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Non-Classical Crystal Morphology and Secondary Phase Directed Growth of Tetragonal SnO Microcrystals

Koushik J[1], Rajeev Kumar Rai[1], and N. Ravishankar[1*].

[1]Materials Research Centre, Indian Institute of Science, Bangalore, KA, India.
* Corresponding author: nravi@iisc.ac.in

Sn(II) oxide (SnO) is a metastable two-dimensional layered oxide, composed of SnO pyramidal units with an inter-layer spacing 4.84 Å. In literature, another metastable phase was also found during oxidation of epitaxial SnO films having an orthorhombic structure [1], equivalent to the high-pressure phase of SnO_2, stabilized at ambient conditions through strain [2]. On the other hand, Moreno *et al*. have shown that SnO is an intrinsically cation deficient non-stoichiometric phase, accommodated by static displacement waves which give rise to a tweed contrast in electron micrographs. This strain coupling caused by metal vacancies is predicted to stabilize the highly disordered nonstoichiometric phase, but open questions regarding charge localization and oxidation states remain [3]. Here, a wet-chemical approach to synthesize SnO single crystalline sheets with an average thickness of ~50 nm having lateral dimension in the micron scale is reported. The microstructural features of the sheets are studied using various electron microscopy techniques. The observed features agree with that in literature and paves path for further studies.

X-ray diffraction and SEM shows the sheets to be textured along the [001] direction agreeing with the reported surface energies for the layered crystal. VLM of the sheets shows a 4-fold symmetric fringe pattern as seen in figure 1(a) and AFM of the sheets reveals an inverse-pyramid morphology. Co-relating the VLM and AFM data allows us to conclude that the fringes seen is due to interference inside the crystal and the synthesis is morphologically uniform. Further, SEM and TEM imaging reveals that the growth occurs via dendrites. Electron diffraction from the sheets along the [001] zone axis shows a 4-fold symmetric pattern and reveals a secondary phase, namely o-SnO_2 in the SnO matrix as shown in figure 1(c). Due to symmetry restriction, two mutually perpendicular variants are observed. The orientation relationship between the two phases is given below and agrees with the thin film literature [1].

[001] SnO || [100] o-SnO_2
(110) SnO || (001) o-SnO_2-I

Further interesting, interrelated features observed are the streaking along <110> in the diffraction pattern in figure 1(c), the tweed microstructure observed at intermediate magnification and modulation of the {110} planes in high-resolution phase contrast imaging shown in figure 1(d). This is in accord with literature where a severe cation deficiency in SnO causes these modulations [3]. Further, high resolution STEM imaging shows us that the edges of the crystals are found to be {110} as shown in figure 2(a). The {110} surface, in projection, is seen to be covered by the secondary phase. Fourier filtering has been performed to filter out the noise and analyse the frequencies present in the image by deconvoluting them spatially. By allowing only the spatial frequencies corresponding to the SnO matrix and one variant of o-SnO_2 to form the image as shown in figure 2(b), we observe that the interface between the two phases is rather diffused. Also, the dendritic growth is incidentally along <110>, i.e., along the strained {110} planes. This might imply that the secondary phase might play a role in the crystal growth if the intrinsic non-stoichiometry is indeed accommodated by forming a secondary coherent phase [4].

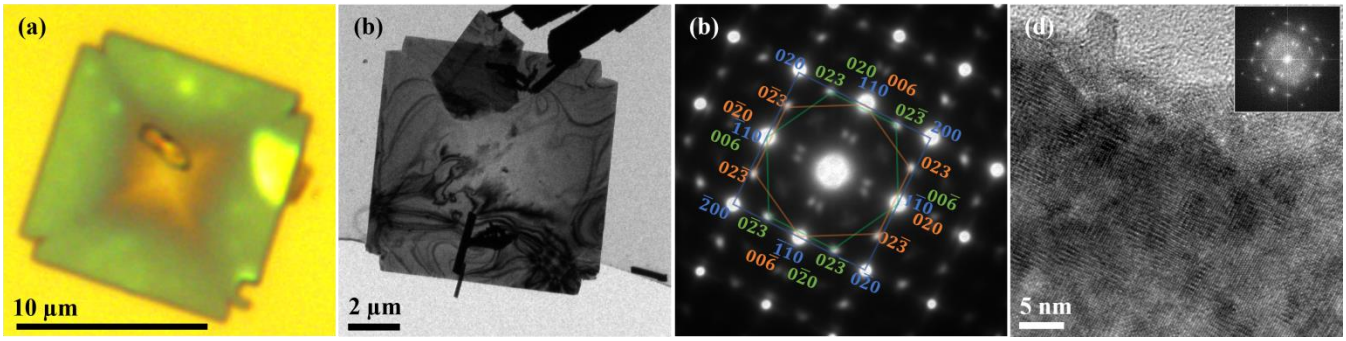

Figure 1. (a) VLM image of the as-synthesized SnO. The 4-fold symmetric dispersion of light is due to the tapered nature of the crystal; (b) Bright-field TEM micrograph of as-synthesized SnO nanosheets displaying bend contours; (c) SAED pattern from the sheets corresponding to t-SnO along [001]. The SnO pattern is denoted by the blue square. Extra spots are indexed to two mutually perpendicular variants of o-SnO_2 (marked in green and orange); (d) HRTEM image of the sheets displaying modulation of the {110} planes.

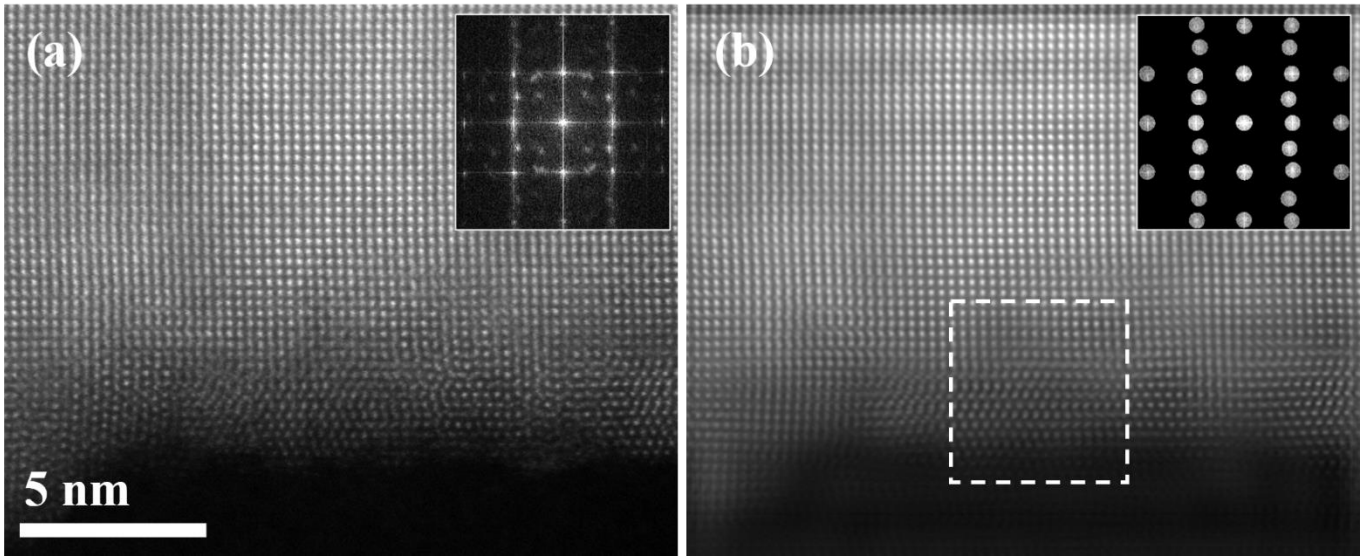

Figure 2. (a) As-acquired High-resolution AC-STEM micrographs of the (110) surface of the sheets as seen along the [001] zone. (b) The Fourier filtered image for frequencies corresponding to t-SnO and one variant o-SnO_2-I. The dashed box marks the interface between the two phases. The FFT of the respective images are shown in insets.

References:

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