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Ferromagnetic properties of $Zn_{1-x}Mn_xO$ epitaxial thin films

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We report on ferromagnetic characteristics of $Zn_{1-x}Mn_xO$ ($x=0.1$ and 0.3) thin films grown on $Al_2O_3(00\cdot1)$ substrates using laser molecular-beam epitaxy. By increasing the Mn content, the films exhibited increases in both the *c*-axis lattice constant and fundamental band gap energy. The Curie temperature obtained from temperature-dependent magnetization curves was 45 K for the film with $x=0.3$, depending on the Mn composition in the films. The remanent magnetization and coercive field of $Zn_{0.9}Mn_{0.1}O$ at 5 K were 0.9 emu/g and 300 Oe, respectively. For $Zn_{0.7}Mn_{0.3}O$, the remanent magnetization at 5 K increased to 3.4 emu/g. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1487927]

There has been much interest in magnetic semiconductors which exploit both the spin and the charge of the carriers, because the combination of the two degrees of freedom promises new functionality of memory, detectors, and light-emitting sources. Possible spintronic devices are spin-valve transistors, spin light-emitting diodes, and nonvolatile storage and logic devices. Much effort is devoted to integrating magnetic and semiconducting phenomena for the applications, as well as the fundamental understanding, of the phenomena. A traditional method in the integration is to substitute magnetic ions such as Mn^{2+}, Cr^{2+}, and Fe^{2+} into nonmagnetic semiconductors.[1] However, with the recent discovery of ferromagnetism in InMnAs,[2] III–V diluted magnetic semiconductor (DMSs) have been extensively studied and GaMnAs exhibited the highest Curie temperature (T_C), 110 K. In this case, it is generally accepted that hole carriers generated by Mn doping induces ferromagnetic ordering in III–V DMSs.[3,4]

Recent theoretical calculations by Dietl *et al*. suggested that Mn-doped ZnO would show ferromagnetic (FM) behavior with a T_C value well above room temperature[4] several $3d$-transition-metal-doped ZnO films have been prepared since the thermal equilibrium solubility of transition metals in the host materials is higher than 10 mol %.[5,6] However, the FM phase has been observed only in Co-doped ZnO.[7] In this letter, we report on the discovery of ferromagnetism in Mn-doped ZnO epitaxial films prepared by laser molecular-beam epitaxy (LMBE).

$Zn_{1-x}Mn_xO$ ($x=0.0$, 0.1, and 0.3) films were epitaxially grown on $Al_2O_3(00\cdot1)$ substrates in an ultrahigh vacuum chamber with a base pressure of mid-10^{-9} Torr. Growth conditions of $Zn_{1-x}Mn_xO$ films are similar to those of ZnO films reported elsewhere.[8] For the growth of $Zn_{1-x}Mn_xO$ films, stoichiometric $Zn_{1-x}Mn_xO$ targets were ablated by the third harmonics (a wavelength of 355 nm) of a Nd:YAG laser. The pulse duration and fluence of the laser beam were 5 ns and 1 J/cm^2, respectively.

The crystal orientation and crystallinity of the as-grown films were investigated using x-ray diffraction (XRD) and *in-situ* reflection high-energy electron diffraction (RHEED). The Mn composition in the films was determined using energy-dispersive x-ray analysis. For investigation of magnetic properties of the films, temperature-dependent magnetization ($M-T$) and magnetic hysteresis ($M-H$) curves were measured using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS*XL*). $M-T$ curves were measured both in zero-field-cooled and field-cooled mode at the applied magnetic field of 1000 Oe and $M-H$ curves at 5 K were measured in the field range $-3000\ \text{Oe} \leqslant H \leqslant 3000\ \text{Oe}$.

The crystal structure and film orientation of the as-grown films were determined from θ–2θ scans of XRD. Only $(00\cdot2)$, $(00\cdot4)$, and $(00\cdot6)$ peaks of $Zn_{1-x}Mn_xO$ were observed, indicating the *c*-axis orientation of $Zn_{1-x}Mn_xO$ ($0.0 \leqslant x \leqslant 0.3$) films. However, the peak position of the $Zn_{1-x}Mn_xO$ $(00\cdot2)$ peak shifted to lower angles with increasing Mn concentration as shown in Fig. 1(a). This presumably results from the substitution of Mn ions with a large ionic radius of 0.91 Å for Zn (0.83 Å) sites.[9] Due to Mn incorporation, the *c*-axis constant of $Zn_{1-x}Mn_xO$ films increased from 5.219 ± 0.003 Å for $x=0.0$ to 5.255 ± 0.012 Å for $x=0.1$ and 5.280 ± 0.005 Å for $x=0.3$ as determined by plotting the $(00\cdot\ell)$ diffraction peak values as a function of $\cos^2\theta/\sin\theta$ and extrapolating to $\theta = 90°$.[10]

Since the θ–2θ scans of XRD only tracks a line in k space, and can not be used to conclude that the film does not contain second phases, we measured RHEED of the films. From the RHEED measurements, in-plane rotational symmetry was clearly observed. The XRD and RHEED results

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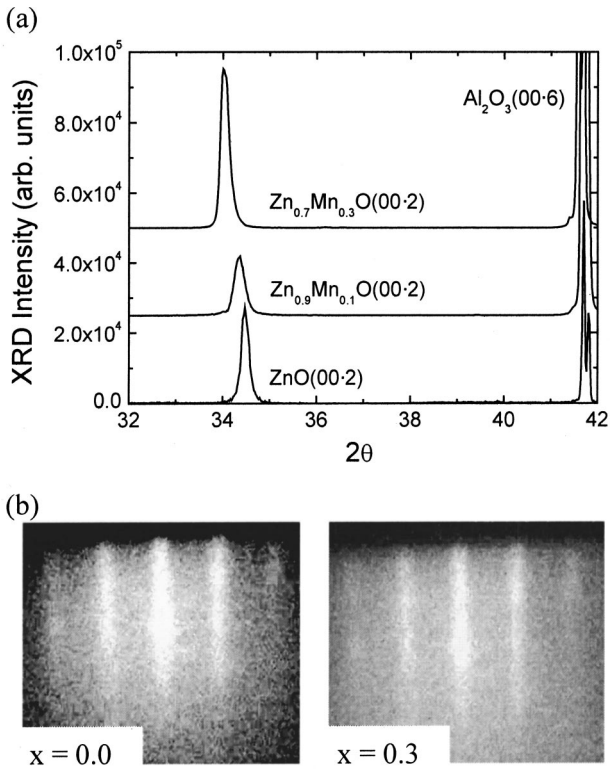

FIG. 1. (a) θ–2θ XRD curves and (b) RHEED patterns of $Zn_{1-x}Mn_xO$ films. The XRD data exhibit only a (00·2) peak of $Zn_{1-x}Mn_xO$ which are shifted to lower angles with increasing Mn concentration. The $Zn_{1-x}Mn_xO$ films yield streaky RHEED patterns along the $[2\bar{1}\bar{1}0]$ direction, aligned with $Al_2O_3[1\bar{1}00]$.

strongly suggest that the films are of high single phase. In addition, as shown in Fig. 1(b), RHEED patterns of the films were streaky, indicating the epitaxial growth of $Zn_{1-x}Mn_xO$ films with smooth surfaces. From analysis of the RHEED patterns, it has also been observed that the $[2\bar{1}\bar{1}0]$ direction of the $Zn_{1-x}Mn_xO$ was aligned with the $[1\bar{1}00]$ direction of $Al_2O_3(00\cdot1)$.[8] The RHEED measurements confirm the epitaxial growth of the $Zn_{1-x}Mn_xO$ films.

The excellent crystallinity of as-grown films was also confirmed by measuring XRD rocking curves. The rocking curves of $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.7}Mn_{0.3}O$ films exhibited a narrow full width at half maximum of 0.07°, comparable to that of undoped films, 0.04°. The small degree of broadening in the rocking curves of the Mn-doped films is presumably due to strain induced from the occupation of Mn ions at Zn ion sites.

We investigated magnetic properties on $Zn_{1-x}Mn_xO$ films using the SQUID system. Figure 2 shows $M-T$ curves of $Zn_{1-x}Mn_xO$ ($x=0.1$ and 0.3) films between 5 and 150 K. The magnetic field was applied parallel to the surface of the substrate. As shown in Fig. 2, $Zn_{1-x}Mn_xO$ films with $x=0.1$ and 0.3 exhibited an abrupt increase in $M-T$ curves at 30 and 45 K, respectively, corresponding to T_C. In addition, the magnetization of $Zn_{0.7}Mn_{0.3}O$ at low temperatures below T_C is three to four times higher than that of $Zn_{0.9}Mn_{0.1}O$. The increases in magnetization and T_C in the highly Mn-doped film imply that Mn doping into ZnO induces ferromagnetism.

Ferromagnetic behavior of $Zn_{1-x}Mn_xO$ films was further investigated measuring $M-H$ curves both below and above T_C. As shown in Fig. 3, the $M-H$ curve of $Zn_{0.9}Mn_{0.1}O$ at 5 K clearly shows a hysteresis loop, resulting from ferromagnetic ordering in the material. Above T_C, however, the $M-H$ curve showed linear paramagnetic behavior. This discovery of ferromagnetism in Mn-doped ZnO contrasts with the previous report, observation of spin–glass behavior in Mn-doped-ZnO films grown by pulsed laser deposition.[5] This controversy might stem from the difficulty in the reproducible preparation of samples, which has also been occurred in Co-doped ZnO.[7] Although ferromagnetic behavior in Co-doped-ZnO films has previously been reported, $M-H$ curves of these films have not clearly shown hysteresis loops, presumably due to very small remanent magnetization (M_r).[7] However, for $Zn_{0.9}Mn_{0.1}O$ in this research, M_r at 5 K was as large as 0.9 emu/g (0.15 μ_B/Mn) and the coercive field (H_C) was 300 Oe. For $Zn_{0.7}Mn_{0.3}O$, M_r at 5 K increased to 3.4 emu/g (0.17 μ_B/Mn).

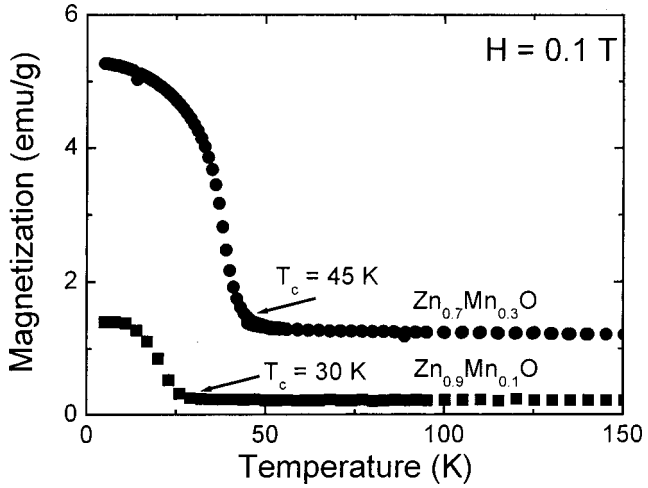

FIG. 2. Temperature-dependent magnetization ($M-T$) curves of $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.7}Mn_{0.3}O$ films at a magnetic field of 0.1 T. The abrupt increase in $M-T$ curves, corresponds to T_C of 30 K and 45 K for $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.7}Mn_{0.3}O$, respectively.

It is also noted that our $Zn_{1-x}Mn_xO$ films in this research are electrical insulators because the substitution of

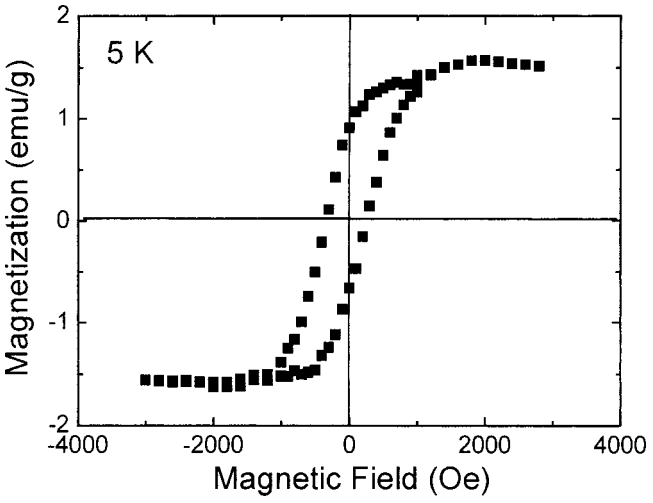

FIG. 3. $M-H$ curve of $Zn_{0.9}Mn_{0.1}O$ measured at 5 K. The magnetic hysteresis curve was clearly observed at 5 K, resulting from ferromagnetic ordering in $Zn_{0.9}Mn_{0.1}O$. The remanent magnetization (M_r) and coercive field (H_c) were 0.9 emu/g and 300 Oe, respectively.

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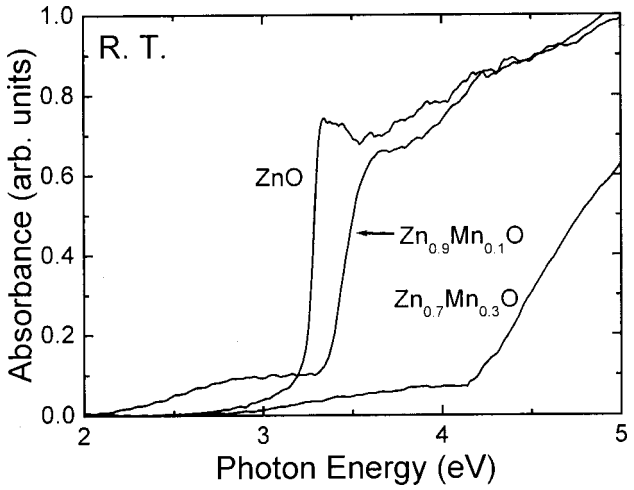

FIG. 4. Room-temperature UV absorbance spectra of $Zn_{1-x}Mn_xO$ ($x=0.0$, 0.1, and 0.3) films. The absorbance spectra show a strong UV absorbance at 3.22–4.2 eV. Note that the absorbance edge of $Zn_{1-x}Mn_xO$ films blueshifts with increasing Mn content.

Mn^{2+} for the group-II cation of Zn would not generate carriers. Similar behavior has also been observed in $Zn_{1-x}Mn_xGeP$.[11] The ferromagnetism in the insulating materials is not consistent with the previous report on ferromagnetism in III–V based DMS:hole carriers induced by doping of Mn^{2+} into the group-III cation mediate the interaction of the magnetic ions, resulting in the ferromagnetic behavior. Instead of generating carriers, the addition of Mn ions into Zn sites affects the electronic band structure of the materials, as previously observed in other II–VI DMSs.[1] Hence, the band gap energy of the material depends on the composition of Mn in the materials, which is experimentally confirmed by absorbance measurements.[5,11] As shown in Fig. 4, the absorbance spectra of the materials exhibited an abrupt increase in near bandedges. Based on the visible-ultraviolet (VIS-UV) absorbance measurements, the band gap energy of the films was obtained by plotting $\alpha^2 E^2$ versus E, where α and E are absorbance and incident photon energy, respectively. The band gap energy of $Zn_{1-x}Mn_xO$ films prepared during the course of this research increased from 3.27 eV for $x=0.0$ to 3.36 and 4.2 for $x=0.1$ and 0.3, respectively, indicating that ZnMnO alloys are formed by the Mn incorporation.

The XRD, VIS-UV absorption, and magnetic characteristics of $Zn_{1-x}Mn_xO$ films strongly suggest that Mn ions substitute for Zn ion sites and prefer FM ordering below T_C of 30 and 45 K for 10% and 30% Mn-doped-ZnO films, respectively. However, it is noted that a secondary phase might exist in the films although a secondary phase was not detectable in our XRD and electron microcopy measurements. The possible secondary phase is manganese oxides. However manganese oxides, MnO and MnO_2 are well known to be antiferromagnetic below the Néel temperature of 116 K and 84 K, respectively. Hence, ferromagnetic behavior of the ZnMnO films might not be explained in terms of the formation of the manganese oxides.

In conclusion, ferromagnetic semiconducting $Zn_{1-x}Mn_xO$ ($x=0.1$ and 0.3) epitaxial films were grown on $Al_2O_3(00.1)$ using LMBE. The Mn-doped films clearly showed ferromagnetic ordering from magnetic hysteresis curves. The T_C obtained from temperature-dependent magnetization curves was 30 and 45 K for the $Zn_{1-x}Mn_xO$ films with $x=0.1$ and 0.3, respectively. The remanent magnetization and coercive field of $Zn_{0.9}Mn_{0.1}O$ measured at 5 K were 0.9 emu/g and 300 Oe. For $Zn_{0.7}Mn_{0.3}O$, remanent magnetization at 5 K increased to 3.35 emu/g.

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