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Ferromagnetism and Anomalous Hall Effect in p-$Zn_{0.99}Mn_{0.01}O$:P

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We report hole-induced ferromagnetism in diluted magnetic semiconductor $Zn_{0.99}Mn_{0.01}O$ films grown on SiO_2/Si substrates by reactive sputtering. The p-type conduction with hole concentration over 10^{18} cm^{-3} is achieved by P doping followed by rapid thermal annealing at 800 °C in a N_2 atmosphere. The p-type $Zn_{0.99}Mn_{0.01}O$:P is carefully examined by x-ray diffraction and transmission electron microscopy. The magnetic measurements for p-$Zn_{0.99}Mn_{0.01}O$:P clearly reveal ferromagnetic characteristics with a Curie temperature above room temperature, whereas those for n-$Zn_{0.99}Mn_{0.01}O$:P show paramagnetic behavior. The anomalous Hall effect at room temperature is observed for the p-type film. This result strongly supports hole-induced room temperature ferromagnetism in p-$Zn_{0.99}Mn_{0.01}O$:P.

Key words : Diluted magnetic semiconductors, Zinc oxide, Ferromagnetism, Anomalous Hall effect

1. Introduction

Diluted magnetic semiconductors (DMS) have recently attracted a great deal of attention due to the possibility of spin source or spin injector for spin electronics devices. Since the discovery of ferromagnetism in Mn-doped GaAs with a Curie temperature (T_C) of ~110 K [1], a lot of works have been carried out to search for high-T_C DMS in wide band gap III-V and II-VI based materials. Among those works, there have been several reports on the observation of room temperature ferromagnetism in Mn-doped GaN, Co- and Mn-doped ZnO [2-4]. However, there are only few reports on the magnetotransport properties of high-T_C DMS such as anomalous Hall effect, which manifests intrinsic nature of ferromagnetism caused by spin-polarized charge carrier. In most of cases, the possibility of an extrinsic origin for the ferromagnetism, such as ferromagnetic clusters, could not be ruled out. Hence, for possibility of practical spin electronics applications, we have to examine the ferromagnetic response due to charge carriers in DMS [5].

Mn-doped ZnO (ZnMnO) is one of the intensively studied DMS for applications to spin electronics devices operable at room temperature, due to several theoretical predictions of the possibility of room temperature ferromagnetism in p-type ZnMnO [6, 7]. Meanwhile, most experimental works have been conducted on n-type ZnMnO, because of much difficulty in making p-type ZnMnO. Recently, there have been some reports on realization of p-type ZnO thin films via P doping and thermal treatment [8, 9]. In this work, we report on the successful growth of p-type ZnMnO thin films by reactive sputtering and the observation of room temperature ferromagnetism and anomalous Hall effect governed by hole doping in ZnMnO.

2. Experiments

Mn-doped ZnO thin film was deposited on SiO_2 (200 nm)/Si substrates by reactive magnetron sputtering from phosphorus-doped ZnO, Zn and Mn targets at 500 °C under Ar/O_2 mixture gas with a ratio of 5/1 to a constant working pressure of 5 mTorr. The sputtering power for ZnO:P, Zn and Mn targets were kept at 50, 70 and 15 W, respectively. Phosphorus was used as p-type dopant in Mn-doped ZnO via ZnO target mixed with 10 wt% P_2O_5. We employed rapid thermal annealing (RTA) at a temperature above 500 °C under a N_2 ambient or vacuum under 10^{-3} Torr to control the carrier concentration and conduc-

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tion type in as-grown insulating films.

3. Results and Discussion

Figure 1 shows the Hall measurement results at 300 K for $Zn_{0.99}Mn_{0.01}O$:P films annealed at various temperatures. The data shown were obtained at room temperature using the van der Pauw configuration. We found that the films annealed under vacuum exhibit n-type conduction in the whole annealing temperature range, whereas those annealed under N_2 ambient display p-type conduction depending on the RTA temperature. The inset in Fig. 1 shows the detailed results of the Hall measurements for the $Zn_{0.99}Mn_{0.01}O$:P films treated by RTA under N_2 ambient. The obtained maximum electron concentration (n) and hole concentration (p) in the films as high as $n = 5.2 \times 10^{18}$ cm^{-3} and $p = 6.7 \times 10^{18}$ cm^{-3}. Here, we did not take into account any influence of a possible anomalous Hall effect on the evaluation of the data shown in Fig. 1. We note that the conduction type of the films annealed under N_2 ambient changes from n-type to p-type with increasing RTA temperature. This result indicates that phosphorus as a p-type dopant in Mn-doped ZnO is more active at high thermal energy under an atmosphere of N_2 to suppress substantially oxygen vacancies and generate free holes. This result is well understood by considering the fact that P_2O_5 (P-O bonding energy is 599.1 kJ/mol and Zn-O bonding energy is 256 kJ/mol [10]) needs high thermal energy to dissociate and play the role as an acceptor.

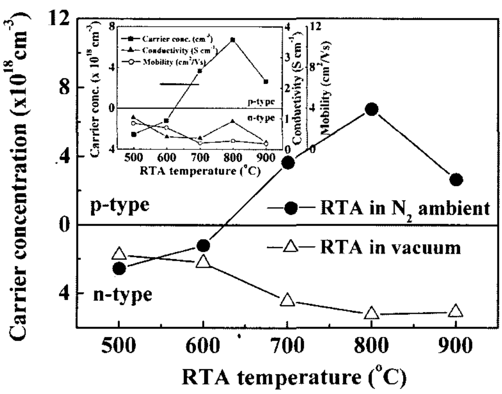

Fig. 1. Carrier concentration of $Zn_{0.99}Mn_{0.01}O$:P films annealed under N_2 ambient (●) or vacuum (△) at various temperatures. The inset shows the Hall measurement results for the film annealed under N_2 ambient.

Figure 2(a) shows x-ray diffraction patterns of as-deposited and annealed $Zn_{0.99}Mn_{0.01}O$:P films under N_2 ambient or vacuum at 800 °C. Only (002) and (004) peaks of wurtzite lattice were observed with no secondary peaks, indicating a c-axis preferred-orientation growth. It is clearly seen that RTA atmosphere has little effect on the structural properties of the films. Transmission electron microscopy (TEM) analysis was conducted to examine possible formation of secondary phases in the nano-sized range, which could be an extrinsic origin for the magnetism observed in the films. A well-defined columnar structure with growth direction parallel to the c-axis of the wurtzite structure is clearly seen in a cross-sectional TEM image of the p-$Zn_{0.99}Mn_{0.01}O$:P/SiO_2, as dispalyed in Fig. 2(b). Also, the interface is quite flat and sharp with no noticeable interfacial reaction. A high resolution TEM (HRTEM) image for the same film, shown in Fig. 2(c), demonstrates the absence of any impurity segregation or clustering. This is further supported by the absence of additional reflections in the corresponding diffraction pattern, shown in the inset of Fig. 2(c).

Figure 3(a) shows the temperature dependence of the magnetization (M-T) for a as-deposited $Zn_{0.99}Mn_{0.01}O$:P film, a n-type film with $n = 5.2 \times 10^{18}$ cm^{-3} and a p-type film with $p = 6.7 \times 10^{18}$ cm^{-3}, measured during warming from 5 to 300 K using a superconducting quantum interference device (SQUID) magnetometer. The data

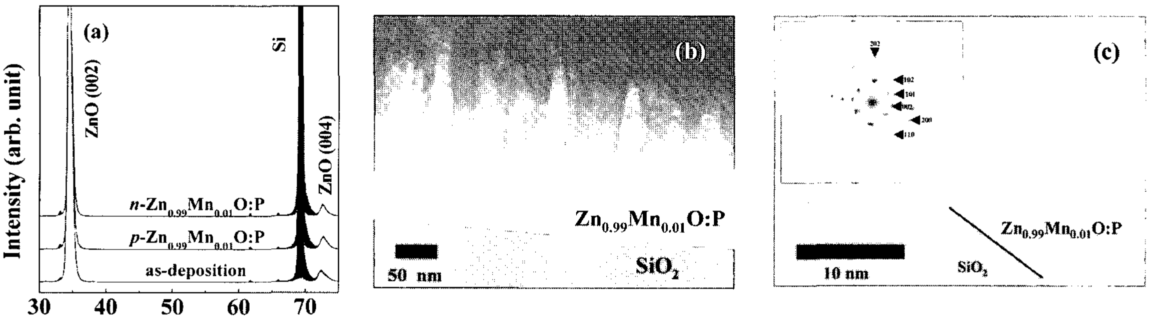

Fig. 2. (a) X-ray diffraction patterns of as-deposited, n-type and p-type $Zn_{0.99}Mn_{0.01}O$:P films. (b) Cross-sectional transmission electron microscopy (TEM) image of p-$Zn_{0.99}Mn_{0.01}O$:P/SiO_2 structure. (c) High resolution TEM image of p-$Zn_{0.99}Mn_{0.01}O$:P interface. The inset shows the corresponding electron diffraction pattern.

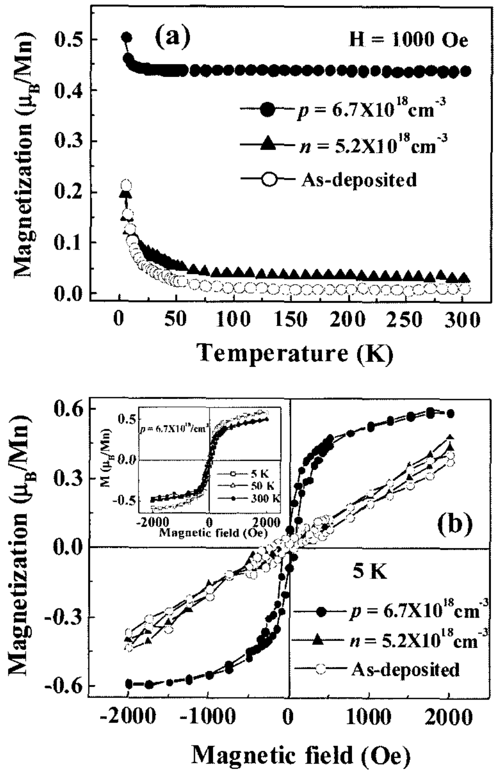

Fig. 3. Magnetic properties of as-deposited, n- and p-type $Zn_{0.99}Mn_{0.01}O$:P films: (a) Temperature dependence of the magnetization measured in a field of 1 kOe, (b) Magnetic field dependence of the magnetization measured at 5 K. The inset shows the magnetic hysteresis curves measured at 5, 50, and 300 K, respectively, for p-type $Zn_{0.99}Mn_{0.01}O$:P film.

were obtained in an applied magnetic field (H) of 1 kOe parallel to the film surface. The diamagnetic contribution due to the substrate was subtracted from the data. We note that the magnetization at room temperature for the p-$Zn_{0.99}Mn_{0.01}O$:P film is eight to nine times as high as that for the as-deposited and n-type films. Also, the magnetization of the p-type film is nearly invariable in the temperature range above around 20 K. These features signify the presence of the ferromagnetism in the p-type film. The field dependence of magnetization (M-H) for the p-type film, shown in Fig. 3(b), gives further evidence for the presence of ferromagnetism. On the other hand, the M-T and M-H data for the as-deposited and n-type films indicate paramagnetic behavior. Our results manifest the occurrence of hole-induced ferromagnetism in Mn-doped ZnO. The observed upturn at very low temperature in the M-T curve for the p-type film can be attributed to the paramagnetic Mn moments. Consequently, the characteristics of the M-T curve for the p-type film are attributed to coexistence of the ferromagnetic and paramagnetic moments, as observed in Mn-doped GaN [11, 12] and Co-doped Cu_2O [13]. The signature of such coexistence behavior is also detected in the M-H curves at several temperatures, shown in the inset of Fig. 3(b). Clear ferromagnetic hysteresis is observed up to room temperature, yielding a remanent magnetization of ~0.3 emu/cm^3 and a coercive field of ~60 Oe.

It is well known that an important criterion for intrinsic ferromagnetism caused by spin-polarized carriers in magnetic semiconductors is the observation of the anomalous Hall effect (AHE). Hall resistivity (ρ_{xy}) in ferromagnets is customarily written as $\rho_{xy} = R_0 B + R_S \mu_0 M$, where R_0 is the ordinary Hall conastant, R_S is the anomalous Hall constant, μ_0 is the magnetic permeability of free space, and M is the magnetization [14]. Here, the first term denotes the ordinary Hall effect (OHE) resulting from the Lorentz force on the carriers in the same manner as in paramagnets, and the second term denotes the AHE due to asymmetric carrier scattering in the presence of an exchange interaction between itinerant carriers and magnetic moments.

Figure 4 shows the magnetic field (H) dependence of ρ_{xy} at three temperatures (T = 100, 200, and 300 K) for a p-type $Zn_{0.99}Mn_{0.01}O$:P film. At T = 300 K, ρ_{xy} increases rapidly up to 1.6 kOe with increasing H, and gradually increases linearly with further increasing H. This behavior shows that the anomalous part of ρ_{xy} (ρ_{AHE}), being proportional to M, is dominant for lower H. The observed AHE further supports the room temperature ferromagnetism in the p-type film. On the other hand, the ordinary part of ρ_{xy} (ρ_{OHE}) at higher H shows the positive linear slope, yielding a hole concentration (p) of 4.6×10^{19} cm^{-3} at 300 K. At T = 200 K, p decreases to 1.3×10^{19} cm^{-3} and ρ_{OHE} becomes more dominant. At length ρ_{AHE} cannot be observed at 100 K because the lower p (= 8.9×10^{18} cm^{-3}) gives the larger ρ_{OHE}. These features demonstrate

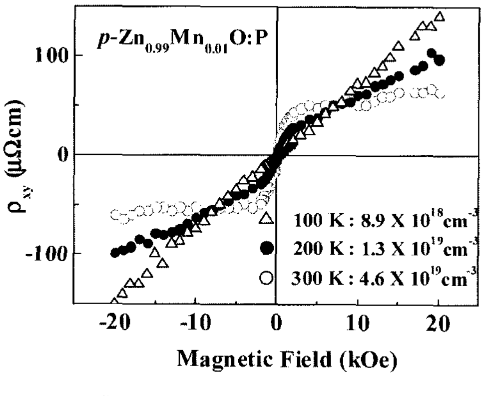

Fig. 4. Magnetic field dependence of Hall resistivity (ρ_{xy}) for a p-type $Zn_{0.99}Mn_{0.01}O$:P film. The applied magnetic field is perpendicular to the film plane. The hole concentration evaluated from the ordinary part of ρ_{xy} is labeled for each curve.

the intrinsic nature of hole-mediated ferromagnetism in Mn-doped ZnO films. We note here that the disappearance of the AHE with decreasing T could be attributed to the reduction of the hole concentration in the film with decreasing T.

4. Conclusion

We have successfully grown p-type Mn-doped ZnO thin films on SiO_2/Si substrates using reactive magnetron sputtering via P doping and thermal treatment in a N_2 ambient. We have presented clear evidence for the occurrence of intrinsic room temperature ferromagnetism by hole doping and the presence of the exchange coupling between itinerant electrical carriers and localized Mn spins in sputtered Mn-doped ZnO films. These features suggest that Mn-doped ZnO could be promising for the possible realization of semiconductor spin electronics devices operable at room temperature.

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