Room-Temperature Ferromagnetic Ordering in Mn-Doped ZnO Thin Films Grown by Pulsed Laser Deposition

W.Y. SHIM,[1] K.A. JEON,[2] K.I. LEE,[1] S.Y. LEE,[2] M.H. JUNG,[3] and W.Y. LEE[1,4]

1.—Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea. 2.—Department of Electrical and Electronic Engineering, Yonsei University, Seoul 120-749, Korea. 3.—Quantum Materials Research Team, Korea Basic Science Institute, Deajeon 305-333, Korea. 4.—E-mail: wooyoung@yonsei.ac.kr

The ferromagnetic ordering in Mn-doped ZnO thin films grown by pulsed laser deposition (PLD) as a function of oxygen pressure and substrate temperature has been investigated. Room-temperature ferromagnetic behaviors in the Mn-doped ZnO films grown at 700°C and 800°C under 10^{-1} torr in oxygen pressure were found, whereas ferromagnetic ordering in the films grown under 10^{-3} torr disappeared at 300 K. The large positive magnetoresistance (MR), ~10%, was observed at 5 K at low fields and small negative MR was observed at high fields, irrespective of oxygen pressure. In particular, anomalous Hall effect (AHE) in the Mn-doped ZnO film grown at 700°C under 10^{-1} Torr has been observed up to 210 K. In this work, the observed AHE is believed to be further direct evidence demonstrating that the Mn-doped ZnO thin films are ferromagnetic.

Key words: Diluted magnetic semiconductors (DMSs), Mn-doped ZnO, anomalous Hall effect (AHE), pulsed laser deposition (PLD), oxygen pressure, ferromagnetism

INTRODUCTION

Diluted magnetic semiconductors (DMSs) have attracted much interest in recent years due to their possibility of exploiting charge and spin degrees of freedom to bring novel functionalities to semiconductor devices.[1–21] In particular, wide bandgap semiconductors continue to be of central importance, since Dietl et al.[2] predicted T_c exceeding room temperature for GaN and ZnO containing 5% of Mn and a high hole concentration (3.5×10^{20} cm^{-3}). Recently, although Mn-doped GaN[3–5] and Mn-doped ZnO[6–17] have been intensively studied, the origins of their ferromagnetism are still not fully understood.

II-VI DMSs such as ZnO are of particular significance because the solubility limit of magnetic ions is very high. However, the magnetic behaviors of Mn-doped ZnO differ for different research groups, for instance, which reported Mn-doped ZnO to be antiferromagnetic[7] and paramagnetic[8,11] and ferromagnetic.[9,10,12–17]Even the origins of ferromagnetic ordering were controversially reported due to a change of electronic band structure,[9] a carrier-induced mechanism,[12] or an oxygen-vacancy-stabilized metastable ferromagnetic phase.[16] The discrepancies can be attributed to different sample growing conditions or different sample growing methods, e.g., pulsed laser deposition (PLD),[7,8,12,15–17] laser molecular-beam epitaxy,[9] ion implantation,[10] magnetron sputtering,[11] and standard solid-state reaction.[6] Furthermore, the magnetic properties of Mn-doped ZnO can be sensitive to Mn content and growth conditions, e.g., substrate temperature, oxygen pressure, and so on.

In the present work, we report the magnetic and magnetotransport properties of Mn-doped ZnO thin films grown by PLD as a function of oxygen pressure and substrate temperature. The origin of room-temperature ferromagnetism in the Mn-doped ZnO films grown at high oxygen pressure is discussed.

EXPERIMENT

Mn-doped ZnO thin films in the thickness range 20–50 nm were grown by PLD on a single-crystal

(Received August 1, 2005; accepted November 22, 2005)

sapphire substrate using ZnMnO targets with 30% of Mn concentrations. The deposition time by ablating targets with Nd:YAG laser (355 nm) and laser pulse energy density were 8.5 min and 2J/cm^2, respectively. The films were grown at various substrate temperatures ranging from 20°C to 800°C under oxygen pressure of 10^{-1} to 10^{-3} torr. X-ray diffraction (XRD) technique and high-resolution transmission electron microscopy (HRTEM) were used to investigate the crystal structure and microstructure of the Mn-doped ZnO thin films. TEM–electron dispersive spectrometry was also used to estimate Mn content in the films. The van der Pauw Hall and magnetoresistance (MR) measurements were performed by applying a magnetic field up to 9 T in the temperature range 4–300 K, in order to investigate the electrical and magnetotransport properties of the Mn-doped ZnO films. Hysteresis loops were measured at temperatures ranging from 4 K to 300 K using a superconducting quantum interference device.

RESULTS AND DISCUSSION

The crystal structure of the 26at.%Mn-doped ZnO film grown at 700°C under 10^{-1} torr in oxygen pressure was investigated by XRD. Figure 1 shows the XRD pattern for the film in which all the peaks were found to be from the wurtzite structure of ZnO, except for peaks of (013), (223) from $Zn_2Mn_3O_8$. As reported in a previous study,[18] $Zn_2Mn_3O_8$ is believed not to be responsible for the origin of ferromagnetic ordering in the Mn-doped ZnO films, since it is nonmagnetic. A representative HRTEM image (see the inset of Fig. 1) provides direct experimental evidence that there are no appreciable Mn nanoclusters or Mn oxides as a secondary phase in the Mn-doped ZnO film, which is suspected to exhibit ferromagnetic ordering in the film. Our results on the crystal structure and microstructures are crucial in addressing the intrinsic origin of ferromagnetic ordering in the Mn-doped ZnO systems.

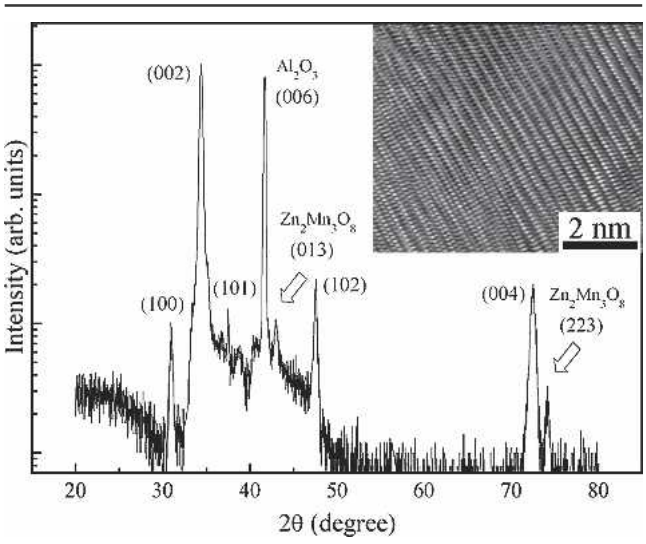

Fig. 1. XRD pattern of the film grown at 700°C under 10^{-1} torr on the Al_2O_3 substrate. The inset is a cross-sectional HRTEM image of 26% Mn-ZnO showing no indication of any embedded Mn clusters or Mn oxides.

The magnetic behaviors for the Mn-doped ZnO films have been investigated as a function of substrate temperature and oxygen pressure. Figure 2 shows M-H loops for the Mn-doped ZnO films grown at 700°C and 800°C under an oxygen pressure of 10^{-1} and 10^{-3} torr, obtained with magnetic fields applied parallel to the plane of the films at 4 K and 300 K. Regardless of the oxygen pressure, the Mn-doped ZnO thin films grown at 700°C and 800°C exhibit ferromagnetic ordering at 4 K. On the other hand, both the Mn-doped ZnO films grown at 700°C and 800°C under 10^{-1} torr are still indicative of ferromagnetic ordering at 300 K, whereas the ferromagnetic behavior in the films at 700°C and 800°C grown under 10^{-3} torr was found to almost disappear at 300 K. In this study, it is of great significance to understand the room-temperature ferromagnetic ordering in the Mn-doped ZnO thin films under 10^{-1} torr. Although room-temperature ferromagnetism in Mn-doped ZnO films[12,15,16] has been previously reported, the origin of ferromagnetic ordering remains controversial. A clear understanding of the room-temperature ferromagnetic ordering can provide us with new experimental approaches to an opportunity to develop spintronic devices based on Mn-doped ZnO films.

The variation of oxygen pressure during the growth in the present work was found to result in a dramatic difference in magnetic behaviors other than the substrate temperature, as seen in Fig. 2. It has been reported that higher oxygen pressure in PLD suppresses the formation of oxygen vacancies, leading to reduction in free electrons in a ZnO system.[19] From the van der Pauw Hall measurements, we found that the electron concentration ($n \approx 1.4 \times 10^{19}$/cm^3) in the Mn-doped ZnO thin film grown under 10^{-1} torr is lower than that ($n \approx 4.1 \times 10^{19}$/cm^3) in the sample grown under 10^{-3} torr at 4 K.

On the assumption that the origin of ferromagnetism in the Mn-doped ZnO thin films is carrier mediated such as (Ga,Mn)As, (In,Mn)As,[1,2] the magnetic moment in Mn-doped ZnO thin film grown under 10^{-1} torr should be lower than that in the sample grown under 10^{-3} torr at 4 K due to lower concentration, as confirmed from Fig. 2a and c. However, the assumption turned out to be incorrect at 300 K, since the magnetic moment in Mn-doped ZnO thin film grown under 10^{-1} torr is higher than that in the sample grown under 10^{-3} torr, although electron concentration in the film grown under 10^{-1} torr is lower than that in the film grown under 10^{-3} torr at 300 K (see Fig. 2b and d).

In order to clarify the origin of ferromagnetic ordering and the effects of substrate temperature and oxygen pressure on the magnetic properties in the Mn-doped ZnO thin films, we investigated temperature dependence of magnetization for the Mn-doped ZnO films grown at 700°C and 800°C

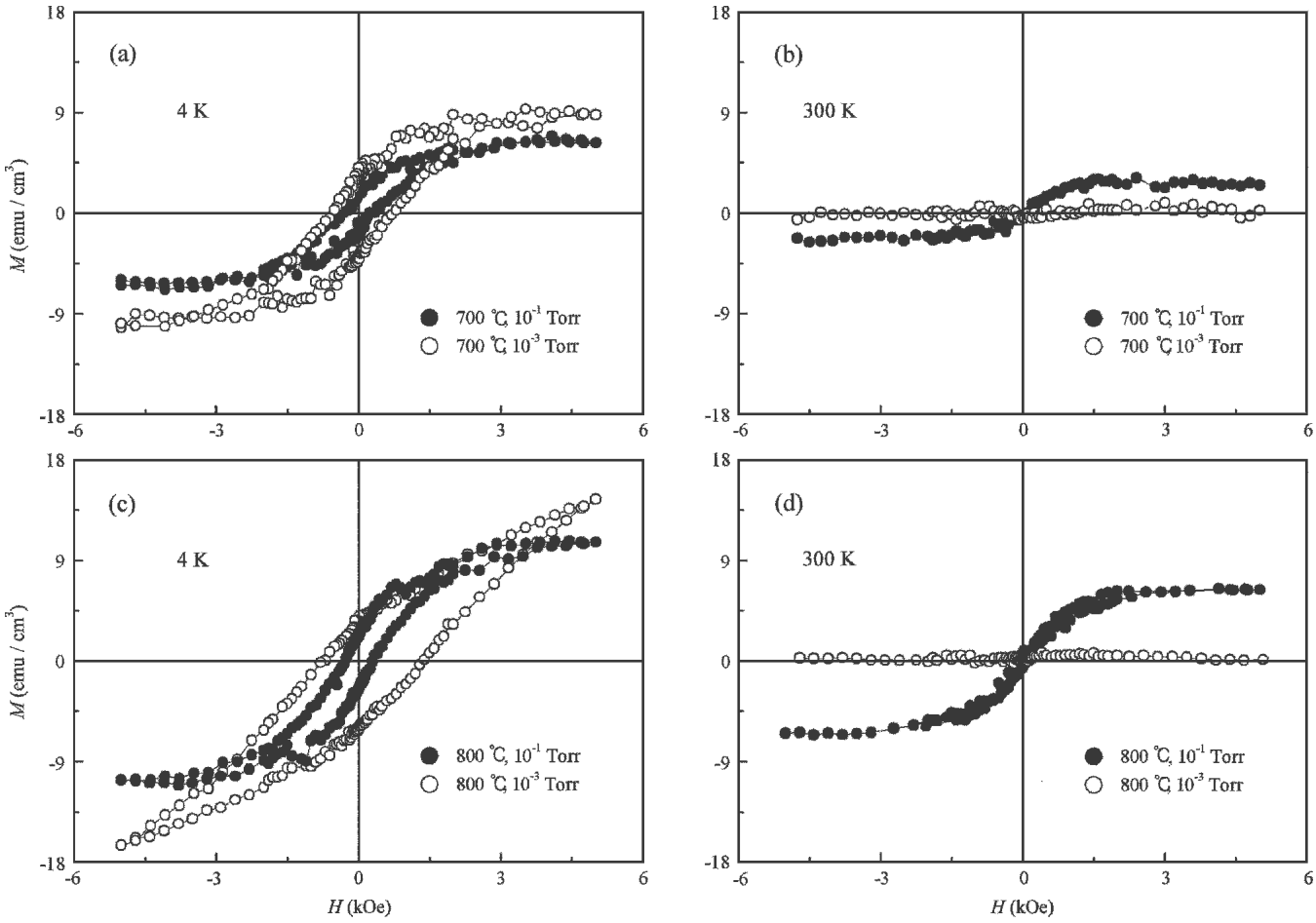

Fig. 2. (a)–(d) M-H loops for the Mn-doped ZnO films grown at 700°C and 800°C under an oxygen pressure of 10^{-1} torr and 10^{-3} torr, measured with magnetic fields applied parallel to the plane of the films at 4 K and 300 K.

under 10^{-1} torr and 10^{-3} torr, respectively. Figure 3 exhibits the magnetization difference (ΔM) between the zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations as a function of temperature under a magnetic field of 100 Oe. This subtraction effectively eliminates the diamagnetic contribution of the substrate, a single-crystal sapphire, from the samples. The FC-ZFC subtraction is particularly effective when there is a small amount of a ferromagnetic material in the presence of a large diamagnetic background.

Ferromagnetic ordering for the Mn-doped ZnO films grown at 700°C and 800°C under 10^{-1} torr and 10^{-3} torr is clearly seen at 4 K. The magnetic moment in the samples grown at 800°C drastically decreases with increasing temperature below 45 K, but the magnetic moment in the samples only grown at 700°C and 800°C under 10^{-1} torr persists up to room temperature. This is in very good agreement with the M-H loops shown in Fig. 2. Crossovers in the M-T curves, at which magnetizations for the samples grown under 10^{-1} torr and 10^{-3} are identical, are found to occur at 12 K and 48 K, respectively, as indicated by arrows in Fig. 3. The detailed reason for this is not clear yet, but it should be noted that it is related to the formation of oxygen vacancies due to oxygen pressure, giving rise to the variation in electron concentration.

Very recently, an oxygen-vacancy-stabilized metastable ferromagnetic phase[16] was reported to be responsible for high-temperature ferromagnetism, indicating that the carrier-induced mechanism is inappropriate as an origin of ferromagnetism in Mn-doped ZnO. On the other hand, there is a theoretical work[20] based on first-principles total energy calculations and Monte Carlo simulations, indicating that hydrogen-mediated spin-spin interactions lead to high-temperature ferromagnetism in ZnO-based dilute magnetic semiconductors. Although the reported origins[16,20] can be adopted to explain the room-temperature ferromagnetic ordering in our samples, they are not available to address the crossovers in magnetization for the samples grown under 10^{-1} torr and 10^{-3} torr.

Figure 4 shows the variation of MR [R(H)/R(0)] against magnetic fields applied perpendicular to the sample plane for the Mn-doped ZnO film grown at 700°C under 10^{-1} torr. The positive MR is striking at 5 K, reaching ~10%, at high fields and negative MR at low fields. The positive MR behaviors are believed to be due to the spin splitting by s-d exchange coupling between the carriers and localized

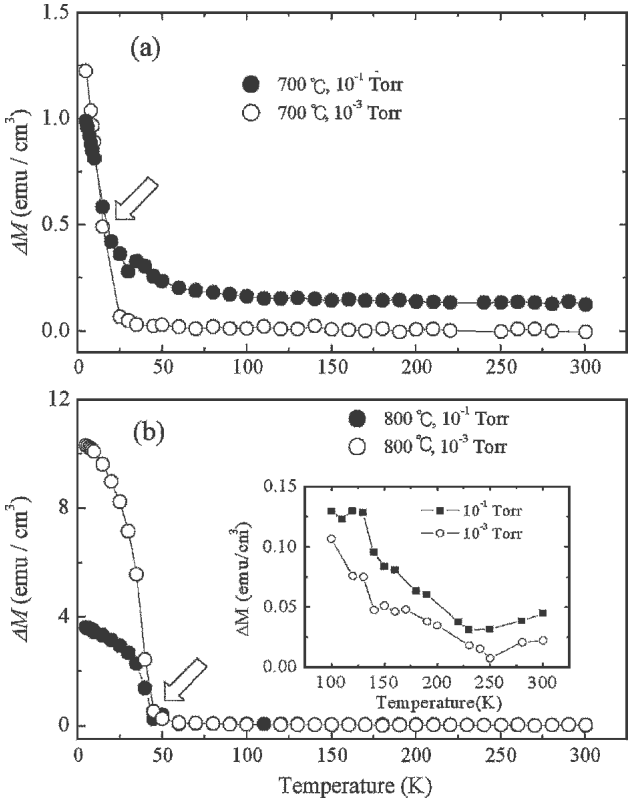

Fig. 3. (a) and (b) Temperature dependence of magnetization for the Mn-doped ZnO films grown at 700°C and 800°C under 10^{-1} torr and 10^{-3} torr, respectively. Magnetization difference (ΔM) between the ZFC and FC magnetizations were measured as a function of temperature under a magnetic field of 100 Oe. The inset in (b) shows the comparison between ΔM of the films grown under 10^{-1} torr and 10^{-3} torr above 50 K.

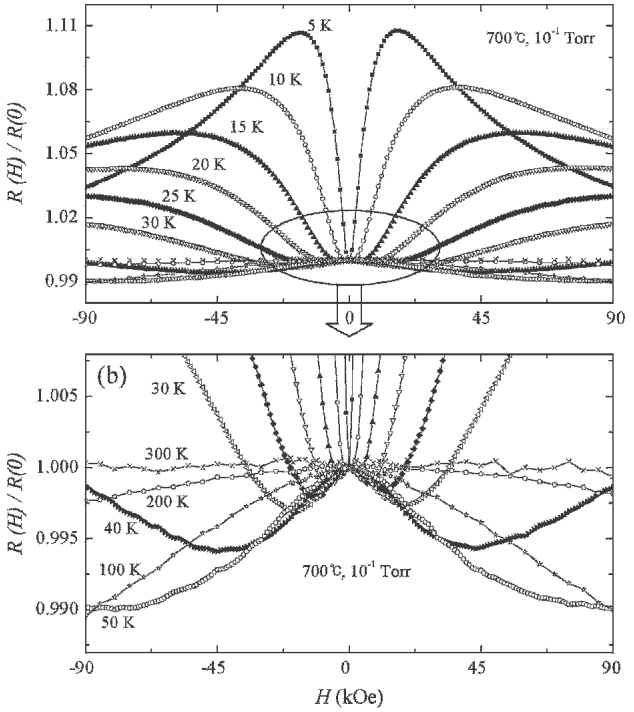

Fig. 4. (a) Variation of MR [R(H)/R(0)] against magnetic fields applied perpendicular to the sample plane for the Mn-doped ZnO film grown at 700°C under 10^{-1} torr. (b) Negative MR at low fields and positive MR at high fields are clearly observed.

spin and the rise of the Fermi level in the majority-spin sub-band.[21] The positive MR decreases with increasing temperature and disappears at room temperature. We also found small negative MR due to a weak localization,[22] as shown in Fig. 4b. Interestingly, we found that the variation of MR for the Mn-doped ZnO film grown at 700°C under 10^{-3} torr is very similar to that for the film grown at 700°C under 10^{-1} torr, suggesting that oxygen pressure does not affect the variation of MR. The MR behaviors cannot be direct evidence for the ferromagnetic ordering in the Mn-doped ZnO films, but reflect doping of Mn into ZnO.

In particular, we demonstrated the ferromagnetic ordering in the Mn-doped ZnO thin film grown at 700°C under 10^{-1} torr by way of finding the anomalous Hall effect (AHE) up to 210 K, which was for the first time observed in Mn-doped ZnO systems to the best of our knowledge. The Hall effect is given to two contributions that are well known as the ordinary Hall effect (OHE) and the AHE.[23] The OHE is a consequence of Lorentz force acting on the current carriers, whereas the AHE arises from spin-orbit interaction and other couplings. The observation of AHE arising from asymmetric scattering due to spin-orbit coupling is clear evidence of the exchange interaction between itinerant carriers and localized spins.

Figure 5 shows the Hall resistivity measured at several temperatures of 5 K, 15 K, 30 K, and 210 K for film grown at 700°C under 10^{-1} torr as a function of applied field. In order to extract the anomalous Hall resistivity, the ordinary Hall resistivity should be subtracted from the measured Hall resistivity. From the linear extrapolation of the Hall resistivity in the high field regime, because the ordinary Hall resistivity is linear to the field, the ordinary Hall coefficients are derived to be $R_0 = -0.133$ cm^3/C to -0.448 cm^3/C, which gives the carrier concentration ranging from 1.40×10^{19}/cm^3 to 4.70×10^{19}/cm^3 at temperatures between 5 and 210 K. The negative sign of R_0 suggests electron conduction to the charge carriers, whereas the anomalous Hall coefficient, R_A, has the positive sign. The opposite signs of R_0 and R_A have been previously observed in (InMn)Sb,[24] half-metallic Sr_2FeMoO_6,[25] and co-doped TiO_2.[26] Even in a single material of (GaMn)As, the different signs of R_A are shown depending only on the growth temperature.[27] The determination of the R_A sign is probably made by asymmetric scattering due to the different density of states for positive and negative orbital orientation.[28] The anomalous Hall resistivity is in good accordance with the M-H curves, as seen in the inset of Fig. 5, where both curves are saturated at almost identical fields, ±2.5 kOe.

For the films grown at 700°C under 10^{-3} torr in oxygen pressure, however, no AHE is observed even though it has higher magnetization at low temperature. One possible origin for the absence of AHE in the sample grown under 10^{-3} torr in oxygen pressure can be a weak coupling between the charge

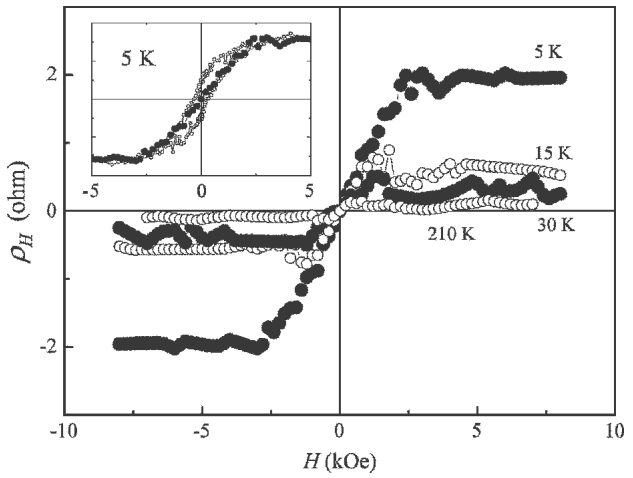

Fig. 5. Hall resistivity measured at several temperatures of 5 K, 15 K, 30 K, and 210 K as a function of magnetic field for the Zn-Mn-O film grown at 700°C under 10^{-1} torr in oxygen pressure. The anomalous part of Hall resistivity is plotted by subtracting the ordinary contribution from the measured Hall resistivity. The open and closed circles in the inset represent magnetic hysteresis and anomalous Hall resistivity at 5 K, respectively.

carriers of conduction electrons and the localized spins of magnetic impurities, as previously reported.[29] The other possibility for describing the lack of AHE in films grown under 10^{-3} torr arises from higher oxygen vacancies that deteriorate the crystalline quality and disturb the homogeneous distribution of Mn ions into the system. However, an understanding of the absence of AHE in the low-temperature regime, where the larger magnetic moment is observed, is not yet clear. This fact might lead to the conclusion that the AHE in our samples is strongly dependent on the anomalous Hall coefficient (R_A) rather than the magnetization (M) in which Hall resistivity is expressed:

$$\rho_{xy} = R_0 H + R_A M$$

In the case of (Ga,Mn)As, skew scattering is responsible for the AHE given by the relationship of $M \sim (1/c)R_{Hall}/R_{xx}$, where c is the constant, which means R_A is linearly proportional to R_{xx}.[1] We have confirmed, however, that c is temperature dependent in the plot of M versus R_{Hall}/R_{xx}. Hence, we exclude the skew scattering mechanism for the presence of AHE in the film grown under 10^{-1} torr. The other well-known mechanism for describing the AHE behavior is the side jump mechanism based on the constant lateral displacement Δy of the charge carrier's trajectory at the point of scattering and expressed as $\tan\theta_S \approx \theta_S \approx \Delta y/\ell \propto \rho_{xy}\Delta y$, where θ_S is the scattering angle, Δy the lateral displacement, and ℓ the mean free path, finally resulting in the form of $R_A \propto \rho^2_{xx}$.[23] Our results suggest that the AHE in our Zn-Mn-O films grown at 700°C under 10^{-1} torr in oxygen pressure is attributed to the side jump mechanism due to its short mean free path.

SUMMARY

In summary, we have investigated the effects of oxygen pressure and substrate temperature on the magnetic and magnetotransport properties of the Mn-doped ZnO thin films grown by PLD. We found that ferromagnetic ordering in the Mn-doped ZnO films grown at 700°C and 800°C under 10^{-1} torr persists up to 300 K, whereas that in the films grown under 10^{-3} torr was found to disappear at 300 K. We also found the large positive MR at high fields and small negative MR at low fields, regardless of oxygen pressure. Although the observed MR behaviors cannot be direct evidence indicating the ferromagnetic ordering in the Mn-doped ZnO films, it reflects doping of Mn into ZnO. On the other hand, the observed AHE reveals intrinsic ferromagnetic ordering in the Mn-doped ZnO thin film grown at 700°C under 10^{-1} torr in oxygen pressure. Our results support that charge carriers mediate the ferromagnetic exchange coupling between the localized magnetic ions due to the presence of significant oxygen vacancies in the Mn-doped ZnO thin film.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science and Technology of Korea through the Cavendish-KAIST Research Cooperation Program and by grant No. R01-2004-000-10195-0 (2005) from the Basic Research Program of the Korea Science and Engineering Foundation.

REFERENCES

1. H. Ohno, *Science* 281, 951 (1998).
2. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* 287, 1019 (2000).
3. G.T. Thaler et al., *Appl. Phys. Lett.* 80, 3964 (2002).
4. K.S. Hur, M.H. Ham, J.M. Myung, J.M. Lee, K.I. Lee, J.Y. Chang, S.H. Han, H.J. Kim, and W.Y. Lee, *Jpn. J. Appl. Phys.* 41, L 1069 (2002).
5. K. Ando, *Appl. Phys. Lett.* 82, 100 (2003).
6. S. Han, T. Jang, Y. Kim, B. Park, J. Park, and Y. Jeong, *Appl. Phys. Lett.* 83, 920 (2003).
7. T. Fukumura, Z. Jin, M. Kawasaki, T. Shono, T. Hasegawa, S. Koshihara, and H. Koinuma, *Appl. Phys. Lett.* 78, 958 (2001).
8. A. Tiwari, C. Jin, A. Kvit, D. Kumar, J. Muth, and J. Narayan, *Solid State Commun.* 121, 371 (2002).
9. S. Jung, S. An, G. Yi, and C. Jung, S. Lee, and S. Cho. *Appl. Phys. Lett.* 80, 4561 (2002).
10. D. Norton, S.J. Pearton, A. Hebard, N. Theodoropoulou, L. Boatner, and R. Wilson, *Appl. Phys. Lett.* 82, 239 (2003).
11. X. Cheng and C. Chien, *J. Appl. Phys.* 93, 7876 (2003).
12. P. Sharma, A. Gupta, K. Rao, F. Owens, R. Sharma, R. Ahuja, J. Guillen, B. Johansson, and G. Gehring, *Nat. Mater.* 2, 673 (2003).
13. Y. Chang, D. Wang, X. Luo, X. Xu, X. Chen, L. Li, and C. Chen, *Appl. Phys. Lett.* 83, 4020 (2003).
14. V. Roy, A. Djurisic, H. Liu, X. Zhang, Y. Leung, M. Xie, J. Gao, H. Lui, and C. Surya, *Appl. Phys. Lett.* 84, 756 (2004).
15. Y. Heo, M. Ivill, K. Ip, D. Norton, S.J. Pearton, J. Kelly, R. Rairigh, A. Hebard, and T. Steiner, *Appl. Phys. Lett.* 84, 2292 (2004).
16. D. Kundaliys et al., *Nat. Mater.* 3, 709 (2004).
17. T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, *Appl. Phys. Lett.* 75, 3366 (1999).
18. P. Sharma, A. Gupta, F. Owens, A. Inove, and K. Rao, *J Magn. Magn. Mater.* 282, 115 (2004).

19. S. Choopun, R.D. Vispute, W. Noch, A. Balsamo, R.P. Sharma, and T. Venkatesan, *Appl. Phys. Lett.* 75, 3947 (1999).
20. C.H. Park and D.J. Chadi, *Phys. Rev. Lett*. 94, 127204 (2005).
21. M. Sawicki, T. Dietl, J. Kossut, J. Igaison, T. Wojtowicz, and W. Plesiewicz, *Phys. Rev. Lett.* 56, 508 (1986).
22. A. Goldenblum, V. Bogatu, T. Stoica, Y. Goldstein, and A. Many, *Phys. Rev. B: Condens. Matter Mater. Phys.* 60, 5832 (1999).
23. C. Chien and C. Westgate, *The Hall Effect and Its Applications* (New York: Plenum Press).
24. T. Wojtowicz et al., *Appl. Phys. Lett.* 82, 4310 (2003).
25. W. Westerburg, D. Reisinger, and G. Jakob, *Phys. Rev. B: Condens. Matter Mater. Phys.* 62, R767 (2000).
26. H. Toyosaki, T. Fukumura, Y. Yamada, K. Nakajima, T. Chikyow, T. Hasegawa, H. Koinuma, and M. Kawasaki, *Nat. Mater.* 3, 221 (2004).
27. W. Allen, E.G. Gwinn, T.C. Kreutz, and A.C. Gossard, *Phys. Rev. B: Condens. Matter Mater. Phys.* 70, 1253201 (2004).
28. A. Fert and O. Jaoul, *Phys. Rev. Lett.* 28, 303 (1972).
29. S.J. Han, J.W. Song, C.H. Yang, S.H. Park, J.H. Park, and Y.H. Jeong, *Appl. Phys. Lett.* 81, 4212 (2002).