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To cite this article: I A Pronin et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 387 012062

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A model of the vacuum level effect on the sensor response of vacuum sensors based on nanostructured semiconductor oxide materials

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Abstract. A mathematical model of the sensor response of vacuum sensors based on wide-band gap semiconductor nanostructured oxides, using a small number of parameters, is proposed. The results of the research can be used to develop a methodology for the synthesis of sensitive elements with a given response for a selected range of vacuum.

1. Introduction
An analysis of recent publications has shown an increasing interest in a new type of vacuum sensors, the sensitive element of which is made on the basis of nanostructured wide-band gap oxides [1, 2]. The principle of operation of such devices is based on the reversible process of chemical adsorption of oxidizing gases and reducing agents, leading to a change in the concentration of free charge carriers in the material [3]. For example, oxygen, being an oxidizing gas, is desorbed from the surface of a sensitive element with an increase in the vacuum level, and returns electrons to the conduction band of the semiconductor, increasing its electrical resistance. The advantage of this type of sensor is low power consumption, the possibility of microminiaturization, and compatibility with planar silicon technology.

At present, there are no model representations describing the change in electrical resistance of a given type of sensitive elements with a change in the vacuum level. Therefore, the aim of the article is to develop a model of the vacuum level effect on the sensor response of vacuum sensors based on nanostructured semiconductor oxide materials.

2. Model development and discussion
To calculate the response of sensory elements during adsorption-desorption of the gases under investigation (the investigated atmosphere can contain both oxidizing gases (usually, oxygen) and reducing gases (for example, hydrogen), it is necessary to analyze the dependence of the carrier concentration in the material on their partial pressure p', i.e., analytically determine the dependence n = f(p'). We will consider the region of low gas concentrations, assuming that there is no direct reaction between them, the chemisorption of the oxygen molecule is accompanied by the capture of the
electron, and the chemisorption of the reducing agent is by transfer of the electron to the conduction band of the semiconductor.

The condition of adsorption equilibrium in the case when adsorption is not accompanied by dissociation has the form [4]:

$$\gamma P (N^r - N) = v^0 N^0 \exp \left( -\frac{q^0}{k_B T} \right) + v^+ N^+ \exp \left( -\frac{q^+}{k_B T} \right) + v^- N^- \exp \left( -\frac{q^-}{k_B T} \right)$$

(1)

where $\gamma$ is Langmuir kinetic coefficient; $P$ is pressure; $N^r$ is surface concentration of adsorption centers; $N$ is surface concentration of all varieties of adsorbed particles; $v^0$, $v^\pm$ are probabilities of particle desorption in neutral, positive and negatively charged forms; $N^0$, $N^\pm$ are surface concentrations of the corresponding forms of adsorbed molecules; $q^0$, $q^\pm$ is differential heat of adsorption of the corresponding forms. However, the equilibrium with the gas phase in the case of a nondegenerate semiconductor is maintained exclusively due to the “weak” neutral form of chemisorbed particles, i.e. “firmly” bound particles do not participate in interaction with the environment. Then equation (1) can be rewritten in the form:

$$\gamma P (N^r - N) = v^0 N^0 \exp \left( -\frac{q^0}{k_B T} \right).$$

(2)

Introducing the notation $p_i = \frac{\gamma P_i}{v_i^0 \exp \left( -\frac{q_i^0}{k_B T} \right)}$ for partial normalized pressures of $i$-th gases, we rewrite the conditions of adsorption equilibrium (2) for oxygen and a reducing agent:

$$\begin{cases}
    p_{go} (N^r - N_{go} - N_{go}) = N_{go} - N_{go}^+ = N_{go}^0, \\
    p_{gr} (N^r - N_{gr} - N_{go}) = N_{go} - N_{go}^- = N_{go}^0,
\end{cases}$$

(3)

where $N_{go}, N_{go}$ is the surface concentration of the adsorbed (charged and neutral) forms of the reducing agent and oxygen, respectively; $N_{go}^+, N_{go}^-$ is the surface concentration of the charged forms of the reducing agent and oxygen, respectively; $N_{go}^0, N_{go}^0$ is the surface concentration of the neutral forms of the reducing agent and oxygen, respectively. The probability that the particle remains neutral on the surface of the semiconductor is described by the Fermi-Dirac statistics:

$$N_{gr}^0 = N_{gr} \left[ \frac{1}{1 + \frac{1}{2} \exp \left( \frac{E_D - E_F}{k_B T} \right) } \right],$$

(4)

$$N_{go}^0 = N_{go} \left[ \frac{1}{1 + \frac{1}{2} \exp \left( \frac{E_A - E_F}{k_B T} \right) } \right],$$

(5)

where $E_D, E_A$ are ionization energies of the donor and acceptor levels, respectively; $E_F$ is Fermi energy of a semiconductor.

For further analysis, let us pass to the counting of energy from the bottom of the conduction band, and add a subexponential expression $(E_C - E_F)$ to each numerator, where $E_C$ is energy of the
conduction band bottom. Then, taking into account equality \( n = N_c \exp \left( \frac{E_D - E_C}{k_B T} \right) \), where \( N_c \) is the effective density of states in the conduction band, equations (4), (5) can be rewritten in the form:

\[
N_{gr}^0 = \frac{2n N_{gr}}{2n + N_c \exp \left( \frac{E_D - E_C}{k_B T} \right)},
\]

\[
N_{go}^0 = \frac{2N_{go} N_c \exp \left( \frac{E_A - E_C}{k_B T} \right)}{2N_c \exp \left( \frac{E_A - E_C}{k_B T} \right) + n}.
\]

Introducing notations \( \Lambda_1 = N_c \exp \left( \frac{E_D - E_C}{k_B T} \right) \), \( \Lambda_2 = N_c \exp \left( \frac{E_A - E_C}{k_B T} \right) \) we rewrite the system of equations (3) in the form:

\[
\begin{align*}
F_{go} (N^* - N_{go} - N_{gr}) &= \frac{2n N_{gr}}{2n + \Lambda_1} \\
F_{gr} (N^* - N_{go} - N_{gr}) &= \frac{2N_{go} \Lambda_2}{2\Lambda_2 + n}
\end{align*}
\]

To calculate the dependence \( n = f(p_{go}) \) at a constant oxygen pressure \( p_{go} \), in addition to system (8), one more equation is needed to exclude the terms \( N_{go} \) and \( N_{gr} \) [5]. For this we introduce the electroneutrality equation:

\[
n V_f + N_{go} S_f = N_D V_f + N_{gr} S_f
\]

where \( V_f, S_f \) are volume and area of the film, respectively; \( N_D \) is concentration of donor impurity in a semiconductor. Dividing both parts of equation (9) by \( S_f \) we get its final version:

\[
n h_f + N_{go}^* = N_D h_f + N_{gr}^*
\]

Rewriting equation (10) taking into account the previously adopted notation, as well as the degree of filling of impurity levels, we arrive at the expression:

\[
\frac{n N_{go}^* - \Lambda_1 N_{gr}^*}{2\Lambda_2 + n} = h_f (N_D^* - n)
\]

To express the desired dependence in the analytic form, we find the parameter \( N_{gr} \) from the first equation of the system (8):

\[
N_{gr} = (N^* - N_{go}) \left( 1 - \frac{2n}{2n p_{gr} + \Lambda_1 p_{go} + 2n} \right)
\]

Then, we divide the first and second equations of the system (8) by each other, and from the obtained identity \( \frac{N_{gr}}{N_{go}} = \frac{p_{gr} \Lambda_2 (2n + \Lambda_1)}{p_{go} n (2\Lambda_2 + n)} \) we substitute \( N_{go} \) to equation (12), as a result of which we express the dependence of the parameter \( N_{gr} \) on quantities that do not depend on \( N_{go} \):

\[
N_{gr} = \frac{N^* p_{gr} \Lambda_2 (2n + \Lambda_1)}{p_{go} n (2\Lambda_2 + n) + 2n p_{gr} \Lambda_2 + \Lambda_1 \Lambda_2 p_{go} + 2n \Lambda_2}.
\]
Substituting equation (13) into the identity obtained earlier by dividing the equations of the system (8), we express the parameter \( N_{gr} \):

\[
N_{gr} = \frac{N^* p_{gr} n(2\Lambda_{2} + n)}{p_{gr} n(2\Lambda_{2} + n) + 2np_{gr}\Lambda_{2} + \Lambda_{1}\Lambda_{2} p_{gr} + 2n\Lambda_{2}}.
\]  

(14)

Substituting (13) and (14) into the electroneutrality equation (11), we arrive at the final expression in which there are no terms \( N_{gr}, N_{go} \):

\[
N^*(p_{gr}n^2 - \Lambda_{1}p_{gr}\Lambda_{2})
p_{gr}n(2\Lambda_{2} + n) + 2np_{gr}\Lambda_{2} + \Lambda_{1}\Lambda_{2} p_{gr} + 2n\Lambda_{2} = h_f(N_D - n).
\]  

(15)

An analysis of (15) shows that expression \( n = f(p_{gr}) \) in the analytical form is very difficult, and involves the solution of a cubic equation with the use of the Cardano formula. Therefore, we express the inverse relationship \( p_{gr} = f(n) \), and further analysis will be carried out with the help of its numerical solution:

\[
p_{gr} = \frac{N^* p_{gr} n^2 - h_f(N_D - n)(p_{gr}n(2\Lambda_{2} + n) + 2n\Lambda_{2})}{N^* \Lambda_{1}\Lambda_{2} - h_f(N_D - n)(2n\Lambda_{2} + \Lambda_{1}\Lambda_{2})}.
\]  

(16)

Within the framework of the developed model, let us analyze the dependence of the concentration of charge carriers in the zinc oxide film on the partial pressure of the reducing agent. We will assume that hydrogen acts as a reducing gas. Let us translate the partial normalized pressures of oxygen and hydrogen into Pa and ppm, respectively. Then the partial pressure of atmospheric oxygen will be 1.167·10^{34} \text{ rel. units}, and the concentration of hydrogen in 1 ppm will be 5.83·10^{28} \text{ rel. units}.

Figure 1 shows the dependence of the electron concentration in the ZnO film on the hydrogen concentration in a gas mixture containing some air. The calculation was carried out for a film thickness of 200 nm. An analysis of the graphs shows that two regions can be distinguished in the gas concentration ranges under study: the first one in which the electron concentration does not depend on the ethanol concentration, and the second one in which the growth of the electron concentration occurs according to a power law.

![Figure 1](image1.png)

**Figure 1.** Dependences of the electron concentration in the ZnO film on the concentration of ethanol in air at various amount values of the donor impurity.

The research of the relative change in the concentration of charge carriers in a semiconductor film under the action of a gas analyzer is of particular interest. Figure 2 shows the dependence \( \frac{\Delta n}{n_0} \). If we

![Figure 2](image2.png)

**Figure 2.** Dependence of the relative change in carrier concentration and film resistance on the concentration of ethanol at various concentrations of the donor impurity.
neglect the dependence of the mobility of the charge carriers on their concentration, then \[ \frac{\Delta n}{\Delta n_0} = \frac{\Delta R}{R_0}, \]

where \( \frac{\Delta R}{R_0} \) is the relative change in resistance.

An analysis of the dependence shows that there is a certain threshold value of the ethanol concentration, below which the relative change in the electron concentration is negligible. When this threshold concentration is exceeded, power-law dependence grows proportional to the square root of the analyzer gas concentration.

3. Conclusions

Thus, in the article a mathematical model of sensor response of vacuum sensors based on nanostructured semiconductor oxide materials is developed. The obtained model can be used for a technical vacuum containing both oxidizing and reducing gases. These results can be used in the design of sensing elements based on ZnO, SnO\(_2\), In\(_2\)O\(_3\) and other wide-band gap oxides obtained in the framework of various synthesis methods.

4. Acknowledgments

The work was carried out with the financial support of the Ministry of Education and Science of the Russian Federation (project No. 16.897.2017/4.6), as well as in the framework of the Presidential Grant and the Presidential Scholarship (project No. MK-1882.2018.8 and SP-84.2018.1).

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