Lack of ferromagnetism in \( n \)-type cobalt-doped ZnO epitaxial thin films

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*New Journal of Physics* 10 (2008) 055010 (18pp)
Received 1 January 2008
Published 23 May 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/5/055010

**Abstract.** Epitaxial thin films of cobalt-doped ZnO (Co : ZnO) were deposited by pulsed laser deposition (PLD) on both \( c \)-plane and \( r \)-plane sapphire (\( \text{Al}_2\text{O}_3 \)). The films exhibited high structural quality with narrow x-ray diffraction (XRD) rocking curve peak widths. X-ray absorption spectroscopy (XANES and EXAFS) confirmed well-ordered Co substitution for Zn in ZnO without the formation of secondary phases. A wide range of \( n \)-type conductivities (\( 10^{-4} \)–\( 10^5 \) \( \Omega \)cm) was achieved by controlling the deposition conditions, post-annealing in vacuum, and/or addition of Al during deposition. Despite the high structural quality of the Co : ZnO thin films, no significant room temperature ferromagnetism was observed under any processing or treatment conditions. The lack of ferromagnetism indicates that itinerant conduction band electrons alone are not sufficient to induce ferromagnetism in Co : ZnO, even when the carrier concentration is a significant fraction of the magnetic dopant concentration. The implications of this observation are discussed.

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1. Introduction

As a wide-bandgap, transparent semiconducting oxide, ZnO has been widely studied for a variety of electrical and optical applications [1]. With the prediction of room temperature ferromagnetism in p-type Mn:ZnO by Dietl et al [2], a considerable effort was undertaken to identify transition-metal-doped ZnO which exhibited ferromagnetism at and above room temperature, in the hopes of developing a ferromagnetic dilute magnetic semiconductor (DMS) for use in potential spintronic devices. A review of the recent literature, however, demonstrates the disparate claims and ensuing controversy resulting from this field of investigation [3]–[6].

Focusing specifically on cobalt-doped ZnO (Co:ZnO), room temperature magnetic results have ranged from no observation of ferromagnetism [7]–[12] to very weak ferromagnetism (<0.1 μB/Co) [13]–[15] to strong ferromagnetism [16]–[19] with ferromagnetic saturation moments approaching the theoretical spin-only value of 3 μB/Co for tetrahedral Co(II). Moreover, a few claims have been made for much higher saturation moments [20, 21].

The role of itinerant n-type carriers in mediating ferromagnetic ordering is equally unclear, with claims of ferromagnetism for Co:ZnO material ranging from highly insulating to highly conductive [3]. A recent report by Behan et al [19] found for a large number of Co:ZnO films that ferromagnetism occurs in films which are insulating (n-type carrier concentration <10^{18} cm^{-3}) and films which are metallic (>10^{20} cm^{-3}), but films with intermediate carrier concentrations are not ferromagnetic. They postulated that the ferromagnetism is mediated by bound magnetic polarons in the insulating regime, and the addition of a few free carriers destabilized the magnetic polarons and destroyed the ferromagnetism; increasing the free-carrier concentration until the metallic regime was reached and allowed free-carrier-mediated ferromagnetism.

Grain boundary defects have also been proposed to play an important role in facilitating magnetic ordering of oxide DMSs. For example, both Co:ZnO and Ni:ZnO colloidal nanocrystals were found to be paramagnetic, but weak ferromagnetism was observed when the colloids were allowed to aggregate aerobically at room temperature [22, 23]. Similar results have been obtained in several oxide DMS nanocrystal studies [24, 25], and a correlation between grain boundary defects and room temperature ferromagnetism has also been observed in...
Cr:TiO$_2$ films grown by oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) [26, 27]. Recently, complex impedance spectroscopic results have been used to investigate the relationship between grain boundary defects and ferromagnetism in Co:ZnO [18].

None of the theoretical models put forth to explain the ferromagnetic ordering in doped oxides, such as Zener-RKKY free-carrier exchange, Zener double exchange and bound magnetic polarons [3, 28], offer a satisfactory quantitative prediction of ferromagnetism persisting at and above room temperature. In a few cases, the observed ferromagnetism has been attributed to secondary phase formation, such as ferromagnetic Co metal inclusions [8, 9, 29, 30]. Many reports of doped ZnO limit materials characterization to x-ray diffraction (XRD), which is a bulk technique that has been shown to be insensitive to small quantities of secondary phases in Co:ZnO [29, 30]. Venkatesan et al [31] illustrated this point by showing that slow, careful XRD scans were necessary to detect Co metal inclusions in Co:ZnO thin films which were missed under conventional measurement conditions. Recently, Dietl et al [32] proposed secondary phase formation by spinodal decomposition of Co:ZnO into Zn-doped wurtzite CoO nanocrystals coherently imbedded within a Co-poor Co:ZnO matrix. Based on magnetic and magnetotransport measurements, the observed room temperature ferromagnetism was proposed to arise from uncompensated spins on the surface of these antiferromagnetic crystallites. However, wurtzite CoO nanocrystals were not directly observed, and coherent crystallites of the same structure as the host lattice would be very difficult to identify with standard materials characterization techniques. Spinodal decomposition into dopant-rich regions has also been proposed to understand the robust ferromagnetism in other DMS systems [33, 34].

The original theoretical prediction of room temperature ferromagnetism in Mn-doped ZnO was based on mean-field theory, and required a high concentration of holes to stabilize the ferromagnetic phase [2]. Since then, several theoretical calculations based on density functional theory (DFT) have been presented to explore the ferromagnetic ordering in Co:ZnO (see for example [35]–[38]). In general, these calculations have indicated that insulating Co:ZnO is not ferromagnetic, and thus defects which add carriers to the system are necessary to stabilize the ferromagnetic phase. The nature of the defect varies with the specific calculation, with some predicting electron-mediated ferromagnetism [35, 36] and others predicting hole mediation [38, 39]; another calculation found that both electrons and holes could promote ferromagnetism in Co:ZnO [37]. One major drawback to these results is the well-known tendency of DFT calculations to significantly underestimate the bandgap of transition metal oxides, making accurate determination of the position of the Co and defect states within the ZnO band structure difficult or impossible [40]. These calculations generally predict half-metallic behavior for doped transition metal oxides, with the Fermi level crossing dopant-induced defect states in the middle of the host oxide bandgap [41]. In contrast, several recent calculations utilizing modified methods (LDA + U [41], pseudo-self-interaction-corrected LDA [42] and B3LYP [40]) have placed the occupied majority-spin Co 3d orbitals of e and t$_2$ symmetry within the ZnO valence band, and the occupied minority-spin e orbitals extending into the lower portion of the bandgap. The unoccupied minority-spin Co 3d t$_2$ orbitals were predicted to lie in the lower portion of the conduction band, and no levels were predicted at midgap. This picture is consistent with photoemission studies of Co:ZnO [43, 44] which show Co:ZnO to be a semiconductor with additional states extending from the top of the valence band and no states observed at the Fermi level. The calculations also showed that defect-free, insulating Co:ZnO is not ferromagnetic [40, 41]. Patterson [40] explored several likely defects and found strong ferromagnetism only
for the singly charged oxygen defect (V$_O^+$), although this defect was predicted to be energetically unfavorable compared to V$_O$ and V$_O^{2+}$.

The lack of consensus in both the experimental and the theoretical literature illustrates the controversy over the claim of intrinsic ferromagnetism in Co:ZnO. There is a demonstrated need in the field of transition-metal-doped ZnO for complete and thorough materials characterization to ensure the observed ferromagnetism (or lack thereof) is truly an intrinsic property of substitutionally doped ZnO, and not the product of precipitates, clusters, or secondary phases [4, 5]. In this work, such a thorough investigation is undertaken for Co-doped ZnO. The structural characteristics, dopant speciation and ferromagnetic ordering of high quality Co:ZnO epitaxial films are investigated for a wide range of n-type doping levels. The magnitude of n-type conductivity in Co:ZnO has been controlled by conventional means, such as modifying the deposition and/or annealing conditions, and in some cases doping with Al, a known n-type dopant. Despite the high structural quality of the Co:ZnO films and the large range of conductivities investigated, no appreciable ferromagnetic ordering was observed in any Co:ZnO film, indicating that charge carriers alone are not sufficient to induce ferromagnetism in high-quality Co:ZnO.

2. Experimental methods

Thin films of Co:ZnO were deposited by pulsed laser deposition (PLD). The PLD chamber is set up in an off-axis configuration to minimize deposition of droplets and particles on the substrate. The base pressure of the system is $< 2 \times 10^{-8}$ Torr. Chamber pressure during deposition is controlled via a combination of a mass flow controller on the O$_2$ inlet and an automatic throttled gate valve between the chamber and the turbopump. Alternatively, oxygen can be introduced through an electron cyclotron resonance (ECR) microwave plasma unit, which produces both atomic and ionic excited oxygen species. A KrF laser (248 nm, 2.4 J cm$^{-2}$ and 1–20 Hz) is utilized for ablation; laser rastering, target rotation and sample rotation allow uniform deposition. Target starting materials were either thoroughly mixed commercially available CoO and ZnO powders, or uncapped Co:ZnO nanoparticles synthesized as in [23]; the starting target materials were mixed with small amounts of deionized water and organic binder (polyethylene glycol), cold-pressed, then sintered for 4–6 h at 1000 $^\circ$C in air. Targets were pre-ablated in oxygen before every deposition to remove surface contaminants.

Substrates were single crystal single-side epi-polished 10 $\times$ 10 $\times$ 1 mm$^3$ r-plane Al$_2$O$_3$(0112) and double-sided epi-polished 10 $\times$ 5 $\times$ 0.5 mm$^3$ c-plane Al$_2$O$_3$(0001). As-received substrates often show residual ferromagnetic contamination, which is presumably deposited on the substrate edges during wafer dicing. To ensure ferromagnetic cleanliness, all substrates were etched (edges and back side only) in concentrated HNO$_3$ [26]. Each substrate was then measured by vibrating sample magnetometry (VSM) at room temperature; residual ferromagnetic signals were generally $<$2 µemu or nonexistent.

Typical Co:ZnO thin film deposition conditions were 10 mTorr molecular O$_2$, 550 $^\circ$C substrate temperature, and 5 or 10 Hz laser repetition rate, resulting in an average deposition rate of 0.25 Å per pulse and final film thicknesses of 100–1000 nm. When the ECR plasma was employed to introduce excited oxygen species, the chamber pressure was reduced to $2 \times 10^{-5}$ Torr. Computer control of the six-target carousel allowed codoped films deposited from two targets. For this case, the laser repetition rate was reduced to 1 Hz. The laser was
incident on one target for only a few pulses; the laser shutter was then closed and the second
target was brought into position (2–3 s); the shutter then opened for a few pulses, and the process
was repeated. Thus, the codoped films experienced both a slower overall deposition rate and
many short periods with no deposition. Vacuum annealing was performed in the PLD chamber
at a pressure of $5 \times 10^{-7}$ Torr or lower.

Magnetic properties were measured at room temperature by VSM with the magnetic
field applied in the plane of the film (unless noted otherwise). Crystallinity was investigated
using high-resolution x-ray diffraction (HRXRD) with a four-circle goniometer and a double-
crystal Ge(220) four-bounce monochromator. Film thickness was measured by x-ray reflectivity
(XRR) for some thinner films, and Rutherford backscattering spectrometry (RBS) for thicker
films. Particle-induced x-ray emission (PIXE) was utilized to confirm the dopant concentration
in several films. Detailed microstructure was investigated with high-resolution transmission
electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) valence band spectra
were acquired at normal take-off angle with a monochromatized Al K$_\alpha$ x-ray source ($h\nu = 1486.6$ eV).

Film resistivity was determined at room temperature using a four-point-probe apparatus
with spring contacts. A Physical Property Measurement System (PPMS) by Quantum Design
was utilized for Hall effect measurements as a function of temperature and magnetic field.
Contacts to the Co : ZnO film surface were made by indium solder, in the van der Pauw
geometry. Measurements were taken in the temperature range of 5–295 K, and in magnetic
fields up to 8 T.

Dopant speciation and lattice location were explored by x-ray absorption near edge
spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS), performed on
the PNC–CAT beamlines 20-BM and 20-ID at the Advanced Photon Source, Argonne National
Laboratory. Fluorescence measurements were taken using a multi-element Ge detector with an
incidence angle in the range of 4–10°. The angle was selected to maximize the signal while still
probing the entire film thickness. The x-ray beam was linearly polarized and oriented with the
electric field vector either parallel to the sample surface (parallel polarization) or perpendicular
to the sample surface (perpendicular polarization). Sample rotation about the surface normal
was utilized to minimize Bragg diffraction effects.

3. Results and discussion

3.1. Crystalline structure and film morphology

Deposition of Co : ZnO in 10 mTorr O$_2$ was found to result in a consistent growth rate of
0.25 Å per pulse, and the Co concentration in the film, as measured by PIXE, was similar
to the nominal concentration in the Co : ZnO target. Deposition in lower oxygen pressure or
vacuum resulted in thinner films with higher Co concentration. However, the total amount of
Co incorporated into the film was equivalent to that expected for the same deposition time in
10 mTorr O$_2$. Thus, it appears that the reduced film thickness results primarily from preferential
loss of Zn/ZnO from the film surface under less oxidizing conditions, and the decrease in
the ablation plume spread with reduced chamber pressure plays a secondary role. A similar
reduction in film thickness was observed at higher substrate temperatures, which again is
attributed to loss of Zn/ZnO from the film surface. There did not appear to be a significant
reduction in film thickness after post-growth annealing in vacuum.
Figure 1. XRD of 5000 Å $c$-Co$_{0.1}$Zn$_{0.9}$O/$c$-Al$_2$O$_3$ deposited in 10 mTorr O$_2$ at 550 °C. (a) $\omega$–$2\theta$ rocking curve of the out-of-plane ZnO(002) reflection (log scale). Inset: wide-angle $2\theta$–$\omega$ scan (log scale); only oriented ZnO(001) is detected. (b) $\omega$–$2\theta$ rocking curve of the in-plane ZnO(104) reflection (log scale). Inset: phi scan of ZnO(104) (linear scale), showing a single in-plane orientation for ZnO.

Figure 2. XRD of 5000 Å $a$-Co$_{0.1}$Zn$_{0.9}$O/$r$-Al$_2$O$_3$ deposited in 10 mTorr O$_2$ at 550 °C. (a) $\omega$–$2\theta$ rocking curve of the out-of-plane ZnO(110) reflection (log scale). Inset: wide-angle $2\theta$–$\omega$ scan (log scale); only oriented ZnO(110) is detected. (b) $\omega$–$2\theta$ rocking curve of the in-plane ZnO(211) reflection (log scale). Inset: phi scan of ZnO(211) (linear scale), showing a single in-plane orientation for ZnO.

Epitaxial films of Co:ZnO were obtained for all deposition conditions on both $c$-sapphire and $r$-sapphire. Representative HRXRD patterns for 5000 Å 10% Co:ZnO(0001) ($c$-plane Co:ZnO) deposited on $c$-sapphire and 5000 Å 10% Co:ZnO(1120) ($a$-plane Co:ZnO) deposited on $r$-sapphire are shown in figures 1 and 2, respectively. Both in-plane and out-of-plane reflections exhibit narrow peak widths (0.06–0.13 °$\theta$), indicative of well-ordered...
Table 1. ZnO lattice parameters determined by XRD $2\theta$–$\omega$ scans of 5000 Å thin films on $c$-Al$_2$O$_3$ and $r$-Al$_2$O$_3$, deposited in 10 mTorr O$_2$ at 550 °C. Values are compared to lattice constants for bulk pure ZnO [45].

| Sample       | Substrate   | $a$ (Å) | % Difference | $c$ (Å) | % Difference |
|--------------|-------------|---------|--------------|---------|--------------|
| Reference ZnO| –           | 3.2495  | –            | 5.2069  | –            |
| Pure ZnO     | $c$-Al$_2$O$_3$ | 3.2524  | −0.09        | 5.1964  | +0.20        |
| 4% Co : ZnO  | $c$-Al$_2$O$_3$ | 3.2701  | −0.63        | 5.1976  | +0.18        |
| 10% Co : ZnO | $c$-Al$_2$O$_3$ | 3.2489  | +0.02        | 5.2257  | −0.36        |
| 4% Co : ZnO  | $r$-Al$_2$O$_3$ | 3.2498  | −0.01        | 5.2343  | −0.53        |
| 10% Co : ZnO | $r$-Al$_2$O$_3$ | 3.2533  | −0.12        | 5.1867  | +0.39        |

crystallinity with little mosaic spread. As the insets show, the films are epitaxial on their respective substrates. For $c$-Co : ZnO on $c$-sapphire, pole figures (not shown) confirm a 30° rotation of the ZnO lattice relative to the substrate, as expected [45]; the crystalline orientations are thus (0001)ZnO || (0001)Al$_2$O$_3$ and [10 0 0]ZnO || [11 2 0]Al$_2$O$_3$. For $a$-Co : ZnO on $r$-sapphire, the orientations are (1 1 2 0)ZnO || (0 1 1 2)Al$_2$O$_3$ and [0 0 0 1]ZnO || [0 1 1 1]Al$_2$O$_3$, in accordance with previous reports [46]. The lattice constants for Co : ZnO films on both $c$-sapphire and $r$-sapphire are given in table 1, along with the lattice constants measured for a pure ZnO film of similar thickness deposited on $c$-sapphire, and the reference lattice parameter values for bulk ZnO [47]. As seen in table 1, there is no systematic dependence of lattice constant on Co incorporation. This is in contrast to previous reports which found a slight increase in the $c$ lattice parameter with increasing Co concentration in epitaxial films on $c$-sapphire [48]–[50]. Presumably under the current deposition conditions, other mechanisms which induce strain in Co : ZnO, such as lattice mismatch and differential thermal expansion, and mechanisms which reduce strain, such as misfit dislocation formation, dominate over Co incorporation in determining the lattice parameters in the epitaxial films. The x-ray absorption spectra discussed below provide unambiguous evidence that Co substitutes for Zn in these films.

The low magnification TEM image in figure 3(a) shows the columnar microstructure of $c$-Co : ZnO deposited on $c$-sapphire. Columnar growth results from the large (18%) lattice mismatch between the $c$-plane of sapphire and the $c$-plane of ZnO (assuming a 30° in-plane rotation of the ZnO lattice relative to the $c$-sapphire surface). As shown in the high resolution image in figure 3(b), the Co : ZnO/sapphire interface within the column is sharp and abrupt without misfit dislocations; the misfit strain is accommodated by the grain boundaries between columns. For comparison, a similar $a$-Co : ZnO film deposited on $r$-sapphire is shown in figure 4. For $a$-Co : ZnO on $r$-sapphire, the lattice mismatch is only 1.53% in the [0001]ZnO direction, but still 18% in the perpendicular [1 1 0 0]ZnO direction [46]. This results in a column-free microstructure for $a$-Co : ZnO/$r$-sapphire, as demonstrated by the low resolution image in figure 4(a). Since the strain misfit is not accommodated by columnar grain boundaries, the $a$-Co : ZnO/$r$-sapphire interface consists of many misfit dislocations, as evidenced by the high-resolution TEM image in figure 4(b). No Co clusters or other secondary phases were observed by high-resolution TEM for Co : ZnO on either substrate. Energy-dispersive x-ray spectroscopy (EDX) did not detect Co segregation to the film surface or interface.
3.2. Dopant speciation and location

Since the very small volume sampled by TEM may not be sufficient to detect highly disperse precipitates, sensitive bulk spectroscopic techniques can be more effective for detecting secondary phase formation. Thus, Co K-edge XANES and EXAFS were employed to investigate the possibility of secondary phase formation. It has been shown previously that XANES and EXAFS of doped transition metal oxides can yield valuable information on both the presence of secondary phases and the detailed local environment of the dopant [51]. Co K-edge XANES spectra for representative as-grown 10% Co:ZnO films on both c-sapphire and r-sapphire are presented in figures 5(a) and (b), respectively. The spectral lineshapes are similar to Zn K-edge XANES spectra (inset to figure 5(a)), indicating Co is in a similar local environment in the ZnO lattice. The single crystal films exhibited an x-ray polarization dependence, as expected [52]. The perpendicular polarization on the a-Co:ZnO (electric field vector $E$ perpendicular to the film surface and aligned with the $a$ lattice vector) is equivalent to the parallel polarization on the c-Co:ZnO ($E$ parallel to the film surface and perpendicular to the $c$ lattice vector), as expected from the 90° rotation of the ZnO lattice between $a$-ZnO and $c$-ZnO. However, the other polarization directions (parallel for $a$-Co:ZnO and perpendicular for $c$-Co:ZnO) are not equivalent, since for the $a$-Co:ZnO film the in-plane direction contains both the $a$ and the $c$ lattice directions (because the sample is spinning during the measurement), while the out-of-plane direction for $c$-Co:ZnO consists only of the $c$ lattice direction. The pre-edge feature at $\sim$7709 eV arises from 1s to 3d transitions, which are formally forbidden at the K edge but become weakly allowed due to Co 3d–O 2p covalency [51, 53]. This pre-edge feature is not observed for Zn K-edge XANES since the Zn 3d orbitals are fully occupied (3d$^{10}$).
Figure 4. TEM of 3000 Å $a$-Co$_{0.1}$Zn$_{0.9}$O/r-$\text{Al}_2\text{O}_3$ deposited in 10 mTorr O$_2$ at 350 °C. (a) Low-resolution image showing lack of columns and flat surface of $a$-Co : ZnO. (b) High-resolution image of the $c$-Co : ZnO/r-$\text{Al}_2\text{O}_3$ interface. Bright regions at the interface indicate the formation of misfit dislocations.

Also plotted in figures 5(a) and (b) are spectra from reference standards of Co metal foil and CoO powder. It is clear that for both Co : ZnO films, the Co absorption edge rises at the same photon energy as CoO, indicating Co is present in Co : ZnO as Co(II). However, the difference in lineshape between CoO and the Co : ZnO films, particularly in the region of 7735 eV where there is a decrease in intensity for the CoO spectrum, indicates the films do not contain CoO or other octahedral Co(II) secondary phases. The lack of intensity in the pre-edge region for the Co : ZnO films confirms the lack of a significant quantity of Co(0) in the films. The sensitivity of XANES to Co(0) is limited to approximately $\geq 5\%$ of the Co dopants forming Co(0); smaller fractions of Co(0) would be difficult or impossible to detect.

The Fourier-transformed EXAFS spectra for Co in $c$-Co : ZnO, Co in $a$-Co : ZnO and Zn in $c$-Co : ZnO are plotted in figure 5(c). The similarity between the three spectra confirms that Co substitutes for Zn (Co$_{Zn}$) in ZnO, without forming metallic or oxide secondary phases. Metallic Co–Co bonding would result in a peak in between the two ZnO peaks ($R \sim 2$ Å). While there is a small signal present in this region, it arises entirely from the ZnO environment. Fitting the Co EXAFS spectra with a combination of Co$_{Zn}$ in ZnO and Co metal sites consistently refined to give essentially pure Co$_{Zn}$ in ZnO, with no significant Co–Co metal bonding. The strong similarity of the Co spectra to the Zn spectrum in ZnO indicates the Co atoms are in well-ordered local environments without significant distortion or disorder. For all films and treatments discussed below, no significant changes were observed in the Co K-edge XANES or EXAFS, indicating negligible if any secondary phase formation under any deposition or annealing conditions explored.
3.3. Electrical and magnetic measurements

As discussed previously, Co : ZnO is generally expected to be ferromagnetic only when \( n \)-type carriers (electrons) are present in the ZnO lattice. Electrons can easily be added to the ZnO lattice by several different methods to induce \( n \)-type conductivity. Table 2 lists the methods employed in this work to obtain \( n \)-type conductivity in Co : ZnO, and the resultant resistivities of some representative films as measured by four-point probe at room temperature. Generally, the addition of Co results in more resistive films than pure ZnO films deposited under the same conditions. Co : ZnO film resistivities range from \( 10^{-4} \) to \( 10^5 \) \( \Omega \) cm, and appear to be a complex function of additional dopants, substrate temperature, oxygen pressure and laser repetition rate and power; in general, more resistive films are obtained at higher oxygen pressure, moderate substrate temperature and faster laser repetition rates. For highly resistive films (> \( 10^4 \) \( \Omega \) cm), the
Table 2. Deposition and subsequent vacuum annealing conditions for Co:ZnO thin films, and the resulting thin film resistivity as measured by four point probe at room temperature. Films from the conventional target contain nominally 10% Co, and films from the nanoparticle target contain nominally 4% Co. Films codoped with Al contain half the Co concentration of non-codoped films.

| Processing condition | O₂ pressure | Substrate temperature | Additional dopant | Conventional target | Nanoparticle target |
|----------------------|-------------|-----------------------|-------------------|---------------------|---------------------|
|                      |             |                       |                   | C-Al₂O₃             | r-Al₂O₃             |
| Deposition           | 10 mTorr    | 550 °C                | –                 | 70.000              | 95.000              |
| Anneal               | Vacuum      | 700 °C                | –                 | 0.13                | 0.11                |
| Deposition           | 10 mTorr    | 550 °C                | 1% Al             | 0.4                 | 0.18                |
| Anneal               | Vacuum      | 700 °C                | 1% Al             | 0.004               |                     |
| Deposition           | 2 × 10⁻⁵ Torr (plasma) | 550 °C | – | 0.15 | 0.54 |
| Deposition           | Vacuum      | 400 °C                | –                 | 0.9                 | 0.025               |
|                      |             |                       | 1% Al             | 0.0014              | 0.0007              |

resistivity exceeded the measurement limit of the four-point probe apparatus; the values reported are thus a lower bound of the true film resistivity. Films codoped with Al show significantly lower resistivities than undoped films, which is attributed to both the presence of Al in the film, and the slower deposition rate during codeposition from Co:ZnO and Al:ZnO targets, as discussed above. Vacuum annealing is an effective method to reduce the resistivity of Co:ZnO thin films, presumably through the creation of oxygen vacancies and/or Zn interstitials under reducing conditions. Changes in resistivity were often observed after annealing for a couple of hours at 550 °C, although annealing for several hours at 700 °C was necessary to obtain the desired magnitude of change in resistivity.

The room temperature saturation magnetization (in μᵥ/Co) of the films listed in table 2, along with other Co:ZnO thin film samples, is plotted as a function of thin film resistivity in figure 6(a). The magnitude of the moments (0.001–0.060 μᵥ/Co) is very small, indicating strong room temperature ferromagnetism has not been activated by the introduction of n-type carriers into Co:ZnO. Based on previously published results [17, 32], Co:ZnO thin films can exhibit strong magnetocrystalline anisotropy, with a substantial change in the ferromagnetic saturation moment depending on the orientation of the magnetic field relative to the film. As shown in figure 6(b), the lack of strong ferromagnetism observed in the present Co:ZnO films with the magnetic field oriented in the plane of the film is not simply an effect of magnetocrystalline anisotropy; the same level of saturation moment is observed when the magnetic field is oriented perpendicular to the film plane (parallel to the c-axis). The very small magnitudes of the observed ferromagnetic moments are near the sensitivity limit of the VSM, and are too weak to conclusively attribute to the Co:ZnO films. This is illustrated in figure 6(c), where the absolute saturation magnetic signals from the VSM (after subtracting a linear background due to the diamagnetic substrate) are plotted for all the samples shown in figure 6(a). Absolute moments less than 5 μemu can easily arise from extrinsic sources such as substrate contamination [54], even on substrates which are ferromagnetically ‘clean’.
Figure 6. (a) Room temperature saturation moment per Co for Co:ZnO thin films, measured by VSM. Film resistivities were measured by four point probe at room temperature. Blue circles: c-Co : ZnO/c-Al₂O₃; red triangles: a-Co : ZnO/r-Al₂O₃; solid lines connect resistivity values (open symbols) before and after vacuum annealing. Asterisks (*) indicate films plotted in figure 7 below. (b) VSM hysteresis loops at room temperature for 4000 Å c-Co₀.₁₅Zn₀.₈₅O/c-Al₂O₃, deposited in vacuum at 400 °C, after subtraction of a linear signal from the diamagnetic substrate. (c) Total saturation moment measured by VSM at room temperature. Dotted line: total saturation moment for 2000 Å pure c-ZnO/c-Al₂O₃. Symbols same as (a).

after etching in HNO₃ [26], as shown by the nonzero moment for pure ZnO deposited on a c-sapphire substrate. The largest magnetic moment shown in figure 6(a), 0.060 μB/Co, is shown in figure 6(c) to arise from an absolute moment of only 5 μemu. Likewise, the largest absolute moment shown (12 μemu) corresponds to an insignificant 0.014 μB/Co. Thus, these small moments indicate negligible ferromagnetism in both insulating and n-type Co : ZnO. Recent magnetization measurements at low temperature have shown that neither ferromagnetism nor a blocking temperature are observed in a similar Co : ZnO film on c-sapphire down to 5 K [55].
Behan et al [19] recently categorized the ferromagnetic properties of many Co : ZnO thin film samples according to the $n$-type carrier concentration in the film. To facilitate a comparison to that work, Hall effect measurements as a function of temperature were performed for two of the Co : ZnO samples plotted in figure 6 (marked with *) to determine the carrier concentration, mobility and resistivity behavior with temperature. Figure 7 plots the saturation magnetization (in $\mu_B$/Co) as a function of room temperature carrier concentration for these two films. Film (a) in figure 7 is insulating, according to the classification scheme of Behan et al with a room temperature resistivity of $6.8 \ \Omega \ \text{cm}$, $4.8 \times 10^{17} \ \text{cm}^{-3}$ $n$-type carriers, and a mobility of $1.9 \ \text{cm}^2/(V \ \text{s})^{-1}$. The film shows a sharp upturn in resistivity as the temperature is decreased, exceeding the measurement capacity of the PPMS at 75 K. Film (b) exhibits metallic conduction, with a resistivity of $3.0 \times 10^{-4} \ \Omega \ \text{cm}$, $5.4 \times 10^{20} \ \text{cm}^{-3}$ $n$-type carriers, 39 cm$^2/(V \ \text{s})^{-1}$ mobility, and a slight monotonic decrease in resistivity as the temperature is lowered to 5 K. In contrast to the results by Behan et al, Co : ZnO films in this work with low carrier concentration ($<10^{18} \ \text{cm}^{-3}$) and very high carrier concentration ($>10^{20} \ \text{cm}^{-3}$) were not found to be ferromagnetic. The discrepancy between the present results and those reported by Behan et al is unresolved. However, it is clear in the present work that controlled introduction of $n$-type carriers does not induce room temperature ferromagnetism in Co : ZnO thin films.

3.4. Location of Co states in ZnO band structure

The position of Co dopant states within the band structure of ZnO can be evaluated by XPS valence band spectra. The XPS valence band spectra of Al-doped ZnO and Al- and Co-codoped ZnO are shown in figure 8. Although the samples were cleaned by UV/O$_3$ treatment...
prior to introduction into the vacuum chamber, significant signals from C and OH surface contamination were detected by XPS (not shown). To minimize the effects of static charging, the samples were irradiated with a low-energy (1–2 eV) electron flood gun during measurement. After data collection, the valence band spectra were shifted (∼1–2 eV) to place the Zn 3d core level at 10 eV binding energy. The spectra were then normalized so the Zn 3d peak area for the 5% Co-doped film was reduced by 5% relative to the peak area of the undoped film. As seen in figure 8, adding Co to Al:ZnO introduces additional intensity off the top of the valence band and extending approximately 1 eV into the bandgap, with no intensity detected at the Fermi level, in agreement with previous photoemission reports [43, 44]. The new intensity presumably arises from a combination of occupied Co 3d orbitals of e symmetry (minority spin) and t$_2$ symmetry (majority spin), as predicted by recent theoretical calculations [40]–[42]. The calculations predict large exchange splitting which places the unoccupied minority-spin Co 3d t$_2$ orbitals at or very near the bottom of the ZnO conduction band. In the electronic structure description proposed by Kittilstved et al [56], the resonant interaction of these orbitals with itinerant electrons in the conduction band leads to electron-mediated ferromagnetic ordering of the Co dopants. Experimentally, the energy mismatch related to this resonance has been determined to be small on the basis of optical absorbance, magnetic circular dichroism (MCD) and photocurrent action spectroscopic measurements, which have identified the relevant Co(II)-electron coupled state within ∼0.3 eV of the ZnO conduction band minimum [56]–[58]. Unfortunately, due to the relatively low itinerant donor electron concentration (10$^{20}$ cm$^{-3}$ or less) present in the Co:ZnO films studied here, as well as extensive lifetime broadening effects in the short-lived resonance state, XPS does not have the sensitivity to detect the electrons potentially participating in the resonant interaction and filling the Co 3d orbitals near the conduction band minimum. However, optical MCD spectra of these Co:ZnO thin films (not shown) are identical to spectra reported previously for Co:ZnO nanocrystals and
thin films [13, 23], with clear features attributed to ligand field, charge transfer and excitonic transitions.

3.5. Discussion

It is clear from the results presented here that appreciable room temperature ferromagnetism has not been induced by adding $n$-type carriers to the conduction band of Co : ZnO. Thus, the interaction of itinerant carriers with Co 3d levels near the conduction band does not appear to be sufficient to align the Co spins in this case. Although XPS cannot confirm the presence of empty minority-spin Co 3d states near the conduction band minimum, optical MCD spectra confirm that there is no change in electronic structure in these high quality Co : ZnO thin films when compared to previous Co : ZnO studies [13, 23]. One potential explanation of the lack of room temperature ferromagnetism involves the role of grain boundaries and grain boundary defects in facilitating ferromagnetic ordering in Co : ZnO. As discussed previously, room-temperature aerobic aggregation of paramagnetic Co : ZnO nanoparticles was found to give rise to weak ferromagnetic signals, implying that interfacial grain boundary defects that are formed upon aggregation facilitate ferromagnetic ordering in Co : ZnO [23]. Such defects may introduce bound charge carriers capable of nucleating bound magnetic polarons, which (if present at sufficient density) may give rise to magnetic ordering [59, 60]. Of particular relevance to the present study are findings that bound magnetic polarons are generally substantially more stable than magnetic polarons involving itinerant charge carriers [61]. Such interfacial defects have now been observed to play important roles in the ferromagnetism of many doped oxides. For example, in Cr-doped anatase TiO$_2$ thin films deposited by OPA-MBE, it was found that increasing the density of low-angle grain boundaries could induce strong ferromagnetism, while Cr : TiO$_2$ films with much higher structural quality (i.e. fewer low-angle grain boundaries resulting in less mosaic spread) showed negligible ferromagnetism [26, 27]. By analogy, the lack of ferromagnetism in the present Co : ZnO films, which also exhibit good structural quality, could be due to a lack of low-angle grain boundaries. However, even in the relatively high crystalline quality films investigated here, the fundamental lattice mismatch of 18% between ZnO and sapphire ensures a reasonable quantity of misfit dislocations and other structural defects will be present. For Co : ZnO deposited on $c$-sapphire, the result is columnar growth; although the individual columns have the same nominal in-plane orientation, there exist clear grain boundaries between columns (as seen in figure 3(a)), which may be structurally similar to the low-angle grain boundaries observed as mosaic spread in other thin films. The microstructure of Co : ZnO deposited on $r$-sapphire is more complex, since columnar growth does not occur and thus other structural defects must accommodate the lattice mismatch strain (18% in one direction and 1.5% in the other). However, none of these defects appear to be able to facilitate interaction of Co dopants with conduction band electrons, precluding ferromagnetism. Thus, room temperature ferromagnetic ordering is not intrinsic to either insulating, defect-free Co : ZnO or highly conductive, high crystalline quality Co : ZnO. Instead, a combination of electronic defects to introduce itinerant electrons and structural defects to facilitate the interaction of Co dopants with the itinerant electrons appears to be required.
4. Conclusions

Thin films of Co-doped ZnO were deposited on sapphire substrates by PLD. The films were epitaxial and of high crystalline quality. The Co dopants were shown to substitute as Co(II) for Zn(II) in the ZnO lattice; no formation of secondary phases or precipitates was detected (within the sensitivity limit of ~5% of the Co dopants). Highly resistive films were obtained by deposition in high oxygen pressure. The resistivity could be lowered several orders of magnitude by deposition in low oxygen conditions or vacuum, addition of Al as an n-type dopant, and/or annealing in vacuum. However, negligible room temperature ferromagnetism was measured for all Co : ZnO films, regardless of n-type doping method or resistivity \((10^{-4} - 10^5 \Omega \text{cm})\). The lack of ferromagnetism in n-type Co : ZnO indicates that, in well-defined epitaxial films, Co spin alignment is not mediated by coupling to donor electron states. It appears that appropriate structural defects, which are not present in these epitaxial films, are required to facilitate the interaction between Co dopants and itinerant electrons in the ZnO conduction band, potentially stabilizing a ferromagnetic ground state.

Acknowledgments

We acknowledge G A Gehring for making a copy of her manuscript [19] available to us prior to publication. Zn K-edge XANES spectra were provided by Y Li. This work was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering Physics. The UW–PNNL collaboration is sponsored by the NSF (CRC-0628252) Additional support to DG from the Sloan Foundation, the Dreyfus Foundation and the Research Corporation is gratefully acknowledged. Use of the Advanced Photon Source was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under contract no DE-AC02-06CH1135.

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