AES and XPS Studies of a por-Si/SnO$_x$ Nanocomposite Formed Using a Powerful Ion Beam of Nanosecond Duration

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Abstract—The results of the X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM) investigations of tin-oxide nanolayers on samples of por-Si/SnO$_x$ composites with varying matrix porosity, formed using a powerful ion beam of nanosecond duration, are presented. It is shown that rapid melting and crystallization of the surface leads to the formation of Si nanoparticles with a maximal size of 200 nm. It is established that tin is included in the structure of the nanocomposite in an oxidized state with a small inclusion of metallic β tin. With increasing porosity, the phase composition of the tin nanolayers becomes closer to the state corresponding to the highest tin oxide (SnO$_2$). It is also shown that, upon an increase in the porosity, the intensity of the tin 4$d$ subvalent line increases, which is, apparently, associated with an enhanced degree of hybridization of tin and oxygen atoms. The changes in the elemental composition of the composite and the depth of tin penetration are estimated from the results of ion etching.

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INTRODUCTION

Porous media are promising materials for micro- and nanosensors. For instance, layers of porous silicon (por-Si) obtained electrochemically exhibit a specific internal surface of up to 600 m$^2$/cm$^3$ [1], great sorption ability, and high sensitivity to different chemicals [2–4]. However, the stability of the sensor characteristic of such structures is rather low due to silicon oxidation.

With the aim of utilizing the developed surfaces of porous structures and high selectivity of metal oxides to chemicals [5, 6], it is efficient to design porous composite structures based on them [7].

Different studies show that using magnetron sputtering and chemical vapor deposition allows the formation of por-Si/SnO$_x$ nanocomposite materials which exhibit sensitivity to chemicals and property stability [7]. Herewith, the formation of SnO$_2$ phase islands commences on the surface of the por-Si skeleton, and the tin penetration depth and depth profile are determined, in particular, by diffusion into por-Si via pore surfaces.

The action of a powerful ion beam of nanosecond duration on porous silicon with a deposited thin film of nonstoichiometric tin oxide is a fundamentally new approach to the creation of a nanocomposite based on the por-Si/SnO$_x$ system. It results in a decrease in the oxidized tin concentration and the formation of a structural phase state of surface layers under conditions of nonequilibrium collective processes of different nature [8, 9]. Supposedly, the porous Si skeleton can transform into a layer of nanocrystalline silicon containing SnO$_x$ islands due to local melting under such treatment [8].

The thus prepared structures show high sensitivity to low NO$_2$ concentrations even at room temperature [8], which makes them promising in sensing elements for micro- and nanosensors. At the same time, the structural phase transformations under nonstationary conditions under the action of powerful ion beams of nanosecond duration, accompanied by segregation and diffusion processes during melting and solidification of these systems, need further investigations. Therefore, the aim of this work is to study the structural and phase changes in the nanocomposite layers of por-Si/SnO$_x$ under the action of powerful ion beams (PIBs) of nanosecond duration.

EXPERIMENTAL

To fabricate silicon layers with differing porosity, 300-μm thick polished single-crystal KDB-0.005 (111) p-type silicon plates were etched anodically. A electrolyte of the composition HF (40%) : C$_3$H$_7$OH = 1 : 1 was used for anodic etching. The etching time for obtaining layers of ~5 μm in thickness was 120 s. The resulting layers exhibited a typical pore size of ~20 to 30 nm [7] with a porosity of 40, 50, 60, and 70%.

Tin-oxide films 100 nm thick were applied to the surface of the obtained porous Si by magnetron sput-
tering in argon plasma at a pressure of 8 Pa. The discharge current was 100 mA, the voltage was 500 V, and the sputtering time was 15 min [7]. A nanocomposite layer was formed under PIB irradiation (30% H, 70% C, energy 300 keV, and duration 60 ns) at a current density of ~20 A/cm² and a carbon implantation dose of ~10¹⁷ at/cm⁻³, which does not induce significant changes in the chemical composition of the sample.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were carried out using a RIBER analytical complex under ultrahigh vacuum in a chamber with a residual pressure of ~10⁻¹⁰ Torr. Layer-by-layer argon etching at a beam energy of 3 keV was used to study the distribution of elements across the thickness of the samples. The morphology of the nanocomposite surface was studied using a Jeol JSM-6610LV scanning electron microscope.

RESULTS AND DISCUSSION

SEM analysis of the surface of the irradiated samples with differing porosity showed that the action of a PIB upon a porous por-Si/SnOₓ nanocomposite yields the formation of layers containing silicon nanoparticles with a maximal size of 200 nm (Fig. 1).

An overview of the photoelectron spectra of all samples showed that the following elements were present on the surface: oxygen, tin, carbon, and silicon (Fig. 2). Analysis of the most intense 3dₓ/₂ line of tin made it possible to establish that its position is shifted toward higher energies to 485.1 to 486.6 eV relative to metal Sn (484.6 eV), which corresponds to binding energies (BEs) typical of SnO₂. However, the presence of bivalent tin cannot be ruled out, because the BEs of SnO and SnO₂ are close [10–15]. This is due to the fact that a small shift in the BE of tin in the XPS spectrum occurs during the transition of the chemical state from Sn²⁺ to Sn⁴⁺ on account of the large valent orbital radius [11]. The technique based on calculation of the so-called modified Wagner Auger parameter α’ is the most accurate way of identifying the chemical state of tin in such structures [12–15]:

$$\alpha' = E_{\text{kin}} + E_b.$$

This parameter is independent of static charge and is the characteristic of a certain element’s chemical state. It is the sum of the photoelectron BE and the Auger electron kinetic energy for the most intense line from the element.

The results of calculations are shown in the diagram in Fig. 3. The value of the Wagner parameter for the samples with differing porosity is close to that of tin dioxide known from published data [12], which also confirms the low metal tin content of the layers (~3 to 5 at %). There is a tendency toward a shift of the Auger parameter with increasing porosity of the initial structures to values typical of tin dioxide (Fig. 3). The value of this parameter closest to SnO₂ is observed for the sample with the maximal porosity of 70%. This is apparently associated with an increase in the pore surface area, uniform tin distribution, and, accordingly, more complete tin oxidation into an oxide with a composition close to stoichiometric SnO₂.

The oxygen line was decomposed using a mixed Gauss–Lorentz model for samples with differing porosity and presented as a superposition of three components corresponding to adsorbed oxygen in different forms: C–O bonds, OH–groups, adsorbed water (energies of 532.2–532.5 eV), and lattice oxygen contained in silicon (529–529.5 eV) and tin (530.4–530.6 eV) chemical compounds [13]. The ratio between the intensities of these oxygen line components changes with sample porosity (Fig. 4). With increasing sample porosity, there is a shift of the oxy-