Low Dimensional Materials and Catalysts

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Investigations of Sn-doped ZnO nanowires with multiple inversion domain boundaries

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One-dimensional nanostructures such as nanowires (NWs) have been synthesized from a wide variety of chemical elements and compounds. Zinc oxide is a direct n-type semiconductor with a band gap of 3.44 eV and an exciton binding energy of 60 meV, making it an interesting material for many applications. Due to its low price and excellent availability, it is envisaged as a promising alternative to materials like GaN and ITO (indium tin oxide).[1] Additions of other main group or transition metal oxides can alter its optical, electrical or magnetic properties. ZnO NWs doped with Sn are a useful material for photoanodes in dye-sensitized solar cells.[2]

Compounds of the general sum formula $ABO_3(ZnO)_m$ (A = In, Fe, $Sn^{IV}_{1/2}Zn_{1/2}$, $Sb^{V}_{1/3}Zn_{2/3}$...; B = In, Fe, Ga...; *m* = integer) exhibit layered structures composed of wurtzite-type ZnO slabs separated by single layers of edge-sharing AO_6 octahedra. These layers act as inversion domain boundaries (IDBs) for the adjacent ZnO domains. Inside each domain, a second inversion occurs at IDBs consisting of pyramidal or tetrahedral sites occupied by B cations.[3] In the case of Sn-doped ZnO, half of both octahedral and pyramidal or tetrahedral sites are expected to contain Sn. The latter has not been reported yet for bulk materials in the system $ZnO\text{-}SnO_2$.

In our work, Sn-doped ZnO NWs were synthesized by thermal evaporation and deposition following a unique growth mechanism involving Au nanoparticles as seeds.[4] A mixture of ZnO, Sn and graphite powders acts as the source for Zn and SnO vapours. These are transported to a substrate (fused silica coated with Au nanoparticles) using purified Ar enriched with O_2 as carrier gas. The NWs measure tens of µm in length and ca. 100 nm in diameter on average. According to EDXS measurements, the relative Sn content of the NWs reaches up to 2.1 at.-% of the cations.

TEM investigations reveal that the NWs indeed exhibit layered structures featuring both basal and pyramidal IDBs perpendicular to the growth direction of the NW (Figure 1). The mean distance between basal IDBs in the shown portion is 22.78 nm. This directly correlates with the relative Sn content and corresponds well with the EDXS measurements. In electron diffraction patterns of zone axes and , the nonperiodic structure gives rise to rows of diffuse reflections in the direction. TEM bright-field images were recorded using an FEI CM300 FEG-UT microscope.

Spatially resolved compositional analysis was performed in an advanced analytical TEM/STEM system (JEOL JEM-ARM 200CF equipped with cold FEG, probe Cs-corrector, X-ray and electron spectrometer (GATAN GIF Quantum ER) attachments). Spectroscopic imaging by X-ray (SIX) reveals that Sn selectively occupies both basal and pyramidal IDBs (Figure 2). The arrangement of the cations inside the IDBs and the adjacent ZnO domains in ZnO NWs as observed in high-resolution HAADF-STEM images is identical to that of well-known compounds such as $InGaO_3(ZnO)_m$ (Figure 3). Thus, we assume that Sn statistically occupies half of the octahedral as well as the pyramidal sites, the other half being occupied by Zn. Occupation of pyramidal or tetrahedral sites by Sn ions is unknown so far in bulk oxides, however, appears possible in nanostructures due to shorter diffusion paths.

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3. N. Kimizuka *et al.*, J. Solid State Chem. 116 (1995), p. 170.
4. H. Simon, T. Krekeler, G. Schaan, W. Mader, Cryst. Growth Des. 13 (2013), p. 572.
5. We thank E. Arzt for continuous support through INM.

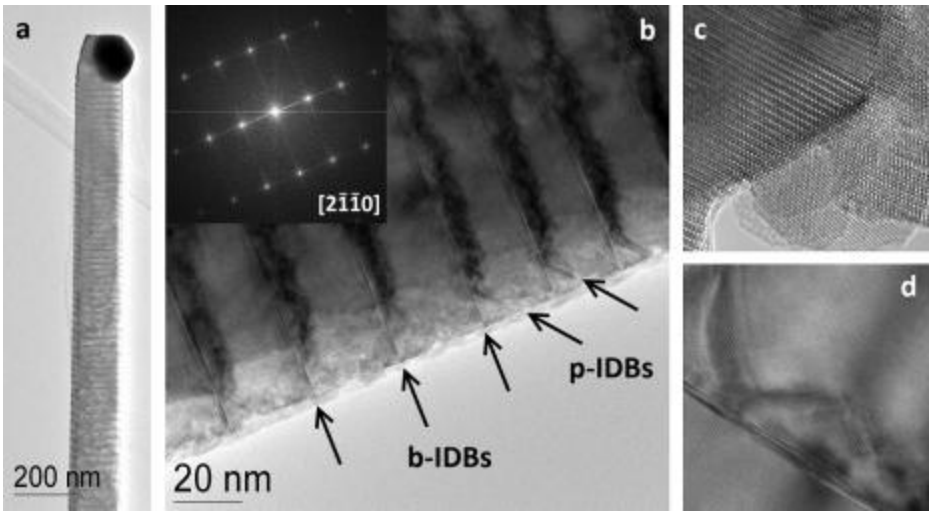

Figure 1. TEM bright-field images of a ZnO NW (a, b) featuring basal (c) and pyramidal (d) IDBs.

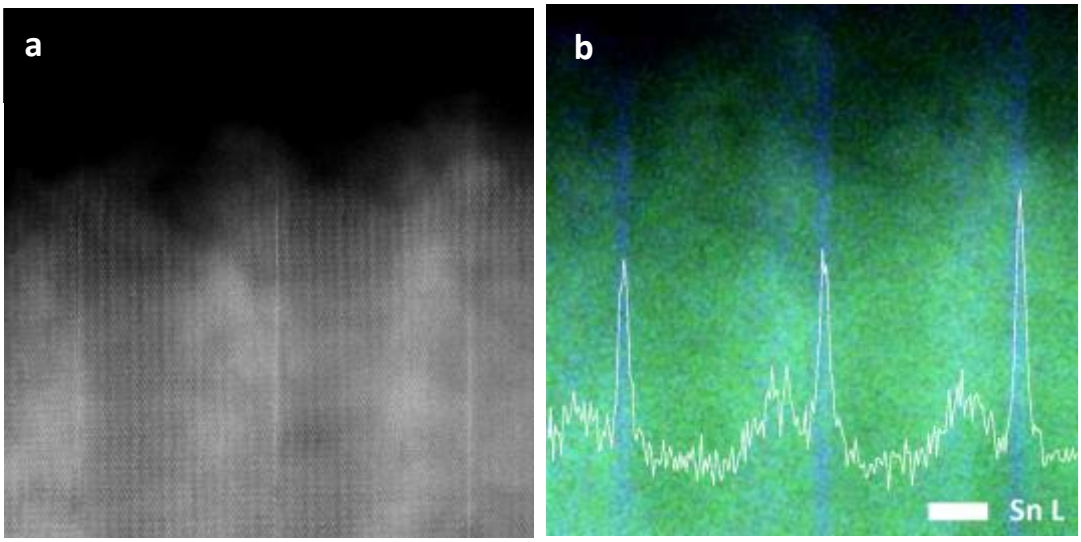

Figure 2. HAADF imaging (a) and element mapping (Sn/Zn overlay) by EDS-SIX spectroscopic imaging (b) shows that Sn selectively occupies both basal and pyramidal IDBs.

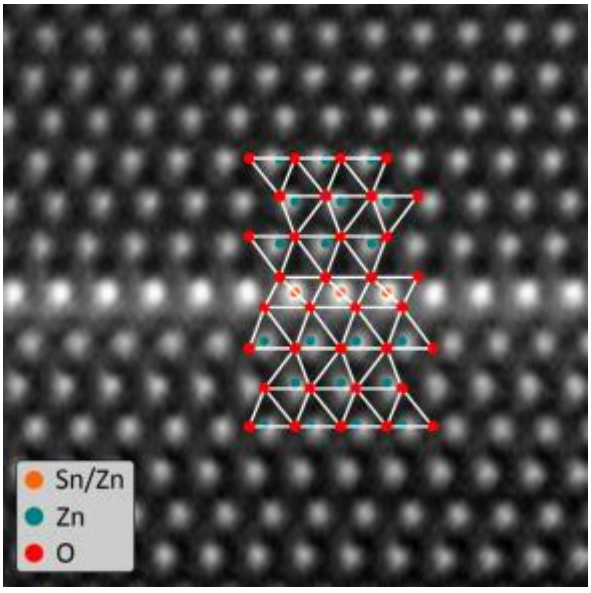

Figure 3. High-resolution HAADF-STEM image of the b-IDB in Sn-ZnO reveals that the stacking sequence of cations is identical to that in compounds with the sum formula $A^{III}B^{III}O_3(ZnO)_m$.