Compositional and Structural Analysis of Al-doped ZnO Multilayers by LEAP

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Atomic layer deposition (ALD) is a technique that uses a cyclical exposure and purging of chemical precursors to create thin films. ALD offers a high degree of control over the thickness and composition of the films. The technique is generally used for binary compounds such as oxide and nitrides. ZnO is grown by ALD as a transparent conductive oxide for photovoltaic and optoelectronic applications.

By doping ZnO, for example with aluminum, the conductivity and optical properties can be controlled. For ALD-grown ZnO the doping is tuned by alternating the cycles of the ZnO deposition with the precursor for Al_2O_3. The resistivity and carrier mobility of the resulting material will depend on the distribution of Al in the ZnO matrix. However, the atomic scale of the interfaces, combined with a high degree of disorder, means that direct imaging is not practicable [1].

The current work demonstrates the use of atom probe tomography to analyze the chemistry and microstructure of ALD-deposited materials. A multilayer of Al-doped ZnO was deposited onto an atom probe coupon. The film contains three 40 nm layers of Al:ZnO with $ZnO:Al_2O_3$ deposition ratios of A 85, B 23 and C 12, deposited using $Al(CH_3)_3$, $Zn(C_2H_5)_2$ and H_2O precursors. XPS determined the average Al fractions ($AF_{XPS} = Al_{at.\%} / (Al_{at.\%} + Zn_{at.\%})$) of the layers as A 1.9%, B 6.9% and C 16.4% [1].

The coated coupons were prepared into atom probe specimens using standard focused ion beam annual milling [2] and successfully measured in a CAMECA LEAP 4000 [3, 4]. Laser pulse energies ranging from 300 fJ to 100 pJ were tried in order to find optimal analysis conditions. Figure 1 shows a 2D profile of the Al concentration of the three layers, respectively labelled A, B and C. Quantification was limited by mass-spectral overlaps, in particular between $^{16}O_2^+$ and $^{64}Zn^{++}$. Despite this, measurements of the Al composition ratios between the three doped layers by APT and XPS were in concordance.

The Al dopants inside the layers were found to have a highly inhomogeneous distribution, forming a laminate structure representing the ALD cycle scheme. Figure 2 shows a one-dimensional composition profile through Al doped region B. The supercycle structure with 11 Al rich layers is clearly observed, showing that a low proportion of Al has diffused into the ZnO layers. Figure 3a shows the $AF_{APT} = 0.018$ isosurfaces in volume A again showing confinement of Al to the AlZnO layers. The intervening layers of 14 nm ZnO have $AF_{APT} \sim 0.005$. Figure 3b shows the same volume with $AF_{APT} = 0.03$ isosurfaces, revealing additional structure within the AlZnO layers: linear features with higher Al composition. It is believed that these correspond to positions of ZnO grain boundaries.

References:
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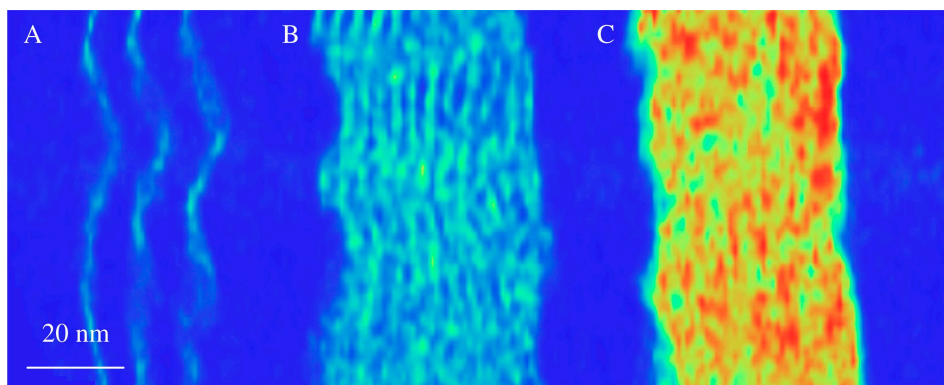[4] T. F. Kelly and D. J. Larson, Annu. Rev. Mater. Res. **42** (2012) p. 1.

Figure 1. 2D concentration plot (80 nm × 200 nm) showing the Al distribution in the Al:ZnO multilayer. Colour ranges from blue $AF_{APT} = 0$ to red $AF_{APT} = 0.16$. The number of $ZnO:Al_2O_3$ supercycles used to grow the three doped volumes are A 3, B 11, and C 19.
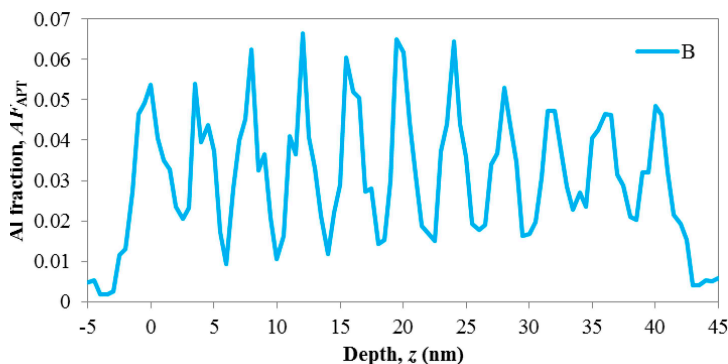

Figure 2. One-dimensional concentration profile from a 10 nm cylinder through the second Al:ZnO volume (labelled B in figure 1). Al diffusion from the AlO_x layers to the ZnO layers is limited, resulting in the laminate structure where the 11 supercycles used during growth are clearly visible.
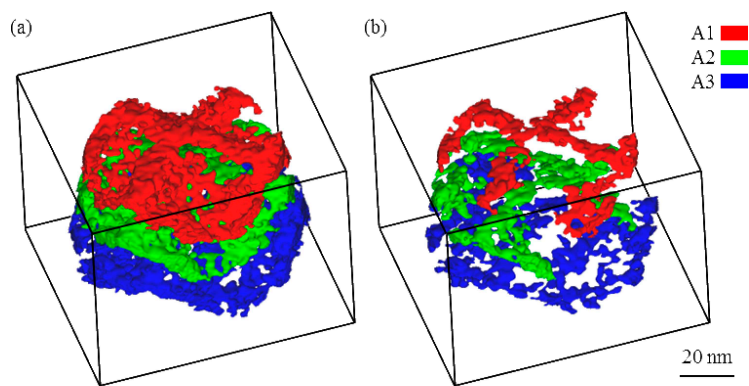

Figure 3. Isosurfaces of the top Al:ZnO volume (labelled A in figure 1). The AlZnO layers in each of the three supercycles are separated by ZnO with a low Al doping. For visual clarity each of the AlZnO layers, A1, A2 and A3, has been assigned a different colour. (a) shows the $AF_{APT} = 0.018$ isosurface and (b) shows the $AF_{APT} = 0.03$ isourface.