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Correlation of magnetic property with electrical transport property for ferromagnetic $(Zn_{1-x}Mn_x)O$ thin films

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The correlation of electrical properties with magnetic properties for As^+-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin films was investigated. For electrical transport measurements, it was clearly observed that the electrical mobility at the cryogenic temperature region is increased with decreasing temperatures. In Arrhenius plots of the carrier mobility, the critical point was observed at 65 K. For Arrhenius plots of Mn^{2+}-related emissions in photoluminescence measurements, the similar behavior was also observed at the same temperature region. The values of critical points are very closed to the value of the Curie temperature, thus it is expected that the increase of carrier mobility might be related to the activation of Mn^{2+} ions. Below the Curie temperature region, the activated Mn^{2+} ions will provide higher magnetic moments, and then the exchange interaction may increase in the material system. As a result, it will lead to enhance the spin-ordering effect and to reduce the probability of spin-disorder scattering. Therefore, the observation of gradual drop below the Curie temperature region in the temperature-dependent resistivity curve is expected to be a result from the spin-ordering effect due to the activation of Mn^{2+} ions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2147845]

I. INTRODUCTION

For the realization of spintronics which utilize both the charge degree of freedom and the spin degree of freedom,[1] the diluted magnetic semiconductor (DMS) continues to be of central importance from physical and technical points of view.[2] Among the various DMS materials, ZnO-based DMS thin films have attracted much attention because of the theoretical prediction of possible ferromagnetism with high Curie temperature (T_C) above 300 K.[3] Moreover, since the host material ZnO has a lot of potential applications for various devices such as varistors, wide band gap high-power devices, surface acoustic wave devices, and ferroelectric memory devices,[4–6] researches on the physical property and the carrier dynamics of ZnO-based DMSs have been of great interest. The lattices of ZnO-based DMS materials consist in part of magnetic ions; for example, V, Cr, Mn, Fe, Co, and Ni, substituting for the Zn site. These magnetic ions carry a local spin due to their partially-filled d shells, and they give rise to the exchange interaction with carriers. An exchange interaction between the magnetic moments mediated by the carriers makes this type of material ferromagnetic. The interest in these materials is mainly stimulated by their potential applications for use in spintronic devices and by imparting the possibility of controlling both spin and charge degrees of freedom. Therefore, for the realization of spintronics applications, it is important to understand the electrical transport properties of carriers in DMS materials. However, systematic studies on the correlation of electrical transport properties with magnetic properties for ferromagnetic ZnO-based DMS thin films have been disregarded up to now except for N. Fujimura's study dealing with the carrier transport properties for ZnMnO/ZnO heterostructures,[7] although experimental and theoretical studies for GaAs-based DMS thin films have been performed systematically.[8–10]

In this paper, we report data on the electrical transport property of p-$(Zn_{1-x}Mn_x)O$ thin films. In order to help understand the electrical transport mechanism in ferromagnetic $(Zn_{1-x}Mn_x)O$ thin films, the correlation of magnetic properties with electrical properties was studied. The $(Zn_{1-x}Mn_x)O$ thin films were grown by a radio frequency (rf) magnetron sputtering method, and the p-type conduction in $(Zn_{1-x}Mn_x)O$ thin films was obtained by As^+ ion implantation into intrinsic $(Zn_{1-x}Mn_x)O$ thin films. The magnetic properties were characterized by means of superconducting quantum interference device (SQUID) measurements, and the electrical transport properties were determined by measurements of the electrical contact probe method and the Hall effect method. The optical properties were characterized by means of photoluminescence (PL) measurements.

II. EXPERIMENTAL DETAILS

The $(Zn_{0.93}Mn_{0.07})O$ thin films were grown on (0001) Al_2O_3 substrates by using an rf magnetron sputtering method. For the formation of p-type $(Zn_{0.93}Mn_{0.07})O$ thin films by ion implantation method, the native donors should be compensated before ion implantation in order to effectively incorporate As species into $(Zn_{0.93}Mn_{0.07})O$ DMS thin films. Thus, in the first place, we have grown intrinsic $(Zn_{0.93}Mn_{0.07})O$ DMS thin films using the control of oxygen partial pressure because the intrinsic $(Zn_{0.93}Mn_{0.07})O$ thin films have a very low density of oxygen vacancies (V_O) acting as native donors. The 700 nm thick $(Zn_{0.93}Mn_{0.07})O$ thin films were grown at 450 °C, and the 40 nm thick

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$(Zn_{0.91}Mn_{0.09})O$ buffer layer grown at 200 °C was employed in order to obtain the mirrorlike surface and the high crystal quality. The role of the buffer layer in detail was reported elsewhere.[11] The rf power of 120 W was applied, and the mixture gases of Ar (15 sccm) and O_2 (15 sccm) were supplied during both growth processes. The As^+ ions were implanted into intrinsic $(Zn_{0.93}Mn_{0.07})O$ DMS thin films with the beam acceleration energy of 70 keV. The dose of implanted As^+ ions was 1.0×10^{16} cm^{-2}, and the ion beam was aligned 7° off the *c* axis of thin film in order to prevent the channeling effect. After ion implantation, samples were annealed to activate the implanted As dopants at 600 °C for 60 s in a nitrogen atmosphere. After postimplantation annealing, we have confirmed that the As^+-implanted $(Zn_{0.93}Mn_{0.07})O$ thin film have *p*-type conduction using several kinds of Hall effect measurement instruments. The hole carrier concentration and mobility at 300 K are 6.1×10^{17} cm^{-3} and 5.4 cm^2/V s, respectively. After formation of the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film, the films were promptly characterized in order to avoid the transmutation of material properties. SQUID measurements were performed by using the Quantum Design MPMSXL system, and PL measurements were performed by using the 75-cm monochromator equipped with the GaAs photomultiplier tube. The excitation source for PL measurements was the 3250-Å line of the He-Cd laser. The temperature-dependent electrical transport properties were determined by the electrical contact probe method and the Hall effect method. The electrical contact probe measurements were performed using the conventional contact probe configuration, and Hall effect measurements were carried out using the van der Pauw configuration. During electrical transport measurements, the magnetic field was applied parallel to the surface in order to find the spin-ordering effect on the easy axis.

III. RESULTS AND DISCUSSION

The magnetic properties of the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film grown on Al_2O_3 (0001) were analyzed using SQUID measurements. Figure 1 shows the magnetization curve as a function of the temperature, and the inset of Fig. 1 shows the magnetization curve as a function of the magnetic field. As shown in the inset of Fig. 1, a sharp hysteresis loop indicative of ferromagnetism appears clearly when an external magnetic filed is applied in-plane parallel to the film surface. This result suggests that the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film grown on Al_2O_3 (0001) is ferromagnetic and that the film has the easy axis of the in-plane direction. The remanent magnetization and the coercive field of the As^+-implanted *p*$(Zn_{0.93}Mn_{0.07})O$ thin films were 2.46 emu/cm^{-3} and 204 Oe, respectively. For the temperature-dependent magnetization curve, the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film exhibits the ferromagnetic behavior and it is kept up to approximately 76 K. Thus the T_C of the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film is expected to be about 76 K. The origin of ferromagnetism in Mn-doped ZnO DMS materials is still controversial.[12,13] However, we have considered that the ferromagnetism in our sample, i.e., the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film, is attributed to the carrier-mediated exchange interaction, because the films showed the *p*-type conductivity resulting from the implantation of As acceptors and the theoretical predictions have strongly claimed that the ferromagnetism in Mn-doped ZnO DMS materials may originate from the hole-induced ferromagnetism. With regard to the secondary phase, there are some possible solid solutions such as MnO, MnO_2, Mn_3O_4, and $(Mn,Zn)Mn_2O_4$. However, since it is well known that MnO and MnO_2 are antiferromagnetic and Mn_3O_4 and $(Mn,Zn)Mn_2O_4$ are ferrimagnetic with lower transition temperature below 43 K,[14–16] it is judiciously considered that the ferromagnetic behavior in our sample might not be related to these secondary phases. Moreover, no secondary phase had been observed in high resolution x-ray diffraction measurements.

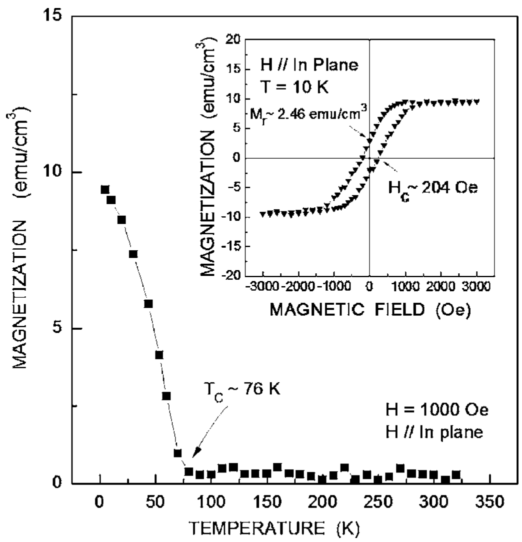

FIG. 1. Magnetization curve as a function of the temperature for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film. The inset shows the magnetization curve as a function of the magnetic field for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film.

Figure 2 shows the temperature-dependent resistivity of As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin films. The closed rectangles are determined from the electrical probe measurements, and the closed triangles are determined from the Hall effect measurements. In both cases, the resistivity curves as a function of the temperature show the typical metallic behavior with an initial increase in the cooling state. The deviation of resistivity values between two curves is considered to be a result of series resistances in electrical contacts for the electrical probe measurements. The resistivity curves show the peak at ~63 K, and the resistivity values drop below 63 K. This critical behavior in the temperature-dependent resistivity characteristics is commonly observed at the temperature region around the T_C of ferromagnetic semiconductors,[9,10] and this phenomenon is ascribed to the scattering of carriers by the magnetic spin fluctuation via exchange interactions.[17] The similar behavior was observed for $(Ga_{1-x}Mn_x)As$ DMS epilayers by I. Yoon *et al.*,[10] and they have explained this behavior originates from the reduction of spin disorder scattering. From their interpretation, the total mobility is given by

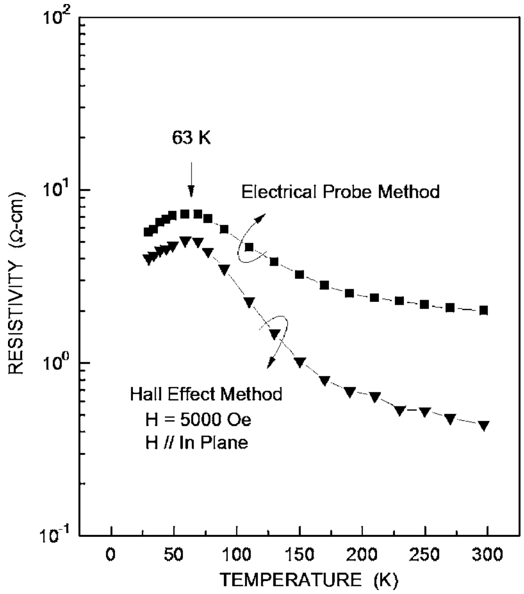

FIG. 2. Temperature-dependent resistivity curves of As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin films.

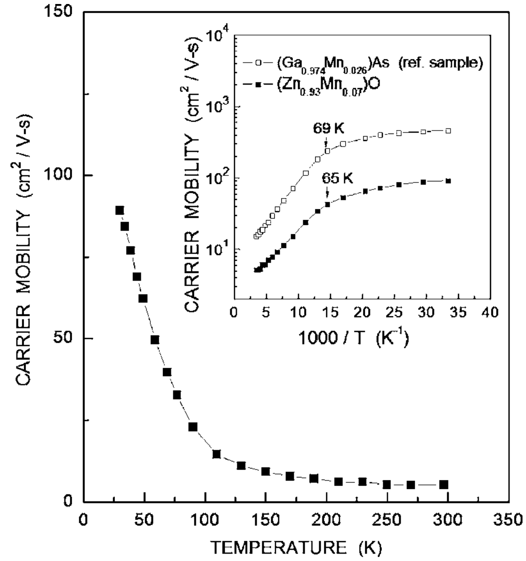

FIG. 3. Variation of the carrier mobility with varying the temperature for the As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin film. The inset shows Arrhenius plots of carrier mobilities for As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin film and the reference sample of the $(Ga_{0.974}Mn_{0.026})As$ epilayer.

$$\frac{1}{\mu} = \sum_i = \frac{1}{\mu_i} + \frac{1}{\mu_{\mathrm{SD}}} + \frac{1}{\mu_a} + \frac{1}{\mu_{\mathrm{ph}}},$$

where μ_i, μ_{SD}, μ_a, and μ_{ph} are mobility terms dependent on ionized impurity scattering, spin disorder scattering, alloy scattering, and polar optical mode scattering, respectively. Alloy scattering of electrons in a semiconductor alloy is caused by the randomness in the distribution of the alloying constituents. The mole fraction of Mn ions is small in the samples used in this experiment, therefore alloy scattering is negligible. In addition, the term of polar optical mode scattering also can be disregarded because the polar optical mode scattering causes low mobility values only at very high temperatures.[18] Thus, one can consider two major scattering mechanisms: ionized impurity scattering and spin disorder scattering.

In order to clarify the scattering mechanism below T_C, we have measured the temperature-dependent mobility for the As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin film. For the measurement of mobilities, it is assumed that the deviation caused by anomalous Hall effect (AHE) in the Hall resistance can be negligible. Indeed, we are aware that the AHE cannot be rigorously neglected in the Hall effect measurement for ferromagnetic semiconductors because of the presence of terms arising from the AHE. In order to minimize the deviation from the existence of AHE, the constant magnetic field with the quite high value of ~1.2 T, where anomalous Hall resistivity is saturated, is applied for all measurements. Thus, the contribution of the AHE term in total Hall effects is expected to be small compared to the ordinary Hall effect term. In addition, because of the relatively low Mn concentration in our samples, the contribution of AHE is expected to be small. Therefore, it can be assumed that the effect of deviations between extraordinary and ordinary Hall effect on determining mobility values is thought to be negligible. Figure 3 shows the variation of the carrier mobility with varying the temperature. As shown in Fig. 3, the mobility is exponentially increased with decreasing the temperature. This result is not consistent with a nonmagnetic semiconductor, because the mobility curve as a function of the temperature generally shows the critical point around cryogenic temperatures.[19] Normally, it is well known that the decrease of mobility below the critical point for nonmagnetic semiconductors is attributed to the increase of ionized impurity scattering.[19] However, the mobility curve of the As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ DMS thin film shows no critical point. Thus, one can expect that the ionized impurity scattering mechanism is not dominant in the ferromagnetic $(Zn_{0.93}Mn_{0.07})O$ DMS material system at the cryogenic temperature region. Since spins in the ferromagnetic solid state are aligned with the same direction below the T_C, the spin disorder scattering will be decreased after ordering spins. Therefore, it is expected that the gradual drop below the T_C for the resistivity curve might be attributed to the increase of the carrier mobility resulting from the decrease of the spin disorder scattering. The inset of Fig. 3 shows Arrhenius plots of carrier mobilities for the As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin film and the reference sample $(Ga_{0.974}Mn_{0.026})As$ epilayer. The $(Ga_{0.974}Mn_{0.026})As$ thin film with the T_C of 72 K had been grown on semi-insulating GaAs (001) at 210 °C by molecular beam epitaxy. In both cases, the mobility is increased with decreasing the temperature, and there are two slopes in curves. The crossover point between two slopes means the critical point at which the activation of carriers concerning increases of mobilities might have occurred. The points are observed at 65 K and 69 K for the As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin film and the $(Ga_{0.974}Mn_{0.026})As$ thin film, respectively. These values are closed to T_C values in each case. For $(Ga_{1-x}Mn_x)As$ thin films, this behavior has already been explained by the reduction of spin disorder scattering below the T_C.[10] Therefore, it is expected that the increase in the carrier mobility of the As$^+$-implanted p-$(Zn_{0.93}Mn_{0.07})O$ thin film might be related to the spin-ordering effect.

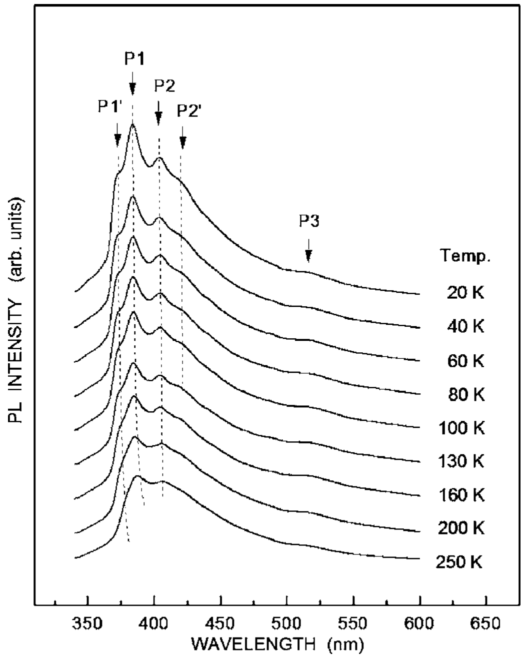

FIG. 4. PL spectra at various temperatures for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film.

This spin-ordering effect could be explained by the activation of Mn^{2+} ions, because the strong magnetic moment resulting from the activation of Mn^{2+} ions would give rise to the increase of exchange interactions. And then, it will lead to increase the effect of ordering spin carriers. In order to find the activation of Mn^{2+} ions, we have measured the temperature-dependent PL characteristics. Figure 4 shows PL spectra at various temperatures for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film. The resolved PL peaks of P1′ at 370 nm, P1 at 382 nm, and P2 at 404 nm are observed clearly. The peaks of P1′, P1, and P2 are originated from the neutral acceptor bound exciton emission,[20] free carrier-acceptor emission,[21,22] and group II vacancy-related emission,[11] respectively. The shoulder of P2′ and the hump of P3 are attributed to Mn^{2+}-related emission[23,24] and V_O-related emission,[21,22] respectively. As shown in Fig. 4, PL intensities of the P1, P1′, P2, and P2′ peaks significantly increase with decreasing the temperature. Among them, especially, it needs to focus on the variation of P2 and P2′ peaks because the increase in PL intensities of P2 and P2′ indicates the activation of Mn^{2+} ions. Figure 5 shows the Arrhenius plot of PL intensities of P2 and P2′ for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film. As observed in the resistivity curve, similarly, it is observed that the crossover points are revealed at 69 K and 61 K for the P2 and P2′, respectively. These values are also closed to the T_C value. Based on these results, we can expect that the *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film will be set on the ferromagnetic state below T_C region due to the activation of Mn^{2+} ions. Under the ferromagnetic state, the activated Mn^{2+} ions will provide higher magnetic moments. Thus, the exchange interaction may increase in the material system; then, it will lead to enhance the spin-ordering effect. Due to this effect, the spin disorder scattering will be decreased in carrier motions and the energy for carrier transport will be minimized sufficiently. Therefore, the carrier mobility will be increased by a result from the decrease in carrier transporting energy, and as a result, the resistivity will be dropped gradually.

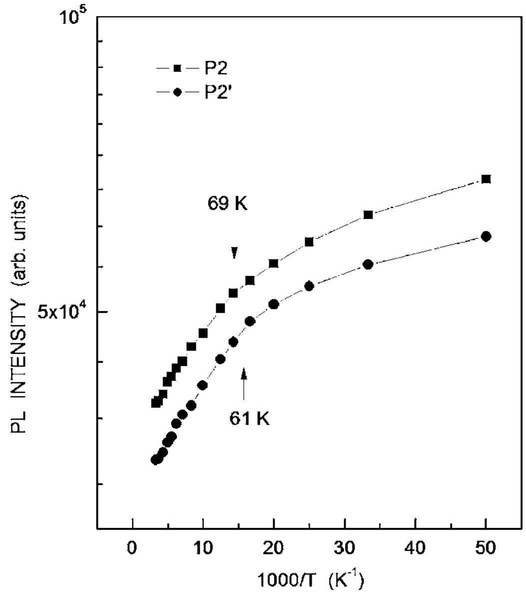

FIG. 5. Arrhenius plots of PL intensities of P2 and P2′ for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film.

IV. CONCLUSION

In summary, the correlation of magnetic properties with electrical properties for the As^+-implanted *p*-$(Zn_{0.93}Mn_{0.07})O$ thin film was investigated. The resistivity curve as a function of the temperature for ferromagnetic *p*-$(Zn_{0.93}Mn_{0.07})O$ thin films showed the typical metallic behavior, and the resistivity curve has the critical point near the T_C. It was observed that the resistivity decreases below the T_C, and this result might be attributed to the increase of the carrier mobility resulting from the decrease of the spin disorder scattering. For temperature-dependent PL measurements, it was observed that the spin-ordering effect might be related to the activation of Mn^{2+} ions. The activated Mn^{2+} ions will provide higher magnetic moments, thus the exchange interaction may increase in the material system. Consequently, the increase of exchange interactions will lead to enhance the spin-ordering effect. Therefore, it is expected that the gradual drop below the T_C shown in the resistivity curve as a function of the temperature might be attributed to the increase of the carrier mobility resulting from the decrease of the spin disorder scattering.

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