1-1-2010

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Additional information on J. Appl. Phys.

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To avoid the occurrence of doped magnetic ion clustering is a challenge in fabrication of diluted magnetic semiconductors (DMSs). In this work, we report the intrinsic ferromagnetic behavior in Co-doped ZnO DMSs induced by Eu codoping. Both structural parameters and magnetic properties demonstrate the existence of an interaction between Co and Eu ions. The observation of multiplet structures for the localized Co $3d$ states in x-ray absorption and x-ray magnetic circular dichroism characterization evidences that the codoped Eu plays an important role in facilitating the Co substitution of Zn, leading to intrinsic ferromagnetism. © *2010 American Institute of Physics.* [doi:10.1063/1.3298507]

I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have attracted enormous interests because of their potential for innovative spintronics application.[1,2] Currently, the most common DMSs are II-VI and III-V compounds (such as CdTe, ZnSe, CdSe, ZnO, GaN, GaAs, etc.), with transition metal ions (e.g., Mn, Fe, or Co) substituting their original cations. Although values of Curie temperature above room temperature have been reported in Co-doped TiO_2,[3] ZnO,[4] and Mn-doped GaN,[5] the possibility of an extrinsic origin of the ferromagnetism, such as ferromagnetic impurity segregation, could not be ruled out in most cases. It was reported that the nanoscale ferromagnetic phase in Co-doped ZnO thin films is due to the Co clusters.[6] This gives rise to an argument: homogeneous films of (Zn,Co)O exhibited a spin-glass behavior while room temperature ferromagnetism was only found in inhomogeneous films attributed to the presence of Co clusters.[7] Such an argument on the origin of ferromagnetism in (Zn,Co)O is caused by the often-performed magnetization measurements with a magnetometer [e.g., superconducting quantum interference device (SQUID)], which is unable to distinguish an intrinsic ferromagnetic signal from an extrinsic one.[8] Recent progress for the investigation of the nature of ferromagnetism in (Zn,Co)O with other advanced materials characterization tools provides a better way to develop the intrinsic DMS materials. Although ion implantation is a common and simple technique to fabricate semiconductor materials with the advantage of creating nonequilibrium doping suited for achieving desired dopant concentrations, it was reported that the occurrence of Co clustering is frequently observed in the (Zn,Co)O thin films prepared by the ion implantation technique.[9] This has impeded the application of ion implantation in the fabrication of DMSs. Therefore, the development of dilute magnetic-impurity-doped functional wide-bandgap semiconductors, such as (Zn,Co)O, with high-temperature ferromagnetism is eagerly awaited if it is unambiguously established to be intrinsic in nature.[8] In this study, we report the experimental evidence of Co substitution in ZnO epitaxial films induced by Co and Eu codoping as well as the results on the localized magnetic moment of Co in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ determined by x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD).

II. EXPERIMENT

The $Zn_{96}Co_{0.04}O$ and $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ materials were prepared by ion implantation.[10] The ZnO (0001) epitaxial thin film, ~100 nm thick grown on *c*-sapphire, was implanted with Co and Eu ion beams perpendicular to its surface under a vacuum pressure of 2×10^{-6} mbar. The TRIM calculation[11] was performed to optimize implanting parameters for the ZnO epitaxial thin film. For the codoped sample of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$, Co was implanted first followed by Eu. The dose concentrations and the ion distribution depth profiles were verified by Rutherford back scattering (RBS) measurements. At the above mentioned implantation parameters, both Co and Eu have an average concentration of 4%. The crystallographic structures of the as-prepared materials were characterized using X'Pert PRO Materials Research Diffractometer that is specially designed for x-ray diffraction (XRD) characterization of thin films with Cu $K\alpha_1$ radiation. The magnetic properties of doped ZnO films were determined using a SQUID magnetometer (Quantum Design MPMS-XL). Local electronic structure and magnetic moments of Co were studied by XAS and XMCD at BL11A Dragon beamline of National Synchrotron Radiation Research Centre in Taiwan. XAS spectra at the Co $L_{2,3}$ edge were measured in total fluorescence yield mode to probe the properties throughout the entire thickness of the films at both

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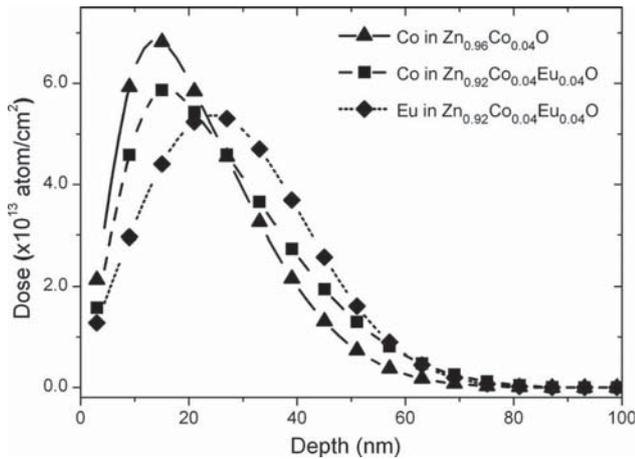a)Electronic mail: sean.li@unsw.edu.au.

FIG. 1. Distribution of Co and Eu ions as a function of depth. X axis is depth (nanometer) from the top surface and Y axis is Co or Eu dose at a particular depth.

FIG. 2. (Color online) θ-2θ XRD patterns of ZnO, $Zn_{0.96}Co_{0.04}O$, and $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ thin films. Inset shows the normalized (0002) peak.

room temperature and 77 K. The propagation direction of the incident circular polarized x-ray ($\sim$80% polarization) was 30° with respect to the surface of the samples. A magnetic field of 1 T was applied along the surface plane of the samples. XMCD spectra originated from the difference of the spin-resolved XAS corresponding to two opposite magnetic fields after proper background subtraction.

III. RESULTS AND DISCUSSION

Figure 1 shows the depth profiles of Co and Eu, which are analyzed with RBS measurement, in the as-prepared thin films. It is discernable that the peak of Co depth profile in $Zn_{0.96}Co_{0.04}O$ (the sample with Co dopants only) is located at $\sim$15 nm underneath the film surface. The subsequent Eu implantation changed the implanted Co distribution profile of depth. Although the peak position of Co depth profile remains unchanged, Co distribution profile broadens, having more Co in the depth range of >25 nm by comparing to $Zn_{0.96}Co_{0.04}O$. In $Zn_{0.96}Co_{0.04}Eu_{0.04}O$, the peak of Eu depth profile is positioned at $\sim$26 nm, similar to the depth estimated by TRIM calculation. It is noted that in this work our strategy is to maintain the similarity of Co distribution profiles between the Co-doped ZnO film and the Co–Eu codoped ZnO film to investigate the subtle interplay between Co and Eu.

XRD spectra of ZnO, $Zn_{96}Co_{0.04}O$, and $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ thin films in Fig. 2 show that the as-implanted films were single phase with a wurtzitelike structure. No secondary phases including Co and Eu alloys were detected in the samples. The strong and sharp (0002) diffraction found in the as-grown ZnO film shows that the ZnO film was well crystallized. A small left shift of the (0002) peak appearing in $Zn_{0.96}Co_{0.04}O$ demonstrates the expansion of c lattice parameter caused by Co dopants. The c was expanded from 5.2084 Å for the ZnO film to 5.2099 Å for the $Zn_{0.96}Co_{0.04}O$. It was reported that the substitution of Zn^{2+} (ion radius of 0.60 Å) with high-spin Co^{2+} (ion radius of 0.58 Å) in tetrahedral coordination results in the reduction in c with large compressive strain.[4,12] Therefore, the expansion of
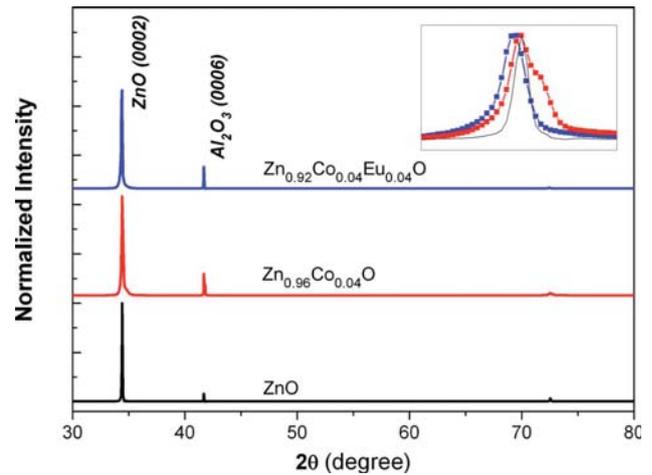
c induced by Co suggests that Co ions do not fully substitute Zn in the wurtzite lattice points with +2 formal oxidation state. It implies that the Co ions may exist with the form of either Co metal nanoclustering or the interstices accommodated in octahedral interstitial sites of the wurtzite structure or both in $Zn_{0.96}Co_{0.04}O$. The lattice constant c of the Co and Eu codoped sample $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ is 5.2127 Å which is larger than that of $Zn_{0.96}Co_{0.04}O$. It is understandable that the addition of large Eu ions into the Co-doped ZnO can result in a larger c than that of $Zn_{0.96}Co_{0.04}O$ due to the substantial difference of ion radii between Zn and Eu, where the radii of Eu^{2+} and Eu^{3+} are 1.17 and 1.03 Å, respectively.[13] The normalized (0002) peaks are shown in the inset of Fig. 2. It is found that the peak of $Zn_{96}Co_{0.04}O$ is asymmetrical and looks like consisting of two peaks in the first glance. However, if it were true, the other peaks of a secondary phase should be observed in the XRD spectra. So the observed phenomenon may be due to inhomogeneous distribution of Co in the Co-doped ZnO film. Furthermore, the full width at half maximum of the (002) peak reduces remarkably for $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ compared to that for $Zn_{96}Co_{0.04}O$. These strongly indicate that Eu and Co couples to reduce inhomogeneous strain, meaning the existence of a subtle interaction between Co and Eu in the codoped materials. The coupling of the compressive and tensile strains caused by the doped Co and Eu individually can minimize the energy of system. This may break the network of the Co metal nanoclusters, thus enhancing Co substitution at Zn lattice sites.

Figure 3 shows isothermal magnetization curves of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$ as a function of the external magnetic field applied parallel to the film surface. It demonstrates that $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$ possesses ferromagnetism at room temperature with a coercive field of 60 Oe as shown in the hysteresis loop. The saturation magnetization (M_s) of 65 emu/cm^3, equivalent to 2.09 μ_B/(Co+Eu), with the remanent magnetization of 5.2 emu/cm^3 and the M_s of 50 emu/cm^3, equivalent to 3.21 μ_B/Co, with the remanent magnetization of 3.0 emu/cm^3 were determined for $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$, respectively. The presence of ferromagnetism
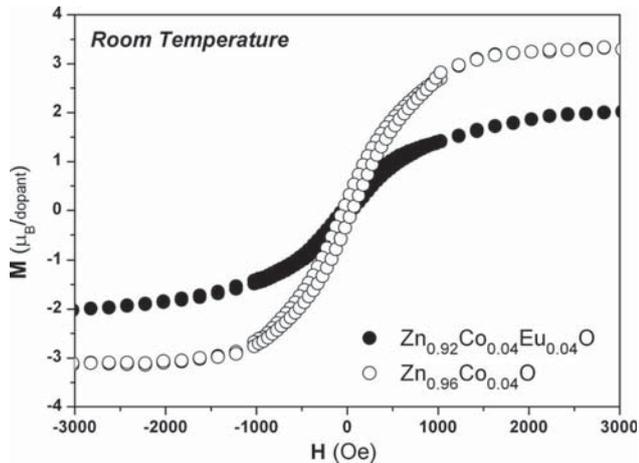
FIG. 3. Magnetization curves of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$ thin films measured by a SQUID magnetometer at room temperature, after the subtraction of diamagnetic contribution of Al_2O_3 substrate. The external applied field was applied parallel to the film surface. (Note: dopants for $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$ refer to Co+Eu and Co, respectively.)

in $Zn_{0.96}Co_{0.04}O$ supports Co's clustering in the film. The ferromagnetism in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ may be sourced from the substitution of the implanted Co and Eu. Our theoretical studies using *ab initio* calculations show that Eu dopants in the ZnO host lattice are preferably substitutional at the Zn site by examining three different possible cases: (i) the octahedral interstitial site of the perfect hexagonal ZnO lattice, (ii) the octahedral interstitial site where a neighboring Zn vacancy exists, and (iii) the substitutional Zn site. Total energy calculations show that in $Zn_{0.875}Co_{0.0625}Eu_{0.0625}O$, the ferromagnetic interaction between Co and Eu is stronger than the ferrimagnetic one where the spin alignment of Eu and Co ions is antiparallel.

Figure 4 shows XAS and XMCD spectra of the Co $L_{2,3}$ edge of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ measured at room temperature and 77 K. The absorption at the Co $L_{2,3}$ edge is associated with Co 2p to 3d transition, which provides information of unoccupied density of Co 3d states by probing the projected
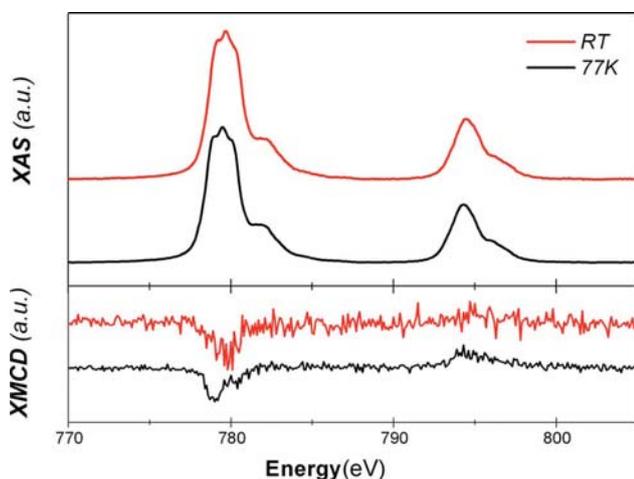

FIG. 4. (Color online) XAS spectra (top) and their derived XMCD spectra (bottom) of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ measured at the Co $L_{2,3}$ absorption edges at room temperature and 77 K.
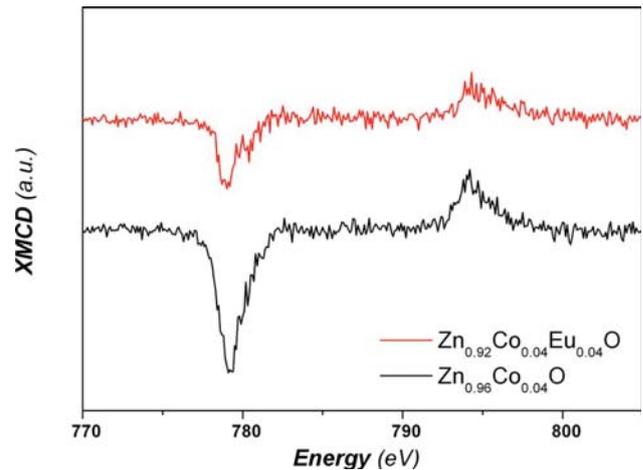

FIG. 5. (Color online) XMCD spectra of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$ measured at the Co $L_{2,3}$ absorption edges at 77 K.

3d magnetism of Co.[14] It can be seen from the XAS and XMCD spectra that the absorption at Co L_2 and L_3 is different from those of Co metals. By comparing with the theoretical XAS results,[15] it is discernable that the observed tetrahedral multiple structures are consistent with the local electronic structure of Co substitution at the tetrahedral Zn site. This provides strong evidence of Co substitution induced by the Eu codoping. From our comprehensive investigation with first-principles density functional calculations, it is interesting to find that the possibility of Eu^{2+} and Eu^{3+} coexistence can be ruled out and only Eu^{2+} can appear in the materials with the spinning state of 7. This detail work will be reported in elsewhere. The Co magnetic spin moment (m_s) of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ derived from XMCD sum rules[16] is 0.082 ± 0.020 μ_B per Co atom at room temperature and 0.096 ± 0.014 μ_B per Co atom at 77 K. It suggests that the temperature has very limit effects on the localized magnetic spin moment of Co in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$. XMCD spectra of the Co $L_{2,3}$ edge of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ and $Zn_{0.96}Co_{0.04}O$ measured at 77 K are compared in Fig. 5. The m_s of Co in $Zn_{0.96}Co_{0.04}O$ is 0.191 ± 0.016 μ_B per Co atom at 77 K, which is obviously larger than that for $Zn_{0.92}Co_{0.04}Eu_{0.04}O$. The large magnetic spin moment from the $Zn_{0.96}Co_{0.04}O$ may be contributed from Co metal nanoclusters presented in the sample. On the other hand, the smaller Co magnetic spin moment in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ may be caused by enhanced Co substitution in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$, indicating a strong interaction between Co and Eu in the codoped sample. This is in agreement with aforementioned magnetic properties which further supports the notion that the Co substitution was facilitated by Eu codoping in ZnO.

It is well known that the Co metal nanoclustering easily forms in vacuum processing environment. It is often observed in the samples prepared with ion implantation techniques,[9] thus resulting in the large localized spin moments.[17] Consequently this process may facilitate the replacement of Zn with Co in the wurtzite lattice. Therefore, the Co magnetic contribution in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ thin films would arise from the intrinsic Co substituting Zn. The energy of Eu L edge is too high to be determined due to the

facility measurement limit. Since the signal at $M_{4,5}$ edge in our measurement is very weak with a strong background of noise, it leaves an open question on the measurement of magnetic spin and orbit moments of Eu for future investigation. It is believed that the Co–Co spin coupling in perfect ZnO lattice structure is antiparallel,[18] similar to Eu–Eu spin coupling. However, total energies calculations show that in its most stable configuration of $Zn_{0.875}Co_{0.0625}Eu_{0.0625}O$ parallel Co–Eu spin coupling is stronger by 57 meV than antiparallel. Therefore, the magnetic contribution in $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ thin films would arise from the ferromagnetic interaction between substitutional Co and Eu. Atomic ratio of Co and Eu needs to be optimized to achieve the best performance. A systematic study on the detailed interaction between Co and Eu on crystal and electrical structures with XAS to analyze the extended x-ray absorption fine structure is currently in progress. Furthermore, the room temperature photoluminescence was used to determine the structural disordering induced by the implantation process and its results show no artifact is induced during the materials preparation.

IV. CONCLUSION

We have studied the structural and magnetic properties of $Zn_{0.92}Co_{0.04}Eu_{0.04}O$ thin films prepared by ion implantation technique. Room temperature ferromagnetism was observed with a saturation magnetization of 65 emu/cm^3, a coercivity of 60 Oe and a remanent magnetization of 5.2 emu/cm^3. XAS spectra of Co $L_{2,3}$ edge show that the Co ions reside in the tetrahedral coordination, demonstrating its substitution of Zn in the wurtzite structure. XMCD spectra of Co $L_{2,3}$ edge also reveal that Co metal nanoclustering may not form in Co and Eu coimplanted ZnO as evidenced by Co tetrahedral multiplet structures. It suggests that Co substitution at the Zn sites may be facilitated by Eu codoping and thus the Co metal clustering is suppressed significantly.

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