Development of gas sensitivity model of nanocomposites based on the tin dioxide - silicon dioxide system

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Abstract. A model of gas sensitivity of nanocomposites based on tin dioxide - silicon dioxide system is developed. The mechanisms of conductivity and chemoresistive response of composites are investigated. The parameters corresponding to the maximum sensitivity of SiO₂-SnO₂ films are determined as well.

The topical task is to develop the new generation of gas sensors with high sensitivity, selectivity and low energy consumption. Promising point is the sol-gel technology, which allows to create gas-sensitive films based on meshy semiconductor composites. Therefore, the aim of this work is to develop model representations of gas sensitivity of films based on SiO₂-SnO₂ obtained by sol-gel technology.

Modern ideas about the nature of conductivity of oxide semiconductors are based on the band theory. The predominantly ionic nature of chemical bindings determines the large band gap ΔE and the relatively low mobility of charge carriers. Donor and acceptor levels can be created not only by impurities, but also by deviations from the composition of stoichiometry – anionic and cationic vacancies. They represent special chemical centers involved in reactions. Anionic vacancies play the role of donors, and cationic vacancies play the role of acceptors. Their ionization energies are determined by the type of anion and cation of the compound [1]:

\[ 0 \rightarrow e^- + h^+ + \Delta E, \quad \Delta E = 3.56\text{eV}; \]
\[ 2O_2 \rightarrow 2O + 2e^- + 2h^+, \quad \Delta H_{O_2} = 1.54\text{eV}; \]
\[ Sn_{Sn} + V'_o \rightarrow Sn_i + V'_{Sn} + \Delta H_{Sn}, \quad \Delta H_{Sn} = 6.5\text{eV}; \]
\[ V_O \rightarrow V'_O + e^- + E_{O}, \quad E_{O} = 0.75\text{eV}; \]
\[ Sn_i \rightarrow Sn_i^1 + e^- + E_{Sn}, \quad E_{Sn} = 1.8\text{eV}; \]
\[ V_{Sn} \rightarrow V_{Sn}^1 + h^+ + E_{Sn}, \quad E_{Sn} = 2.1\text{eV}. \]

In SnO₂ there are donor levels with activation energies of 0.21, 0.33, 0.52, 0.6, 0.72 eV. In film samples of SnO₂ donor levels are usually shallow. The values of their activation energies are not more than 0.15 eV. It is lower while \( N \) concentration is higher. At \( N \approx 10^{19} \text{cm}^{-3} \), the levels close to the
impurity zone, which, with an increase in $N$ to $10^20$ cm$^{-3}$, overlaps with the conduction zone. The energy band diagram of SnO$_2$ single crystals (figure 1) shows the following levels [2]:

- the stable fully compensated level of e-traps, which lies 0.21 eV below the bottom of the conductivity;
- the stable level of hole traps lying at 0.33 eV above the ceiling of the valence band which can act as a center of sensibilization at low temperatures;
- two important levels of electronic traps: the smaller one is fully compensated and is usually at a distance of 0.52 eV below the conduction band, the deeper one (partially compensated) at a distance of 0.6 eV below the conduction band;
- other discrete levels lie at a distance of 1, 1.3, 1.8 eV from the bottom of the conduction band.

![Energy band diagram of SnO$_2$.](image)

Unalloyed SnO$_2$ has only an electronic type of conductivity. It also has a bilateral area of homogeneity – figure 2 [1]. To analyze the conductivity of tin dioxide, it is necessary to calculate the equilibrium concentrations of defects in the clusters of tin dioxide obtained by the Sol-gel technology. According to equations (1), ionized oxygen vacancies make an overwhelming contribution to the conductivity. The energy of formation of other defects is much greater than the energy of formation of oxygen defects by Schottky.

![The diagram of tin dioxide state.](image)

The formation of defects in the crystal volume is accompanied by an increase in entropy:

$$S = k \ln W,$$

where $W$ characterizes a thermodynamic probability equal to the number of ways in which a given state of the system can be realized, $k$ is the Boltzmann constant. The number of ways in which $nV$ vacancies can be distributed across $N$ nodes is expressed:

$$W = \frac{N!}{(N-n_v)!n_v!}.$$
Using Stirling’s formula, we transform expressions (2) and (3) to form:

\[ S = k(N \ln N - (N - n_v) \ln(N - n_v) - n_v \ln n_v). \]  \(\text{(4)}\)

If \(E_{\text{def}}\) energy is expended on the formation of one Schottky defect, the internal energy of the crystal will increase by \(n_v E_{\text{def}}\). Then the expression for free energy will be written as:

\[ F = n_v E_{\text{def}} - kT \left[ (N \ln N - (N - n_v) \ln(N - n_v) - n_v \ln n_v) \right]. \]  \(\text{(5)}\)

where \(T\) is temperature.

Find the concentration of defects from the condition \(\frac{\partial F}{\partial n_v} = 0\). Then the number of thermodynamic vacancies is as:

\[ N_D = n_v = N \exp \left( - \frac{E_{\text{def}}}{kT} \right). \]  \(\text{(6)}\)

In equation (6), the pre-exponential factor is the concentration of nodes in tin dioxide. For a polycrystalline material, this parameter is determined by the density \(\rho_0\), the molar mass \(M\). It is calculated from the equation:

\[ N = \frac{\rho_0 N_A}{M}, \]  \(\text{(7)}\)

where \(N_A\) is Avogadro number.

When growing gas-sensitive films Sol-gel technology equation (7) is not applicable because of the fractal organization of clusters of tin dioxide [3, 4] – figure 3.

![Figure 3. Clusters of tin dioxide obtained by Sol-gel technology: a) – Witten-Sender fractal aggregate; b) – morphology of SiO\(_2\)-SnO\(_2\) film; c) – increased area of the cluster.](image)

The density of the fractal aggregate \(\rho\) is calculated by this equation:

\[ \rho = \rho_0 \left( \frac{R}{r_0} \right)^{3-D}, \]  \(\text{(8)}\)

where \(R\) is the cluster radius; \(r_0\) is the radius of the tin hydroxide molecule deposited from the solution (Sn(OH)\(_2\), Sn(OH)\(_4\)); \(D\) is the fractal dimension of the cluster (for the Witten-Sender aggregate – figure 3,a – \(D = 2.5\)). Subject to expressions (1), (6), (7) and (8) the concentration of ionized oxygen defects in the cluster as a function of temperature and size is equal to:

\[ n_v = \frac{\rho_0 N_A}{M} \exp \left( - \frac{E_{\text{def}}}{kT} \right) \exp \left( - \frac{E_O}{kT} \right) \left( \frac{R}{r_0} \right)^{3-D}, \]  \(\text{(9)}\)

where \(E_O\) is the ionization energy of the oxygen vacancy. For clusters of 50 nm, 200 nm and 600 nm in the temperature range (1000 – 1300) K, the calculation results for equation (9) are shown in figure 4.
Figure 4. Temperature dependence of the concentration of ionized oxygen vacancies in tin dioxide clusters of different sizes.

We analyze the mechanism of gas sensitivity of own tin dioxide. The most interesting fact is reducing gases such as ethanol and acetone vapors, methane, carbon monoxide and some others. Their adsorption on the semiconductor surface leads to the following effects:

- molecules or atoms of the reducing gas are adsorbed on the surface of $p$-type semiconductors as donors, injecting electrons into the volume. Adsorption may be accompanied by dissociation or decomposition of molecules;
- gas molecules adsorption destroy jobs oxygen on the surface of the semiconductor via oxidation-reduction reactions. In this case, the concentration of donors, both on the surface and in the volume, changes, including due to the diffusion of vacancies in the semiconductor volume;
- the reducing gas reacts to the surface of the semiconductor with chemisorbed oxygen, returning the localized electrons to the conduction band.

The contribution of each mechanism is obtained by different conditions – operating temperature, composition of the gas medium, synthesis conditions, type of contacts and some others. However, studies have shown that neither the reconstructed surface of natural tin oxide nor the stoichiometric surface have surface States in the band gap of the semiconductor. Consequently, the surface of the unalloyed stoichiometric SnO$_2$ does not contain chemisorbed ions, including oxygen ions. Oxygen can be adsorbed only when the negative charge of its ions is compensated by ionized bulk donors in the near-surface region of the semiconductor. Such donors are formed in non-stoichiometric SnO$_2$ layers due to volumetric oxygen vacancies.

Thus, the last processes make the main contribution to the chemoresistive effect for unalloyed tin dioxide [5]. However, vacancies on the surface of tin dioxide unlike other semiconductor materials are not donors. They become of such type only when diffusing into the depth of the material, which proceeds intensively at temperatures ($550 – 700$) K. Therefore, in the future we will evaluate all processes on the surface and in the volume of SnO$_2$ at a temperature of 600 K.

Thus, to obtain the dependence of the change in the resistance of the sensor based on SnO$_2$, it is necessary to know the ratio between the partial pressure of oxygen in the medium and the density of adsorbed oxygen molecules per unit area – $N_0$. The equation of balance of adsorbed oxygen:

$$\alpha P(1-\theta) = v^0\theta^0 \exp\left(-\frac{Q_0}{kT}\right) + v\theta \exp\left(-\frac{Q}{kT}\right) + v^2\theta^2 \exp\left(-\frac{Q_2}{kT}\right) + ...$$

where $\alpha$ is the kinetic coefficient of Langmuir isotherm equal to $\frac{\kappa s_0}{(2\pi mkT)^{1/2}}$, where $\kappa$ is the coefficient of adhesion of gas molecules to the surface; $s_0$ is the effective area of the adsorbed atom; $m$ is the mass of the gas molecule; $k$ is the Boltzmann constant; $T$ is the temperature; $\theta$ is the degree of coating of the semiconductor surface with various forms of oxygen, defined as $\frac{N_s}{N_0}$, where $N_s$ is the
maximum possible number of adsorption centers per unit surface; \( P \) is the partial pressure of oxygen in the medium; \( \nu \) is the frequency of phonons for all forms of adsorbed oxygen; \( Q \) is the adsorption heat.

Using equation (10) and equation of electroneutrality of semiconductor:

\[
N_D V = n V + N_o S,
\]

where \( V \) is the volume of a semiconductor spherical aggregate; \( S \) is the area of the aggregate, is the surface density of oxygen, we obtain the ratio between the partial pressure of the reducing gas and the concentration of charge carriers:

\[
p_a = \frac{-p_o n^2 + \eta_1 n + \eta_2 n}{2n_1 n^2 - \eta_3 n - \eta_4 n},
\]

where 
\[p_a\] – partial pressure of oxygen in the medium.

Using (12), we obtain that the region of maximum sensitivity of gas sensors with the growth of cluster sizes is shifted towards high pressures, and with an increase in the concentration of oxygen vacancies – towards low partial pressures of the reducing gas (figure 5).

**Figure 5.** Dependence of charge carrier concentration on partial gas pressure: a) – for different cluster sizes; b) – for different concentrations of oxygen vacancies.

Thus, a model of gas sensitivity of mesh nanocomposites based on the vacancy mechanism and chemisorption processes on the surface of SiO\(_2\)-SnO\(_2\) films synthesized by sol-gel technology [6] has been developed.

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