

PHYSICS OF SEMICONDUCTORS AND DIELECTRICS

THE EFFECT OF WATER VAPOR ON THE ELECTRICAL PROPERTIES AND SENSITIVITY OF THIN-FILM GAS SENSORS BASED ON TIN DIOXIDE

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The results of theoretical and experimental studies into the effect of water vapor on the electrical conductance of a gas sensor and the sensor response to hydrogen action are discussed. A relation describing the dependence of electrical conductance G_0 on absolute humidity in the pure air is derived using a hypothesis of the presence of space-charge regions depleted of electrons between the SnO_2 grains in a polycrystalline tin dioxide film. Due to dissociative chemisorption of water molecules, the energy-band bending at the SnO_2 grain interfaces decreases and the oxygen-vacancy concentration in the grains increases, resulting in an increase in G_0 . An equation for the sensor response to hydrogen action is derived (the G_1/G_0 ratio, where G_1 is the sensor conductance in a gas mixture containing molecular hydrogen). The expression describes the dependence of G_1/G_0 on the hydrogen concentration n_{H_2} in the interval $50\text{--}6\cdot 10^3$ ppm, band bending at the SnO_2 grain interface, and sensor temperature. The dependences of the sensor conductance, highest possible conductance, and energy-band bending on temperature and absolute humidity resulting from processing of the experimental data are in good agreement with the theoretical predictions.

INTRODUCTION

It is shown in a number of studies that the presence of water vapor in gas mixtures significantly affects the conductance and sensitivity to gas of sensors based on tin dioxide. However, no physical model describing the effect of gas-mixture humidity on sensor characteristics is developed so far. In this work, an attempt is made to solve this problem.

A physical model of a hydrogen sensor based on a polycrystalline tin-dioxide film is developed in [1]. In this model, a tin-dioxide film is assumed to consist of SnO_2 microcrystals interconnected by conductance bridges of the same material. Electrical properties of the sensors and their sensitivity to gas depend on these bridges, since they exhibit high resistance. However, no effect of humidity on sensor characteristics is considered in this theory. In addition, due to refinement of the technology, we developed sensors highly sensitive to hydrogen, whose characteristics cannot be described using the model put forward in [1].

In view of these facts, the effect of water vapor on the characteristics of hydrogen sensors will be considered using the model assuming that in the presence of oxygen, SnO_2 grains in tin-dioxide films are separated by the Schottky-barrier layers [2] (Fig. 1). This model allows adequate description of experimental data.

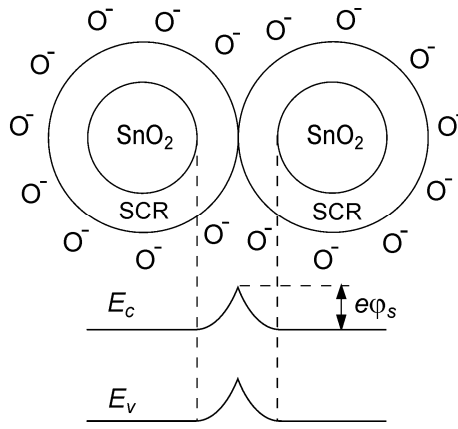


Fig. 1. A model of an intergrain barrier in an SnO₂ film.

CONDUCTANCE AND RESPONSE OF SENSORS TO HYDROGEN IN THE PRESENCE OF WATER VAPOR IN GAS MIXTURES

Let us assume that the electron exchange between SnO₂ grains takes place due to thermal electron emission alone. In this case, the conductance of a tin-dioxide film can be written in as [3]

$$G_0 = ge\mu_n n_0 \exp\left(-\frac{e\phi_s}{kT}\right), \quad (1)$$

where g is the geometrical factor depending on the parameters of the film and SnO₂ grains and their contacting areas, e is the electron charge, n_0 and μ_n are the electron concentration and mobility in grains, respectively, $e\phi_s$ is the energy-band bending at the grain boundary, ϕ_s is the surface potential, k is the Boltzmann constant, and T is the absolute temperature of the sensor.

We also assume that the formation of space charge regions (SCR) depleted of electrons around the SnO₂ grains is due to oxygen atom adsorption alone. In the sensors under study, a discontinuous platinum layer deposited on the tin-dioxide film enhances dissociation of O₂ molecules into atoms. According to [2–4], oxygen is adsorbed on the SnO₂ surface in the form of O⁻ ions at $T > 423$ – 523 K. In the case of heavy depletion in the SCR, the surface concentration of oxygen ions is $N_{O^-} = N_i = N_d \cdot d$, where N_d is the donor impurity concentration in SnO₂ and d is the SCR width.

Taking this into account, for a dry gaseous mixture (absolute humidity $A = 0$), we obtain from the solution to the Poisson equation [2]

$$e\phi_s(0) = \frac{e^2 N_i^2}{2\epsilon_r \epsilon_0 N_d}, \quad (2)$$

where ϵ_r is the relative permittivity of SnO₂ and ϵ_0 is the dielectric constant.

In [5, 6], concerning the effect of water vapor on the characteristics of gas sensors, it is noted that tin-dioxide conductance increases going from dry to humid air. Equation (1) shows that an increase in G_0 can result from either a decrease in $e\phi_s$ or an increase in the electron concentration in the SnO₂ grains, depending on the types of reactions on the SnO₂ surface under adsorption of water molecules.

By analogy with [7], we expect that at high temperatures, a water molecule is chemisorbed on the SnO₂ surface as a result of dissociation into an OH⁻ hydroxyl group and an H⁺ proton. The hydroxyl group is localized on the surface atom of tin lattice, whereas proton is captured by an O⁻ to form a neutral OH group. Upon neutralization of the OH⁻ group (an electron transits into the SnO₂ conduction band), both hydroxyl groups can be desorbed. Thus, under adsorption of an H₂O molecule on the SnO₂ surface, two hydroxyl groups are formed and the negative charge of the O⁻ ion disappears, resulting in a decrease in $e\varphi_s$. In so doing, the rate of neutralization of the OH⁻ groups should be much higher than that of desorption of the neutral groups.

The concentration N_{g1} of hydroxyl groups of both types is equal to that of protons adsorbed on the centers occupied by O⁻ ions. This makes it possible to use a well-known solution to the kinetic equation for gas particle adsorption to determine N_{g1} . For a steady state, we have [8]

$$N_{g1} = \frac{N_i(\alpha/\nu)\exp[\Delta E_p/(kT)]mP}{1 + (\alpha/\nu)\exp[\Delta E_p/(kT)]mP}. \quad (3)$$

Here (α/ν) is a quantity proportional to the ratio of probabilities of proton adsorption and desorption per unit time, $\Delta E_p = E_{p,des} - E_{p,ads}$, where $E_{p,des}$ and $E_{p,ads}$ are the activation energies of proton desorption and adsorption, P is the partial water vapor pressure, and m is the coefficient taking into account the fact that protons can adsorb not only on the centers occupied by O⁻ ions ($m < 1$). It is assumed in Eq. (3) that all water molecules approaching the sensor surface dissociate, and the concentration of protons is equal to that of H₂O molecules.

In accordance with [9], we have

$$P = 126(1 + 3.67 \cdot 10^{-3} t^0)A, \quad (4)$$

where A is the absolute humidity in g/m³, if P is expressed in Pa, and t^0 is the water vapor temperature in Celsius degrees. Substituting Eq. (4) into Eq. (3) and replacing N_i for $N_i - N_{g1}$ in Eq. (2), we obtain

$$e\varphi_s(A) = \frac{e\varphi_s(0)}{(1 + \chi A)^2}, \quad (5)$$

where

$$\chi = 126m(1 + 3.67 \cdot 10^{-3} t^0)(\alpha/\nu)\exp[\Delta E_p/(kT)]. \quad (6)$$

Thus, at $T = \text{const}$, $e\varphi_s(A)$ should decrease with increase in the absolute humidity of a gaseous mixture.

It is pointed out in [6, 7] that oxygen lattice vacancies can be formed due to the dissociative adsorption of water molecules. Oxygen vacancies are formed as a result of interaction between protons and oxygen lattice atoms. These vacancies diffuse deep into the SnO₂ grains, where they act as donors. Let us designate the concentration of electrons generated due to ionization of oxygen vacancies as n_V . With allowance for the foregoing facts, Eq. (1) can be rewritten as follows:

$$G_0 = G_{0m} \exp(-\beta N_{ib}^2), \quad (7)$$

where $\beta = e^2 / (2\varepsilon_r \varepsilon_0 N_d kT)$, $N_{ib} = N_i / (1 + \chi A)$ is the O⁻ ion surface concentration at a given humidity level.

$$G_{0m} = ge\mu_n(n_0 + n_V), \quad (8)$$

where G_{0m} is the maximum possible conductance of the tin-dioxide film at $e\varphi_s = 0$.

Under exposure of our sensor to a gaseous mixture containing hydrogen, H_2 molecules dissociate on the sensor surface into atoms which further adsorb on the centers occupied by O^- ions. The surface reaction corresponding to this process is described by the equation



where OH^- is desorbed in the form of a neutral hydroxyl group upon preliminary neutralization, and the electron transits into the SnO_2 conduction band. If the rate of neutralization of OH^- groups significantly exceeds that of desorption of neutral groups, adsorption of hydrogen atoms should result in a decrease in N_{ib} and an increase in the sensor conductance.

The surface concentration N_{g2} of hydroxyl groups resulting from adsorption of hydrogen atoms on the centers occupied by O^- ions can be written using Eq. (3). To this end, let us replace N_i by N_{ib} and ΔE_p by $\Delta E = E_{des} - E_{ads}$, where E_{des} , E_{ads} are the activation energies of hydrogen-atom desorption and adsorption, respectively. We express the partial pressure of hydrogen in the gaseous mixture using the concentration of H_2 molecules ($P_{H_2} = kTn_{H_2}$).

With allowance for the foregoing substitutions, we obtain

$$N_{g2} = \frac{N_{ib}\eta n_{H_2}}{1 + \eta n_{H_2}}, \quad (10)$$

where

$$\eta = m(\alpha/v)\exp[\Delta E/(kT)]kT. \quad (11)$$

When writing the relation for the sensor conductance G_1 in the hydrogen-containing gaseous mixture, we take into account the fact that the O^- -ion concentration decreases from N_{ib} down to $N_{ib} - N_{g2}$ and thus, we derive

$$G_1 = G_{0m} \exp(-\beta(N_{ib} - N_{g2})^2). \quad (12)$$

Dividing Eq. (12) by Eq. (7), we have

$$G_1 / G_0 = \exp(\beta N_{g2} (2N_{ib} - N_{g2})). \quad (13)$$

Substituting Eq. (10) into Eq. (13) and taking into account Eqs. (2) and (5), we obtain

$$G_1 / G_0 = \exp\left[\frac{e\varphi_s(A)}{kT} \frac{\eta n_{H_2}}{(1 + \eta n_{H_2})} \left(2 - \frac{\eta n_{H_2}}{1 + \eta n_{H_2}}\right)\right]. \quad (14)$$

Equation (14) shows that at low hydrogen concentrations, where $\eta n_{H_2} \ll 1$, the exponent index and G_1/G_0 ratio increase according to the linear and exponential laws, respectively, with the increase in n_{H_2} . At high hydrogen concentrations, where $\eta n_{H_2} \gg 1$, G_1/G_0 tends to the highest possible value $(G_1/G_0)_{\max} = \exp[e\varphi_s(A)/(kT)]$. By

and large the dependence of G_1/G_0 on n_{H_2} is described by a curve, where two regions can be marked out, namely: the region of superlinear dependence of G_1/G_0 on n_{H_2} (low hydrogen concentrations) and the region of sublinear dependence of G_1/G_0 on n_{H_2} (high hydrogen concentrations).

EXPERIMENTAL TECHNIQUE

The technology for producing sensors under study was similar to that described in [10]. The tin-dioxide films were obtained by magnetron sputtering at constant current in the oxygen-argon plasma of a tin target containing 1.5 at.% Sb.

For measurements, the sensor was placed into a 600-ml quartz chamber. Laboratory air was pumped through the chamber and the chamber was hermetically sealed. The required gaseous mixture composition was prepared by injection of a certain portion of hydrogen into the measuring chamber using a special dosing unit. The concentration dependence of sensor conductance was measured by repeated adding the required quantity of hydrogen into the chamber. In so doing, the gaseous mixture in the chamber was constantly stirred using a fan.

In studying the dependence of sensor conductance on the humidity of gaseous mixture, the zeolite-dried air was pumped through the chamber to obtain low values of the relative (RH) and absolute humidity. Then, to increase the humidity, the air entering the chamber was pumped through the bubbler for a certain time. Relative humidity was determined using an HIH-400 capacitance detector placed in the measuring chamber. The absolute humidity of the gaseous mixture was calculated by the formula adopted in the World Standardizing Authority using a metrological calculator designed in the Scientific-Industrial Complex "Mikrofor" (Moscow).

The dependence of sensor conductance on the temperature, hydrogen concentration, and humidity of gaseous mixture were studied using an automatized test unit, which allowed us to measure the G_1 values every 2 s. To verify the theory proposed in the first section of the paper, we used the stationary G_1 values. The experiments show that the time required for establishing the stationary G_1 value significantly depends on the sensor temperature and hydrogen concentration. In the temperature range from 523 to 723 K, this time can be reduced from about of 10 minutes to some tens of seconds at $n_{H_2} = 10^3$ ppm.

TEMPERATURE DEPENDENCE OF SENSOR CHARACTERISTICS

Figure 2 shows that the dependence of G_1/G_0 on n_{H_2} (1) corresponds to the theoretical predictions. At $n_{H_2} < 900$ ppm, a superlinear increase in G_1/G_0 with increase in hydrogen concentration is observed. At $n_{H_2} > 900$ ppm, the dependence of G_1/G_0 on n_{H_2} becomes sublinear.

To determine the theory parameters, it is convenient to analyze the dependence of $\ln(G_1/G_0)$ on n_{H_2} (2). At high n_{H_2} , for which $\eta n_{H_2} \gg 1$, $\ln(G_1/G_0)$ achieves the highest possible value $\ln(G_1/G_0)_{\max} = e\varphi_s(A)/(kT)$. For the sensors under study, the highest value of $\ln(G_1/G_0)$ is obtained at about $n_{H_2} \geq 6 \cdot 10^3$ ppm.

The experimental data obtained at $RH \cong 25\%$ ($A \cong 5.4$ g/m³) show that $e\varphi_s(A)$ linearly increases with increase in temperature from 523 to 723 K (Fig. 3, 1).

In accordance with Eqs. (2) and (5), this temperature dependence of $e\varphi_s(A)$ can be due to the sublinear increase in $N_{ib} = N_i/(1 + \chi A)$ ($N_{ib} \sim T^{1/2}$) at $T > 523$ K. The sublinear dependence of N_{ib} on T is supported by the data obtained in [4]. The numerical estimations show that at $N_d = 10^{18}$ cm⁻³ and $\varepsilon_r = 13$ [2, 11], N_{ib} increases from $2 \cdot 10^{12}$ to $2.7 \cdot 10^{12}$ cm⁻² in the considered temperature range. These values should be considered as the approximate ones, since N_d is unknown in the sensors under study, however, the value of N_d can agree by the order of magnitude with the data of [11].

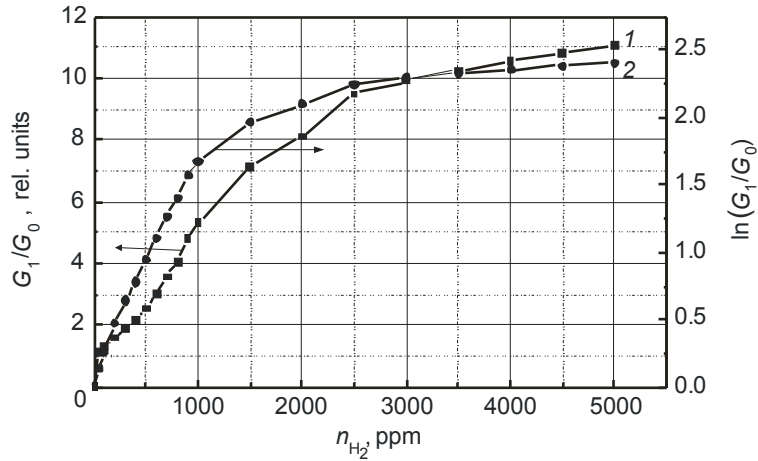


Fig. 2. Sensor response G_1/G_0 (1) and $\ln(G_1/G_0)$ (2) versus hydrogen concentration at $T = 573$ K and $A = 6.9$ g/m³.

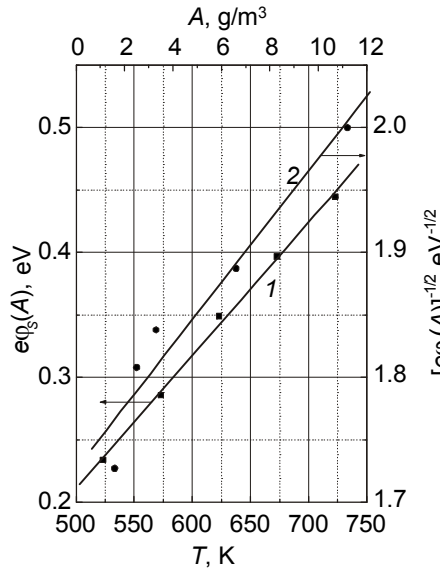


Fig. 3. Temperature dependence of the energy-band bending $e\varphi_s(A)$ at $A = 5.4$ g/m³ (1) and the dependence of $[e\varphi_s(A)]^{-1/2}$ on A (2).

In the room atmosphere, the sensor conductance G_0 decreases by a factor of 7.3 with increase in T from 523 to 723 K (Fig. 4, 1). The temperature dependence of the highest possible conductance G_{0m} is much weaker (Fig. 4, 2). These data show that the observed decrease in G_0 with increase in T is mainly due to increase in $e\varphi_s(A)$. In accordance with Eq. (7), $G_0 = G_{0m} \exp(-\beta N_{ib}^2) = G_{0m} \exp[-e\varphi_s(A)/(kT)]$. As T increases from 523 to 723 K, $e\varphi_s(A)$ increases from 0.23 to 0.44 eV, whereas $\exp[-e\varphi_s(A)/(kT)]$ decreases by a factor of 7.

The temperature dependence of G_{0m} cannot be unambiguously interpreted. A weak increase in G_{0m} with temperature at $T < 630$ K can be due to ionization of donor impurity atoms (Sb) or oxygen vacancies. At high temperatures, the intensity of adsorption of water molecules drastically decreases, which should result in a decrease in

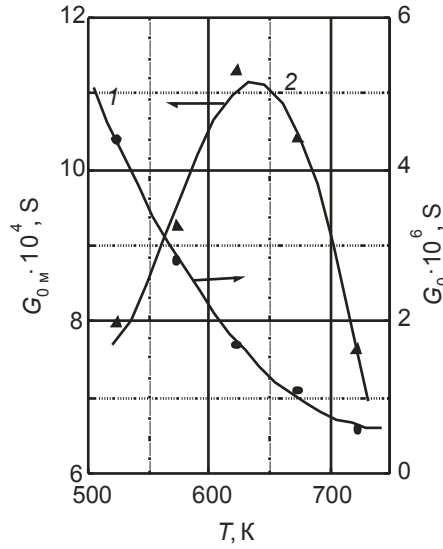


Fig. 4. Temperature dependences of the sensor conductance G_0 (1) and highest possible conductance G_{0m} (2) at $A = 5.4 \text{ g/m}^3$.

the concentration of oxygen vacancies in the SnO_2 grains [6, 7]. Therefore, the decrease in G_{0m} at $T > 630 \text{ K}$ can be caused by decrease both in n_V and μ_n .

In accordance with Eq. (14), the theory parameter η was calculated using the formula

$$\eta = \frac{1}{n_{\text{H}_2}} \left[\sqrt{1 + \frac{\ln(G_1/G_0)}{e\varphi_s(A)/(kT) - \ln(G_1/G_0)}} - 1 \right]. \quad (15)$$

The results obtained show that η is independent of n_{H_2} and temperature. In the temperature range from 523 to 723 K at $A \approx 5.4 \text{ g/m}^3$, $\eta = (1.25 \pm 0.07) \cdot 10^{-3} \text{ ppm}^{-1}$. Therefore, in accordance with Eq. (11), the product $\exp[\Delta E/(kT)] \cdot kT$ is independent of T . This, in turn, is indicative of low ΔE , that is, E_{des} differs little from E_{ads} in the case of adsorption of a hydrogen atom on the center occupied by O^- ions.

DEPENDENCE OF SENSOR CHARACTERISTICS ON THE ABSOLUTE HUMIDITY OF A GASEOUS MIXTURE

At $T = 573 \text{ K}$, an increase in the absolute humidity from 1.6 g/m^3 ($RH = 8 \%$) to 11.2 g/m^3 ($RH = 53 \%$) results in a decrease in $e\varphi_s(A)$ from 0.33 down to 0.25 eV. It follows from Eq. (5) that $[e\varphi_s(A)]^{-1/2} = [e\varphi_s(0)]^{-1/2} (1 + \chi A)$. This dependence of $[e\varphi_s(A)]^{-1/2}$ on A is confirmed by experiment (Fig. 3, 2). At $T = 573 \text{ K}$, $e\varphi_s(0) \cong 0.33 \text{ eV}$ and $\chi \cong 1.4 \cdot 10^{-2} \text{ g}^{-1} \cdot \text{m}^3$. The wide scatter of experimental points in Fig. 3 seems to be due to errors in determination of A . At $T = 723 \text{ K}$, $e\varphi_s(0) \cong 0.4 \text{ eV}$ and $\chi \cong 8 \cdot 10^{-4} \text{ g}^{-1} \cdot \text{m}^3$. Drastic weakening of the dependence of $e\varphi_s$ on A with increase in temperature is accounted for by the fact that $\chi \sim \exp[\Delta E_n/(kT)]$ (Eq. (6)). In accordance with Eq. (6), the decrease of χ by a factor of 17.5 at $\Delta E_p = 0.63 \text{ eV}$ can take place in the considered temperature interval in the case of weak dependence of (α/v) on T .

At $T = 573 \text{ K}$, the sensor conductance G_0 linearly increases with A

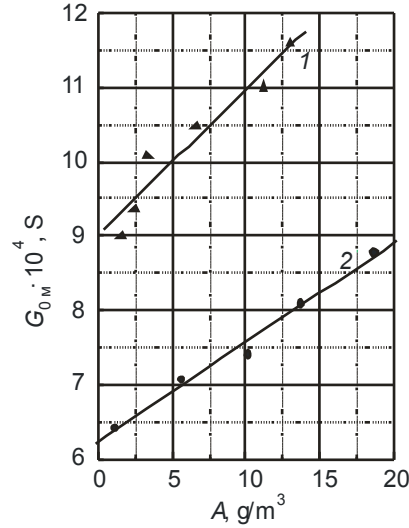


Fig. 5. Dependence of the highest possible sensor conductance G_{0m} on the absolute humidity A at T , K: 573 (1) and 723 (2).

$$G_0(A) = G_0(0)(1 + \gamma_0 A), \quad (16)$$

where $G_0(0) = 5 \cdot 10^{-7}$ S and $\gamma_0 = 0.94 \text{ g}^{-1} \cdot \text{m}^3$. As A increases from 1.6 to 11.2 g/m^3 , G_0 increases by a factor of 6.7. At $T = 723$ K, $G_0(0) = 4 \cdot 10^{-7}$ S, and $\gamma_0 = 0.2 \text{ g}^{-1} \cdot \text{m}^3$. Equations (7) and (8) show that the increase in G_0 with A can be explained by the decrease in N_{ib} or $e\varphi_s(A)$ and increase in n_V . The higher the absolute humidity of the gaseous mixture, the more H_2O molecules are adsorbed on the SnO_2 surface, and the more oxygen vacancies appear [6, 7], which results in an increase in n_V . The highest possible conductance G_{0m} is also linearly increased with increase in A (Fig. 5) as

$$G_{0m}(A) = G_{0m}(0)(1 + \gamma_M A), \quad (17)$$

where $G_{0m}(0) = 9 \cdot 10^{-4}$ S, $\gamma_M = 2.2 \cdot 10^{-2} \text{ g}^{-1} \cdot \text{m}^3$ at $T = 573$ K and $G_{0m}(0) = 6.2 \cdot 10^{-4}$ S, $\gamma_M = 2.3 \cdot 10^{-2} \text{ g}^{-1} \cdot \text{m}^3$ at $T = 723$ K. An increase in G_{0m} with A is caused by an increase in n_V alone, therefore, $\gamma_M \ll \gamma_0$.

Analysis of the experimental data obtained at different T (523 and 723 K) shows that the parameter η is independent of A . This testifies to the fact that the adsorption mechanism of hydrogen atoms on the centers occupied by O^- ions is independent of the humidity of gaseous mixture. In addition, it follows from Eq. (14) at $\eta = \text{const}$, that the dependence of the sensor response G_1/G_0 on the absolute humidity is determined by $e\varphi_s(A)$ alone. The higher the humidity of the gaseous mixture, the lower the response.

CONCLUSION

The results presented in this paper show that the effect of water vapor on the sensor characteristics can be described using the hypothesis of the presence of the Schottky-barrier layers between the SnO_2 grains in a polycrystalline tin-dioxide film. The experimental dependence of the sensor response G_1/G_0 on hydrogen concentration and temperature can be well described by Eq. (14) based on the conception of dissociation of H_2

molecules under interaction with a discontinuous platinum layer on the surface of the SnO₂ film followed by adsorption of H atoms on the centers occupied by O⁻ ions.

The dependence of sensor response on the absolute humidity of the gaseous mixture A is due to dissociative chemisorption of H₂O molecules. The possible variants of corresponding surface reactions are considered in [7]. In the first variant, a water molecule dissociates into a hydroxyl group and an H⁺ proton which is adsorbed on the center occupied by an O⁻ ion. As a result, each H₂O molecule compensates the charge of one O⁻ ion, which decreases $e\varphi_s(A)$ (Eq. (5)) and G_1/G_0 (Eq (14)).

In addition, the protons resulting from dissociation of water molecules interact with the oxygen lattice atoms, which results in the formation of oxygen vacancies [6, 7] which, diffusing into the volume of SnO₂ grains, act as donors. This variant of chemisorption of H₂O molecules results in a linear increase in the highest possible sensor conductance G_{0m} with increase in A (Eq. (17)). The sensor conductance G_0 has the strongest dependence on absolute humidity. An increase in G_0 with A is due to an increase in the electron concentration in the SnO₂ grains and a decrease in $e\varphi_s(A)$.

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