PHYSICS OF SEMICONDUCTORS AND DIELECTRICS

DEPENDENCES OF CHARACTERISTICS OF SENSORS BASED ON TIN DIOXIDE ON THE HYDROGEN CONCENTRATION AND HUMIDITY OF GAS MIXTURE

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An expression is obtained for the energy band bending $e\varphi_{sH}$ on the surface of the SnO_2 film in the clean air + hydrogen mixture. It is assumed that the value of $e\varphi_{sH}$ depends not only on the surface charge density of adsorbed oxygen ions O^-, but also on the negative charged hydroxyl groups (OH^-). The results of the analysis of the dependences of $e\varphi_{sH}$ on the hydrogen concentration n_{H_2} and the absolute humidity of the gas mixture obtained during the operation of the sensor in the thermo-cyclic mode are presented. A method for the determining n_{H_2} in the examined gas mixture is proposed. The method based on the dependence of $e\varphi_{sH}$ on the hydrogen concentration established during the calibration of the sensor is proposed. The dependences of the energy band bending on the SnO_2 surface at $n_{H_2} = 0$ and the conductivity of the sensor on its temperature during the heating period are discussed.

Keywords: tin dioxide, hydrogen, thermo-cyclic mode, energy band bending, hydroxyl groups, kinetic equation, absolute humidity, adsorption centers.

INTRODUCTION

It was shown in [1, 2] that the concentration of molecular hydrogen n_{H_2} in a clean air + H_2 mixture can be determined using sensors based on thin polycrystalline tin dioxide films operating in the thermo-cyclic mode. To determine the hydrogen concentration, it is proposed to use the following expression [2]:

$$\eta_H n_{H_2} = \sqrt{\frac{e\varphi_{s0}(T_2) - kT_2}{e\varphi_{sH}(T_2) - kT_2}} - 1, \tag{1}$$

where η_H is the coefficient proportional to the probability of adsorption of a gas particle to the probability of its desorption [2], T_2 is the absolute temperature of the sensor operating in the thermo-cyclic mode during the heating period, e is the electron charge, $e\varphi_{s0}$ is the bending of energy bands at the interfaces of SnO_2 microcrystals in the tin dioxide film in the atmosphere of clean air, $e\varphi_{sH}(T_2) = e\varphi_{s0}(T_2) - kT_2\ln(G_H(T_2)/G_0(T_2))$ is the energy band bending at the interfaces of SnO_2 microcrystals in the gas mixture clean air + H_2, $G_0(T_2)$ and $G_H(T_2)$ are the conductivities of the sensor in the clean air and in a gas mixture containing hydrogen, respectively, and k is the Boltzmann constant.

The sensor manufacturing technology and methods for determining η_H, $e\varphi_{s0}(T_2)$ and $G_H(T_2)/G_0(T_2)$ are described in [1, 2]. Unlike previous works, this report takes into account the contribution of kT_2 to the bending of the SnO_2 energy bands in an atmosphere of clean air, and it is determined using the expression

$$e\varphi_{s0}(T_2) = \frac{kT_1T_2}{T_2 - T_1} \ln\left(\frac{G_0(T_2)}{G_0(T_1)}\left(\frac{T_2}{T_1}\right)^n\right) + kT_2, \qquad (2)$$

where T_1 is the sensor temperature during the cooling period and $n = 0.75$.

Experimental data obtained during calibration of sensors show that with increasing hydrogen concentration, the coefficient η_H decreases. Therefore, to determine n_{H_2} with the aid of Eq. (1), the mean η_H values were used in the investigated hydrogen concentration intervals.

However, the expression for η_H presented in [2] does not contain an explicit dependence of this coefficient on n_{H_2}. This discrepancy between theory and experiment may be due to the inconsistency of the applicability conditions of Eq. (1) with the real regularities of the adsorption process of molecular hydrogen on the surface of SnO$_2$ microcrystals.

Equation (1) is valid under the following conditions [3]: 1) hydrogen molecules on the surface of SnO$_2$ coated with dispersion Pt and Pd layers dissociate into atoms that at the sensor temperature $T_2 > 473$ K, are adsorbed mainly on centers occupied by oxygen ions O$^-$; 2) as a result of adsorption of hydrogen atoms on the surface of SnO$_2$, hydroxyl groups (OH$^-$) are formed, which in the process of formation give electrons to the conduction band and are neutral particles prior to desorption. Due to this, the surface density of O$^-$ ions decreases by the number of neutral hydroxyl groups (OH) on an area of 1 cm^2 of the SnO$_2$ surface.

It follows from the conditions formulated above that on the surface of the SnO$_2$ microcrystals under the action of a gas mixture containing hydrogen, there must be two types of particles: O$^-$ ions and neutral OH groups. However, the assumption on the neutralization of all hydroxyl groups in the process of their formation has no physical justification. The charge state of the hydroxyl groups should be determined by the function of electron distribution over the local energy levels in the forbidden band of SnO$_2$, which arises when these particles are formed. This implies the possibility of presence of three types of particles on the SnO$_2$ surface: O$^-$ ions, neutral and charged hydroxyl groups. Taking this fact into account, in order to obtain formulas for the determining the concentration of hydrogen in a gas mixture, it is necessary to establish a relationship between $e\varphi_{s0}$, $e\varphi_{sH}$, and n_{H_2}, if there are three types of particles (O$^-$, OH$^-$, OH) on the SnO$_2$ surface.

1. DEPENDENCE OF THE ENERGY BAND BENDING ON THE TIN DIOXIDE SURFACE ON THE HYDROGEN CONCENTRATION IN A GAS MIXTURE

The problem of establishing the functional dependence of $e\varphi_{sH}$ on n_{H_2} can be solved by considering the process of dissociative hydrogen adsorption on the SnO$_2$ surface only in an atmosphere of clean dry air with the absolute humidity $A = 0$. In this case, we cannot take into account the presence and charge state of adsorption centers occupied by hydroxyl groups that appear on the SnO$_2$ surface due to the dissociative adsorption of water molecules [3–6].

Taking into account high concentration of oxygen in the air (approximately 20%), we assume that at $A = 0$ before the start of the hydrogen adsorption, all the adsorption centers on the SnO$_2$ surface are occupied by O$^-$ ions. In this case [2]

$$e\varphi_{s0} = \frac{\left(eN_i(e\varphi_{s0})\right)^2}{2\varepsilon_r\varepsilon_0 N_d} + kT, \qquad (3)$$

where $e\varphi_{s0} = e\varphi_{s0}(A = 0)$, $N_i(e\varphi_{s0})$ is the number of O$^-$ ions on the area of 1 cm^2 of the SnO$_2$ surface, ε_r is the relative permittivity of SnO$_2$, ε_0 is the electric constant, and N_d is the concentration of the donor impurity ions in the space charge regions (SCR) on the surface of the SnO$_2$ microcrystals of the tin dioxide film.

When the sensor is exposed to hydrogen, some of O^- ions on the SnO_2 surface are replaced by hydroxyl groups. Taking this fact into account, we can write the following equality:

$$N_i(e\varphi_{s0}) = N_i(e\varphi_{sH}) + N_{OH}f_{tOH} + N_{OH}(1 - f_{tOH}),\tag{4}$$

where $N_i(e\varphi_{sH})$ is the surface density of O^- ions in the presence of hydrogen in a gas mixture, N_{OH} is the number of hydroxyl groups on an area of 1 cm^2, f_{tOH} is the distribution function of electrons over the local energy levels of hydroxyl groups in the forbidden band of SnO_2, the second and the third terms after the sign of equality are the surface densities of the negatively charged and neutral hydroxyl groups, respectively.

The expression for $e\varphi_{sH}$ can be obtained by substituting in Eq. (3) instead of $N_i(e\varphi_{s0})$ the surface density of particles having a negative charge at $n_{H_2} \neq 0$. In accordance with Eq. (4), the surface density of such particles is

$$N_i(e\varphi_{sH}) + N_{OH}f_{tOH} = N_i(e\varphi_{s0}) - N_{OH}(1 - f_{tOH}).\tag{5}$$

As a result, we have

$$e\varphi_{sH} = \frac{e^2\left(N_i(e\varphi_{s0}) - N_{OH}(1 - f_{tOH})\right)^2}{2\varepsilon_r\varepsilon_0 N_d} + kT.\tag{6}$$

Solving the kinetic equation for the adsorption process of hydrogen atoms on O^- ions, we express N_{OH} in terms of $N_i(e\varphi_{s0})$. Such an equation can be written in the same form as for the process of adsorption of gas particles on the neutral centers [7, 8]. However, in this case, one should take into account that only neutral hydroxyl groups can desorb from the SnO_2 surface.

In the experiment, stationary values of $e\varphi_{s0}$ and $e\varphi_{sH}$ were determined at the sensor temperatures T_1 and T_2 [1, 2]. Given this fact and also the fact that the hydrogen atoms are adsorbed only on the centers occupied by O^- ions, the kinetic equation can be written in the following form:

$$\alpha_H \exp(-E_{aH}/(kT))\cdot n_H \cdot (N_i(e\varphi_{s0}) - N_{OH}) = \nu_{OH}\exp(-E_{d,OH}/(kT))\cdot N_{OH}(1 - f_{tOH}),\tag{7}$$

where $\alpha_H = K_a S_M \sqrt{kT/(2\pi M_0)}$, K_a is the probability of an unactivated adsorption of a gas particle on the center, S_M is the effective cross-section area of the adsorbed particle, M_0 is the mass of the particle, E_{aH} is the activation energy of the process of adsorption of hydrogen atoms on the O^- ions, n_H is the concentration of hydrogen atoms on the SnO_2 surface, ν_{OH} is the frequency of natural oscillations of hydroxyl groups, and $E_{d,OH}$ is the activation energy of the desorption process of neutral OH groups.

The left-hand side of Eq. (7) is equal to the number of hydroxyl groups formed on an area of 1 cm^2 on the surface of SnO_2 per unit time due to the adsorption of hydrogen atoms on the centers occupied by O^- ions, and the right-hand part is equal to the number of desorbed OH groups during the same time. Equation (7) does not take into account the term describing the possible process of desorption of hydrogen atoms from O^- ions, which can be justified by the presence of a large binding force between these particles in the hydroxyl groups.

The solution of Eq. (7) has the form

$$N_{OH} = \frac{N_i(e\varphi_{s0})\eta_{Hr}n_{H_2}}{\eta_{Hr}n_{H_2} + (1 - f_{tOH})},\tag{8}$$

where $\eta_{Hr} = r\cdot\eta_{OH}$ is the coefficient characterizing the effectiveness of the effect of the adsorption of H_2 molecules on the surface density of O^- ions, $r = n_H/n_{H_2}$ is the degree of dissociation of molecular hydrogen on the SnO_2 surface,

the maximum value of which is 2, since H_2 molecules dissociate on the surface of the Pd particles with a probability close to unity [9],

$$\eta_{OH}(T) = \left(\alpha_H(T)/\nu_{OH}\right)\exp\left((E_{d,OH} - E_{aH})/(kT)\right) \tag{9}$$

is the coefficient proportional to the ratio of the probability of adsorption of a hydrogen atom on the O^- ion to the probability of desorption of the hydroxyl group.

Substituting Eq. (8) in Eq. (6) and using Eq. (3), after some transformations we obtain

$$e\varphi_{sH} = \frac{e\varphi_{s0} - kT}{(1 + \eta_{Hr}\gamma n_{H_2})^2} + kT , \tag{10}$$

where

$$\gamma = \frac{1 - f_{tOH}(1 + M)}{1 - f_{tOH}} , \tag{11}$$

$$M = \sqrt{\frac{e\varphi_{s0} - kT}{e\varphi_{sH} - kT}} - 1 . \tag{12}$$

At low hydrogen concentrations at which $e\varphi_{sH} \approx e\varphi_{s0}$, and $M \ll 1$, the coefficient $\gamma \approx 1$. As n_{H_2} increases, $e\varphi_{sH}$ decreases and M increases, which should lead to a decrease in γ.

In the laboratory conditions or in industrial premises, the hydrogen concentration in the air is usually determined at $A \neq 0$. In this connection, we consider the possible effect of the adsorption of water molecules on the energy band bending on the surface of the SnO_2 microcrystals.

A possible variant of dissociation of an H_2O molecule upon adsorption on the SnO_2 surface coated with the dispersed layers of Pt and Pd is one, in which a hydrogen atom and a neutral OH group are formed. In this case, hydroxyl groups desorb from the surface of SnO_2, while hydrogen atoms interacting with O^- ions create hydroxyl groups, whose charge state is determined by the function f_{tOH}. Thus, the problem of the effect of water molecules on $e\varphi_{s0}$ is analogous to the problem considered above. The only difference is that under the dissociation of an H_2O molecule, one hydrogen atom is formed, whereas under the dissociation of an H_2 molecule, two hydrogen atoms are formed. In addition, the degrees of dissociation of these molecules may differ.

Carrying out calculations similar to those performed for the process of adsorption of hydrogen molecules, we obtain

$$e\varphi_{s0}(n_{H_2O}) = \frac{e\varphi_{s0} - kT}{(1 + \eta_{H_2O}\gamma_{H_2O}n_{H_2O})^2} + kT , \tag{13}$$

where $\eta_{H_2O} = r_{H_2O} \cdot \eta_{OH}$ is the coefficient characterizing the effectiveness of the effect of adsorption of H_2O molecules on the surface density of O^- ions and $r_{H_2O} \leq 1$. The expressions for γ_{H_2O} and M_{H_2O} are similar to Eqs. (11) and (12).

When hydrogen is added to the humid clean air, the process of formation of hydroxyl groups on the surface of SnO_2 will continue, causing a further reduction in the bending of the energy bands. The regularities of this process can be described by Eqs. (10)–(12) by replacing $e\varphi_{s0}$ by $e\varphi_{s0}(A)$ and G_H/G_0 by $G_H(A)/G_0(A)$. Taking this fact into account, we use the following formula to analyze the experimental data:

TABLE 1. Dependence of the Sensors' Characteristics on the Absolute Humidity

The sensor number	A, g/m^3	$e\varphi_{s0}(A)$, eV	$M(n_{H_2} = 1, A)\cdot 10^3$	$m(A)$
	0	0.65	9.7	–
	3.9	0.60	8.1	0.29
1	6.8	0.57	7.2	0.22
	10.9	0.55	5.7	0.18
	17.7	0.51	4.3	0.13
	0	0.60	11.4	–
	3.9	0.58	10	0.3
2	6.8	0.54	8.9	0.25
	10.9	0.52	7.6	0.23
	17.7	0.49	5.5	0.18

$$M = \sqrt{\frac{e\varphi_{s0}(A) - kT}{e\varphi_{sH}(A) - kT}} - 1 = \eta_{Hr}\,\gamma(n_{H_2})\,n_{H_2}. \tag{14}$$

It follows from Eqs. (10)–(12).

2. EXPERIMENTAL RESULTS

2.1. Dependence of the sensor characteristics on the hydrogen concentration and humidity level of the gas mixture

Investigations of the dependence of $e\varphi_{sH}$ on n_{H_2} in the range from 10 to 10^3 ppm were carried out for four values of A: 3.9, 6.8, 10.9, and 17.7 g/m^3. At $T_2 = 673$ K, relative humidity values of clean air equal to 19, 33, 53, and 82% correspond to these values of A, respectively. All the measurements needed to determine $e\varphi_{s0}(A)$ and $e\varphi_{sH}(A)$ were performed in the thermo-cyclic mode at $T_2 = 673$ K and $T_1 = 473$ K. For all A, the values of $e\varphi_{s0}(A)$ were determined (Table 1). To calculate $e\varphi_{s0}(0)$, extrapolation of the dependence of $e\varphi_{s0}$ on A to $A = 0$ was used.

An analysis of the results obtained showed that starting from $n_{H_2} = 10$ ppm, $\log M$ linearly increases with $\log n_{H_2}$ (Fig. 1, curve 1) for all values of A. In this case, $d(\log M)/d(\log n_{H_2}) < 1$. It is established that such a dependence of $\log M$ on $\log n_{H_2}$ is observed up to $n_{H_2} = 5\cdot 10^3$ ppm. It can be seen from Eq. (14) that an increase of M with increasing n_{H_2} is due to a decrease of $e\varphi_{sH}$. For all values of A, $e\varphi_{sH}$ decreases by approximately 3.2 to 3.6 times with the change of n_{H_2} from 10 to 10^3 ppm. For example, for $A = 6.8$ g/m^3, $e\varphi_{sH}$ decreases from 0.53 to 0.15 eV for the sensor No. 1, and for sensor No. 2, it decreases from 0.45 to 0.14 eV.

At $\eta_{Hr} = $ const, the linear increase of $\log M = \log\eta_{Hr} + \log(\gamma(n_{H_2})\,n_{H_2})$ with $\log n_{H_2}$ at $d(\log M)/d(\log n_{H_2}) < 1$ can be observed only, if $\gamma(n_{H_2})$ decreases by the power law $\gamma \sim n_{H_2}^{-m}$ with the exponent $m < 1$. Taking this fact into account, the dependence of γ on n_{H_2} can be described by the expression

$$\gamma(n_{H_2}) = \gamma(n_{H_2} = 1)(n_{H_2}/n_{H_2} = 1)^{-m}, \tag{15}$$

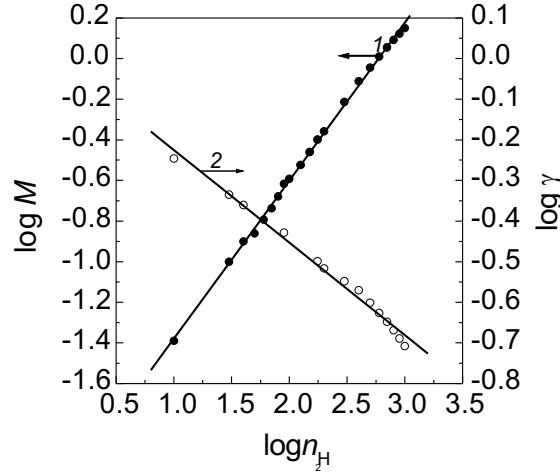where $\gamma(n_{H_2} = 1)$ is the value of the coefficient at $n_{H_2} = 1$ ppm.

Fig. 1. Dependences of $\log M$ (1) and $\log \gamma$ (2) on $\log n_{H_2}$ at $A = 6.8$ g/m³.

Extrapolation of curve 1 in Fig. 1 to $\log n_{H_2} = 0$ allows to determine $\log M(n_{H_2} = 1)$ and calculate $M(n_{H_2} = 1)$ = $\eta_{Hr} \cdot \gamma(n_{H_2} = 1) n_{H_2} = 1$. Taking into account this equation and using Eq. (14), we obtain

$$M(n_{H_2}) = M(n_{H_2} = 1)\left(\frac{n_{H_2}}{n_{H_2} = 1}\right)\left(\frac{\gamma(n_{H_2})}{\gamma(n_{H_2} = 1)}\right). \tag{16}$$

Substituting Eq. (15) in Eq. (16), we have

$$M(n_{H_2}) = M(n_{H_2} = 1)(n_{H_2} / n_{H_2} = 1)^{1-m}. \tag{17}$$

Hence,

$$\log M(n_{H_2}) = \log M(n_{H_2} = 1) + (1 - m)\log n_{H_2}. \tag{18}$$

Thus, from the plot depicting the dependence of $\log M$ on $\log n_{H_2}$, we can determine $M(n_{H_2} = 1)$ and the exponent m. The results of calculations of these values are presented in Table 1.

From the data presented in Table 1, it is evident that for all values of A, $M(n_{H_2} = 1) \ll 1$. Hence, in accordance with Eq. (11), $\gamma(n_{H_2} = 1) \approx 1$. Taking this equation into account, we obtain from Eq. (16) $\gamma(n_{H_2}) = \left(M(n_{H_2}) n_{H_2} = 1\right) / \left(M(n_{H_2} = 1) n_{H_2}\right)$. The results of the calculation (Fig. 1, curve 2) showed that with an increase in n_{H_2} from 10 to 10^3 ppm, $\gamma(n_{H_2})$ for the sensor No. 1 decreases from 0.55 to 0.19. In this case, $d(\log M)/d(\log n_{H_2}) = m = 0.22$, which coincides with the value of m obtained from the dependence of $\log M$ on $\log n_{H_2}$. For the sensor No. 2, we have $\gamma(10$ ppm$) = 0.56$, $\gamma(10^3$ ppm$) = 0.16$, and $m = 0.25$.

Using the obtained values of $M(n_{H_2})$ and $\gamma(n_{H_2})$, we can calculate the function f_{tOH} with the help of Eq. (11). It is found as a result of these calculations that with the increase in n_{H_2} from 10 to 10^3 ppm, $f_{tOH} = N_{OH^-}/N_{OH}$ decreases at $A = 6.8$ g/m³ from 0.90 to 0.36 for both sensors. Thus, at low concentration of hydrogen in the gas mixture, most of the hydroxyl groups on the SnO_2 surface have a negative charge.
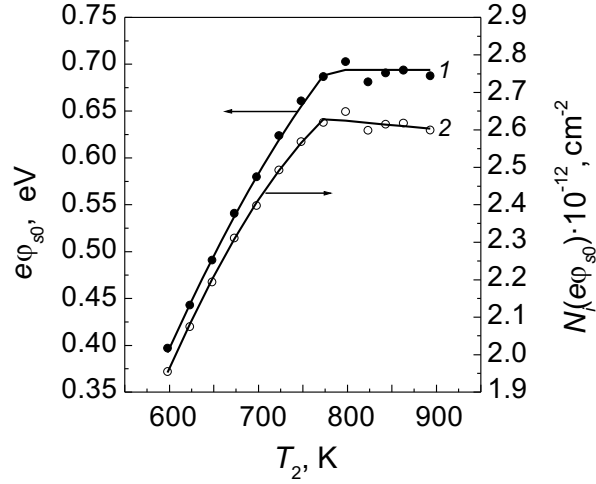
Fig. 2. Temperature dependences of $e\varphi_{s0}$ (*1*) and $N_i(e\varphi_{s0})$ (*2*) at $A = 7$ g/m^3.

An analysis of the experimental results showed that the observed dependence $M(n_{H_2} = 1)$ on A (see Table 1) is caused by the decrease in $e\varphi_{s0}(A)$ and $G_H(A)/G_0(A)$ with increasing humidity level of the gas mixture. Due to this, in the region of low hydrogen concentrations ($n_{H_2} \leq 100$ ppm), $M(n_{H_2})$ decreases with increasing A, while in the region of large concentrations, it increases. As a result, the slope of curve *1* in Fig. 1*d* $(\log M(n_{H_2}))/d(\log n_{H_2}) = 1 - m$ increases with increasing A, and m decreases. The dependence of $M(n_{H_2} = 1)$ on A is described by the expression

$$M(n_{H_2} = 1, A) = M(n_{H_2} = 1, A = 0) - \frac{dM(n_{H_2} = 1, A)}{dA} A, \tag{19}$$

where $dM/dA = 0.33 \cdot 10^{-3}$ m^3/g and $M(n_{H_2} = 1, A = 0)$ are $9.7 \cdot 10^{-3}$ and $11.4 \cdot 10^{-3}$ for the sensors Nos. 1 and 2, respectively.

After the determining $M(n_{H_2} = 1)$ and m, the thin-film sensor based on tin dioxide can be used to determine n_{H_2} in the gas mixture under study using Eq. (17). For this, it is necessary to determine only $M(n_{H_2}, A)$, but for the same value of A, at which the sensor calibration was carried out. This requirement for $A \neq$ const can be fulfilled in a small time interval between the end of the sensor calibration and the measurements of $e\varphi_{s0}(A)$ and $G_H(A)/G_0(A)$ needed to calculate $e\varphi_{sH}(A)$ and $M(n_{H_2}, A)$.

2.2. Temperature dependences of characteristics of sensors

One of the most important characteristics of sensors is $e\varphi_{s0}(N_i, N_d)$. The results of the experiment showed that with an increase of T_2 from 598 to 773 K, $e\varphi_{s0}$ increases from 0.40 to 0.69 eV according to the sublinear law (Fig. 2, curve *1*). Taking into account high values of T_2 and $e\varphi_{s0}$, we assume that in the SCR of the sensor, the donor impurity (shallow and deep) is completely ionized, that is, $N_d =$ const in the entire temperature range, where the experiment was performed (from 598 to 893 K)

At $N_d =$ const, in accordance with expression (3), the temperature dependence $e\varphi_{s0} - kT$ is proportionate to $(N_i(e\varphi_{s0}))^2$. Calculation using Eq. (3) at $N_d = 10^{18}$ cm^{-3} and $\varepsilon_r = 10$ showed that when the temperature of the sensor increases from 598 to 773 K, $N_i(e\varphi_{s0})$ increases from $1.95 \cdot 10^{12}$ to about $2.62 \cdot 10^{12}$ cm^{-2} (Fig. 2, curve *2*). With a further
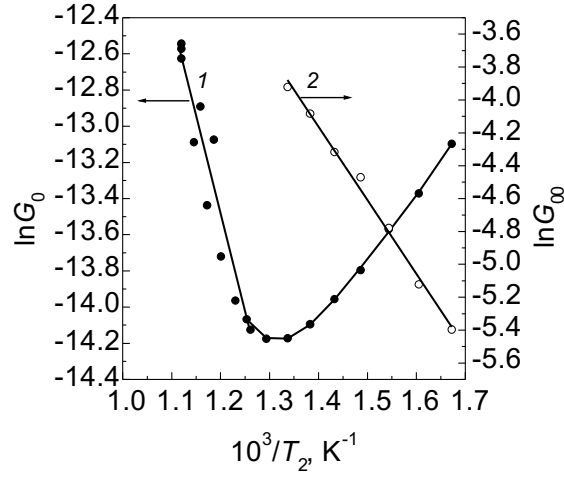
Fig. 3. Dependences of $\ln G_0$ (1) and $\ln G_{00}$ (2) on T_2^{-1} at $A = 6.7–7$ g/m³.

increase of T_2 to 893 K, $N_i(e\varphi_{s0})$ decreases slightly. A similar form of the temperature dependence of the surface density of adsorbed oxygen atoms with a maximum at $T = 773$ K is presented in [6].

The increase of $N_i(e\varphi_{s0})$ at $T_2 > 598$ K is due to the fact that the binding energy of the hydroxyl groups with the adsorption centers is apparently smaller than that of the O^- ions. Therefore, the surface density of hydroxyl groups decreases [6] and the number of adsorption centers for oxygen atoms increases.

For the sensors under study, in whose tin dioxide films the over-barrier electron drift mechanism is realized, the temperature dependence of the conductivity is described by the following expression [3]:

$$G_0(T) = G_{00}(T)\exp\left(-e\varphi_{s0}(T)/(kT)\right),\tag{20}$$

where $G_{00}(T) \sim n_0(T)$ and $n_0(T)$ is the equilibrium electron concentration in SnO_2 microcrystals.

Polycrystalline films of tin dioxide appear to be partially compensated n-type semiconductors. In this case, $n_0(T) \sim T^{3/2}\exp(-\Delta E_d/(kT))$, where ΔE_d is the activation energy of the ionization process of donor impurity. Substituting $n_0(T)$ in the expression for $G_{00}(T)$ [3], we obtain

$$G_{00}(T) = K_0 \exp\left(-\Delta E_d/(kT)\right),\tag{21}$$

where $K_0 \approx$ const can slightly depend on T. After substitution of Eq. (21) in Eq. (20), we have

$$G_0(T) = K_0 \exp\left(-\frac{e\varphi_{s0}(T)+\Delta E_d}{kT}\right).\tag{22}$$

It follows from the experimental results that the dependence of $\ln G_0$ on T_2^{-1} passes through the broad minimum at $T_2 = 748–773$ K (Fig. 3, curve 1). For ceramic sensors having the shape of a bead, a maximum is observed in the dependence of $\ln R$ on T^{-1}, where R is the resistance at $T = 735$ K [4].

Numerical estimates showed that when the sensor temperature increases from 598 to 773 K, $\exp\left(-e\varphi_{s0}(T_2)/(kT_2)\right)$ decreases by 13.58 times due to the increase of $e\varphi_{s0}(T_2)$. In the same temperature range, G_0 decreases only by 2.94 times, which indicates an increase in G_{00} with an increase in T_2. The calculation using Eq. (20) showed that the temperature dependence of G_{00} can be described by Eq. (21) at $\Delta E_d = (0.39 \pm 0.01)$ eV (Fig. 3, curve 2). Hence, the conclusion follows that the SnO_2 microcrystals contain a deep donor impurity.
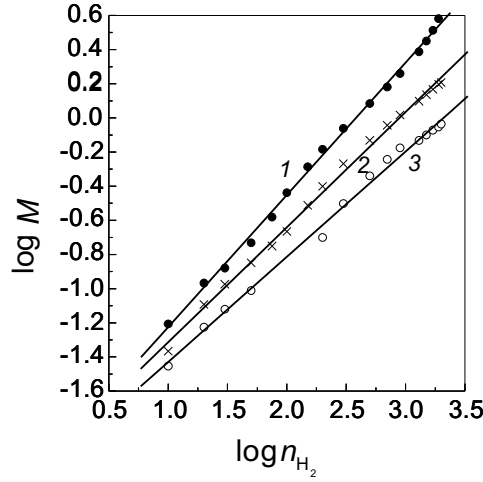
Fig. 4. Dependences of $\ln M$ on $\log n_{H_2}$ at $A \approx 7$ g/m^3 and T_2, K: 623 (*1*), 673 (*2*), and 773 (*3*).

Figure 2 (curve *1*) shows that at $T_2 = 773$ K, $e\varphi_{s0}$ reaches a maximum value of $e\varphi_{s0M} = 0.69$ eV and does not depend on the sensor temperature up to 893 K. Taking this into account, the temperature dependence of G_0 at $T_2 > 773$ K should be described by Eq. (22) at the activation energy $\Delta E_a = e\varphi_{s0M} + \Delta E_d = (1.08 \pm 0.05)$ eV. An estimate of the activation energy of the temperature dependence of G_0 with the help of curve *1* in Fig. 3 (at $10^3/T \leq 1.294$ K^{-1}) gave approximately the same result $\Delta E_a = (1.01 \pm 0.08)$ eV.

The influence of the sensor temperature T_2 in the range from 623 to 773 K on the dependence of $\log M$ on $\log n_{H_2}$ is shown in Fig. 4. It follows from the results obtained that $M(n_{H_2} = 1)$ is practically independent of T_2 and m increases with increasing temperature. For the sensor No. 1, $M(n_{H_2} = 1)$ is $(8 \pm 1) \cdot 10^{-3}$ and for the sensor No. 2, it is $(9.6 \pm 0.4) \cdot 10^{-3}$. With an increase in T_2 from 623 to 773 K, m increases from about 0.23 to 0.39.

In accordance with Eq. (14), $M(n_{H_2} = 1, T_2) = \eta_{Hr}(T_2) \cdot \gamma(n_{H_2} = 1, T_2)$, where $\eta_{Hr} \sim r\sqrt{T_2} \exp\left((E_{d,OH} - E_{aH})/(kT_2)\right)$ and $\gamma(n_{H_2} = 1, T_2) \approx 1$, because $M(n_{H_2} = 1, T_2) \ll 1$ (see Eq. (11)). If in the high-temperature region 623–773 K, the degree of dissociation of H$_2$ molecules upon adsorption on the SnO$_2$ surface $r =$ const, then, independence of η_{Hr} on T_2 is due to the fact that a weak growth of this coefficient due to $\sqrt{T_2}$ is compensated by a decrease of $\exp\left((E_{d,OH} - E_{aH})/(kT_2)\right)$.

The data in Fig. 4 indicate that for any $n_{H_2} > 1$ ppm, an increase in T_2 leads to a decrease in $M(n_{H_2})$. To explain this fact, we write Eq. (12) in the following form:

$$M(n_{H_2}) = \sqrt{\frac{1}{1-\Omega} - 1}, \tag{23}$$

where $\Omega = kT_2\ln(G_H(T_2)/G_0(T_2))/(e\varphi_{s0}(T_2) - kT_2)$. It follows from the obtained experimental data that at $n_{H_2} = 2 \cdot 10^3$ ppm with increasing T_2 from 623 to 773 K, Ω decreases from 0.94 to 0.73 for the sensor No. 1 and it decreases from 0.93 to 0.72 for the sensor No. 2. Due to this, $M(T_2)$ decreases from 3.2 to 0.92 and from 2.8 to 0.9 for the sensors Nos. 1 and 2, respectively. Since η_{Hr} does not depend on the sensor temperature, the observed decrease of $M(T_2)$ is caused by the change in the coefficient γ (see Eq. (15)) due to an increase in the exponent m in the above limits (0.23–0.39).

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CONCLUSIONS

Based on the analysis of the experimental data, the model of the process of dissociative adsorption of molecular hydrogen on the SnO_2 surface coated with adsorbed oxygen ions O^- is proposed for the operation of the sensor in thermo-cyclic mode with a temperature drop from $T_1 = 473$ K to $T_2 = 598-893$ K.

The model assumes that: 1) the hydrogen atoms are adsorbed only on the centers occupied by O^- ions; 2) the charge state of the hydroxyl groups formed in this case is determined by the distribution function of electrons f_{tOH} over the local levels of OH groups in the forbidden band of SnO_2; 3) only neutral OH groups can desorb from the SnO_2 surface; 4) the absolute humidity A of the gas mixture clean air + H_2, in which the sensor is located, is zero.

As a result of the solution of the kinetic equation for the hydrogen adsorption process taking into account the above statements, the expression is obtained that describes the dependence of the surface density of hydroxyl groups N_{OH} on the hydrogen concentration n_{H_2} in the gas mixture (see Eq. (8)). This allowed in the expression for the energy band bending on the SnO_2 surface $e\varphi_{sH}$ (see Eq. (10)) to take into account that its value depends not only on the surface density of oxygen ions O^- ($N_i(e\varphi_{sH})$), but also on the negatively charged hydroxyl groups ($N_{OH^-} = f_{tOH} \cdot N_{OH}$).

If there is no hydroxyl groups on the SnO_2 surface ($f_{tOH} = 0$), then, it follows from the expression for $e\varphi_{sH}$ that $\sqrt{e\varphi_{s0}(T_2) - kT_2 / e\varphi_{sH}(T_2) - kT_2} - 1 = M \sim n_{H_2}$ (see Eq. (1)). However, in accordance with the experimental data obtained, $M \sim n_{H_2}^{1-m}$, where $m < 1$ (see Eq. (17)). This fact indicates that the formation of OH^- groups on the SnO_2 surface slows down the decrease of $e\varphi_{sH}$ with increasing n_{H_2}.

It is shown that the theoretical formulas describing the characteristics of the sensors are valid at any humidity level of the gas mixture. This made it possible to carry out a detailed analysis of the experimental dependences of $e\varphi_{s0}$, $e\varphi_{sH}$, and M on the absolute humidity of the gas mixture.

The experimentally established dependence of M on n_{H_2} at A = const can be used after preliminary calibration of the sensor to determine the hydrogen concentration in the examined gas mixture. Since the humidity level of the gas mixture can change over time, the characteristics of the sensor, required for the calculation of n_{H_2}, should be the determined immediately after its calibration. In this case, the absolute humidity of the gas mixture, in which the calibration is carried out, and that of the test gas mixture must have the same values.

The results of studying the dependences of $e\varphi_{s0}$, M, and the sensor conductivity G_0 in an atmosphere of clean air on its temperature T_2 during the heating are presented. It is shown that the sublinear growth of $e\varphi_{s0}$ with increasing T_2 in the range from 598 to 773 K is due to an increase in $N_i(e\varphi_{s0}(T_2))$ on the SnO_2 surface (see Fig. 2). It follows from the analysis of the temperature dependence of G_0 (see Fig. 3) that the SnO_2 microcrystals contain a deep donor impurity, whose activation energy is 0.39 eV. The experimental data for M (see Fig. 4) indicate that the coefficient $\eta_{Hr} = r \cdot \eta_{OH}$ is independent of the sensor temperature T_2, where r is the degree of dissociation of H_2 molecules on the SnO_2 surface and 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 formed.

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