A novel approach to the electronic structure and surface composition investigations of tin-oxygen system materials by means of X-ray absorption spectroscopy combined with ab initio calculations

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ARTICLE INFO

ABSTRACT

A novel approach to the comprehensive study of the tin-oxygen compounds electronic structure and phase composition is reported. X-ray absorption fine structure relative to Sn $M_{4,5}$ edge and reflecting density of p- and f-electronic states in the conduction band for tin metallic foil, bulk SnO and SnO_2 oxides and tin oxide nanolayers have been obtained using synchrotron radiation. Same absorption edges of metallic tin single crystal, SnO, tetragonal and orthorhombic SnO_2 have been ab initio calculated for the first time. Peculiarities of the experimental spectra fine structure transformation have been precisely analyzed and connected with changes in the surface composition of materials under study. The technique of materials composition semiquantitative estimation in tin-oxygen system by means of linear combination fitting of the calculated spectra was discussed.

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1. Introduction

Tin dioxide is a well-known semiconductor, wide-spread in the modern technologies [1] to produce resistive gas sensors [2,3], transparent conducting electrodes [4,5] and solar cells [6]. Tin dioxide demonstrates a strong dependence of electronic structure and other properties on presence of defects in its lattice [7,8]. The most of defects are caused by deviation of tin to oxygen atoms ratio from stoichiometry, that is accompanied by formation of intermediate oxide phases. As a result, the precise control of SnO_2 phase and chemical composition becomes extremely important for its application in industry and technology.

Nanotechnology progress resulted in the critical influence of surface composition on properties of many newly synthesized materials. Phase and chemical composition of surface layers can substantially differ from bulk composition of a material, that is why it is necessary to use surface sensitive techniques to study them, e.g. X-ray absorption near-edge structure spectroscopy, that implies using of highly intensive synchrotron radiation sources. This technique provides information on local partial density of unoccupied electronic states in surface layer of a materials under study [9,10]. Using bulk sensitive techniques (i.e. X-ray diffraction – XRD) to investigate the surface composition of a substance is accompanied by the risk of getting incorrect results and suggesting possibly wrong interpretation.

XANES technique is widely used to study tin oxides. To date, different SnO_2 nanostructures like nanoparticles [8], nanowires [11], nanoribbons [12] and nanolayers [13] have been studied. $M_{4,5}$ tin spectrum often becomes the main object under study in such materials. It is located in the ultrasoft range of X-ray radiation, exhibiting the distinctive fine structure and pronounced features of the absorption spectrum, and its form is highly sensitive to structural changes in a sample [7]. These facts simplify interpretation of registered spectral data and its comparative analysis.

The reference SnO_2 (T) (tetragonal tin dioxide) spectra, presented in different studies [7,11,14–16], correlate with each other well. On the other hand, the reference tin monoxide (SnO) spectra [7,14,17] demonstrate notable distinctions. There are very few spectra of metallic tin (β-Sn) [14] and we deem them to be quite questionable. Even less data is available on SnO_2 (O) orthorombic tin dioxide [17].

As XANES spectrum fine structure is highly sensitive to local atomic surrounding [9], changes in a distribution of the main spectral features are caused by differences in condition and phase composition of a studied sample's surface. The question of the

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relationship between Sn $M_{4,5}$ XANES spectra shape and characteristics of tin oxides like stoichiometry is actively studied [11,12] and remains an open issue. Addressing this issue may provide possibility to evaluate a surface phase composition of samples by shape of their experimental spectra.

The aim of this work is the detailed investigation of regularities and peculiarities in tin oxides' conduction band electronic structure. For this purpose, the evolution of Sn $M_{4,5}$ XANES spectra depending on phase composition of different tin-oxygen materials' surface layers is studied by using both synchrotron radiation and ab initio calculations. The work presents the theoretically simulated XANES Sn $M_{4,5}$ spectra of metallic tin and its different oxides as well. The novel approach to the electronic structure and surface composition study of tin-oxygen system materials is suggested by means of X-ray absorption spectroscopy combined with ab initio calculations.

2. Experimental

Sn $M_{4,5}$ XANES spectra that reflect distribution of the local partial density of unoccupied p- and f-electronic states in the conduction band have been experimentally registered with the depth of informative layer of about 10 nm. The following commercial Alfa Aesar [18] reference samples have been studied: tin foil (referred as "Sn foil initial"), SnO powder, and small lumps of pressed and sintered SnO_2 tin dioxide. A few samples that we prepared ourselves have also been investigated. The first one (referred as "Sn foil fused") was prepared by in-situ gradual heating of the tin foil (Sn foil initial) in ultra-high vacuum 10^{-10} Torr in the spectrometer (end-station) preparation chamber. The resulting temperature was about 240 °C that is slightly higher that the metallic tin melting point. Formation of a droplet was visually observed on the horizontally disposed holder during the process. After 15 min in such conditions the sample was gradually cooled to room temperature. The second sample (referred as "Sn foil refresh") represented a piece of the same initial metallic tin foil that was mechanically refreshed in the UHV spectrometer preparation chamber. As a consequence, the yellowish color of the foil that is common for tin oxides turned into "metallic" light-grey. The third sample (referred as "SnO$_x$/Si initial") was formed by magnetron sputtering of 100 nm tin film on a silicon substrate. Finally, another sample that is referred as "SnO$_x$/Si 170" was produced by 170 °C annealing of the identical tin film at air for an hour [19].

XANES investigations have been performed at the RGBL Russian-German beamline of BESSY II synchrotron (Helmholtz-Zentrum Berlin). The HIRES end-station with UHV preparation and experimental chambers was used during the experiment. The photon flux was equal to 10^{12}–10^{13} photons/s, the storage ring current was about 150–300 mA. Instrumental broadening was of the order of 0.1 eV. Vacuum was maintained at the level of 10^{-10} Torr in the end-station chambers. XANES spectra were registered in the TEY (total electron yield) mode by measuring sample current, occurring to compensate the yield of photo- and Auger electrons from a sample's surface. The registered spectra have been normalized using the standard normalization procedures [9,10].

3. Calculation

The calculation of electronic structure have been conducted using the linearized augmented plane wave method in Wien2k [20] code. Lattice parameters from the database [21] have been used to simulate metallic tin (β-Sn), tin monoxide (SnO) and tin dioxide tetragonal phase (SnO$_2$ [T]). Orthorhombic SnO$_2$ (O) simulation was performed with the lattice parameters from the article

[22]. The Generalized Gradient Approximation (GGA) was used to take into account the exchange–correlation energy [23].

The following supercells [24] parameters were used in order to calculate Sn $M_{4,5}$ X-ray absorption spectra: $2 \times 2 \times 4$ for β-Sn, $3 \times 3 \times 3$ for SnO, $2 \times 2 \times 3$ for SnO$_2$ (T) and $2 \times 2 \times 2$ for SnO$_2$ (O). These supercells contained 1 tin atom with a core hole [25] on the $3d_{5/2}$ level. Such sizes of supercells almost allow to exclude mutual interaction of atoms containing core holes, as was demonstrated previously during calculation of bulk SnO$_2$ (T) XANES spectra [26].

3d level spin–orbit splitting wasn't taken into account in ab initio calculation of the absorption spectra, so the theoretical curves that describe only the M_5 ($3d_{5/2}$) edge have been obtained. The calculated M_5 edge was shifted on the amount of spin–orbit splitting of the $M_{4,5}$ metallic tin level (8.4 eV) and multiplied on 2/3 to semi-empirically locate Sn M_4 ($3d_{3/2}$) absorption edge. For that reason, only results for the range of M_5 absorption edges for calculated spectra were compared to analyze the experimental data.

Analysis of the experimental XANES results was performed by means of linear combination fitting (LCF) of the calculated spectra. The detailed information on this technique can be found in [27,28]. According to the LCF, an experimental X-ray absorption spectrum of an object with unknown phase composition can be represented as a linear combination of the known reference spectra of phases this object includes $M = \sum_i f_i \cdot S_i$, where M is a model of a spectrum in the chosen range (obtained by means of the least-squares method) and f_i is a weight coefficient for intensity of every S_i reference spectrum in the same range. The sum of weight coefficients is described as follows $\sum_i f_i = 1$. That's why contribution of every reference spectrum to resulting model spectrum equals to relative weight of a component in a sample. Accuracy of LCF analysis results is limited by accuracy of reference calculated spectra in a representation of phases that samples consist, as well as by uniqueness of near-edge fine structure distribution in absorption spectra of different references. The LCF technique was previously used by different authors to analyze XANES spectra of different compounds [29], including ones containing tin [30].

4. Results and discussion

Fig. 1a shows the experimental XANES spectra of the studied samples. The spectrum of the reference SnO$_2$ sample is characterized by tin M_5 ($3d_{5/2}$) absorption edge at the energy of ~490 eV and distinctive ternary structure (peaks B, C and D in Fig. 1a). The second absorption edge Sn M_4 ($3d_{3/2}$) is located at the energy over 499 eV that corresponds to the tin 3d level spin–orbit splitting equal to 8.4 eV. Fine structure of other reference samples spectra (SnO and Sn foil initial) is similar to SnO$_2$. They also demonstrate three peaks, but features B and C are substantially smeared. These spectra also introduce a slight double pre-peak A (sometimes referred as peak A due to its intensity) at the energy of about 486.5–488.3 eV. The peculiarities of these reference spectra have been closely analyzed in [7,11].

Compared to SnO and Sn foil initial, Sn foil fused absorption spectrum exhibits much more differences from SnO$_2$, and the most notable one is high intensity of peaks A and D. The form of spectral curves obtained for SnO$_x$/Si initial and SnO$_x$/Si 170 nanofilms is substantially different from the spectra described above. Peaks B and C merge in one wide maximum, exceeded by the intensive peaks A and D. Besides, there is a low-energy shoulder at the energy of 485 eV in the spectrum of the SnO$_x$/Si initial film. This energy range contains Sn M_5 absorption edge of the Sn foil refresh sample represented as a "step" with a weak fine structure. Energy range between Sn M_5 (485.0 eV) and Sn M_4 (493.4 eV) levels