## Characterization of SnO<sub>2</sub> Nanorods grown under oxidizing conditions

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Tin dioxide  $(SnO_2)$  is an n-type semiconductor with a wide bandgap of 3.6 eV. Its distinctive reactivity towards reducing gases is beneficial for gas detection of CO, H<sub>2</sub>, CH<sub>4</sub> etc. [1]. A high surface to volume ratio is crucial for fast response and low detection limit of the sensor material, therefore proper control of the sensor material morphology is important. In this work we describe the structural characterisation of quasi one-dimensional  $SnO_2$  nanorods produced via an autocatalytic vapor-liquid-solid (VLS) [2] mechanism with gold particles as a seed. Furthermore, the influence of oxygen and water vapor on the morphology is examined and determined.

The nanorods are grown via a chemical vapor deposition on fused silica covered with gold particles as catalyst. The particles are produced by magnetron sputtering and are 50 to 100 nm in size. By heating a source composed of either tin oxide (SnO) or tin and tin dioxide (Sn + SnO<sub>2</sub>) in a two-zone furnace with argon as a carrier gas the required SnO vapor is formed. The substrate with the catalyst particles is heated to 600 °C. The vapor condenses on these particles, liquefies and forms the mono-crystalline SnO<sub>2</sub> nanorods.

The disproportionation of SnO to Sn and SnO<sub>2</sub> at the catalytic particle results in large tin droplets on top of the nanorods and increasing diameter of the SnO<sub>2</sub> nanorod (Fig. 1). The surplus of tin remains in the catalytic particle. Measurements of shape and size and calculations confirm this mechanism of SnO<sub>2</sub> nanostructure growth. The morphology of the structures resembles "tadpoles" [3]. The growth direction of the nanorod is along the [100] axis (Fig. 3 and 4). This axis corresponds to the corner-connected SnO<sub>6</sub> chains in the rutile structure of SnO<sub>2</sub>. During the growth process a significant increase of the thickness along [010] of the nanorod and formation of a twin boundary is observed (Fig. 2). The observed growth direction is unusual, since the prevalent growth direction for SnO<sub>2</sub> is either <101> [4] or [001] [5] depending on the synthesis method.

Careful addition of oxygen or water to the carrier gas alters the morphology into thin nanorods with small Au-Sn alloy particles on top. Here the excess tin is oxidized to  $SnO_2$ . Hence, presence of oxygen or water hinders the increase of thickness and twinning of the rods (Fig. 5 and 6).

The growth morphology of the nanorods is determined by SEM and TEM imaging. Growth direction and chemical composition was determined by electron diffraction and EDS, respectively.

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Figure 1. SEM image of "tadpole"  $SnO_2$  nanorods synthesized in pure argon atmosphere.



**Figure 2.** SEM image of twinned "tadpole" SnO<sub>2</sub> nanorod.



**Figure 3.** TEM bright field image of "tadpole"  $SnO_2$  nanorod with growth direction in [100].



Figure 4. corresponding diffraction pattern in the [001] axis of tetragonal  $SnO_2$ .



**Figure 5.** SEM image of  $SnO_2$  nanorods grown with water vapor in argon.

**Figure 6.** TEM bright field image of  $SnO_2$  nanorod grown with water vapor in argon.