Role of valence-band Co 3*d* states on ferromagnetism in $Zn_{1-x}Co_xO$ nanorods

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This work investigates the electronic and ferromagnetic properties of $Zn_{1-x}Co_xO$ nanorods using x-ray absorption, x-ray magnetic circular dichroism, and scanning photoelectron microscopy methods. The magnetic moment of Co ions in $Zn_{1-x}Co_xO$ nanorods is found greatly reduced relative to that of the Co metal. The intensities of valence-band features near the valence-band maximum/Fermi level (E_F) of ferromagnetic nanorods are substantially larger than those of weaker ferromagnetic nanorods, suggesting that the occupation of near-E_F valence-band Co 3*d* states is important in determining the ferromagnetic behavior in $Zn_{1-x}Co_xO$ nanorods. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2432234]

Dilute magnetic semiconductors[1] (DMSs) have been intensively investigated because they have a great potential for use as spintronic materials.[2] Transition metal (TM)-doped ZnO is of particular interest because its Curie temperature exceeds room temperature, so that it can be used in practical devices.[3] UV lasing at room temperature has been observed in highly oriented ZnO nanorods.[4] TM-doped ZnO nanorods, with a combination of excellent room-temperature ferromagnetic and optical properties, have attracted much interest in versatile functional nano-spintronic-device applications. However, ferromagnetism (FM) depends strongly on the sample preparation condition[5] and the nature of FM in DMSs remains controversial.[6,7] Various theoretical models[3,8–10] have been proposed to understand FM in DMSs. Thin film and polycrystalline $Zn_{1-x}M_xO$ (M=Mn and/or Fe, Co) samples have been studied using x-ray absorption[11–14] and photoemission spectroscopy.[12,15] Recently, highly oriented ZnO,[16,17] $Zn_{1-x}Co_xO$, and $Zn_{1-x}Mg_xO$ (Ref. 18) nanorods have been studied by Chiou *et al.* using x-ray absorption near-edge structure (XANES) and scanning photoelectron microscopy (SPEM). Here, a combination of XANES, x-ray magnetic circular dichroism (XMCD), and SPEM measurements was performed for ferromagnetic and weak ferromagnetic types of $Zn_{1-x}Co_xO$ nanorods to better understand the role of Co 3*d* states in influencing the ferromagnetic properties of Co-doped ZnO.

Room-temperature O *K*- and Co $L_{3,2}$-edge XANES, Co $L_{3,2}$-edge XMCD, and SPEM measurements were performed at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Highly oriented $Zn_{1-x}Co_xO$ nanorods and reference ZnO (x=0) were deposited on the Si substrate using chemical vapor deposition method. The x=0.057 and 0.078 nanorods were grown at a temperature of 525 °C, while x=0.061 and 0.082 nanorods were grown at 500 °C. Details of the preparation and characterization of the $Zn_{1-x}Co_xO$ nanorods have been presented elsewhere.[19] Scanning electron microscope (SEM) and high-resolution transmission electron microscope (TEM) measurements revealed that $Zn_{1-x}Co_xO$ and ZnO nanorods were approximately 540±50 nm long and 80±20 nm in diameter, as shown in the inset of Fig. 1.

Figure 1 presents x-ray diffraction (XRD) spectra of $Zn_{1-x}Co_xO$ and ZnO nanorods and the reference CoO powder and Co metal. $Zn_{1-x}Co_xO$ nanorods have a predominant reflection of (002) at ~34.2°, indicating that Co doping does not alter the ZnO hexagonal (wurtzite) structure. XRD spec-
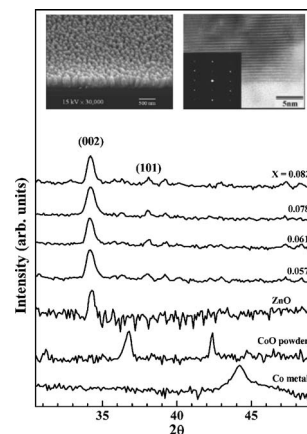

FIG. 1. (a) XRD measurements of well-aligned $Zn_{1-x}Co_xO$ and ZnO nanorods and the reference CoO powder and Co metal (the intensity in log unit). The insets show representative SEM and TEM images and the corresponding electron diffraction from $Zn_{1-x}Co_xO$ (x=0.057) nanorods.

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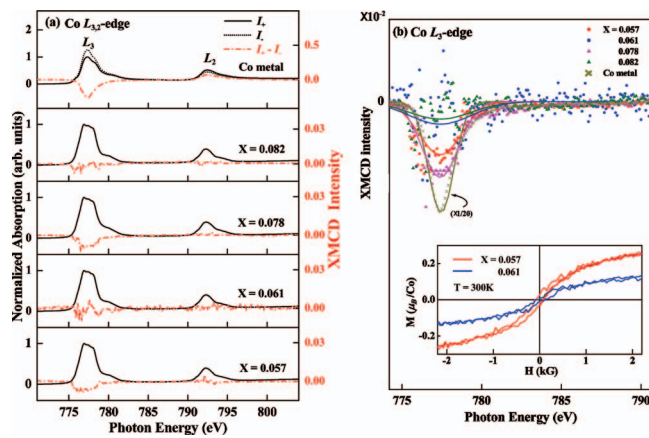
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FIG. 2. (Color) (a) Normalized Co $L_{3,2}$-edge XANES and XMCD spectra of $Zn_{1-x}Co_xO$ nanorods and the reference Co metal. (b) Magnified view of XMCD features of $Zn_{1-x}Co_xO$ nanorods and the reference Co metal at the Co L_3 edge. (The intensity of Co metal has been scaled by a factor of 1/20.) The inset plots hysteresis loops of $Zn_{1-x}Co_xO$ nanorods with $x=0.057$ and 0.061 at room temperature.
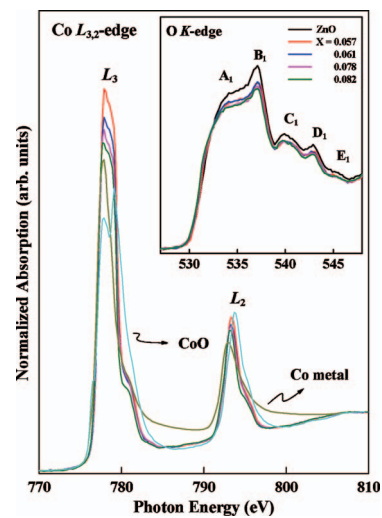

FIG. 3. (Color) Co $L_{3,2}$-edge XANES spectra of $Zn_{1-x}Co_xO$ and ZnO nanorods and the reference CoO and Co metal. The inset shows the O K-edge XANES spectra of the $Zn_{1-x}Co_xO$ and ZnO nanorods.

tra of $Zn_{1-x}Co_xO$ nanorods do not exhibit any Bragg peaks of CoO and Co metals which excludes CoO crystallite phase segregation and formation of Co clusters/precipitates in $Zn_{1-x}Co_xO$ nanorods. However, XRD measurements cannot exclude the existence of the amorphous CoO phase.[20] Structural characterization of $Zn_{1-x}Co_xO$ nanorods has also been performed using high-resolution TEM. The analyses of the bottom, middle, and top regions of those nanorods show the absence of segregated clusters of impurity phase throughout the nanorods, indicating that $Zn_{1-x}Co_xO$ nanorods have mainly a single-phase structure.

Figure 2(a) presents normalized Co $L_{3,2}$-edge XANES and XMCD (i.e., I_+-I_-) spectra of $Zn_{1-x}Co_xO$ nanorods and the reference Co metal. I_+ (I_-) refers to the absorption spectrum obtained by projecting the spin of the incident photons parallel (antiparallel) to the spin direction of the Co 3*d* majority-spin states. The general line shapes of the Co $L_{3,2}$-edge XANES spectra are very similar to those of polycrystalline $Zn_{1-x}Co_xO$ samples, reported by Wi *et al.*[12] The XMCD spectra of $Zn_{1-x}Co_xO$ nanorods show the presence of a magnetic moment, though they differ noticeably from those of the Co metal. Figure 2(b) displays the smoothly fitted curves of the noisy magnified Co L_3-edge negative XMCD data, which suggests that the nanorods ($x=0.057$ and 0.078) prepared at a higher temperature (525 °C) have larger magnetic moments than those ($x=0.061$ and 0.082) prepared at a lower temperature (500 °C). The lower inset of Fig. 2(b) shows the magnetization hysteresis loops (*M-H* curves) of the $x=0.057$ and 0.061 nanorods, respectively, which illustrates that both samples are ferromagnetic at room temperature and the one grown at 525 °C has a larger magnetic moment in consistent with the XMCD result. The magnetic moments of the Co ions in $Zn_{1-x}Co_xO$ nanorods can be estimated from the saturation of the *M-H* curves to be $\sim 0.4 \mu_B$/Co for $x=0.057$ and $0.2 \mu_B$/Co for $x=0.061$ with magnetic fields up to 1 T (not fully shown), which are about 23% and 13% of that of the Co atom in the Co metal $(1.7 \mu_B$/Co),[6] respectively. The reduction of the Co magnetic moment in $Zn_{1-x}Co_xO$ nanorods relative to that of the Co metal can be interpreted due to hybridization with the O 2*p* orbitals that delocalize Co 3*d* orbitals and can also be due to geometrical frustration of the wurtzite ZnO matrix, which

results in imperfect alignment of the spin moments of Co 3*d* electrons.

Figure 3 shows that the intensities of white-line features at the Co $L_{3,2}$ edge decrease monotonically with *x*. This trend suggests that the occupation of the Co 3*d* states increases as the Co concentration increases of $Zn_{1-x}Co_xO$ nanorods. The O K-edge spectra in the inset of Fig. 3 show that the intensities of XANES features A_1–E_1 of $Zn_{1-x}Co_xO$ nanorods are nearly identical but smaller than those of ZnO nanorods. In contrast, the O K-edge XANES spectra of the ferromagnetic Co-doped ZnO films obtained recently by Krishnamurthy *et al.* have somewhat different line shapes and have additional features relative to those of undoped film, which was interpreted by hybridization between O 2*p* and Co 3*d* and oxygen vacancies.[14] Since features A_1–E_1 are associated with electron excitations from O 1*s* to $2p_\sigma$ (along the bilayer) and O $2p_\pi$ (along the *c* axis) states,[16–18] this suggests that the occupation of O 2*p* derived states is enhanced through Co 3*d*-O 2*p* hybridization.
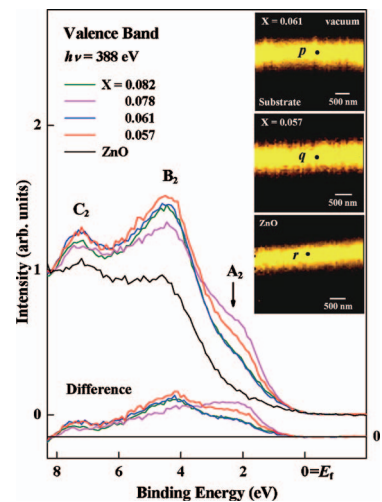
Figure 4 displays spatially resolved valence-band photo-

FIG. 4. (Color) Valence-band photoemission spectra obtained from selected positions *p*, *q*, and *r* in Zn 3*d* SPEM cross-sectional images of well-aligned $Zn_{1-x}Co_xO$ ($x=0.061$ and 0.057) and ZnO nanorods. The lower inset plots difference valence-band spectra between $Zn_{1-x}Co_xO$ and ZnO nanorods.

emission spectra of $Zn_{1-x}Co_xO$ and ZnO nanorods. The Zn $3d$ SPEM images in the insets show cross-sectional views of nanorods with $x=0$, 0.057, and 0.061, in which the bright areas have maximum Zn $3d$ intensities. Figure 4 shows photoelectron yields from the selected positions in the sidewall regions of $Zn_{1-x}Co_xO$ nanorods with $x=0.061$, 0.057, and 0.0 indicated by *p*, *q*, and *r* in the images. The zero energy refers to the valence-band maximum (VBM), which is the threshold of the emission spectrum and is also the Fermi level (E_F). The spectra exhibit two main features, B_2 and C_2. Feature B_2 is dominated by occupied O $2p$ states and feature C_2 is associated with the O $2p$ and Zn $3d/4sp$ hybridized states of ZnO nanorods.[16–18] This figure generally shows that the intensities of features B_2 and C_2 are enhanced with the Co doping. The smaller shoulder, A_2, at ~ 2 eV below E_F is attributable to the Co $3d$ partial density of states (DOSs) inferred by band structure calculations,[15,21] which can also be inferred from the comparison of the valence-band photoemission spectra of pure ZnO and $Zn_{1-x}Co_xO$ nanorods shown in Fig. 4 and of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Mg_xO$ nanorods of Ref. 18, which shows Mg doping does not increase the DOSs near E_F. Since deep-defect and dangling-bond or surface states usually lie in the vicinity of E_F, these states can also contribute to feature A_2. The monotonically decrease of the intensity of the Co L_3-edge XANES white-line feature shown in Fig. 3 with the Co content suggests an increase of the Co $3d$-orbital occupation with the Co content. However, the intensity of feature A_2 does not show the trend of $I(0.082) > I(0.078) > I(0.061) > I(0.057)$, but has an order of $I(0.078) > I(0.057) > I(0.082) \approx I(0.061)$, which does not necessarily imply an inconsistency between Co L_3-edge XANES and valence-band SPEM data, because delocalization of Co $3d$ orbitals may spread the Co $3d$ band into a region deeper than the region of feature A_2. Delocalization of the Co $3d$ band for $x=0.082$ and 0.061 is indicated by the enhancement of the intensities of their spectra relative to that of $x=0.082$ for binding energies deeper than ~ 3.7 eV.

The difference valence-band spectra between $Zn_{1-x}Co_xO$ and ZnO nanorods are plotted at the bottom of Fig. 4. The intensities of SPEM features A_2 and B_2 for $x=0.57$ nanorods are larger than those for $x=0.061$ and 0.082 nanorods. The intensities of features A_2 and B_2 are enhanced and reduced, respectively, for $x=0.078$ nanorods relative to those of $x=0.057$ nanorods. Since a larger intensity of feature A_2 corresponds to more localized Co $3d$ orbitals and consequently larger Co magnetic moment, the SPEM result suggests that the $x=0.078$ sample has the largest Co magnetic moment, followed by the $x=0.057$ sample and both $x=0.082$ and 0.061 samples have the smallest Co magnetic moment in consistent with that inferred from the XMCD and the magnetization hysteresis loop data. Note that Sato and Katayama-Yoshida in a theoretical study also correlated ferromagnetism in $Zn_{1-x}Co_xO$ nanorods with high DOSs of Co $3d$ minority-spin states at/near E_F.[22]

The combination of Co $L_{3,2}$-edge XMCD and valence-band SPEM results shows that the density of the Co $3d$ states in the vicinity of E_F plays an important role in the determination of the ferromagnetic property of $Zn_{1-x}Co_xO$ nanorods. The present result is different from those of Krishnamurthy *et al.*[14] and Venkatesan *et al.* and Coey *et al.*[10] for $Zn_{1-x}Co_xO$ thin films. They proposed that Co magnetic moments are

closely related to the overlapping of unoccupied TM $3d$ states with *shallow* donor states, which lie about 3.2 eV (band gap of ZnO) above VBM. Durst *et al.* argued that defects tend to form bound magnetic polarons that couple with Co $3d$ moments within its orbits and the overlapping of two similar magnetic polarons induces spin-spin interactions between Co ions, which stabilizes the ferromagnetic ordering in $Zn_{1-x}Co_xO$ nanorods.[23] The validity of this argument requires relatively long ranged spin polarization of O ions by the defects, which is incompatible with the present observation of the lack of correlation between O K-edge spectra of $Zn_{1-x}Co_xO$ nanorods and their magnetic properties as shown in the inset of Fig. 3.

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