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Study on Magnetic Behavior of $Zn_{1-x}Mn_xO$ Films Grown on Si and α-Al_2O_3 Substrates by Sol-gel Method and Powders

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Abstract : We report on the ferromagnetic characteristics of $Zn_{1-x}Mn_xO$ films (x = 0.3) prepared by sol-gel method on the silicon and (0001) α-Al_2O_3 substrates at the annealing temperature of 700℃. Magnetic measurements show that Curie temperature (T_C) and the coercive field (H_C) for the film on the silicon are about 32 K and about 275 Oe, while those for that on the sapphire are about 32 K and 425 Oe, respectively. Energy dispersive spectroscopy and transmission electron microscopy measurements suggest that ferromagnetic precipitates originated by manganese oxide compound formed at the interfaces of the both substrates may be responsible for the observed ferromagnetic behavior of the films. Electron paramagnetic resonance study of the powders up to the concentration of x=0.15 supports the result.
Keywords : ZnO, DMS, Manganese oxide, EDS, EPR

INTRODUCTION

Spintronics is a growing research area due to recent developments in physics of spin-related phenomena and their potential in new applications. For use as spintronics materials, many researchers have studied diluted magnetic semiconductors (DMSs), in which transition metal (TM) atoms are introduced into the lattice. Recently ferromagnetic ordering in some of TM-doped ZnO with Curie temperature (T_C) was theoretically predicted by Dietl et al[1] and experimentally observed in Co, Mn and Ni-doped ZnO films.[2] On the contrary,

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$Zn_{1-x}TM_xO$ films prepared by pulsed-laser deposition have not shown any ferromagnetic ordering down to 5 K.[3] Although strong efforts are currently devoted to verify the physical origin and mechanism of ferromagnetic behavior in $Zn_{1-x}TM_xO$ films, it is still challenging since, in general, the material characterization tools such as the X-ray diffraction (XRD), Reflection High-Energy Electron Diffraction (RHEED) diffraction are not sensitive enough to distinguish the signal of TM-doped DMS from that of TM precipitates.

In this paper, we report on the synthesis and the physical origin of the ferromagnetic characteristics in $Zn_{0.7}Mn_{0.3}O$ films prepared by sol-gel method on the silicon and (0001) α-Al_2O_3 substrates. We will also discuss the electron paramagnetic resonance (EPR) spectra of the $Zn_{1-x}Mn_xO$ powders.

EXPERIMENTAL

The Mn-doped ZnO coating solution was prepared as follows. The zinc acetate dihydrate ($Zn(CH_3COO)_2 2H_2O$, > 99.9%) and manganese acetate tetrahydrate ($Mn(CH_3COO)_2 4H_2O$, > 99.9%) were dissolved in ethanol. This solution was stirred for 1 hour at room temperature. We added acetylaceton as a chelating agent and HCl as a catalyst to the solution with 1 hour stirring. Mn-doped ZnO films were deposited on sapphire and silicon substrates of 22 cm^2 by spin coating at room temperature, with a spinning rate of 2500 rpm for 20 sec. After deposition, the films were heat-treated in air at 400 ℃ for 10 min to remove organic materials in the film. Finally, the Mn-doped ZnO films were annealed in N_2 at 700 ℃ for 1 hour. The powder samples were also prepared according to the same procedure of the films. The sample preparation procedure is shown in Fig. 1.

Two methods for the temperature dependence of the magnetization were used. For the zero-field-cooled (ZFC) magnetization measurement (M_{ZFC}), the sample was first cooled down to 5 K without applied magnetic field and then magnetization of the sample was measured up to 100 K with applied magnetic field. On the other hand, for the field-cooled (FC) magnetization measurement (M_{FC}), the sample was cooled down to 5 K with applied magnetic field and then measurements of magnetic moment at each intermediate temperature were carried out.

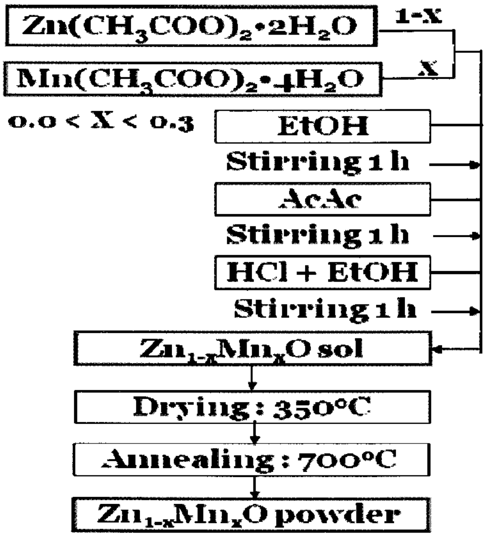

Fig. 1. Sample preparation procedure.

Magnetic properties were investigated by a SQUID magnetometer (MPMS5, Quantum Design) at temperature ranging from 5 to 50 K under different applied magnetic fields. A FE-TEM (F20-UT, Philips-Tecnai) operated up to 200 keV, XRD (X'pert pro, Philips), scanning electron microscope (SEM, S-4700, Hitach) and energy dispersive spectrometer (EDS) were used to determine the grain shape of the particles and their chemical components. Electron paramagnetic resonance (EPR) spectra were obtained with an ESP-300S X-band spectrometer.

RESULTS AND DISCUSSION

The crystal structure was determined from XRD. X-ray diffraction measurement revealed that the crystal structure of $Zn_{1-x}Mn_xO$ ($0.1 \le x \le 0.3$) films is wurtzite structure showing a relatively strong (002) peak. As Mn content increases, the (002) peak slightly shifts to lower angle, which suggests that Mn atoms substitute for Zn sites in the film without changing the wurtzite structure up to x = 0.3.[4]

Fig. 2 shows the magnetization *vs* the temperature (M-T) curve at the applied field of 150 Oe for $Zn_{0.7}Mn_{0.3}O$ film on the sapphire (Fig. 2(a)) and silicon (Fig. 2(b)) substrate under ZFC and FC conditions. An abrupt decrease of MFC near 30 K shows a transition of magnetic phase at this temperature. The magnetization with ZFC shows a deviation from MFC and disappears at ~32 K, corresponding to T_C for the films on both substrates. The experimental result that the magnetic transition temperatures of the $Zn_{0.7}Mn_{0.3}O$ films are similar means that the origin of the ferromagnetic ordering in the both films may be common.

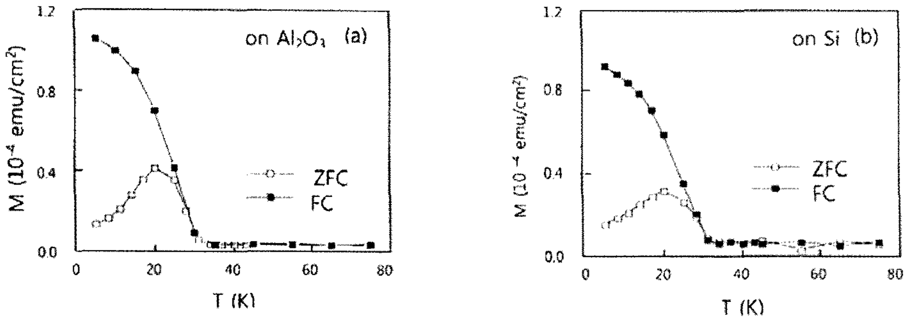

Fig. 2. Temperature dependence of magnetizations of $Zn_{0.7}Mn_{0.3}O$ films under ZFC and FC conditions at applied field of 150 Oe on the (a) sapphire and (b) silicon substrates.

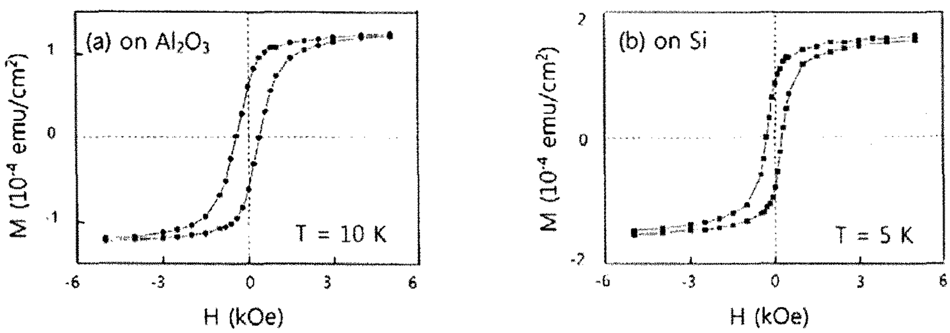

Fig. 3. M-H loops for $Zn_{0.7}Mn_{0.3}O$ films on the (a) sapphire and (b) silicon substrates.

Magnetic behavior of the films was further investigated by measuring the magnetization as a function of field (M-H loop) below T_C. As shown in Fig. 3, the M-H curves for the films clearly show hysteresis loops with coercive field of 425 Oe for sapphire substrate (Fig. 3(a)) and 275 Oe for silicon substrate (Fig. 3(b)), resulting from ferromagnetic ordering in the material.

High-resolution TEM image of a cross-section for $Zn_{0.7}Mn_{0.3}O$ shows typical interfacial area revealing the film surface (notated by A in Fig. 4(a)), film bulk (notated by B), the interface (notated by C) and Si substrate. While energy dispersive x-ray spectroscopy (EDS) performed on B area (center of $Zn_{0.7}Mn_{0.3}O$ film) in Fig. 4(a) indicates that Zn, O, Mn elements are distributed over the film, the EDS focused on the interface, C area (interface between $Zn_{0.7}Mn_{0.3}O$ film and Si substrate) shows significant amount of Mn compared to Zn (See Fig. 4(b)). This experimental result suggests that there might be precipitates of Mn at the interface, which has been known to be easily formed in transition metal doped ZnO film.[4] Recently, Guo et al. reported magnetic properties of Mn_3O_4 film grown on MgO (001) substrate by plasma-assisted MBE.[5] It has been found that the Mn_3O_4 shows ferromagnetic long-range order below the Curie temperature (T_C = 46 K) owing to the exchange interaction of Mn atoms.

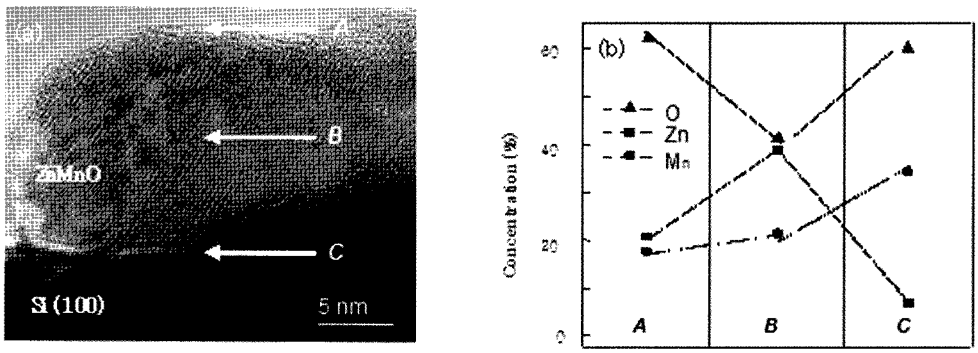

Fig. 4. (a) TEM image of $Zn_{0.7}Mn_{0.3}O$ film. A, B and C are typical areas for the surface, center and the interface of the film. (b) concentrations of Zn, Mn, O by EDS at A, B, C.

The magnetic moments of the powder samples showed a typical Curie-Weiss paramagnetic behavior even at the low temperature of 5 K.[6] The electron paramagnetic spectrum for the powder sample of x = 0.15 at room temperature is shown in Fig. 5. In the figure we can observe only paramagnetic Mn^{2+} hyperfine transitions with fine transition ones. However, we cannot find any ferromagnetic phase in the spectrum at room temperature. If manganese is successfully diluted in the film and powder samples, they should show a ferromagnetic behavior even at room temperature according to the report by Dietle et al.[1] However, we cannot find any ferromagnetic ordering at room temperature and even at 5 K in our experiments.

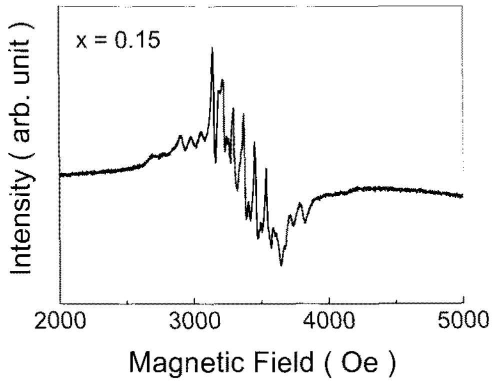

Fig. 5. EPR spectrum for $Zn_{0.85}Mn_{0.15}O$ powder sample.

On the basis of our experimental evidence, there may be two possibilities in the physical origin of the ferromagnetic properties of the sample. First, the observed ferromagnetism does not come from the Mn-doped DMS but from the manganese oxide precipitates.[5] Second, these magnetic properties may come from both manganese oxide precipitates and Mn-doped DMS. Our experimental results suggest that the effect from the precipitates of the manganese oxide, Mn_3O_4, may be dominant factor to the magnetic properties of the film.

CONCLUSION

We have studied the magnetic characteristics of $Zn_{0.7}Mn_{0.3}O$ films prepared by sol-gel method on the silicon and sapphire substrates at the annealing temperature of 700 ℃. The Curie temperatures of the two films are about 32 K independent of the substrates. The ferromagnetic ordering in the films may come from ferromagnetic precipitates originated by manganese oxide compound formed at the interfaces of the both substrates below 32 K. However, we suggest that one should reexamine carefully it with more refined techniques to verify the mechanism of ferromagnetism in Mn-doped ZnO films.

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