of the sensors based on thin Pt/Pd/SnO₂:Sb films (the first series) are compared with those of Au/SnO₂:Sb, Au films (the second series). It is found that the degree of dissociation of molecular hydrogen into atoms during adsorption on the sensor under interaction with Au particles on the SnO₂ surface is 4 times greater than that under interaction with Pt/Pd particles. The degree of dissociation of H₂O molecules into hydrogen atoms and hydroxyl groups in pure moist air on the surface of the sensors of the second series is 1.6 times greater than that for the sensors of the first series. Thus, gold is a more effective stimulator of the dissociation of H₂ and H₂O molecules than platinum and palladium. A formula is obtained that describes more accurately the dependence of the response of the sensors of both series to the effect of hydrogen on the concentration of this gas and on the temperature of the measuring devices.

Keywords: tin dioxide, hydrogen, thermo-cyclic mode, energy band bending, catalytic modifiers, absolute humidity.

INTRODUCTION

The most important problem in the development of gas sensors based on polycrystalline tin dioxide films is to establish the role of catalytic modifiers in the formation of electrical and gas sensitive properties of such devices. In accordance with this problem, a comparison of characteristics of hydrogen sensors based of thin-film structures Pt/Pd/SnO₂:Sb (the first series) and Au/SnO₂:Sb, Au (the second series) was performed in [1]. It follows from the presented experimental results that at the sensor temperature $T = 673$ K, variation of the absolute humidity A of the gas mixture in the range from 2.8 to 10 g/m³, and concentration of molecular hydrogen $n_{\text{H}_2} = 600$ ppm, the responses G_{H}/G_0 of the sensors from the first series (where G_{H} is the conductivity of the sensor in the gas mixture pure air + hydrogen and G_0 is the conductivity of the sensor in the pure air) have 7–12 times higher values than the responses of sensors from the second series. In the same interval of variation of A , the ratio G_{02}/G_{01} (where G_{02} and G_{01} are the conductivities of the sensors of the second and first series, respectively, in the atmosphere of pure air) increases from 14 to 19.

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It was assumed in [1] that these facts can be caused by different conductivity mechanisms in the tin dioxide films of the first and second series: in the sensors of the first series, the over-barrier conductivity mechanism is the main one, whereas in the sensors of the second series, the channel conductivity predominates [2]. However, there is no evidence in favor of this assumption in [1]. Therefore, taking into account high values of the energy band bending [1] at the interfaces of SnO₂ nanocrystals in the tin dioxide films of the sensors of both series, it can be considered that the over-barrier mechanism of conductivity predominates.

In order to clarify the role of modifiers (Pt + Pd and Au) in the operation of hydrogen sensors, an analysis of a wider range of characteristics of such devices is presented in the temperature range from 623 to 773 K. To calculate the characteristics of sensors, we used formulas based on the refined model of dissociative adsorption of hydrogen and water molecules on the surface of SnO₂ [3].

1. DEPENDENCE OF THE SENSOR RESPONSE ON THE HYDROGEN CONCENTRATION

The response of the sensor to the effect of hydrogen in the realization of the over-barrier electron drift mechanism in the tin dioxide film can be described by the following expression [3]:

$$G_H/G_0 = \exp\left(\frac{e\varphi_{s0} - e\varphi_{sH}}{kT}\right), \quad (1)$$

where $e\varphi_{s0}$ and $e\varphi_{sH}$ are the values of the energy band bending at the interfaces of the SnO₂ nanocrystals of the polycrystalline tin dioxide film in an atmosphere of pure air and in a pure air + H₂ gas mixture, respectively, e is the electron charge, φ_{s0} and φ_{sH} are the surface potentials, and k is the Boltzmann constant. The values of the sensor characteristics: G_H , G_0 , $e\varphi_{s0}$, and $e\varphi_{sH}$ depend on the sensor temperature and humidity level of the gas mixture.

In accordance with [3], we have

$$e\varphi_{sH} - kT = \frac{e\varphi_{s0} - kT}{(1 + M(n_{H_2}))^2}. \quad (2)$$

Here,

$$M(n_{H_2}) = \eta_{Hr} \cdot \gamma(n_{H_2}) n_{H_2}, \quad (3)$$

$$\eta_{Hr} = r \cdot \eta_{OH} \sim r \exp((E_{D,OH} - E_{aH})/(kT)), \quad (4)$$

where $r = n_H/n_{H_2}$ is the coefficient proportional to the degree of dissociation of molecular hydrogen on the surface of the modifying particles (for the sensors of the first series, they are Pt and Pd particles, and for the sensors of the second series, they are Au particles), n_H is the concentration of hydrogen atoms on the surface of SnO₂ at the total dissociation of molecular hydrogen $n_H = 2n_{H_2}$, the maximum possible value of r is 2, η_{OH} is the coefficient proportional to the ratio of the probability of adsorption of the hydrogen atom on the O⁻ ion to the probability of desorption of the hydroxyl group from the SnO₂ surface, $E_{D,OH}$ is the activation energy of the desorption process of neutral OH-groups, and E_{aH} is the activation energy of the adsorption process of hydrogen atoms on the O⁻ ions.

Since the coefficient $\gamma(n_{H_2}) = \gamma(n_{H_2} = 1)(n_{H_2}/(n_{H_2} = 1))^{-m}$, where $\gamma(n_{H_2} = 1) \approx 1$ and $m < 1$ [3], then

$$M(n_{H_2}) \cong \eta_{Hr} (n_{H_2}/(n_{H_2} = 1))^{1-m}. \quad (5)$$

Substituting Eqs. (2) into Eq. (1), we obtain

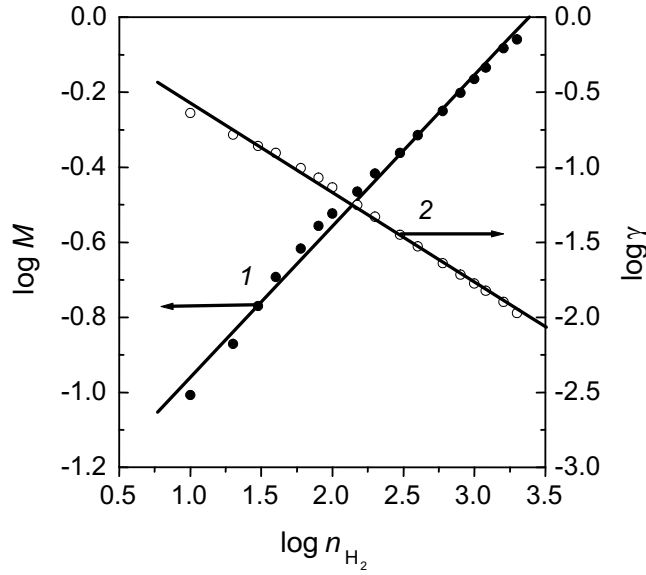


Fig. 1. Dependences of $\log M$ (1) and $\log \gamma$ (2) on $\log n_{H_2}$ at $T_2 = 673$ K and $A = 8$ g/m³.

$$G_H/G_0 = \exp\left(\frac{(e\varphi_{s0} - kT)D(n_{H_2})}{kT}\right), \quad (6)$$

where

$$D(n_{H_2}) = \frac{M(n_{H_2})(2 + M(n_{H_2}))}{(1 + M(n_{H_2}))^2}. \quad (7)$$

It follows from Eqs. (6) and (7) that the dependence G_H/G_0 on n_{H_2} can be calculated, if the values of $e\varphi_{s0}$ and $M(n_{H_2})$ are known. In accordance with Eq. (2), to calculate $M(n_{H_2})$, the following expression can be used:

$$M(n_{H_2}) = \sqrt{(e\varphi_{s0} - kT)/(e\varphi_{sH} - kT)} - 1. \quad (8)$$

2. EXPERIMENTAL RESULTS

All the measurements necessary to determine the characteristics of the sensors were carried out in the thermocyclic mode for the rapid changes of temperature from $T_1 = 473$ K to $T_2 = 623, 673, 723,$ and 773 K. For the sensors of both series, the dependences of G_H/G_0 , M , and γ on n_{H_2} were studied in the interval from 10 to $2 \cdot 10^3$ ppm at $T_2 = 673$ K and four values of A in the range of about from 2.5 to 20 g/m³. At $A \approx 8$ g/m³, the dependences of the same characteristics on n_{H_2} at variation of T_2 from 623 to 773 K were investigated.

As a result of the conducted studies, linear dependences of $\log M = \log \eta_{H_2} + (1-m)\log n_{H_2}$ and $\log \gamma$ on $\log n_{H_2}$ were established for the sensors of the second series (Fig. 1). These dependences have the same form for the sensors of

TABLE 1. Dependence of the Sensors' Characteristics on T_2 at $A \approx 6.8\text{--}8 \text{ g/m}^3$

The series No.	T_2 , K	$e\varphi_{s0}$, eV	$M(n_{\text{H}_2} = 1) \cdot 10^2$	$m(A)$
1	623	0.46	1.1	0.26
	673	0.54	1.0	0.32
	723	0.63	1.0	0.39
	773	0.69	0.8	0.37
2	623	0.42	3.7	0.59
	673	0.49	4.1	0.61
	723	0.57	4.5	0.63
	773	0.66	3.6	0.64

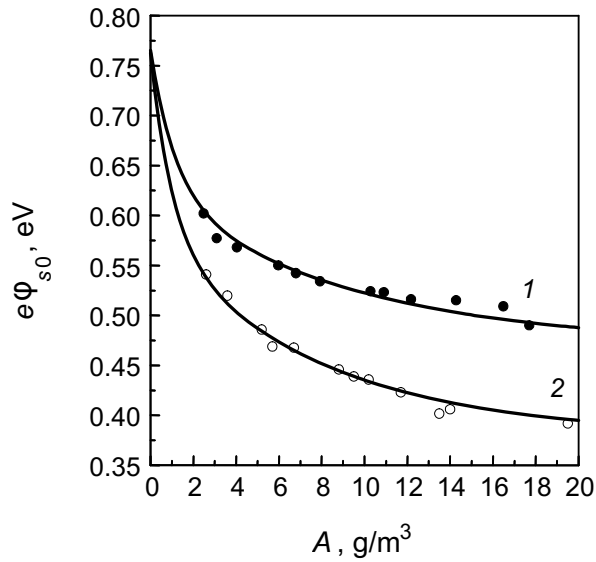


Fig. 2. Dependences of $e\varphi_{s0}$ on A for the sensors from the first (1) and second (2) series at $T_2 = 673 \text{ K}$ (solid lines – calculation, points – experiment).

the first series [3], which confirms the assumption that tin dioxide films in the sensors of both series have the same mechanism of conductivity.

From the results of processing the experimental data presented in Table 1, it is evident that the values of $M(n_{\text{H}_2} = 1) \cong \eta_{\text{H}_r}$ for the sensors of the second series are approximately 4 times greater than those for the sensors of the first series [3]. In accordance with Eqs. (4) and (5), this result is due to the fact that the degree of dissociation r of molecular hydrogen in interaction with Au on the surface of SnO_2 is 4 times greater than that in the interaction with Pt + Pd. After the H_2 molecule is dissociated, two hydrogen atoms are adsorbed on the O^- ions in that part of the SnO_2 surface that is free from the particles of catalytic modifiers. Thus, η_{OH} and the energies $E_{\text{D,OH}}$ and E_{aH} (see Eq. (4)) should have the same values for the sensors of both series.

Similarly, catalytic modifiers also affect the degree of dissociation of H_2O molecules in pure moist air, which leads to the inequality of $e\varphi_{s0}$ for the sensors of the first and second series at the same values of A (Fig. 2). When A varies from 2.5 to about 20 g/m^3 , $e\varphi_{s0}$ for the sensors of the first series is 1.11–1.25 times greater than that for the sensors of the second series.

An analysis of the experimental data presented in Fig. 2 showed that the dependence of $e\varphi_{s0}$ on A can be described using the approximation formula

$$e\varphi_{s0}(A) = B_0 + B_1 \exp(-A/A_1) + B_2 \exp(-A/A_2), \quad (9)$$

where for the sensor of the first series, $B_0 = 0.47$, $B_1 = 0.14$, $B_2 = 0.155$ eV and $A_1 = 1.16$, $A_2 = 9.2$ g/m³, for the sensor of the second series, these characteristics are 0.38, 0.18, 0.203 eV and 0.99, 7.7 g/m³, respectively. From the results of the approximation (solid lines in Fig. 2), it is seen that $e\varphi_{s0}(0) \approx 0.76$ eV for the sensors of both series.

The dependence of $e\varphi_{s0}$ on the concentration of water molecules $n_{\text{H}_2\text{O}}$ in pure moist air is described by the expression [3] similar to Eq. (2) as follows:

$$e\varphi_{s0}(n_{\text{H}_2\text{O}}) - kT = \frac{e\varphi_{s0}(0) - kT}{(1 + M(n_{\text{H}_2\text{O}}))^2}. \quad (10)$$

Here,

$$M(n_{\text{H}_2\text{O}}) = \eta_{\text{H}_2\text{O}} \cdot \gamma(n_{\text{H}_2\text{O}}) n_{\text{H}_2\text{O}}; \quad (11)$$

$$\eta_{\text{H}_2\text{O}} = r_{\text{H}_2\text{O}} \cdot \eta_{\text{OH}}; \quad (12)$$

$r_{\text{H}_2\text{O}} = n_{\text{H}}/n_{\text{H}_2\text{O}}$ is the degree of dissociation of H₂O molecules under interaction with the modifying particles into hydrogen atoms and hydroxyl groups. Since as a result of the dissociation of a water molecule, only one hydrogen atom is formed (H₂O → H + OH), the maximum possible value $r_{\text{H}_2\text{O}} = 1$. The coefficient $\gamma(n_{\text{H}_2\text{O}}) = \gamma(n_{\text{H}_2\text{O}} = 1)(n_{\text{H}_2\text{O}} / (n_{\text{H}_2\text{O}} = 1))^{-m}$, $m < 1$.

To calculate $M(n_{\text{H}_2\text{O}})$ by Eq. (10), the data of Fig. 2 taking into account that $n_{\text{H}_2\text{O}}$ (ppm) = 1.245 A (mg/m³) [4] were used. It follows from the obtained results that under the variation of A from 2.5 to 20 g/m³ and the corresponding increase of $n_{\text{H}_2\text{O}}$ from $3.1 \cdot 10^3$ to $24.9 \cdot 10^3$ ppm,

$$\log M(n_{\text{H}_2\text{O}}) = \log M(n_{\text{H}_2\text{O}} = 1) + (1 - m) \log n_{\text{H}_2\text{O}}, \quad (13)$$

where $M_1(n_{\text{H}_2\text{O}} = 1) = 3.47 \cdot 10^{-3}$ for the sensor from the first series and $M_2(n_{\text{H}_2\text{O}} = 1) = 5.62 \cdot 10^{-3}$ for the sensor from the second series. For the sensors of both series, $m = 0.56$. Thus, the dependence $\log M(n_{\text{H}_2\text{O}})$ on $\log n_{\text{H}_2\text{O}}$ is similar to the dependence $\log M(n_{\text{H}_2})$ on $\log n_{\text{H}_2}$ at $A = \text{const}$ (see Fig. 1, curve 1). This fact indicates the absence of fundamental differences between the processes of dissociative adsorption of H₂ and H₂O molecules on the surface of SnO₂.

Since $\gamma(n_{\text{H}_2\text{O}} = 1) \cong 1$ at $M_1(n_{\text{H}_2\text{O}} = 1) \ll 1$ and $M_2(n_{\text{H}_2\text{O}} = 1) \ll 1$ [3], it follows from Eq. (11) that $M_2(n_{\text{H}_2\text{O}} = 1)/M_1(n_{\text{H}_2\text{O}} = 1) \cong r''_{\text{H}_2\text{O}}/r'_{\text{H}_2\text{O}} = 1.62$, where $r''_{\text{H}_2\text{O}}$ and $r'_{\text{H}_2\text{O}}$ are the values of $r_{\text{H}_2\text{O}}$ for the sensors of the second and first series, respectively. Thus, in pure moist air, the degree of dissociation of H₂O molecules on the particles of gold is greater than that on the particles of platinum and palladium. This fact mainly causes the differences in the values of $e\varphi_{s0}$ and G_0 for the sensors of both series. The lower values of $r_{\text{H}_2\text{O}}$ for the sensors of both series ($3.47 \cdot 10^{-3}$ and $5.62 \cdot 10^{-3}$) in comparison with r (10^{-2} and $4 \cdot 10^{-2}$) are due to the fact that the binding energy of particles in H₂O molecules is greater than that in H₂ molecules [5, 6].

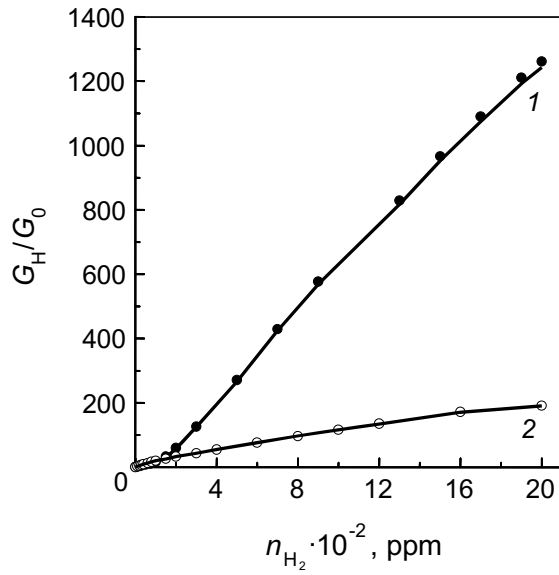


Fig. 3

Fig. 3. Dependences G_H/G_0 on n_{H_2} for the sensors from the first (1) and second (2) series at $T_2 = 673$ K and $A = (7-8)$ g/m³ (solid lines – calculation, points – experiment).

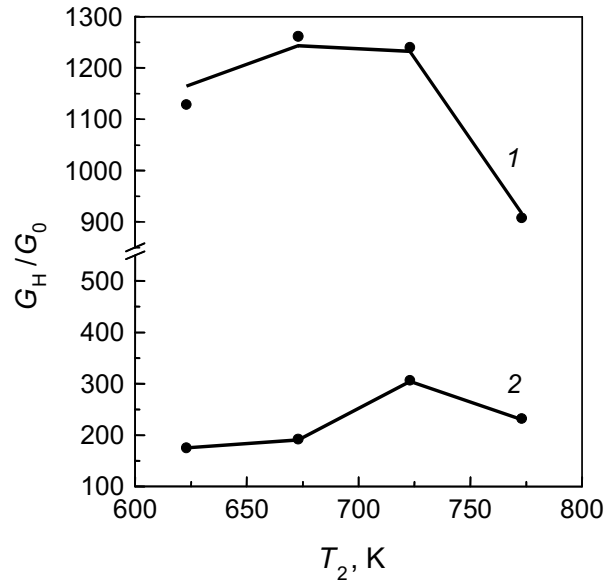


Fig. 4

Fig. 4. Dependences G_H/G_0 on T_2 for the sensors from the first (1) and second (2) series at $A = (7-8)$ g/m³ and $n_{H_2} = 2 \cdot 10^3$ ppm (solid lines – calculation, points – experiment).

The dependences of the response (G_H/G_0) of the sensors of both series on n_{H_2} (Fig. 3) are described with great accuracy by Eqs. (5)–(7). To calculate curves 1 and 2 in Fig. 3 using these expressions, we used the values of $e\varphi_{s0}$, $M(n_{H_2} = 1)$, and m presented in the Table 1 for $T_2 = 673$ K. For the same values of the characteristics, we calculated the dependences of the response on temperature for the sensors of both series (Fig. 4).

It follows from the obtained experimental data that the temperature dependences of $e\varphi_{s0}$ at $A = \text{const}$ for the sensors of both series are similar to each other (see Table 1). The temperature dependences of conductivity for the sensors of both series are described by the same expression [3]

$$G_0(T) = K_0 \exp \left[-\frac{e\varphi_{s0}(T) + \Delta E_d}{kT} \right], \quad (14)$$

where $K_0 \approx \text{const}$, ΔE_d is the donor impurity ionization energy, equal to (0.37 ± 0.05) eV and (0.32 ± 0.05) eV for the sensors from the first and second series, respectively.

CONCLUSIONS

The results of studies of electrical and gas sensitive characteristics of hydrogen sensors based on thin-film Pt/Pd/SnO₂:Sb (series 1) and Au/SnO₂:Sb, Au (series 2) structures are presented. Analysis of the obtained experimental data showed that the degree of dissociation of molecular hydrogen in interaction with Au particles in the sensors of the second series is 4 times greater than that in interaction with Pt + Pd particles in the sensors of the first series (see

Table 1). A similar effect is exerted by these modifiers on the degree of dissociation of water molecules in an atmosphere of pure moist air. In the sensors of the second series, the degree of the dissociation of H₂O molecules is 1.6 times greater than in the sensors of the first series.

Hydrogen atoms, which appear due to the dissociation of H₂ and H₂O molecules, adsorbing on the centers with O⁻ ions, reduce the density of the negative charge on the SnO₂ surface and, as a result, the values of the energy band bending $e\varphi_{s0}$ and $e\varphi_{sH}$ for the sensors of both series. It follows from the data obtained that the gold particles more effectively affect the decrease in the initial value of the energy band bending on the SnO₂ surface $e\varphi_{s0}(0) = 0.76$ eV (see Fig. 2) due to the adsorption of hydrogen atoms, whose concentration n_H is proportional to the absolute humidity A of pure air.

The dependences of the response to the effect of hydrogen (G_H/G_0) on n_{H_2} and temperature for the sensors of both series are described by Eq. (6). Equation (14) describes the temperature dependence of the conductivity G_0 for the sensors of both series at the same values of the donor impurity ionization energy. It follows from these facts that catalytic modifiers do not have a noticeable effect on the model of the mechanism of conductivity in the sensors of both series.

Thus, the main role of the modifier particles on the SnO₂ surface is to set certain values of the degree of dissociation of H₂ and H₂O molecules in the pure air + hydrogen gas mixture, which ultimately leads to the differences in the electrical and gas sensitivity characteristics of sensors from the first and second series.

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