Ferromagnetism in Cu-doped ZnO films: Role of charge carriers

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We report the observation of room temperature ferromagnetism in Cu-doped (5%) ZnO films grown on *c*-plane sapphire substrates. Films were prepared by pulsed laser deposition technique and were thoroughly characterized using several state-of-the-art characterization techniques. Hall measurements showed that the films are of *n*-type with a carrier concentration of 3×10^{17} cm^{-3}. Magnetization measurements showed that the films exhibit room temperature ferromagnetism with a saturation magnetization of $\sim1.45\mu_B$/Cu atom. When additional carriers were introduced in the films, ferromagnetism was completely vanished. Our results show that the *p*-type nature of the film is not essential for realizing ferromagnetic characteristics; however, the concentration of *n*-type carriers should not exceed a critical value. © *2008 American Institute of Physics*.
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Spintronics represents a unique paradigm of electronics that utilizes both the electron's charge as well as its spin degrees of freedom. The most critical step in the operation of a functional spintronic device is the injection of spin-polarized carriers into its semiconductor structure. Despite considerable efforts, efficient injection of spins into nonmagnetic semiconductors still continues to be a major hurdle in this field. Recent studies have predicted that dilutely doped magnetic semiconductors (DMSs) can provide an enabling breakthrough in achieving high spin-injection efficiency.[1–3] However, until recently, most of the DMS systems showed ferromagnetism below room temperature only. For realizing practical spintronic devices, it is essential that the DMS systems display ferromagnetism at room temperature.

A major boost to the experimental efforts to realize room temperature ferromagnetic semiconductors was provided by a theoretical work by Dietl *et al.*[4] in which they predicted room temperature ferromagnetism in Mn doped ZnO and GaN. This work led to a cascade of experimental efforts to explore the possibility of inducing ferromagnetism in ZnO by doping various different transition metal (TM) elements.[5–7] Room temperature ferromagnetism has indeed been reported in many of these systems. However, a major problem with these systems is that the TM dopant material can undergo a segregation to form magnetic precipitates. Therefore, there is a lot of controversy about whether the observed ferromagnetism is an intrinsic or extrinsic property of the material.

In this context, recent reports about the observation of room temperature ferromagnetism in copper doped ZnO have been taken with great enthusiasm by the scientific community. This is mostly because of the fact that the metallic copper (Cu), as well as all possible Cu-based secondary phases, are nonferromagnetic. So, if any ferromagnetism is observed in a Cu-based system, then it will undoubtedly be the intrinsic property of the material. Despite the above interest, the Cu:ZnO sytsem is not beyond controversies.[8] There are several contradicting reports where some authors have confirmed[8] the occurrence of FM in this system while others have ruled it out.[9] Even in studies where room temperature ferromagnetism is reported, the effect of carrier type on the ferromagnetic properties is unclear.[10] Buchholz *et al.*[10] found that *p*-type carriers are essential for realizing ferromagnetism in the ZnO:Cu system. In sharp contrast to this, Hou *et al.*[11] reported ferromagnetism in *n*-type ZnO:Cu films.

In this paper, we report some of our very exciting results about the observation of room temperature ferromagnetism in *n*-type Cu-doped ZnO films and its disappearance on introducing additional electrons in the system. All the films were grown on *c*-plane sapphire substrate by pulsed laser deposition technique. The targets used for deposition were synthesized by a sol-gel technique developed in our laboratory.[12] Thin film deposition was performed at a substrate temperature of 650 °C with 1 mTorr of oxygen pressure. Films were characterized using x-ray diffraction (both θ-2θ scan and Φ-scan), transmission electron microscopy, optical absorption spectroscopy, Hall coefficient, and magnetic property measurements.

The x-ray diffraction pattern from $Zn_{0.95}Cu_{0.05}O$ films grown on Sapphire (0001) substrate is shown in Fig. 1. Only the diffraction peaks corresponding to (0001) family of planes of wurtzite $Zn_{0.95}Cu_{0.05}O$ are observed, indicating strong *c*-axis alignment of the film. Comparison of (0002) peak of $Zn_{0.95}Cu_{0.05}O$ with the corresponding peak of pure ZnO (see the upper inset of Fig. 1) suggests an increase in the lattice parameter. This increase in *c* parameter as a function of Cu concentration is consistent with substitution of Zn by Cu. Lower inset of Fig. 1 shows the four circle high-resolution x-ray Φ-scan from $Zn_{0.95}Cu_{0.05}O$ DMS film for $(10\bar{1}1)$ plane. The Φ-scan peaks at 60° intervals reveal the hexagonal symmetry of the epitaxial ZnO wurtzite structure.

Figure 2 shows the optical transmittance data for $Zn_{0.95}Cu_{0.05}O$ film. For comparison, we have also shown the corresponding data for undoped ZnO. As can be seen in this figure, the absorption edge for $Zn_{0.95}Cu_{0.05}O$ is located at slightly lower energy compared to undoped ZnO. In the inset of this figure, we have shown the plot of α^2 versus energy.

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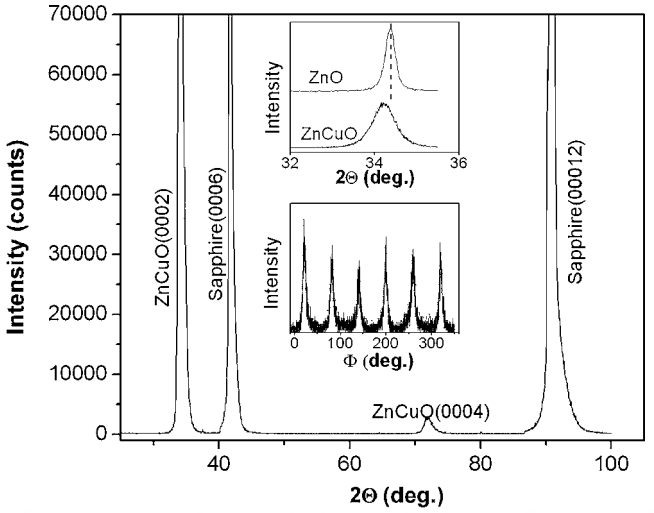

FIG. 1. X-ray diffraction (XRD) θ-2θ patterns for $Zn_{0.95}Cu_{0.05}O$ thin film. Upper inset shows the (0002) peak of $Zn_{0.95}Cu_{0.05}O$ along with the corresponding peak of pure ZnO. Lower inset shows the x-ray Φ-scan from $Zn_{0.95}Cu_{0.05}O$ film for $(10\bar{1}1)$ plane.

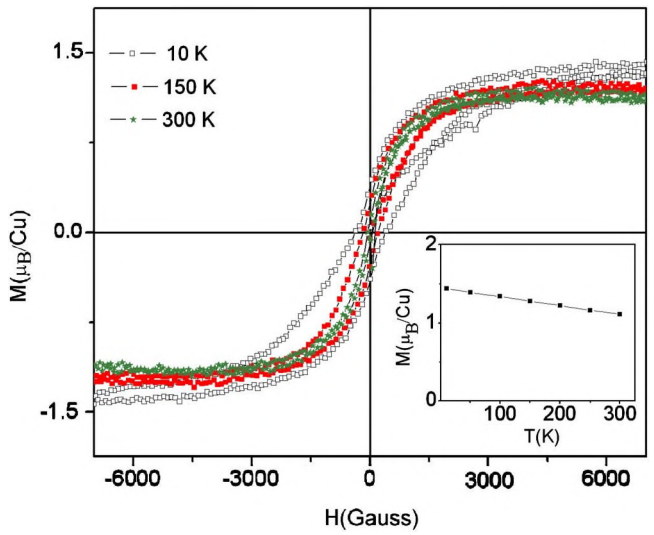

FIG. 3. (Color online) Magnetization field curves for $Zn_{0.95}Cu_{0.05}O$ film at different temperatures. The inset shows the saturation magnetization as a function of temperature.

By the extrapolation of this curve, we estimated the bandgaps of $Zn_{0.95}Cu_{0.05}O$ and ZnO as 3.1 and 3.5 eV, respectively. Decrease in the bandgap of $Zn_{0.95}Cu_{0.05}O$ compared to undoped ZnO confirms the matrix incorporation of Cu in the system.[13]

Hall effect measurements showed that $Zn_{0.95}Cu_{0.05}O$ films are of *n*-type in character. Carrier concentration was estimated to be 3×10^{17} cm^{-3} and these films showed semiconductorlike electrical characteristics. Carrier concentration of undoped ZnO film prepared under the identical concentration was 1×10^{19} cm^{-3}. Therefore, our results show that the doping of copper reduces the effective number of *n*-type carriers in the system. This is understood to arise because of the incorporation of holes in the material due to copper doping. However, the overall nature of the ZnO–Cu film still remains *n*-type.

In Fig. 3 we have shown the magnetization versus field curves of a $Zn_{0.95}Cu_{0.05}O$ film recorded at 10, 150, and 300 K. Thickness of the film was 100 nm and the measurements were performed by applying magnetic field parallel to film surface. $Zn_{0.95}Cu_{0.05}O$ shows room temperature ferromagnetism with about 150 G of corecivity at room temperature, which becomes about 600 G at 10 K. Inset of Fig. 3 shows the saturation magnetization of the $Zn_{0.95}Cu_{0.05}O$ film as a function of temperature. Magnetization at 10 K is $\sim1.45\mu_B$/Cu atom and shows a small and almost linear drop in the moment with increase in temperature over the entire temperature range (10–300 K) of investigation. This indicates that the ferromagnetic transition temperature of $Zn_{0.95}Cu_{0.05}O$ film is much higher than the room temperature. To see how the total magnetization scales with film thickness (for the same substrate area), two more films with thickness values of 50 and 200 nm were investigated. We observed almost a linear increase in total magnetization as the film thickness increases.

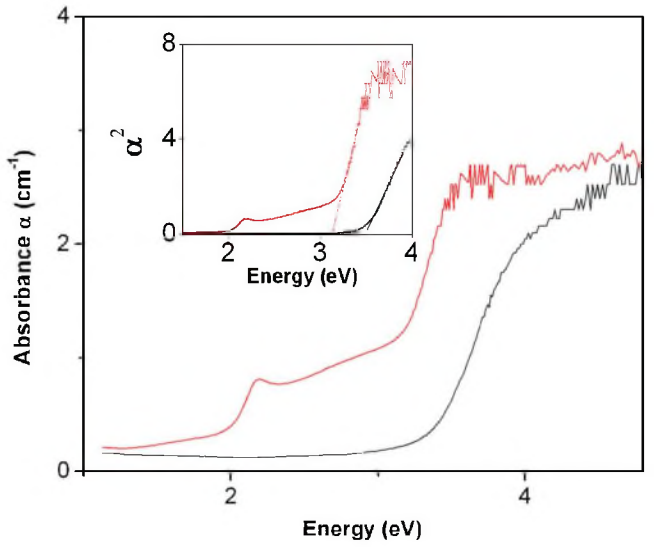

FIG. 2. (Color online) Optical absorbance (α) data of (a) $Zn_{0.95}Cu_{0.05}O$ and (b) ZnO. The inset shows the plot of α^2 energy.

In order to understand the observed magnetic moment of the films, it is essential to have an insight into the possible electronic configurations of Cu ions in the material. Cu atoms in unionized state have an outer cell electronic configuration of $3d^{10}4s^1$ and, hence, Cu^+ and Cu^{2+} ions are expected to posses $3d^{10}$ and $3d^9$ configurations, respectively. In $3d^{10}$ configuration, all the *d* electrons are paired and, hence Cu^+ ions does not posses any magnetic moment. On the other hand, in the case of Cu^{2+} ions with d^9 configuration, one unpaired electron is available. This will give rise to a spin angular momentum of $\frac{1}{2}$ which can result in a net magnetic moment of $M\sim1.73\mu_B$ $[M=g\mu_B\sqrt{S(S+1)};\ g=2,\ S=1/2]$.[14] Observed magnetic moment value of $1.45\mu_B$/Cu atom in our films is quite close to above estimated magnetic moment value for Cu^{2+} ions, implying that Cu ions in our $Zn_{0.95}Cu_{0.05}O$ films are predominant (about 85%) in magnetically active Cu^{2+} state.

Observation of room temperature ferromagnetism in *n*-type $Zn_{0.95}Cu_{0.05}O$ films is indeed very intriguing. This also confirms that the holes are not essential for realizing ferromagnetism in ZnO:Cu system. To extend our study still further, we introduced additional electrons in the system by doping a very slight amount of Ga in $Zn_{0.95}Cu_{0.05}O$. In our earlier studies, we have shown that Ga is an excellent donor for ZnO.[15] Carrier concentration in our $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$

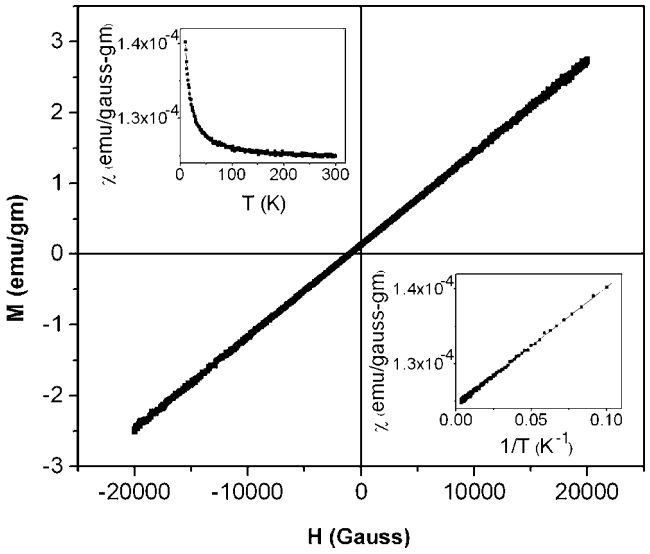

FIG. 4. Magnetization field curves for $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$ film recorded at 10 K. Upper inset shows the magnetic susceptibility ($\chi = M/H$) temperature (T) variation. Lower inset shows χ 1/T.

films prepared in the present study was 1×10^{18} cm^{-3}, about three times higher than that in $Zn_{0.95}Cu_{0.05}O$ film. Figure 4 shows the magnetization versus field curves for $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$ film recorded at 10 K. Linear variation of magnetization with field implies the absence of any kind of ferromagnetic ordering in the material. Upper inset of Fig. 4 shows the magnetic susceptibility ($\chi = M/H$) versus temperature variation for $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$ film. Magnetic susceptibility data fit well in an expression of the kind $\chi = \chi_0 + C/T$ (see lower inset). Using the value of the parameter C in the expression[14] $C = N\mu^2/3k_B$ for Curie paramagnetism, we derived a value of effective magnetic moment per Cu ion to be $0.3\mu_B$.

So we observed that the additional doping of electrons not only spoils long range ferromagnetic ordering in $Zn_{0.95}Cu_{0.05}O$ but also reduces the net magnetic moment per Cu ion. In Fig. 5, we have proposed a plausible mechanism which can explain the observed magnetic behavior of the system. In this mechanism, the reduction in the net magnetic moment of Cu ions occurs because of the transfer of a fraction of additional electrons introduced in the system to the d orbitals of Cu ions. The d orbitals of magnetically active Cu^{2+} ions possess nine electrons. So, if an additional electron is transferred into the d orbital, it will become completely filled and, hence, the magnetic moment of the Cu ion will vanish. A simple estimate showed that in $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$ film (magnetic moment $\sim 0.3\mu_B$/Cu), only about 17% of Cu ions exist in magnetically active Cu^{2+} ions. Reduction in the number of Cu^{2+} ions results in an increase in the distance between the nearest magnetically active ions. When this distance becomes more than a critical value, magnetic interaction may no longer be sufficient to mediate long range magnetic ordering.

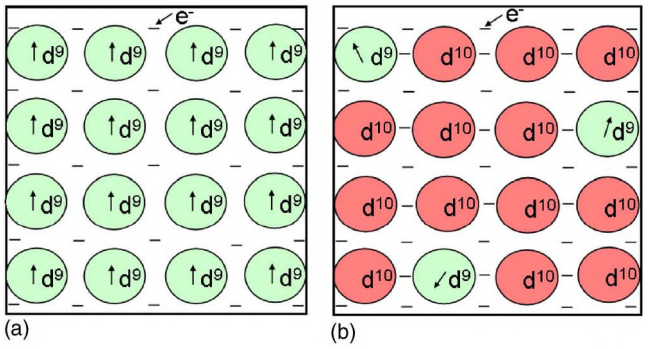

FIG. 5. (Color online) Schematic diagram showing Cu ions embedded in (a) $Zn_{0.95}Cu_{0.05}O$ film with carrier concentration of $\sim 3 \times 10^{17}$ cm^{-3}. In these films, Cu ions exist predominantly ($\sim 85\%$) in magnetically active Cu^{2+} (d^9) state, and (b) $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$ film with carrier concentration of $\sim 1 \times 10^{18}$ cm^{-3}. Because of the enhanced carrier concentration, a fraction of additional electrons gets transferred to the d orbitals of Cu ions, resulting in the completely filled d orbitals. In $Zn_{0.94}Ga_{0.01}Cu_{0.05}O$ films, only about 17% of Cu ions exist in magnetically active Cu^{2+} state.

To summarize our results, we have observed room temperature ferromagnetism in n-type ZnCuO films grown on sapphire (0001) substrate by pulsed laser deposition technique. Films showed T_C above room temperature with a magnetic moment of $1.4 \pm 0.1\mu_B$/Cu atom at 10 K. Our results show that the p-type nature of the film is not essential for realizing ferromagnetic characteristics: however, the concentration of n-type carriers should not exceed a critical value.

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