

## Atomic scale EELS study of the origin of ferromagnetism in Co-doped ZnO epitaxial thin films.

Q.M. Ramasse<sup>1</sup>, A.P. Kuprin<sup>2,3</sup>, M. Chi<sup>4</sup>, T.C. Kaspar<sup>5</sup>, S.A. Chambers<sup>5</sup>, and N.D. Browning<sup>2,6</sup>

<sup>1</sup>Lawrence Berkeley National Laboratory, National Centre for Electron Microscopy, 1 Cyclotron Road, Berkeley CA 94720, U.S.A.

<sup>2</sup>Dept. of Chemical Engineering and Materials Science, University of California-Davis, Davis CA 95616, U.S.A.

<sup>3</sup>Dept. of Chemistry, University of Washington, Seattle WA 98195-1700, U.S.A.

<sup>4</sup>Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, U.S.A.

<sup>5</sup>Pacific Northwest National Laboratory, P.O. box 999, Richland WA 99352, U.S.A.

<sup>6</sup>Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore CA 94550, U.S.A.

The potential for revolutionising electronic devices by controlling the spin degree of freedom has led to an extensive body of research [1]. Practical applications of spintronics, however, rely on the ability to develop materials that remain stable at room temperature and, whilst there have been many reports of ferromagnetism at room temperature in doped semiconducting oxides, the origin of the observed ferromagnetic behaviour is still the subject of ongoing research. Recent reports in the case of Co-doped ZnO (Co:ZnO) epitaxial thin films have shown that a Zn diffusion treatment (annealing in Zn-rich vapour) of the Co:ZnO films dramatically improved the resulting ferromagnetic moment, suggesting that the ferromagnetism might not be intrinsic to the Co doping but could in fact arise from the formation of defects during Zn treatment [2, 3]. Analytical results hinted in particular at the presence of nano-scale ferromagnetic phases, rich in reduced Co(0), albeit at a very dilute level, which makes them extremely difficult to detect with most bulk characterisation techniques such as XRD or XANES [4].

Aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) were used here to investigate  $\text{Co}_{0.1}\text{Zn}_{0.9}\text{O}$  thin films grown epitaxially on either the *r* or *c* plane of sapphire (*r*- $\text{Al}_2\text{O}_3$  or *c*- $\text{Al}_2\text{O}_3$ ). A detailed quantification of the Co  $L_{3,2}$  EELS edge showed no detectable segregation of the Co dopants at the interface or at the surface of the films. In the case of the Zn-diffused film grown on *r*- $\text{Al}_2\text{O}_3$  (*r*- $\text{Zn}_i\text{:Co:ZnO}$ ), although overall the valence of Co throughout the film was determined to be 2+, it was possible to observe small variations in the  $L_3/L_2$  edge ratio, which correlate spatially with contrast differences in the image. As both as-grown and Zn-diffused films exhibited very good structural integrity with no observed defect in high resolution images, these variations are likely to arise from surface effects at the entrance or exit plane of the cross-sectional specimens and could possibly correspond to Co valence changes due to the suggested presence of Co(0) nanophases. The O K edges recorded in the *r*- $\text{Zn}_i\text{:Co:ZnO}$  film exhibited a very prominent pre-peak, uncharacteristic of reference spectra or multiple scattering simulations for either bulk ZnO or dilute Co-doped ZnO. Significantly, this pre-peak was not observed in non Zn diffused films and was significantly reduced in the *r*- $\text{Zn}_i\text{:Co:ZnO}$  film, coinciding with measurements of much weakened ferromagnetism in the as-grown or Zn-diffuse *r*-grown films [4]. Although the presence of a pre-peak could be linked to defects within the film, the surface mediation of this phenomenon is further suggested by its dependence on growth direction, as well as its dramatic decrease in intensity with irradiation time at constant Co signal intensity and image contrast. Finally, the apparition of hexagonal Moiré patterns in high resolution images after long scanning

times, likely due to a re-arrangement of the film's topmost layers, confirm the suggestion that defects at the surface may play a crucial role in the observed properties of the films.

## References

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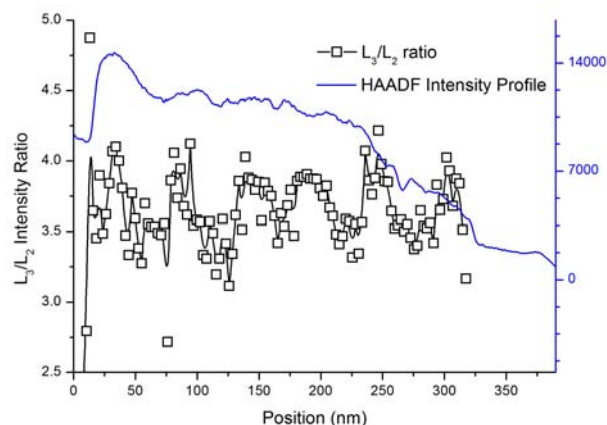


Figure 1.  $L_3/L_2$  ratio for the Co edge across the Zn-diffused Co-doped ZnO film grown on  $r\text{-Al}_2\text{O}_3$ . An aberration-corrected VG HB501 operated at 100 kV was used to perform the EELS measurement.

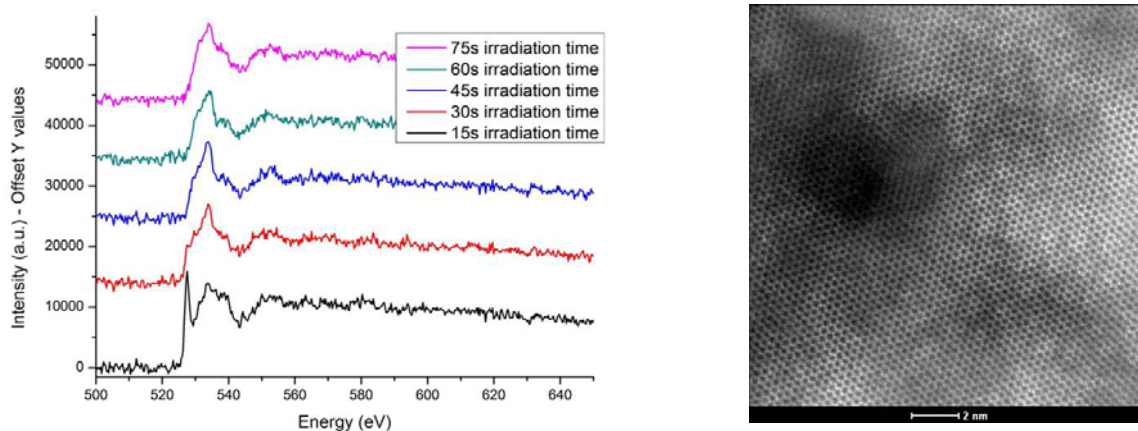


Figure 2. Left: Time-resolved O K EELS spectra for the  $r\text{-Zn}_i\text{:Co:ZnO}$ , acquired on an aberration-corrected VG HB501, showing the very prominent pre-peak disappearing with irradiation time, the Co signal (not shown) remaining constant. The EELS signal was acquired whilst constantly rastering the beam across a 20nm $\times$ 20nm area. Right: Moiré pattern appearing in the high resolution HAADF images after rastering the beam over the area for 5 minutes.