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Modeling of sensor properties for reducing gases and charge distribution in nanostructured oxides: A comparison of theory with experimental data

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ABSTRACT

The theory is developed of sensory response to reducing gases of nanostructured semiconductor oxides such as In_2O_3 with large concentration of electrons in the conduction band. The charge distribution in nanoparticles is determined by the functional relationship between the density of negative and positive charges inside the nanoparticles and electrons on the surface. The capture of conduction electrons by adsorbed oxygen atoms causes redistribution of electrons in the nanoparticles, thereby decreasing the near-surface electron density and the conductivity of the system. Thus, there is a functional relationship between negative charge on the surface and charge structure inside the nanoparticle, which has to be considered. The conditions for the association-dissociation reactions of oxygen molecules on the surface also change. On adsorption of a reducing gas, the O^- ions react with the gas molecules and the electrons are released into the volume of the nanoparticles. The conductivity of the system thereby increases, which constitutes the sensory effect. The radial distributions of the conduction electrons and electrostatic potential in a nanoparticle are here calculated as a function of the hydrogen concentration in the ambient air. A kinetic scheme is developed of chemical reactions corresponding to the above sensory mechanism, and the associated equations are solved. As a result, the theoretical functional relationships of sensitivity to temperature and hydrogen concentration are established. The theoretical results are in good agreement with the experimental data.

1. Introduction

The mechanism of conductometric sensor effect is well known [1–7]. Such sensors typically utilize nanostructured films of semiconductor metal oxides as the sensitive layer. The electronic levels of donor impurities in nanoparticles are located below the bottom of the conduction band [4]. The concentration of conductive electrons occurs as a result of thermal ionization of donor impurities. In air ambience, oxygen molecules are adsorbed on the surface of the nanoparticles and dissociate, and the resulting oxygen atoms effectively capture a significant proportion of the conduction electrons from the bulk of the nanoparticle. This leads to the formation of a negatively charged layer on the surface of the nanoparticle. Consequently, the film conductivity in air is significantly less than the conductivity in vacuum.

If there is a reducing gas in the air ambience, its molecules are also adsorbed on the surface of the nanoparticles and react with the

adsorbed oxygen ions. The reaction products are removed from the surface through the ambient environment, and the electrons are transferred into the bulk of the nanoparticle. The density of electrons in the surface traps decreases, and the density of conductive electrons increases. The conductivity of the film thereby increases, constituting the sensory effect.

Conductometric sensors may be divided into two classes depending on the density of conductive electrons in the sensor material. The first class includes sensors with a low electron density in the conduction band, when the number of such electrons is not more than a few electrons per particle. In this case, there is no negatively charged layer on the surface of the nanoparticles, and only the concentration of conduction electrons affects current flow in the sample. An example of the sensitive layer of this first class of sensors is tin oxide. The theory of sensory effect in such sensors has been developed [6,8], and the dependence of sensitivity on temperature, average size of the

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nanoparticles, and the hydrogen concentration has been established. These theoretical relationships were found to be in good agreement with the experimental data [8–11].

The second class of conductometric sensors utilize sensitive layers with high density of conduction electrons, for example, In_2O_3 -sensors, in which there is a high density of negative charges in the surface traps of the nanoparticles. A simple estimate indicates that one nanoparticle with diameter $d = 100$ nm contains $(\pi/6)d^3n_c \leq 10^4$ electrons, and a significant proportion of the electrons is captured by the traps (i.e. oxygen atoms) on the nanoparticle surface. On adsorption of reducing gas, the surface electron density decreases significantly due to different surface reactions. The electrons return to the bulk of the nanoparticle, the concentration of conductive electrons increases, and the resistance of the film decreases.

Although a number of studies have developed the theory of sensory effect, they are not without shortcomings. Some studies [12–15] consider an idealized plane boundary between nanoparticles, where the surface charge density is not related to the density of conduction electrons inside the nanoparticle. This approach contradicts the apparent dependence of the number of electrons in the surface traps on the total number of conduction electrons in the nanoparticle. The distribution of electrons in spherical semiconductor nanoparticles has also been studied [16,17], but the density of surface charges was set arbitrarily, and the positive charges were assumed to be immobile and distributed evenly. This assumption leads to errors in the density of conduction electrons near the surface of the nanoparticle by several orders of magnitude [18].

It should be noted that the location of adsorbates, i.e. electron traps on the surface, is approximately uniform, and for a large number of trapped electrons it can be assumed that the surface of a spherical particle is charged uniformly. Therefore, according to the Gauss theorem, the field from this charge inside the nanoparticle is zero. The field outside the nanoparticle, due to its electro-neutrality, also will be zero. Consequently, the effect of surface charged layer should take into account the distribution of all charges inside the nanoparticle. In order to determine the conductivity of a nanostructured film associated with the near-surface density of conduction electrons, it is necessary to know the distribution of all the charges in the system, i.e. the conduction electrons, donor ions, and the density of electrons in surface traps (oxygen atoms), which are related to each other.

In addition, in this case, conductivity should not be considered as a result of the transmission of electrons through a near-surface potential barrier. For small difference between potentials of neighboring nanoparticles, the charge distribution is largely unaffected by the electron transfer. Thus, the equilibrium distributions of electrons in nanoparticles can be used to determine the effective current.

All these problems have been solved for the nanoparticles of the second class of sensors [18]. The study considered spherical semiconductor nanoparticle with adsorbed oxygen atoms on the surface. The distribution of conduction electrons, positive charges, and the number of electrons in surface traps were obtained by minimizing the total free energy of the system for different temperatures and sizes of the nanoparticle at a single independent value, namely the surface concentration of oxygen atoms. This value was determined by external conditions comprising the density, composition and temperature of the surrounding atmosphere.

This assumption, i.e. the fact that the surface concentration of neutral oxygen atoms is a function of the density of gases in the surrounding atmosphere including reducing gases like hydrogen, and the characteristics of the surface of the nanoparticle, formed the basis of the theory developed for the second class of sensors [19]. In the present study, we consider in addition, the mechanism that chemical reactions on the surface are associated with surface charges, the density of which is functionally determined by the charge state of the entire nanoparticle. The dependence on radius, charge density and surface density of oxygen atoms are related to one another and are incorporated in a

single free energy functional, the minimum of which determines these quantities. As a result, the indium oxide sensor sensitivity is obtained at various hydrogen pressures and temperatures. The theoretical functional relationships are also compared with the experimental dependence of sensitivity on temperature and hydrogen pressure.

2. Relationship between sensory effect and electron distribution in semiconductor nanoparticle

The current in nanostructured film flows naturally in the region of contacts between the particles. Therefore, the conductivity of contacts, the area of which is much smaller than the cross-sectional area of the film, determines the total conductivity of the sensor. The current from one nanoparticle to another can be due to both the conventional conductivity and the tunneling transfer of electrons between negatively charged ions and oxygen atoms. As for the tunneling conductivity, it most likely does not play a significant role, since the average distance of electron transfer along the surface of one nanoparticle and between nanoparticles is more than 3 nm for realistic oxygen densities on the surface of one nanoparticle. Therefore, as will be shown subsequently, the probability of tunneling transitions at typical distances between O atoms is much smaller than the probability of conduction electron transfer.

The external electric field is much smaller than the fields inside the nanoparticle at voltages typically applied for sensor film measurements. Therefore, the current can be calculated at an equilibrium distribution of charges in neighboring nanoparticles in the first order of the smallest external field. The chemical potential is shifted by the magnitude of the potential difference between these particles. The current from one nanoparticle to another is proportional to the difference of potential between them and the equilibrium near-surface density of conduction electrons in the nanoparticles – $n_c(R, T)$, where R is the radius of the nanoparticle. Thus, the conductivity of the film is proportional to the near-surface density of the conduction electrons $n_c(R, T)$ in the nanoparticles composing the film. Sensitivity of the sensor is defined as the ratio of the film conductivity in the presence of hydrogen with pressure P_{H_2} to the conductivity without it, which is equivalent to the ratio of the corresponding near-surface densities of conduction electrons in the nanoparticles, thus

$$\Theta(T; P_{H_2}) = n_c(R; T, P_{H_2})/n_c(R; T, 0). \quad (1)$$

Oxygen atoms capture a significant amount of the conduction electrons, leading to a redistribution of electrons and ions inside the nanoparticle. The conductivity is determined by the concentration of electrons near the surface, so the conductivity and adsorption of oxygen atoms are interconnected. To determine the sensory effect from the equilibrium condition of oxygen on the nanoparticle surface and in the surrounding atmosphere, it is necessary to find the concentrations on the surface without hydrogen – $n_O(0)$ and with hydrogen – $n_O(P_{H_2})$. Next, the concentrations $n_c(R; T, 0)$ and $n_c(R; T, P_{H_2})$ can be calculated by minimizing the free energy functional, and the sensitivity of the sensor can be determined using the Eq. (1).

3. Determination of reagent concentrations

To determine the electron density distribution in a semiconductor nanoparticle having large concentration of conduction electrons we minimize the free energy of the nanoparticle charge system by analogy to a previous approach [18] as follows,

$$F = F_1 + F_2 + F_3 + F_4, \quad (2)$$

Here F_1 is the free energy of the electron gas, F_2 is the potential energy of interaction of all negative and positive charges of the nanoparticle, F_3 is the free energy associated with the positive charges on the donors, i.e. on ionized donors, and F_4 is the free energy of electrons on adsorbed

oxygen atoms. The first three terms in Eq. (2) are defined and described in details in the previous study [18]. However, the fourth term F_4 in the present study uses the following more complex form than in the paper [18] thus,

$$F_4 = -N_O^-(\varepsilon_0 + kT \ln 2) - kT \left[N_O(N_O^-) \ln \frac{N_O(N_O^-)}{N_O(N_O^-) - N_O^-} + N_O^- \ln \frac{N_O(N_O^-) - N_O^-}{N_O^-} \right] \quad (3)$$

where N_O (N_O^-) is the total number of adsorbed oxygen atoms, which, due to the impossibility of recombination of negatively charged oxygen ions, explicitly depends on their number on the nanoparticle surface (N_O^-). It is precisely the consideration of the functional dependence N_O (N_O^-) that significantly changes the procedure for minimizing the total free energy and its results in comparison with the previous studies [18,19]. In these studies, the value of N_O was determined only by the properties of the surface and composition of surrounding medium (see the Supporting information to the paper [18]). The value ε_0 is the binding energy of electron on the O^- ion, and the second term in the first parentheses in Eq. (3) corresponds to two possible values of the O^- ion spin. Because of the spherical shape of the nanoparticles and the uniform distribution of oxygen atoms on the surface, the density n_O is expressed thus,

$$n_O(n_O^-) = N_O(N_O^-)/4\pi R^2 \quad (4)$$

The conservation of the total charge in a nanoparticle is determined by the expression,

$$N_O^- = \int_0^R 4\pi r^2 [n_+(r) - n_c(r)] dr \quad (5)$$

where $n_+(r)$ is the density of donor ions. The free energy F should be minimized with respect to three independent variables: $n_+(r)$, $n_c(r)$ and N_O^- considering the complete neutrality of the nanoparticle expressed in Eq. (5). In fact, one may use $n_+(r)$, $n_c(r)$ and N_O as independent variables in the total free energy if the function N_O^- (N_O) is substituted in Eq. (3). The function N_O^- (N_O) will be obtained from the solution of subsequent Eqs. (6), (7) and (12)–(14).

In analogy to the previous study [18], the charge distribution is obtained from the solution of equations which may be found by minimizing the total free energy F of the nanoparticle charge system. The equations are solved assuming that donor centers can be considered as uniformly distributed inside the particle and electron traps i.e. adsorbed oxygen atoms, are uniformly distributed over a spherical surface.

Oxygen atoms (O) which are the traps of electrons on the surface result from the adsorption of oxygen molecules and their dissociation into atoms that remain on the surface. First, we consider the surface processes in the absence of hydrogen. It should be noted that it is impossible to consider all intermediate stages in the complex process of adsorption, dissociation and association of molecules, as well as their reactions on the surface of a nanoparticle. Therefore, only the gross processes with efficient rate constants, allowing us to find the values of stationary atomic and molecular concentrations are considered in Eqs. (6), (7) and (12)–(14). To avoid the additional complications associated with the effect of humidity on sensory properties (see, for example, [1,20,21]), the humidity of the air is maintained constant during the experiments [19]. Let us write the equations for stationary concentrations of adsorbed molecules (n_{O_2}) and adsorbed atoms O (n_O) thus,

$$\frac{dn_{O_2}}{dt} = K_{O_2}^{ad}(1 - n_{O_2}/n_{O_2}^{lim}) - K_{O_2}^{des}n_{O_2} - K_{dis}n_{O_2}(1 - n_O/n_O^{lim})^2 + K_{rec}[(n_O)^2 - n_On_O^-] = 0 \quad (6)$$

$$\frac{dn_O}{dt} = 2K_{dis}n_{O_2}(1 - n_O/n_O^{lim})^2 - 2K_{rec}[(n_O)^2 - n_On_O^-] = 0 \quad (7)$$

The first term in Eq. (6) describes the adsorption of oxygen

molecules from air with the adsorption constant $K_{O_2}^{ad}$, and $n_{O_2}^{lim}$ is the limiting density of oxygen molecules on the surface. The second term corresponds to desorption of oxygen molecules, and the third, to the dissociation of adsorbed oxygen molecule on two adsorbed atoms (n_O^{lim} is the limiting surface density of oxygen atoms).

The fourth term in Eq. (6) (the second term in (7)), corresponding to the recombination of oxygen atoms, requires special consideration. Atoms on the surface can remain neutral or, upon capturing an electron from the bulk of the nanoparticle, become O^- . Recombination can involve either two neutral atoms or a neutral atom with an ion. Two ions cannot recombine due to Coulombic repulsion. Thus, the recombination term in Eqs. (6) and (7) should be of the form $K_{rec}[(n_O^0)^2 + n_O^0n_O^-]$, where n_O^0 is the density of neutral oxygen atoms (here, it is assumed that the recombination constants K_{rec} for different pairs are approximately the same). Taking into account that $n_O = n_O^0 + n_O^-$ we obtain the expression for recombination term in Eqs. (6) and (7).

Note that the above Eqs. (6) and (7) for stationary surface concentrations are equations of gross processes on the surface. In fact, the chemical reactions on the nanoparticle surface may be multi-stage types, but the details of these stages are unknown. However, for stationary concentrations of molecules and oxygen atoms, gross reactions are sufficient.

The reaction rate constants in Eqs. (6) and (7) depend on the temperature and can be written as follows:

$$K_{dis} = \nu_{O-O} \exp\{-\varepsilon_{dis}/kT\} \quad (8)$$

$$K_{rec} = a_O^2 \nu_O \exp\{-\varepsilon_a^O/kT\} \quad (9)$$

$$K_{O_2}^{ad} = \frac{1}{4} \tilde{n}_{O_2} \sqrt{\frac{3kT}{m_{O_2}}} \alpha_{O_2} \quad (10)$$

$$K_{O_2}^{des} = \nu_{O_2} \exp\{-\varepsilon_{des}/kT\} \quad (11)$$

Here, ν_{O-O} and ε_{dis} are respectively, the frequency of inter-atomic vibrations and dissociation energy of adsorbed oxygen molecule, ε_a^O , ν_O and a_O are respectively, the binding energy, vibration frequency in the well and characteristic length of jump along the surface of oxygen atom, m_{O_2} and \tilde{n}_{O_2} are respectively the mass and concentration of oxygen molecules in air, and α_{O_2} is the sticking coefficient of oxygen molecule on collision with the nanoparticle surface.

Solving Eqs. (6) and (7), we obtain n_O as a function of n_O^- , $n_O(n_O^-)$. After substituting this function into the expression (3) and minimizing the total free energy (2), we obtain the equilibrium radial distributions of the conduction electrons and the electrostatic potential in the nanoparticle in the absence of hydrogen in the atmosphere, as well as the equilibrium values, n_O^- . Thus, the adsorption of oxygen in a nanoparticle is determined not only by the surface properties of the nanoparticle, but also by the charge characteristics of the whole nanoparticle. If for example, the density of donors changes inside the nanoparticle, the electron distributions both inside the nanoparticle and on the surface will change. The n_O value will also change consequently. Next, the values of the near-surface density of conduction electrons in the absence of hydrogen $n_c(R; T, 0)$, i.e. the denominator in the formula (1) are calculated.

To calculate the surface concentrations of oxygen $n_O(n_O^-)$ in the presence of hydrogen with a surface concentration n_{H_2} , we write the gross equations for stationary concentrations of oxygen and hydrogen, thus

$$\frac{dn_{O_2}}{dt} = K_{O_2}^{ad}(1 - n_{O_2}/n_{O_2}^{lim}) - K_{O_2}^{des}n_{O_2} - K_{dis}n_{O_2}(1 - n_O/n_O^{lim})^2 + K_{rec}[(n_O)^2 - n_On_O^-] - 2K_{HO}n_{O_2}n_{H_2} = 0 \quad (12)$$

$$\frac{dn_O}{dt} = 2K_{dis}n_{O_2}(1 - n_O/n_O^{lim})^2 - 2K_{rec}[(n_O)^2 - n_On_O^-] - K_{HO}n_O(P_{H_2})n_{H_2} = 0 \quad (13)$$

$$\frac{dn_{H_2}}{dt} = K_{H_2}^{ad} (1 - n_{H_2}/n_{H_2}^{lim}) - K_{HO} n_O n_{H_2} - 2K_{HO} n_{O_2} n_{H_2} = 0 \quad (14)$$

In Eqs. (12)–(14), K_{HO} is the gross constant of the water molecule formation, $K_{H_2}^{ad}$ is the hydrogen adsorption constant, which is proportional to the hydrogen concentration P_{H_2} in air, and $n_{H_2}^{lim}$ is half of H atoms limiting concentration on the surface (we assume that the molecule H_2 immediately dissociates into atoms upon adsorption).

The constants are determined from the following expressions:

$$K_{H_2}^{ad} = \frac{1}{4} \tilde{n}_{H_2} \sqrt{\frac{3kT}{m_{H_2}}} \alpha_{H_2} \quad (15)$$

$$K_{HO} = a_H^2 \nu_H \exp\{-\varepsilon_H/kT\} \quad (15a)$$

where \tilde{n}_{H_2} is the density of hydrogen molecules with mass m_{H_2} in air, α_{H_2} is the sticking coefficient of hydrogen molecule upon collision with the nanoparticle surface; a_H is the characteristic length of hydrogen atom jump between potential wells on the nanoparticle surface; ε_H and ν_H are respectively, the binding energy and vibration frequency of H atoms in these potential wells.

Hydrogen molecules do indeed quickly and irreversibly dissociate into atoms whose binding energy to the surface is very high, thus we do not consider the hydrogen desorption. The water molecules produced quickly evaporate from the surface due to the highly exothermic reactions. Therefore, the reverse reactions of decomposition of these molecules cannot be taken into account. The stationary surface density of hydrogen, as well as the density of adsorbed oxygen, is determined by the charge structure of the whole nanoparticle.

By solving Eqs. (12)–(14), and taking into account the formula in Eq. (4) we obtain the expression for $n_O(n_O^-; P_{H_2})$, which should be substituted into the Eq. (3). Minimizing the free energy of the system, we find the distribution of conduction electrons and the potential in a nanoparticle in the presence of hydrogen, and the value of the near-surface electron density $n_c(R; T, P_{H_2})$, which is the numerator in the Eq. (1). Thus, taking into account the previously obtained value $n_c(R; T, 0)$, one can find the measured sensitivity of the sensor.

4. Comparison of theoretical results with experimental data

We consider In_2O_3 nanoparticle of 35 nm radius, which is the average radius of the sensor nanoparticles in a previous experimental study [19]. The electron distribution in In_2O_3 nanoparticle is calculated based on the method developed in paper [18] and associated computer program [22]. The energetic parameters of In_2O_3 and the density of donors used as input to the free energy (see Eqs. (2) and (3)) are obtained from the measurement of conductivity in vacuum and air [18]. Specifically, the ionization energy of donor, $\varepsilon_d = 1.1 \times 10^{-2}$ (0.3 eV), the binding energy of electron on a surface oxygen atom, $\varepsilon_O = 2 \times 10^{-2}$, and the donor density, $n_d = 1.25 \times 10^{-7}$ ($8.4 \times 10^{17} \text{ cm}^{-3}$) (wherein and hereafter, the values of all parameters are given in atomic units). However, most of the parameters in the equations of chemical equilibrium (Equations (6), (7) and (12)–(14)), that strictly determine the value of $\Theta_{theor}(T; P_{H_2})$ are unknown. To determine these parameters, it would be necessary to minimize the value of the functional

$$\delta(\{p_N\}) = \sum_i \int_{T_{min}}^{T_{max}} |\Theta_{exp}(T; P_{H_2}^i) - \Theta_{theor}(T; P_{H_2}^i; \{p_N\})| dT \quad (16)$$

where $\Theta_{exp}(T; P_{H_2}^i)$ are the experimental curves [19] (see Fig. 1), $\{p_N\}$ is the set of unknown parameters in the Eqs. (8)–(11), and (15). All parameters $\{p_N\}$ in the functional (16) should fall into the range of physically reasonable values. If we take into account that every value of δ in the multidimensional space $\{p_N\}$ is obtained by minimizing the free energies (2) and (3), then becomes clear that such a problem has no solution.

Then the procedure for selecting the parameter values was simplified, and the parameters were chosen so as to minimize the following:

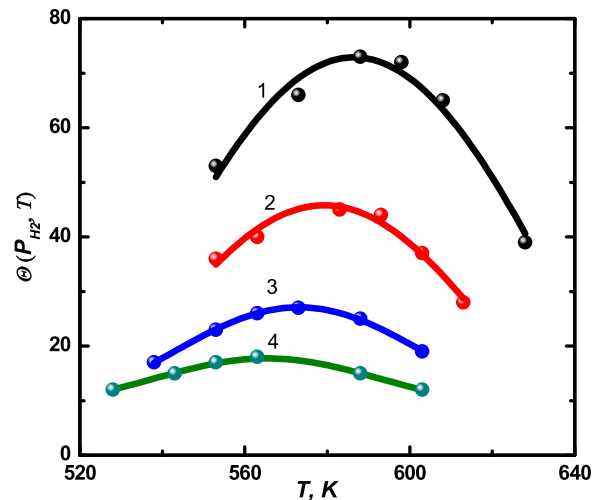


Fig. 1. Experimental temperature dependence of the film sensitivity to hydrogen for various hydrogen concentrations P_{H_2} (black colour of plot (1) – $P_{H_2} = 1100$ ppm; red line (2) – $P_{H_2} = 570$ ppm; blue line (3) – $P_{H_2} = 260$ ppm; green line (4) – $P_{H_2} = 120$ ppm). The data are obtained in Ref. [19] (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

- the difference between the calculated and experimental temperatures at which the maximum of Θ_{exp} and Θ_{theor} , corresponding to the curves $P_{H_2} = 1100$ ppm and $P_{H_2} = 120$ ppm are obtained;
- the difference between the calculated and experimental values of maximal sensitivity for these hydrogen concentrations.

This approach allows a comparison of only two points on two curves rather than a comparison of several curves. As a result, the following values of system parameters were obtained: $\nu_O = 4 \times 10^{-3}$, $\nu_{O_{lim}} = 7 \times 10^{-3}$, $\nu_{O_2} = 2 \times 10^{-4}$, $n_{O_2}^{lim} = 7 \times 10^{-3}$ ($2.5 \times 10^{14} \text{ cm}^{-2}$); $n_{H_2}^{lim} = 7.5 \times 10^{-2}$ ($2.67 \times 10^{14} \text{ cm}^{-2}$); $n_O^{lim} = 7.4 \times 10^{-5}$ ($2.63 \times 10^{12} \text{ cm}^{-2}$); $a = 13$; $\alpha_{O_2}[T] = \beta_0 T + \gamma_0$, где $\beta_0 = 3.64 \times 10^{-7}$, $\gamma_0 = -1.05 \times 10^{-4}$; $\alpha_{H_2}[T] = \beta_1 T + \gamma_1$, где $\beta_1 = -1.29 \times 10^{-5}$, $\gamma_1 = 9.27 \times 10^{-3}$; $\varepsilon_{dis} = 5.2 \times 10^{-2}$ (1.4 eV); $\varepsilon_{des} = 3.1 \times 10^{-2}$ (0.84 eV); $\varepsilon_a^O = 3.08 \times 10^{-2}$ (0.83 eV); $a_H^2 = 20$; $\nu_H = 0.027$; $\varepsilon_H = 0.052$ (1.4 eV). The functions $\Theta_{theor}(T; P_{H_2}^i)$ were calculated using these parameter values (see Fig. 2). The closeness of the theoretical and experimental sensitivity curves indicates the validity of the developed

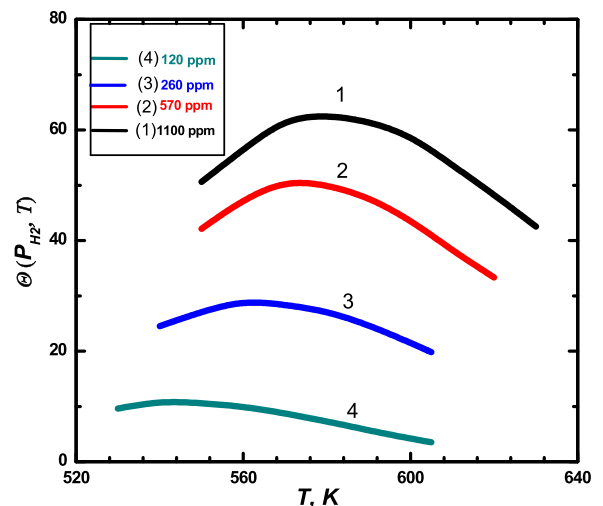


Fig. 2. Theoretical temperature dependence of the film sensitivity to hydrogen for various hydrogen concentrations P_{H_2} , corresponding to experimental data in Fig. 1 (see inset in Fig. 2).

approach.

Note that the curves of sensitivity dependence on temperature $\Theta(T; P_{H_2})$ have a bell shape. This can be qualitatively explained as follows. When the temperature decreases in the range to the left of bell top, the surface concentration of oxygen atoms also decreases due to the exponential temperature dependence of the rate constant for the dissociation of oxygen molecules (Eq. (8)). This trend corresponds to the decrease of electron traps density. The density of traps decreases much faster than the density of conduction electrons, since the ionization energy of donors, $\varepsilon_d = 1.1 \times 10^{-2}$ (0.3 eV) is significantly less than the dissociation energy $\varepsilon_{dis} = 5.2 \times 10^{-2}$ (1.4 eV). This means that the relative increase in conductivity due to the removal of oxygen at hydrogen adsorption becomes smaller when the temperature decreases. This corresponds to decrease of $\Theta(T; P_{H_2})$ with decreasing temperature. On the other hand, when the temperature rises in the range to the right of the bell top, the density of adsorbed oxygen molecules decreases sharply due to an increase in their desorption, $\varepsilon_{des} = 3.1 \times 10^{-2}$ (0.84 eV), which corresponds to a decrease in the density of electron traps, and the number of conduction electrons increases with temperature. Then the value of $\Theta(T; P_{H_2})$ should also fall.

In performing the calculations, we took into account only classical transport of electrons between nanoparticles. In general, the electron transfer can occur also by a tunneling mechanism. To determine the contribution of different mechanisms of electron transfer to the conductivity of a nanostructured film, we represent a film between the cathode and anode as a set of parallel chains of contiguous nanoparticles. The elementary conductivity σ_i , for each contact of two i -th and $(i + 1)$ -th nanoparticles is proportional to the flow of electrons J_i from one particle to another, i.e. $\sigma_i = bJ_i$ where b is the coefficient of proportionality. Then the resistance Ω of the N -nanoparticle chain ($N = L/2R$, L is the length of film) is equal to

$$\Omega = \sum_{i=1}^{i=N} (bJ_i)^{-1} \quad (17)$$

The total flow J_i consists of a conduction electron flux J_c , which is the same for all junctions of the nanoparticles, and a tunnel flow J_i^t from the O^- ion on the surface of one nanoparticle to the O atom on the surface of the adjacent nanoparticle, depending on the distance between them, thus

$$J_i = J_c + J_i^t. \quad (18)$$

The electron flux J_c is given by the expression

$$J_c = n_c(R, T)sv \quad (19)$$

Here s is the contact area between the two nanoparticles, and v is the electron thermal velocity. In our case $s = \pi\rho^2 < \pi R^2$, where radius of nanoparticle $R = 700$, and radius of the contact area $\rho \approx 40$. The tunneling current J_i^t is the probability of tunneling transfer of electron between the donor – O^- ion and the acceptor – O atom, which for sufficiently large distances r between them takes the form

$$J_i^t \approx 10^{-2} r^{-2} \exp \{-2\sqrt{2m\varepsilon_0}r\}, \quad r \gg 1. \quad (20)$$

Here the factor 10^{-2} is the characteristic probability of electron transfer at the contact of the donor and acceptor [18], $m \approx 1$ is the effective mass of electron in the conduction band, and $\varepsilon_0 = 0.02$ is the binding energy of electron in the O^- ion on the surface of the In_2O_3 nanoparticle. For these values of parameters, the exponent in the formula (20) is $-0.4r$.

Let us calculate the classical and tunneling electron flows in the absence of hydrogen in the ambient atmosphere near the sensor. In this case, the value of $n_c(R)$ is minimal, and the surface densities of atoms and oxygen ions are maximal [18]. According to our calculations, $n_c(R) = 4 \times 10^{-10}$ (this value corresponds to $2.7 \times 10^{15} \text{ cm}^{-3}$) and $v \approx 0.1$, then the flow at classical electron transfer (19) is equal to

$$J_c \approx 2 \times 10^{-7} \quad (21)$$

The tunnel transfer of an electron should be considered only if $J_i^t \gtrsim J_c$. To find the probability P of such an inequality, it is necessary at first to determine the value of “” corresponding to this inequality. Equating the expressions (20) and (21), we obtain $r \leq 15$. It is evident that the probability of the donor and the acceptor being at such a distance is $P = P_D \times P_A$, where P_D is the probability of a donor penetration in the area of contact between the nanoparticles, and P_A is the probability of the acceptor reaching the circle of radius $r_A = 15$ with respect to the donor. Modeling provides the surface densities: $n_{O^-} = 2 \times 10^{-5}$ for donors and $n_O^0 = 2 \times 10^{-6}$ for acceptors. Then $P_D = n_{O^-} \times \pi\rho^2 \approx 0.1$, and $P_A = n_O^0 \times \pi r_A^2 \approx 10^{-3}$. Consequently, the probability that the tunnel transfer will prevail over the classical transfer is $P = 10^{-4}$.

Thus, the value of J_i^t should be taken into account only in one of the 10^4 terms in the expression for the resistance of nanoparticles chain of Eq. (17). This term is significantly smaller than the neighboring ones, and can be ignored, i.e., the resistance of the chain is equal to $\Omega = N/bJ_c$ with an accuracy of 10^{-4} . Then, the conductivity Σ of the entire sample consisting of N_{ch} chains is

$$\Sigma = N_{ch}/\Omega = (N_{ch}/N)bJ_c = (N_{ch}/N)bsv \times n_c(R, T) \quad (22)$$

with the same accuracy. It follows from the formula (22) that the total conductivity of a nanostructured film is proportional to the near-surface density of conduction electrons in a nanoparticle and is not related to the electron tunneling between the oxygen atoms. Similar conditions will be satisfied also in the presence of hydrogen in the air ambience. In other words, the sensory effect, in accordance with the Eq. (1), is determined only by classical electron transitions.

A comparison of Figs. 1 and 2 show that the theory indeed gives the dependence of the sensitivity on the temperature and hydrogen concentration that is sufficiently close to the experimental data. The good agreement between experiment and theory is observed for varying concentration of hydrogen and reasonable values of input parameters. Thus, the temperatures of maximal sensitivity are close to the experimental values for different hydrogen concentrations. In addition the maxima of the theoretical curves are shifted toward lower temperatures with decreasing hydrogen concentrations as in the experiment. These features collectively indicate that the developed theory of films sensitivity correctly describes the processes in the nanostructured sensor. There are, however, several reasons for the discrepancy between the theoretical and experimental curves. It should be noted that there is a significant dispersion of nanoparticle sizes in a real sensor, and only the average radius was used in our calculations. In addition, the calculations assumed spherical nanoparticle, while real nanoparticles are markedly different from being spherical.

The effect of hydrogen in air ambience on the radial distributions of conduction electrons and electrostatic potential in the nanoparticle can be readily calculated, using the values of parameters obtained from the above fitting procedure. Figs. 3 and 4 show the result obtained in the absence of hydrogen, as well as for various hydrogen concentrations. We consider in Fig. 3 the relative density of conduction electrons, that is the ratio of local density to average density. It is interesting to demonstrate the inhomogeneity of charge density, regardless of the total number of charges.

When hydrogen reacts with O^- ions on the surface of nanoparticles, the resulting water evaporates, and the released electrons escape into the bulk. A change in the number of surface charges (the number of charged electron traps on the surface) dramatically changes the charge distribution and the electrostatic potential throughout the nanoparticle, and not only near the surface. The lower the concentration of hydrogen in the atmosphere, the more charges are concentrated in the surface oxygen traps. In turn, the greater the potential difference between the center of the nanoparticle and its surface (Fig. 4), the greater the change in the density of conduction electrons from the center to the edge (Fig. 3). It is evident that the distributions of both the electrons and the potential become more homogeneous with increasing hydrogen concentration. This homogeneity can be attributed to the reduction in

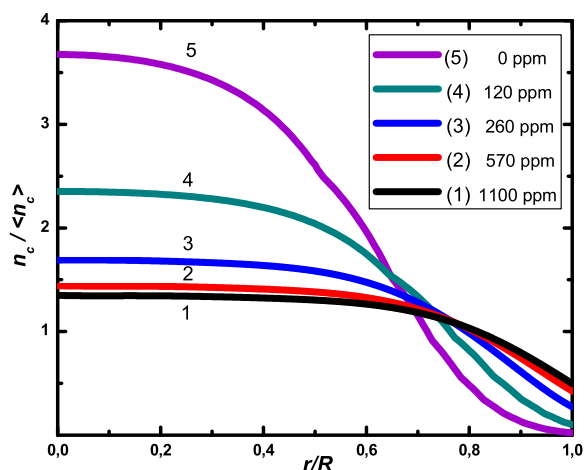


Fig. 3. The calculated radial dependence of the relative density of conduction electrons for various hydrogen concentrations P_{H_2} (see inset in Fig. 3).

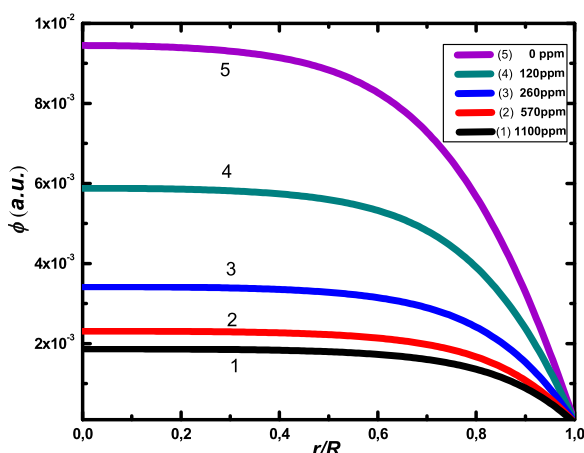


Fig. 4. The calculated radial dependence of the electrostatic potential inside the nanoparticle for various hydrogen concentrations P_{H_2} (see inset in Fig. 4).

the number of electron traps i.e. oxygen atoms, due to the reaction with hydrogen. This reduction leads to a decrease in the density of surface charges. The concentration of the conduction electrons in the bulk of the nanoparticles increases and approaches the number of positively charged ions. As a result, the electric field inside the nanoparticles decreases, the potential is equalized, and we obtain a uniform distribution of the conduction electrons. Therefore, the near-surface density of conduction electrons, which determines the conductivity of a nanostructured semiconductor system, can be found only by solving the general problem of distribution of charges and the electrostatic potential over the entire particle by minimizing the total free energy of the system of nanoparticle charges.

5. Conclusions

The paper develops the theory of sensitivity of the second kind of nanostructured conductometric sensors to reducing gases, i.e. sensors with a large number of conduction electrons in the nanoparticle. The near-surface electron density in nanoparticles determines the conductivity. This density becomes smaller with increasing number of electron traps, i.e. the oxygen atoms on the surface. If hydrogen is in the air ambience, the hydrogen is absorbed on the sensor surface and reacts with oxygen on the nanoparticles. In this case, the number of electron traps decreases, the density of conduction electrons near the surface increases, and the conductivity of the sensor film consequently increases. Calculation of the equilibrium electron density in a

nanoparticle is performed by minimizing the total free energy of the system.

The amount of oxygen atoms on the surface is determined by the gross reactions of adsorption-desorption of oxygen molecules and their dissociation-recombination on the O atoms, i.e. electron traps. The impossibility of recombination of two O^- ions, the number of which is determined by the charge structure of the entire nanoparticle and not only its surface, leads to an unusual phenomenon. Specifically, it leads to the fact that the surface density of adsorbed oxygen atoms depends not only on the surface properties, but also on the charge distribution throughout the nanoparticle. In other words, in this paper, the mutual influence of the charge structure inside the nanoparticle and the negative charge on its surface is taken into account. The surface density of oxygen atoms in turn affects this relationship and ultimately determines the sensory effect. The inhomogeneity of the charge and potential distribution inside the particle is strongly associated with the surface charge density in oxygen traps. It is shown that the tunneling transitions of electrons between oxygen atoms on neighboring nanoparticles do not contribute significantly to the conductivity of system.

The curves of sensitivity dependence on temperature for different hydrogen concentrations calculated by taking into account these factors demonstrate good qualitative and quantitative agreement with the experimental data with reasonable selection of a relatively small number of system parameters in the theoretical model. A good agreement between the theoretical and experimental results was demonstrated by the developed calculation method of radial dependence of the conduction electron density for various hydrogen concentrations in the surrounding atmosphere. Specifically, considering the mutual influence of the negative charge on the surface and the distribution of charges inside the nanoparticle produces noticeable improvement in the agreement between the theory developed and the experimental data obtained in a previous study.

In this study, we consider the sensory effect for reducing gases with hydrogen response used as an example. The same approach can be readily used for consideration of the sensitivity of nanostructured detectors for other reducing gases. Indeed, the only place in the paper where hydrogen is considered are the gross equations for stationary concentrations (Eqs. (12)–(14)) and the rate constants Eqs. (15) and (15a) for the corresponding physico-chemical processes. Replacing these equations with those for another reducing gas allows us to determine the sensitivity on the particular gas. In other words, this paper could be considered as proposing a standard procedure for determination of the sensitivity of semiconductor detector with high concentration of conductive electrons on different reducing gases. Of course, it is necessary to take into account the peculiarities of the corresponding physical and chemical processes when considering each new case.

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