Tailoring the coercivity in ferromagnetic ZnO thin films by 3d and 4f elements codoping
J. J. Lee, G. Z. Xing, J. B. Yi, T. Chen, M. Ionescu, and S. Li

View online: http://dx.doi.org/10.1063/1.4861165
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/1?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Enhanced room temperature ferromagnetism in electrodeposited Co-doped ZnO nanostructured thin films by controlling the oxygen vacancy defects

Dose dependence of ferromagnetism in Co-implanted ZnO

Magnetic, electrical, and microstructural characterization of ZnO thin films codoped with Co and Cu

Magnetic circular dichroism of ferromagnetic Co 2 + -doped ZnO

Ferromagnetism in 200 - MeV Ag + 15 -ion-irradiated Co-implanted ZnO thin films
Tailoring the coercivity in ferromagnetic ZnO thin films by 3d and 4f elements codoping

J. J. Lee, G. Z. Xing, J. B. Yi, T. Chen, M. Ionescu, and S. Li

School of Materials Science and Engineering, The University of New South Wales, Sydney, New South Wales 2052, Australia
Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong
Australian Nuclear Science and Technology Organization, Sydney, New South Wales 2234, Australia

(Received 21 November 2013; accepted 17 December 2013; published online 8 January 2014)

Cluster free, Co (3d) and Eu (4f) doped ZnO thin films were prepared using ion implantation technique accompanied by post annealing treatments. Compared with the mono-doped ZnO thin films, the samples codoped with Co and Eu exhibit a stronger magnetization with a giant coercivity of 1200 Oe at ambient temperature. This was further verified through x-ray magnetic circular dichroism analysis, revealing the exchange interaction between the Co 3d electrons and the localized carriers induced by Eu$^{3+}$ ions codoping. The insight gained with modulating coercivity in magnetic oxides opens up an avenue for applications requiring non-volatility in spintronic devices.

Beyond the conventional semiconductor electronics, the spintronics has attracted much attention due to the possibility to forge a new era in information technology. As one of the key constitutes in spintronics, the diluted magnetic semiconductors (DMSs) have received enormous interests because of their potential for innovative magneto-optoelectronic applications. With a wide band gap of ~3.37 eV at room temperature, ZnO is one of the most promising candidates as the host material for DMSs. However, the majority of the reported magnetism and coercivity in ZnO-based DMSs is often weak and small, there is a pressing need to improve their magnetic properties to explore the reliable data storage applications with controllable magnetism and coercivity. It is believed that the codoping of two transition metals (TMs) [(Fe,Co)] can increase the saturation magnetization in ZnO system. Compared with TMs, rare earth (RE) dopants may offer stronger magnetism due to the higher 4f orbital magnetic moments. The RE ions (Gd, Er, and Nd) doped DMSs have invoked great interest as Gd-doped GaN exhibits a colossal magnetic moment. However, the reported paramagnetic behaviour from ZnO codoped with Gd/Sm and Mn was related to the secondary phase formation of RE oxides. Nevertheless, the solubility of RE in ZnO is strongly limited by the lattice distortion associated with much larger ionic radius of RE atoms.

The ion implantation was widely used to achieve the controlled dose of magnetic elements doping in ZnO matrix, including TM and RE-doped ZnO. Although the intensive research efforts have been carried out, the reported results in this field were still controversial due to the tendency of ferromagnetic segregation. But most recently, the experimental results have demonstrated that the aggregation of Co magnetic ions can be controlled by codoping with RE element of Eu and this has also been further verified by the first-principles calculation based on the density functional theory. However, the origin of this mechanism is still unclear and the interaction between 3d and 4f elements in the codoping systems has not been revealed. In this work, we experimentally investigated the effects of Co (3d) and Eu (4f) codoping on the structural and magnetic properties in ZnO systems and the corresponding mechanism is proposed and discussed in detail.

The Co and Eu mono-doped and codoped ZnO thin films were prepared by ion implantation with meticulous post-annealing treatments. Commercial 100 nm thick ZnO (001) epitaxial films grown on c-sapphire (Nanovation, France) substrates were implanted with Co and Eu ion beams perpendicular to the film surface, under a vacuum pressure of $1 \times 10^{-4}$ Pa. Prior to experiments, the Stopping and Range of Ions in Matter (SRIM) technique was employed to optimize the stopping powers and implantation depth of Co and Eu ions. The accelerated voltage for Co and Eu was calculated to be 30 kV and 45 kV to generate an average implantation depth of 15 nm. The fluence of Co and Eu was regulated at $1.65 \times 10^{16}$ atoms/cm$^2$, which corresponds to a Co and Eu nominal doping concentration of 4 at.%, in the implanted region of ZnO film. All samples were annealed at 600°C for 30 min in the flowing argon (2 l/min) environment.

Rutherford Backscattering Spectroscopy (RBS) was carried out to investigate the implantation dose and the depth profile of implanted species. Figure 1(a) shows the distribution profile of Co and Eu species as a function of implantation depth. Clearly, the implanted Co and Eu ions are located in the near surface of the film and the depth distribution is close to our SRIM results. Fig. 1(b) shows the x-ray diffraction (XRD) patterns obtained on the as-received and implanted ZnO thin film samples in $\theta$-2$\theta$ geometry. Both the virgin and implanted ZnO films exhibit single phase with a typical wurtzite ZnO structure, showing a c-axis out-of-plane orientation with only (002) and (004) diffraction peaks. No secondary phases, such as Co or Eu metallic clusters and corresponding oxides, were detected in the samples within the detection limit. The (002) diffraction peaks of implanted films were normalized against the (006) planes of Al$_2$O$_3$ substrates [Fig. 1(c)]. It shows that the (002) peak in Zn$_{0.96}$Co$_{0.04}$O sample shifts towards higher diffraction angle

---

$^{a}$Email: guozhong.xing@unsw.edu.au

0003-6951/2014(104(1))/012405/5/$30.00

104, 012405-1 © 2014 AIP Publishing LLC

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 149.171.195.101 On: Mon, 06 Jul 2015 00:00:03
in comparison with the undoped ZnO, demonstrating that the c lattice undergoes a shrinkage of \(-0.115\%\) from 5.2131 Å to 5.2125 Å after doping. The shifting of (002) towards higher diffraction angle is due to the four-fold coordinated ion radius of Co\(^{2+}\) (0.058 nm) being smaller than that of Zn\(^{2+}\) (0.06 nm). In contrast, the introduction of Eu ions into ZnO causes (002) peaks to shift towards lower diffraction angle. In this case, c lattice expands \(-0.38\%\) from 5.2131 Å in ZnO to 5.2331 Å in Zn\(_{0.96}\)Eu\(_{0.04}\)O. The incorporation of both Co and Eu ions in ZnO lattice causes the ZnO (002) peak shift to the lower angle indicating a net c-axis expansion of \(-0.31\%\) from 5.2131 Å to 5.2294 Å. This suggests that the substitution of large Eu ions, with the four fold coordinated ionic radii of Eu\(^{2+}\) and Eu\(^{3+}\) of 0.117 nm and 0.095 nm, respectively, into the small Zn ion sites in ZnO induced a considerable lattice distortion.

There have been a few reports attributing ferromagnetism to extrinsic sources such as ferromagnetic clusters or secondary phases. Raman measurements were carried out on the as-received and Co and Eu ions implanted ZnO thin films with 514.5 nm laser excitation. The results show that there were no Co and Eu-related secondary phase within the detection limit, as shown in Fig. 1(d). The A\(_1\)(TO) peaks at 380 cm\(^{-1}\) and E\(_2\) (high) mode peaks at 437 cm\(^{-1}\) were observed in all samples while the A\(_1\)(LO) mode only appears in some samples and this could be associated with the wide coverage of the strong sapphire E\(_g\) mode centred at 576 cm\(^{-1}\). The additional Raman modes (AM) centred at 560 cm\(^{-1}\) were detected in all implanted samples and were ascribed to the multiphonon scattering induced by a disordered ZnO structure. The \textit{ab-initio} calculations results predicted that the Raman modes around 560–580 cm\(^{-1}\) were contributed by B\(_1\) (high) silent mode of wurtzite ZnO, and it can be caused by the relaxation of the Raman selection rules associated with the breakdown of translational symmetry, triggered by the remarkable difference in mass between the Eu and Zn ions. As a consequence, the observed AM can be strongly related to the intrinsic defects in ZnO host, e.g., oxygen vacancies (V\(_O\)) or Zn interstitials (Zn\(_i\)). This assumption is supported by the fact that no AM appears in the as-received undoped ZnO thin films.

Figure 2 shows the field dependence of magnetization (M-H) curves, which were taken at 300 K and 5 K on the undoped and doped thin films. Both mono-doped and codoped ZnO films exhibit clear hysteresis loops at 300 K and 5 K, suggesting the room temperature ferromagnetism. It
has been reported that the pure ZnO alone can give a weak ferromagnetism if they contain sufficient intrinsic defects.\textsuperscript{5,21,22} To examine this possibility, the undoped ZnO was first measured by superconducting quantum interference device (SQUID) magnetometer and the results showed only diamagnetic contribution [insets of Figs. 2(a) and 2(b)]. The diamagnetic contribution from the undoped ZnO was subtracted from the magnetic signal of the doped ZnO samples. After calculation, the saturation moments ($M_s$) for Zn$_{0.96}$Co$_{0.04}$O, Zn$_{0.96}$Eu$_{0.04}$O, and Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O are $7\text{emu/cm}^3$, $9\text{emu/cm}^3$, and $18.2\text{emu/cm}^3$ at room temperature while $8.5\text{emu/cm}^3$, $11\text{emu/cm}^3$, and $28.6\text{emu/cm}^3$ at 5 K, respectively. The possible secondary phase such as metallic europium is antiferromagnetic with a $T_N = 91$ K, and europium oxide (Eu$_2$O$_3$) is paramagnetic at room temperature.\textsuperscript{23} On the other hand, the contribution of both Co and Eu mono-doped samples, indicating that the magnetic contribution is not simply collinear, but more complex and warrants further investigation as follows.

The coercivity ($H_c$) of Zn$_{0.96}$Co$_{0.04}$O, Zn$_{0.96}$Eu$_{0.04}$O, and Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O are 150 Oe, 286 Oe, and 1200 Oe at 300 K, while the $H_c$ at 5 K are 200 Oe, 370 Oe, and 1340 Oe, respectively. Compared with the mono-doped ZnO thin films, the codoped samples with 3$d$ and 4$f$ elements exhibit a much higher $H_c$. Surprisingly, the observed giant $H_c$ of our codoped samples at 5 and 300 K are the highest values among all the diluted magnetic oxides reported up to date, and even rivals some of the manganite compounds.\textsuperscript{11} There are two basic theories have been developed since Néel published the fundamental work on the coercive force of magnetic materials.\textsuperscript{27} The potential theory,\textsuperscript{28} which deals with rigid domain walls of a finite length, and the domain wall bowing theory,\textsuperscript{29} which considers the domain wall to be flexible in one dimension. In the former case, the coercive force is determined by spatial fluctuations of the defect concentration, which plays the role of the rigid domain wall pinning centres. In the latter case, it studies the interaction between domain wall and localized pinning centres. The giant coercivity observed in our Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O films may be associated with both domain-wall pinning effects and the stress anisotropy originated from the defects, which were induced during ion implantation process. The intrinsic defects create energy levels within ZnO band gap, which presumably hybridize with the electrons located at Co 3$d$ shell and Eu 4$f$ shell, thus triggering the onset of magnetic orderings with higher reversal field energy.\textsuperscript{11,25} On the other hand, the lattice distortion in ZnO host due to different ionic radii between Eu and Zn can induce a large strain, which acts as the pinning centres for the domain walls, thus impeding the rotation of the magnetization. Since $H_c$ between 350 and 4000 Oe is often desirable for the typical magnetic storage media, the observed $H_c$ makes the Co and Eu codoped ZnO thin films a promising candidate for the data storage applications that particularly require a non-volatility feature.\textsuperscript{26}

The x-ray photoelectron spectroscopy (XPS) was employed to study the electronic structure of Co and Eu codoped ZnO thin films. Prior to XPS measurements, the surface of samples was sputtered with an Ar ion beam for 40 s (equivalent to a depth of 16 nm). A typical XPS survey scan obtained on Co and Eu codoped ZnO film is shown in Fig. 3(a), in which only Zn, O, Co, Eu, and C elements were detected. Taking the standard spectra of metallic Co, CoO, and Co$_2$O$_3$ as reference, the spectra of Co 2$p$ core level of Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O show only Co$^{2+}$ valence state in the samples and the signals of Co$^{3+}$ and Co$^{4+}$ were undetectable within the resolution of the technique,\textsuperscript{30} excluding any potential metallic Co clusters existence, which is consistent with XRD and Raman experimental results. The core-level spectrum of Eu 3$d$ can be de-convoluted into two groups due to the multiple spin-orbit interactions belonging to $J = 3/2$ and 5/2 components, exhibiting a dominant peak that corresponds to Eu$^{3+}$ trivalent ions and a satellite peak characteristic of Eu$^{2+}$ divalent ions. One possible reason for the
occurrence of Eu$^{2+}$ is due to the preferential sputtering of Argon ions, wherein a cation charge compensation process might be responsible for the Eu valence transition from 3$^+$ to 2$^+$ within a few atomic layers. Nonetheless, no 2$^+$ valence was present in the x-ray absorption spectroscopy (XAS) studies, with an overall investigation sampling the entire implanted layer in Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O film sample [Fig. 3(c)].

In order to gain deeper insight into the origin of ferromagnetism and giant coercivity in Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O films, x-ray magnetic circular dichroism (XMCD) measurements were performed at WERA beam line in Germany. The XMCD signals were collected with a magnetic field applied up to ±2 T. Fig. 3(b) shows the XAS and XMCD spectra of the Co L$_{2,3}$-edge of Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O thin films measured under total electron yield (TEY) mode at 10 K. The absorption at the Co L$_{2,3}$-edge is associated with Co 2p to 3d transition, which provides the information of unoccupied density of Co 3d states by probing the projected 3d magnetism of Co. The XAS and XMCD spectra show that the absorption at Co L$_{2,3}$-edge are different from those of Co metals. By comparing with the theoretical XAS results, it is discernible that the observed tetrahedral multiple structures are consistent with the local electronic structure of Co substitution at the tetrahedral Zn lattice site. Metallic Co cluster would exhibit strongly different spectral shapes and nearly quenched orbital moments. This again excludes the possibility of formation of Co clusters. The XAS spectra in Fig. 3(c) show the Eu M$_{4,5}$ edge photon absorption of Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O films. The absorption at M$_{5}$ edge (3d$_{5/2}$ → 4f) shows at least 2 peaks that may be associated with the multiplet splitting of Eu$^{3+}$ ions. The position of the multiplet peaks in M$_{4,5}$ absorption edge is in good agreement with the theoretical analysis reported in literature. From the XAS spectra of Eu M$_{4,5}$ edge, no trace of Eu$^{2+}$ ions was observed. Although the Eu$^{3+}$ ground state $J$ is 0, the XMCD signal shows the evidence with the presence of Eu paramagnetic moment in Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O films, which was ascribed to the paramagnetism with temperature independent susceptibility arise in the low temperature known as Van Vleck paramagnetism.

XMCD loops at 10 K as a function of magnetic field that was applied perpendicular to the film plane are shown in Fig. 3(d). The magnetization curve of the Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O film shows a large hysteresis loop with a coercive field of 1200 Oe, a characteristic of ferromagnetism at low magnetic field and a paramagnetic component at high magnetic field. The observed giant coercivity of Zn$_{0.92}$Co$_{0.04}$Eu$_{0.04}$O film from XMCD hysteresis loop is consistent with SQUID measurements. The origin of paramagnetic components at 10 K might be associated...
with the exchange interaction with the localized carriers resulted from Eu\(^{3+}\) ions bearing with the van Vleck paramagnetism. This suggests that the ferromagnetic component in the Co (3d) and Eu (4f) elements codoped ZnO films should be predominantly originated from the Co elements in ionic states. The formation of metallic clusters and secondary phases were excluded in Zn_{0.92}Co_{0.04}Eu_{0.04}O films from our extensive XRD, Raman, XPS, and XAS measurements. The observed giant \(H_c\) in the Co XMCD loop at \(L_3\) edge corroborates the interaction between the Co 3d electrons and the localized carriers induced by Eu\(^{3+}\) ions codoping, which is in line with our SQUID measurements.

In summary, our experimental results demonstrated that the coercivity modulation in cluster free Co and Eu codoped ZnO thin films can be achieved through doping engineering, which favours the exchange interaction between Co 3d electrons and the localized carriers induced by Eu\(^{3+}\) ions codoping. These findings highlight the potential of 3d and 4f elements codoping technique for tailoring the magnetic properties in transparent magnetic oxides for fabricating a wide range of components for spintronics applications requiring non-volatility.

This work was supported by Australian Research Council DP1096769, AINSE, Vice-Chancellor’s Fellow Program No. (SIR50/PS26746), Faculty of Research Grant Nos. (IR001/PS30560), ARC FT100100956, and DP110105338 at University of New South Wales. The authors thank the support from WERA beam line in ANKA, Kaisruhe Institute Technology University (KIT) for XAS/XMCD measurements.