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Journal of Crystal Growth 287 (2006) 66–69
JOURNAL OF CRYSTAL GROWTH
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Magnetic and optical properties of $Zn_{1-x}Mn_xO$ thin films prepared by pulsed laser deposition

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Available online 28 November 2005

Abstract

We report on ferromagnetic characteristics of $Zn_{1-x}Mn_xO$ thin films grown on Al_2O_3 substrates by using pulsed laser deposition. The effects of oxygen pressure on the ferromagnetism in the Mn-doped ZnO thin films are discussed. The carrier concentration was found to be controlled by varying the oxygen pressure. By decreasing oxygen pressure, the films exhibited increases in both the lattice constant and fundamental band gap energy. Large magnetoresistance (MR) was observed in the film grown at 700 °C, especially over 10% in the positive MR. The results indicate the spin splitting caused by strong s–d exchange coupling between the conducting carriers and localized spins of Mn ions.

PACS: 75.50.Pp

Keywords: A3. Physical vapor deposition processes; B1. Zinc compounds; B2. Magnetic materials

1. Introduction

Since the ferromagnetism in $Ga_{1-x}Mn_xAs$ was discovered [1], there has been a great deal of interest in the physical properties of diluted magnetic semiconductors (DMSs) for their potential technological applications to optoelectronic, magnetoelectronic, and microwave devices. The replacement of the cations of III–V or II–VI nonmagnetic semiconductors by host magnetic transition metal (TM) ions such as Mn, Fe, and Co leads to a number of magnetic, optical, magnetooptical, and magnetotransport phenomena. The presence of TM ions in these materials leads to an exchange interaction between itinerant sp band electrons or holes and the d electron spins localized at the magnetic ions, resulting in various magnetic-field-induced functionalities. Theoretical calculations have predicted for the possibility of ferromagnetic phenomenon in TM-doped ZnO even at room temperature [2,3]. Because ZnO also has a well-known piezoelectric and electro-optic properties, the incorporation of ferromagnetism in ZnO can lead to a variety of new multifunctional phenomena. However, this prediction is confirmed only in several groups based on their measurements of magnetic properties for TM-doped ZnO thin film samples [4,5]. And $Zn_{1-x}TM_xO$ films investigated by Ando et al. have not shown any ferromagnetic ordering down to 5 K [6,7]. These controversial results seem to come from either the low quality or the poor reproducibility of thin film. Here, it is necessary to investigate the factors of growth parameters that enhance ferromagnetic ordering in Mn–Zn–O systems. In this paper, we report on the discovery of ferromagnetism in Mn-doped ZnO (ZMO) films and the effect of oxygen pressure on ferromagnetic ordering.

2. Experiment

The ZMO thin films were fabricated by using a pulsed laser deposition (PLD). To prepare the ceramic target, prescribed amounts of ZnO (0.7 mol%) and Mn_2O_3 (0.3 mol%) were mixed, calcined at 700 °C for 5 h, and sintered at 1100 °C for 12 h in air. No intentional carrier doping was used. The target

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0022-0248/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jcrysgro.2005.10.044

was ablated by the third harmonics (wavelength of 355 nm) of Nd:YAG laser. The films were grown on (0 0 0 1) Al_2O_3 substrates at 700 °C. After the evacuation of vacuum chamber to the pressure of 1.0×10^{-6} Torr, oxygen gas was injected into the chamber by a mass flow controller and maintained at a constant pressure. The partial oxygen pressure (PO) during the deposition was 1.0×10^{-1} (sample A) and 1.0×10^{-3} Torr (sample B). The thicknesses of the deposited films determined by scanning electron microscopy were in the range of 50–70 nm. The crystalline phase was investigated by using X-ray diffraction (XRD) with a Ni-filtered CuK (= 1.5406 Å) source. The magnetic measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer as functions of temperature and magnetic field. The van der Pauw technique was used for measuring the Hall resistance and magnetoresistance (MR) in fields up to 9 T at temperatures ranging from 5 to 300 K by using a Physical Property Measurement System (PPMS).

3. Results and discussion

The crystal structures of thin films were characterized by XRD. The XRD $\theta - 2\theta$ patterns of thin films are shown in Fig. 1. All the peaks correspond to standard ZnO diffraction pattern with wurzite structure. It seems that the addition of Mn did not affect the structure of ZnO. The XRD spectra of ZMO (0 0 2) peak at 34.4–35.6° besides the substrate peak of Al_2O_3 (0 0 6). It seems that the films are well oriented towards the *c*-axis, indicating that Mn ions tend to substitute for Zn sites without changing the crystal structure of ZnO (wurtzite structure) in the present Mn composition region. However, the position of the ZMO (0 0 2) peak shifted to lower angles with decreasing oxygen pressure as shown in Fig. 1. From variation of the (0 0 2) peak position with the oxygen pressure, the *c*-axis lattice parameter of the alloys is found to increase with a decrease in oxygen pressure. It shows the expansion of the unit-cell volume of the crystal [7]. It can be explained in terms of the larger covalent radius of Mn than that of Zn [8]. Also, the (0 0 2) peak exhibits significant broadening as pressure decrease, and this is attributed to an increase in disorder.

As shown in Fig. 2, the absorption spectra of the samples exhibited an abrupt increase in near band edges. Based on the transmittance spectra, the band gap energy of the films was calculated by using α^2 versus E plot where α is the absorption coefficient and E is the photon energy. The band gap expansion of ZMO films from 3.6 eV (sample A) to 3.7 eV (sample B) indicates that ZnMnO alloys are formed by the Mn incorporation. Also the development of midgap absorption is observed as other II–Mn–VI alloys [7]. The broadening of the absorption edge is due to Mn states extending into the band gap. The blue-shifted of absorption edge and the development of states within the gap are clear evidence 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 [9,10].

Fig. 3 shows the difference between field-cooled (FC) and zero-field-cooled (ZFC) magnetization as a function of

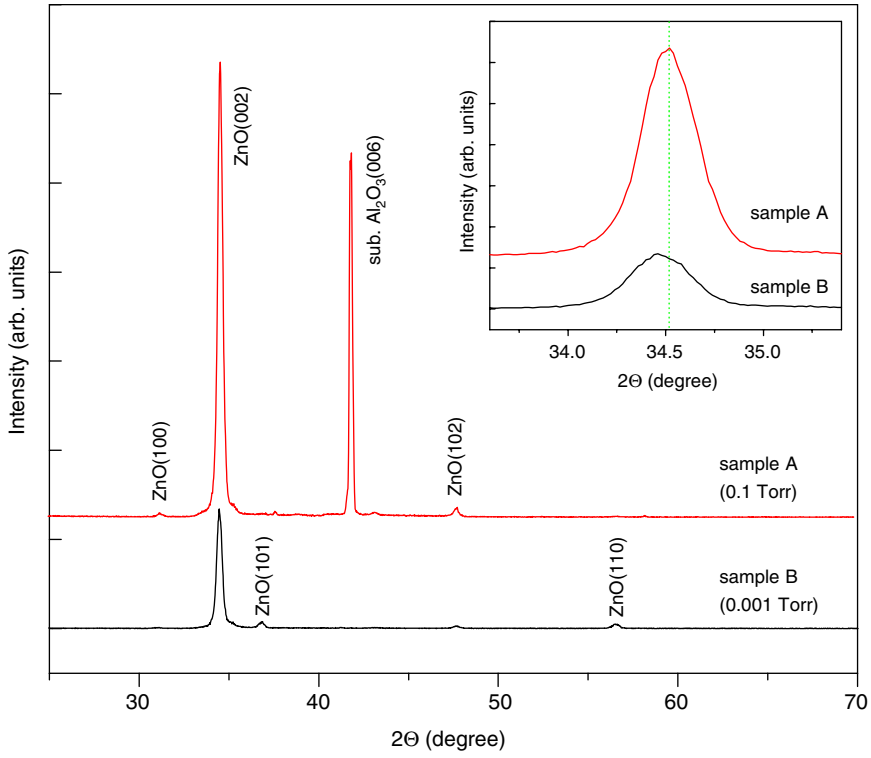

Fig. 1. X-ray diffraction patterns for the samples A and B. Inset shows enlarged ZnO (0 0 2) peaks.

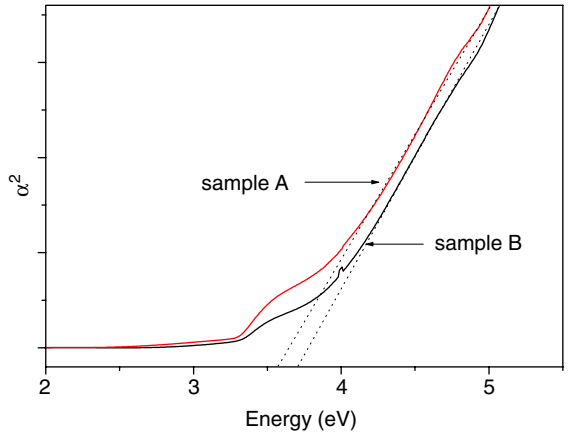

Fig. 2. Room temperature absorption spectra for the samples A and B.

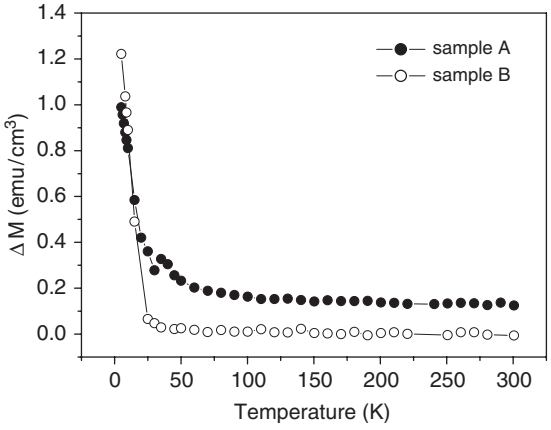

Fig. 3. Temperature dependence on the difference between field-cooled and zero-field-cooled magnetizations measured in a field of 100 Oe for the samples A and B.

temperature in an applied field of 100 Oe parallel to the plane for films grown at 700 °C under 1×10^{-1} and 1×10^{-3} Torr of oxygen pressure, respectively. In order to eliminate paramagnetic and diamagnetic contributions to the magnetization, we subtracted the ZFC data from the FC data, denoted as $\Delta M = M(\mathrm{FC})$–$M(\mathrm{ZFC})$. It implies the presence of hysteric behavior if ΔM does not converge to zero value [11,12]. In the low-temperature region below 25 K, abrupt increase of ΔM is observed and the sample B shows higher magnetization than the sample A. On the other hand, sample A shows the nonzero value of ΔM all over the range of measuring temperature including room temperature, which indicates the presence of ferromagnetism.

These phenomena could be explained again by hysteresis loops in Fig. 4. For all the samples, the field dependence of magnetization (M–H curves) measured at 5 K show well-defined hysteresis loops. At room temperature, however, ferromagnetic behavior disappears in the sample B and the sample A is still indicative of ferromagnetic ordering. In the growth of n-type ZnO thin film, higher PO suppresses the

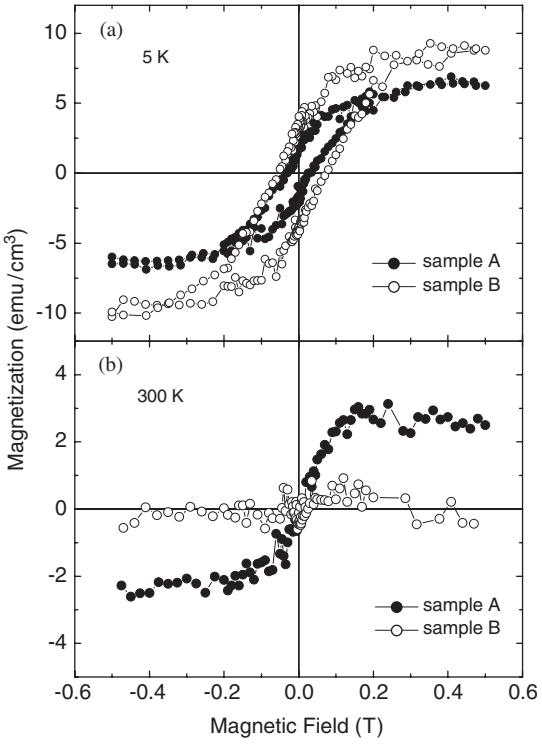

Fig. 4. Hysteresis loops measured at (a) 5 K and (b) 300 K for the samples A and B.

formation of oxygen vacancies that leads to the decrease of charge carriers [13]. Similarly with our Hall measurements, the carrier concentration measured at 5 K is 1.40×10^{19}/cm^3 and 4.13×10^{19}/cm^3 for samples A and B, respectively. The sample A has higher electrical resistivity than the sample B. Therefore, it is suggested that the electric transport is mediated with the hopping of charge carriers between the defect sites. The oxygen vacancies trap the charge carriers of electrons, and then the trapped electrons surrounded by cations of Zn and Mn mediate ferromagnetic exchange interactions between the localized spins of Mn ions. During the cooling down through a critical temperature, the formation of such oxygen-vacancy-induced magnetic clusters is stabilized and the magnetization is strongly enhanced. This suggestion can explain the experimental result that the sample B has higher magnetization than the sample A in the low-temperature region. This is well agree with the previous report by J. Han et al. They suggested that the magnetic properties of ZMO were not related with the magnetic exchange interaction, but hopping conduction at low temperatures below 18 K [14].

Fig. 5 shows the isothermal MR measured at different temperature for ZMO films grown under various PO in magnetic fields up to 9 T perpendicular to the plane of films. The samples A and B show the positive MR ratio of $R(H)/R(0) = 10\%$ and 8% at 5 K, respectively. The positive MR at low fields decrease with increasing magnetic field (H) and the maximum of resistivity (ρ) decreased as increasing temperature. The MR behaviors were thought

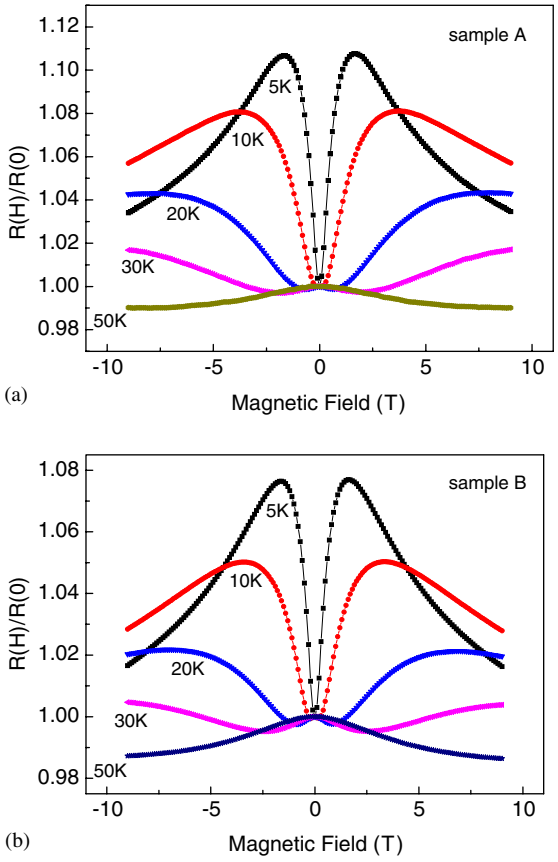

Fig. 5. Normalized magnetoresistance measured at various temperatures; 5, 10, 20, 30, and 50 K for the (a) sample A and (b) sample B.

to come from the spin splitting by s–d exchange coupling [15] and the rising of the Fermi level in the majority-spin subband [16] in the previous reports. It can also be explained by the oxygen-vacancy-induced magnetic cluster model, as described above. The strong s–d exchange interaction at low temperature stabilizes the forming of oxygen-vacancy-induced magnetic cluster. When the magnetic field is applied, however, ferromagnetic ordering of the localized spins is induced; therefore the charge carriers are not necessary to be trapped in order to align the localized spins ferromagnetically. Hence, the charge carriers lead to the negative MR at high fields. Moreover, the value of H at maximum ρ decreases with decreasing temperature. One of the reasons of this reduction is suggested that the spins of Mn ions are more easily aligned at the lower temperature. These results indicate that Mn doping provides localized spin interaction of conducting carriers in ZnO.

4. Conclusion

In conclusion, highly c-axis oriented ZMO thin films have been fabricated by using a pulsed laser deposition. Large MR was observed in the film grown at 700 °C under PO $= 1 \times 10^{-1}$ Torr, especially over 10% in the positive MR. The presence of significant oxygen vacancies have been detected in our system, where the spin-polarized charge carriers are expected to mediate the ferromagnetic exchange coupling between the localized magnetic ions.

Acknowledgment

This work was supported by the Government (R01-2004-000-10195-0(2004)) from the Basic Research Program of KOSEF (Korea Science and Engineering Foundation).

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