

Study of porous sol-gel nanocomposites based on silicon dioxide and tin dioxide modified by fullerenol $C_{60}(OH)_n$ ($n = 22-24$)

E V Maraeva¹, M S Istomina¹, V A Moshnikov^{1,2}, S S Nalimova¹, A I Maximov¹,
N I Alexeev¹ and K N Semenov³

¹ Department of Micro-and Nanoelectronics, Saint Petersburg Electrotechnical University "LETI", 5 Prof. Popova str., St. Petersburg 197376, Russia

² Department of Integral Electronics, St.Petersburg Polytechnic University, 29 Polytechnicheskaya str., St.Petersburg 195251, Russia

³ Department of Chemical Thermodynamics and Kinetics, Saint-Petersburg State University, 7-9 Universitetskaya emb., St. Petersburg 199034, Russia

E-mail: jenvmar@mail.ru

Abstract. In this study silicon dioxide – tin dioxide nanomaterials modified by fullerenol were obtained through the sol-gel technology. The results of nitrogen thermal desorption, atomic force microscopy and X-ray diffraction measurements are discussed. It was shown that introducing fullerenol $C_{60}(OH)_n$ ($n = 22-24$) at the stage of preparing a sol greatly affects the microstructure of composites and results in the formation of an additional system of pores with an average radius of 16 nm.

1. Introduction

Fullerenols are among the most important and promising fullerene derivatives which can be easily synthesized with the properties readjusted by varying the number of hydroxyl groups. The analysis of the literature shows a wide range of possible applications of fullerenols in such areas as mechanics, construction, medicine, pharmacology, material science [1-3]. In particular, high adhesion to metals, alloys and semiconductor (A^3B^5 , A^2B^6 , A^4B^4) surfaces, high transparency in the visible and infrared ranges of the spectrum, high chemical and thermal stability allow their active use in conjunction with other nanomaterials in micro- and optoelectronics [1]. The aim of this study was to investigate the possibility of modifying the sol-gel system based on silicon dioxide and tin dioxide by introducing water-soluble forms of fullerene – fullerenols $C_{60}(OH)_n$ ($n = 22-24$).

2. Experiment

In this study a $C_{60}(OH)_n$ ($n = 22-24$) inorganic salt $SnCl_2 \cdot 2H_2O$ as a precursor of tin dioxide and tetraethoxysilane as a precursor of silicon dioxide were selected. Buthanol C_4H_9OH was used as a solvent. The modifying agent (fullerenol $C_{60}(OH)_n$ ($n = 22-24$)) was introduced at the stage of preparing the solution, i.e. a sol, and the concentration of fullerenols in the alcohol was 1 mg/l.

To obtain powders, 10 % aqua ammonia (NH_4OH) was added to the solutions-sols. Adding ammonia is accompanied by changes in pH of the solution ranged from 2 to 8, and an immediate condensation of the hydrolysis products takes place resulting in a much faster gelation process. After



the gelation, evaporation of the solvent at indoor temperature was performed, and then the powders received were heat-treated for 30 minutes at the temperature of 600 °C.

To control the properties of the synthesized nanomaterial surface, the nitrogen thermal desorption and atomic force microscopy were used. To control the phase composition the X-ray diffraction method was used.

AFM experiments were performed using an NTEGRA-Therma nanolaboratory (NT-MDT, Zelenograd, Russia). Commercial etched silicon tips NSG 01 with typical resonance frequency of 150 kHz were used as AFM probes. X-ray diffraction experiments were carried out using a «DRN Farad» (*Cr-K α*) diffractometer.

Specific surface area measurements were made using a Sorbi № 4.1 analyzer (CJSC «META», Novosibirsk, Russia) that realizes physical adsorption of noble gas by the sample to be studied [4, 5]. Before the measurements, all the samples were pretreated in a SorbiPrep sample preparation station. The principle of operation of the station is based on the degassing dispersed and porous materials by heating in a stream of an inert gas (helium). The station allows you to set the temperature and time of heating in the ranges of 50–400° C and 0–99 minutes, respectively.

3. Results and discussion

During the experiments, a series of samples of the "silicon dioxide – tin dioxide" system was obtained using the sol-gel method which was both modified and not modified by fullerenols, with different ratios of components (mol. %): 90% SiO₂ – 10% SnO₂; 50% SiO₂ – 50% SnO₂.

The samples received were examined by the X-ray phase analysis. As an example, figure 1 shows the results of phase composition investigation for the powders containing 90% SiO₂ – 10% SnO₂ not modified (1) and modified by fullerenols (2). The value 1 in the vertical axis corresponds to the intensity of x-ray reflexes and depends on measurement process conditions.

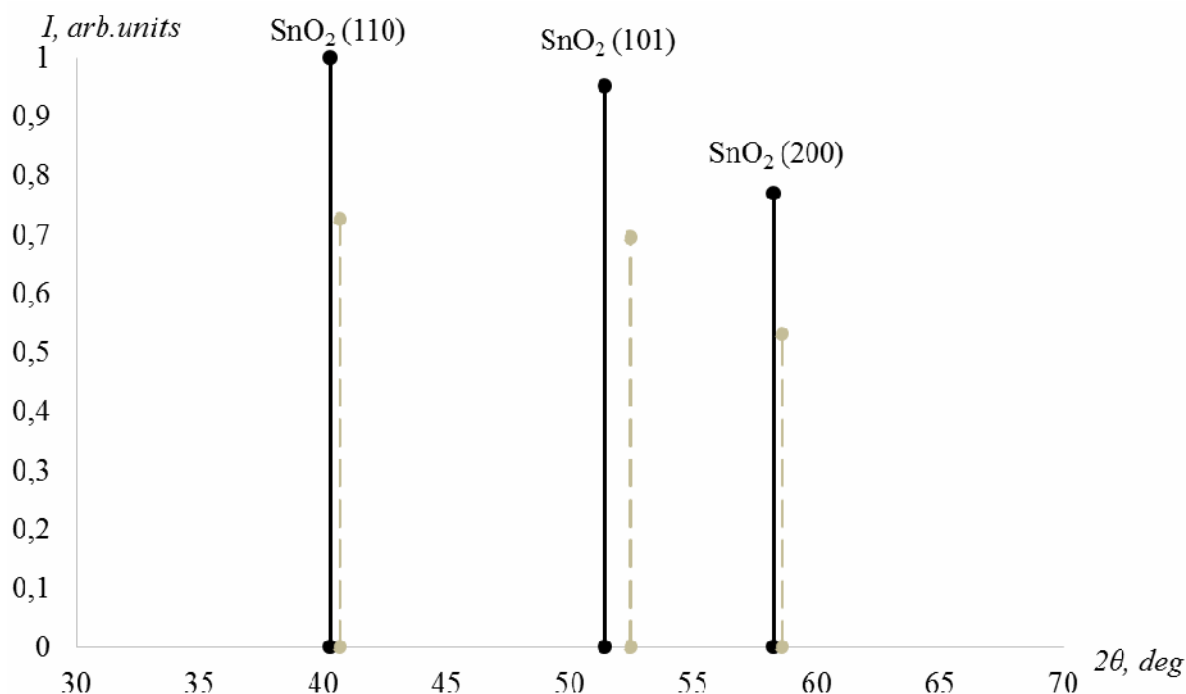


Figure 1. Line diagrams of powder pattern of the samples containing 90% SiO₂ – 10% SnO₂ not modified (1) and modified by fullerenols (2)

As can be seen from figure 1, the X-Ray diffraction pattern shows peaks corresponding to the crystalline structure SnO_2 . A set of diffraction reflections (110), (101), (200) seen on the X-Ray diffraction pattern gives evidence of a tetragonal (space group $P4_2/nmm$) crystalline structure of the rutile type. At the same time, other crystalline structures were not observed. As can be seen from the figure, a reflex corresponding to the (101) planes, containing fullereneol $\text{C}_{60}(\text{OH})_n$ as a sample, was shifted toward larger angles, which corresponds to a decrease in the interplanar space in the direction of the axis 4 of the order in the crystalline structure of the rutile type. It should be noted that for the samples containing 50% SiO_2 – 50% SnO_2 , the color change from white to grey was observed after the oxygen-free heat treatment in a SorbiPreb sample preparation station. This is presumably due to the formation of tin oxide (SnO) phase in an amorphous state.

The microstructure of the synthesized samples was investigated by the atomic force microscopy method in the tapping mode in an NTEGRA nanolaboratory. Figure 2 illustrates the morphology of the sample surface containing 10 mol. % SnO_2 and 90 mol. % SiO_2 . Figure 3 shows an AFM image of a sample of the same composition synthesized with the addition of the $\text{C}_{60}(\text{OH})_n$ ($n = 22-24$) fullereneol. It has been found that the addition of the fullereneol greatly affects the morphology of the surface of the oxide composite: the density of grain distribution and their average size increases. The atomic force microscopy data indicate that on the surface of the sample prepared with the addition of the fullereneol the aggregates of ~ 2 microns, observed in figure 2(a), are not formed. The results are confirmed by cross-section profiles of the AFM images on enhanced lines shown in figure 2(b) and 3(b).

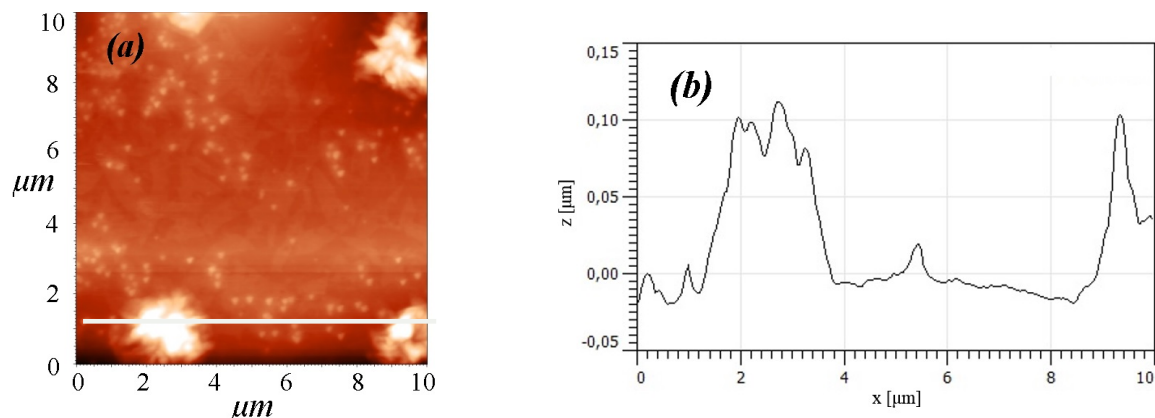


Figure 2. AFM images of the sample containing 90 SiO_2 – 10 SnO_2 (mol. %) synthesized without adding the fullereneol: (a) – the surface relief (scan space size - $10 \times 10 \mu\text{m}^2$), (b) – the cross-section profile.

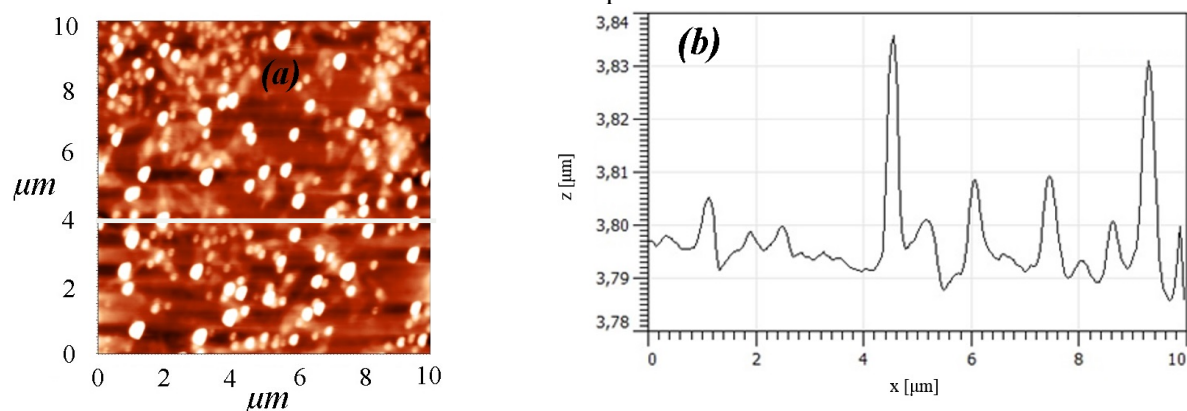


Figure 3. AFM images of the sample containing 90 SiO_2 – 10 SnO_2 (mol. %), synthesized with the addition of the fullereneol: (a) – the surface relief (scan space size - $10 \times 10 \mu\text{m}^2$), (b) – the cross-section profile.

To investigate the influence of fullerenol insertion on the porosity of silicon dioxide – tin dioxide nanocomposites, the powders were examined with the use of the capillary condensation method. The features of the method are discussed in [4]. The results are shown in tables 1-3.

Table 1. Sizes of pores of the 90% SiO₂ – 10% SnO₂ powder taken by a full adsorption isotherm

R_i , nm	V_i/V_{total} , %
1.8	13
2.2	8
3	25
4.2	21
8	34

Table 2. Sizes of pores of the 50% SiO₂ – 50% SnO₂ powder taken by a full adsorption isotherm

R_i , nm	V_i/V_{total} , %
2.2	20
2.9	27
4	23
7	27
12	3

Table 3. Sizes of pores of the 50% SiO₂ – 50% SnO₂ powder modified by fullerenol taken by a full adsorption isotherm

R_i , nm	V_i/V_{total} , %
2.2	16
2.9	27
4	23
7	23
12	8
16	3

It was determined that all the patterns have a multilevel pore system. This fact correlates with the previous investigation of the authors [6-9]. As it can be seen from the table 1, a sample of 90% SiO₂ – 10% SnO₂ has the smallest pores. Estimation of pore size distribution showed that in a sample of 50% SiO₂ – 50% SnO₂ the volume fraction of mesopores with an average radius of 7 nm with respect to the total pore volume is the largest (27 %). Modification of a sample of 50% SiO₂ – 50% SnO₂ results in the formation of an additional system of pores with an average radius of 16 nm that is apparently caused by burning out of fullerenols. Such systems can be promising for injection of lead chalcogenide and cadmium chalcogenide quantum dots.

4. Conclusions

Porous nanocomposites based on silicon dioxide – tin dioxide both modified and not modified by fullerenols were obtained using the sol-gel method. It was found that introducing fullereneol $C_{60}(OH)_n$ ($n = 22-24$) in silicon dioxide – tin dioxide nanocomposites results in the formation of an additional system of pores with an average radius of 16 nm. The fullerenols also greatly affect the microstructure and crystalline structure of composites. The obtained results are promising for optimizing the production technology of porous matrices with required parameters.

Acknowledgments

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References

- [1] Semenov K N, Charykov N A and Keskinov V N 2011 *Journal of Chemical & Engineering Data* **56** 230
- [2] Semenov K N, Charykov N A, Murin I V and Pukharens Y V 2015 *Journal of Molecular Liquids* **202** 1
- [3] Sidorov L N, Yurovskaya M A, Borschevskii A Y, Trushkov I V and Ioffe I N 2005 *Fullerenes, in Russian* (Moscow: Ekzamen)
- [4] Belorus A O, Maraeva E V, Spivak Yu M and Moshnikov V A 2015 *Journal of Physics: Conference Series* **586** 012017
- [5] Lenshin A S and Maraeva E V 2011 *Izvestiya Sankt-Petersburgskogo Elektrotehnicheskogo Universiteta, in Russian* **6** 9
- [6] Maximov A I, Moshnikov V A, Tairov Yu M and Shilova O A 2008 *Basics of sol-gel technology of nanocomposites, in Russian* (St. Petersburg: Elmor)
- [7] Gracheva I E, Moshnikov V A, Karpova S S and Maraeva E V 2011 *Journal of Physics: Conference Series* **291** 012017
- [8] Gracheva I E, 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 and Olchowik J M 2012 *Journal of Non-Crystalline Solids* **358** 433
- [9] 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