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Synchrotron Characterization of Functional Tin Dioxide Nanowires

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Abstract. Wire-like crystals of tin dioxide were synthesized by a gas-transport technique. The wires, of mainly nanometric diameters, were characterized by spectroscopy and microscopy techniques with the use of highly brilliant and intense synchrotron radiation. We studied the influence of the surface chemical state and the oxygen vacancies on the atomic and electronic structure of the nanowires. The surface of the nanowires is covered by a few nanometers of tin suboxides. The lack of oxygen over the surface layers leads to specific sub-zone formation in a gap, as shown by synchrotron studies.

INTRODUCTION

Tin oxide crystalline nanowires are presently attracting enormous attention. They are characterized by high surface-to-volume ratio and are being considered for applications in gas sensing, memory, and light-emitting device technologies [1, 2]. For samples with zero bulk defects and high surface perfection, values for mechanical strength, charge carrier mobility, and other parameters can approach theoretical values. Nondestructive X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) techniques that are sensitive to the local atomic environment (Sn or O in our case) in surface nanolayers are highly informative [3, 4] and in fact essential for characterization of such materials [4, 5].

EXPERIMENTAL

Undoped tin dioxide nanowires were formed by the vapor-liquid-solid mechanism with the use of gas-transport synthesis [6]. Samples modifications, spectroscopy, and microscopy measurements were performed at the Russian–German Beamline of the Helmholtz Zentrum Berlin BESSY II storage ring (Berlin, Germany) and at the Synchrotron Radiation Center (SRC) at the University of Wisconsin–Madison (Stoughton, Wisconsin, USA). The storage ring current was at ~100 ÷ 250 mA, providing radiation with an intensity of $\sim 2.5 \times 10^{11}$ photons/s. The energy resolution was ~ 0.1 eV. The pressure in the analytical chamber was permanently supported at $\sim 10^{-8}$ Pa. The SPECS Phoibos 150 electron energy analyzer attached to the Russian–German Beamline at BESSY II was used for the XPS studies. For XANES investigations performed at the same beamline, the sample current technique registration was applied in the total electron yield mode, i.e., measurements of the current compensating the total electron yield from the sample surface were applied. The photoemission electron microscopy (PEEM) technique was applied with the use of the ELMITEC PEEM III microscope attached to the VLS-PGM beamline at the SRC. The standard samples (examined by X-ray diffraction and microanalysis) were used as references for all measurements in the same load with the investigated samples.

RESULTS AND DISCUSSION

The spectromicroscopy PEEM technique (Fig. 1) proved to be effective for characterization after sedimentation of wire-like crystals onto prepared substrates; sharp images were registered for separated nanowires for the first

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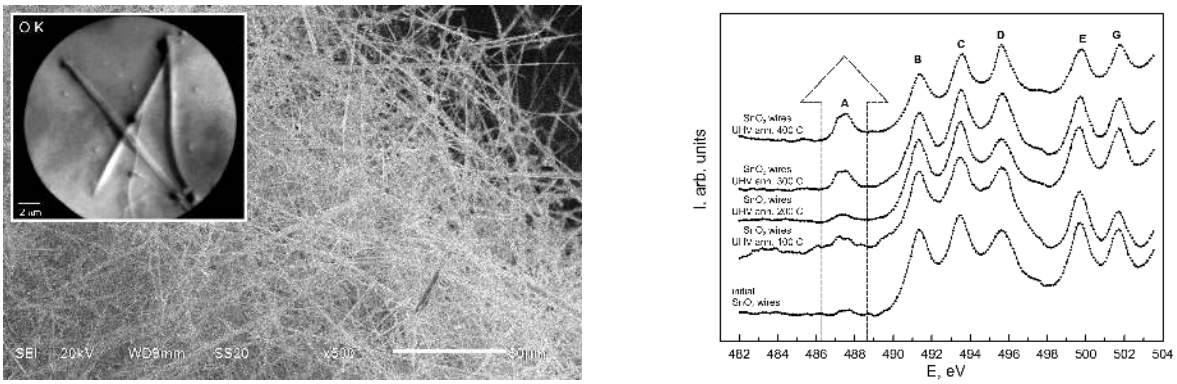
time. Nevertheless, the nonuniformity of the sample surface after sedimentation can be a serious obstacle; it prevented the extraction of spectroscopic information from the separated SnO_2 wire at the microscopic level.

The XPS data obtained demonstrated that binding energy values for our reference samples tended to increase along with the increase in the degree of oxidation (Fig. 1). Oxide observed at the nanowire surface is similar to the oxide covering the reference metallic tin foil. For the first time, the $M_{4,5}$ absorption edge of pure metallic tin was registered for the reference sample after the native oxide was mechanically removed *in situ*. This approach allowed us to clearly separate the absorption edge of metallic tin states and the "defect" pre-peak observed in a gap near the absorption edge of SnO_2; the peaks can be distinguished by their shape and energy position (Fig. 1). This pre-peak is most likely caused by oxygen vacancy states that exist over the surface layer. It is observed for both reference samples and studied wires. Thus, the localized states of lattice defects in the band gap at a distance of ~2.6 eV from the bottom of the conduction band corresponding to the main absorption edge (~490 eV) were detected in the Sn $M_{4,5}$ XANES spectra of the SnO_2 wire-like crystals.



(a) (b)

FIGURE 1. (a) Scanning microscopy image of a sample of nanowires. Inset: synchrotron PEEM image of single nanowires measured at the K absorption edge of oxygen. (b) Sn $M_{4,5}$ XANES of initial wires and *in situ* annealed wires. Arrow shows influence of oxygen vacancies.

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