The study of metal-oxide sol-gel nanocomposites using scanning probe microscopy and X-ray photoelectron spectroscopy

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Abstract. With the use of atomic-force microscopy (AFM) technique and X-ray photoelectron spectroscopy (XPS) morphology and composition of the surface in SnO$_2$-SiO$_2$ nanocomposites were investigated. The samples were obtained by sol-gel method for their use as sensor agents. It was found that the obtained nanocomposites differ from each other as by the distribution of cluster sizes at the surface layer as by the pores size in a dependence on the composition and preparation technique. The study by X-ray photoelectron microscopy demonstrated that in the composites obtained with the use of the above-named technique tin was present mainly in the form of dioxide with a little admixture of non-oxidized metallic tin. This fact can have a certain impact on the functional characteristics of the sensor structures.

1. Introduction
Currently a great attention of researchers and engineers is focused on the materials for multi-sensor systems, multi-functional optoelectronics as well as those semiconducting devices based on the use of these materials [1,2]. Creation of gas-sensitive composite materials with a high sensitivity and selectivity including those ones on the basis of tin matched with silicon technology is also of an important interest for non-invasive medical express-diagnostics [2-4]. Additionally, deposition of thin metal-containing layers can improve current flow in the system. In this case nanostructures and nanocomposites on the basis of silicon and metal oxides such as sol-gel SnO$_2$-SiO$_2$ composites, the structures of metal oxide/por-Si, can demonstrate some new and technically attractive adsorption and optical properties [5-7].

Composition and properties of metal-containing layers are varied in a wide range depending on the deposition technique, thickness and morphology of the obtained film [6,7]. In the work we investigated morphology and composition of SnO$_2$-SiO$_2$ nanocomposites formed by sol-gel technique under different technological parameters applying X-ray photoelectron spectroscopy and atomic-force microscopy for the analysis.
Sol-gel technique was based on hydrolysis and condensation of the precursor molecules. In a dependence of the used precursors it was possible to obtain nanomaterials in a wide range of compositions as well as the size and shape of the particles [8].

2. Experimental technique
Nanocomposites of SnO$_2$-SiO$_2$ with different composition were obtained by sol-gel technology from the alcohol solutions of the components. In order to prepare solutions for the reaction iso-propyl alcohol, distilled water, tin chloride (II) bi-hydrous and tetraethoxysilane (TEOS) were applied. The prepared solutions were deposited onto glass and quartz substrates. pH value of the original solutions-sols was of 2-3. The temperature of anneal was of 600 °C. AFM-images of the nanocomposite samples were obtained with microscope INTEGRA (NT-MDT, Russia) with the use of silicon probes of NSG brand having radius of curvature equal 10 nm in semi-contact mode. Image processing with the use of the program Gwiddion allowed estimation of the spread for the particles over their dimensions.

Investigations of the samples by XPS technique were performed with the laboratory spectrometer produced by SPECS company. XPS spectra were excited with the use of Mg K$_\alpha$ irradiation. Analysis of the composition in the studied composites applying this method was conducted in the surface layers of ~ 1-2 nm in thickness after cleaning of the sample surface by argon ions with the energy of 4 keV (for 3 s.); ion current density was of 30 µA/cm$^2$.

Processing of the experimental data was performed with the use of the program suite Origin 9.0. A technique for determination of the background as well as its subtraction according to the algorithms proposed by Shirley [9], were also realized applying the same program. While determining binding energies of the core levels for the elements comprising nanocomposites C1s line of the natural hydrocarbon contaminations on the surface of any sample that was not subjected to a special cleaning procedure was taken as a reference one. It was reduced to the energy of $E_b[\text{C1s}]=285$ eV.

Identification of the elements core levels according to XPS data and their chemical state was made with the use of X-ray photoelectron spectra database at National Institute of Standards (USA) [10].

3. Results and discussion
Figure 1a represents a typical morphology of the surface in nanocomposite sample with a composition of 15%SnO$_2$-85%SiO$_2$. Figure 1b provides AFM-image of the nanocomposite sample with 85%SnO$_2$-15%SiO$_2$ composition. Figure 1c illustrates morphology of the sample surface of 85%SnO$_2$-15%SiO$_2$ composition obtained under the speed of centrifuge rotation 1000 rpm, while in all other cases the speed of rotation was of 5000 rpm. A decrease in the speed of rotation resulted in the formation of porous structure.

The obtained data mean that nanocomposite samples with a tin dioxide content of 85 mol. % are characterized by porous structure. Pore sizes for these samples depends on the speed of centrifuge rotation. Decrease of the speed resulted in the formation of porous structure with a large pore size. Therefore, a speed of a centrifuge rotation among some other technological conditions of sol-gel synthesis proves to be an important parameter determining the size of pores.

Processing of the images in the program suite known as Gwiddion allowed an estimation of a spread of the particles by their sizes (fig. 2) It should be noted that these distributions are characteristic ones just for the selected scanned area of 5 x 5 µm in size.
Figure 1. a) AFM-image of the layer of 15%SnO$_2$-85%SiO$_2$. b) 85%SnO$_2$-15%SiO$_2$, obtained under the speed of centrifuge rotation equal to 5000 rpm, c) AFM-image of 85%SnO$_2$-15%SiO$_2$ layer obtained under 1000 rpm. The scan size area is 5x5 µm, height range 0-20nm.

Figure 2. Distribution of the particles by their sizes in the samples obtained by sol-gel technique: a) 15%SnO$_2$-85%SiO$_2$, b) 85%SnO$_2$-15%SiO$_2$ (5000 rpm), c) 85%SnO$_2$-15%SiO$_2$ (1000 rpm).
It was found that the distribution of the particles by their sizes mainly depends on the sample composition. The number of particles in the layer of 15%SnO$_2$-85%SiO$_2$ composition is monotonously reduced with the increase of their size. For the samples of 85%SnO$_2$-15%SiO$_2$ composition minimum can be observed in the range of ~ 50 nm. The changes in the particles distributions after different treatments can be explained by the fact that with an increase of tin content in the sol the independent polymer chains of tin dioxide are being formed, that leads to a phase separation in the material. It was discussed in details previously [11].

XPS of Sn 3d5/2 and O1S spectra with their decomposition into the spectral components are presented in Fig 3 for sol-gel nanocomposites of SnO$_2$-SiO$_2$ (85%:15%); centrifugal separation was performed at 3000 rpm and 4000 rpm, respectively.

Analysis of the shape and position for XPS Sn 3d5/2 spectra and their decomposition into spectral components demonstrated that Sn in the surface layer of nanocomposites is present mainly in the form of oxide SnO$_x$, where x is close 2 (spectral component with $E_b = 486.5$-487 eV). At the same time relatively small amount of non-oxidized metal tin is also observed (spectral component with $E_b = 485$ eV) [10,12], that can nevertheless play a considerable role, for example, in the adsorption processes on the surface of nanocomposites and result in the change of the functional characteristics of devices using these materials. Due to the relatively small concentration of silicon in the composite XPS Si 2p spectra of the samples were rather low-intensive. Therefore, these spectra were not presented in our work.

![Figure 3](image_url)

**Figure 3.** XPS of Sn 3d5/2 and O1S spectra for sol-gel nanocomposites of SnO$_2$-SiO$_2$ (85%:15%) with a decomposition into the components; centrifugal separation was performed at 3000 rpm and 4000 rpm.

Analysis of O1s spectra in nanocomposites confirmed the presence of the presumable amount of tin dioxide in the surface layer of the foil (spectral component with $E_b = 530.5$ eV). The obtained XPS
spectra also include two components. The first one more intensive peak is related with oxygen bound with tin. The second one, less intensive component is due to the oxygen in silicon oxide SiO₂ and oxygen adsorbed on the surface with Eb=532,5 eV [12,13 ].

4. Summary
Morphology and composition of the surface in SnO₂-SiO₂ nanocomposites were investigated. It was found that the distribution of the particles by their sizes mainly depends on the sample composition. The number of particles is monotonously reduced with the increase of their size. It was demonstrated that in the composites obtained with the use of the above-named technique tin was present mainly in the form of dioxide with a little admixture of non-oxidized metallic tin.

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