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Ferromagnetism in Fe-doped ZnO bulk samples with additional Cu doping

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Room-temperature (RT) ferromagnetism (FM) has been observed in Fe-doped ZnO bulk samples fabricated by a coprecipitation method, and the effect of additional Cu doping on magnetic properties of the samples has been investigated. The results of XRD show that all doping samples are single-phase with a wurtzite structure. X-ray photoelectron spectroscopy reveals that Fe is in 3+ state substituting for Zn in the sample without Cu doping, however, Fe shows a mixed oxidation state of 2+ or 3+ in the sample with additional Cu doping, where Cu is 1+ valence. Magnetic measurements indicate that additional Cu doping enhances the FM of the system, and the magnetization increases gradually with the increasing Cu content x up to 1%. The observed RT FM was attributed to the ferromagnetic coupling between Fe^{3+} ions mediated by holes.

1 Introduction Numerous technological breakthroughs are envisaged with the use of magnetic semiconductor materials that show a ferromagnetic ordering at or above room temperature. Oxide diluted magnetic semiconductors (DMSs) have recently attracted a lot of research effort due to their potential application in the field of spintronic devices [1–3] designed to process information by manipulating the spin of electronic currents, such as spin light-emitting diodes (spin-LEDs) [4–7], spin-polarized solar cells [8], and magneto-optical switches [9].

Room-temperature (RT) ferromagnetism (FM) in ZnO doped with transition-metal elements (V, Cr, Mn, Fe, Co, and Ni) has been predicted by Dielt et al. [10] and Sato and Katayama-Yoshida [11]. Following the original report by Ueda et al. [12], many experiments have been carried out to confirm the theory prediction and the initial result. Some results dealing with RT FM of Fe-doped ZnO samples have also been published [13–20]. However, there remain some questions regarding the origin of the magnetic behavior in these DMS materials. Additional Cu doping is deemed essential to achieve RT FM in Fe-doped ZnO bulk samples [18]. Contrarily, Shim et al. [19] showed that RT FM in Fe-doped ZnO with additional Cu doping stems from nanocrystalline $ZnFe_2O_4$ with an inverted spinel structure. Zhou et al. [20] reported that the metallic α-Fe nanocrystals may be responsible to the FM in Fe-implanted ZnO single-crystal samples. A detailed structural, chemical bonding states, and magnetic investigation with high-quality codoped samples is essential to resolve the controversy.

Most recently, we have reported RT FM in Fe-doped ZnO single-phase bulk samples prepared by a coprecipitation method, with the highest doping concentration of $x = 2\%$ [21]. In the present work, we prepared Fe-doped ZnO bulk samples that are codoped with Cu under similar preparation conditions and experimentally study the effect of additional Cu doping on the magnetic properties of Fe-doped ZnO bulk samples, attempting to clarify the origin of FM in these DMS materials.

2 Experimental Bulk samples with a nominal component $Zn_{0.98-x}Fe_{0.02}Cu_xO$ ($x = 0$, 0.25, 0.5, and 1%) were prepared by a coprecipitation method. Appropriate proportions of $Zn(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ high-purity (99.9%) powders were thoroughly mixed according to the desired stoichiometry, the powders were dissolved in distilled water to get a homogeneous solution. The mixture was stirred strongly while a proper amount of Na(OH) aqueous solution was introduced, controlling the pH to 7 to deposit all cations completely. The obtained precipitate was thoroughly washed

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with distilled water and dried in air at 200 °C, and then prefired at 400 °C for 8 h. The prepared powders were ground, pelletized, and sintered at 600 °C for 12 h in an Ar gas atmosphere. The crystal structure of $Zn_{0.98-x}Fe_{0.02}Cu_xO$ samples was characterized by X-ray diffraction (XRD, X'Pert PRO) using Cu Kα radiation ($\lambda = 1.5406$ Å). Chemical bonding states and chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) with Al K radiation ($h\nu = 1486.6$ eV). A physical properties measurements system (PPMS, Quantum Design) was used to investigate the magnetic properties of the doped samples.

3 Results and discussion

The crystal structure of the samples was characterized by XRD using Cu Kα radiation. Data were collected using a step scan of 0.017° in 2θ. Figure 1 presents the typical powder XRD patterns for pure ZnO, $Zn_{0.98}Fe_{0.02}O$, and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$. No clear difference was found in XRD patterns for all the samples, an additional 1% Cu doping has induced no change in structure. All the diffraction peaks can be indexed to a wurtzite structure as ZnO, no spurious phase was found within our detection limit of less than 5%. This means that iron and copper have been incorporated into the lattice structure, forming a solid solution instead of precipitates. In addition, the position of the diffraction peak of $Zn_{0.98}Fe_{0.02}O$ was found a shift to higher angles compared with pure ZnO, suggesting the possibility of Fe^{3+} substitution for Zn^{2+} because of its smaller ionic radius of 0.064 nm compared to 0.074 nm for Zn^{2+}.

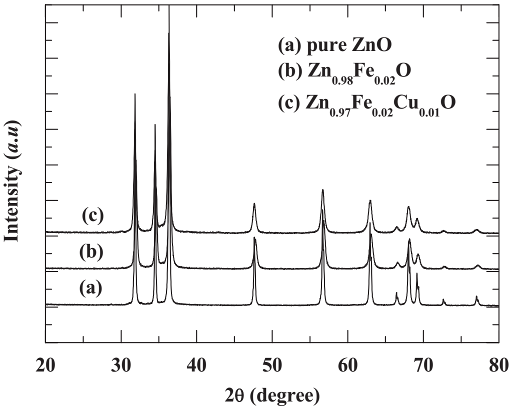

Figure 1 Typical powder XRD patterns for pure ZnO, $Zn_{0.98}Fe_{0.02}O$, and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$.

Chemical bonding states in $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ bulk samples were characterized by XPS measurement. The XPS spectra have been charge corrected to the adventitious C 1s peak at 284.6 eV and the core states of Zn 2p, Fe 2p peaks for $Zn_{0.98}Fe_{0.02}O$ and Zn 2p, Fe 2p, Cu 2p peaks for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ were presented in Fig. 2. The binding energy of the Zn $2p_{3/2}$ state is typical located at 1021.8 eV for $Zn_{0.98}Fe_{0.02}O$ and 1021.9 eV for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, respectively. The Fe $2p_{3/2}$ peak for $Zn_{0.98}Fe_{0.02}O$ occurs at 710.7 eV as presented in Fig. 2c, suggesting that Fe ions in the sample should have a valence of 3+, consistent with the results of XRD. For $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, the main peak of Fe $2p_{3/2}$ at 711.2 eV splits into two peaks with the binding energy of 710.5 and 710.9 eV, as shown in Fig. 2d, which corresponds to a mixed oxidation state of 2+ or 3+. In addition, the peak of Cu $2p_{3/2}$ is located at 931.8 eV, corresponding to Cu^{1+}, in agreement with another report [17]. According to the experimental results, we can exclude the possibility of the formation of Fe metal clusters, since, if Fe exists as a metal cluster itself in the samples, the binding energy of the Fe $2p_{3/2}$ state should be typical located at 706.9 eV [22].

The magnetic properties of $Zn_{0.98-x}Fe_{0.02}Cu_xO$ were studied by checking the temperature and magnetic field dependence of the magnetization. Figure 3 shows the magnetic field dependence of magnetization (M–H) for $Zn_{0.98}Fe_{0.02}O$ bulk samples both without and with additional

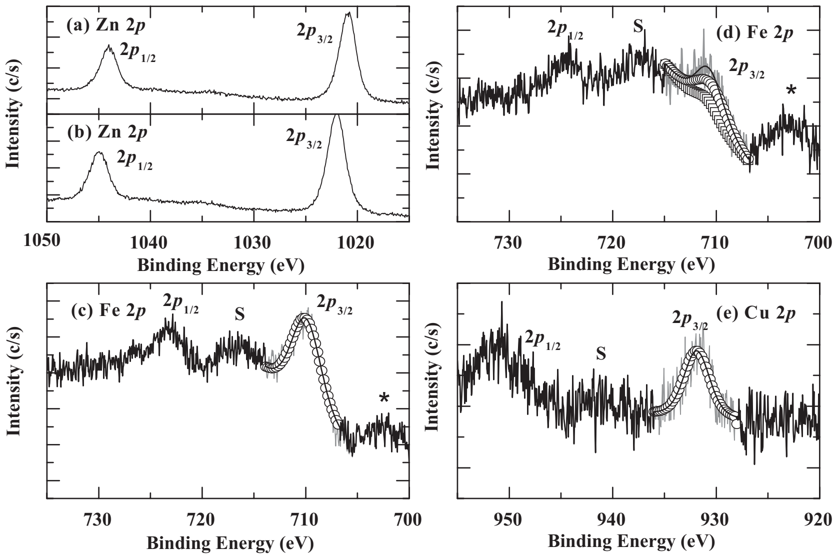

Figure 2 XPS spectra for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ bulk samples: (a) Zn $2p_{3/2}$ XPS spectrum for $Zn_{0.98}Fe_{0.02}O$; (b) Zn $2p_{3/2}$ XPS spectrum for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$; (c) Fe $2p_{3/2}$ XPS spectrum for $Zn_{0.98}Fe_{0.02}O$; (d) Fe $2p_{3/2}$ XPS spectrum for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$; (e) Cu $2p_{3/2}$ XPS spectrum for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$. The peaks marked by "S" are satellite peaks.

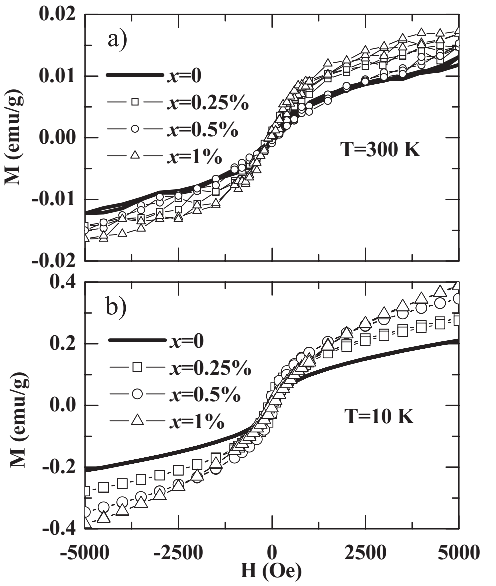

Figure 3 *M–H* curves for $Zn_{0.98-x}Fe_{0.02}Cu_xO$ ($x = 0$–1%) bulk samples at 300 K (a) and 10 K (b).

Cu doping. Even though the coercive force (H_C) and the remnant magnetization (M_R) are modest, the hysteresis loops that can be seen clearly from the *M–H* curves ensure all samples are FM at RT, as shown in Fig. 3a. A small amount of additional Cu doping ($x = 0.25\%$) brought a slight increment in *M*, and *M* gradually increases with the increase of Cu concentration up to $x = 1\%$. The saturation magnetization (M_S) of the $Zn_{0.98-x}Fe_{0.02}Cu_xO$ series samples is estimated to be $0.009\mu_B$/Fe, $0.011\mu_B$/Fe, $0.011\mu_B$/Fe, and $0.012\mu_B$/Fe for the $x = 0$, 0.25, 0.5, and 1% samples, respectively.

Figure 3b presents the *M–H* curves of $Zn_{0.98-x}Fe_{0.02}Cu_xO$ ($x = 0$–1%) at 10 K. One can find that the H_C are quite small, and the *M–H* curves show superparamagnetic behavior, indicating the existence of small ferromagnetic clusters. The saturation magnetization (M_S) of the series of samples is estimated to be $0.15\mu_B$/Fe, $0.21\mu_B$/Fe, $0.25\mu_B$/Fe, and $0.28\mu_B$/Fe for the $x = 0$, 0.25, 0.5, and 1% samples, respectively.

From the above, a RT ferromagnetic behavior has been observed in a Fe-doped ZnO bulk sample. One can find that additional Cu doping is beneficial to the FM of the system, but not very crucial as theories have predicted. This result is different from some previous publications [18, 23]. In those reports, additional Cu doping is quite important to achieve and enhance RT FM in Zn–Fe–O and Zn–Co–O system.

Further studies on magnetic behaviors of $Zn_{0.98-x}Fe_{0.02}Cu_xO$ were performed through measuring the magnetization as a function of temperature (*M–T*). Figure 4 shows the *M–T* curves typical for the $x = 0$ and 1% samples in an applied field of 1000 Oe.

For the two samples, no clear magnetic transition is found in the whole temperature range from 10 to 300 K, showing a paramagnetic-like behavior. However, it is clear that both the $x = 0$ and 1% samples are in magnetization saturation at about 15 K. Furthermore, the nonzero magnetization values and the hysteresis loops (seen in Fig. 3) at 300 K indicate that both the samples are FM at 300 K. So one can conclude that the Curie temperature of $Zn_{0.98-x}Fe_{0.02}Cu_xO$ ($x = 0$–1%) series samples is higher than 300 K.

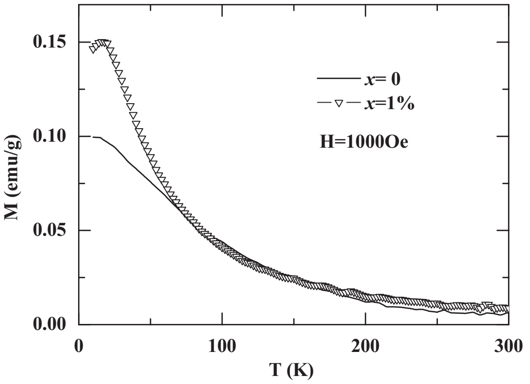

Figure 4 Magnetization as a function of temperature (*M–T*) for $Zn_{0.98-x}Fe_{0.02}Cu_xO$ ($x = 0$–1%) bulk samples in an applied field of 1000 Oe from 10 to 300 K.

It is noted that M_S of the samples is quite small, for example, the M_S is only $0.25\mu_B$/Fe for the $x = 0.5\%$ sample at 10 K, however, the theory magnetic moment of Fe^{3+} ions is $3\mu_B$/Fe, the experiment value is one order of magnitude less than the theory value, meaning that the ferromagnetic exchange interaction is quite weak.

To further clarify this issue, *M* as a function of *T* for the $x = 0.25$ and 0.5% samples were measured in zero-field-cooling (ZFC) and field-cooling (FC) modes with an applied field of 1000 Oe, as shown in Fig. 5.

A clear discrepancy between the ZFC and FC curves can be observed in the whole temperature range, indicating clear superparamagnetic behavior with a blocking temperature at about 20 K. The results further show that there are many small ferromagnetic clusters in our samples. Most of these clusters are isolated due to the long distance between them, fixed by the low doping concentration, therefore they have a small contribution to the long range ferromagnetic order, so the *M* of the system is lower than the theory value. It is noted that the *M* in the ZFC mode are even larger than the *M* in the FC mode in the temperature range from 20 to 300 K. The anomaly may be ascribed to the existence of small ferromagnetic clusters. In the FC mode, magnetic clusters only felt the applied magnetic field at high-temperature. With the decrease of temperature to *T*, the applied magnetic field turned the magnetic moments of these small magnetic clusters against the thermal fluctuation. In the ZFC mode, all ferromagnetic clusters were turned by the applied magnetic field at low temperature. Every magnetic cluster was in the applied magnetic field and the internal magnetic field stemmed from the near-neighbor ferromagnetic

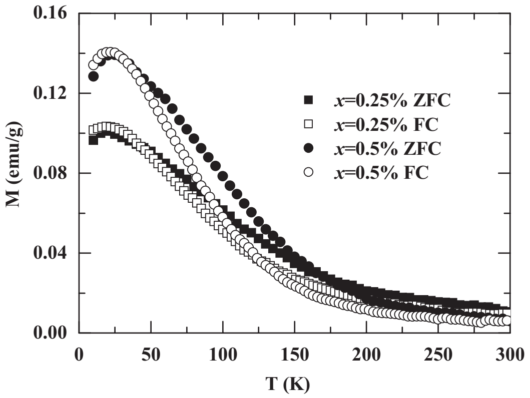

Figure 5 M–T curves for $x = 0.25$ and 0.5% samples in ZFC and FC modes.

clusters. To break the ferromagnetic ordering of these small magnetic clusters, the thermal fluctuation must overcome the applied magnetic field and the internal magnetic field, which need a higher temperature than T. So, one can find that the contribution of these small ferromagnetic clusters to the M of the system in the ZFC mode is larger than is the case in the FC mode in a specific temperature range.

Although the precise mechanism for ferromagnetic coupling between magnetic ions is still being discussed and debated in the literature, there is wide consensus that carrier doping has an important effect on magnetic properties of ZnO-based DMSs. Especially, as a p-type dopant in semiconductors, additional Cu doping is deemed essential to achieve RT FM in Fe-and Co-doped ZnO bulk samples [18, 23]. In this research, however, RT FM is observed in an Fe-doped ZnO sample without additional doping, additional Cu doping has a positive effect on the FM of $Zn_{0.98}Fe_{0.02}O$. The possibility of the formation of Fe metal clusters and Fe_3O_4 clusters can be excluded because Fe ions show 3+ valence according to the results of XPS. The only possible Fe-based oxide is Fe_2O_3, however, Fe_2O_3 is a typical anti-ferromagneic oxide with a T_N of 963 K. Obviously, the FM observed in our samples should be intrinsic, and additional Cu doping enhances the intrinsic ferromagnetic interaction to a certain extent. Considering that Cu is a typical p-type dopant in DMS, the substitution of Cu^{1+} ions for Zn^{2+} ions will increase the hole concentration, one can conclude the FM of Zn–Fe–O system must be dependent on the hole concentration. So, we suppose that the ferromagnetic behavior observed in this experiment should stem from the ferromagnetic coupling between Fe^{3+} ions mediated by the holes formed during the preparation process. The Cu^{1+} ions substitution for Zn^{2+} increases the hole concentration of the samples and enhance the ferromagnetic coupling between Fe^{3+} ions, therefore, the FM is enhanced. On the other hand, the introduction of Cu^{1+} ions induce an enhanced compensation effect that results in the onset of Fe^{2+} in the samples, accordingly decreasing the concentration of Fe^{3+} ions in the samples, thereby, weakening the ferromagnetic coupling of the samples. For this reason, the additional Cu doping increase the FM of $Zn_{0.98}Fe_{0.02}O$, but not very crucial as theories have predicted. Further research on this issue might need to be done in the future to clarify the supposition.

4 Conclusion In conclusion, RT FM is observed in a single-phase Fe-doped ZnO bulk sample prepared by a coprecipitation method. The effect of additional Cu doping on the magnetic properties of an Fe-doped ZnO sample was investigated. Based on the results of XRD and XPS, the observed FM is attributed to the ferromagnetic coupling between Fe^{3+} ions mediated by holes formed during preparation process. Additional Cu doping is beneficial to the FM of the system to some extent, but as marked as theories have predicted.

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