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Net-like structured materials for gas sensors

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Abstract. Silicon dioxide-based fractal aggregates as an example of self-assembly in sol-gel processes were prepared. Main evolution stages of tin dioxide-silicon dioxide fractal systems were demonstrated by atomic force microscopy (AFM): diffusion-limited aggregation, cluster-cluster aggregation, formation of percolation net and 3D-net nanostructures. The formation possibilities of porous nanomaterials based on different metal oxides, including those based on tin dioxide, iron oxide and zinc oxide, were shown. New chemical etching method to obtain microreactors was developed. Specific surface area of nanostructures was investigated by thermal desorption of nitrogen and gas sensitive properties of tin dioxide nanocomposites were also studied.

1. Introduction

Developing methods for synthesis of materials with hierarchical architecture is one of the most advancing directions among nanotechnologies of functional materials. Such materials consist of elements of different scales; they are organized so that the elements of smaller scales are built into the elements of larger scales. New unique properties of hierarchical materials arise from composition changing, size changing and (or) from construction of substructures (clusters, blocks) on one or several different levels [1]. One of the methods to obtain such hierarchical nanomaterials is self-assembly [2, 3]. Hierarchical self-assembly processes can be realized not only due to ionic or covalent interactions or by metallic, hydrogen or coordination bonds, in this case weaker forces, such as Van der Waals forces, Coulomb interaction, Casimir forces, forces caused by special features of medium and outer fields characteristics (colloidal, capillary, π-bonds, convective, magnetic, electrical, optical, gravity forces and hydrophilic-hydrophobic interactions), generally take place [4].

The main point of hierarchical self-assembly is synthesis of initial constructive "blocks" with different sizes and shapes (and size-dependent properties) and their further integration. Hierarchical self-assembly can be a multilevel one, when the integrated blocks are basic elements for larger consolidations (with lager interaction radius).

The products of hierarchical self-assembly are materials with hierarchical porous structure. One of the simplest idealized examples of such self-assembly is Julien fractal (Figure 1) [5]. It is an appropriate example for understanding of the principal possibility to obtain the materials with pores of calibrated sizes. That is very important for development of new-generation devices, because the pores with different sizes have different functions (nanoreactors with different capillary phenomena, canals for reaction products delivery and withdrawal, adsorption centers etc.).

The sol-gel processes are based on hierarchical self-assembly [6]. In sol-gel processes the initial fractal aggregates are created throughout the volume of colloid as a result of diffusion-limited

aggregation. The subsequent processes are caused by growing role of cluster-cluster interactions [7]. The processes of formation, growth and evolution of fractal aggregates in sol-gel synthesis can be controlled. Sol-gel methods are ones of the molecular design technologies [8]. Fractal aggregates in the process of their growth can be transformed into percolation composites with pores of controlled and reproducible sizes from nanometer to micrometer (Figure 2), or formation of porous structure can take place because of spinodal decomposition and phase separation. Sol-gel techniques are often supplemented with the template synthesis methods [9, 10, 11], such as insertion of dendrites, fullerenes or carbon nanotubes, which are burnt later. Large surface area (Figure 2) and high modulation of current canal sections during gas adsorption on the surface can be effectively used in new generation of semiconductor gas sensors, including multisensor "electronic-nose" systems [12].

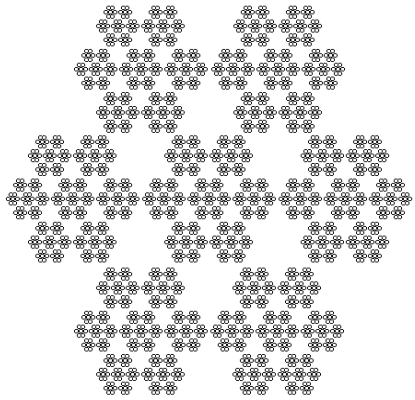


Figure 1. Projection of 3-D Julien fractal.

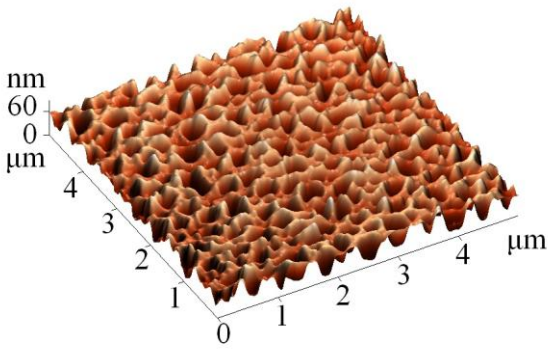


Figure 2. AFM image of fractal SiO_2-SnO_2 nanocomposite synthesized by sol-gel method.

The systems based on n-type semiconductor metal oxide nanocomposites (such as SnO_2, ZnO, Fe_2O_3, NiO, V_2O_3, WO_3, Co_3O_4) are very sensitive to surface states at high temperatures, so they are suitable materials for detection and identification of minute quantity of explosive, narcotic and dangerous substances.

2. Experimental details

AFM was used to measure the surface morphology of the thin-film nanostructures synthesized from sol solutions in the precursor medium based on tetraethoxysilicate (TEOS). Tapping mode AFM experiments were performed using NTEGRA-Therma nanolaboratory (NT-MDT, Zelenograd, Russia). Commercial etched silicon tips NSG 01 (NT-MDT, Zelenograd, Russia) with typical resonance frequency of 150 kHz were used as AFM probes.

Specific surface area measurements were made using Sorbi № 4.1 (CJSC «META», Novosibirsk, Russia) that realizes physical adsorption of noble gas by the sample to be studied. Operating principle of the instrument is based on the comparison of the volume of gas-adsorbate which is absorbed by the studied sample with the volume of gas absorbed by the standard sample with known value of specific surface area. In current research standard sample pressed in globe-shaped granules (diameter is 2 mm, weight is 0.01 g) and having specific surface area 67 m^2/g was used for calibration of Sorbi. Nitrogen was used as gas-adsorbate. For the measurement of absorbed gas volume the thermal desorption method was applied. A thermal conductivity sensor was a detector of gas mixture composition. The signal of thermal conductivity sensor (TCS signal) is a desorption curve (Figure 3). The measurements were made under variation of the relative partial pressure (P/P_0) of gas-adsorbate (Figure 4, where V is absorbed gas volume normalized to 1 gram of the sample). Specific surface area was calculated according to the model of Brunauer, Emmett, Teller.

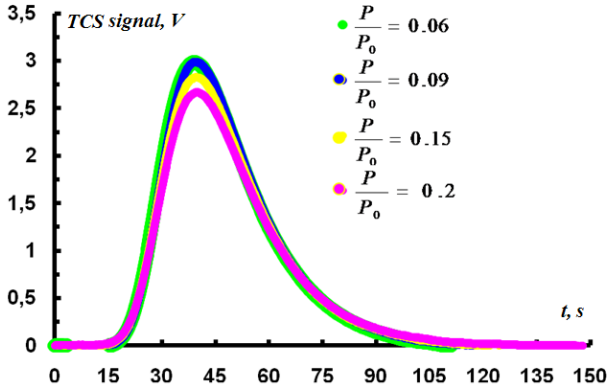


Figure 3. Typical desorption curves for porous nanocomposites based on the tin dioxide (the relative partial pressure of nitrogen are 0.06, 0.09, 0.15 and 0.20).

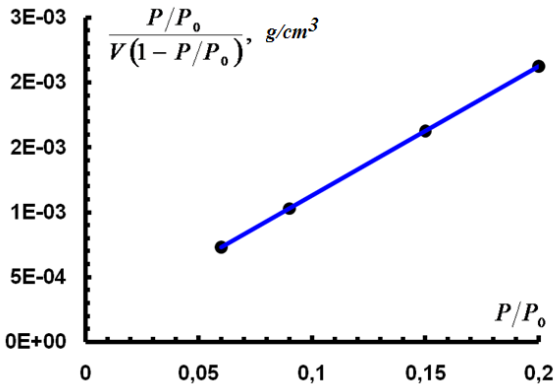


Figure 4. Typical plot $\frac{P/P_0}{V(1-P/P_0)} = f(P/P_0)$ for porous nanostructures.

Preliminary thermal action influence on the structures was studied with the use of SorbiPrep (the station for preliminary treatment of the samples). Operating principle of the station is based on the degassing of disperse and porous materials by their heating in the stream of noble gas (helium). The station works in various operation modes: temperature and time can be changed as 50-400 ºC, 0-99 minutes. In this work the SiO_2-SnO_2 nanomaterials with various SiO_2 content (0 – 100 %) obtained by sol-gel method under other equal conditions (pH level, temperature, annealing time) were chosen for studying.

Gas-sensitivity measurements were done to acetone and ethanol vapors. Value of sensitivity was calculated as $S = (Rair - Rgas)/Rgas$, where *Rair* is the electrical resistance in dry air, *Rgas* is the electrical resistance in the presence of gas to be tested. Automatic cycle of sensitivity measurement consists of several stages: heating of sensor film composite to required temperature in air atmosphere; measurement of the sensor resistance while the temperature is maintained; gas-reagent supply (the concentration of gas-reagent is 1000 ppm) until the sensor resistance in the presence of gas vapors is stabilized.

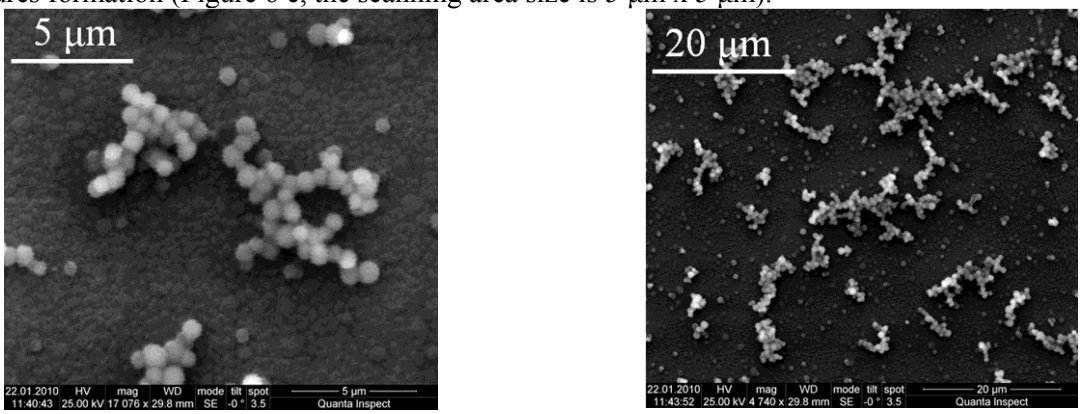
3. Results and discussion

Figure 5 illustrates the self-assembly in sol-gel processes and shows SEM (in secondary electron mode) microphotographs of SiO_2 fractal aggregates synthesized by sol-gel method. The series of images (Figure 5 a – d) was analysed and the film structure was found to consist of rather large clusters of spherical particles. The size of these clusters ranges from several to tens of micrometers. In sol-gel processes growth of fractals according to the model of diffusion-limited aggregation occurs simultaneously with the random cluster-cluster aggregation. In that case occasional contacts among fractal aggregates and particles, cross-linking reactions among the branched structures and also the formation of large percolation clusters take place.

Sol-gel processes occurring in unstable states lead to the spontaneous formation of materials with different morphology as a result of spinodal decomposition [14]. In unstable states any fluctuation gains energy so that the fluctuations spontaneously develop without activation energy [15].

Generally the results of AFM studies show that evolution of fractal aggregates based on metal oxides can be controlled by varying the thermodynamic and kinetic conditions of sol-gel nanotechnology (composition of the materials, precursors, amount of solvent, polymer sol solutions aging time, annealing temperature). Several stages of evolution for fractal-aggregated systems based on tin dioxide and silicon dioxide were determined: spherical structures formation (nucleophilic

growth) (Figure 6 a, the scanning area size is 25 μm x 25μm); co-continuous structures formation (spinodal decomposition) (Figure 6 b, the scanning area size is 10 μm x 10 μm); percolation net-like structures formation (Figure 6 c, the scanning area size is 5 μm x 5 μm).

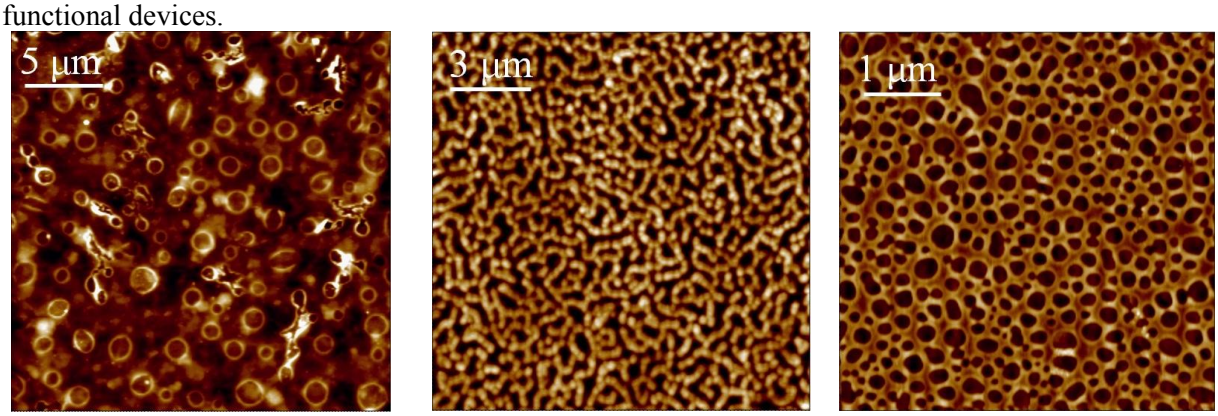


a b

Figure 5. SEM images of SiO_2 fractal structures synthesized by sol-gel method.

The formation possibilities of porous nanomaterials based on different metal oxides, including those based on tin dioxide (Figure 2, Figure 6), iron oxide (Figure 7), zinc oxide (Figure 8), were shown in this work.

The shape and size of obtained particles depend on the synthesis conditions [16, 17]. The specific advantages of zinc oxide micro- and nanocrystlas are related to the chemical properties but also strongly dependent on the size and shape of the crystals. Thus control over the size and morphology of nanometer- and micrometer-sized semiconductor materials is a great challenge to realize new functional devices.



a b c

Figure 6. Stages of evolution for fractal-aggregated systems based on tin dioxide and silicon dioxide.

It was found for ZnO-SiO_2 nanocomposites that particles are formed inside the pores at low annealing temperatures (300°C) and the shape and size of these particles depend on amount of solvent used for preparation of sol solution. When the amount of solvent is small crystalline structures with a size of about 1 micron grow perpendicular to the substrate surface inside the pores (Figure 8 a, the scanning area size is 20 μm x 20 μm). When the amount of solvent increases the nanoparticles smaller than 100 nm are observed inside the pores (Figure 8 b, the scanning area size is 2 μm x 2 μm). It was suggested that zinc oxide phase crystallizes in the pores as a result of spinodal decomposition and phase separation processes. However, the proof of this fact requires further experiments. It is found

that ZnO-SiO_2 samples annealed at higher temperatures do not contain crystalline structures inside the pores.

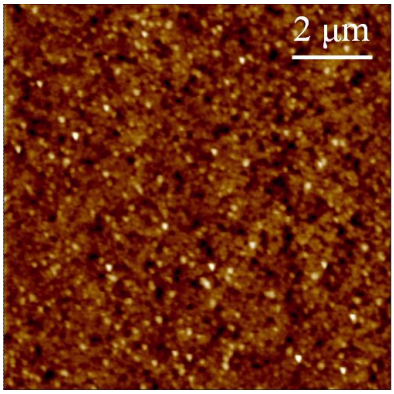
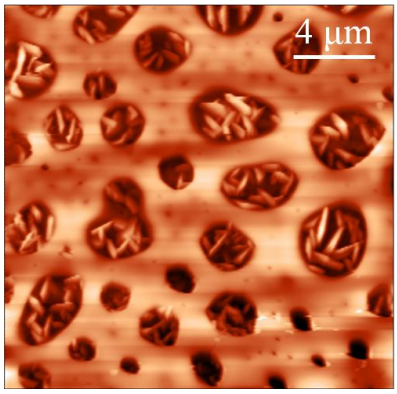


Figure 7. AFM image of iron oxide – silicon dioxide nanocomposite.



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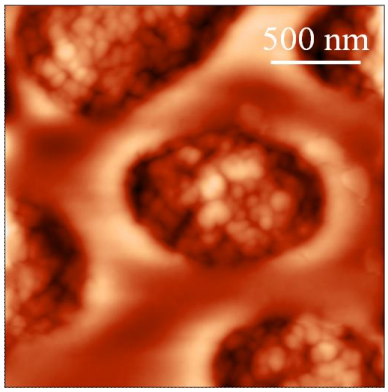


b

Figure 8. AFM images of zinc oxide-silicon dioxide nanocomposites annealed at 300 °C.

It should be noted that sol-gel derived porous silica (Figure 9, the scanning area size is 80 μm x 80 μm) has been used as a matrix for synthesis of different nanoparticles [18, 19]. Synthesis of such functional materials is usually requires several stages: first the porous matrix is produced by sol-gel method and then nanoparticles are precipitated into the pores. The advantage of the proposed method for synthesis of ZnO-SiO_2 nanocomposites is the ability to synthesize nanomaterials and porous matrix in a single process.

There is no doubt that studies on the compatibility of sol-gel synthesis with other methods at nanoscale are promising. The compatibility of sol-gel processes with spray pyrolysis is of particular interest. It is associated with the fact that the formation of new phases occurs in the vapor phase in spray pyrolysis and in the liquid phase in sol-gel processes [20]. The combination of two technologies similar in physical and chemical laws along with the easy introduction of catalyst particles by spray pyrolysis is promising for development of multisensor systems. Formation of intermediate porous layers having a special form is often required to create the multi-layer structures. The effective method for formation of microreactors was developed. It is etching (in hydrofluoric acid, HF) of net-like percolation nanocomposites based on tin dioxide (Figure 10 a, the scanning area size is 5 μm x 5 μm). Decreasing conductive branches (Figure 11) and formation of hexagonal pores are occurred (Figure 10 b, the scanning area size is 20 μm x 20 μm) during etching processes.

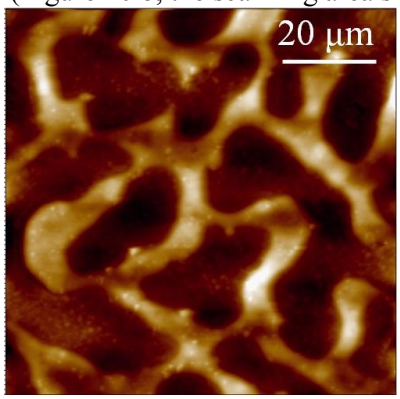
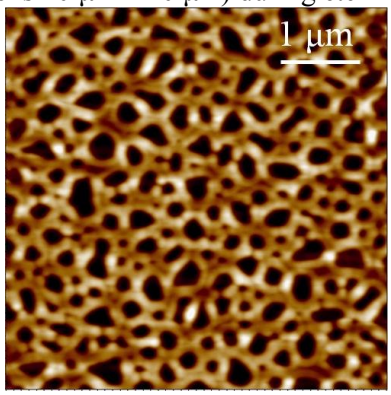


Figure 9. AFM image of sol-gel derived porous silica.



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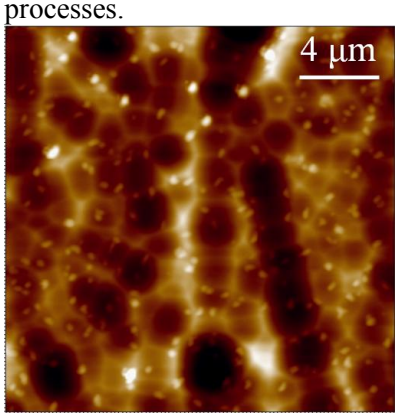

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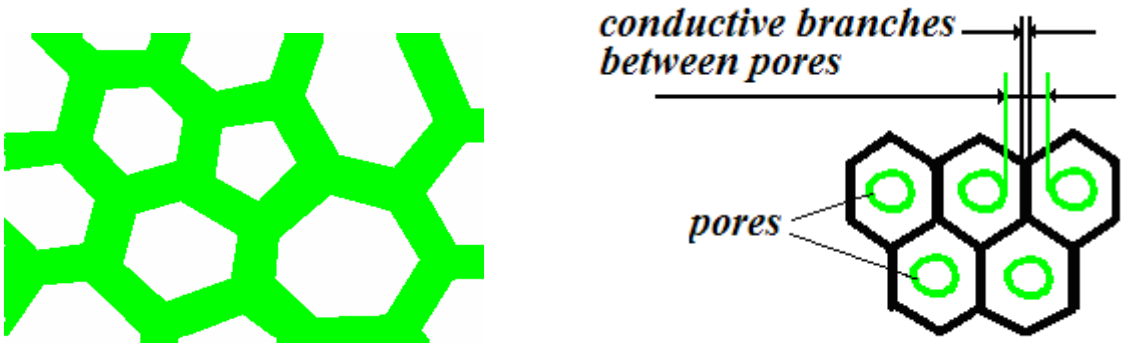
Figure 10. AFM images of tin dioxide net-like nanocomposite before (a) and after (b) etching.



a b

Figure 11. Schemes of microreactors obtained by etching of net-like nanocomposites (a), of decreasing conductive branches and the formation hexagonal pores (b).

High specific surface area and the porous structure with different sizes of pores are very important factors which are necessary for gas-sensitive structure to work efficiently. That is why studying the specific surface is one of the crucial methods for analysis of gas sensor characteristics.

In Figure 12 the dependence between specific surface area (SSA) of sol-gel SiO_2-SnO_2 nanocompisites and SnO_2 content is shown. The character of concentration dependence was repeated while several xerogel series were studied, so it can be considered that the specific surface area dependence reflects a common regularity for sol-gel system SiO_2-SnO_2.

It can be seen from Figure 12 that the plot can be divided in two parts having different characters of concentration dependence of specific surface area. In each part the experimental data can be approximated by a linear function. In the first area where tin content is low (0 – 10 % SnO_2) prompt growth of specific surface area is observed with increasing tin dioxide content. It is supposed that at low SnO_2 content monomeric branches of tin dioxide are incorporated into polymeric net of silicon dioxide, i.e. a monophase polymer solution in the binary system SiO_2-SnO_2 is created. The second area (10 – 100 % SnO_2) is characterized by gradual recession of the specific surface area with increasing tin dioxide content. An increase in tin oxide content leads to the formation of tin dioxide monophase aggregates, aggregate's size increases in the process of gel annealing resulting in decreasing porosity and descending the specific surface area of the samples.

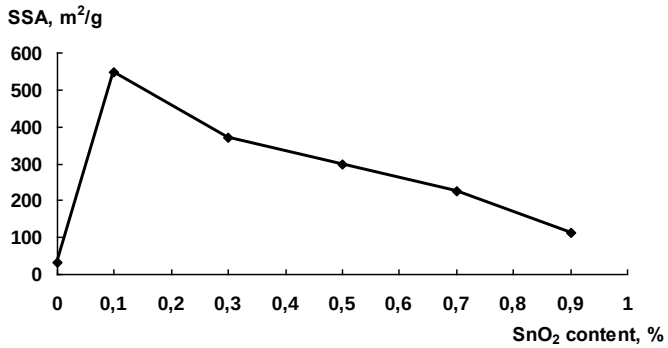


Figure 12. The dependence between specific surface area of sol-gel SiO_2-SnO_2 nanocompisites and SnO_2 content.

Preliminary thermal action influence on the structures was studied under various temperatures and times: T = 150 °C, 200 °C, 250 °C; t = 60, 90 minutes. Optimal conditions for preliminary treatment

of xerogels with high specific surface area were determined (T=200 °C, t=60 minutes). Necessity of using stricter conditions of preliminary degassing of powders in SorbiPrep can be connected with changing the character of porosity when SnO_2 content is increasing (more than 10%). The micropores arise along with macro- and mesopores, i.e. under those conditions the xerogels with multilevel system of pores are formed. Removal of residual gases adsorbed in micro- or ultramicropores takes stricter conditions in comparison with larger pores.

Gas sensitivity is determined by the processes in the near-surface layer, namely, by adsorption of gas molecules and their reactions with chemisorbed oxygen ions on the surface. The electrical resistance of sensor changes reversibly under exposing to reducing gases (in proportion to the gas concentration).

Typical time dependence of the netting nanocomposite resistance in the presence of gas-reagent is shown in Figure 13. The main results of the investigation of tin dioxide gas-sensitive nanostructures are following:

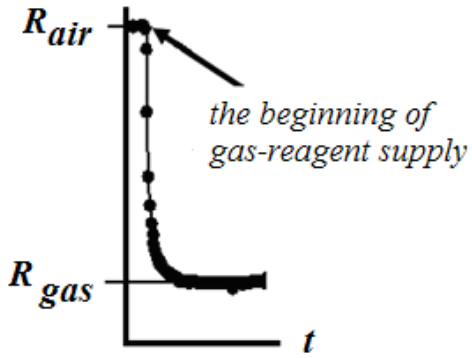


Figure 13. Typical time dependence of the netting nanocomposite resistance when gas-reagent is supplied and stopped.

- the nanostructures formed during nucleophilic growth (Figure 6 a) and co-continuous structures caused by spinodal decomposition (Figure 6 b) have very low sensitivity to acetone and ethanol vapors ($S \leq 0.5$);
- value of sensitivity to gas-reagents is $S > 20$ for netting percolation nanostructures (Figure 6 c).

4. Conclusions

The experimental results show that handling of self-assembly during sol-gel processes allows one to control the structure of fractal systems and their gas-sensitive properties. Main evolution stages of fractal systems based on tin dioxide were demonstrated by atomic force microscopy: diffusion-limited aggregation, cluster-cluster aggregation, formation of percolation net. Gas sensitive properties of nanocomposites under exposing to reducing acetone and ethanol vapors were investigated. The chemical etching method resulting in decreasing conductive branches of nanostructures and generation of hexagonal pores was developed for effective formation of microreactors. It was found that at low annealing temperatures pores of zinc oxide nanomaterials contain particles. The shape (sheet-like or spherical) and size (10-1000 nm) of these particles depend on amount of solvent used for preparation of sol solution. Study of the material properties by nitrogen thermal desorption after preliminary thermal action showed that the tin dioxide xerogels with multilevel porous system can be formed in sol-gel processes.

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