Evidence for carrier-induced ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films: Anomalous Hall effect

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The intrinsic origin of the ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films grown by pulsed-laser deposition was investigated. The ferromagnetic behaviors for a $Zn_{1-x}Mn_xO$ ($x=0.26$) film grown at 700 °C under oxygen pressures of 10^{-1} Torr were observed at 4 and 300 K. The anomalous Hall effect (AHE) was found at temperatures of up to 210 K for the $Zn_{0.74}Mn_{0.26}O$ thin film. The anomalous Hall coefficients (R_A) were determined to be approximately proportional to the square of resistivity in the low field region, indicating the side-jump process for the AHE. Our results provide direct experimental evidence that a carrier-mediated mechanism is responsible for the ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films grown by pulsed-laser deposition. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743728]

I. INTRODUCTION

There has been great interest in transition-metal-doped ZnO as a diluted magnetic semiconductor (DMS) for use in spintronics. In particular, $Zn_{1-x}Mn_xO$ thin films have attracted much attention due to the large solubility of Mn (<35%) into high-quality epitaxial ZnO thin films[1] and its high Curie temperature (T_c).[2] Since Dietl *et al.*[2] predicted on the basis of the mean-field Zener model of ferromagnetism T_c exceeding room temperature for *p*-type ZnO containing 5% Mn, $Zn_{1-x}Mn_xO$ thin films has continued to be of central importance for DMSs research due to its high Curie temperature. However, the magnetic properties in $Zn_{1-x}Mn_xO$ thin films differ for different research groups, for instance, reporting $Zn_{1-x}Mn_xO$ thin films to be anti-ferromagnetic,[1] paramagnetic[3] and ferromagnetic.[4–9] The discrepancies can be attributed to different growth methods, e.g., pulsed laser deposition (PLD),[1,6–9] laser molecular-beam epitaxy,[4] ion implantation,[5] and, magnetron sputtering.[3] The ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films is known to be sensitive to growth conditions, such as substrate temperature,[9] oxygen pressure,[9] annealing temperature,[7] and annealing atmosphere.[10]

This controversy leads to different conclusions on the origins of ferromagnetic ordering, e.g., a change in electronic band structure,[4] carrier-induced mechanisms,[6] or metastable system phases.[8] Very recently, Ramachandran *et al.*[11] also suggested that the ferromagnetic ordering in a $Zn_{1-x}Mn_xO$ system can be induced through bound magnetic polaron (BMP) mechanism at low temperatures. Thus, a more understanding of the intrinsic origin of ferromagnetism in the $Zn_{1-x}Mn_xO$ thin films is essential for realizing practical spintronic devices based on $Zn_{1-x}Mn_xO$ films.

The anomalous Hall effect (AHE) has been recognized as a useful tool for demonstrating the ferromagnetic ordering to be intrinsic due to spin-polarized carriers, which mediate ferromagnetic exchange interaction with localized magnetic moments. AHE is well-known to be caused by the emergence of voltage transverse to both an applied current and an external magnetic field proportional to magnetization.[12] The observation of the AHE in $Zn_{1-x}Mn_xO$ thin films can provide the evidence of carrier-induced ferromagnetism since the AHE is able to rule out spurious origins of the ferromagnetic ordering, such as magnetic impurities in an Al_2O_3 substrate and nano-sized ferromagnetic segregation as a secondary phase.

In the present work, we report anomalous Hall effect (AHE) observed in the range of 4–210 K for a $Zn_{1-x}Mn_xO$ ($x=0.26$) thin film grown by pulsed laser deposition. Our results demonstrate a carrier-mediated mechanism for the ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films, since AHE originating from asymmetric scattering due to spin-orbit coupling is clear evidence of exchange interaction between itinerant carriers and localized spins. The mechanism of the observed AHE is discussed in detail.

II. EXPERIMENT

The $Zn_{1-x}Mn_xO$ thin films were grown by pulsed-laser deposition (PLD) on a single crystal sapphire substrate using ZnMnO targets. Thin films of 40 nm in thickness were deposited at a laser repetition rate of 2 Hz and a pulse-energy density of 2 J/cm^2 for 8.5 min at a substrate temperature of 700 °C in the oxygen pressure range of 10^{-1}–10^{-3} Torr. Mn concentration of 26 at. % for the film of 10^{-1} Torr was determined from energy dispersive x-ray spectroscopy (EDS). An x-ray diffraction (XRD) technique was used to investi-

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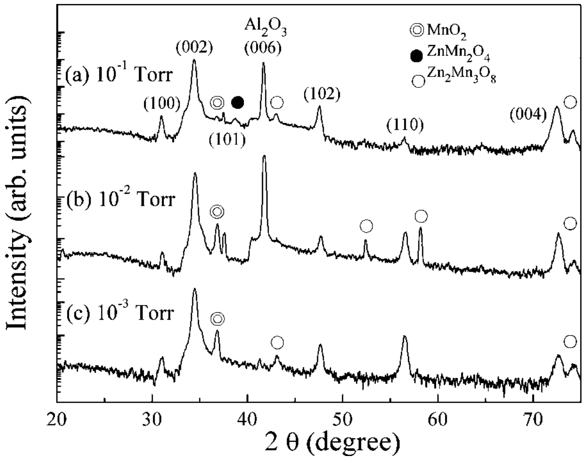

FIG. 1. XRD patterns for the $Zn_{1-x}Mn_xO$ films grown at 700 °C with the oxygen pressure of 10^{-1} Torr (a), 10^{-2} Torr (b), and 10^{-3} Torr (c). The marks (◎, ●, ○) indicate the possible presence of MnO_2, $ZnMn_2O_4$, and $Zn_2Mn_3O_8$.

gate the microstructures of the $Zn_{1-x}Mn_xO$ thin films. The magnetic hysteresis (*M-H*) loops were measured in the range of 4–300 K using a superconducting quantum interference device (SQUID). The van der Pauw Hall and magnetoresistance (MR) measurements were also performed by applying magnetic fields from −9 to +9 kOe in the range of 4 −300 K in order to investigate the electrical and magnetotransport properties of the $Zn_{1-x}Mn_xO$ films.

III. RESULTS AND DISCUSSION

Figure 1 exhibits x-ray diffraction patterns of $Zn_{1-x}Mn_xO$ films grown at 700 °C under oxygen pressures of 10^{-1} Torr [Fig. 1(a)], 10^{-2} Torr [Fig. 1(b)], and 10^{-3} Torr [Fig. 1(c)]. Peaks [(002) and (004)] of $Zn_{1-x}Mn_xO$ were observed, showing the *c*-axis orientation of the wurtzite structure in the films grown at 700 °C under oxygen pressures of 10^{-1} Torr [Fig. 1(a)], 10^{-2} Torr [Fig. 1(b)], and 10^{-3} Torr [Fig. 1(c)]. The peaks corresponding to $Zn_2Mn_3O_8$ appeared in all films [Figs. 1(a)–1(c)], while a suspicious peak indexed to $ZnMn_2O_4$ was observed for the films grown at 700 °C under 10^{-1} Torr as seen in Fig. 1(a). $Zn_2Mn_3O_8$ is unlikely to be responsible for the origin of ferromagnetic ordering in $Zn_{1-x}Mn_xO$ films since it is non-magnetic.[13] Moreover, the possible presence of $ZnMn_2O_4$ observed only in the films grown at 700 °C under 10^{-1} Torr does not account for the magnetic behavior of the film since it is not relevant to the ferromagnetic ordering at room temperature.[10] In the case of the films grown under 10^{-2} [Fig. 1(b)] and 10^{-3} Torr [Fig. 1(c)], the obvious diffraction peaks from MnO_2 were indexed, whereas it almost disappeared in the film grown under 10^{-1} Torr as seen in Fig. 1(a). MnO_2 is known to be anti-ferromagnetic, showing Neel temperature (T_N) of 84 K. Therefore, the presence of MnO_2 phases could neither be relevant to the ferromagnetic transition temperature of 22 (10^{-2} Torr) and 25 K (10^{-3} Torr) nor the room-temperature hysteresis of the film grown at 700 °C of 10^{-1} Torr. In this study, the ferromagnetic behavior of the films grown under 10^{-1} Torr, 10^{-2} Torr, and 10^{-3} Torr was found not due to the formation of secondary phases, such as $Zn_2Mn_3O_8$, $ZnMn_2O_4$, and MnO_2.

Figure 2(a) and 2(b) show *M-H* loops for the $Zn_{1-x}Mn_xO$ films grown at 700 °C under oxygen pressures of 10^{-1} Torr, 10^{-2} Torr, and 10^{-3} Torr, obtained with magnetic fields applied parallel to the plane of the films at 4 and 300 K. Regardless of the oxygen pressure, all the $Zn_{1-x}Mn_xO$ thin films exhibited ferromagnetic ordering at 4 K. On the other hand, only the $Zn_{1-x}Mn_xO$ film grown at 700 °C under 10^{-1} Torr is still indicative of ferromagnetic ordering at 300 K, whereas the ferromagnetic behavior in the films grown at 700 °C under 10^{-2} Torr and 10^{-3} Torr was found to almost disappear at 300 K. This is in agreement with the *M-T* curves

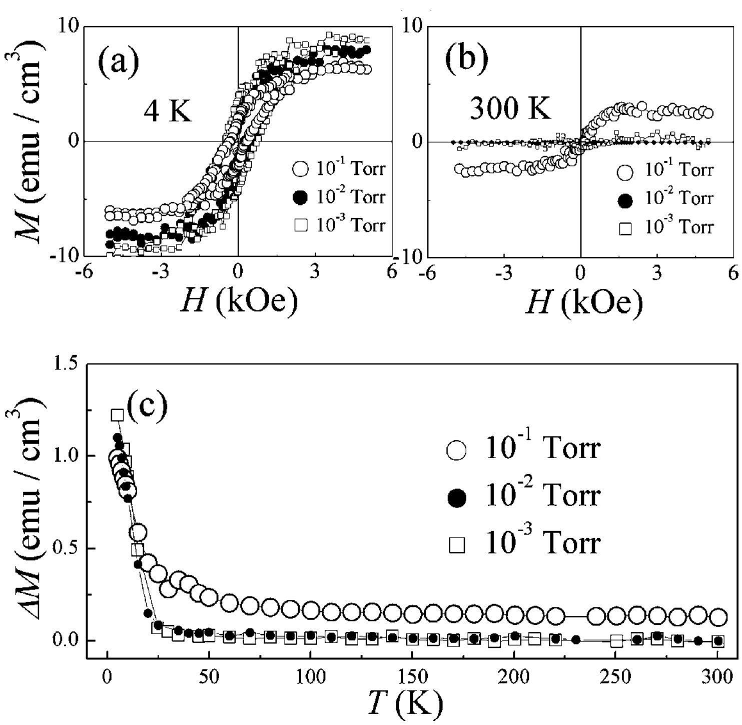

FIG. 2. *M-H* loops for the $Zn_{1-x}Mn_xO$ films grown at 700 °C under oxygen pressures of 10^{-1}, 10^{-2}, and 10^{-3} Torr at (a) 4 K and (b) 300 K. (c) Temperature dependence of magnetizations for the $Zn_{1-x}Mn_xO$ films. The magnetization difference (ΔM) between the zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations were measured as a function of temperature under a magnetic field of 100 Oe.

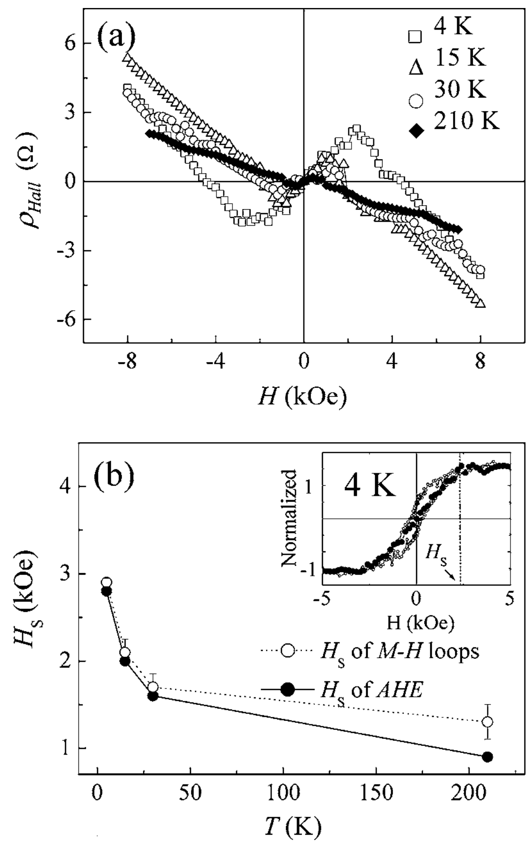

FIG. 3. (a) Hall resistivity measured at temperatures of 4, 15, 30, and 210 K as a function of magnetic fields for the $Zn_{1-x}Mn_xO$ film grown at 700 °C under an oxygen pressure of 10^{-1} Torr. (b) The variation of H_s, a magnetic field to reach saturation magnetization (M_s), with increasing temperature. The values of H_s were determined from *M-H* loops and *R-H* curves. The inset in (b) exhibits *M-H* loop and *R-H* curve obtained at 4 K, respectively. In particular, the anomalous part of Hall resistivity in the inset was plotted by subtracting the ordinary contribution from the measured Hall resistivity.

as shown in Fig. 2(c). Ferromagnetic behaviors for all the films are clearly seen at 4 K. The magnetic moments for the films grown at 700 °C under 10^{-2} Torr and 10^{-3} Torr were found to exhibit an abrupt decrease in the *M-T* curves at 22 and 25 K, corresponding to T_c, respectively. However, it was found that the magnetization in the sample grown at 700 °C under 10^{-1} Torr persists up to room temperature. Our findings suggest that oxygen pressure as a growth condition have remarkable influence upon the magnetic properties in the $Zn_{1-x}Mn_xO$ thin films. This dependence of the magnetic behaviors on the oxygen deficiency in the thin films is not fully understood. However, the oxygen pressure during the film growth is inferred to play a critical role in tuning the room-temperature ferromagnetic ordering in $Zn_{1-x}Mn_xO$ films, which may be attributable to oxygen vacancies.[11] In fact, the strongly concave *M-T* behaviors observed in our samples follow the polaron percolation theory $M(T) \propto \ln T_C/T$,[14] which is strikingly different from the usual Weiss mean-field prediction $M(T) \propto (T_C - T)^{0.3}$.[15] The formation of the magnetic polarons mediated by oxygen vacancies is believed to be responsible for ferromagnetic ordering in $Zn_{1-x}Mn_xO$ films and will be discussed in detail in subsequent works.

The Hall measurements were carried out to clarify the origin of the ferromagnetic ordering of 26 at. % $Zn_{1-x}Mn_xO$ thin film grown at 700 °C under oxygen pressure of 10^{-1} Torr. Figure 3 shows the Hall resistance [Fig. 3(a)] measured as a function of the magnetic field and [Fig. 3(b)] the variation of H_s, a magnetic field to reach saturation magnetization (M_s), with temperature determined from *M-H* loops and *R-H* curves. In Fig. 3(a), the Hall resistance is linear up to high fields as expected, with a vertical shift at low fields indicating typical anomalous Hall effect (AHE). The Hall resistance ρ_{Hall} can be expressed phenomenologically as

$$\rho_{\text{Hall}} = R_0 H + R_A M, \tag{1}$$

where R_0 is the Hall effect coefficient resulting from the Lorentz force on the carriers in the same manner as in paramagnetic materials, and R_A is referred to as the anomalous Hall coefficient. It is noted that the sign of R_A is opposite to R_0, which is positive. The opposite signs of R_A and R_0 were previously reported in various DMS systems, which is believed to be due to the different density of states for positive and negative orbital orientation.[16] It was found that AHE was observed up to 210 K even though the magnetic hysteresis persisted to room-temperature. The magnetic property measured by SQUID is only related to M of the samples, whereas AHE is determined by R_A as well as M according to Eq. (1), where R_A is defined $R_A = a\rho + b\rho^2$. R_A is expected to decrease with the increase of the temperature, since ρ decrease due to the thermal excitation of the electrons. In other words, the reduction of R_A at elevated temperature in addition to the decrease in M can cause the further reduction of anomalous Hall resistance. Thus, one can assume that AHE may exhibit weaker signals at certain temperature, compared to the magnetic hysteresis. The other possible explanation for the lack of anomalous Hall effect at elevated temperature can be a weak coupling of the conduction electrons to magnetic degrees of freedom, as assumed in $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$ system.[17]

In order to directly compare H_s for the *R-H* curves with that for the *M-H* loops, the ordinary Hall part at high fields where M saturates has been subtracted because of the small magnitude of the anomalous Hall resistance, as seen in the inset of Fig. 3(b). It was found that H_s obtained from the *R-H* curve is in good accordance with H_s obtained from *M-H* loop as shown in Fig. 3(b). The ferromagnetic behaviors of the $Zn_{1-x}Mn_xO$ film observed in the Hall measurements are found to be identical to the ferromagnetic behaviors measured by a SQUID magnetometer. In the present work, these results are able to exclude spurious origins of the ferromagnetic ordering in the $Zn_{1-x}Mn_xO$ film, such as magnetic impurities in an Al_2O_3 substrate and nano-sized ferromagnetic segregation as a secondary phase.

Two types of the mechanism are well-recognized to be responsible for anomalous Hall effect. One is the skew-scattering process ($R_A \propto \rho$) and the other is the side-jump process ($R_A \propto \rho^2$).[12] Thus, the effect of the mechanisms can be analyzed by examining $R_A \propto \rho^n$ scaling relation where n is the scaling exponent. Figure 4(a) shows the anomalous Hall coefficient R_A with resistivity ρ for the $Zn_{0.74}Mn_{0.26}O$ film and Figure 4(b) the variation of magnetizations with temperature, calculated from the AHE and measured by the SQUID magnetometer. Figure 4(a) shows a plot of R_A versus

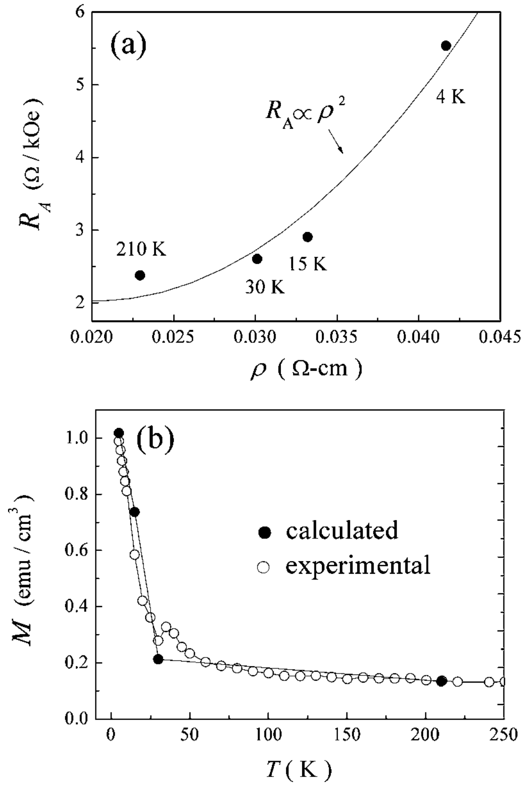

FIG. 4. (a) The anomalous Hall coefficient R_A with resistivity ρ for the $Zn_{0.74}Mn_{0.26}O$ film. The plot of R_A vs ρ appears to obey $R_A \propto \rho^2$, where R_A is calculated from $\rho_{Hall}/M_{(measured)}$ at $H=500$ Oe. (b) The variation of magnetizations with temperature, calculated from the AHE and measured by the SQUID magnetometer at $H=100$ Oe. The absolute value of M obtained from the AHE is scaled to fit the SQUID data at $T=210$ K.

ρ for the $Zn_{0.74}Mn_{0.26}O$ film, appearing to obey $R_A \propto \rho^2$, where R_A is calculated from $\rho_{Hall\ An}/M_{(measured)}$ at $H=500$ Oe. Our results suggest that the side-jump mechanism plays an important role in the asymmetric scattering process, which is responsible for the AHE in the $Zn_{0.74}Mn_{0.26}O$ films.

The magnetizations obtained from the AHE are calculated with the relation of $\rho_{Hall\ An}/R_A = M$, extracting the anomalous Hall resistance by subtracting the ordinary Hall resistance in Eq. (1). The values of R_A were substituted by assuming a power law of $R_A = a\rho + b\rho^2$, where $a=0$ and $b=1\ \Omega^{-2}\ C^{-1}$, indicating the side-jump mechanism rather than the skew scattering. The calculated magnetizations from the AHE are very consistent with that obtained from SQUID measurements as clearly seen in Fig. 4(b). It is noted that the side-jump mechanism gain relative importance over the skew scattering mechanism in a system with shorter mean free path, i.e., higher Mn concentration.[12] With the highly degenerate electron model using the equation,[18] $l=(h/2e) \times (3n_e/\pi)^{1/3} \cdot \mu_e$, where electron mobility μ_e is defined $\mu_e = (en_e\rho)^{-1}$ with n_e the electron concentration, the mean free path of electrons in the film was found to be 5.29×10^{-10} m at 4 K and 2.88×10^{-10} m at 210 K. The obtained l is fairly short and is believed to be governed by the scattering due to the high magnetic impurities (26 at. % Mn concentration) in the system. Taking into account the relatively low mobility ($5.85-10.75\ cm^2\ V^{-1}\ s^{-1}$) in this film, it is considered that the deflected carrier travels a considerably short distance due to the high Mn concentration. Therefore, the mechanism of the observed AHE demonstrating carrier-induced ferromagnetism in $Zn_{0.74}Mn_{0.26}O$ thin film is attributable to the side-jump process.

IV. CONCLUSIONS

In summary, the intrinsic origin of the carrier-induced ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films has been investigated with respect to anomalous Hall effect (AHE). The AHE was observed in the range of 4–210 K for a $Zn_{0.74}Mn_{0.26}O$ thin film grown by pulsed-laser deposition. The ferromagnetic behaviors for the thin film obtained from the AHE are found to be very consistent with that observed from M-H loops and M-T curves. Our results suggest that the AHE is clear evidence of exchange interaction between itinerant spin-polarized carriers and localized magnetic moments, demonstrating a carrier-mediated mechanism responsible for ferromagnetic ordering in $Zn_{1-x}Mn_xO$ thin films. Furthermore, the side-jump process is found to be a dominant mechanism for the AHE due to high magnetic impurities.

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