Kinetic models for sensory response of multicomponent oxide nanomaterials with a hierarchical pore system

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Abstract. A kinetic model for sensory response of multicomponent oxide nanomaterials used as sensing elements of gas sensors and vacuum gauges is proposed. It is shown that gas-sensitive properties of nanomaterials depend both on their qualitative and quantitative composition, and morphology to determine the presence of a hierarchical pore system therein.

Formation of new generation devices is based on the development of novel technologies for synthesis, research, and modeling of nanocomposite material properties, including multicomponent oxide nanomaterials of SiO₂–Meₓ₁O₃ₙ–Meₓ₂O₄ and SiO₂–Meₓ₃O₅ₙ–…–Meₓₙ₋₁Oₓ₂ composition (Me is Zn, In, etc.) [1–2]. Such nanomaterials made in the form of thin nanostructured films with controllable and reproducible pore sizes are used as sensing elements of gas sensors [3–4], and next-generation vacuum gauges [5–6]. The latter are based on change in material electrical conductivity during adsorption/desorption of oxidizing and reducing agents. The research results prove the importance of both qualitative and quantitative composition of a gas-sensitive layer, and consideration of its morphology, which determines the presence of a hierarchical pore system in the nanomaterial.

To specify physical processes of gas-film interaction based on semiconductor oxides, the models of thin continuous layer; potential barriers at grain boundaries; open bridges; closed bridges; and of grain resistance complete modulation are used. However, in real gas sensors, individual material sections act according to one or another model, which is determined by the material properties, the size of crystallites, and the adsorption capacity in this section [7]. In turn, to describe sensory response of vacuum gauge sensing elements based on semiconductor oxides, there are models to consider desorption predominance of charged oxygen species, and nanomaterial fractal structure [8].

The internal volume of multicomponent oxide nanomaterials with a hierarchical pore system is accessible for gas-phase molecules, wherein the active surface significantly exceeds the external geometric dimensions of the gas-sensitive layer. It is almost impossible to predict the pore geometry due to its end-to-end structure. Nevertheless, calculation problems concerning gas molecule flows in a porous medium are still relevant. For solving thereof, idealized models are adopted, approximate design ratios are used, and numerous approximations are introduced. It should be noted that current gas sensitivity models do not consider the porosity of nanostructured films. Therefore, they are poorly
applicable for modeling sensory response kinetics of sensing elements of both gas sensors and vacuum gauges.

There is matter (gas molecules) transfer in nanomaterials with a hierarchical pore system when molecules collide with each other (Fickian molecular diffusion), or with pore walls (Knudsen diffusion). Besides, depending on the gas pressure, pore size, and form factor thereof, either the first or the second type process dominates, since the probability of molecular collision is rather small at low pressure.

The theoretical diffusion coefficient \( D_T \) considering both processes has the form:

\[
D_T = \frac{D_K D_M}{D_K + D_M},
\]

where \( D_K \) and \( D_M \) are Knudsen and molecular diffusion coefficients, respectively, determined by the relations:

\[
D_K = 4 \frac{r}{3} \sqrt{\frac{2RT}{\pi m}},
\]

\[
D_M = \frac{3}{8} \frac{1}{\sqrt{\xi}} \frac{kT}{p \sqrt{\pi m}},
\]

where \( r \) is the pore radius; \( R \) is the universal gas constant; \( k \) is the Boltzmann constant; \( T \) is temperature; \( M \) is the molar mass of a gas (in case of a multicomponent mixture, its average molar mass is used); \( \xi \) is the average molecular size; \( m^* \) is the average molar mass of a gas (it is determined by the ratio of \( m^* = \frac{m_1 m_2}{(m_1 + m_2)} \) for a mixture of two gases).

The distribution of gas molecules with concentration of \( C_{gas(x,t)} \) in porous films based on semiconductor oxides can be described by the following equation [9]:

\[
\frac{\partial C_{gas(x,t)}}{\partial t} = D_T N_p \frac{\partial^2 C_{gas(x,t)}}{\partial x^2} - KC_{gas(x,t)} ,
\]

where \( 0 \leq x \leq L \) is the coordinate to calculate the gas concentration; \( L \) is gas-sensitive film thickness; \( \partial \xi \leq \xi_{max} \) is gas exposure time; \( N_p \) is the number of pores in the film; \( K \) is the constant of surface reaction \([s^{-1}]\).

The solution to this equation is the function:

\[
C_{gas(x,t)} = C_0 \exp(\lambda t) \frac{\text{sh} \left( x \frac{K + \lambda}{ND_T} \right) + \text{sh} \left( 2L - x \frac{K + \lambda}{N_p D_T} \right)}{\text{sh} \left( 2L \frac{K + \lambda}{N_p D_T} \right)},
\]

with initial and boundary conditions being considered:

\[
\begin{align*}
C_i (0) &= C_0, \\
C_i (\xi_{max}) &= C_{max} , \\
C_s (0) &= C_s, \\
C_s (2L) &= C_{max} ,
\end{align*}
\]

where \( C_0 \rightarrow 0 \) and \( C_{max} \) is initial and maximum concentration of gas molecules, respectively; \( C_s = C_0 \exp(\lambda t) \) is the concentration of gas molecules on the porous film surface at \( t \) time; \( \lambda \) is some
constant; \( L \) is the thickness of the multicomponent oxide nanomaterial synthesized on the substrate surface.

An analysis of equation (5) shows that the concentration of gas molecules is not constant, being dependent on gas exposure onset; the greater the distance from the surface, the lower the concentration is. Considering that gas-sensitive nanomaterial structure is a porous layer array of infinitely small thickness, the change in its electrical conductivity linearly depends on concentration thereof, being exposed to reducing or oxidizing agents:

\[
\sigma(x,t) = \sigma_0 + \sigma_0 a C(x,t),
\]

where \( \sigma_0 \) is electrical conductivity of air-exposed films; \( a \) is some quantity depending on the type of gas (it is positive for reducing agents, and negative for oxidizing agents), and specific interaction mechanisms of gases and films based on multicomponent oxide nanomaterials [ppm⁻¹].

Integration of equation (7) makes it possible to determine the resistance of the gas-sensitive layer in air \( (R_0) \), and when exposed to gas molecules \( (R_g) \):

\[
\frac{1}{R_0} = \int_0^L \sigma_0 dx = \sigma_0 L, \quad (9)
\]

\[
\frac{1}{R_g} = \int_0^L (\sigma_0 + \sigma_0 a C(x,t)) dx = \sigma_0 L + \sigma_0 a \frac{N_p D_T}{K + \lambda} \left( \frac{L}{N_p D_T} \right)^{1/2} \exp(\lambda t). \quad (10)
\]

In this case, taking into account (9) and (10), the kinetics of sensory response of gas-exposed multicomponent oxide nanomaterials has the form:

\[
\frac{R_g}{R_0} = 1 + \frac{a}{L} \frac{N_p D_T}{K + \lambda} \left( \frac{L}{N_p D_T} \right)^{1/2} \exp(\lambda t). \quad (11)
\]

A characteristic feature of chemoresistive gas sensors is an increase in sensory response with a decrease in the size of crystallites that form a multicomponent oxide nanomaterial. Provided the crystallite size is commensurable with the Debye screening length, the concentration of free charge carriers is modulated throughout the entire volume due to chemical adsorption and formation of charged forms on the surface thereof. A further decrease in size leads to an increase in the concentration modulation efficiency and, accordingly, to an increase in the relative change in the concentration of charge carriers and electrical resistance under the influence of the analyzed gases. However, a decrease in the crystallite size simultaneously contributes to a decrease in the pore size in the material, which slows down the diffusion of the analyzed gas into the material, i.e. diffusion enters the Knudsen regime, when the mean free path is limited by the pore geometric size. In this case, it is important to determine the prevailing type of diffusion in a given material for further predicting sensor parameters, having analyzed equation (11).

The diffusion regimes of a nanomaterial with a hierarchical pore system can be estimated through the calibration parameter \( D_i / L_p^2 \), where \( D_i \) is the diffusion coefficient (molecular or Knudsen, respectively), and \( L_p \) is the pore length. In this case, Fick diffusion dominates if the calibration parameter calculated from the experimental data is about \( 10^5 \) s⁻¹, and Knudsen diffusion prevails if it is about \( 10^9 \) s⁻¹ [10].

We rewrite expression (11) as:

\[
\frac{R_g}{R_0} = \frac{F N_p}{S \sigma} \sqrt{\frac{D_T}{L_p^2 (K + \lambda)}} \exp(\lambda t) = \left( \frac{R_g}{R_0} \right)^{1/2} \exp\left( \frac{S \sigma}{F N_p} \sqrt{\frac{L_p^2 (K + \lambda)}{D_T}} \right), \quad (12)
\]
where \( s = \frac{V_p}{V_f} = \frac{N_r L_r F}{L S} \) is porosity estimated from the ratio of pore volume \((V_p)\) to the volume of the gas-sensitive layer \((V_f)\), and its form factor \((F)\), taking into account the presence of a hierarchical system of pores, represented by macro-, meso- and micropores in a nanomaterial with a surface area \((S)\).

Further, to find the calibration factor, we represent (12) in the form of a system of equations:

\[
\begin{align*}
\left\{ \begin{array}{l}
f_1 \left( \frac{D_f}{L_p^2} \right) = \frac{R_a}{R_0} \frac{FN_p}{S_S} \sqrt{L_p (K + \lambda)} C_0 \exp(\lambda t) \\
f_2 \left( \frac{D_f}{L_p^2} \right) = \left( 1 - \frac{R_a}{R_0} \right) \left[ \frac{S_S}{FN_p} \sqrt{L_p (K + \lambda)} \right]
\end{array} \right.
\end{align*}
\]

where \( f_1 \left( \frac{D_f}{L_p^2} \right) = f_2 \left( \frac{D_f}{L_p^2} \right) \) are functions characterizing the relative change in resistance of multicomponent oxide nanomaterials depending on the calibration factor.

The calibration factor can be calculated by a graphical method (figure 1) using experimental data on the sensory response in region II (the inset in figure 1, a).

**Figure 1.** Determination of the calibration factor (a), and AFM image of the surface morphology of multicomponent oxide nanomaterials \( \text{SiO}_2-\text{SnO}_2-\text{ZnO} \) (b).

Thus, for the considered \( \text{SiO}_2-\text{SnO}_2-\text{ZnO} \) nanomaterials with oxide mass fractions of 20, 65, and 15 wt\%, respectively, a value of \( D_f / L_p^2 \approx 1.48 \times 10^3 \text{s}^{-1} \) indicates the predominance of Fickian diffusion. This fully corresponds to the surface morphology of the gas-sensitive layer, which is characterized by the presence of a large number of macropores (figure 1, b). These pores serve to supply the analyzer gas to the nanomaterial and remove the reaction products. Taking into account the form factor, their size significantly exceeds the mean free path of gas particles, which does not allow diffusion to enter the Knudsen regime.

The proposed model can be used in the development and prediction of output parameters for sensing elements of gas sensors and vacuum gauges based on multicomponent oxide nanomaterials with a hierarchical pore system. Knowing the prevailing diffusion type allows controlling sensitivity, selectivity, and response time thereof.

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