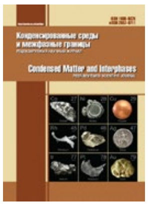

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Synchrotron XANES studies of epitaxial tin-silicon solid solutions nanolayers

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Abstract

Objective: Functional tin and silicon-based materials and thin-film structures based on them are promising objects for microelectronics devices. An important issue for the study and subsequent application of such materials and structures is the properties control under formation technological regimes variations.

Experimental: The specificity of the local atomic surrounding and the features of the electronic structure of tin-silicon solid solutions have been studied by X-ray absorption near edge structure spectroscopy using synchrotron radiation. Nanolayer structures of tin-silicon solid solutions on buffer silicon nanolayers were formed using molecular beam epitaxy.

Conclusions: The possibility of forming an epitaxial tin-silicon solid solution in the concentration range significantly exceeding the known solubility limits of Sn in Si is shown. The rearrangement of the local density of the electronic states of tin and silicon indicates the formation of solid solutions with tin concentrations of 2, 8, and 15 at. %.

Keywords: Tin, Silicon, Tin and silicon oxides, Electronic structure, Density of states, Local atomic surrounding, Composition, Epitaxial solid solutions, X-ray absorption near edge structure, Synchrotron investigations

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1. Introduction

The formation of new promising functional materials with new properties and characteristics for the creation of modern devices based on them is an urgent task. The creation of solid solutions based on silicon, the most common and widely used material for microelectronic devices, is a promising way to achieve new properties of the structures being formed. For example, the introduction of tin atoms into a silicon crystal lattice can lead to changes in the optical properties, processes of generation, recombination, and transfer of charge carriers in the obtained objects [1, 2]. Varying the concentration of embedded tin atoms can make it possible to control the properties of the material, which affect the electronic structure, optical, and electrophysical properties of solid solutions. Obtaining uniform tin-silicon solid solutions is possible using nonequilibrium growth methods such as molecular beam epitaxy, due to the noticeable difference in the lattice parameters of structures based on these atoms and their low mutual solubility [1]. The above makes $Si_{1-x}Sn_x$ solid solutions suitable for creating electronic devices, in particular, various thermoelectric devices, optoelectronic devices such as lasers and LEDs. This paper presents the results of the electronic structure specificity studying for nanolayers of $Si_{1–x}Sn_x$ epitaxial solid solutions grown on crystalline silicon buffer layers and substrates with concentrations exceeding the limits of tin solubility in silicon ($x > 0.1$ at.%) [3]. The studies were carried out using a non–destructive X-ray absorption near edge structure (XANES) method sensitive to the local surrounding of surface atoms using high-intensity synchrotron radiation [4–6].

2. Experimental

The studied samples, which we designate as “SiSn”, were obtained by molecular beam epitaxy on a Si (001) substrate with a 20 nm Si buffer layer [7]. During the formation of the samples, the purified and dried substrates were transported to an ultra-high vacuum film growth chamber, where thermal oxide was desorbed at the temperature of 840 °C. Then, silicon atoms (~ 98, 92 and 85 at. %) and tin atoms (~ 2, 8 and 15 at. %) were simultaneously deposited on a 20 nm thick silicon buffer layer from an electron beam evaporator (Si) and an effusion cell (Sn) sources. The thickness of the deposited SiSn layer was about 5 nm. As a result, the following samples were obtained: $Si_{0.98}Sn_{0.02}$, $Si_{0.92}Sn_{0.08}$ and $Si_{0.85}Sn_{0.15}$. Before conducting synchrotron experiments, the samples were stored in laboratory conditions for several weeks.

The electronic structure of the samples was studied using the non-destructive XANES method, which allows obtaining information about the specificity of the local surrounding of absorbing silicon, tin, and oxygen atoms and the effects of ordering in the structural grid of these atoms of the analyzed surface layer [8]. The XANES method makes it possible to obtain direct experimental information on the distribution of the local partial density of free electronic states in the conduction band of the studied surface layer [4–6, 9–11]. The high-intensity radiation of the ultrasoft X-ray range of BESSY-II synchrotrons, the Russian-German beamline (Helmholtz-Zentrum-Berlin, Berlin, Germany) [12] and KISI-Kurchatov, the NANOPES beamline (NRC Kurchatov Institute, Moscow, Russia) [13] were used. The photon flux was 10^9–10^{11} photons/s, and the storage rings beamcurrent was 50–300 mA. The depth of the analyzed surface layer [14, 15] and the energy resolution for the edges of Si $L_{2,3}$, Sn $M_{4,5}$, and O K were ~5 nm for silicon, ~10 nm for tin and oxygen, and 0.1 eV, respectively. The total electron yield (TEY) was detected by recording the compensation current of the sample. The vacuum in the experimental chambers was ~ 10^{-10} Torr. The angle of incidence of synchrotron radiation was 90° to the surface plane.

3. Results and discussion

XANES Si $L_{2.}3$ (2*p*) absorption spectra represent the distribution of *s* states in the conduction band, which reflect transitions from core 2p states to free *s* and *d* states in the conduction band. Fig. 1 shows the XANES Si L2,3 spectra for the reference materials (single crystalline silicon c-Si, amorphous silicon a-Si, thermally grown silicon oxide SiO_2 and the epitaxial buffer layer c-Si Buffer on silicon) and the studied samples of epitaxial solid solutions $Si_{0.98}Sn_{0.02}$, $Si_{0.92}Sn_{0.08}$ and $Si_{0.85}Sn_{0.15}$. Analysis of the obtained spectra shows that the epitaxial silicon buffer layer (c-Si

Buffer) has a well-defined fine structure with two pairs of features corresponding to the spin–doublet splitting of the excited $L_{2.3}$ silicon core level at 0.6 eV, in the energy range of synchrotron radiation quanta of 100–104 eV, characteristic of the reference single crystalline silicon (c-Si). Note that in this region, the spectrum of the a-Si reference has a simpler, thinner structure without the paired maxima noted above, due to the blurring of the density of electronic states of amorphous silicon. The following absorption edge and the fine structure of XANES Si $L_{2.3}$ for SiO_2 are located above the energies of 104 eV, similar features can be detected for the spectra of the c-Si and a-Si references, since they are covered by a natural oxide.

XANES Si $L_{2.3}$ spectra fine structure of the studied epitaxial solid solutions samples has a number of features (Fig. 1). Thus, in a solid solution with 2% tin atoms $Si_{0.98}Sn_{0.02}$, XANES spectrum fine structure in the absorption region of elementary silicon (100 eV < hn < 104 eV) is well expressed and corresponds to crystalline silicon (Fig. 1). And in the region silicon oxide 105-111 eV the characteristic fine structure features are not observed in the spectrum. Here, the fine structure is generally blurred, and the main peak at energies of ~ 108 eV is broadened and shifted to lower values, which may indicate an underoxidized state of silicon atoms from the sample surface [10, 16]. In a solid solution with a higher tin content of 8% $Si_{0.92}Sn_{0.08}$, the fine structure of the spectrum in the region of elementary silicon is somewhat blurred, which may indicate a slight deviation from the ordering in the lattice of silicon atoms. The fine structure in the area of silicon oxides remains, in general, as unexpressed as in the case of a solid solution with a 2% of the tin content $Si_{0.98}Sn_{0.02}$. As the tin content increases to 15% $Si_{0.85}Sn_{0.15}$, the fine structure of the XANES Si $L_{2,3}$ spectrum in the elementary silicon region becomes even more blurred. However, the width of the characteristic fine structure features in this part of the XANES Si $L_{2,3}$ spectra for $Si_{0.85}Sn_{0.15}$ and their general appearance differ from the characteristic structureless absorption edge of the amorphous silicon reference. In the silicon oxide region, the fine structure becomes more pronounced and corresponds to that of the natural oxide covering crystalline silicon c-Si reference (Fig. 1). This indicates possible distortions in the lattice of silicon atoms and, at the same time, greater oxidation of silicon atoms from the surface, which are even more noticeable than with a lower tin content in solid solution. Finally, for all nanolayers of solid solutions, there was a slight shift in the position of the absorption edge at 99.9 eV towards lower energies.

Thus, it can be concluded that as the number of tin atoms in solid SiSn solutions increases, the fine structure of the Si $L_{2,3}$ absorption spectra changes. With an increase in the concentration of tin atoms in the nanolayer of the solid solution, the fine structure of the spectrum is smoothed, that is, the density distribution of free electronic states in the conduction band [8, 10]. In the region of the absorption edge of elementary silicon, corresponding to the position of the bottom of

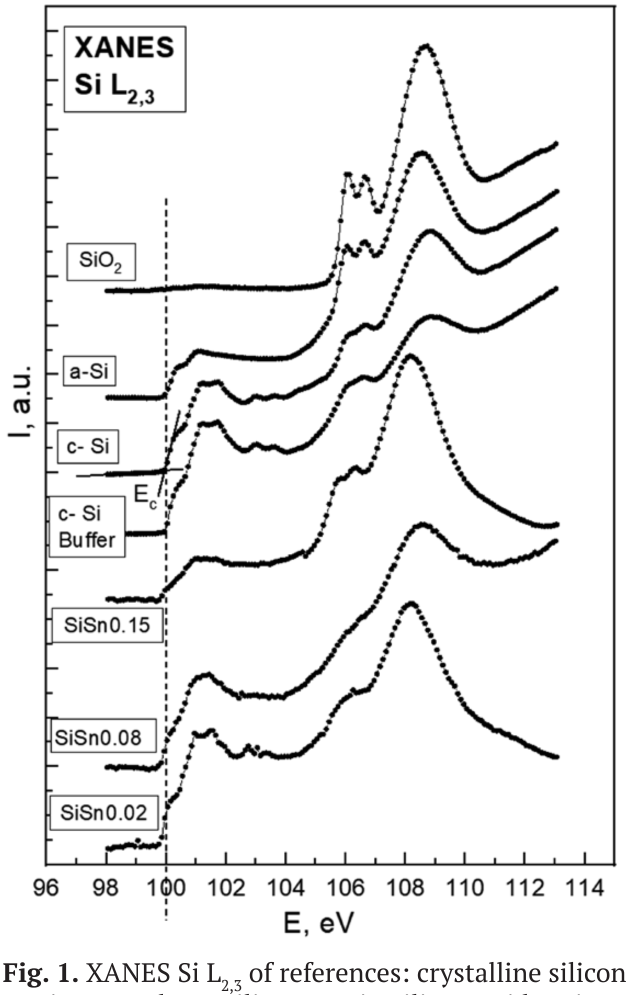

Fig. 1. XANES Si $L_{2,3}$ of references: crystalline silicon (c-Si), amorphous silicon (a-Si), silicon oxide (SiO_2), buffer layer of c-Si (c-Si Buffer) and epitaxial solid solutions $SiSn_{0.02}$, $SiSn_{0.08}$, $SiSn_{0.15}$

the conduction band relative to the excited core level (Si $L_{2,3}$), electronic states are “dragged” into the band gap compared with the data on the fine structure of the crystalline silicon reference spectrum and the E_c position (Fig. 1). The order in the structural grid of silicon atoms as a whole is undergoing some distortions. That is, the mechanical stresses that probably occur during the formation of nanolayers of solid solutions lead to distortion in the electronic structure of these nanolayers. This includes natural silicon oxide formed during storage in the laboratory. The observed general smoothing of the XANES Si $L_{2,3}$ spectra fine structure may occur as a result of the tin atoms incorporation into the lattice of silicon atoms during the formation of a solid solution nanolayer.

Fig. 2 shows the XANES Sn $M_{4.5}$ spectra of reference materials (experimentally obtained for tetragonal SnO_2(T), metal foil without natural oxide “Sn foil refresh”, metal foil “tin Sn foil” with natural oxide [4-6] and *ab-initio* calculated for orthorhombic SnO_2(O) and tetragonal SnO [11]) and the studied samples of epitaxial solid solutions $Si_{0.98}Sn_{0.02}$, $Si_{0.92}Sn_{0.08}$ and $Si_{0.85}Sn_{0.15}$. XANES Sn $M_{4.5}$ (3*d*) absorption spectra represent the distribution of *p* states in the conduction band, which reflect transitions from core 3*d* states to free *p* and *f* states in the conduction band. A detailed discussion of the reference spectra fine structure is given in [4-6, 11]. It is only worth noting that the distribution of the main spectral features and their relative intensities (Fig. 2) of XANES Sn $M_{4.5}$ show a significant difference for the references of each compound of the tin-oxygen system. The fine structure of the studied solid solutions is quite similar to each other in terms of the observed spectral features at energies of 487, 493, 497 eV, corresponding to the M5 absorption edge in tin. In general, the fine structure of XANES Sn $M_{4,5}$ of the studied solid solutions, based on the presence and location of characteristic peaks and their relative intensity, is a combination of contributions from orthorhombic SnO_2(O), tin monoxide SnO, and tetragonal SnO_2(T) with a noticeable number of oxygen vacancies. At the same time, there is a redistribution in the intensities of the above-mentioned features. Thus, with an increase in the concentration of tin in solid solutions, the intensity of the double peak increases at an energy of ~ 488 eV (M_5 edges), associated with a lack of atoms in the oxygen sublattice of tin oxide [4, 5] and its high-energy component at an energy of ~ 495 eV. It is also worth noting that with increasing tin concentration, changes in the pre-edge region of the spectrum become more and more apparent, namely, a small shoulder is formed from the bottom of the conduction band towards lower energies. This may indicate the presence of additional electronic states in the band gap, close to the bottom of the conduction band. Thus, it can be concluded that an increase in the concentration of tin atoms in solid solutions of SiSn leads to a change in the fine structure of the tin absorption edge near the bottom of the conduction band with a stable state of the nearest surrounding of tin atoms. The observations made indicate the formation of a stable set of tin compounds in the studied nanolayers of solid

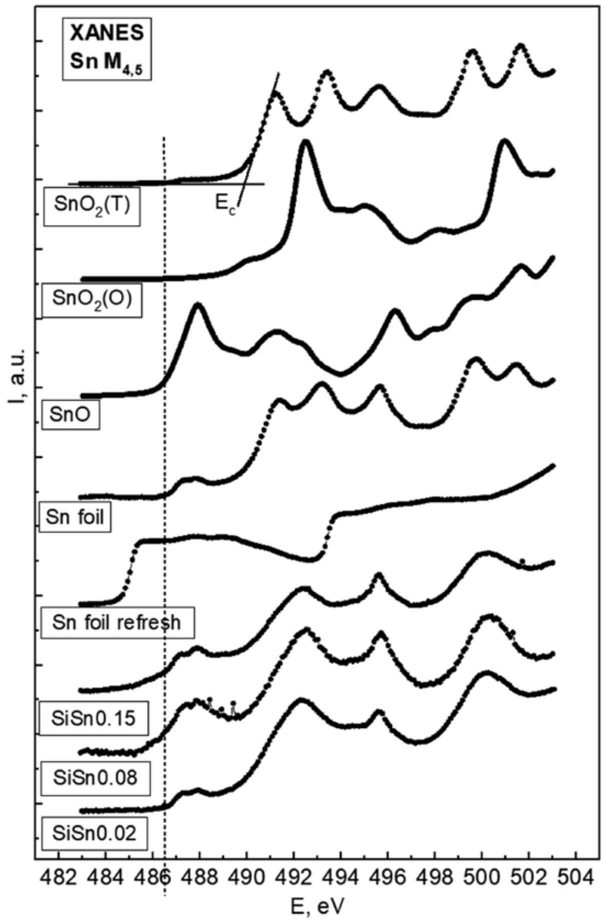

Fig. 2. XANES Sn $M_{4,5}$ of references SnO_2(T), SnO_2(O), SnO, Sn foil, Sn foil refresh and epitaxial solid solutions $SiSn_{0.02}$, $SiSn_{0.08}$, $SiSn_{0.15}$

solutions. There is a good correlation with the data for the absorption edges of silicon, where "dragging" of electronic states near the E_c was also observed. Thus, the effects of changes in the electronic structure of nanolayers of solid solutions of SiSn are observed as a result of disturbances in the Si atoms local surrounding when Sn atoms are embedded in their lattice and oxygen redistribution during formed solid solutions nanolayers surface natural oxidation with a lack of oxygen for tin atoms.

Fig. 3 shows the O K XANES spectra of references (SnO_2(T), Sn foil, c-Si (natural oxide), SiO_2, and c-Si Buffer (natural oxide)) and studied samples of $Si_{0.98}Sn_{0.02}$, $Si_{0.92}Sn_{0.08}$, and $Si_{0.85}Sn_{0.15}$ epitaxial solid solutions. XANES O K (1*s*) absorption spectra are the result of transitions from the core 1s oxygen level to free *p* states in the conduction band. It can be seen that the spectra of the presented reference samples differ in their fine structure. Thus, tetragonal tin dioxide has pronounced peaks at energies of 533.9 and 540.2 eV, as well as features at 536–549 eV. In the tin metal foil, the main peaks are most pronounced at the same energies, while the remaining features of the fine structure are smoothed out. The spectra for c-Si (natural oxide), SiO_2, and c-Si Buffer (natural oxide) are similar to each other and have a wide peak in the energy range of 537–539 eV. The difference is in a more pronounced step at an energy of 535 eV and a pronounced peak at an energy of 537.3 eV for SiO_2. The lack of data on the oxygen edge in orthorhombic tin dioxide and tin single oxide makes the interpretation of the oxygen edge of the studied samples insufficiently complete and is the subject of further research. When considering the edges of oxygen O K absorption (Fig. 3) in the studied solid solutions, it can be seen that the fine structure of the spectra consists of two features at energies of 533.9 eV and in the energy range of 537–539 eV, which corresponds to the features of tin oxides and silicon oxides, respectively. The spectra of solid solutions differ from each other by a slight redistribution of the intensities of these peaks. Thus, the fine structure of the oxygen absorption edge in the studied samples indicates the predominant oxidation of atoms of more electronegative silicon; nevertheless, tin oxides contribute to the electronic spectrum of nanolayers of tin-silicon solid solutions.

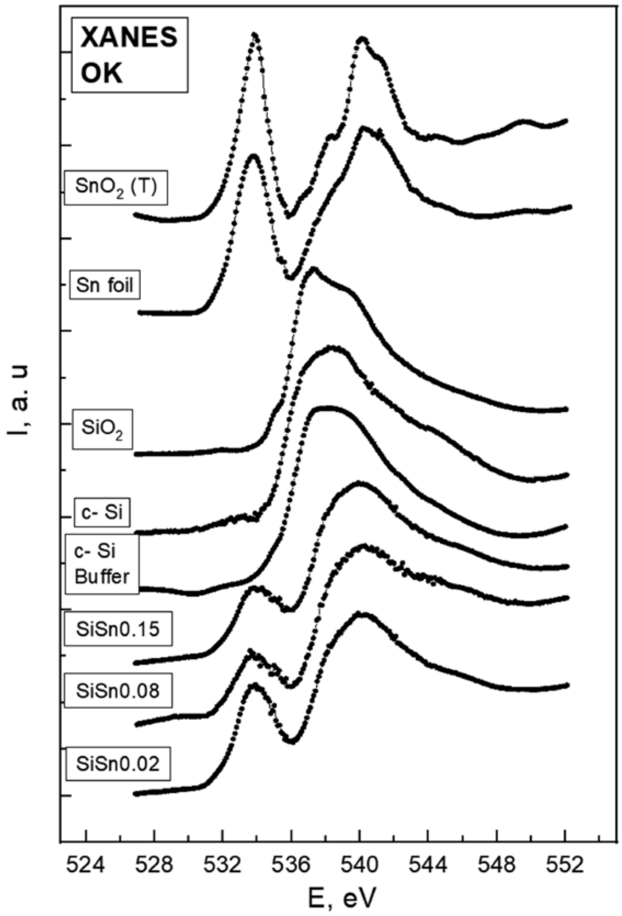

Fig. 3. XANES O K of references SnO_2(T), Sn foil, c-Si, SiO_2 and epitaxial solid solutions $SiSn_{0.02}$, $SiSn_{0.08}$, $SiSn_{0.15}$

4. Conclusions

There is a general agreement of data from the analysis of synchrotron XANES spectra of silicon (Si $L_{2,3}$), tin (Sn $M_{4,5}$), and oxygen (O K) for tin-silicon solid solutions formed by molecular beam epitaxy exceeding the known limits of solubility of Sn in Si (2, 8, and 15%) in the form of thin nanolayers on a crystalline silicon buffer layer. It is shown that even the lowest concentration of tin atoms of 2% during the formation of a solid solution of SiSn makes changes in the specificity of the nearest surrounding of Si and Sn atoms. The appearance of tin atoms surrounded by silicon atoms, during the formation of a solid solution, leads to the effect of electronic states "dragging" into the band gap near the E_c. When structures are stored in the laboratory conditions, natural and intermediate oxides of silicon and tin are formed on the surface. An increase in the tin content (up to 15%) leads to a blurring of the density of the electronic states near the bottom of the conduction band.

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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