Magnetic properties of epitaxial Mn-doped ZnO thin films

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Epitaxial ZnO thin films doped with 7% Mn have been made by reactive rf magnetron sputtering onto $(11\bar{2}0)$ sapphire substrates at 400 °C. X-ray diffraction measurements reveal that the $Zn_{0.93}Mn_{0.07}O$ film has a (0001) wurtzite single-crystal structure with a rocking curve width of 0.98°. UV–VIS absorption spectra show a band gap of 3.25 eV for pure ZnO films and 3.31 eV for the $Zn_{0.93}Mn_{0.07}O$ film with states extending into the gap. The Auger electron spectroscopy shows homogeneous distribution of Mn in the film. The magnetic properties of the $Zn_{0.93}Mn_{0.07}O$ film have been measured by a superconducting quantum interference device magnetometer at various temperatures with fields up to 5 T. No ferromagnetic ordering has been observed at temperature at 5 K. Instead, paramagnetic characteristics with a Curie–Weiss behavior have been observed.
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I. INTRODUCTION

Diluted magnetic semiconductors (DMS) obtained by doping magnetic impurities into host semiconductors have been of standing interest for the exploration of magnetoelectronics.[1–6] Doping of Mn into II–VI semiconductors such as (Zn–Mn)S, (Zn–Mn)Se, and (Cd–Mn)Te, has been extensively studied since two decades ago.[1] While the magnetic ordering temperatures of Mn-doped II–VI semiconductors depend on the Mn concentration, their values are generally quite low (<30 K) and the ordering is often spin glass. With these characteristics, Mn-doped II–VI semiconductors are undesirable for magnetoelectronics. In contrast, Mn-doped III–V semiconductors, especially (Ga–Mn)As, exhibit ferromagnetism with Curie temperature as high as 172 K.[7–9]

Recently, ZnO-based DMS have attracted much attention due to the theoretical prediction of the possibility of ferromagnetic ordering above room temperature in *p*-type Mn-doped ZnO.[10,11] A number of experimental studies have recently been reported using samples that have been made by pulsed-laser deposition (PLD) and molecular-beam epitaxy (MBE).[12–14] Fukumura *et al.* observed only spin glass behavior with significant antiferromagnetic interactions among the Mn ions in $Zn_{0.64}Mn_{0.36}O$.[12] In contrast, very recently, Jung *et al.* reported ferromagnetic ordering in $Zn_{1-x}Mn_xO$ ($x=0.1$ and 0.3) thin films grown by laser molecular-beam epitaxy with Curie temperature T_C of 30 K for $x=0.1$ and 45 K for $x=0.3$.[14] To date, epitaxial Mn-doped ZnO thin films have been made by either PLD and MBE. There appears to be disagreement among the reports concerning the magnetic properties of Mn-doped ZnO films. In this work, we report the epitaxial growth of ZnO thin films doped with 7% Mn by reactive rf magnetron sputtering. We have found only paramagnetic characteristics without ferromagnetic ordering.

II. EXPERIMENTS

We have fabricated epitaxial Mn-doped ZnO thin films on $(11\bar{2}0)$ sapphire substrates by reactive rf magnetron sputtering. Sputtering targets were made by sintering prescribed amounts of ZnO (99.95%) and MnO (99.9%) powders. The base pressure of the sputtering chamber was better than 1.0×10^{-7} Torr. The Ar/O_2 mixture gas with a ratio of 5:1 was introduced into the chamber with the sputtering pressure maintained at 6 mTorr. Both ZnO and Mn-doped ZnO thin films were deposited at a rf power of 100 W with the substrate temperature maintained at 400 °C.

The composition of the $Zn_{1-x}Mn_xO$ thin film was measured to be $x\approx0.07$ by energy-dispersive x-ray spectroscopy. The crystal quality of the thin film was characterized by x-ray diffraction using the $\theta/2\theta$ scan, rocking curve, and pole-figure measurements on a four-circle x-ray diffractometer (Philips X'Pert-MRD) with Cu $K\alpha$ ($\lambda=1.5405$ Å) radiation. The UV–VIS absorption spectra were used to measure the energy band gap and the electronic states of the Mn ions. The magnetic properties of the $Zn_{0.93}Mn_{0.07}O$ films, 3.3×3.3 mm^2 in size and about 3500 Å in thickness, were measured by a superconducting quantum interference device magnetometer (Quantum Design, MPMS) at various temperatures with fields up to 5 T.

III. RESULTS AND DISCUSSION

X-ray diffraction results of a 3500-Å-thick Mn-doped ZnO film on a $(11\bar{2}0)$ sapphire substrate are shown in Fig. 1. The $\theta/2\theta$ scan [Fig. 1(a)] shows only the (0002) and (0004) peaks of the wurtzite structure of ZnO indicating that it is a *c*-axis oriented film. The rocking curve of the (0002) peak [Fig. 1(b)] shows a full width at half maxima (FWHMs) of 0.98°. The epitaxial nature of the Mn-doped ZnO thin film has been revealed by the pole-figure scan [inset of Fig. 1(b)], where the $(10\bar{1}2)$ spots observed at a tilt angle of $\Psi=42.8°$ have the expected sixfold symmetry. These x-ray diffraction results demonstrate that the (0001) $Zn_{0.93}Mn_{0.07}O$ film is epitaxial to the $(11\bar{2}0)$ sapphire substrate. The Auger

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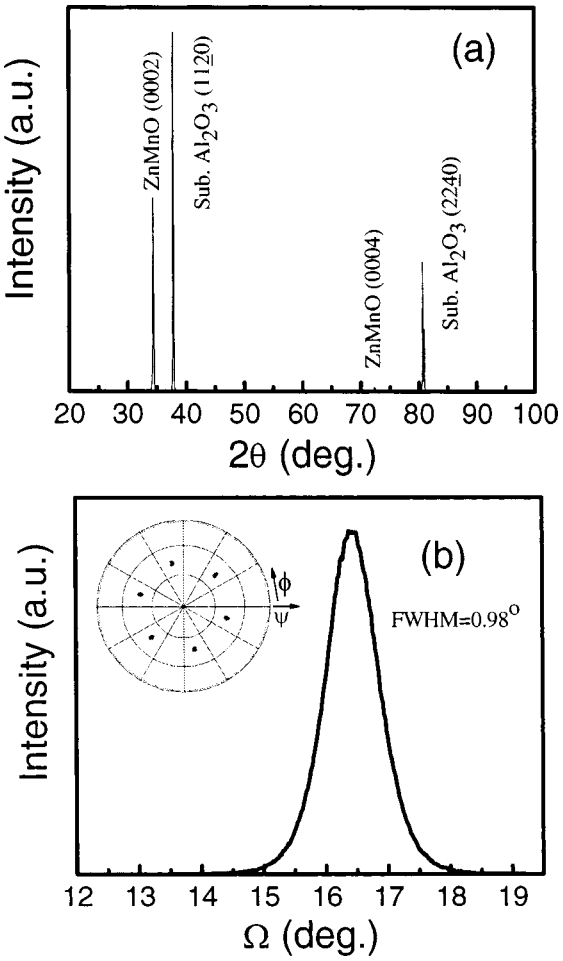

FIG. 1. X-ray diffraction patterns of epitaxial $Zn_{0.93}Mn_{0.07}O$ thin films on (11$\bar{2}$0) sapphire substrate: (a) $\theta/2\theta$ scan showing only the (0002) and (0004) peaks, (b) rocking curve of the (0002) peak with a FWHM of 0.98°, and pole figure of the (10$\bar{1}$2) peak showing the expected sixfold symmetry.

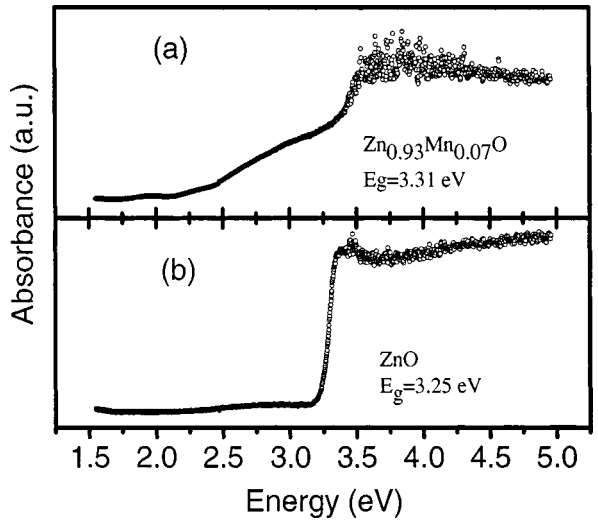

FIG. 2. UV–VS absorption spectra of (a) $Zn_{0.93}Mn_{0.07}O$ thin film with a blueshifted absorption edge at 3.31 eV and states in the gap and (b) undoped ZnO thin film with a band gap of 3.25 eV.

electron spectroscopy depth profiling of the $Zn_{0.93}Mn_{0.07}O$ thin film shows that Mn is uniformly distributed throughout the epitaxial thin film.

The epitaxial $Zn_{0.93}Mn_{0.07}O$ film is transparent with a slight brown color, whereas the epitaxial ZnO thin films are transparent and colorless. The UV–VIS absorption spectra of ZnO and $Zn_{0.93}Mn_{0.07}O$ thin films are shown in Fig. 2. The ZnO thin film shows a sharp absorption edge at 3.25 eV [Fig. 2(b)]. In contrast, the absorption edge of the $Zn_{0.93}Mn_{0.07}O$ thin film is blueshifted to 3.31 eV and the absorption edge is less sharp due to Mn states extending into the band gap [Fig. 2(a)]. The blueshifted absorption edge and the development of states within the gap are clear indications that the Mn ions have entered into the ZnO lattice. These characteristics have also been observed in Mn-doped ZnO thin films fabricated by pulsed-laser deposition and other Mn-doped II–VI semiconductors.[1,15]

Figure 3(a) shows the magnetic-field dependence of magnetization (M vs H) at various temperatures with fields up to 5 T. The raw data contain a large diamagnetic background due to the much thicker sapphire substrate. The contribution from the sapphire substrate was separately measured and subtracted from the raw data. The results shown in Fig. 3(a) reveal no ferromagnetic characteristics, and the results can be well described by paramagnetic moments. The data have been quantitatively analyzed using the Brillouin function expressed as

$$M = n_{\text{eff}} g S \mu_B B_{5/2}\left[\frac{g S \mu_B H}{k_B (T-\Theta)}\right], \tag{1}$$

where $B_{5/2}[x]$ is the Brillouin function with spin $S=5/2$, the Lander factor $g=2$ as expected for Mn^{2+}, μ_B is the Bohr magneton, and k_B is the Boltzmann constant. The results in Fig. 3(a) can be well described by using $n_{\text{eff}}=1.9\times10^{21}/\text{cm}^3$ and $\Theta=1.01$ K. As indicated by Eq. (1), the $M-H$ curves in Fig. 3(a) at different temperatures should collapse into a single curve of M vs $H/(T-\Theta)$. This is indeed the case as shown in Fig. 3(b), where all the data in Fig. 3(a) fall onto a single curve of M vs $H/(T-\Theta)$. The solid curve in Fig. 3(b) is the calculated results of Eq. (1) using the same parameters as mentioned above.

The magnetic characteristics of our epitaxial $Zn_{0.93}Mn_{0.07}O$ films are clearly paramagnetic. The small value of $\Theta=1.01$ K indicates that there are essentially no interactions among the Mn moments that could lead to ferromagnetic ordering with a substantial T_C. The value of $n_{\text{eff}}=1.9\times10^{21}/\text{cm}^3$ obtained corresponds to an effective Mn content of $x_{\text{eff}}=0.047$, which is slightly smaller than the value of 0.07 as determined from composition analyses. This discrepancy may be due to a small amount of clustering of the Mn ions.

The temperature dependence of magnetization (M vs T) at a field of 1 kOe from 5 to 300 K is shown in Fig. 4. The results can be well described by the Curie–Weiss law

$$\frac{M}{H} = \frac{C}{T-\Theta'}, \tag{2a}$$

$$C = \frac{n'_{\text{eff}} S(S+1) g^2 \mu_B^2}{3 k_B}, \tag{2b}$$

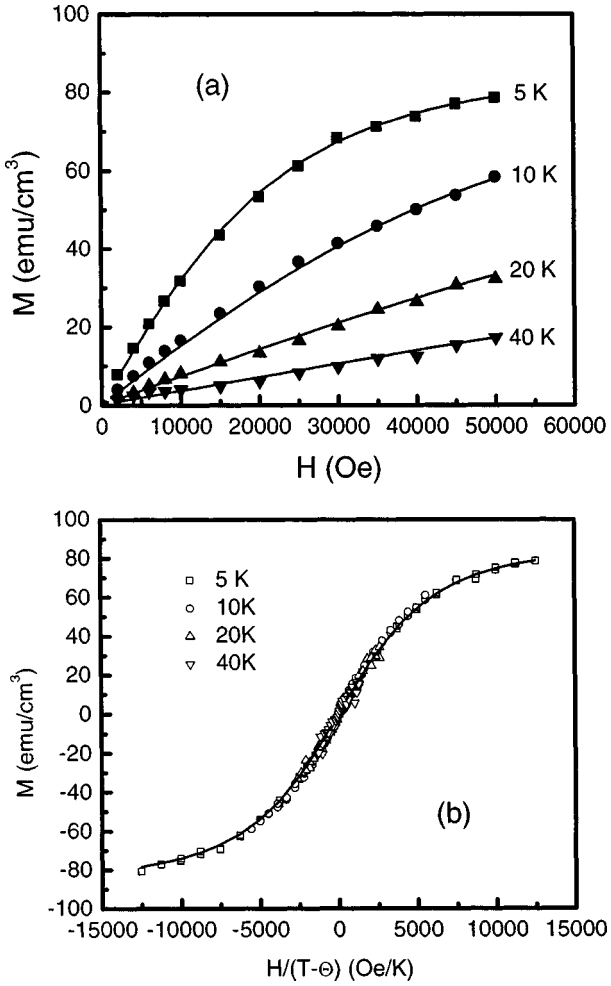

FIG. 3. (a) Field dependence of magnetization (M vs H) at 5, 10, 20, and 40 K, (b) a plot of M vs $H/(T-\Theta)$ of epitaxial $Zn_{0.93}Mn_{0.07}O$. The solid lines are best-fit results using Brillouin function.

using the best-fit parameters of $\Theta' = 1.17$ K, and $n'_{\text{eff}} = 2.2 \times 10^{21}/\text{cm}^3$. These parameters agree well with those obtained from the $M-H$ data.

The magnetic properties of our epitaxial $Zn_{0.93}Mn_{0.07}O$ film show conclusively that it is paramagnetic. The small value of Θ shows that the Mn moments are nearly noninteracting. Indeed, we have found no evidence of ferromagnetic ordering. However, since Mn composition x in our $Zn_{1-x}Mn_xO$ film (0.07 from composition analyses, or 0.047 from magnetic data) is lower than 0.1 as reported in Ref. 10, the absence of ferromagnetic ordering might not be surprising. On the other hand, no ferromagnetic ordering has been observed in samples with $x = 0.36$ as reported in Ref. 8. Among these few reports, there are apparent disagreements concerning the magnetic properties of Mn-doped ZnO. The magnetic properties of Mn-doped ZnO are expected to be strongly influenced by the carrier type (p or n) and carrier density.[10,11] Sato *et al.* predicted p-type (Zn–Mn)O to be ferromagnetic and n-type (Zn–Mn)O to be antiferromagnetic.[11] However, these characteristics of Mn-doped ZnO films are not well known experimentally at present.

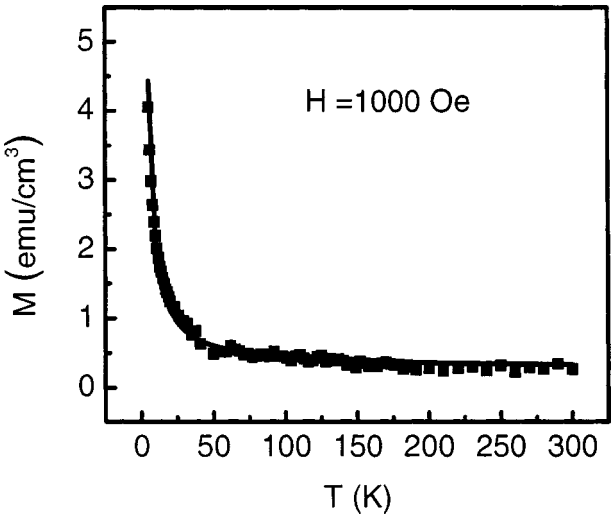

FIG. 4. Temperature dependence of magnetization of $Zn_{0.93}Mn_{0.07}O$ at 1 kOe.

IV. CONCLUSIONS

Epitaxial (0001)-oriented Mn-doped ZnO thin films were fabricated on $(11\bar{2}0)$ sapphire substrates by reactive rf magnetron sputtering method at 400 °C. In addition to PLD and MBE, epitaxial Mn-doped ZnO films can also be made by reactive sputtering. The doped Mn^{2+} ions cause a shift in the absorption edge and the development of states in the band gap. Magnetic properties of the epitaxial $Zn_{0.93}Mn_{0.07}O$ thin films show conclusively that it is paramagnetic with no evidence of ferromagnetic ordering.

ACKNOWLEDGMENT

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