Research of materials for porous matrices in sol-gel systems based on silicon dioxide and metallic oxides

E.V. Maraeva¹, A.A. Bobkov¹, A.I. Maximov¹, V.A. Moshnikov¹,², S.S. Nalimova¹

¹Saint Petersburg Electrotechnical University "LETI", ul. Prof. Popova, 5, 197376, Saint Petersburg, Russia
²Peter the Great St.Petersburg Polytechnic University, 29, Polytechnicheskaya st., 195251, St.Petersburg, Russia

E-mail: jenvmar@mail.ru

Abstract. In this study silicon dioxide – stannic oxide and silicon dioxide – zinc nanomaterials oxide were obtained through sol-gel technology. The results of nitrogen thermal desorption measurements, atomic force microscopy measurements and particle sizes measurements are discussed.

1. 1. Introduction

Currently, the “quantum dots – poromeric inert matrices” hybrid systems have become broadly used. The advantage of quantum dots in porous inert matrices is stability of sizes; in systems with quantum dots the density of radiating centers can be significantly higher than that in polycrystalline materials. Porous matrices must be optically transparent when photoluminescent particles are introduced into them. To develop electroluminescent structures, it is necessary to form highly-conductive wide-gap layers. In this respect the materials of sol-gel systems based on silicon dioxide and metallic oxides are most promising.

The purpose of this study is researching different stages of sol-gel synthesis of materials in silicon dioxide – stannic oxide and silicon dioxide – zinc oxide systems [1-4].

2.  Experiment

In this study an inorganic salt Zn(NO₃)₂·6H₂O as the precursor of zinc oxide, SnCl₂·2H₂O as the precursor of stannic dioxide and tetraethoxysilane as the precursor of silicon dioxide were selected. To control properties of the synthesized nanomaterial surface, the nitrogen thermal desorption and atomic force microscopy were used.

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 [5].
3. Results and discussion

In the course of this study the samples of xerogels in the “silicon dioxide – stannic oxide” and “silicon dioxide – zinc oxide” systems were obtained, and specific influence of sol-gel synthesis conditions on the specific surface area and morphology of samples surface was investigated. As an example figure 1 presents AFM images of 85% SiO$_2$ – 15% SnO$_2$ layer obtained with various centrifuge speeds.

As it can be seen from figure 1 the reducing of centrifuge speed leads to formation of porous structure with a large pore size. This structure may be promising for deposition of the quantum dots. So by varying the centrifuge speed we can change the porous matrix and the sizes of deposited quantum dots.

Analysis of adsorption-desorption, capillary condensation and study of the pore size distribution were carried out on powders. Figure 2 presents the full adsorption/desorption isotherm for the sample of 85% SiO$_2$ – 15% SnO$_2$ powder. A relative error of the method is 6 %. The features of method are discussed in [6]. The results are shown in table 1.

![AFM images](image1.png)

**Figure 1.** AFM images of 85% SiO$_2$ – 15% SnO$_2$ layers obtained with various centrifuge speeds: a – 5000 rpm, b – 1000 rpm (scan size area is 5 * 5 µm)

![Adsorption/Desorption Isotherm](image2.png)

**Figure 2.** Full adsorption/desorption isotherm for the sample of 85% SiO$_2$ – 15% SnO$_2$ powder
Table 1. Sizes of pores of the 85% SiO₂ – 15% SnO₂ powder taken by full adsorption isotherm

| D, nm | V/Vₜₜ₀, % |
|-------|-----------|
| 2.5   | 7         |
| 3     | 17        |
| 4     | 30        |
| 7     | 29        |
| 15    | 17        |

It was determined that the lion’s share of pores in SiO₂ – SnO₂ materials has average dimensions of 3 nm, and 15 nm. Such systems can be perspective for injection of lead chalcogenide and cadmium chalcogenide quantum dots.

In case of silicon dioxide – zinc oxide system, the dependence of the heating temperature on layer structure was analyzed. Figure 3 presents AFM images of the surface of 80%ZnO-20%SiO₂ nanocomposites obtained at different annealing temperatures: a - 300°C, b - 400°C, c- 500°C, d - 600°C.

Figure 3. AFM images of 80%ZnO-20%SiO₂ layers obtained at different annealing temperatures: a - 300°C, b - 400°C, c- 500°C, d - 600°C (scan size area is 10 * 10µm)
As it can be seen from figure 3, the annealing temperature directly affects the distribution and size of the particles formed. Increasing of the annealing temperature leads to the reduction of particle sizes. The most uniform distribution of the particles is observed for the sample annealed at 500°C.

Conclusions
The experimental results show that by varying the synthesis parameters (such as centrifuge speed, annealing temperature) we can change the porous matrix and the sizes of deposited nanoparticles, for example quantum dots. The obtained results are perspective for optimizing the conditions of production of xerogels with required parameters.

Acknowledgments
The reported study was supported by by Russian Ministry of Education state task № 16.2112.2014 / K.

References
[1] Maximov A I, Moshnikov V A, Tairov Yu M and Shilova O A 2008 Basics of sol-gel technology of nanocomposites (SPb: Elmor)
[2] Gracheva I E, Moshnikov V A, Karpova S S, Maraeva E V 2011 Journal of Physics: Conference Series 291 012017
[3] Gracheva E I, Moshnikov V A, Maraeva E V, Karpova S S, Alexandrova O A, Alekseyev N I, Kuznetsov V V, Olchowik G, Semenov K N, Startseva A V, Sitnikov A V, Olchowik J M 2012 Journal of Non-Crystalline Solids 358 433
[4] Moshnikov V A, Gracheva I E, Kuznezov V V, Maximov A I, Karpova S S and Ponomareva A A 2010 Journal of Non-Crystalline Solids 356 2020
[5] Lenshin A S, Maraeva E V 2011 Izvestiya of Saint-Petersburg Electrotechnical University 6 9
[6] Belorus A O, Maraeva E V, Spivak Yu M, Moshnikov V A 2015 Journal of Physics: Conference Series 586 012017