Surface Nanotechnology. Experiments and Theory in Harmony: SnO_2: A Landscape to be explored

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Modeling of nanocrystals supported by advanced morphological and chemical characterization is a unique tool for the development of reliable nanostructured devices, which depends on the ability to synthesize and characterize materials on the atomic scale. Among the most significant challenges in nanostructural characterization is the evaluation of crystal growth mechanisms and their dependence on the shape of nanoparticles and the distribution of doping elements. This comunication presents a new strategy to characterize nanocrystals, applied here to antimony-doped tin oxide (Sb-SnO_2) (ATO) by the combined use of experimental and simulated high-resolution transmission electron microscopy (HRTEM) images and surface energy ab initio calculations. The results show that the Wulff construction can not only describe the shape of nanocrystals as a function of surface energy distribution but also retrieve quantitative information on dopant distribution by the dimensional analysis of nanoparticle shapes. In addition, a novel three dimensional evaluation of an oriented attachment growth mechanism is provided in the proposed methodology. This procedure is a useful approach for faceted nanocrystal shape modeling and indirect quantitative evaluation of dopant spatial distribution, which are difficult to evaluate by other techniques.

In recent years, advanced tools have been developed for nanocrystal characterization in order to obtain accurate chemical, structural, and morphological information, such as crystal-lographic habit, surface chemistry, and growth mechanisms from self-assembled arrangements. Although a number of techniques based on X-ray, scanning probe microscopy, and transmission electron microscopy (TEM) have been successfully applied to retrieve compositional and morphological information about nanostructures, several challenges still remain, especially with regard to three-dimensional reconstruction and chemical mapping.
In this work we present a novel approach based on high resolution transmission electron microscopy (HRTEM) characterization and surface energy ab initio calculation (atomistic simulation). By combining information from HRTEM images of faceted nanocrystals, Wulff construction, and surface energies obtained by atomistic simulation for selected facets, the 3D morphological and compositional features of ATO nanocrystals and their growth mechanisms were elucidated.

Wulff construction was applied to build theoretical crystals by using the ab initio calculated surface energies and the SnO_2 $P4_2/mnm$ crystal structure. HRTEM multislice simulated images of theoretical ATO nanocrystals were obtained by use of JEMS software. Surface energy calculations for ATO nanocrystals were performed with the CRYSTAL06 program package. Oxygen atoms were described by the standard 6-31G* basis sets and the tin and antimony centers in the PS-21G* scheme, where PS stands for Durand-Barthelat's nonrelativistic large effective core potential. Becke's three-parameter hybrid nonlocal exchange functional combined with the Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) was used. Full optimization of the

cell parameters (*a* and *c*) and internal coordinate (*u*) for the bulk SnO_2 was carried out. The low index (110), (101), (100), and (001) surfaces were modeled by unreconstructed (truncated bulk) slab models by use of the calculated equilibrium geometry. Because these surfaces have a different number of atoms in each layer, the low-index surfaces were modeled with different thicknesses in the *z*-direction but were periodic in *x*and *y*-directions. After the corresponding convergence test on the
undoped systems, slab models containing nine SnO_2 layers for the (110), (100), and (101) surfaces and 11 layers for the (001) surface were selected. For the models used here, the top and bottom planes are equivalent in symmetry so the substitution of Sn for Sb atoms was done on both sides of each slab model. Supercells were used to model the lower percentages of doping (~7%). A complete relaxation of all the atoms in each model was performed.

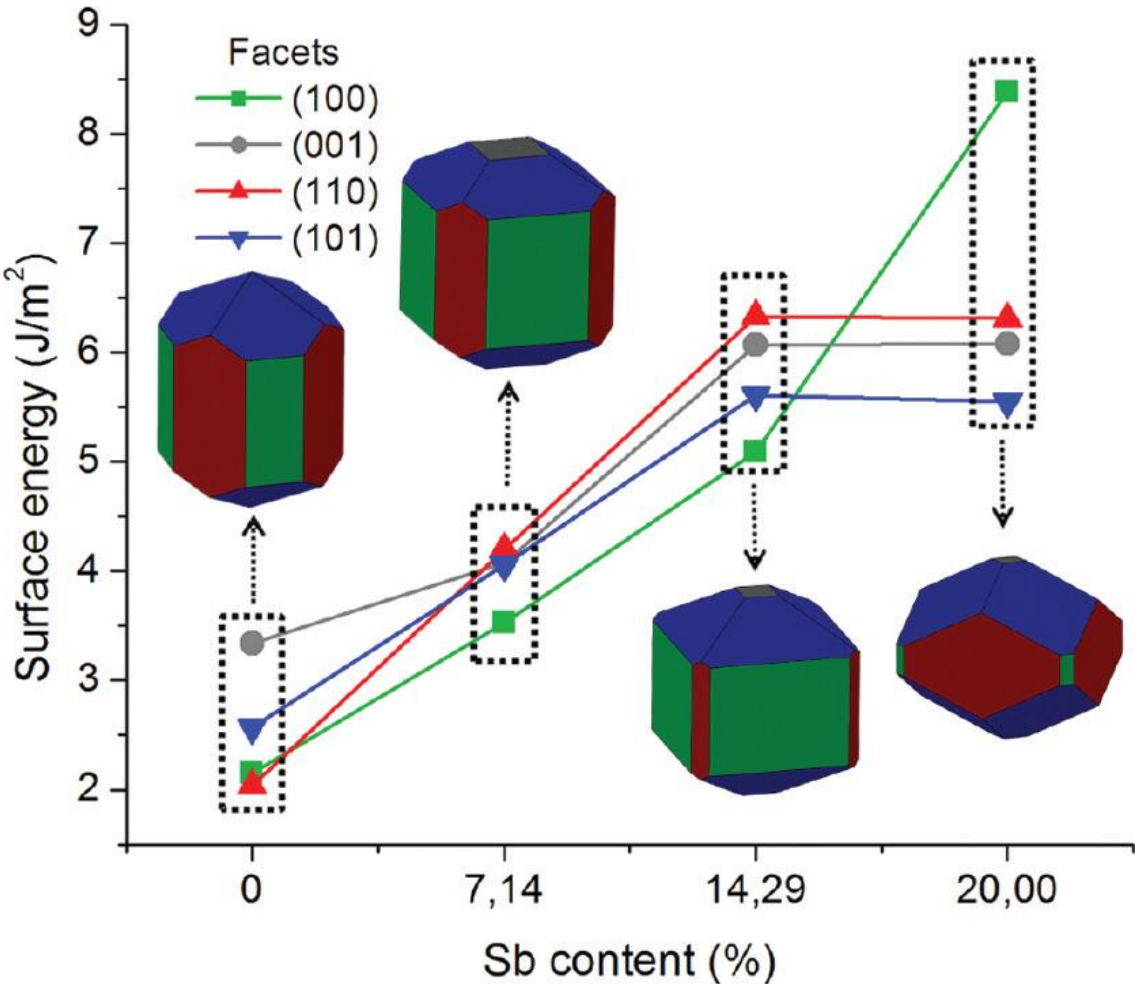

Fig. 1.- Surface energies for different Sb contents and Wulff constructed nanocrystals for each dopant content considering a homogeneous Sb distribution. The figure shows the ab initio calculated surface energies for the selected crystalline planes with different Sb contents. The facets on the constructed Wulff crystals are indicated by a color code.

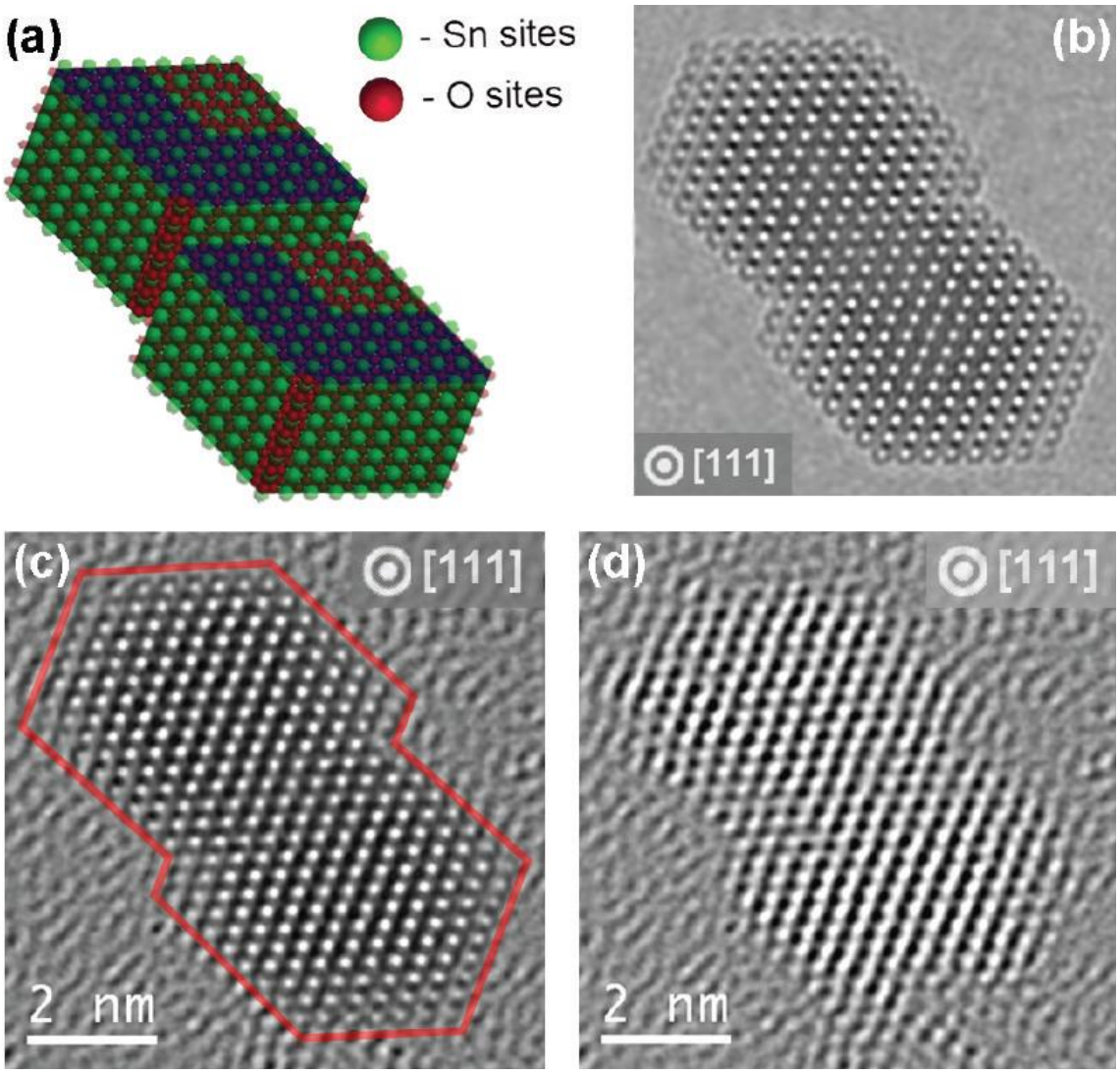

Fig 2.- Proposed ATO nanocrystal ensemble and its simulated HRTEM image. (a) Atomic arrangement of the ATO (Sb-SnO_2) nanocrystal ensemble superimposed on its Wulff construction. (b) Multislice simulated HRTEM image obtained from the proposed nanocrystal ensemble. (c, d) Comparison of the simulated nanocrystal image (c) and the experimental image (d).

Based on indirect quantitative measurements, this methodology is a novel approach for the evaluation of surface dopant distribution on nanoparticles. It is a powerful tool for the analysis of nanocrystals, where usual quantitative techniques such as X-ray photoelectron spectroscopy (XPS), X-ray energy dispersive spectroscopy (XEDS), high-angle annular dark field (HAADF), and electron energy loss spectroscopy (EELS) would require a much greater effort and/or would be restricted by system dimensions and/or small atomic weight differences between the material elements. In addition, the combined use of surface energy ab initio calculations and Wulff construction applied to nanocrystal modeling was applied successfully to study the oriented attachment growth mechanism in ATO nanocrystals and can be used to carry out such studies in a number of nanostructured systems. Modeling hypothetical nanocrystals as building blocks with known surface energy distribution and faceting enables one to produce a three-dimensional description of the oriented attachment growth mechanism, which can be further investigated by HRTEM imaging and HRTEM multislice image simulation.