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NEXAFS spectral peculiarities in Sn:SiO_2 composite layer

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ABSTRACT

Synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy has been used to investigate a novel Sn:SiO_2 composite thin layer grown by organometallic chemical vapor deposition technique (CVD) on a single crystalline silicon wafer with additional treatment by argon ions. According to a previously reported thermodynamic anomaly, an efficient exchange of oxygen between the silicon and tin dioxide surfaces occurs during the growth of the metal oxide thin layer. The present study focuses on the visualization of the atomic and electronic structure of tin nanostructures localized in silica matrix. It is found that no significant chemical alterations are observed during argon ions treatment of the initial composite layer. The removal of atmospheric residues, which partially passivated defects in the highly defective SnO_{2-x} top layer, did not significantly change the initial NEXAFS Sn $M_{4,5}$ edge spectrum. Based on these results, we found that the main state in which tin nanoparticles localized in the amorphous silica matrix is the metallic state. In addition, based on the NEXAFS Si $L_{2,3}$-edge studies, we found that silica is most associated with the stoichiometric structure of thermally deposited SiO_2 layer with the presence of silicon suboxides. These results provide insights into the atomic and electronic structure of Sn:SiO_2 composites and contribute to the possible implementation of such materials in various application concepts related to thermal energy storage and novel photonic devices.

Introduction

The main task of science is to understand the nature of materials and the means of controlling their behavioral state. Given the significant progress of human society over the last couple of centuries and the development provided by the reduction of the size of materials thanks to modern nanotechnology. In the 1990 s a bridge between the macro- and nanoworld was built, making new unexplored effects and properties of materials available. Precise controlling of the formation and chemical composition of the thin layer during its growth plays a crucial role in the further implementation of this layer in various devices as an active building block. The development of reliable energy storage technologies has been pushed to the front at the time. The thermal energy storage using phase change materials (PCMs) is one of the most effective ways to solve the above tremendous energy losses problems. PCMs as latent heat storage materials have high energy storage density and relatively constant operating temperature, which have been widely investigated for promising applications in solar thermal energy storage [1,2], waste heat recovery [3,4], thermal management [5–7] and modern architecture [8,9] etc. Tin-silica composite material belongs to the middle range of PCM materials due to the low melting point of metallic tin, below 250 °C, which makes it very promising in the field of thermal energy storage [10]. In recent years, the formation and characterization of this type of materials has attracted increased interests due to the lack of knowledge of this type of materials.

In our previous publication [11], we reported a significant surface charge effect in the Sn 3d core level XPS spectrum as a result of the conducting/insulating nature of the constituent elements of the Sn:SiO_{2-x} composite layer, but due to this strong surface charge effect in the XPS spectra, the atomic and electronic structure of the obtained new composite thin layer is not completely clear. Therefore, in this work, a technique less sensitive to the charging effects was applied. We used NEXAFS spectroscopy in order to experimentally evaluate the atomic and electronic structure of the Sn:SiO_{2-x} composite layer. The tin-silica

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composite layer was grown at the 725 °C using CVD technique. The detailed growth procedure and methodology is presented in our previously published paper [12]. Scanning electron microscopy (SEM, FEI HELIOS nanolab 600i) and high-resolution transmission electron microscopy (TEM, Neoarm 200F, JEOL Ltd., Japan) at an accelerating voltage of 200 kV were used to obtain high-resolution images. The characteristic "volcano"-like morphology with the presence of the globular structures with the diameter of about 200 nm is clearly visible in SEM planar view image, as shown in Fig. 1*a*. In parallel, TEM studies were performed using Pt/Au protection layer to avoid the damage of the initial layer structure during the FIB lamella preparation as pointed in the TEM micrograph. The cross-sectional TEM image of the obtained composite layer is presented in Fig. 1*b*, and confirms the presence of the bigger features about 200 nm in the above 50 nm thin layer on silicon surface grown by CVD. As was proposed in our previous studies, the bigger NPs are related to the metallic tin and the layer itself is a tin-silica composite. Additionally, the top layer is related to the highly porous tin oxide layer. In the present article, we intend to gain a further insight in the composition of the layer and provide additional proof of the previously suggested model. In order to remove the adsorbed atmospheric residues from the surface we applied Ar^+ sputtering. Sputtering with argon ions with energies ranging from 1 to 1.5 kV and at a pressure of 1-5x10^{-5} mbar was carried out. In current work we focused on NEXAFS Si $L_{2,3}$-edge and Sn $M_{4,5}$-edge spectra which reveal the local partial density of free electronic states in the conduction band. Studies were approved at two synchrotron radiation facilities: GELEM dipole beamline of BESSY II operated by Helmholtz Zentrum Berlin (GER) [13] and at VerSoX B07-B Diamond Light Source (UK)[14]. The probing depth at Si $L_{2,3}$ and Sn $M_{4,5}$ edges recorded in total electron yield mode were estimated as 5 nm [15] and about 10 nm, respectively. NEXAFS spectra were normalised to the ring current and the photon flux of the beamline. Energy calibration was performed using a reference of a sintered SnO_2 lump [99,9% ThermoScientific; CAS: 18282–10-5], where the first Sn(IV) peak from the five-features structure was set to 491.2 eV. NEXAFS Sn $M_{4,5}$ spectra of the initial and Ar^+-treated surfaces in comparison with the reference spectra of metallic tin foil (ThermoFisher (Kandel) GmbH, Puratronic, CAS [7440–31–5], Germany) and sintered lump of tin dioxide (ThermoFisher (Kandel) GmbH, CAS [18282–10-05], Germany) are presented in Fig. 1*c*. In order to interpret the spectrum of the composite layer we compare experimental data with those of the reference compounds and literature. NEXAFS Sn $M_{4,5}$-edge spectrum of SnO_2 crystal is characterized by the presence of five maxima in the photon energy range between 491 eV and 501 eV [16], while metallic tin foil exhibits a "step" at photon energy around 485 eV. Spectral characteristics of the SnO_2 can be partially identified in the spectra of the initial composite layer: by the presence of a broad unresolved features in the energy range 491–493 eV, above 500 eV and sharp peak at 496 eV. In the sample after Ar^+ sputtering we do not observe these components, while metal-related step arises at lower photon energies. Additionally, component at 489 eV arises. According with the theoretically calculated NEXAFS spectrum it can be also attributed to the metallic tin state [18]. Moreover, we observe components at 488 eV and 497 eV which appear as shoulders in the initial spectrum, whereas in the spectrum of the Ar^+ treated sample these are more pronounced and better resolved. These components can be attributed to Sn(II) oxide that agrees well with the theoretically calculated NEXAFS spectrum reported in Ref [18]. Furthermore, the defect-rich nature of tin(IV) is confirmed by the presence of a clearly resolved component in the 486–487 eV region, which, according to the current knowledge, can be referred to the presence of oxygen vacancies in the Sn(IV) oxide [16,17]. These results suggest that tin dioxide has a highly defect-rich nature, where tin oxide can be represented as SnO_{2-x}, where x is closer to unity. Moreover, NEXAFS Sn $M_{4,5}$-edge confirms the

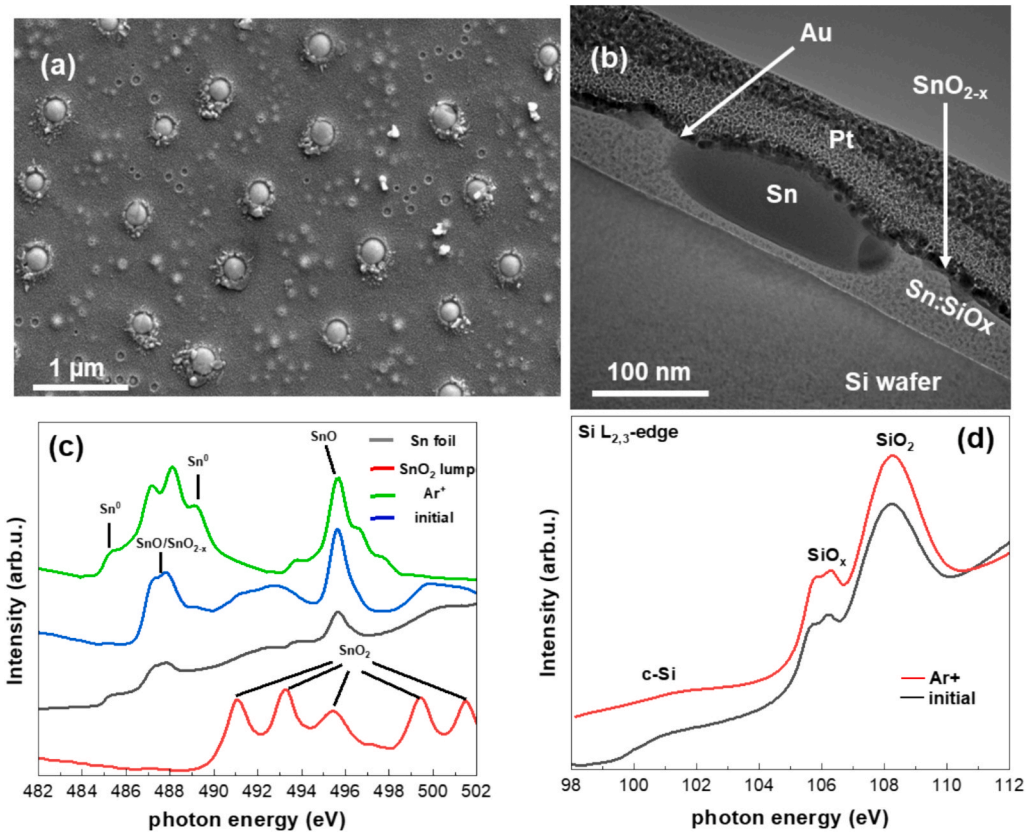

Fig. 1. Sn:SiO_2 composite layer deposited at 725 °C (a) scanning electron microscopy planar view; (b) TEM cross – sectional view with Au-Pt protection layer; (c) NEXAFS Sn $M_{4,5}$-edge spectra: initial and after soft Ar^+ ions sputtering in comparison with the references NEXAFS spectra of tin foil and tin dioxide lump; (d) NEXAFS Si $L_{2,3}$-edge: initial and after soft Ar^+ ions treatment.

presence of metallic Sn phase, that is related to Sn nanoparticles. Closer look at Fig. 1(d) with Si $L_{2,3}$ NEXAFS spectra does not reveal any significant changes upon the Ar^+ treatment. Sputtering only removes the adsorbed atmospheric residues from the surface, passivating the highly defective SnO_{2-x} top layer without significant transformation of the surface chemical composition of the matrix. The presence of the feature at 108 eV in Si $L_{2,3}$ NEXAFS can serve as a signature of SiO_2 and corresponds well to the spectrum of the thermally deposited stoichiometric silica layer on silicon [19]. On the other hand, a doublet at above 106 eV is an indication of the presence of silicon suboxides, SiO_x, where x is about 1.7 that well correlates with the Si $L_{2,3}$ NEXAFS spectrum for $SiO_{1.7}$ suboxide reported by Barranco et al. [20]. In summary, based on the previous studies and current NEXAFS investigation we found that the composition of the layer observed due to the thermodynamic anomaly growth of tin oxide layer in CVD can be presented as a mixture of porous highly defective tin(IV) and tin(II) oxide as a top layer (with the thickness below 5 nm based on TEM studies) following the main layer which can be identified as Sn:SiO_2. These fundings provide a deeper understanding of the surface structure of obtained tin-silica composite layer composition and their specificity, which can further be used for different applications and functional material engineering.

CRediT authorship contribution statement

Vladimir Sivakov: Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Poting Liu:** Writing – review & editing, Visualization, Investigation, Formal analysis. **Katharina Freiberg:** Writing – review & editing, Methodology, Investigation. **Shivani Yadav:** Writing – review & editing, Methodology, Investigation. **David C. Grinter:** Writing – review & editing, Methodology, Investigation. **Anna Makarova:** Writing – review & editing, Visualization, Validation, Methodology, Investigation.

Declaration of competing interest

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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Data availability

Data will be made available on request.

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