Defects in paramagnetic Co-doped ZnO films studied by transmission electron microscopy

A. Kovács,1,a) A. Ney,2 M. Duchamp,1 V. Ney,2 C. B. Boothroyd,1 P. L. Galindo,3 T. C. Kaspar,4 S. A. Chambers,4 and R. E. Dunin-Borkowski1
1Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52425 Jülich, Germany
2Institut für Halbleiter- und Festkörperphysik, Johannes Kepler Universität, Altenberger Str. 69, 4040 Linz, Austria
3Departamento de Ingeniería Informática, Universidad de Cádiz, 11510 Cádiz, Spain
4Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, USA

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We study planar defects in epitaxial Co:ZnO dilute magnetic semiconductor thin films deposited on c-plane sapphire (Al2O3), as well as the Co:ZnO/Al2O3 interface, using aberration-corrected electron microscopy and electron energy-loss spectroscopy. Co:ZnO samples that were deposited using pulsed laser deposition and reactive magnetron sputtering are both found to contain extrinsic stacking faults, incoherent interface structures, and compositional variations within the first 3–4 Co:ZnO layers next to the Al2O3 substrate. The stacking fault density is in the range of 10^{17} cm^{-3}. We also measure the local lattice distortions around the stacking faults. It is shown that despite the relatively high density of planar defects, lattice distortions, and small compositional variation, the Co:ZnO films retain paramagnetic properties. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4851015]

I. INTRODUCTION

The prospect of combining ferromagnetic and semiconducting properties1 is attractive for the design of spin-electronic devices, whose magnetic and transport properties can be controlled by the introduction of transition metal ions into a semiconducting host. Of the different doped oxides2 that have been investigated as diluted magnetic semiconductors (DMSs), Co-doped ZnO (Co:ZnO) thin films, and nanostructures are among the most intensely studied materials because of the promising electronic and optical properties of the ZnO host material. A high Curie transition temperature (T_C) was predicted for transition-metal-doped zinc oxide by Dietl3 et al. using a Zener type p-d exchange interaction model based on high concentrations of localized spins and delocalized free carriers (holes). At the same time, Sato and Katayama-Yoshida4 used an ab initio local density approximation to predict that doping ZnO with Mn should lead to a ferromagnetic ground state in the presence of hole doping, but that Co, V, Cr, and Fe doping should show ferromagnetic ordering without additional carrier doping. These theoretical predictions were followed by contradictory experimental activities that either proved or disproved the existence of a high T_C in Co:ZnO.

In the last few years, however, there has been an emerging consensus of theoretical and experimental investigations showing that epitaxial Co:ZnO thin films with high crystalline quality are intrinsically paramagnetic,5 with antiferromagnetic Co-O-Co interactions.6,7 Recently, we have correlated the observed ferromagnetism in ZnO with the presence of secondary Co-rich phases.8 These conclusions about the intrinsic magnetic properties of Co:ZnO relied on avoiding measurement artefacts when performing very sensitive superconductive quantum interference device (SQUID) magnetometry9 in combination with synchrotron-based x-ray absorption spectroscopy (XAS), x-ray linear dichroism (XLD), and x-ray magnetic circular dichroism (XMCD).5 The detection of small quantities of local structural or chemical variations using these techniques poses a significant analytical challenge and is ideally complemented by the application of advanced transmission electron microscopy (TEM) techniques to the same materials.5,8 The need for high-spatial resolution studies of DMS materials, such as doped ZnO is even more important in view of the recent proposals that ferromagnetism in these materials may be related to the presence of structural defects.10,11

Here, we make use of recent advances in aberration-corrected TEM and optimized specimen preparation techniques for TEM to study the structure and chemistry of Co:ZnO layers that have been deposited onto c-plane sapphire using two common preparation techniques: pulsed laser deposition (PLD) and reactive magnetron sputtering (RMS). We use a combination of scanning TEM (STEM) imaging and electron energy-loss spectroscopy (EELS) to characterize grain boundaries, planar defects and interfaces in order to reveal structural features and possible chemical inhomogeneities, some of which have not been previously reported in transition-metal-doped oxides. We demonstrate that the presence of extended defects, which can be distinguished from simple point defects,12 as well as non-stoichiometric layers of Co:ZnO, should be considered in realistic models of such DMS layers.

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a)Author to whom correspondence should be addressed. Electronic mail: a.kovacs@fz-juelich.de
II. EXPERIMENTAL DETAILS

Thin epitaxial films of Co:ZnO were deposited onto c-plane sapphire substrates using PLD\textsuperscript{13,14} and RMS.\textsuperscript{3} Careful pre-characterization using x-ray diffraction, XAS, XLD, XMCD, and SQUID has been performed before for the PLD-10 (Refs. 5, 13, and 15) and RMS-10 (Ref. 15) samples, respectively, which has revealed that the samples are virtually phase pure and paramagnetic. These measurements suggest that Co occupies predominantly Zn lattice sites and is therefore likely to be in its formal 2\textsuperscript{+} oxidation state, i.e., that the samples are devoid of metallic Co precipitates. In addition, it has been found that in both samples the single ion anisotropy D(S)\textsuperscript{2}, which is induced by the anisotropic crystal field, is reduced to D/k\textsubscript{B} = 3 K, as compared to the bulk value of 4 K reported for impurities in single crystals.\textsuperscript{15}

In the present study, the two Co:ZnO samples with nominal Co\textsubscript{x}Zn\textsubscript{1-x}O compositions of x = 0.10 grown by RMS and PLD are complemented with another RMS sample with x = 0.20 (Table I) and all three were studied in cross-sectional geometry using TEM. The characterization of the RMS-20 sample using XAS, XLD, XMCD, and SQUID has also revealed that this sample is phase pure and paramagnetic and these findings will be published in Ref. 16.

TEM specimens were prepared using either conventional preparation (mechanical polishing followed by broad-beam ion milling) or focused ion beam (FIB) milling. In both cases, the specimens were finished using low-energy Ar ion milling at 500 eV, in order to remove ion-beam-induced artefacts. Image and probe aberration-corrected TEM and STEM studies were carried out at 300 keV using FEI Titan 80–300 microscopes, each of which is equipped with a double-hexapole corrector and a Gatan imaging energy filter. TEM and STEM images were recorded using a Gatan 2 k x 2 k charge-coupled device camera and a Fischione 3000 detector, respectively. Strain maps were calculated from high-resolution TEM images using geometrical phase analysis\textsuperscript{17} (GPA).

III. RESULTS AND DISCUSSION

TEM studies involved the characterization of grain boundaries and planar defects in the Co:ZnO layers, as well as the interface between each Co:ZnO layer and its c-plane sapphire substrate. Figure 1 summarizes the representative structural features in the Co:ZnO samples. All of the samples exhibit good epitaxy with the sapphire substrate, with a columnar but highly oriented grain structure that results from the presence of a large (~18\%) lattice mismatch between c-plane sapphire and the c-plane of Co:ZnO. The Co doping of ZnO does not change significantly the growth process, thus a 30° rotation of Co:ZnO basal planes is expected with respect to the sapphire.\textsuperscript{14} A strain field on both sides of the interface can be seen in a dark-field (DF) TEM image of the RMS-10 sample shown in Fig. 1(a), recorded using the 002 reflections of Co:ZnO and Al\textsubscript{2}O\textsubscript{3}. A detailed analysis of TEM images recorded from all three samples reveals that the grain diameters of the columns parallel to the substrate surface normal in the RMS-deposited and PLD-deposited layers are in the ranges 10 nm to 90 nm and 50 nm to 100 nm, respectively, as summarized in Table I.

Figure 1(b) shows a high-resolution aberration-corrected high-angle annular DF (HAADF) STEM image of a 15 nm wide Co:ZnO grain in the RMS-10 sample. This grain is aligned along [010], while the two adjacent grains have different in-plane directions. The three grains that are visible in Fig. 1(b) exhibit a perfect match of their respective (002) planes with no additional phase visible at the grain boundaries. The interface between the Co:ZnO is abrupt. Interestingly, misfit dislocations are rarely observed in Co:ZnO, probably the strain is accommodated by the grain boundaries. The epitaxial relationship between the Co:ZnO layers and sapphire is determined as Co:ZnO[010]/[001]//Al\textsubscript{2}O\textsubscript{3}[110]/[001]. Chemical composition measurements (not shown), acquired using energy dispersive X-ray spectroscopy from the PLD and RMS-10 samples, revealed homogenous chemical compositions of Co, Zn, and O across the grain boundaries. Figure 1(c) shows an aberration-corrected high-resolution TEM image of nanometer-sized planar defects (stacking faults) in the PLD-deposited sample (circles), which may be responsible for some of the local contrast variations that are visible within the

| TABLE I. Properties of the paramagnetic RMS-deposited and PLD-deposited Co:ZnO layers on c-plane Al\textsubscript{2}O\textsubscript{3} studied here. |
|---|---|---|---|
| Co [at. %] | Layer thickness [nm] | Grain size [nm] | Stacking fault density [cm\textsuperscript{-2}] |
| RMS-10 | 10 | 158 | 15–90 | 2 x 10\textsuperscript{17} |
| RMS-20 | 20 | 128 | 10–50 | 6 x 10\textsuperscript{17} |
| PLD | 10 | 113 | 50–100 | 3 x 10\textsuperscript{17} |
grains in Fig. 1(a). The typical length of each extra lattice plane in the Co:ZnO is \( \sim 2.5 \) nm in the PLD-deposited sample and \( \sim 5 \) nm in the RMS-deposited samples (see below). By estimating the thickness of the studied region using EELS and counting the stacking faults on high-resolution TEM images, the density is estimated as \( 2 \times 10^{17} \text{cm}^{-2} \), \( 6 \times 10^{17} \text{cm}^{-2} \), and \( 3 \times 10^{17} \text{cm}^{-2} \) in RMS-10, RMS-20, and PLD samples, respectively (Table I). The error in the measured stacking fault density is expected to be \( \sim 20\% \).

The structures of the stacking faults and their local environments were studied in detail in sample RMS-10, as shown in Fig. 2. Figure 2(a) shows a high-resolution aberration-corrected TEM image of a stacking fault in this sample. The negative spherical-aberration imaging (NCSI) technique was used to enhance the contrast of the atomic columns in the image. Aberration coefficients were corrected up to fourth order, with the negative spherical aberration coefficient \( (C_2) \) set to \( \sim 10 \mu \text{m} \) and the objective lens defocus set to \( \sim 1 \) nm to optimize the imaging conditions. The \( \sim 4 \) nm-long additional plane distorts the surrounding Co:ZnO lattice. The resulting strain distribution was visualized using GPA, as shown in Fig. 2(b). Surprisingly, the strain map was found to be affected strongly by the defocus used to record the image. Therefore, an exit wave function reconstruction was obtained from a defocus series of TEM images.22 In Fig. 3(a), Al and Zn(Co) columns appear bright, with semi-circular regions that are in tension above and below the stacking fault, extending by \( \sim 5 \) nm into the lattice. Figure 2(c) shows a high-resolution HAADF STEM image of a similar stacking fault, in which the bright spots correspond to Zn(Co) columns. Such defects were determined to be basal plane extrinsic stacking faults, with Frank partial dislocations and displacement vectors of \( 1/2[001] \). By matching the locations of the Zn(Co) atomic columns in the HAADF STEM image with a wurtzite structure model, a possible core structure of the stacking fault was determined, as shown in Fig. 2(d). The model suggests that the atomic columns in the core regions form tetragonally coordinated 5/7 rings, with strongly distorted bond angles and lengths. Such stacking faults, with their associated strain distributions, are expected to affect carrier localization and local transport properties around the defects, according to first-principles total energy calculations.20,21 Interestingly, these calculations also show that such extrinsic faults have high formation energies per unit cell compared to other intrinsic faults. Their presence in all three samples highlights the strongly off-equilibrium nature of both deposition techniques.

The interface structure between Co:ZnO and sapphire was also studied in more detail. Figure 3 shows an aberration-corrected high-resolution TEM image of the PLD sample viewed along the \([1-100]\) direction of \( \text{Al}_2\text{O}_3 \). The image was recorded using the NCSI method, so that the Al and O columns in \( \text{Al}_2\text{O}_3 \) could be distinguished in the TEM image.22 In Fig. 3(a), Al and Zn(Co) columns appear bright, with semi-circular regions that are in tension above and below the stacking fault, extending by \( \sim 5 \) nm into the lattice. Figure 3(b) shows a high-resolution HAADF STEM image of a similar stacking fault, in which the bright spots correspond to Zn(Co) columns. Such defects were determined to be basal plane extrinsic stacking faults, with Frank partial dislocations and displacement vectors of \( 1/2[001] \). By matching the locations of the Zn(Co) atomic columns in the HAADF STEM image with a wurtzite structure model, a possible core structure of the stacking fault was determined, as shown in Fig. 2(d). The model suggests that the atomic columns in the core regions form tetragonally coordinated 5/7 rings, with strongly distorted bond angles and lengths. Such stacking faults, with their associated strain distributions, are expected to affect carrier localization and local transport properties around the defects, according to first-principles total energy calculations.20,21 Interestingly, these calculations also show that such extrinsic faults have high formation energies per unit cell compared to other intrinsic faults. Their presence in all three samples highlights the strongly off-equilibrium nature of both deposition techniques.

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whereas O columns appear dark. The enlarged section of the interface shown in Fig. 3(b) reveals that the sapphire is O-terminated and that steps are present on the Al$_2$O$_3$ surface. Interpretation of the nature of the first Co:ZnO atomic layer is not straightforward, as the observed atomic structure does not represent the expected wurtzite structure, suggesting the presence of structural or chemical disorder in the first layer(s) of Co:ZnO. Figure 3(c) shows a high-resolution HAADF STEM image of the Co:ZnO-PLD layer viewed along [1100] direction of the Al$_2$O$_3$ substrate. In the HAADF STEM image, the recorded intensity of the Co:ZnO film is higher than that of the Al$_2$O$_3$ substrate primarily due to the higher atomic numbers of Zn (Z = 30) and Co (Z = 27) compared to that of Al (Z = 13). The interface structure is incoherent, with 7 (110) Al$_2$O$_3$ planes matching 6 (100) Co:ZnO planes, as indicated in Fig. 3(c). The area shown in Fig. 3(c) does not contain any obvious steps or defects at the interface and appears to be structurally abrupt. However, the intensity of the Zn(Co) columns decreases close to the interface, which is suggestive of compositional variation or strain. Yu et al.\textsuperscript{25} showed that the presence of strain at a SiO$_2$/Si interface causes a change in ADF STEM image intensity, which depends on inner detector semi-angle and specimen thickness. In the present specimens, the contrast of the Co:ZnO layers close to the interface in the ADF STEM image series was not observed to reverse as a function of collection angle over the range 20 to 120 mrad. It is therefore likely that a compositional variation is present in the Co:ZnO layers, probably dominated by a change in the relative concentration of Zn. In order to clarify the origin of the observed contrast, elemental analysis using the StripeSTEM\textsuperscript{24} EELS technique was performed across the interface for O, Co, and Zn core-loss EELS edges. In this technique, an isochronous recording of EEL spectra and HAADF images provides spectroscopic information from individual atomic layers using an optimized irradiation dose.\textsuperscript{25} Figure 3(d) displays measurements of elemental concentration profiles for O, Co, and Zn. Al was not included in the present measurement. The Zn concentration (upward pointing blue triangles in Fig. 3(d)) decreases faster compared to the Co concentration, while approaching the interface. At the same time, the O concentration increases towards the interface, suggesting the formation of a Co-containing interface layer, which is deficient in Zn. This conclusion is consistent with the observed decrease in HAADF STEM intensity in Fig. 3(c).

The compositional variation at the interface was also studied in detail in sample RMS-20, which contains the highest Co concentration of the three samples. Figure 4 shows an atomic-resolution HAADF STEM image and background-subtracted EELS measurements acquired across the interface between the Co:ZnO layer and the substrate viewed along the [1120] direction of the Al$_2$O$_3$. Schematic ball-and-stick models of the Co:ZnO and Al$_2$O$_3$ structures are inserted for illustrative purposes. The presence of a monoatomic step on the Al$_2$O$_3$ surface is highlighted by a dotted line in Fig. 4(a). The contrast of the Zn(Co) columns decreases close to the interface in a similar manner to that found in the PLD sample in Fig. 3.

**Figure 4.** (a) HAADF STEM image of the sample RMS-20 viewed along the [1120] direction of Al$_2$O$_3$. The inner ADF detector semi-angle used was 78 mrad. The insets show schematic models of the crystal structures (red = O, blue = Zn, green = Co, dark grey = Al). The dotted line at the interface marks a monoatomic step on the Al$_2$O$_3$ surface. (b) Representative background-subtracted EELS spectra showing the O K, Co L$_{2,3}$, and Zn L$_{2,3}$ edges acquired across the interface at the positions marked in (a).
observed for O in Al2O3. This chemical shift is not abrupt, but changes in position gradually within the first 4 layers in Co:ZnO, which is in agreement with our speculation previously.11 The extrinsic stacking faults that are present in each Co:ZnO layer introduce regions of both compressive and tensile strain into the wurtzite structure. The stacking fault densities in the RMS and PLD deposited films are in the 1017 cm−3 range (Table I). The presence of the observed lattice distortions may be responsible for the reduction of the single ion anisotropy D, which was reported before for the RMS-10 and PLD-10 samples.15

Taking together the decrease in ADF STEM intensity, the decrease in Zn concentration measured using EELS and the chemical shift of the O edge suggest that the first monolayers of Co:ZnO are deficient in Zn, while the Co oxidation state remains essentially 2+.

IV. SUMMARY

We have used advanced TEM and EELS methods to study the structure and chemistry of grain boundaries and plate-like stacking faults in three Co:ZnO samples, as well as the interface between the Co:ZnO films and their sapphire substrate. Thin films of Co:ZnO with Co concentrations of 10% and 20% are deposited on sapphire substrates using RMS and PLD methods. The TEM characterization confirms the high crystalline quality of the films, thus no formation of secondary phases or precipitates is detected. Since all three samples are known to be paramagnetic, the presence of the defects cannot be associated with magnetic order, as speculated previously.11 The extrinsic stacking faults that are present in each Co:ZnO layer introduce regions of both compressive and tensile strain into the wurtzite structure. The stacking fault densities in the RMS and PLD deposited films are in the 1017 cm−3 range (Table I). The presence of the observed lattice distortions may be responsible for the reduction of the single ion anisotropy D, which was reported before for the RMS-10 and PLD-10 samples.15

The chemical compositions and electronic structures of the first few monolayers of Co:ZnO adjacent to the Al2O3 substrate were also studied. In each sample, the interface is incoherent but atomically abrupt. Variations in chemical composition are found only in the first 2–4 layers in the Co:ZnO film, which are Zn-deficient. In these first few layers, the Co appears to remain in its 2+ valence state. These findings are supportive of the formation of an interfacial layer, which facilitates subsequent growth of the polar c-oriented wurtzite ZnO structure.

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