Functional nanomaterials based on metal oxides with hierarchical structure.

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Abstract. The depending on evolution morphology of hierarchical porous nanostructured films based on metal oxide systems was investigated using atomic force microscopy. Gas sensitive properties of these structures were investigated. It was found that the characteristics of the degree of maturation of sols are gas-sensitive parameter to create functional porous layers.

1. Introduction
Sol–gel processes [1-3] are finding ever-increasing applications in various fields of science and engineering. Models of various hierarchies formed during the sol–gel transition are of great scientific and practical interest. It is worth noting that these hierarchies [4-7] can be different in shape and origin.

In modern materials science, the principle of hierarchical self-assembly has acquired great importance. In essence, this principle lies in the synthesis of “building blocks” (modules) with specified sizes and shapes and in the further process of their integration. The hierarchical self-assembly can represent a multilevel process, when the integrated modules are the initial elements of larger sized aggregates (with larger characteristic interaction radii).

This work is aimed at investigating the mechanisms responsible for the formation of objects with a hierarchical porous structure by means of the self-assembly in sol–gel processes in which the initial fractal aggregates are formed over the entire volume of the colloid as a result of the diffusion-limited aggregation and the subsequent (more retarded) processes occur already with an increasing role of cluster–cluster interactions. The processes of formation, growth, and evolution of fractal aggregates can be controlled in the sol–gel synthesis.

2. Purposes
This work is aimed at investigating the mechanisms responsible for the formation of objects with a hierarchical porous structure by means of the self-assembly in sol–gel processes in which the initial fractal aggregates are formed over the entire volume of the colloid as a result of the diffusion limited aggregation and the subsequent (more retarded) processes occur already with an increasing role of cluster–cluster interactions. The processes of formation, growth, and evolution of fractal aggregates can be controlled in the sol–gel synthesis.
3. Experiment
Solutions of sols were obtained on the basis of binary heterochain inorganic polymers, where atoms form ion-covalent bonds between each other. The initial pre-courses used for the preparation of sol solutions are easily hydrolyzed components. Such components form polymolecules, or poly-solvated groups, due to their interaction with water. Tetraethoxysilane (TEOS, Si(OC₂H₅)₄) was chosen to obtain the nanostructured films of silicon dioxide. TEOS solutions helped to improve the film-forming qualities and have the ability to spread over the surface of porous silicon. To obtain the two-component oxide materials 10SiO₂–90SnO₂ (mol. %), the hydrolysis and polycondensation of TEOS in the presence of inorganic salt of tin. Five types of film structures with a gradual increase in the exposure time of sol were obtained.

The optimum ratio of the basic components in an initial solution provides fast partial or full hydrolysis of alkoxides forming sol. The prepared sol solution is deposited on a rotating (3000 rev / min) glass substrate surface leading to a fuller hydrolysis of the alkoxides. The subsequent polycondensation and deposit of a sol thin layer on the substrate surface results in the formation of gel spatial at an annealing temperature of 600 °C.

Observations of nanostructured layer morphology of two component systems, using dynamic AFM (atomic force microscopy) methods, were carried out using an NTEGRA-Thera nanolaboratory (NT-MDT). Si-AFM probes NSG01 (NT-MDT) with a spring constant varying between 2.5 N/m and 10 N/m were used. The radius of curvature of the probes was ≥10 nm. We recorded AFM images at a resolution of 256 by 256 elements. Fractal dimension was calculated using Gwyddion.

Using impedance spectroscopy, we performed studies on the electrical properties of the nanomaterials. Measurements of the impedance spectra were carried out in the frequency range from 1 Hz to 0.5 MHz at 300 °C using an impedance meter «Z-500 P» (LTD «Elins»).

4. Results and Discussion
The sol–gel methods belong to technologies of molecular design. During the growth, fractal aggregates transform into percolation composites with controlled and reproducible sizes of pores in the range from several nanometers to several micrometers, or a porous structure is formed as a result of the spinodal decomposition and phase separation.

The main evolution stages of fractal aggregated systems were demonstrated using atomic force microscopy (figure 1–5).

![Figure 1. First type structures.](image1)

![Figure 2. Second type structures.](image2)
We revealed that local areas of irregular shape (figure 1: scanning area size is $5 \mu m \times 5 \mu m$; first type structures) in film nanocomposites formed in the early stages of ripening sols in nucleophilic growth. The fractal objects (figure 2: scanning area size is $10 \mu m \times 10 \mu m$; second type structures) are formed inside these areas with increasing exposure time of sols.

The formation of nanocomposites is determined by diffusion-limit aggregation and cluster–cluster aggregation conditions. It was shown that a further increase in the exposure time of sols leads to the formation of hierarchical structures with porous percolation isthmuses between the pores (figure 3: scanning area size is $10 \mu m \times 10 \mu m$; third type structures) in terms of spinodal decomposition. Revealed that hierarchical nanocomposites formed on glass substrates have pores with a size of two types 150-200 and 400-700 nm (figure 3), and on oxidized silicon substrates – 20 nm and 230-400 nm.

It was found that the fourth type structure corresponds to a porous structure with pore sizes of 10, 20 and 30 nm (figure 4: scanning area size is $10 \mu m \times 10 \mu m$), and the fifth type structures – corpuscular porous structure in which pores (with dimensions of about 10 nm) are the spaces between the particles (with size of about 40 nm) (figure 5: scanning area size is $1 \mu m \times 1 \mu m$).

It was found that the molecular weight distribution of the inorganic polymer chains in the sol strongly influences supramolecular structure of nanocomposites. It was shown that the longer the polymer chains in the sol, the more there is a strong tendency for spinodal decomposition. The dependence of the fractal dimension of the films on the degree of maturity of the sol is nonmonotonic (figure 6).
The principle of operation of semiconductor gas sensors based on metal-oxide layers [8-13], which represent porous nanostructured composites, consists in changing the electrical conductivity of the material as a result of the chemisorption of gases. The first and necessary stage in the process of gas detection is the adsorption of oxygen on the surface of the semiconductor film. In the process, electrons are transferred from the bulk of the semiconductor to oxygen located on the surface of the film, which leads to a bending of the energy bands in the near-surface region to a depth determined by the Debye screening length. During the interaction of the reducing gas with negatively charged oxygen molecules on the surface of the semiconductor film, electron pass back into the bulk of the semiconductor and the reaction products leave the surface in the neutral form; in this case, the electrical resistance of the semiconductor material decreases. The measurements of the gas sensitivity were carried out using the reducing vapors of ethanol. The gas-sensitivity was calculated two ways:

\[ S(Re) = \frac{Re(Z_{air}) - Re(Z_{gas})}{Re(Z_{air})} \times 100\% \]

\[ S(Im) = \frac{Re(Z_{air}) - Re(Z_{gas})}{Re(Z_{gas})} \times 100\% \]

where \( Re(Z_{air}) \) and \( Im(Z_{air}) \) – the value of active and reactive components of the complex impedance in air, \( Re(Z_{gas}) \) and \( Im(Z_{gas}) \) – the value of active and reactive components of the complex impedance in the presence of ethanol vapour (table 1). It was shown that gas-sensitive thin film layers decreases with increasing degree of maturation of the sol.

| Table 1. The calculated sensitivity for the samples. |
|-----------------------------------------------|
| Sample type | first | second | third | forth |
| S(Re),% | 400 | 130 | 90 | 14 |
| S(Im), % | 900 | 180 | 130 | 40 |
5. Conclusion
In this work, it has been shown that the control of the self-assembly in sol–gel processes provides a means for controlling the structure of fractal clusters and their gas-sensitive properties. Five different stages of the evolution of fractal aggregated systems of tin and silicon dioxide have been determined, namely, the formation of local areas of irregular shape in nucleophilic growth, diffusion-limited aggregation, cluster–cluster aggregation, formation of spherical species, the formation of hierarchical structures with porous percolation isthmuses between the pores in terms of spinodal decomposition, the formation of porous structure with pore sizes of 10, 20 and 30 nm corpuscular porous structure in which pores (with dimensions of about 10 nm) are the spaces between the particles. Investigated gas sensitive properties of these structures with respect to ethanol vapor. It was found that the characteristics of the degree of maturation of sols are gas-sensitive parameter to create functional porous layers.

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