Grain Boundary Effects on Charge Transport In ZnO:Al Transparent Conducting Films

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Abstract:

The work function of transparent conducting oxides is critical in determining the efficiency of charge transfer in certain solar cells and light emitting diodes. Previous research has indicated that this quantity is not well-described by the known properties of bulk zinc aluminum oxide (ZnO:Al), and may be strongly affected by grain boundaries. We have used Kelvin force microscopy for high resolution measurements of the work function, which is found to vary significantly on and off the grain boundaries. Our results show that work function granularity increases with oxygen content, due to the oxygen species segregated at the grain boundaries. This suggests that the work function can be tuned with post-processing treatments. Both exposure to UV/ozone and annealing in a hydrogen gas atmosphere are found to affect the material work function and the electronic granularity. It remains to be seen whether these treatments can be used to increase the efficiency of optoelectronic devices.

Introduction:

Transparent conducting oxides (TCOs) are materials commonly used in photovoltaics and other optoelectronic devices. Although indium tin oxide (In_2O_3:Sn) is currently the most widely used material on, zinc aluminum oxide (ZnO:Al) is becoming an attractive alternative due to improvements in processing techniques and lowered cost [1]. ZnO:Al films are also non-toxic and highly stable after heat cycles [2]. Thus, it is increasingly important to understand the electronic properties of this doped metal oxide on a nanostructure scale.

Kelvin force microscopy (KFM) is a powerful technique that uses an atomic force microscope to measure work function with nanometer resolution. We are interested in the work function, because it affects the performance of devices such as solar cells and light-emitting diodes. We have demonstrated through KFM measurements that work function varies significantly on and off grain boundaries of ZnO:Al. We have also shown that post-processing treatments affecting the distribution of oxygen species at the grain boundaries can further modify the work function level and granularity of the material.

Methods:

Film Growth. ZnO:Al thin films were grown on soda lime glass by RF magnetron sputtering from a Zn:Al 1.2 wt.% target (99.99%, ACI Alloys, Inc.). The RF power, substrate heater temperature, Ar gas flow rate, and total process pressure were held constant at 100 W, 100°C, 40 sccm, and 2.5 mTorr, respectively, and all film thicknesses were nearly 350 nm. The maximum temperature attained at the substrate surface during growth is estimated to be 160°C. The three films measured differ only in oxygen content, controlled by O_2 process pressure which varied between 0.32 mTorr (oxygen-deficient), 0.36 mTorr (optimal), and 0.41 mTorr (oxygen-rich).

Kelvin Force Microscopy. In Kelvin force microscopy, a conductive tip scans across the sample surface, and an external bias is applied to null the electrostatic force between the tip and the sample. The magnitude of the bias is equal to the contact potential difference (CPD), which can then be used to calculate the work function of the sample. KFM was performed with MikroMasch DPE and DPER probes, and an Asylum Research MFP-3D atomic force microscope.

Post-Processing Treatments. The three ZnO:Al films of varying oxygen content were exposed to ultraviolet radiation and ozone under 500 Torr O_2 for one hour and two hours. The films were also annealed inside a Lindberg furnace at 400°C under Forming gas (95% He, 5% H_2) flowing at 300 sccm for one hour and two hours.

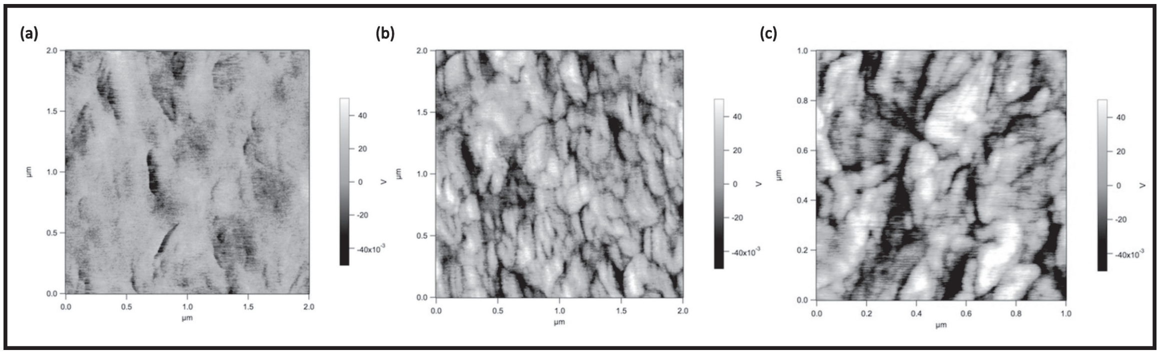

Figure 1: KFM measurements of (a) oxygen-poor, (b) optimal, and (c) oxygen-rich ZnO:Al films. Data has been flattened in order to emphasize electronic granularity.

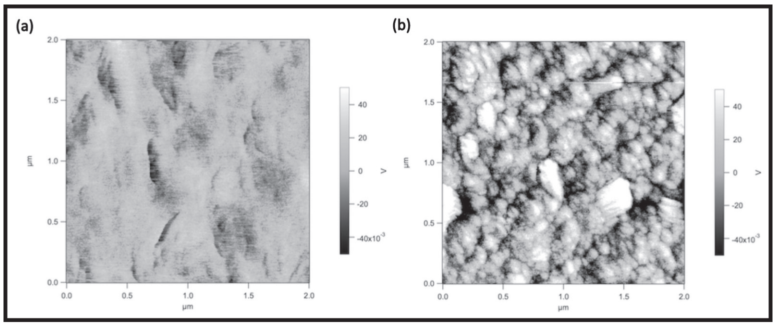

Figure 2: KFM measurements of oxygen-poor ZnO:Al film (a) as-grown, and (b) after exposure to UV/ozone for 2h.

Results and Discussion:

As shown in Figure 1, the work function of ZnO:Al films varied significantly on and off grain boundaries. Both average work function levels and electronic granularity increased with oxygen content. We propose that this is due to the chemisorbed oxygen species at the grain boundaries, which form surface dipoles that increase work function. This implies that the work function can be further tuned with post-processing treatments that affect oxygen content at the grain boundaries. In Figure 2, work function granularity increased after exposure to UV/ozone for 2h.

Conclusion:

Our study has presented a novel use of KFM to measure work function across grain boundaries. With this technique, we have shown an increase in both work function level and electronic granularity due to oxygen content in ZnO:Al films. We have also demonstrated that post-processing treatments can be used to further tune the work function. We hope that these results will impact further investigation of the material properties of ZnO:Al as a transparent conducting oxide for electronic devices.

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References:

[1] E. Fortunato, D. Ginley, H. Hosono, and D. Paine, MRS Bull. 32, 242 (2007).

[2] M.L. Addonizio, A. Antonaia, G. Cantele, and C. Privato, Thin Solid Films 349, 393 (1999).