Transmission electron microscopy of Co:ZnO magnetic semiconductor layers

A. Kovács\textsuperscript{1}, M. Duchamp\textsuperscript{1}, A. Ney\textsuperscript{2}, V. Ney\textsuperscript{2}, C.B. Boothroyd\textsuperscript{1}, P. L. Galindo\textsuperscript{3} M. Luysberg\textsuperscript{1} and R.E. Dunin-Borkowski\textsuperscript{1}

1. Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Peter Grünberg Institute, Jülich Research Centre, D-52425, Germany
2. Fakultät für Physik and CeNIDE, Universität Duisburg-Essen, D-47057, Germany
3. Departamento de Ingeniería Informática, Universidad de Cádiz, E-11510, Spain

a.kovacs@fz-juelich.de
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The prospect of combining ferromagnetic and semiconducting materials is attractive for use in spin-electronic devices, whose magnetic and transport properties can be controlled by the introduction of transition metal ions into the semiconducting host\cite{1}. Poor structural characterization of these materials has led to controversial publications, in which the origin of ferromagnetism has been misinterpreted. In this work, transmission electron microscopy (TEM) is used to study the structure and chemistry of Co-doped ZnO layers that can help us to understand the magnetic structure in these layers. Both image and probe aberration-corrected TEM and scanning TEM (STEM) studies were carried out using FEI Titan microscopes operated at 300 kV. Information about local concentrations of elements was obtained by using a combination of STEM and electron energy-loss spectroscopy (EELS).

Co-doped ZnO layers were deposited using reactive magnetron sputtering onto c-plane sapphire substrates. Composition changes of the Ar:O\textsubscript{2} sputter gas lead to either paramagnetic properties, or super-paramagnetic properties\cite{2}. The nominal Co composition in Co\textsubscript{x}Zn\textsubscript{1-x}O was varied between 10<x<20. Great care was devoted to cross-sectional TEM specimen preparation in order to minimize the amount of artefacts. Both conventional and focused ion beam specimen preparation methods were used. Each specimen was finished using low-energy Ar ion milling at 500 eV.

Figure 1 (a) shows a bright-field TEM image of a cross-sectional specimen of a paramagnetic Co:ZnO layer grown on sapphire. The layer is columnar with slight in-plane misalignments of the individual columns. Selected area electron diffraction from the layer and the substrate confirmed the quality of the epitaxy, as shown in Fig. 1 (b). The layer was found to contain I\textsubscript{1} type intrinsic stacking faults. Figure 2 shows an aberration-corrected high-resolution TEM image of a stacking fault that is \approx 5 nm long. Negative spherical-aberration (Cs) imaging\cite{3} was used to image the planar defect. The strain distribution around the defect was determined by applying geometrical phase analysis to a phase image reconstructed from a defocus series of aberration-corrected images of the defect, as shown in Fig. 2 (b). Aberration-corrected high-angle annular dark-field (HAADF) STEM images were used to confirm the structure of the defect. Figure 2 (c) shows a schematic image of the inferred structure of the dislocation core, which contains a 5/7-atom ring, in which the atoms are tetrahedrally coordinated.

Figure 3 shows an aberration-corrected HAADF STEM image of the interface between a Co:ZnO layer and a sapphire substrate. Elemental analysis performed using StripeSTEM EELS\cite{4} was performed across the interface by collecting core-loss signals of O, Co and Zn. The signal-to-noise ratios of the spectra were improved by using principal component analysis. The background-subtracted EEL spectra acquired from the interface suggest the presence of a Co-rich monolayer.

References

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Figure 1. (a) Cross-sectional bright-field TEM image of a Co:ZnO layer deposited on sapphire. (b) Selected area electron diffraction pattern acquired from the layer and the substrate demonstrating good epitaxy.

Figure 2. (a) Aberration-corrected TEM image of an intrinsic stacking fault in a Co:ZnO layer acquired using negative Cs imaging conditions. (b) Strain component in the vertical direction measured from a reconstructed phase image of a stacking fault determined using geometrical phase analysis. (c) Structure of the dislocation core marked in (a) inferred from aberration-corrected HAADF STEM images (not shown). Grey and red atoms are Zn and O, respectively.

Figure 3. (a) Aberration-corrected HAADF STEM image of the interface between a Co:ZnO layer and a sapphire substrate. The viewing direction is [110] for the sapphire. The inner detector semi-angle used was 78 mrad. Ball models of the crystal structures are inserted, with red=O, blue=Zn, green=Co and dark grey=Al. (b) Background-subtracted EEL spectra acquired from the interface from the positions marked on the right of (a). Spectrum 3 is suggestive of a Co-rich monolayer formation.