The Witten-Sander stochastic fractal approximation as the basis for a model of sensory response of multicomponent oxide nanomaterials to changes in environmental pressure

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\textbf{Abstract.} A model developed on the Witten-Sander fractal approximation of sensory response of vacuum sensors with sensitive elements, based on multicomponent oxide nanomaterials, is proposed. A key feature of the model is a mechanical contact of three-dimensional fractal aggregates consisting of conductive and non-conductive nanoparticles. It leads to the formation of a conductive channel, being a two-dimensional fractal. An agreement between the simulation results and experimental data for a two-component tin dioxide-silicon dioxide system with a labyrinthine structure, synthesized using the sol-gel technology, has been demonstrated in a wide range of pressures.

At present, most modern technological processes take place in a vacuum and require pressure control in a wide range. However, there is no such a physical phenomenon that could be effectively used in vacuum gauges to measure the entire required pressure range from atmospheric to deep vacuum. Therefore, devices based on different operation principles, and using a wide class of physical phenomena, are implemented in various ranges. An idea of using wide bandgap semiconductor metal oxides as sensitive elements of vacuum sensors was first outlined in a number of modern papers [1–3]. We have extended this idea to multicomponent oxide nanomaterials, for example, based on a two-component SiO\textsubscript{2}-SnO\textsubscript{2} system, in our earlier work [4, 5]. At the same time, a number of questions on the mechanisms of sensitivity of such nanomaterials to changes in environmental pressure remain unsolved. It has been reliably established that a decrease in the resistance of a two-component SiO\textsubscript{2}-SnO\textsubscript{2} system with a decrease in pressure below atmospheric is due to the processes of adsorption/desorption of gases. In this case, the key role belongs to O\textsubscript{2} form of oxygen, the existence of which is possible on highly defective surfaces in a wide range of temperatures, including those close to room temperatures, and has been confirmed in a number of studies [6].

However, the processes occurring during adsorption/desorption of oxygen, which are generally determined by both the qualitative composition of the used multicomponent oxide nanomaterial and the structure that it forms during the synthesis, are not completely clear [7, 8]. The formation of three main types of structures (spherical, labyrinthine, and percolation net) has been observed for a two-
component system based on tin dioxide-silicon dioxide, synthesized by the sol-gel technology. The model proposed in [9] is in fairly good agreement with the experimental data for nanomaterials with a spherical structure; it satisfactorily describes samples with labyrinthine formations, but is inapplicable for multicomponent oxides with a percolation net structure. This model is based on the barrier mechanism of conductivity associated with the integration of single crystals of nanometer size into aggregates from 100 nm to 1-2 µm. It is assumed that the sensitive layer of the vacuum sensor is formed by three-dimensional fractal aggregates (according to the Jullien model) of conductive (SnO$_2$) and non-conductive (SiO$_2$) nanoparticles. The aggregates are in mechanical contact with each other and form an electric current flow channel, the diameter of which is determined by the size of the depletion region resulting from the adsorption of oxygen and the capture of electrons from SnO$_2$.

Desorption of O$_2$ at pressures below atmospheric leads to a reduction in the size of the depletion region, an increase in the conductive channel, and a decrease in the resistance of the nanomaterial, respectively.

Using the three-dimensional fractal Jullien model to describe the basic elements that form SiO$_2$-SnO$_2$-based multicomponent oxide nanomaterials with a spherical structure is quite acceptable and agrees well with atomic force microscopy data. However, obvious shortcomings of this model, consisting in its deterministic nature, which are not consistent with the stochastic processes of the sol-gel synthesis, show the incomplete agreement of experimental data and simulation results for labyrinthine structures. Therefore, the purpose of this work is to simulate the sensory response of vacuum sensors with sensitive elements based on multicomponent oxides in the Witten-Sander fractal approximation.

Focusing on this model, we will assume that the basic elements that form the structure of a nanomaterial are fractal aggregates of radius $R$ according to the Witten-Sander model, which are in mechanical contact with each other, resulting in a conductive channel with a diameter:

$$d_k = 2aR,$$

where $0 < a < 1$ is the overlap coefficient of aggregates under their mechanical contact.

The stochastic nature of the studied aggregates makes it very difficult to estimate their radius, the overlap coefficient, and, as a consequence, the diameter and shape of the conductive channel. The assumption about the continuous nature of the conductive channel is impractical, given the known experimental data, according to which two-component systems based on SiO$_2$-SnO$_2$ are characterized by high porosity, due to the presence of macro-, meso- and micropores. As a result, it is more acceptable to choose a model of two-dimensional Witten-Sander fractal to describe such a channel (figure 1).

![Figure 1](image_url)

**Figure 1.** Three-dimensional Witten-Sander fractal as a model of basic elements that form multicomponent oxide nanomaterials, and two-dimensional Witten-Sander fractal as a model for describing a conductive channel.
Then, the current flowing through the considered channel will include two components, the first of which characterizes the movement of charge carriers through its center, and the second one through the depletion region \( w \):

\[
I = j_b S_b + j_w S_w,
\]

where \( j_b \), \( j_w \) are current densities corresponding to the movement of charge carriers through the center of the channel of \( S_b \) area, and through the area depleted by charge carriers of \( S_w \) area, respectively.

The formula (2) determines \( j_b \) and \( j_w \) by the coefficients known from the physics of semiconductors:

\[
\begin{align*}
  j_b &= q \mu_b n_b E, \\
  j_w &= q \mu_w n_w E,
\end{align*}
\]

where \( n_b \), \( n_w \) and \( \mu_b \), \( \mu_w \) are concentration and mobility of charge carriers in the center of the channel and in the depletion region, respectively; \( E \) is the electric field strength applied to the channel.

The area of the central channel and the area of the depletion region will be determined based on the model of the two-dimensional Witten-Sander fractal as:

\[
\begin{align*}
  S_b &= \pi r_0^2 N_{prb}, \\
  S_w &= \pi r_0^2 N_{prw} = \pi r_0^2 (N_{prk} - N_{prb}),
\end{align*}
\]

where \( r_0 \) is the radius of a single nanoparticle, \( N_{prb} \), \( N_{prw} \) is the amount of conductive nanoparticles having a cross section \( \pi r_0^2 \), contained both in the center of the channel and in the depletion region, respectively; \( N_{prk} = N_{prb} + N_{prw} \) is the total number of conductive nanoparticles in the channel.

The generalized formula for the number of conductive particles in a deterministic fractal aggregate of any spatial organization can be written as \( [9] \):

\[
N_{pr} = \frac{M_{diel}}{M_{diel} + (1 - \omega)M_{pr}} r_0^{-D} R^D,
\]

where \( D \) is the fractal dimension corresponding to a specific model of the aggregate, \( \omega \) is the mass fraction of tin dioxide in the nanomaterial, \( M_{diel} \) and \( M_{pr} \) are molar masses of dielectric and conductive material, respectively.

The formula (7) is inaccurate for fractals of a stochastic nature, since aggregates of the same size may contain different amounts of nanoparticles \( N = N_{pr} + N_{diel} \), where \( N_{pr} \) and \( N_{diel} \) is the number of conductive and dielectric particles, respectively. The coefficient of the number of conductive and non-conductive particles does not depend on the type of the fractal aggregate, that is, \( N_{pr}/N_{diel} = M_{diel}/(1 - \omega)M_{pr} \). However, the results of numerical calculations in accordance with the diffusion-limited aggregation (DLA) of the cluster-particle model show a good agreement with the values determined by the formula (7). According to the DLA, the average number of conductive particles \( N_{pr}^{DLA} \) deviates from the calculated value in (7) by less than 10%. Therefore, to find the total number of conductive nanoparticles in the electric current flow channel, you can use the formula (7), taking into account that the fractal dimension \( D \approx 1.7 \) will correspond to the two-dimensional Witten-Sander fractal aggregate.

Then, the total number of conductive particles in the channel, taking into account the overlap coefficient of fractal aggregates, is defined as:

\[
N_{prk} = \frac{M_{diel}}{M_{diel} + (1 - \omega)M_{pr}} r_0^{-D} \left( \frac{d_k}{2} \right)^D = \frac{M_{diel}}{M_{diel} + (1 - \omega)M_{pr}} r_0^{-D} (aR)^D.
\]

Based on the total number of conductive particles in the channel, it is possible to estimate the number of nanoparticles contained in the center of the channel and in the depletion region, respectively. A more accurate estimate is due to a numerical calculation in accordance with the DLA.
using $N_{DLA}^0$, and the use of the formula (7) inevitably leads to a small error, since the sum of $N_{prb}^*$ and $N_{prw}^*$, calculated assuming a fractal aggregate radius $r_b = d_k / 2 - w$ and the depletion region $w$, is not exactly equal to $N_{prk}$, that is, $N_{prk}^* \neq N_{prb}^* + N_{prw}^*$. This inequality is a consequence of the Witten-Sander stochastic fractal anisotropy for which there is growth direction preferred within the DLA (figure 1). However, it should be noted that the error in assessing $N_{prb}$ and $N_{prw}$ can be reduced by introducing a correction factor $c$ connecting $N_{prb}^*$ and $N_{prk}^*$, as well as $N_{prw}^*$ and $N_{prk}^*$. In view of the above, the amount of conductive nanoparticles having a cross-sectional area $\pi r_0^2$, contained in the center of the channel, is defined as:

$$N_{prb}^* = cN_{prb} = \left[ \frac{aR}{aR-w} \right]^2 cN_{prk} = \left[ \frac{aR}{aR-w} \right]^2 \frac{cM_{diel}}{M_{pr} + (1-\omega)M_{pr}} r_b^{-D} (aR)^D.$$  \hfill (9)

Taking into account (8), the area of the central channel and the depletion region is defined as:

$$S_b = \pi \left[ \frac{aR}{aR-w} \right]^2 \frac{cM_{diel}}{M_{diel} + (1-\omega)M_{pr}} r_b^{2-D} (aR)^D,$$  \hfill (10)

$$S_w = \pi \left[ 1 - \left[ \frac{aR}{aR-w} \right]^2 \right] \frac{cM_{diel}}{M_{diel} + (1-\omega)M_{pr}} r_b^{2-D} (aR)^D.$$  \hfill (11)

Taking into account (2), (3), (4), (10), and (11), we get the following expression for the current flowing through the channel:

$$I = q \frac{d_k}{U} \left( \mu_b n_b S_b + \mu_w n_w S_w \right).$$  \hfill (12)

where $E=U/d_k$ if the voltage drop $U$ occurs mainly at the boundary of the mechanical contact of the fractal aggregates.

**Figure 2.** Pressure dependence of the sensory response of vacuum gauges of a labyrinthine structure with sensitive elements based on SiO$_2$-SnO$_2$. 

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$$S_w = \pi \left[ 1 - \left[ \frac{aR}{aR-w} \right]^2 \right] \frac{cM_{diel}}{M_{diel} + (1-\omega)M_{pr}} r_b^{2-D} (aR)^D.$$  \hfill (11)

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**Figure 2.** Pressure dependence of the sensory response of vacuum gauges of a labyrinthine structure with sensitive elements based on SiO$_2$-SnO$_2$. 

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Then, the channel resistance, and as a consequence of this, the resistance of multicomponent oxide nanomaterials, used as sensitive elements of vacuum sensors, is defined as:

\[
R = \frac{2aR}{q\pi_0 2^{-D} cM_{\text{dil}}}{M_{\text{dil}} + (1 - \omega)M_{\text{pr}}} \left[ \mu_{\text{b}}n_{\text{b}} \left( \frac{aR}{aR - w} \right)^2 \right] + \mu_{\text{w}}n_{\text{w}} \left( 1 - \left( \frac{aR}{aR - w} \right)^2 \right) \right].
\] (13)

Figure 2 shows the dependence of the sensory response \((S=R/R_0)\) of vacuum sensors with sensitive elements based on a two-component SiO\(_2\)-SnO\(_2\) system. A set of curves 1 and 2 corresponds to nanomaterials with different size of branches (basic fractal aggregates), forming labyrinthine structures. The solid curves correspond to the simulation results in the Witten-Sander fractal approximation; the dotted curves correspond to the Jullien fractal; the experimental data are indicated by the markers.

The analysis of the presented dependences shows that with a decrease in pressure below atmospheric the resistance of sensitive elements of vacuum sensors based on multicomponent oxides also decreases. This process corresponds to a change in the size of the depletion region as a result of oxygen desorption from the surface and from the volume of the nanomaterial. The use of the Witten-Sander approximation allows one to improve the agreement of experimental data and simulation results in the low-pressure region.

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