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Characterization of individual SnO$_2$ nanobelts with STM

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**A B S T R A C T**

The surface morphology of tin oxide nanobelts (NB) was studied with scanning tunneling microscopy (STM), dry-deposited on TiO$_2$ substrates. XPS shows carbon contamination on as-grown, air-exposed SnO$_2$ nanobelts, which was removed by oxygen plasma cleaning. The thermal stability of the NBs was studied with SEM and critical temperatures, where structural changes occur in UHV, O$_2$ atmosphere, and air, were determined. Atomically resolved STM images show a SnO$_2$(101)-(1$	imes$1) structure on the top NB surface.

Tin oxide is widely used as a solid-state gas sensor for detection of combustible and toxic gases [1,2]. The sensing mechanism relies on a change in the electrical conductivity due to the interaction with ambient reducing and oxidizing gases. Charge transfer between the substrate and the adsorbed species leads to a depletion or injection of charge carriers into the active region of the material. This results in band bending in the vicinity of charged adsorbates [3,4]. The shift of the conduction band relative to the Fermi level changes the number of charge carriers and, as a consequence, results in a measurable change in conductivity.

Tin oxide nanobelts and nanoribbons [5] have been suggested as novel materials for gas sensing applications [6–10]. For small single crystals charge carrier depletion may run across the whole crystal, influencing nearly all electrons inside. This may result in drastic conductivity changes as a function of the adsorbing gas partial pressure [11]. The large surface-to-volume ratio of the nanobelts, and lateral dimensions that are comparable to their charge carrier screening length, make them highly sensitive and efficient transducers of surface chemical processes into electrical signals.

The surface properties as well as molecular processes at the surface of tin oxide define its sensitivity and selectivity towards target gases [1,2]. Well-defined facets of SnO$_2$ single crystals are considered model systems for studying SnO$_2$ based gas sensing materials. Their structure, composition, electronic properties [11–16], surface oxygen chemistry [3,17,18], Pd growth [19–22], and adsorption of water [13,23–25] have been studied extensively by our group and by others. As a continuation of our studies of SnO$_2$ we have begun surface investigations of nanobelt systems, which can provide a more direct comparison with realistic gas sensing devices. In order to fully exploit the potential of these novel materials it is important to characterize their surface morphology, modification with reactive metal clusters (which allows to functionalize the NBs), and molecular adsorption on the surface of NBs. Commercial solid-state gas sensors are usually operated at high temperatures (300–400 °C) [2,7], thus it is important to know the safe operation limits for NBs based gas sensors.

The purpose of the present work is two-fold: First, probing the surfaces of the NBs with surface science techniques is challenging because of their reduced dimensionality. We want to find best practices for applying state-of-the-art surface science techniques to oxide nanobelts and nanoribbons as a new class of materials, in particular scanning tunneling microscopy (STM), which allows a direct inspection of the surfaces of individual nano-objects. Second, identifying the differences and similarities between macroscopic SnO$_2$ single crystals and NBs will allow to apply the fundamental knowledge of their surface properties to SnO$_2$ NB-based devices.

SnO$_2$ nanobelts were synthesized using physical vapor transport following established techniques [5,26]. SnO powder was evaporated in an alumina tube in a horizontal furnace under Ar flow. Products condensed onto an alumina crucible placed at the downstream end. Dry-deposition from the edge of the crucible was a found a practical way to minimize the surface contaminations during handling of the samples. Mica, HOPG, a Si(111) single crystal covered with a native oxide layer, an Au film evaporated on...
a Si wafer, and TiO$_2$(011) single crystals were tested as substrates. Dry deposition was only successful on the (oxide-covered) Si(1 1 1) and TiO$_2$(011) single crystals. We speculate that SnO$_2$ nanobelts cling to the substrate electrostatically, as metallic materials did not show any appreciable adhesion. Initial tries on HOPG showed adhesion of the NB’s, but further inspection showed that these were only located at rough (improperly cleaved) parts of the crystal, and that the nanobelts were moved by the tip the STM measurements.

The as-grown NBs, deposited on a Si wafer, were characterized with SEM (Hitachi S4800), see Fig. 1. They have a rectangular cross section and are uniform in width and thickness. The typical widths/thickness of the NBs (determined from the STM line profile analysis) are in the range of 100–700 nm/80–300 nm, although there was some variation between batches. The NBs were tens to hundreds of microns long.

X-ray photoelectron Spectra (XPS) (not shown here) were acquired at normal emission using Mg Kx radiation and showed carbon contamination. On macroscopic single crystals [21,22], such carbon deposits are usually removed by Ar$^+$ sputtering; a subsequent anneal to 750 °C is necessary to render large and flat terraces in STM. Attempts to use the same cleaning recipe for the NB’s resulted in structural damage of the NBs. The thermal stability of the NBs in different environments was studied with SEM (Fig. 1). NBs deposited on the Si substrate were heated to different temperatures (in increments of 20–30 °C) in air (Lindbergh/Blue box furnace), UHV, and an O$_2$ atmosphere (~100 mbar in the load lock of the UHV chamber). Decomposition of the NBs material in UHV and in air was observed at 830 °C and 1100 °C, respectively. The NBs heated in O$_2$ to 800 °C (temperature limit of the experimental setup in the load lock of the UHV chamber) were not observed to decompose. The SEM images in Figs. 1a and b show the features characteristic of the onset of thermal decomposition.

In order to avoid damaging the samples, and altering their surface morphology from the as-grown state, sample cleaning for the STM experiments was performed by exposing the dry-deposited NBs to oxygen plasma for 20 min at 1 × 10$^{-5}$ mbar (OSMiPlas, Oxford Scientific Inc.) in the UHV chamber. This resulted in a significant reduction of the carbon deposits below the detection limit of XPS. Stable tunneling in STM was only possible after the plasma-treated the NBs were briefly heated to 350 °C in UHV.

STM measurements (Omicron UHV STM/AFM) were performed in the constant-current mode at room temperature with the sample at positive bias voltages in the range of ~0.5–5 V. One challenge in obtaining atomically-resolved images of the relatively high, large nanostructures was to determine the correct loop gain and Z-input gain, i.e. the signal amplification value of the z-piezo of the STM. It is crucial to set up these parameters properly in order to accommodate rapid changes in the vertical position of the STM tip.

Parts of three NBs, dry-deposited on a slightly-reduced TiO$_2$(011) substrate, are shown in Fig. 2a. No apparent registry was found between the orientation of the NBs and the atomic-scale structure of the TiO$_2$(011) [27]. An STM image obtained on the surface of an individual NB is shown in Fig. 2b. Previous HRTEM results [5] showed that SnO$_2$ NB exhibit a rectangular cross section terminated by (101)/(100) facets on the wide/narrow sides. The image in Fig. 2b were taken on the wide side of a NB, and the morphology is similar to one obtained on a macroscopic SnO$_2$(101) single crystal [21]. Large, flat terraces are bordered by straight step edges oriented along the (101) direction and short, jagged steps that are mainly aligned along [010] (Fig. 2b). The terrace size appears slightly larger than that for the reduced surface of a macroscopic SnO$_2$(101) single crystal. Bright features observed on the terraces can possibly be attributed to contaminants that still remain on the surface after the plasma cleaning.

An atomically-resolved STM image (Fig. 2c) of a NB (large facet) reveals the $1 \times 1$ structure of SnO$_2$(101). The SnO$_2$(101) surface (and the SnO$_2$(100) surface, present on the narrower sides of the NB’s) can be prepared reproducibly in either fully-oxidized or reduced form [12,13]. In both cases, the surface maintains the $(1 \times 1)$ unit cell, as indicated in the STM image (Fig. 2c). Fully-oxidized surfaces exhibit essentially a bulk-termination (with some relaxations [3]), and contain two-fold coordinated O atoms and 5-fold coordinated Sn atoms. Upon heating to 300 °C in UHV, all two-fold coordinated oxygen atoms desorb from the surface, leaving behind 3-fold Sn atoms with a (formal) oxidation state that is reduced from 4+ (as in the bulk) to 2+. Thus, on can assume that annealing of the NBs to 350 °C followed after plasma treatment will also result in the reduced surface formation. Such a reduced surface has a stoichiometry of SnO, and is characterized by a pronounced, 5$\sqrt{2}$ – derived surface state located at the upper edge of the valence band [13]. The reversible surface oxidation/reduction is accompanied by large changes in work functions (on the order of ~1 eV), which influences the adsorption of water [25] and benzene [18]. A top-view ball model of the reduced SnO$_2$(101) surface (unit cell 3.2 Å × 4.7 Å), is shown in Fig. 2c. Under empty-states tunneling conditions, cations are often imaged on metal oxide surfaces, because these have a higher density of empty states than the surface oxygen atoms [28]. Sn surface atoms are imaged on top of the NB, which is consistent with STM studies of the reduced SnO$_2$(101) surface reported earlier [13,21]. Morphologically, the top surface of the SnO$_2$ nanobelts closely resembles the reduced SnO$_2$(101) surface of a macroscopic single crystals [21].

To the best of our knowledge, this is the first report of atomically resolved STM images on metal oxide nanobelts. Obtaining
such measurements paves the way for STM studies of more complex processes on the surface of SnO2 NBs, such as details of metal nucleation and growth [9], molecular adsorption [29], and following changes in surface morphology and electronic structure with repeated adsorption/desorption cycles. The similarity between the surface morphology of SnO2 nanobelts and macroscopic single crystals encourages to apply knowledge of the surface properties of SnO2 single crystals to NB material.

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References