

Room temperature magnetism in semiconducting films of ZnO doped with ferric ions

S. D. Yoon^{a)} and Yajie Chen

Center for Microwave Magnetic Materials and Integrated Circuits, Northeastern University, Boston, Massachusetts 02115

Don Heiman

Departments of Physics, Northeastern University, Boston, Massachusetts 02115

Aria Yang, Nian Sun, C. Vittoria, and V. G. Harris

Center for Microwave Magnetic Materials and Integrated Circuits, Northeastern University, Boston, Massachusetts 02115 and Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

(Presented on 3 November 2005; published online 20 April 2006)

Films consisting of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ were prepared by alternating-target laser ablation deposition. The Fe doping levels ranged from $x=0.016$ to 0.125 at. %. X-ray diffraction and energy dispersive x-ray spectroscopy measurements showed only (002n) reflections of the ZnO host and confirmation of the Fe concentration, respectively. For films grown on (001) Al_2O_3 at 300 K, room temperature average saturation magnetization, $\langle 4\pi M_s \rangle$, measured from superconducting quantum interference device (SQUID) hysteresis loops for $x=0.125 \pm 0.025$ was 172 G. Although SQUID measurements were sensitive to the average value of the saturation magnetization, ferrimagnetic resonance measurements appeared to be sensitive only to the saturation magnetization of the so-called magnetic layer containing ferric ions. We believe that we have produced a host semiconductor material doped with impurities of ferrimagnetic ordering. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172916]

INTRODUCTION

Room temperature magnetically ordered semiconductors have attracted much attention in recent years due to their potential in spintronics devices where the spin degree of freedom of the electron is utilized in addition to its carrier concentration.¹⁻⁷ Researchers have traditionally diluted mostly conventional compound semiconductors (i.e., III-V alloys) with 3d-transition metals (TM) to obtain dilute magnetic semiconductors (DMS).^{1,2} However, it remains a key goal of this technology to understand magnetism in DMS and to achieve ordering temperatures (T_C) well above 300 K.

Recently, ZnO films have been diluted successfully with Mn and Co (Refs. 3 and 8) using traditional pulsed laser deposition (PLD) (i.e., using a single alloy target),⁹ ion beam sputter deposition,¹⁰ or PLD followed by ion implantation.¹¹ Other experimental works have claimed that for Co doped in ZnO ordered ferromagnetically with $T_C \sim 280$ K.^{12,13} It has been suggested that the origin of ferromagnetism in this system was a result of clustering in which magnetic ions interact within a small distance where exchange interaction predominates.¹² The films in previous works⁹⁻¹¹ were deposited from a single target of a mixture of ZnO and TM oxide. Although clustering may be possible from their preparation techniques, it is rather difficult to quantify a local distribution of magnetic ions within the clustering. As such, the origin of magnetism can only be described in qualitative terms.

In Refs. 9-11 they have concluded that the magnetic

ordering was ferromagnetic in nature as manifested in TM ions doped in ZnO. This is very interesting in view of the fact that not many oxide compounds contain TM ions which exhibit ferromagnetic order. These compounds are usually ferrimagnetic. We have simplified the approach in producing magnetic semiconductors for the purpose of determining the local distribution of magnetic ions. We have deposited the films from two separate targets of ZnO and Fe_2O_3 and monitored precisely the deposition from either target. We have deposited a thick layer of ZnO as the “host” crystal and followed this with the deposition of a thin layer of Fe_2O_3 much less than a unit cell in thickness. In so doing we believe that we have effectively doped the host with ferric ions. Our results indicate that magnetic ordering is ferrimagnetic well above 300 K.

EXPERIMENTAL DETAILS

Thin films of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$, where $x=0.016$ to $x=0.125$, were deposited on both (001) sapphire ($\alpha\text{-Al}_2\text{O}_3$) and quartz substrates by laser ablation deposition (LAD) using binary oxide targets of zinc oxide (ZnO) and hematite ($\alpha\text{-Fe}_2\text{O}_3$).¹⁴ Alternate layers of ZnO and Fe_2O_3 were deposited sequentially to produce films whose crystal structure is the same as that of pure ZnO. Targets of ZnO and Fe_2O_3 were mounted on a target rotator driven by a servomotor and synchronized with the trigger of the pulsed excimer laser ($\lambda=248$ nm). In each deposition cycle, the ratio of laser pulses incident upon the ZnO target to those upon the Fe_2O_3 target varied from 1:0 to 48:1. The substrate temperature, laser energy density, and pulse repetition rate were kept at 700 °C, 400 mJ, and

^{a)}Author to whom correspondence should be addressed; electronic mail: syoon@ece.neu.edu

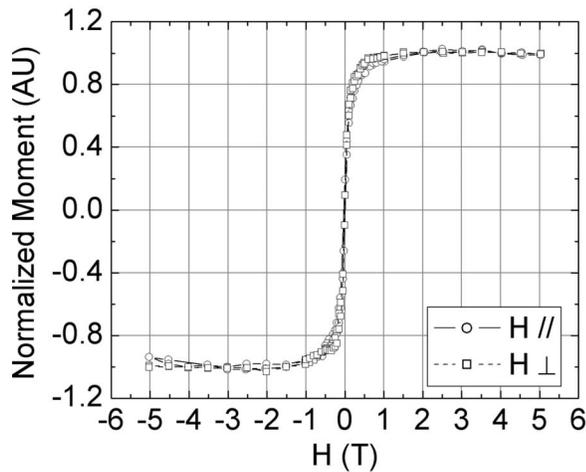


FIG. 1. Room temperature hysteresis loops for $Zn_{1-x}Fe_xO$ films on a (001) sapphire ($\alpha-Al_2O_3$) substrate $x=0.125$.

1 Hz, respectively. The deposition was carried out in pure oxygen background of 10 mTorr. There were a total of 7200 laser pulses for each film resulting in a thickness of approximately 300 nm as measured by a Dek-Tak 3 step profilometer. Structural properties of the ZnO films were examined by a Phillips X'pert Pro x-ray diffractometer (XRD). Surface morphology and Fe doping concentration of the $Zn_{1-x}Fe_xO$ films were examined by Hitachi S4800 high resolution field emission scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS), respectively. The hysteresis loops and magnetization were obtained using a Quantum Design MPMS XL-5 superconducting quantum interference device (SQUID) magnetometer at temperatures from 10 to 300 K. Microwave properties were measured using a cavity operating in the TE_{102} mode at X band. Room temperature ferrimagnetic resonance (FMR) spectra were obtained using the differential power absorption technique utilizing a Varian E-102 microwave bridge and an E-line console for lock-in detection of the absorption signal.

In order to explore the short range order structure and cation site distribution, all samples were subjected to extended x-ray absorption fine structure (EXAFS) measurements and analysis. Data collection was performed using beamline X23B at the National Synchrotron Light Source in fluorescence yield at room temperature. EXAFS analysis followed the well established refinement procedures outlined by Sayers and Bunker¹⁵ leading to the Fourier transform of the extended fine structure. The Fourier transform of the extended fine structure allows one to qualitatively assess the local structure often providing identification of ion sites.

RESULTS AND DISCUSSIONS

X-ray diffraction spectra on all the films showed strong (001) reflections of ZnO coinciding with (001) sapphire peaks. There were no other evidences for secondary phases present in the spectra. XRD analysis indicated that the films were epitaxial and single crystal.

In Fig. 1, the hysteresis loops for the $Zn_{1-x}Fe_xO$ film, where $x=0.125\pm 0.025$ Å, are shown for room temperature measurements. The total thickness was 3000 Å, and the av-

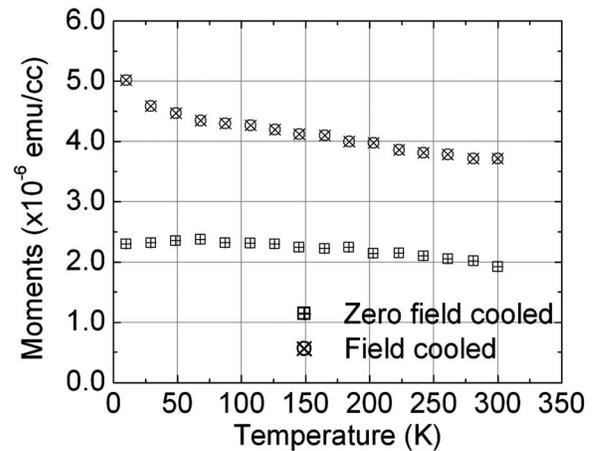


FIG. 2. SQUID measurement of moment vs temperature for $Zn_{1-x}Fe_xO$ films $x=0.125$ on (001) sapphire substrate.

erage saturation magnetization, $\langle 4\pi M_S \rangle$, and average remanence magnetic moment were deduced to be 172 and 69 G, respectively. In Fig. 2, the remanance magnetization and magnetization in a field of 100 Oe (slightly greater than coercive field) is plotted as a function of temperature (K). Clearly, there is a spontaneous magnetic moment at low temperatures as well as for temperatures exceeding room temperature. We may conclude that the films in question are magnetically ordered with transition temperatures well above room temperature. Let us now focus in identifying the type of magnetic ordering in these films.

In Fig. 3, the FMR resonance field, H_r , is plotted as a function of the angle, α , between the external magnetic field and the film plane. These data were compared with our theoretical prediction of the angular variation of H_r , as shown below,

$$\frac{\omega}{\gamma} = \sqrt{H_r(H_r + 4\pi M_S \cos^2 \alpha)}. \quad (1)$$

There were a number of assumptions that entered into Eq. (1): (i) the dc demagnetizing field is small, since the average saturation magnetization, $\langle 4\pi M_S \rangle$, is only 172 G; and (ii) as shown in a previous work¹⁶ $4\pi M_S$ in Eq. (1) was assumed to be the saturation magnetization pertaining to the single magnetic layer within the structure that made up the film. This $4\pi M_S$ should not be confused with the average saturation magnetization, $\langle 4\pi M_S \rangle$, measured from SQUID measurements [see Figs. 1(a) and 1(b)]. The saturation magnetization from the SQUID was an average moment that can be related to the $4\pi M_S$ of FMR by the following equation:

$$\langle 4\pi M_S \rangle = 4\pi M_S \left(\frac{t_1}{t_1 + t_2} \right), \quad (2)$$

where $t_1 \equiv$ thickness of magnetic region and $t_2 \equiv$ thickness of nonmagnetic region. The period of the magnetic region, $(t_1 + t_2) \sim 3$ Å, was estimated from the number of shots required to deposit 3000 Å. Hence, Eq. (1) was derived on the basis that there were no dc "magnetostatic charges" induced for H_r perpendicular, where $\alpha=90^\circ$, to the film plane. Although we see no physical evidence for a layered structure we believe

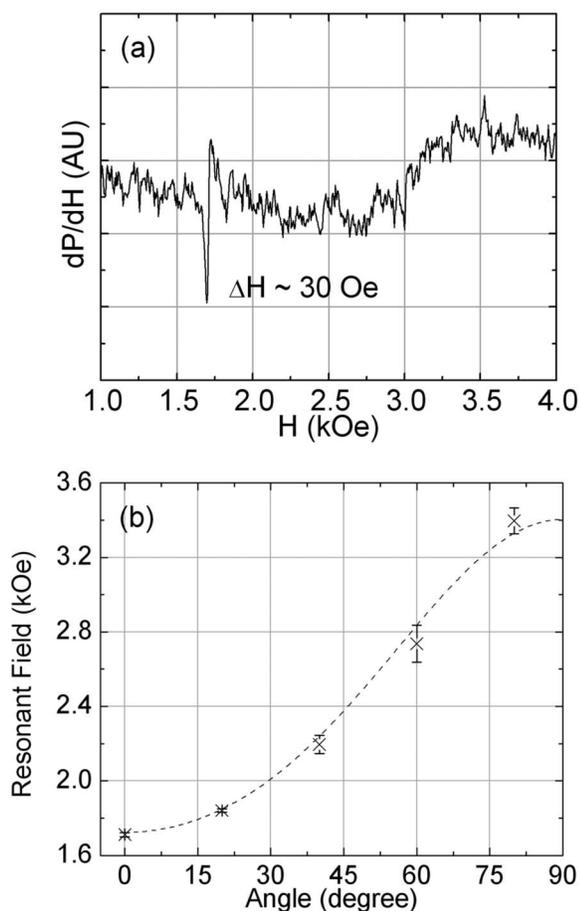


FIG. 3. (a) FMR spectrum acquired from the $\text{Zn}_{0.875}\text{Fe}_{0.125}\text{O}$ on the sapphire substrate at X-band frequency with applied field (H) parallel the film plane and (b) resonant field vs angle between the applied magnetic field and the film plane.

that the Fe ions form an enriched region that we refer to as a “layer.”

The fit between the measured angular variation of H_r and that predicted by Eq. (1) was reasonable. There was no angular variation of H_r for H_r rotated in the film plane. Assuming $g \cong 2$, $4\pi M_S$ for a single magnetic layer of 5000 G was deduced from the fit simulation, which was well above $\langle 4\pi M_S \rangle$. From Eq. (2), the ratio of magnetic to nonmagnetic layer was about 3.3%. Interestingly, this ratio did not scale as a percentage of Fe ions substituted in the film as measured from EDAX. The magnetic layer was mostly Fe_2O_3 , since depositions were made from ZnO and Fe_2O_3 sintering targets. Our deduced value of $4\pi M_S = 5000$ Oe compared remarkably well with the value of saturation magnetization reported in the literature for bulk Fe_2O_3 (also 5000 G).¹⁶

Preliminary EXAFS results indicate that the local environment of ferric ions does not resemble that of the Zn ions

in ZnO. Hence, it is unlikely that ferric ions are entering the lattice via substitution. However, there are some similarities with the short range structure of Fe_2O_3 . This is consistent with the FMR results and the nature of the alternating-target laser ablation deposition (AT-LAD) processing. Since XRD shows no evidence of long range order of the Fe oxides, we can conclude that this ordering is short range in nature. We conclude that the magnetic regions in the doped ZnO host lattice order ferrimagnetically corresponding to the magnetic ordering of $\gamma\text{-Fe}_2\text{O}_3$ which also orders ferrimagnetically.¹⁷

CONCLUSIONS

The basic question that we were addressing was the type of magnetic ordering induced in magnetic semiconductors. Specifically, did the preparation technique affect the magnetic ordering? We conclude that magnetic ordering was only a result of local coordination and distance between magnetic ions, via the oxygen. As it is well known superexchange interaction between nearest neighbor distance between magnetic ions (via the oxygen) is the most important factor. Our FMR and EXAFS results suggest that the Fe ions form short range order Fe-oxide regions within the host. These regions have short range symmetry similar to that of $\gamma\text{-Fe}_2\text{O}_3$ and possess $4\pi M_S$ values near 5000 G, also consistent with this crystal structure. Thus, it is not surprising that the magnetic ordering was ferrimagnetic well above room temperature.

¹H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, *Appl. Phys. Lett.* **69**, 363 (1996).

²H. Ohno, *Science* **281**, 951 (1998).

³T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, *Appl. Phys. Lett.* **75**, 3366 (1999).

⁴S. W. Jung, S.-J. An, G.-C. Yi, C. U. Jung, S.-I. Lee, and S. Cho, *Appl. Phys. Lett.* **80**, 4561 (2002).

⁵T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).

⁶Y. Matsumoto *et al.*, *Science* **291**, 854 (2001).

⁷A. H. MacDonald, P. Schiffer, and N. Samarth, *Nature (London)* **4**, 195 (2005).

⁸K. Rode, A. Anane, R. Mattana, J.-P. Contour, O. Durand, and R. LeBourgeois, *J. Appl. Phys.* **93**, 7676 (2003).

⁹C. Vittoria, U.S. Patent No. 5,227,204 (1993).

¹⁰S. G. Yang, A. B. Pakhomov, S. T. Hung, and C. Y. Wong, *IEEE Trans. Magn.* **38**, 2877 (2002).

¹¹D. P. Norton, S. J. Pearton, A. F. Hebard, N. Theodoropoulou, L. A. Boatner, and R. G. Wilson, *Appl. Phys. Lett.* **82**, 239 (2003).

¹²S. A. Chambers and R. F. C. Farrow, *MRS Bull.* **28**, 729 (2003).

¹³K. Ueda, H. Tabata, and T. Kawai, *Appl. Phys. Lett.* **79**, 988 (2001).

¹⁴X. Zuo, F. Yang, R. Mafhoum, R. Karim, A. Tebano, G. Balestrino, V. G. Harris, and C. Vittoria, *IEEE Trans. Magn.* **40**, 2811 (2004).

¹⁵D. E. Sayers and B. A. Bunker, *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES* (Wiley, New York, 1988), Vol. 92, pp. 211–253.

¹⁶H. How and C. Vittoria, *Phys. Rev. B* **39**, 6823 (1989).

¹⁷A. E. Berkowitz, W. J. Schuele, and P. J. Flanders, *J. Appl. Phys.* **39**, 1261 (1968).