Identifying nucleation and growth mechanisms in nano-grained polycrystalline thin films

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Understanding the three-dimensional evolution of grain size and orientation during the growth of polycrystalline thin films with nano-scale grains presents a significant challenge for structural characterization. Here, we tackle this challenge for the analysis of low pressure metalorganic chemical vapour deposition grown ZnO thin films developed for applications as transparent electrodes in photovoltaic and other optoelectronic devices. The films, which grow non-epitaxially from (semi-)randomly oriented nuclei on amorphous glass substrates, undergo self-texturing and grain coarsening as they thicken, as a result of an orientation dependent growth competition. In order to quantify this process, we develop a characterization methodology that combines TEM-based automated crystal orientation mapping (ACOM), using the NanoMEGAS ASTAR system, with a "double wedge" TEM sample geometry [1]. Using this methodology, we obtain unprecedented statistics on the films' nature, measuring the size and orientation of over 10'000 grains across a series of calibrated heights within each thin film sample; data which can be used for precise comparison of growth competition between films deposited under different conditions [2].

Further to these statistics, the spatially-resolved nature of the data allows their mining in order to identify other structural characteristics. For instance, in *a*-texture films, correlation of nearest-neighbor grains uncovers an abundance of coherent twinning between grain pairs. These twins are further coordinated by small grains existing at triple points, which grow with a minor but persistent (10-13) texture component that was too small to detect by XRD (Fig. 1). By combining these results with high-resolution (HR-)TEM analysis of triple points (Fig. 2), and comparing to analysis of *c*-texture films [3], this is explained by polytypism driven re-nucleation occurring during film growth. In this mechanism, which breaks the classical competitive grain growth model, few nm diameter cores of metastable zinc blende phase lead to formation of tetrahedrally-coordinated wurtzite phase grains, some at the minor (10-13) orientation.

Within individual *a*-texture ZnO grains, additional growth phenomena are discovered. In SEM cross-section imaging, the grains show a bimodal intensity distribution in the secondary electron emission, suggestive of some difference in electronic structure. When the ZnO film is B-doped during deposition for better electrical conductivity, correlative NanoSIMS studies show that the B is also bimodally segregated. This is explained through a new growth model, based on structural TEM cross section analysis of individual grains, in which the wedge-shaped grains present opposing growth fronts of differing surface polarity; B adatoms incorporate on only the c- polarity faces, and hence into just one side of each growing wedge [4].

[1] Spiecker, E., et al., Acta Materialia 55 (2007) 3521 - 3530
[2] Aebersold, A.B., et al., Ultramicroscopy 159 (2015) 112 - 123
[3] Aebersold, A.B., et al., Acta Materialia 130 (2017) 240 - 248
[4] Fanni, L., et al., ACS Applied Materials & Interfaces 9 (2017) 7241 - 7248

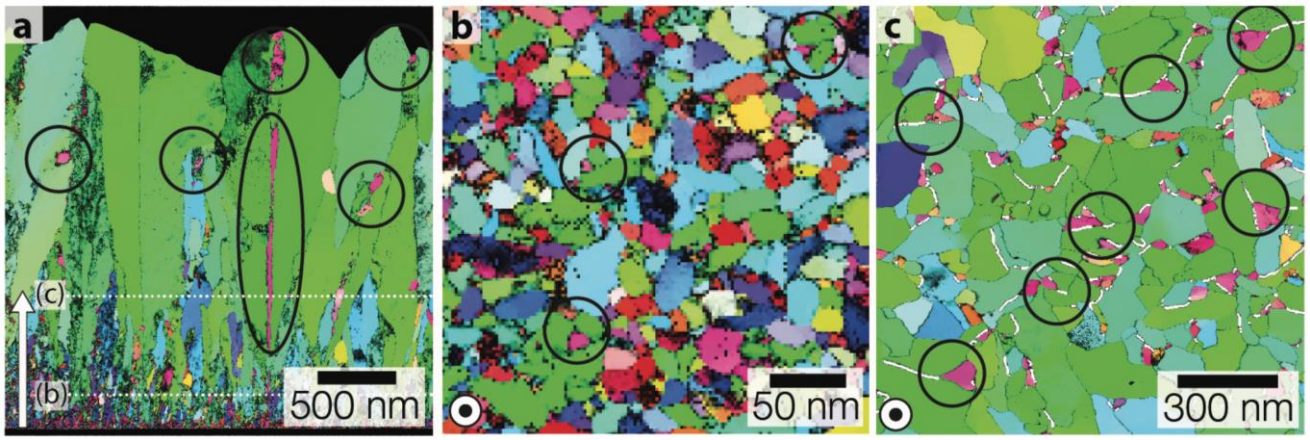

Figure 1. Cross-section (a) and plan-view TEM orientation maps, at film heights of (b) 220 nm and (c) 850 nm, showing rose colored (10-13) grains between twinned *a*-texture grains.

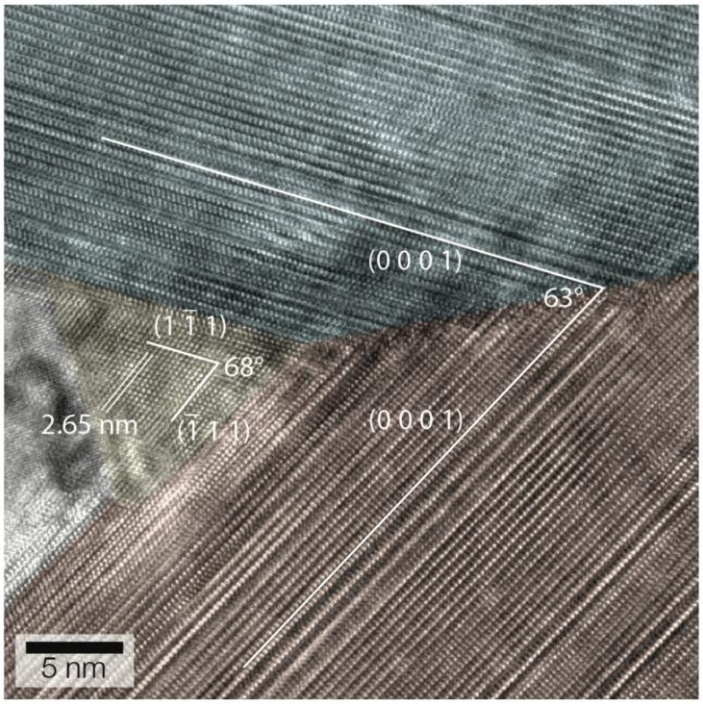

Figure 2. HRTEM image showing zinc blende at the core of a triple junction.