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XPS investigations of MOCVD tin oxide thin layers on Si nanowires array

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ABSTRACT

Tin oxide thin layers were grown by metal-organic chemical vapor deposition technique on the top-down nanostructured silicon nanowires array obtained by metal-assisted wet-chemical technique from single crystalline silicon wafers. The composition of the formed layers were studied by high-resolution X-ray photoelectron spectroscopy of tin (Sn 3d) and oxygen (O 1 s) atoms core levels. The ion beam etching was applied to study the layers depth composition profiles. The composition studies of grown tin oxide layers is shown that the surface of layers contains tin dioxide, but the deeper part contains intermediate tin dioxide and metallic tin phases.

In the last decades, there has been a growing interest in the research and development of silicon nanowires (SiNWs) for various applications in the fields of optoelectronics, photonics, and photovoltaics, as well as in the sensor field [1–4]. The top-down metal-assisted wet chemical etching (MAWCE) formation mechanism is a simple and perspective approach since it is involving only processes under the near ambient conditions and leading to low-cost processes. The formed SiNWs array and their developed surfaces prepared under controlled regimes are promising candidates to be applied as a matrix for subsequent functionalization in a large field of applications [5–8]. At the same time, tin oxides, and especially, tin dioxide belongs to the functional materials [9–11] which can be widely used for different electronic applications and devices such as gas sensing electronic nose [12,13]. In the present paper, the well-known metal-organic chemical vapor deposition (MOCVD) technique was applied for the deposition of tin oxide layers on the nanostructured silicon surfaces. The controlled flexibility of two material classes, electronic and optical properties under alignment in certain structure can open up more available forms of functional composite materials. However, the role of surface composition is a significant aspect due to the fact that such kind of composite structures and techniques are sensitive to the surface physico-chemical properties than can influence their functionality. X-ray photoelectron spectroscopy (XPS) is an ultra-high vacuum and non-destructive technique that provides direct experimental information on materials surface's atoms charge states allowing to explore composition of the materials surface. Even more, XPS technique in combination with focused ion beam etching can be applied for the step-by-step study of materials surface and matrix depth profiles. The tin-oxygen system has been previously studied using lab-based XPS technique or synchrotron-based experimental systems [14–18].

Silicon nanowires were prepared by metal-assisted chemical etching of highly boron doped (doping concentration 10^{20} cm^{-3} with resistivity < 0.005 Ωcm) (1 0 0) single crystalline silicon (Si) wafers using the similar procedure as published in our previous work [6]. Silver particles were deposited on the silicon surface and than immediately immersed in a mixture of 5 M HF and 30% H_2O_2 (volume ratio 10:1) water solutions. The wafer etching process is based on the galvanic displacement of Si-surface thereby oxidizing the Si to form silicon dioxide (SiO_2) so that the HF component of the solution can remove the SiO_2 and in parallel by reducing the silver ions to metallic silver at the Si surface [6]. The typical 4 μm vertically-aligned SiNWs array was observed. The gas phase pyrolysis of the tin(IV) *tert*-butoxide ($Sn(O^tBu)_4$) precursor, was studied in a horizontal home-built cold-wall CVD reactor [19]. Tin precursor vapors were created by heating the precursor reservoir to 30–35 °C using an auxiliary heater. The precursor flux was guided to an inductively heated substrate by applying reduced pressure (10^{-4} mbar). Tin oxide thin layer were deposited into the SiNWs matrix at 600 °C with the total growth time of 10 min that guided to the formation of few tens of nanometers thick tin oxide layer around silicon nanowires.

UHV XPS spectrometer was equipped with high resolution SPECS Phoibos 150 hemispherical electron energy analyzer with monochromatic Al X-ray source (excitation energy was 1486.61 eV) and focused ion etching source. Energy resolution was found in the range of 0.1 eV

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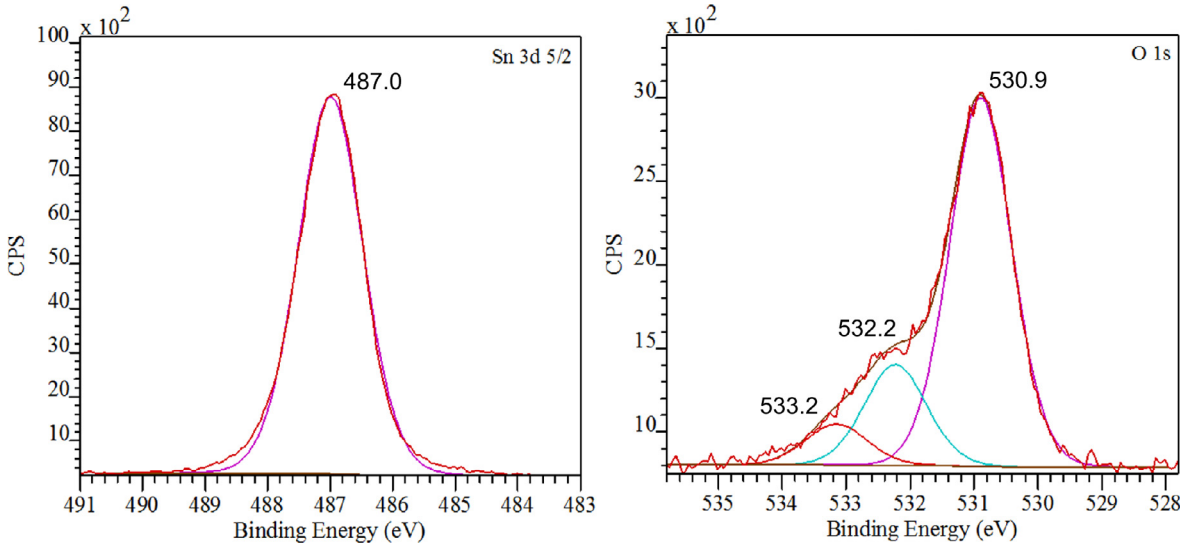

Fig. 1. High resolution XPS spectra for the surface of the MOCVD tin oxide covered silicon nanowires array. Left: Sn $3d_{5/2}$ core level with fitting curve. Right: O 1 s core level with fitting curves.

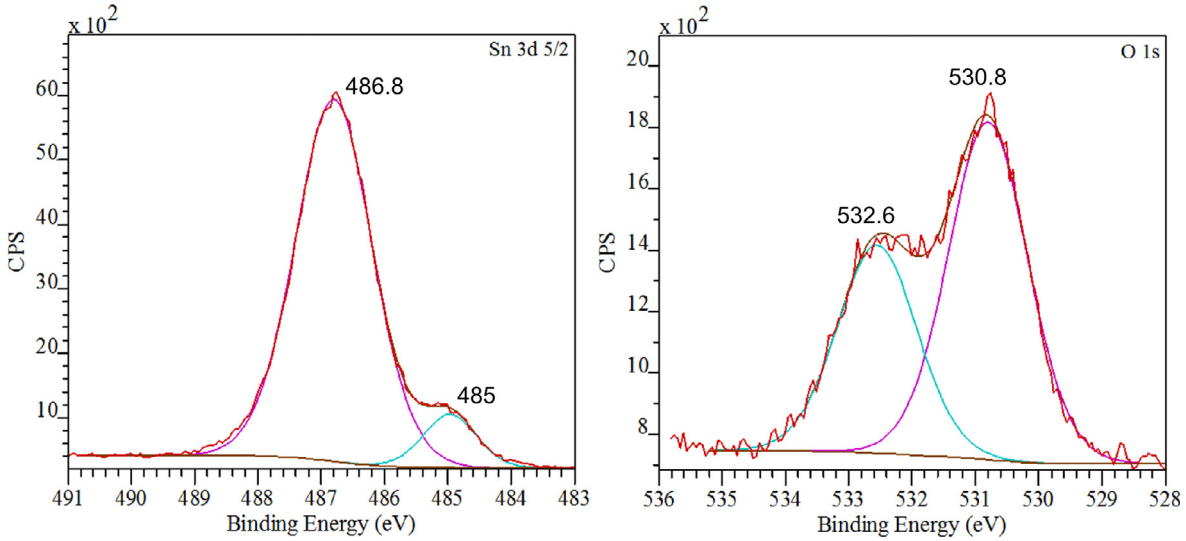

Fig. 2. High resolution XPS spectra for the ion beam treated part of the tin oxide covered silicon nanowires array. Left: Sn $3d_{5/2}$ core level with fitting curves. Right: O 1 s core level with fitting curves.

with the analysis depth estimation of about 3 nm for excited Sn 3d and O 1 s core levels. The calibration of the spectra was carried out using a signal of pure gold film and the position of its core 4f level together with C 1 s level of hydrocarbon contaminations residuals on the investigated sample surfaces reduced to the known value of 285.0 eV [20]. Stepwise combination of 1 kV (3 times, 15 min each) followed by 1 kV (2 times, 1 min each) acceleration voltages for Ar^+ ions was used for ion beam surface treatment. The formed etching area was larger in comparison with area of X-rays photons illumination.

Sn $3d_{5/2}$ and O 1 s core levels XPS spectra were registered with the resolution of 0.1 eV for the silicon nanowires arrays covered by MOCVD formed tin oxide layers as presented in Fig. 1. In present study we used standard Shirley procedure of background removal and so we can estimate components of each registered spectrum by Lorenz and Gauss peaks fitting. The binding energy value of the Sn $3d_{5/2}$ line is 487.0 eV. This value well correlates to the known binding energy of SnO_2 given in previous publications [18,20]. O1s fitting results allowed us to detect three components. The main component at 530.9 eV is a quite close to the published binding energy of oxygen in SnO_2 [18,20]. At the same time the rest two low intensity and high energy components can be attributed to the adsorbates containing oxygen: OH groups (532.2 eV) or water molecules (533.2 eV) [15,18,20].

The surface treatment with ion beam results on the removal of about 11 nm of the initial tin oxide layers than allowed us to estimate deeper the composition in SiNWs matrix. The composition of the etched area i.e. the layer bulk was estimated by Sn $3d_{5/2}$ and O 1 s core levels XPS spectra as shown in Fig. 2 (registered under the same conditions as spectra in Fig. 1). As it clearly visible, the Sn $3d_{5/2}$ core level is transformed into two component lines. The low intensity component at 485.0 eV is specific to the metallic tin phase [18,20]. Sn atoms binding energy of 486.8 eV is characteristic for the intermediate tin oxide SnO_{2-x} compositions previously discussed in the literature [16–18]. Taking into account that ion beam etching can change oxidation state of SnO_2 surface one should note the unexpectedly high intensity of metallic tin component if compared with obviously shifted tin oxide main feature (Fig. 2). O 1 s component fitting with two observed peaks are in a good agreement to the achieved results of Sn 3d5/2 core level. Lowest binding energy value of 530.8 eV is observed for oxygen atoms in SnO_{2-x} [16–18] while another observed peak at 532.6 can be attributed to surface OH groups residuals and probably to natural SiO_2

covering silicon wires (that is reachable because of the SnO_{2-x}/SiO_2 interface non-uniformity).

To summarize, our observations strongly suggest that formed tin oxide MOCVD layer on a top of silicon nanowires array and in the SiNWs matrix under applied formation conditions has a complex composition containing a tin dioxide as a main phase on a top of layer, but deeper the presence of intermediate tin dioxide and metallic tin phases was observed after ion beam etching applied.

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