doi:10.1017/S1431927622009369
Microsc. Microanal. 28 (Suppl 1), 2022

Topotactic Phase Transformation of Single Crystalline Tetragonal SnO to Orthorhombic SnO_2

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

[1]Materials Research Centre, Indian Institute of Science, Bangalore, Karnataka, India - 560012.
* Corresponding author: nravi@iisc.ac.in

Tin oxide has two well-known phases, namely metastable layered-SnO in the Sn^{2+} state and the stable rutile-SnO_2 in the Sn^{4+} state, both having a tetragonal crystal structure. Being metastable, SnO disproportionates into SnO_2 and β-Sn at temperatures around 475°C. The existing literature on this transformation deals mainly with thin films. In literature, during oxidation of Sn thin films on NaCl, a metastable phase of tin oxide was discovered, namely orthorhombic SnO_2 [1]. This has been rationalized as possible due to the close inter-relation between the columbite-brookite-cassiterite phases [2]. Another report shows that epitaxial SnO on sapphire is oxidized to t-SnO_2, with the transformation giving rise to crystallographic shear planes and twins [3]. Yet another orthorhombic polymorph of o-SnO_2 was found in an oxidized film having hierarchical branched structure [4]. Further, depending on synthesis method, atmosphere and sample history, intermediate oxides like Sn_3O_4 may be formed and are poorly understood. The exact nature of the transformation needs further careful study to control the transformation for practical applications. Also, since plan view transmission electron microscopy is not possible on films, a different procedure is required to study such phenomena. Here, we have used free-standing sheets grown chemically to study such a transformation using TEM techniques.

SnO sheets having an average thickness of ~50 nm and lateral dimension of a few micrometers are prepared by using a wet-chemical route. The sheets are oxidized and drop cast on a lacey C coated Cu grid for TEM analysis. From an initial analysis, the XRD pattern from the oxidized sample can be indexed to t-SnO_2 as well as o-SnO_2. However, the SAED pattern can be indexed only to the [100] zone of o-SnO_2 with two mutually perpendicular rotational variants as shown in figure 1 (b). The planes bounding the edges of the sheets in the original t-SnO was known to be of the {110} type, and the o-SnO_2 phase was known to be an impurity in the crystal with a definite orientation relationship (OR). Using these information, we show that the orthorhombic phase is growing while maintaining the original OR, as well as the macroscopic shape of the crystal i.e., the transformation is topotactic.

High resolution imaging reveals the two variants, and lots of stacking defects in the structure as shown in figure 1 (c) and figure 2 (a). A pseudo-12-fold symmetry is observed at the intersection of the two variants as seen in figure 2 (b). This can be interpreted as due to the projection of the two rotational variants of the o-SnO_2 overlapping along [100], as substantiated by the movement of the boundary in defocus variation experiments. Thus, we can conclude that the boundary between the two variants must not be perpendicular to the imaging direction, i.e., o-SnO_2 [100].

In conclusion, the oxidation behavior of metastable SnO sheets is studied using TEM and STEM. While X-ray diffraction poses a dilemma over the phase present, electron diffraction undisputedly reveals that the SnO transforms into another metastable phase, namely o-SnO_2. The transformation is topotactic and allows crystallographic investigations into the decomposition of SnO. Further diffraction and microscopy studies on such single crystalline sheets is expected to provide subtler insights into the phase

transformation, which might be difficult to study in other form. Also, this method can be used to obtain morphology controlled metastable orthorhombic SnO_2 sheets, to measure its intrinsic properties.

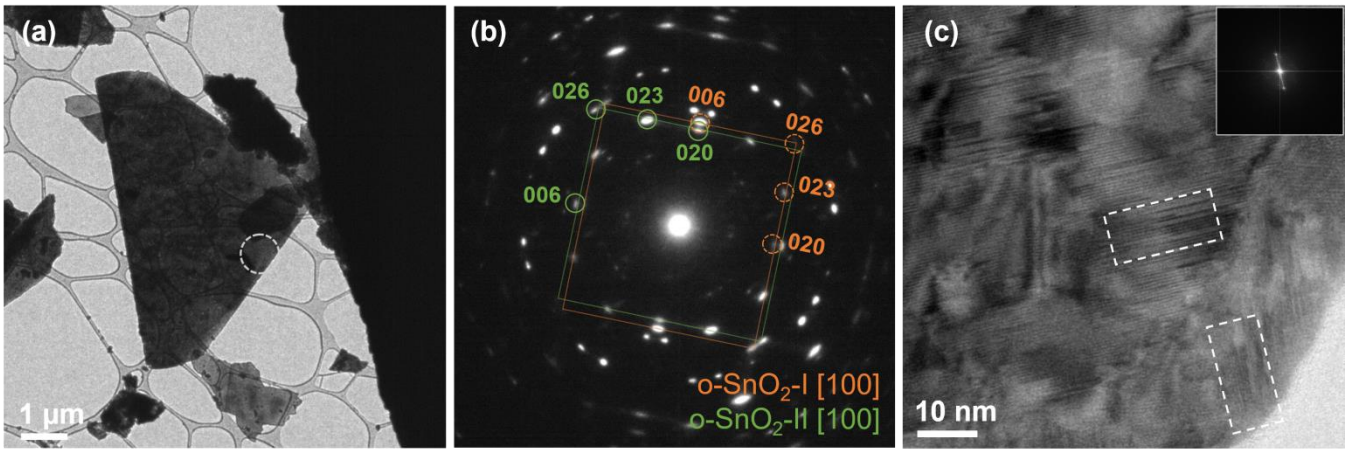

Figure 1. (a) Bright field micrograph of the sheet showing the transformation is topotactic. (b) SAED pattern obtained from the region marked in (a), displaying a spot pattern which can be indexed to two mutually perpendicular variants of o-SnO_2 along [100]. (c) High resolution phase contrast micrograph from the edge of the crystal displaying defects in the stacking. The two variants are marked.

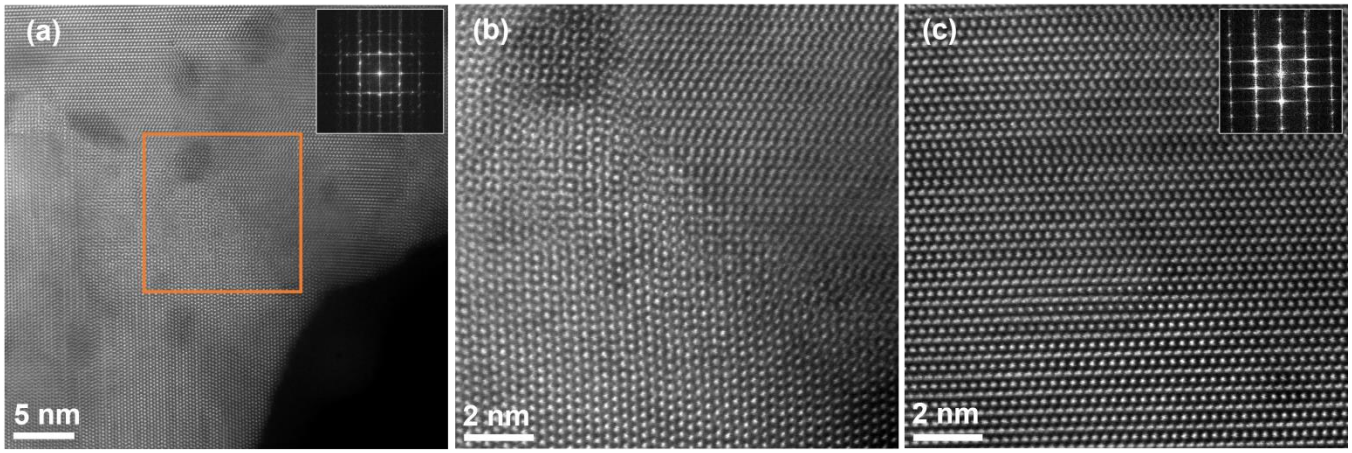

Figure 2. (a) High-resolution HAADF-STEM micrograph of the same region as in figure 1 (c) where the same two variants are seen at atomic resolution. (b) A pseudo-12-fold symmetric pattern is observed at the junction between the two variants. (c) Atomically resolved STEM micrograph of one of the variant, the FFT pattern in the inset can only be indexed to [100] o-SnO_2, confirming the phase.

References:

[1] V. Krasevec et al., physica status solidi (a) **87** (1985), p. 127 – 133. doi: 10.1002/pssa.2210870110
[2] A. Prodan et al., Thin Solid Films, 147 (1987), p. 313 – 319. doi: 10.1016/0040-6090(87)90027-7
[3] X. Q. Pan and L. Fu, Journal of Applied Physics, 89 (2001), p. 6048 – 6055. doi: 10.1063/1.1368865
[4] Jeong Ho Shin, Hyun Min Park, Jae Yong Song, Journal of Alloys and Compounds, 551 (2013), p. 451 – 455. doi: 10.1016/j.jallcom.2012.11.039

https://doi.org/10.1017/S1431927622009369 Published online by Cambridge University Press