Original articles

XPS investigations of thin epitaxial and magnetron tin layers surface physico-chemical state

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Abstract

Thin layers of the tin-oxygen system with nanometer thicknesses and structures based on them are relevant objects of development for use in modern devices, for example in microelectronics. The general miniaturization of electronic devices, the achievement of energy efficiency in the operation of such devices, and the optimal modes of their operation determine the strategies for using the tin-oxygen system structures. First of all, the justification of the tin-oxygen system nanolayers formation technique. The dependence of the formed nanolayers properties on the state of their surface is significant.

The article contains the results of direct experimental studies of the composition and physico-chemical state of the tin-oxygen system thin nanolayers surface. To form the studied structures, the popular and in-demand methods of magnetron sputtering and molecular beam epitaxy were used. The X-ray photoelectron spectroscopy was applied with the use of the synchrotron radiation which has a high intensity and the possibility of spectrum excitation energy optimal selection, which is important for a small amount of the studied material. After formation, the research objects were stored in laboratory conditions for several weeks before synchrotron studies.

Differences in the surface composition and physico-chemical state of the thin tin layers formed by magnetron sputtering or epitaxially, and then oxidized naturally, are shown. Five monolayers of tin formed by the molecular beam epitaxy make it possible to diffuse atmospheric oxygen, which oxidizes the Si buffer layer located under the Sn nanolayer on a silicon substrate. At the same time, the surface of the tin film obtained by magnetron sputtering is close to the natural oxide SnO_{2-x} in its physico-chemical state.

The results of the work can be useful for determining the optimal approaches to the formation and subsequent modification of thin and ultrathin layers of tin oxides for the tasks of creating active layers of modern electronic devices.

Keywords: Tin and its oxides, Physico-chemical state, Composition, Epitaxial nanolayers, Magnetron nanolayers, X-ray photoelectron spectroscopy, Synchrotron studies

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1. Introduction

Nanostructures of the tin-oxygen system attract wide interest of researchers and are used to solve various modern problems of science, engineering and technology [1–3]. Tin oxide SnO_2 is actively used in microelectronics, for example, to create structures of resistive gas sensors [4–6] and a number of other devices. Planar layered tin oxide structures including ones characterized by nanometer thicknesses are an important class of objects with high manufacturability realization of them together with relative simplicity of their creation [7–9]. By varying the formation and processing techniques, it is possible to control the morphology, composition, structure, physico-chemical state as a whole and, as a result, the properties of the structures being formed, obtaining optimal sizes, energy consumption of devices based on them, response speed and other functional characteristics. The molecular beam epitaxy makes it possible to obtain ordered layers of tin of minimal thickness (up to few nanometers) that may have a set of unique characteristics with variations in their composition e.g. after certain subsequent modification. The use of layered epitaxial heterostructures of tin and silicon for thermoelectrics may be promising [10]. At the same time, the magnetron sputtering is a common formation approach of the tin-oxygen system thin layered structures [11]. This technique allows significant variations of the composition and structure of the formed and modified tin layers in combination with simplicity and flexibility in managing the formation regimes. It is obvious that the properties of thin tin-oxygen layers will be significantly influenced by the composition of the surface and interface boundaries, largely determining the properties of structures based on them. Therefore, the use of direct experimental techniques for studying the composition-sensitive, surface physico-chemical state of thin layers is extremely important. Such techniques include X–ray photoelectron spectroscopy (XPS). XPS allows us to obtain high-precision experimental data on the charge state of atoms that make up several nanometers of the object under study surface without destruction, and to study the phase composition. The use of high-intensity synchrotron radiation makes it possible to select the quantum energy for excitation of the photoelectron spectrum. This makes the XPS technique an accurate universal tool for studying the physico-chemical state of the surface even with a small amount of matter, which is typical for layers of nanoscale thickness, including the tin-oxygen system [12–15]. This paper presents the results of XPS studies using synchrotron radiation on the physico-chemical state of the surface of thin epitaxial and magnetron layers of tin formed on crystalline silicon substrates.

2. Experimental

The molecular beam epitaxy was used to obtain tin nanolayers on a 50 nm thick Si buffer layer grown on a Si (001) substrate [10]. We will call these samples «Epitaxy Sn/Si». The substrates prepared after cleaning and drying were moved to an ultrahigh vacuum chamber. After desorption of thermal oxide at a temperature of 840 °C, 5 monolayers of tin atoms (~ 1.6 nm) from an effusion cell were grown (deposited) on the formed 50 nm thick silicon buffer layer. After formation, the samples were kept in the laboratory for several weeks before synchrotron studies. The control by atomic force microscopy showed the continuity and uniformity of the formed tin layer.

Magnetron sputtering was used to form 30 nm thickness tin layers on silicon substrate. We will call these samples «Magnetron Sn/Si». Sputtering of a tin target with a purity of 99.999% was carried out in a direct current argon plasma. Prepared and cleaned Si (100) substrates were used. The argon pressure in the working chamber was 10^{-3} Torr, the discharge current was 60 mA, the voltage was 360 V. The film thickness was determined by the deposition time. The morphology was controlled by scanning electron microscopy. Solid uniform granular nanolayers with granule sizes comparable to the layer thickness have been formed. The «Magnetron Sn/Si» samples

were also stored in the laboratory for several weeks before measuring the photoelectron spectra.

Investigations of the samples surface physico-chemical state were carried out using the non-destructive XPS technique. The XPS is based on the kinetic energies spectrum analysis for photoelectrons emitted by atoms under the irradiation of X-rays (synchrotron) radiation and allows determining the binding energies of electrons levels excited by radiation [e.g. 12, 16]. The high-intensity radiation of the ultra-soft X-ray range of BESSY-II synchrotron, the Russian-German beamline (Helmholtz - Zentrum-Berlin, Berlin, Germany) [17] and KISI-Kurchatov synchrotron, the NANOPES beamline (National Research Center «Kurchatov Institute», Moscow, Russia) [18] were used. The photon flux was 10^9–10^{11} photons/s, the storage ring current was 50–300 mA. The depth of the analyzed surface layer [12] and the instrumental broadening were ~2 nm and 0.1 eV, respectively. The photon energies of synchrotron radiation of 800 eV were used, which corresponded to the maximum intensity of synchrotron radiation of both beamlines. The vacuum in the experimental chambers was ~ 10^{-10} Torr. Calibration and normalization of the spectra were carried out using a pure gold film based on the position of the core 4f gold level and the Fermi level under the same registration conditions as for the studied samples. Additionally, the position of the core levels was also controlled by C1s level of carbon-containing contaminants on the surface of the samples, reduced to a value of 285.0 eV according to [16]. To ensure charge drain during spectra registration, standard sample mounting on Omicron flag type holders was used.

3. Results and discussion

Fig. 1 shows the survey XPS spectra of the studied samples with epitaxial (Epitaxy Sn/Si) and magnetron (Magnetron Sn/Si) tin layers. The spectrum of the sample obtained by magnetron sputtering of tin (Magnetron Sn/Si) shows intense lines of oxygen O 1s, tin Sn $3d_{3/2,5/2}$, Sn 4d, carbon C 1s, and Auger $M_5N_{4;5}N_{4;5}$ and $M_4N_{4;5}N_{4;5}$ lines [14, 16, 19]. The C 1s line is clearly defined,
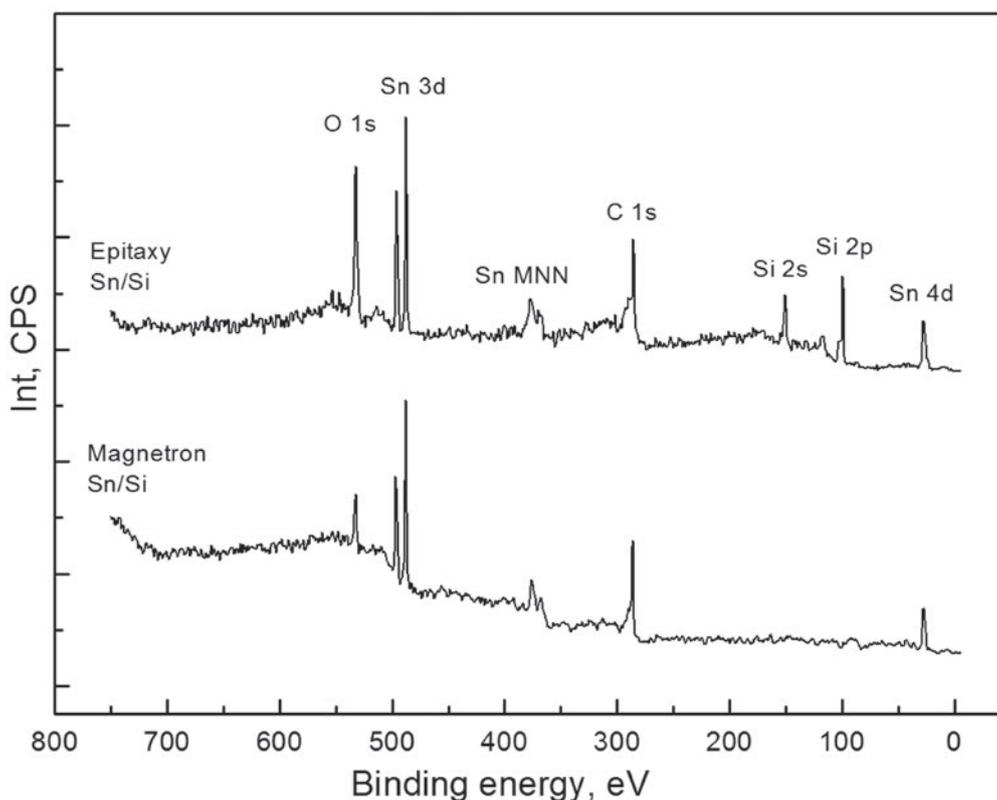

Fig. 1. Survey XPS spectra of the studied samples of epitaxial (Epitaxy Sn/Si) and magnetron (Magnetron Sn/Si) tin layers

which indicates a sufficient carbon-containing contaminants amount formed on the surface as a result of samples storage in the laboratory conditions. In the spectrum of the sample obtained by molecular beam epitaxy (Epitaxy Sn/Si), in addition to the above, silicon lines Si $2p_{1/2,3/2}$, Si $2s$ are observed. The observation of the lines related to the silicon buffer layer is the result of the small thickness of the formed layer of epitaxial tin. This means that the tin-silicon layer interface is available for study. At the same time, the oxygen line O $1s$ in its intensity is noticeably higher than that in the «Magnetron Sn/Si» sample. The intensity of this line, in our opinion, consists of a signal from the naturally oxidized upper epitaxial Sn layer, as well as from oxygen atoms bound to the surface of the silicon buffer layer. This observation, in our opinion, is the result of atmospheric oxygen diffusion through the epitaxial tin layer to its interface with the more electronegative silicon of the buffer layer. The C1s carbon line is also quite intense, which may indicate the presence of a sufficiently large amount of carbon on the surface of this sample in the form of carbon-containing contaminants.

For a detailed analysis of the physico-chemical state of the surfaces and interfaces of the studied samples, the spectra of the main core lines of tin and oxygen were taken with high resolution. Fig. 2 shows the XPS spectra of tin Sn $3d_{5/2}$ of the reference sample of tin dioxide SnO_2 [15], epitaxial «Epitaxy Sn/Si» and magnetron «Magnetron Sn/Si» in the binding energy range 483 – 491 eV. It can be seen that the Sn $3d5/2$ line of the sample obtained by magnetron sputtering is single-component, with a binding energy of 486.7 eV, which is slightly lower than the binding energy of this line for the reference tin dioxide SnO_2, which is 487.2 eV [14–16]. This value of the binding energy of tin atoms indicates a relatively incomplete oxidation of the surface of the «Magnetron Sn/Si» sample to SnO_2 and corresponds to the binding energy value for the intermediate oxide SnO_{2-x} previously shown in [15, 20, 21], e.g. for the surface of a metal foil. In the spectrum of the «Epitaxy Sn/Si» sample obtained by molecular beam epitaxy, two components are observed at binding energies of 487.5 eV and 486.0 eV, respectively (Fig. 2). The high-energy component shows a binding energy value close

to the SnO_2 reference sample. The low-energy component of low intensity corresponds to the binding energy of tin atoms in SnO monoxide, specified in [20]. Thus, the surface of the studied «Magnetron Sn/Si» tin layers with a thickness of 30 nm is single-phase and is characterized by an intermediate «surface» tin oxide SnO_{2-x}. The formation of such an oxide occurs with a sufficient number of tin atoms in a layer available for natural
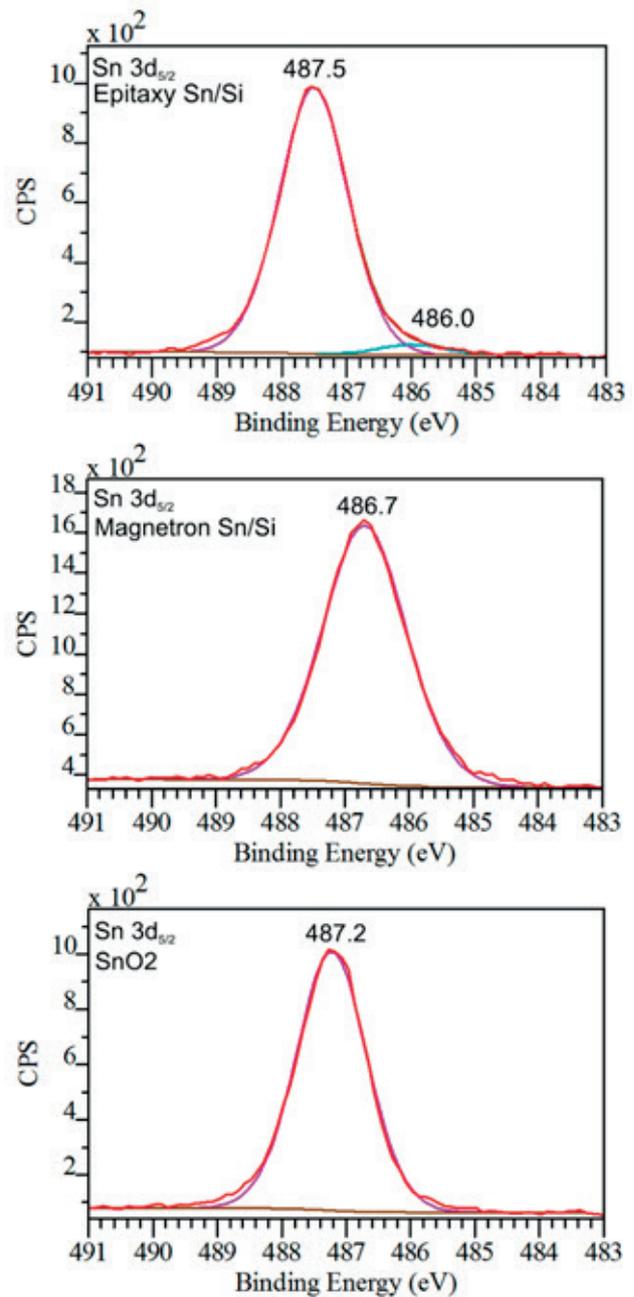

Fig. 2. XPS spectra of Sn $3d_{5/2}$ of the reference SnO_2 and the studied samples of epitaxial (Epitaxy Sn/Si) and magnetron (Magnetron Sn/Si) tin layers

oxidation during storage in the laboratory. The thickness of the epitaxial layer of tin is extremely small, moreover, there is a surface of more electronegative buffer silicon under it. In the process of interaction with atmospheric oxygen, during storage in laboratory conditions, complete oxidation of tin atoms of the entire epitaxial layer occurs, with the formation of a thin transition layer of SnO. In our opinion, this layer borders on a buffer layer of silicon, which is also oxidized as a result of atmospheric oxygen diffusion, as was suggested above when considering the intensities of the tin and oxygen core level lines of the survey spectrum. The mutual oxidation of the tin and silicon epitaxial layers interface occurs before the equilibrium state is established, keeping the thin transition layer of tin in the SnO state. A detailed study of the fine structure of high-resolution photoelectron spectra of 2p silicon states seems to us to be a priority task in further studying the epitaxial structures of tin-silicon.

Fig. 3 shows the XPS O $1s$ spectra of the reference SnO_2 and the studied samples of epitaxial «Epitaxy Sn/Si» and magnetron «Magnetron Sn/Si» tin layers. The spectrum of the «Magnetron Sn/Si» sample has two components with a binding energy of 530.5 eV and a binding energy of 532.1 eV, which correspond to oxygen atoms in the surface oxide SnO_{2-x} [15, 20, 21] and various types of atmospheric oxygen compounds adsorbed by the surface [see for example 14–16]. In a sample with an epitaxial tin nanolayer, 3 components are observed in the O $1s$ spectrum at energies 531.5, 532.6 and 533.3 eV. The states of oxygen atoms with the binding energy of 531.5 are close to SnO_2 dioxide (Fig. 3). A slight increase in the binding energy of the states of oxygen atoms (as well as tin atoms, see above) may be due to the influence of an additional surface charge forming by the layered structure of the sample during its phase transformations as a result of natural oxidation [12]. The components of the O $1s$ spectrum with binding energies of 533.3 and 532.6 eV are connected, in our opinion to various types of atmospheric oxygen compounds adsorbed by the surface [see for example 14–16] and are observed in the spectrum of the reference SnO_2 (Fig. 3). However, the peak at 532.6 eV has a significantly higher intensity compared to the SnO_2 standard, which is associated with the

binding energies of silicon oxide, having a close value. This confirms the above assumption about the oxidation of the silicon buffer layer located under the epitaxial layer of tin. Finally, the fact that we do not observe a state in the O1s spectrum of the «Magnetron Sn/Si» sample with the binding energy of ~ 533.3 eV indicates somewhat different storage conditions for this sample.
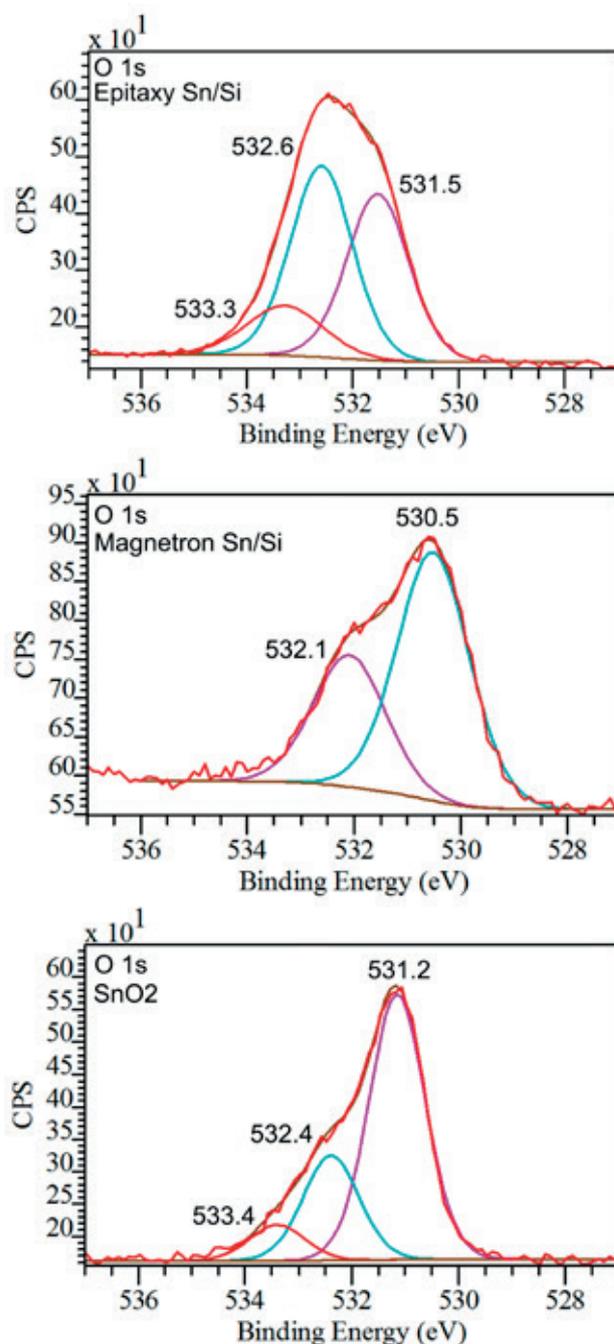

Fig. 3. XPS spectra of O $1s$ of the reference SnO_2 and the studied samples of epitaxial (Epitaxy Sn/Si) and magnetron (Magnetron Sn/Si) tin layers

4. Conclusions

The physico-chemical state of the thin tin layers surface obtained by magnetron sputtering and molecular beam epitaxy after storage in laboratory conditions is studied. There is a general agreement of data on the analysis of synchrotron photoelectron spectra, including high-resolution data for the Sn $3d_{5/2}$ and O $1s$ lines. The differences in the composition of the studied structures surface layers are shown. When using the magnetron sputtering to form a 30 nm Sn layer with subsequent storage in laboratory conditions, a single-phase surface of natural tin oxide SnO_{2-x} is formed. The tin layer formed by the molecular beam epitaxy after storage of the same duration in laboratory conditions is completely oxidized to SnO_2. The surface of the silicon buffer layer is oxidized by atmospheric oxygen atoms as a result of their diffusion through the epitaxial layer of tin, while a thin transition layer of SnO is formed. The results obtained can be used in the controlled formation of functional nanolayers of the tin-oxygen system and structures based on them for various tasks, for example, in the creation of modern microelectronic devices.

Contribution of the authors

All authors made an equivalent contribution to the preparation of the publication.

Conflict or interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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