Mn-doped ZnO and (Mn, Cu)-doped ZnO thin films: Does the Cu doping indeed play a key role in tuning the ferromagnetism?

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(Received 15 October 2004; accepted 13 January 2005; published online 17 February 2005)

$Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.1}Cu_{0.05}O$ thin films were grown by the pulsed laser deposition technique on *R*-cut Al_2O_3 substrates under various conditions. Both $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.1}Cu_{0.05}O$ films that were fabricated at 650 °C under an oxygen pressure of 0.1 Torr show ferromagnetism (FM) above room temperature. It appears that by applying appropriate conditions, doping Mn alone can induce FM in ZnO itself, while co-doping with Cu might enhance the magnetic moment for some extent in some specific cases, but not very crucially as theories have predicted. Growth conditions likely play more important roles to result in ferromagnetic samples. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1875752]

During the last few years, there has been much interest in diluted magnetic semiconductors (DMS), i.e., semiconductors that have been doped slightly with magnetic element in order to result in room temperature ferromagnetism (FM) that is very essential for applications.[1–5] Based on the local spin density approximation (LSDA), Dietl *et al.* predicted that a high Curie temperature (T_C) FM could be obtained in ZnO if ZnO was doped with Mn along with a certain concentration of holes.[6] On the other hand, simulations of Sato and Katayama-Yoshida predicted that FM could also be achieved in V, Cr, Fe, Co and Ni-doped ZnO while in Mn-doped ZnO, since the energy of the antiferromagnetic state is lower than that of the ferromagnetic one, doping Mn alone in ZnO might not result in FM but co-doping with holes might tune it.[7] Recently, also by LSDA, Spandil theoretically showed that doping Mn or Co could not result in FM in ZnO, except if adding holes to stabilize the ferromagnetic state. As consequences, that author suggested that experimentalists co-dope Mn or Co with Cu in ZnO in order to bring out some good candidates for devices, since the resulting materials are not only ferromagnetic but also piezoelectric.[8] Other theoretical work of other groups, which was based on B3LYP hybrid density functional method or gradient corrected functional density theory, also confirmed that antiferromagnetism is the ground state of Mn-doped ZnO.[9,10] In this study, we undertook an investigation on Zn–Mn–O and Zn–Mn–Cu–O thin films to experimentally verify the effects of Cu doping in magnetism of this specific system.

Thin films of $Zn_{0.9}Mn_{0.1}O$ (ZMO) and $Zn_{0.85}Mn_{0.1}Cu_{0.05}O$ (ZMCO) with a typical thickness of 200 nm were fabricated by the pulsed laser deposition technique (KrF, 248 nm) from ceramic targets on *R*-cut Al_2O_3 substrates. Two main sets of growth conditions were used. One is the same as the optimal condition for Co-doped ZnO or V-doped ZnO thin films (hereafter called C1),[3,11] i.e., the substrate temperature was kept as 650 °C, the repetition rate was 3 Hz, the energy density was 2 J/cm^2, the partial oxygen pressure (P_{O_2}) was 0.1 Torr during deposition, and 300 mTorr for cooling down to room temperature. Another set of growth conditions is the same as the optimal one used for (Mn, Co)-doped ZnO films (hereafter called C2),[12] i.e., the substrate temperature was 400 °C, the repetition rate was 5 Hz, the energy density was 2 J/cm^2, the P_{O_2} was 10^{-6} Torr during deposition, and 20 mTorr for cooling down to room temperature. Structural properties were studied by x-ray diffraction (XRD). Compositions were checked by Rutherford backscattering spectroscopy method. Magnetization (M) vs temperature (T) from 5 to 400 K and vs magnetic field (H) from 0 to 0.5 T were measured by a superconducting quantum interference device magnetometer.

All films of ZMO and ZMCO films are lightly yellow, very transparent with a very smooth surface. XRD data in log scale showed that all films are well formed as wurtzite with a good crystallinity. There is only one very-high-intensity peak of the 110 orientation appearing in the spectra (see a typical example in Fig. 1), and no peak of other phases has been seen. Within our detection limit of less than 5% (with a step of 2θ as of 0.02°), there is no trace of Mn or Mn oxides. It is not possible to rule out completely some possi-

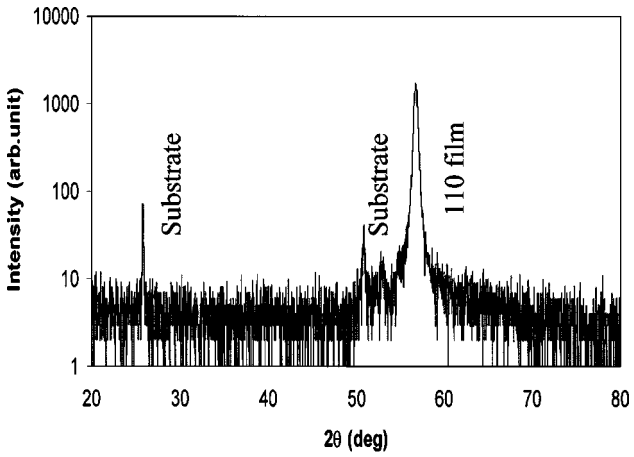

FIG. 1. XRD pattern of a $Zn_{0.9}Mn_{0.1}O$ film grown under the C1 condition.

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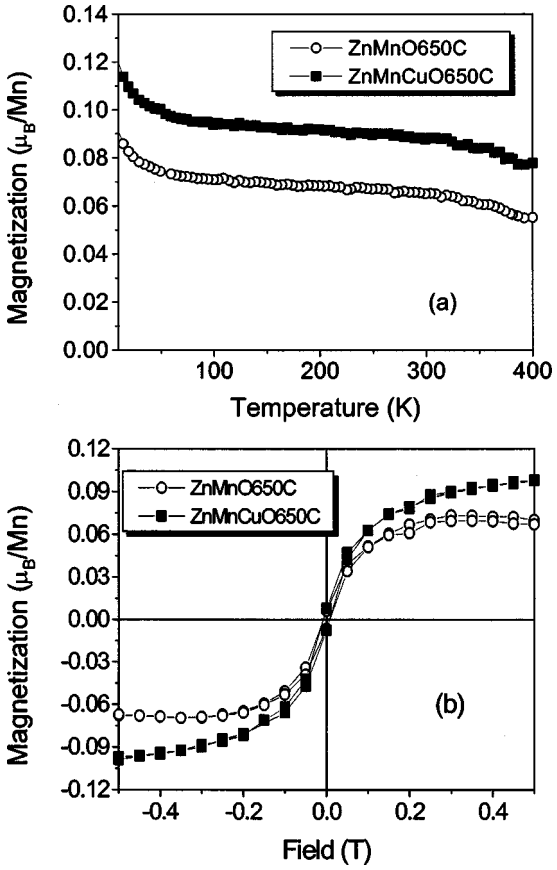

FIG. 2. Magnetization vs (a) temperature at 0.5 T, and (b) magnetic field at 300 K for the $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.1}Cu_{0.05}O$ thin films fabricated under the C1 condition.

bility for some nanometer-sized particles to exist, since it might be below this detection limit, transmission electron microscopy measurements might need to be done in the future to verify this issue. Magnetic force microscopy measurement in a small scale also might help to elucidate it, but since the samples have very small magnetic moments (shown later in this letter), it must be difficult to perform those.

Different from what theories had predicted, Mn doping, under some appropriate conditions, could indeed induce room temperature FM in ZnO. ZMO films grown under the C1 condition are ferromagnetic at room temperature. From Fig. 2(a), one can see that ZMO films have a T_C higher than 400 K, with the saturated magnetization (M_s) as of about 0.075 μ_B/Mn. Even though this value is rather modest, the hysteresis loop that can be seen clearly from *M-H* curve taken at 300 K [Fig. 2(b)] ensures the FM at room temperature of those films. Doping Cu enhanced the magnetic moment of the system for some extent (from Fig. 2, one can see that the ZMCO film fabricated under the C1 condition has a M_s of about 0.1 μ_B/Mn, i.e., 0.025 μ_B larger than that of the ZMO film), but it does not change the magnetic properties of the Mn-doped ZnO films drastically.

The room temperature FM is not obtained in both ZMO and ZMCO films grown under the C2 condition. Films are very weak ferromagnetic below 75 K and paramagnetic in a wide range of temperature (see *M-T* curves taken at 0.5 T in Fig. 3). No big difference can be seen in magnetism of ZMO in the cases of doping with or without Cu. Thus, in fact, Cu doping does not play a very crucial role in tuning the FM in Mn-doped ZnO thin films, or in other words, we must assume that the growth conditions would cause a more crucial effect than the additional carriers. The temperature and oxygen pressure during the film growth may create necessary oxygen vacancies that may lead to *n*-type doping, as one among several assumptions that the authors of Ref. 13 gave, in order to explain the magnetism they observed in HfO_2 films. One should notice clearly that the LSDA alone could not cover all things that have been happening in DMS thin films. Bergqvist *et al.* claimed that the magnetic percolation may strongly influence the ordering in DMS, and they were aware that the agreement between theory and experiment could be achieved only when the magnetic atoms are randomly positioned. One must say that the magnetic ordering in the semiconductor lattices critically depends on the preparation conditions of the samples that may result in a wide range of ordering temperatures.[14]

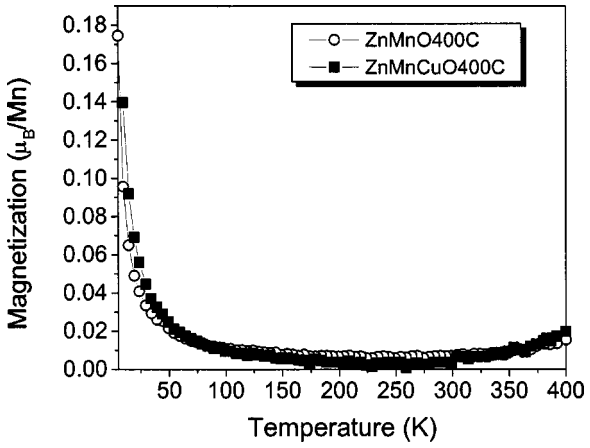

FIG. 3. Magnetization vs temperature at 0.5 T for the $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.1}Cu_{0.05}O$ thin films fabricated under the C2 condition.

In conclusion, magnetism of laser ablated $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.1}Cu_{0.05}O$ thin films on *R*-cut Al_2O_3 substrates under different conditions was investigated. Either without or with 5% of Cu doping, the $Zn_{0.9}Mn_{0.1}O$ films that were fabricated at 650 °C under oxygen pressure of 0.1 Torr clearly show ferromagnetism (FM) above room temperature while in other conditions, they both can be paramagnetic. It appears that by applying suitable conditions, doping Mn alone can induce FM in ZnO system itself, while co-doping with Cu might just enhance the magnetic moment slightly. Growth conditions, that may influence the magnetic ordering in the host lattices, may be an appropriate explanation for the friction between the observed experiment and some theoretical predictions.

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