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Quantification of Interfacial Roughness of In_2O_3/ZrO_2 Superlattice Films in 3D

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Conducting oxides are of interest in a variety of current and future energy applications, including solid oxide fuel cells and solar cells. Obtaining better understanding of the structure/property relations of conducting oxide interfaces is key to providing needed control and enhancement of the transport behavior that is critical to these usages. In this study we focused on understanding interfacial proximity effects on the behavior of a model ZrO_2/In_2O_3 heterostructure that has potential to exhibit novel mixed conduction behavior, i.e., may have both enhanced ionic and electronic transport This enhanced conductivity could arise because of the electronic structure of sharp interfaces and/or local intermixing. Knowledge of the chemistry and structure of oxide interfaces on an atomic level is therefore essential for understanding changes in conductivity. A thin film sample of 20 alternating, controlled thickness, layers of ZrO_2 and In_2O_3 was deposited on yttria-stabilized zirconia (YSZ) (001) by rf-magnetron sputtering. To vary the layer thicknesses, deposition times were doubled after each two bilayers of ZrO_2 and In_2O_3 (i.e., the sample contained five distinct interfacial spacings). Following growth, the sample was annealed 20 minutes in 10^{-3} Torr of O_2, and then was cooled to room temperature.

Cross-sectional samples were prepared from this superlattice for TEM imaging. Elemental maps of Zr and In were calculated from energy filtered TEM (EFTEM) images. An interface roughness of up to 5nm was measured from these elemental maps, as well as high-resolution TEM (HRTEM) images. Under these circumstances conventional TEM imaging and analysis is hampered by projecting a 3D structure into two dimensions. Therefore, we used a series of energy-filtered tomographic images to reconstruct 3D elemental maps of this complex interface. A disadvantage of standard thin foil preparation for TEM tomography is the increase of sample thickness projected along the electron beam at higher tilt angles. In this case background subtraction is different for each tilt angle and, therefore, the number of counts of the elemental map depends on the tilt angle. Multiple scattering effects complicate the calculation of elemental maps when the projected sample thickness is greater than the electron mean free path, which is very likely for higher tilt angles. This problem can be solved by preparing cylindrical samples using focused ion beam (FIB) milling. This sample geometry has the advantage that the sample thickness projected along the electron beam is constant with tilt angle and facilitates background subtraction for calculating elemental maps for all tilt angles. A Tecnai F20ST with a Gatan imaging filter and a sample stage from Hummingbird Scientific were used to acquire tomographic image series with a tilt increment of 2º between -80º and +80º.

The Zr $M_{4,5}$ edge (onset at 181eV) was used for elemental mapping. The simultaneous iterative reconstruction technique SIRT algorithm [1] provided the best results with respect to its ability to reduce noise and minimize distortions induced by the missing wedge for EFTEM tomography and was used to reconstruct the 3D distribution of Zr in a ZrO_2/In_2O_3 multilayer. The buried interfaces of ZrO_2 phases were extracted from the reconstructed volume and analyzed via the SPIP software. The 2D (Figure 1a) and the 3D map (Figure 1b) show the interface roughness of several ZrO_2/In_2O_3

interfaces on a nanometer scale. Resolution is limited due to lens aberrations and delocalization of energy-loss electrons to ~2nm.

The 3D shape of the surfaces of the ZrO_2 layers can be extracted from the Zr map in Figure 2b. Figure 1c shows the topography of the bottom surface of the first ZrO_2 layer. The roughness of the interface according to the 3D Zr map is 4 nm. The length scale of the roughness in the interface plane is 10 to 20nm (Figure 1c). The roughness of the interfaces where the In_2O_3 layer is closer to the substrate is significantly higher than that of interfaces with the ZrO_2 closer to the substrate (i.e., the magnitude of the roughness is larger at every second interface). The interface roughness of the different layers and its correlation to growth direction and layer thickness will be discussed.

3D elemental mapping extends the analytical capabilities of TEM to arbitrarily shaped interfaces. This will allow a better understanding of growth mechanisms of thin films and the correlation of interface properties to the conductivity at the interface ZrO_2/In_2O_3 and other thin film systems.

References

[1] L.J. Gauckler and K. Sasaki, *Solid St. Ionics* 75 (1995) 203.

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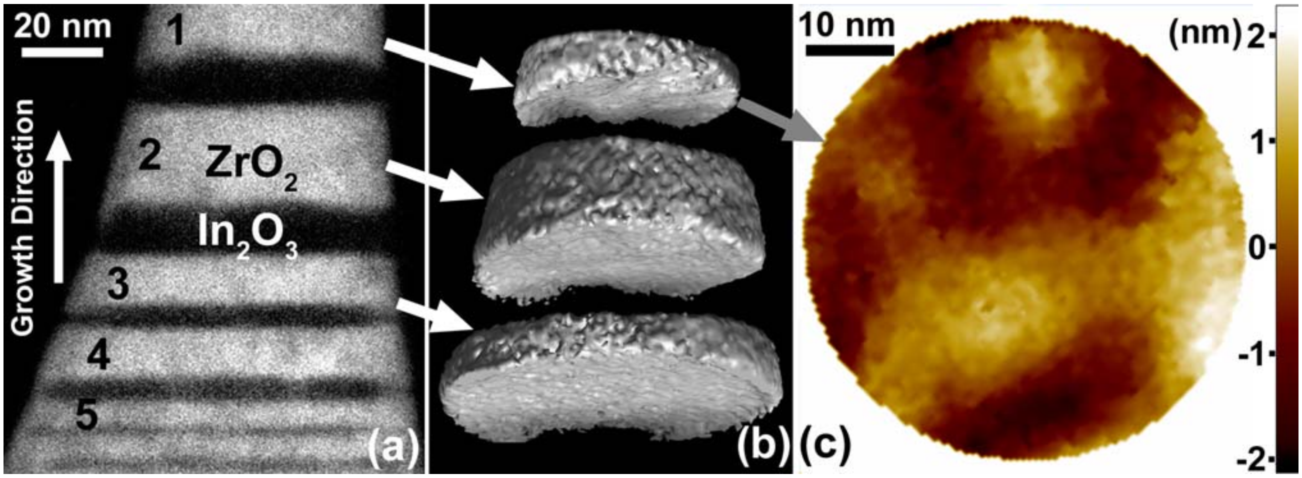

Figure 1: Elemental maps of Zr distribution of the ZrO_2/In_2O_3 multilayer films in 2D (a) and 3D (b), (c) Color-coded roughness of the bottom surface of the first ZrO_2 layer.