Magnetic order in Co-doped and (Mn, Co) codoped ZnO thin films by pulsed laser deposition

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Co-doped $Zn_{1-x}Co_xAl_{0.01}O$ ($x=0.15,0.3$) and (Mn, Co) codoped $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ thin films were fabricated on Al_2O_3 (0001) by pulsed laser deposition. The doped ZnO thin films with well wurtzite structures could be deposited at a low temperature of 400 °C and low oxygen pressure of 5×10^{-5} Pa. The Co-doped ZnO showed metallic conductivity with low resistance, while the (Mn, Co) codoped ZnO was semiconductor with high resistance, which was confirmed by the resistance vs temperature measurements. All the three doped ZnO films showed room temperature (290 K) ferromagnetism, with the saturated magnetic moments of $0.08\mu_B$/Co, $0.17\mu_B$/Co, and $0.19\mu_B$/(0.5Co+0.5Mn) for $Zn_{0.85}Co_{0.15}Al_{0.01}O$, $Zn_{0.7}Co_{0.3}Al_{0.01}O$, and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$, respectively. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1757652]

I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) are alloys with magnetic elements embedded in semiconductor material. DMSs have been extensively studied in last decade for their unique semiconducting and magnetic properties.[1,2] The observation of ferromagnetism in the Mn-doped III-V semiconductor at fairly high temperatures[3] has made DMS a promising candidate for spintronics applications where the coexistence of semiconducting and ferromagnetic properties is in high demand.[4] Theoretical studies have further predicted that room-temperature ferromagnetism may be achieved in several classes of DMS,[5] such as transition-metal-doped TiO_2 (Ref. 6) and ZnO (Refs. 7–9). These discoveries inspired researchers to have greater zeal in this field.

ZnO is a direct band-gap semiconductor with a wurtzite structure. Several theoretical calculations have suggested that Mn-doped *p*-type ZnO (Refs. 5 and 10) and Fe/Co/Ni-doped *n*-type ZnO (Ref. 11) may have ferromagnetic order even at room temperature. Many experiments were then carried out to confirm these predictions. While most of the experiments failed to produce ferromagnetic order in transition-metal-doped ZnO, several groups did claim that they have observed ferromagnetism in their samples. The first experimental observation of ferromagnetism in Co-doped *n*-type ZnO was reported by Ueda *et al.*[7,12,13] They have successfully fabricated $Zn_{1-x}M_xO$ ($x=0.05-0.25$,$M=$Co/Mn/Cr/Ni) films on α-Al_2O_3 (1120) by a pulsed laser deposition (PLD) method. They observed that all the Cr/Ni/Mn-doped and most of the Co-doped ZnO films did not show ferromagnetism with the Curie temperature above 280 K. However, the reproducibility of the experiment is quite poor (less than 10%) and the origin of the ferromagnetism is not clear. Using a reactive magnetron cosputtering technique, Cho *et al.* have grown $Zn_{1-x}(Co_{0.5}Fe_{0.5})_xO$ films on Si/SiO_2 substrate using Zn and CoFe targets. In addition to the observation of ferromagnetic behaviors in their samples, they have also found that the rapid thermal annealing under vacuum leads to a remarkable increase of the Curie temperature as well as the spontaneous magnetization. However, $Zn_{1-x}Mn_xO$ ($x=0.1$ and 0.3) films deposited on Al_2O_3 (0001) substrate using laser molecular-beam technique were also reported to show a ferromagnetic order at low temperature.[14,15] These films are also reported to be electrical insulators.

However, the experimental results from the other authors are contradictory and the repeatability of the ferromagnetism is poor. The problem remains unsettled. In fact, doping process is strongly dependent on various deposition parameters, especially deposition temperature and ambient oxygen pressure. Our present study showed that the successful doping of Co and (Mn, Co) codoping in ZnO without forming second phases can only be realized at a low deposition temperature (400 °C) and a low oxygen pressure (5×10^{-5} Pa). At high deposition temperature and oxygen pressure, cobalt will not substitute Zn in the lattice, instead, second phase of Co or Co_2O_3 will be formed. In this paper, we report the structural, electrical, and magnetic properties of Co-doped and (Mn, Co) codoped ZnO thin films prepared by PLD.

II. EXPERIMENTS

The Co-doped targets for PLD were prepared by the conventional solid-state reaction process. Fine powders of high purity (>99.9%) ZnO, Co_3O_4 with MnO_2 with different molar ratios are weighed and mixed. In some targets, 1 mol % Al_2O_3 was also included in order to increase the carrier density in the samples. The powders were ground in an agate ball-milling machine for 30 min to get homogeneous mix-

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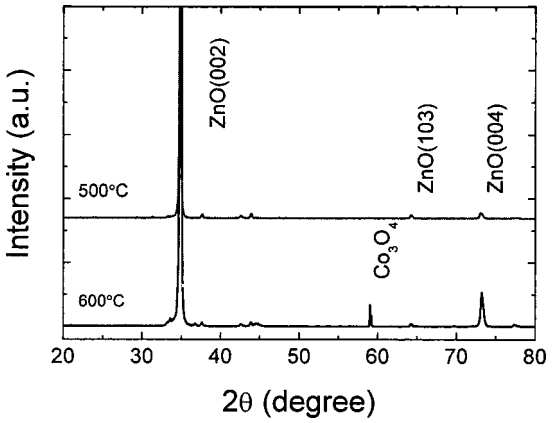

FIG. 1. XRD patterns of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin films deposited at 500 and 600 °C at oxygen pressure 5×10^{-5} Pa.

tures. They were then uniaxially cold pressed and sintered at 1000 °C for 10 h. The resultant high-density targets showed different colors. Pure ZnO target showed white with slightly yellow color, while the Co-doped and (Mn, Co) codoped ZnO had a dark green color which becomes even darker with increasing Co concentration.

$Zn_{1-x}Co_xAl_{0.01}O$ $(x=0.15,0.3)$ and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ thin films were deposited on polished Al_2O_3 (0001) substrates with a dimension of $10\times5\times0.5$ mm^3 using a KrF excimer laser of 248 nm wavelength. The deposition was carried at a laser repetition of 5 Hz, with an energy density of 250 mJ/pulse. The deposition time was 120 min leading to a film thickness of ~3 μm. The deposition temperature was from 400 to 600 °C and the ambient oxygen pressure was fixed at 5×10^{-5} Pa. The structure and the surface morphology of the doped ZnO films were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The resistance vs temperature (R-T) properties of the doped ZnO were measured at temperatures ranging from 80 to 300 K. The in-plane magnetic properties were probed by an Oxford Instrument superconducting vibrating spectrometer (VSM) at 290 K.

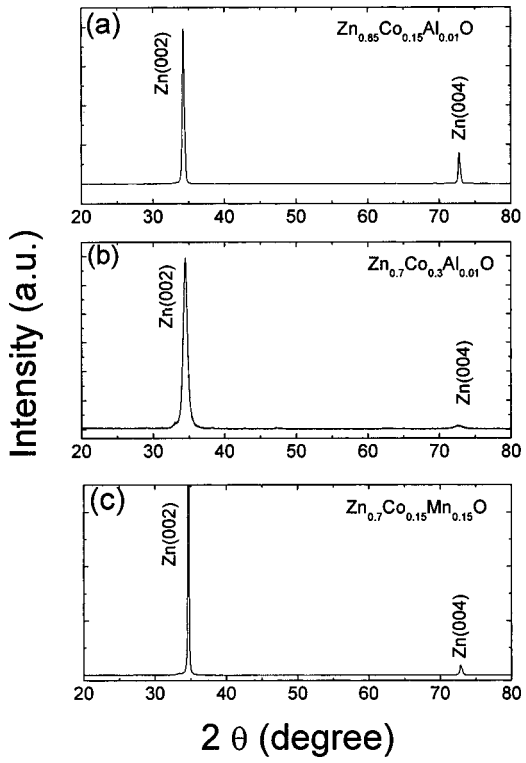

FIG. 2. XRD patterns of the $Zn_{0.85}Co_{0.15}Al_{0.01}O$ (a), $Zn_{0.7}Co_{0.3}Al_{0.01}O$ (b), and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ (c) thin films deposited at 400 °C at the oxygen pressure 5×10^{-5} Pa.

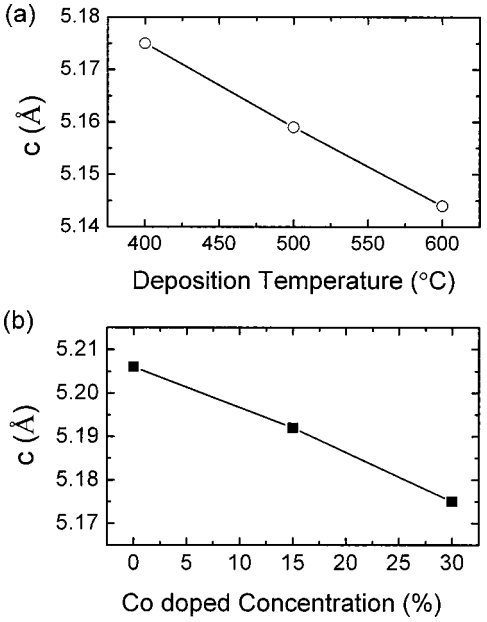

FIG. 3. The lattice constant c of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin films deposited at 400, 500, and 600 °C (a) and the lattice constant c of the pure ZnO, $Zn_{0.85}Co_{0.15}Al_{0.01}O$, and $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin films deposited at 400 °C (b).

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin films deposited at 500 and 600 °C at the oxygen ambient pressure 5×10^{-5} Pa. Single phase ZnO with high orientation is obtained for the 500 °C sample.

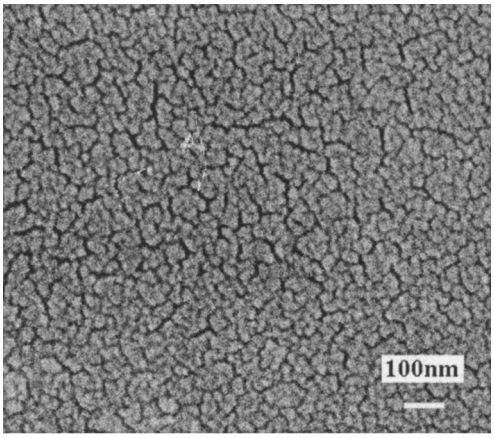

FIG. 4. SEM image of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ deposited on Al_2O_3 (0001) at 400 °C at oxygen pressure 5×10^{-5} Pa.

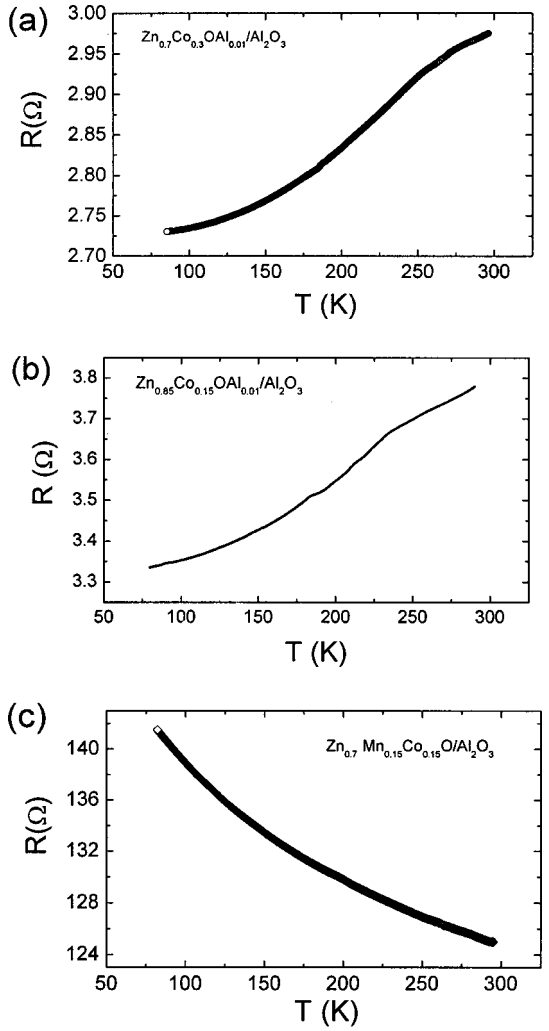

FIG. 5. *R-T* curves of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ (a), $Zn_{0.85}Co_{0.15}Al_{0.01}O$ (b), and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ (c) thin films.

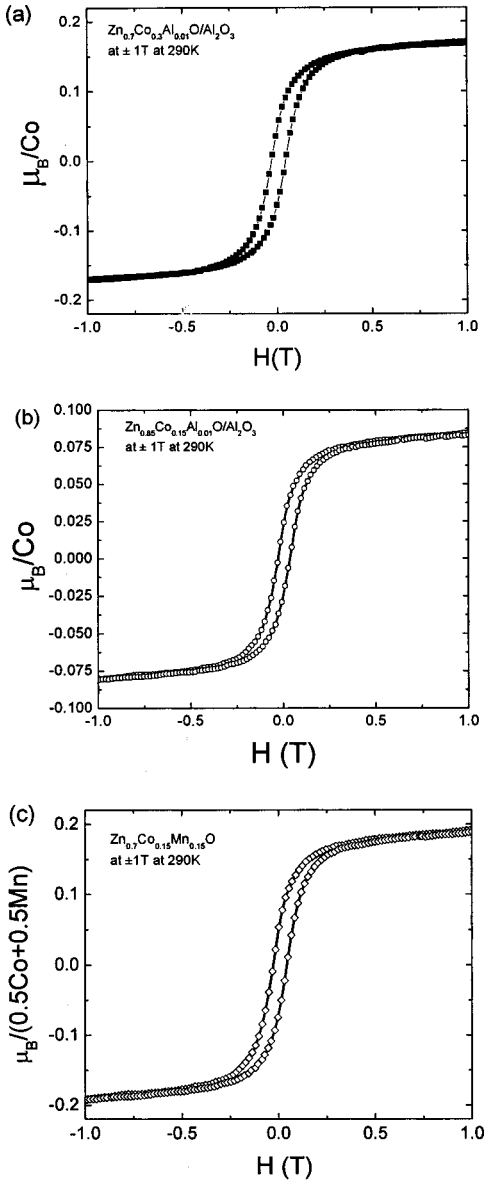

FIG. 6. VSM curves of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ (a), $Zn_{0.85}Co_{0.15}Al_{0.01}O$ (b), and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ (c) thin films at room temperature (290 K).

However, second phase (Co_3O_4) can be readily observed as the deposition temperature was above 600 °C.

Figures 2(a)–(c) show the XRD patterns of the $Zn_{0.85}Co_{0.15}Al_{0.01}O$, $Zn_{0.7}Co_{0.30}Al_{0.01}O$, and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ thin films deposited on Al_2O_3 (0001) at 400 °C. Except for ZnO (002) and (004) orientations, no peaks of other orientations of ZnO are observed, which means that they are strongly *c*-axis orientated wurtzite structure. From the XRD results, it is concluded that the film properties are strongly dependent on the deposition temperature. Low temperature deposition is crucial to have high quality ZnO thin films.

The lattice constant *c* of the pure ZnO, $Zn_{0.85}Co_{0.15}Al_{0.01}O$, and $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin films deposited at 400 °C are 5.206, 5.192, and 5.175 Å, respectively, showing a decrease with increasing Co concentration. This is probably due to the fact that the radius of Co^{2+} (72 pm) is smaller than that of Zn^{2+} (74 pm). For the $Zn_{0.85}(Mn_{0.15}Co_{0.15})O$ thin film deposited at 400 °C, the lattice constant *c* is 5.197 Å, which is slightly larger than that of pure ZnO, which is because the radius of Mn^{2+} (80 pm) is much larger than that of Zn^{2+}. It is also found that the lattice constant *c* of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin films decreases with increasing deposition temperature, indicating the incorporation of more Co atom in the films [Fig. 3(b)].

The surface morphology of the doped ZnO thin films has been examined by SEM. Figure 4 shows a typical SEM image of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ thin film deposited on Al_2O_3 (0001) at 400 °C. The surface of the doped ZnO is very smooth and the crystallites are very fine. No big particles can be found from the SEM image.

Figure 5 shows the *R-T* curves of the $Zn_{0.7}Co_{0.30}$ $Al_{0.01}O$ [Fig. 5(a)], $Zn_{0.85}Co_{0.15}Al_{0.01}O$ [Fig. 5(b)], and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ [Fig. 5(c)] thin films. Both Co-doped ZnO films demonstrate a metallic behavior, with the resistance of the 30% Co-doped ZnO being slightly lower than that of the 15% Co-doped ZnO. However, the (Mn, Co) codoped ZnO has a semiconducting property, whose resistance is higher than that of the Co-doped ZnO thin films.

This is probably attributed to the shallow acceptor nature of the Mn impurity.

The magnetism curves of all the samples were measured at room temperature (290 K) using VSM at the magnetic field ± 1 T. Figure 6 shows the VSM curves of the $Zn_{0.7}Co_{0.3}Al_{0.01}O$ [Fig. 6(a)], $Zn_{0.85}Co_{0.15}Al_{0.01}O$ [Fig. 6(b)] and $Zn_{0.7}(Mn_{0.15}Co_{0.15})O$ [Fig. 6(c)] thin films. All the samples showed ferromagnetic hysteresis with $m_s = 0.17\mu_B/\text{Co}$, $0.08\mu_B/\text{Co}$, and $0.19\mu_B/(0.5\text{Co}+0.5\text{Mn})$ for the 30%, 15% Co-doped, and 15% Co+15% Mn codoped samples, respectively. It is suggested that the value of m_s increases as the concentration of Co increases. The codoping of (Mn, Co) also results in an increase in the value of m_s.

IV. CONCLUSIONS

The properties of Co-doped ZnO and (Mn, Co) codoped ZnO thin films were strongly dependent on substrate temperature and ambient oxygen pressure, when deposited on Al_2O_3 (0001) substrates using PLD method. Single phase doped/codoped ZnO thin films, with room-temperature ferromagnetism, could be only obtained at a substrate temperature of 400 °C and oxygen pressure of 5×10^{-5} Pa. The Co-doped ZnO thin films showed a metallic conducting characteristic with low resistance, while the (Mn, Co) codoped ZnO thin film had semiconductor conductivity with high resistivity.

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