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Electron concentration dependent magnetization and magnetic anisotropy in ZnO:Mn thin films

Z. Yang and J. L. Liu[a]
Quantum Structures Laboratory, Department of Electrical Engineering, University of California, Riverside, California 92521, USA

M. Biasini and W. P. Beyermann
Department of Physics and Astronomy, University of California, Riverside, California 92521, USA

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Well-above room temperature and electron concentration dependent ferromagnetism was observed in *n*-type ZnO:Mn films, indicating long-range ferromagnetic order. Magnetic anisotropy was also observed in these ZnO:Mn films, which is another indication for intrinsic ferromagnetism. The electron-mediated ferromagnetism in *n*-type ZnO:Mn contradicts the existing theory that the magnetic exchange in ZnO:Mn materials is mediated by holes. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2838753]

There is tremendous potential with using both the spin and charge properties of the electrons in semiconductor applications.[1] Diluted magnetic semiconductors (DMSs) can meet this expectation.[1,2] ZnO based DMS materials have attracted much attention because theoretical calculations have predicted that the Co-doped ZnO will be ferromagnetic in an electron rich environment while the Mn-doped ZnO will be ferromagnetic in a hole rich environment at above room temperatures.[3–5] Recent experimental studies on ZnO:Mn materials resulted in very controversial results,[6–19] showing both ferromagnetism[6–14] and nonferromagnetic states[15–18] in ZnO:Mn. Most recently, different groups reported hole-mediated ferromagnetism in *p*-type ZnO:Mn thin films.[10–14] This seems to be consistent with the theoretical predictions. However, ferromagnetism has also been observed in *n*-type ZnO:Mn.[7–9] So the circumstances under which ZnO:Mn can be ferromagnetic is still debatable. In this letter, we report our experimental results on *n*-type ZnO:Mn thin films, showing strong evidence for electron concentration dependent magnetization, supporting an electron-mediated ferromagnetic exchange mechanism in ZnO:Mn.

ZnO thin films were grown on *r*-plane sapphire substrates using plasma-assisted molecular-beam epitaxy. The ZnO thin film samples A, B, C, and D with electron carrier concentration of 1.2×10^{20}, 4.7×10^{19}, 8.4×10^{18}, and 3.5×10^{18} cm^{-3}, respectively, were obtained by different amounts of Ga dopant incorporation. The Mn ions were implanted into these thin films. The implantation energy and dose are 50 keV and 3×10^{16} cm^{-2}, respectively. The implanted samples were annealed at 900 °C for 5 min to activate the implanted ions and recover the crystallinity. Hall effect measurements were carried out before and after implantation. The carrier concentration of the samples shows the same trend after Mn implantation. X-ray diffraction (XRD) measurements were performed to check the crystallinity of the ZnO thin films. Secondary ion mass spectroscopy (SIMS) measurements were performed to characterize the Mn ion profile along the depth of the ZnO films. The magnetic properties were measured with a Quantum Design MPMS-XL superconducting quantum interference device magnetometer using an in-plane geometry (magnetic field parallel to the film) on all samples, unless specified differently.

Figure 1 shows the XRD spectra for sample A before and after Mn implantation. Both the ZnO and the ZnO:Mn thin films show high crystallinity. Only the $(11\bar{2}0)$ peaks associated with the ZnO wurtzite structure were observed at 56.8° and 56.7° in the ZnO and ZnO:Mn thin films, respectively. Figure 2 shows the SIMS data for (a) the ZnO sample A, (b) the Mn-implanted ZnO sample A, and (c) the Mn-implanted ZnO sample A after annealing. As shown in Fig. 2(a), nearly uniform Zn and Ga concentrations are observed in the ZnO thin film before implantation. In the Mn-implanted sample in Fig. 2(b), the profile of the Mn concentration follows an approximate Gaussian distribution, which is a common implantation profile. The Gaussian peak is near the surface, which was intentionally designed using a relatively small implantation energy to prevent a large amount of Mn ions from reaching the sapphire substrate. The Mn ions redistribute to a comparatively uniform profile along the depth of the film after annealing, as shown in Fig. 2(c). The density of residual Mn penetrated into the substrate is more than one order of magnitude smaller than the Mn in the ZnO film layer. Furthermore, the weak ferromagnetic contribution from sapphire is purely from the tiny amount of implanted Mn ions that reach the substrates because no continuous

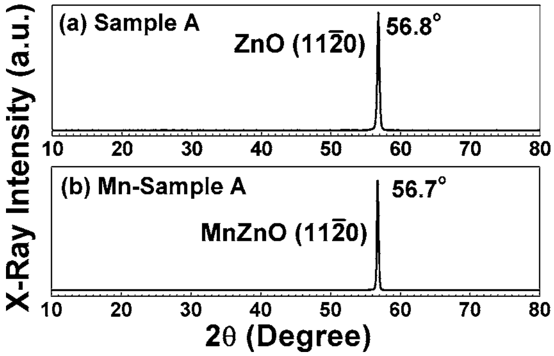

FIG. 1. XRD spectra of (a) sample A before Mn implantation and (b) sample A after Mn implantation.

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[a] Author to whom correspondence should be addressed. Electronic mail: jianlin@ee.ucr.edu.

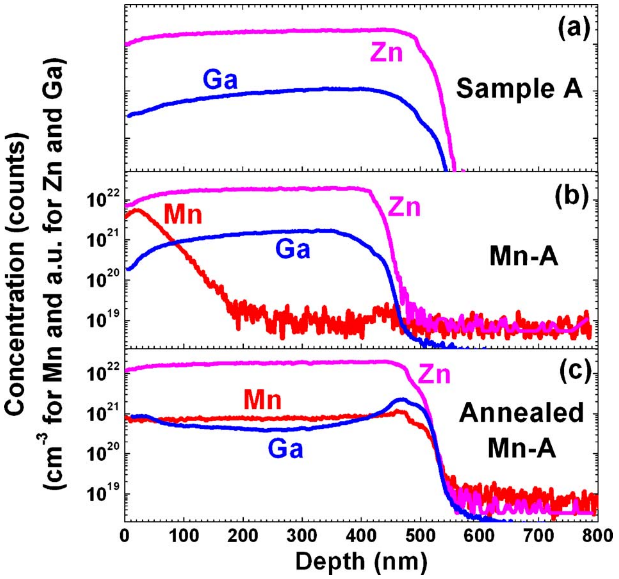

FIG. 2. (Color online) SIMS spectra of (a) sample A before Mn implantation, (b) sample A after Mn implantation, and (c) Mn-implanted sample A after annealing.

long-range magnetic exchange was observed. To remove any possible contributions from the substrates to the magnetic measurements, we began by measuring the ZnO:Mn film on the sapphire substrate. Then, we completely etched away the ZnO:Mn layer and measured just the sapphire substrate. The magnetic response of the ZnO:Mn films was obtained by subtracting the two data sets.

Figure 3 shows the magnetization as a function of the applied magnetic field at 300 K for ZnO:Mn (sample A), indicating ferromagnetic hysteresis. The saturated magnetization value is $\sim 5.0\mu_B$ per Mn ion, which greatly exceeds the previously reported values for ZnO:Mn DMS materials,[10–14,19] but it is smaller than the giant magnetic moment ($\sim 6.1\mu_B$ per Co) observed for $Zn_{0.96}Co_{0.04}O$.[20] The upper inset shows the magnetic field dependence of the magnetization on the same sample at 10 K with a slightly larger coercivity than that at 300 K. The bottom inset shows the temperature dependence of the magnetization measured from 2 to 300 K. The magnetization is almost temperature independent up to 300 K, indicating that the Curie temperature is well-above room temperature. As we know, neither Mn metal nor any oxide of Mn is ferromagnetic (such as MnO, MnO_2, and Mn_2O_3), although Mn_3O_4 has a Curie temperature around 45 K.[2] Since the ZnO:Mn thin film has a much higher Curie temperature than 45 K, the possibility of ferromagnetism in our ZnO:Mn films originating from the segregated Mn, or Mn related oxides is excluded.

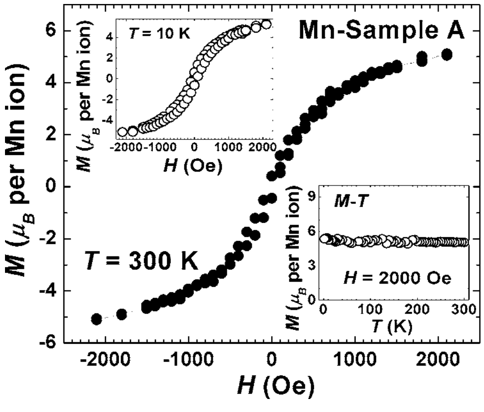

FIG. 3. Magnetic field dependence of the magnetization for the Mn-implanted ZnO sample A measured at 300 K. The upper inset shows the magnetic field dependence of the magnetization on the same sample at 10 K. The bottom inset shows the temperature dependence of the magnetization measured from 2 to 300 K.

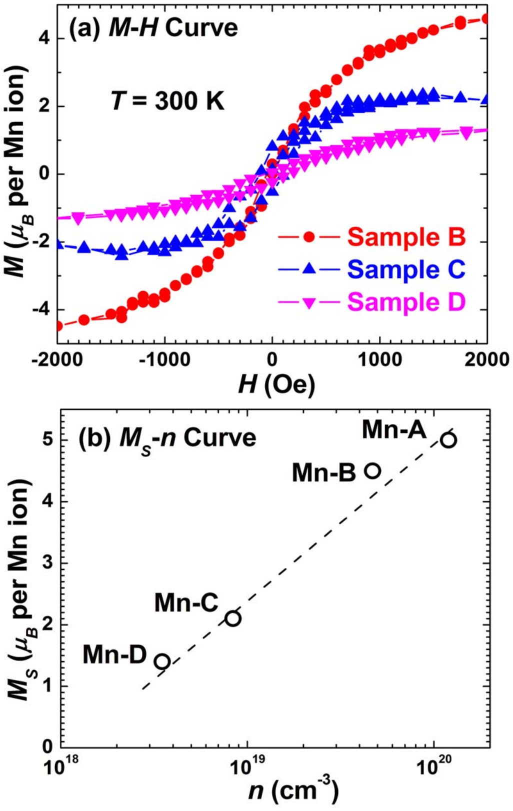

FIG. 4. (Color online) (a) Magnetic field dependence of the magnetization for the Mn-implanted ZnO samples B, C, and D measured at 300 K. (b) The relation between the saturated magnetization M_S and the electron carrier concentration (n). The M_S of the samples show an electron concentration dependent behavior.

Figure 4(a) shows ferromagnetic hysteresis loops for ZnO:Mn thin films with different electron concentrations, and in Fig. 4(b) the relationship between the saturated magnetization (M_S) and the free electron carrier concentration (n) is plotted. ZnO:Mn samples A, B, C, and D with electron concentrations of 1.2×10^{20}, 4.7×10^{19}, 8.4×10^{18}, and 3.5×10^{18} cm^{-3}, show 5.0, 4.5, 2.1, and $1.4\mu_B$ per Mn ion magnetization, respectively. They reveal a strong reduction of M_S as the electron concentration decreases. Based on the theoretical calculations,[4] the Mn-doped ZnO should be ferromagnetic with an excess of hole, however, all of our ZnO:Mn thin films are strongly n type. We conclude that the ferromagnetic exchange inside these ZnO:Mn thin films is mediated by electrons from shallow donor impurities.

Figure 5 shows the out-of-plane (magnetic field perpendicular to the film) and in-plane (magnetic field parallel to the film) magnetic field dependences for a ZnO:Mn thin film (sample B). The out-of-plane magnetization shows a smaller saturated magnetization but larger coercivity than in-plane magnetization. The inset shows the M-H curve measured over a larger magnetic field range. The magnetic anisotropy is a further proof of the intrinsic nature of the ferromagnetism in ZnO DMS materials,[21,22] since cluster-related fer-

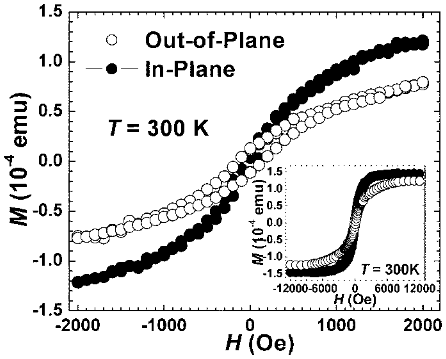

FIG. 5. Anisotropic magnetism for a ZnO:Mn thin film (sample B). The out-of-plane magnetization shows a smaller saturated magnetization but larger coercivity than in-plane magnetization. The inset shows the *M-H* curve measured over a larger magnetic field range of up to 12 000 Oe.

romagnetism is generally isotropic. The ZnO thin films were epitaxially grown on *r*-plane sapphire with the growth direction along the *a* direction $[(11\bar{2}0)]$ as shown in the XRD spectra. The easy axis of the magnetization is in the plane while the hard axis of magnetization is parallel to the *a* axis. Similar anisotropic results were also observed in ZnO:Co DMS materials.[21]

In summary, ferromagnetism with a transition temperature well-above room temperature, electron concentration dependent magnetization, and magnetic anisotropy was observed in *n*-type ZnO:Mn thin films. The dependence of the magnetization on electron concentration provides strong experimental evidence for an electron-mediated exchange mechanism for ferromagnetism in ZnO:Mn materials, contrary to the requirement of a hole-rich environment predicted by theory.

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