Determination of the fractal dimension of mesopores in metal-oxide structures obtained via sol-gel synthesis

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Abstract. The work is devoted to the development of a combined method of analyzing the porous structure of metal oxide materials. The method is based on a combination of fractal analysis from data obtained by the sorption method using a thermodynamic approach and fractal analysis of atomic force microscopy images. The objects under research are optically transparent materials of the SiO₂ – SnO₂ – ZnO system, obtained by the sol-gel technology.

1. Introduction
According to [1], at present the main materials for products of transparent electronics are metal oxide ZnO, SnO₂ and In₂O₃. These compounds have a wide band gap, high transparency in the visible range and electrical properties that allow them to be used for the manufacture of products of transparent electronics.

The main methods for producing micro- and nanostructures based on zinc and tin oxides can be classified into the following types: thermal evaporation, high-temperature calcination, mechanical grinding, sol-gel synthesis, hydrothermal method and synthesis based on ion exchange reactions. The structures under consideration are used as materials of transparent electronics [1], in solar cells [2], gas sensitive [3–7] and catalytic [8] structures, and materials for lithium batteries [9]. In most cases, the key characteristics of such structures are the porous structure parameters of the functional metal oxide layer.

2. Experiment
In the present work, the synthesis of metal oxides was carried out using the sol-gel technology. To eliminate the ion exchange reaction when mixing precursors as sources of metal oxides, the most rational choice is the salt with the same acid residues. The following metal precursors were selected: zinc and tin salts (ZnCl₂, SnCl₂·2H₂O). Butanol -1 was chosen as the solvent. After obtaining a stable solution of the starting metal salts in butanol without sedimentation, the solution was mixed with the gel-forming substance tetraethoxysilane (TEOS), which is one of the most studied precursor for gel formation, as well as a source of silicon dioxide [10]. The parameters affecting the result of the sol-gel process were the composition of the initial solution of the sol, pH level of the solution and centrifugation parameters.

The evaluation of the specific surface area of the synthesized nanocomposites, the average pore size and pore size distribution was carried out using the method of thermal desorption of inert gases carried out on the Sorby MS instrument. The device allows one to investigate porous systems of
various sizes, in particular, measuring the total specific surface by the method of Brunauer, Emmett, Teller and to investigate the processes of capillary condensation in mesopores, to obtain inert gas adsorption-desorption isotherms in the relative partial pressure range from 6 to 97%. The device is equipped with a «SorbiPrep» preparation station that can be used for controlled heating of samples in an inert gas flow.

The study of the surface morphology of porous thin films was carried out using scanning probe microscopy using an atomic force microscope Ntegra Therma (NT-MDT). The study used several methods for estimating the fractal dimension (decomposition, counting cubes, triangulation, power spectrum) for areas of AFM images of different sizes to determine the area in which the surface can be described in the fractal approximation.

3. Results and discussion

For the preparation of film samples, the formation of extended polymers is necessary. To do this, when mixing precursors it is necessary to maintain a weakly acidic medium in the sol solution (pH=2). This was achieved by introducing a small amount of acid corresponding to the acid residue of the metal salt. Several sols with different molar ratios of the components were prepared (0.1SiO₂–0.3ZnO–0.6SnO₂ - type 1, 0.1SiO₂–0.45ZnO–0.45SnO₂ - type 2, 0.1SiO₂–0.6ZnO–0.35SnO₂ - type 3). After maturation, sol solutions of different composition were deposited on glass substrates by centrifuging. After a series of preliminary experiments, centrifugation modes were selected (centrifugation speed of 1500 rpm, application time of 15 seconds). As a result, visually transparent films with a thickness of about 100 nm were obtained.

Powders were also prepared from the sol solutions of each composition for their study by the nitrogen thermal desorption method. In the preparation of powders, it is necessary to form a branched structure that can form at high pH values. Ammonia was used to increase the pH of the solution up to pH=8. All series of the samples were heat treated at T = 600 °C, since this temperature is sufficient to remove organic residues.

Figures 1 - 6 show the AFM - images of the surface for the samples of the composition 1, 2, 3 with different sizes of scanning areas.

![Figure 1. AFM-image of the type 1 film (scan size area is 5 x 5μm)](image1)

![Figure 2. AFM-image of the type 1 film (scan size area is 1.5 x 1.5μm)](image2)

When studying the surface of nanocomposites using AFM methods, it was found that all the samples are characterized by the presence of a porous structure with a pore size from 85 nm to 250 nm, depending on the composition of the initial sol solution. Thus, the average pore diameter on the surface of films for type 1 is 88 nm, for type 2 - 135 nm, for type 3 - 260 nm. The average value of
pore diameters on the surface of each sample was determined by collecting statistical data in the Gwyddion program based on analysis of 2x2 and 5x5 μm AFM images.

Figure 3. AFM-image of the type 2 film (scan size area is 5 x 5μm)

Figure 4. AFM-image of the type 2 film (scan size area is 2 x 2μm)

Figure 5. AFM-image of the type 3 film (scan size area is 5 x 5μm)

Figure 6. AFM-image of the type 3 film (scan size area is 2 x 2μm)

Regardless of the composition, height range on different parts of the nanocomposites’ surface is 20–120 nm. The values of the fractal dimension of the samples calculated in the Gwyddion program lie in the range of 2.25 - 2.5 (2.39 for the type 1; 2.47 for the type 2; 2.27 for the type 3).

The study on the processes of nitrogen adsorption and desorption was carried out in the range of relative partial pressures of gas-adsorbate from 0.06 to 0.20 when determining the specific surface area by BET method, and in a wide range of relative partial pressures from 0.06 to 0.97 for analyzing the mesopore distribution over sizes. Figures 7-12 show nitrogen adsorption isotherms obtained in the study of sol-gel powders deposited from sol solutions with different ratios of components, and the mesopore distribution over sizes calculated on the basis of sorption analysis. The term “desorption line” is understood to mean the reverse course of hysteresis, which occurs when the relative partial pressures decrease.
Figure 7. Full adsorption/desorption isotherm for the $0.1\text{SiO}_2-0.3\text{ZnO}-0.6\text{SnO}_2$ powder (type 1)

Figure 8. The histogram of the pore distribution over sizes (type 1)

Figure 9. Full adsorption/desorption isotherm for the $0.1\text{SiO}_2-0.45\text{ZnO}-0.45\text{SnO}_2$ powder (type 2)

Figure 10. The histogram of the pore distribution over sizes (type 2)
Figure 11. Full adsorption/desorption isotherm for the 0.1SiO$_2$–0.6ZnO–0.3SnO$_2$ powder (type 3)

Figure 12. The histogram of the pore distribution over sizes (type 3)

From the Figure 8 it can be seen that there are no pore systems with an average radius of 18 nm and in the powder of 0.1SiO$_2$–0.3ZnO–0.6SnO$_2$ composition.

The fractal dimension of the mesopores according to the sorption analysis was calculated using the Neimark-Kisilev method [11]. Table 1 presents data on the surface fractal dimension $D_s$, calculated on the basis of sorption analysis data; the data on the specific surface area of the materials under study (SSA), as well as the values of fractal dimension $D$ obtained on the basis of atomic force microscopy data.

Table 1. The data on the specific surface area by the BET method and fractal dimension of sol-gel nanocomposites

| Type | Initial sol composition | SSA, m$^2$/g | $D_s$ (sorption methods) | $D$ (AFM) |
|------|-------------------------|--------------|--------------------------|-----------|
| 1    | 0.1SiO$_2$–0.3ZnO–0.6SnO$_2$ | 92           | 2.78                     | 2.39      |
| 2    | 0.1SiO$_2$–0.45ZnO–0.45SnO$_2$ | 70           | 2.73                     | 2.47      |
| 3    | 0.1SiO$_2$–0.6ZnO–0.3SnO$_2$ | 82           | 2.77                     | 2.27      |

As it can be seen from the Table 1, trends in the changes of the surface fractal dimension of mesopores are consistent with changes in the specific surface area of nanocomposites (the largest value is for the type 1, the smallest is for the type 2). Most likely, the presence of larger pores in the nanocomposites of types 2, 3 (Figures 10, 12) causes a lower value of the specific surface area and surface fractal dimension.

However, in all cases the value of the fractal dimension $D$ determined on the basis of atomic force microscopy data is less than the value of $D_s$ determined on the basis of sorption analysis data. We explain this by the difference in sol-gel synthesis of thin films and powders (namely, different pH values in sol solutions). At high pH values of the solution prepared for the deposition of
nanocomposite powders, a more branched structure is formed, which in all cases causes higher values of the surface fractal dimension.

4. Conclusions
The nanocomposites based on silicon dioxide and metal oxides (zinc, tin) are obtained via sol-gel method. The porous structure parameters of the synthesized nanocomposites are investigated and the surface fractal dimension is determined on the basis of atomic force microscopy data and sorption analysis data. In all cases, the fractal dimension takes on adequate values and lies in the range from 2 to 3. It has been established that the parameters of sol-gel synthesis, in particular, the pH level in the initial sol solution, significantly affect the value of the surface fractal dimension. The higher the pH values during the formation of nanocomposites, the more branched structure is formed, which causes high values of the nanocomposite’s surface fractal dimension.

5. Acknowledgment
The reported study was funded by RFBR according to the research project № 18-32-00712.

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