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The Magnetic Properties of $Zn_{0.98}Fe_{0.02}O$ with Additional Cu Doping

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Abstract

Samples $Zn_{0.98}Fe_{0.02}O$ doped with additional Cu have been fabricated by a coprecipitation method. It is found that $Zn_{0.98}Fe_{0.02}O$ without additional doping shows weak ferromagnetism at room temperature. The Cu doping has induced a light increase of magnetization in low temperature of 10 K. This result is consistent with bound magnetic polaron model relative to holes.

Keywords

Ferromagnetism, $Zn_{0.98}Fe_{0.02}O$, Magnetic Field, Magnetization

1. Introduction

Diluted magnetic semiconductors (DMS) have attracted a lot of attention for their potential applications in the field of spin-dependent semiconductor electronics and optoelectronics, or so-called spintronics and optospintronics [1]. Simulations of Sato *et al.* predicated that the ferromagnetism could also be achieved in V, Cr, Fe, Co, and Ni-doped ZnO [2]. Copper (Cu) is a typical non-magnetic transition metal dopant, because metallic Cu and Cu related oxides are non ferromagnetic materials. Theoretical and experimental studies have confirmed that there is room temperature ferromagnetism (RTFM) in Cu Doped ZnO. For this reason, Cu doped ZnO is considered as an ideal candidate to study the mechanism of ferromagnetism in ZnO based DMS. Room-temperature ferromagnetism in ZnO doped with Fe has been achieved; however, there remain some questions regarding the origin of the magnetic behavior in Fe-doped ZnO materials. It is deemed that additional Cu doping is essential to achieve RTFM in Fe-doped ZnO bulk samples [3]. Howerver, Shim *et al.* found that the ferromagnetism in Fe- and Cu-codoped ZnO stems from the secondary phase $ZnFe_2O_4$ [4].

In the present work, we have introduced additional Cu in $Zn_{0.98}Fe_{0.02}O$ bulk samples by a coprecipitation method, and compared the ferromagnetism of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ system.

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2. Experimental

Bulk samples with nominal component $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ 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 (99.99%) powders were weighed and mixed according to the desired stoichiometry, the powders were dissolved in distilled water to get homogeneous solution. The mixture were stirred strongly while proper amount of Na(OH) aqueous solution were poured into it, controlling the PH = 7 to deposit all cations of Zn^{2+}, Fe^{3+}, Cu^{2+} and completely. The obtained precipitate was thoroughly washed with distilled water and dried in air at 200˚C, and then prefired at 400˚C for 8 hours. The prepared powders were ground, palletized, and sintered at 600˚C for 12 hours. To aviod the formation of secondary phase as far as possible, the sintering process was executed in Ar gas atmosphere. X-ray diffraction (XRD, PANalytical B.V.) was used to determine the crystallinity and secondary phase formation. Chemical bonding states and chemical compositions of the samples were analyzed by x-ray photoelectron spectroscopy (XPS, VG Multilab 2000). Physical Properties Measurements System (PPMS, Quantum Design) was used to characterize magnetic behavior of the doped samples.

3. Results and Discussions

The crystal structure of the samples was characterized by x-ray diffraction using Cu Kα radiation. Data were collected using a step scan of 0.017˚ in 2θ. **Figure 1** presents the typical powder x-ray diffraction patterns for ZnO, $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$. No clear difference in XRD patterns can be found between pure ZnO and doping samples, suggesting that the doping has not changed the structure of ZnO. All the diffraction peaks can be indexed to a wurtzite structure as ZnO, and there is no indication of secondary phase within our detection limit. It suggests that all samples are of single phase and iron, stannum and copper have been incorporated into the lattice structure, forming a solid solution instead of precipitates.

The magnetic properties of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ were investigated by checking the temperature (T) and magnetic field (H) dependence of the magnetization (M). **Figure 2** shows the M as a function of T (M-T) for all samples in an applied field of 1000 Oe from 10 to 300 K. For $Zn_{0.98}Fe_{0.02}O$, M gradually increases with the decrease of T above 25 K, and the curve becomes flat below 25 K, the maximum value of M (M_{max}) can be estimated to about 0.74 μB/Fe site. The result hints probable low-temperature ferromagnetism in $Zn_{0.98}Fe_{0.02}O$ bulk sample. $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ shows a similar M-T behavior to $Zn_{0.98}Fe_{0.02}O$ with an equal value of $M_{max.}$

The inverse of M as a function of T (M^{-1}-T) for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ was plotted to understand the magnetism, as shown in **Figure 3**. The solid lines are extrapolation fits to the data in the range of 180 - 300 K for these samples. According to the discussion by Spacek *et al.* [5], the Curie-Weiss temperature Θ_0 is evaluated to be 140 K for $Zn_{0.98}Fe_{0.02}O$ and 90 K for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$. The positive Θ_0 for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ suggests that ferromagnetic interaction is dominant in the two samples, which confirms the low-temperature ferromagnetism in $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ and $Zn_{0.98}Fe_{0.02}O$.

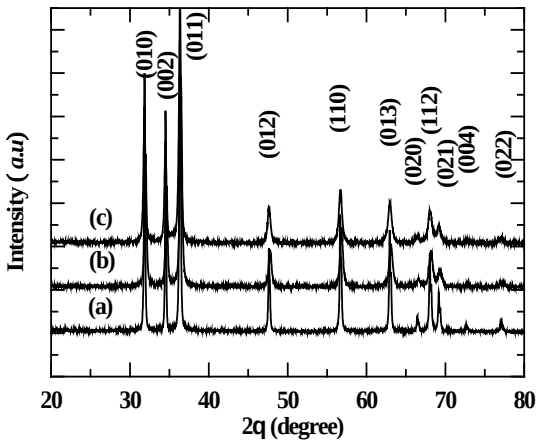

Figure 1. Powder XRD patterns for (a) pure ZnO; (b) $Zn_{0.98}Fe_{0.02}O$; (c) $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$.

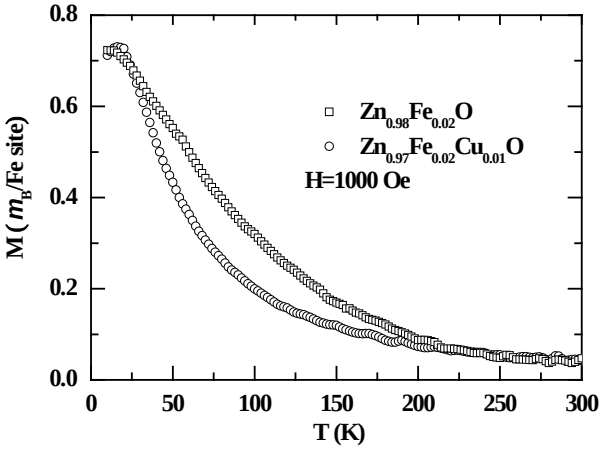

Figure 2. Temperature dependence of magnetization (*M-T*) for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ bulk samples in an applied field of 1000 Oe.

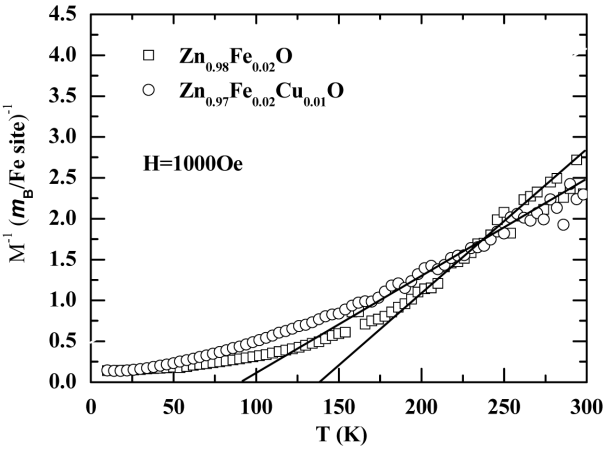

Figure 3. Curie-Weiss plot for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ bulk samples. The solid line represents the linear extrapolation line fit to the data for 180 - 300 K.

Figure 4 shows the *M-H* curves of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ taken at 300 K, the inset gives a partial enlarged detail. All samples show a room-temperature ferromagnetic behavior with a modest hysteresis loops, which suggests that their Curie temperature (TC) are higher than RT. This result is consistent to the theoretical predictions [2] [6] and essential for practical application in spintronics. From the inset, the Coercive force (HC) and residual magnetization (MR) can be estimated to about 90 Oe and 0.005 μB/Fe site for $Zn_{0.98}Fe_{0.02}O$, 100 Oe and 0.006 μB/Fe site for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$. Simultaneously, the saturation magnetization (MS) also can be estimated to about 0.08 μB/Fe site for $Zn_{0.98}Fe_{0.02}O$, 0.085 μB/Fe site for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ from **Figure 4**. From the above, we can see that additional Cu doping has not induced remarkable change in magnetic properties at 300 K. This result is very different to the previous results [4], in there, a small amount of additional Cu doping in $Zn_{0.95}Fe_{0.05}O$ bulk sample caused a drastic change in *M*, the MS at room temperature of the sample with 1% Cu doping becomes 30 times larger than that of the sample without Cu.

The *M-H* curves of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ also have been measured at 10K, as shown in **Figure 5**, a partial enlarged detail also has been given in the inset. Both $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ show "S" shaped hysteresis loops. The MS of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ is about 1.5 μB/Fe site and 1.85 μB/Fe site, respectively. It seems that additional Cu doping causes an enhancement of ferromagnetism at low temperature of 10 K.

The observation of RT FM in Zn-Fe-O system is consistent with the prediction by theory, it has been proved

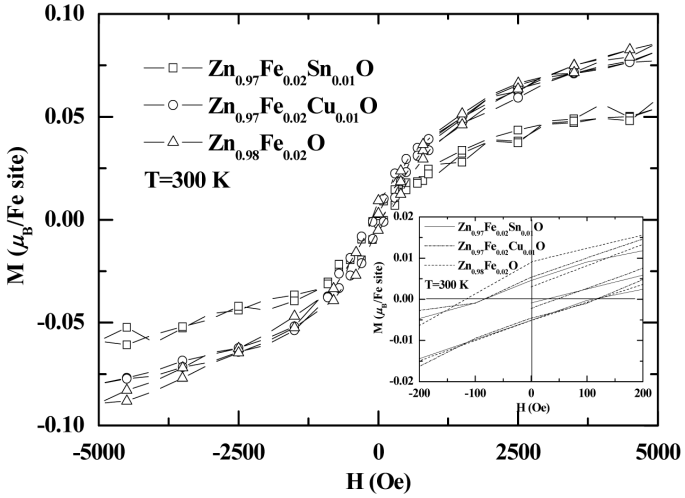

Figure 4. The magnetization as a function of magnetic field (*M-H*) for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$.

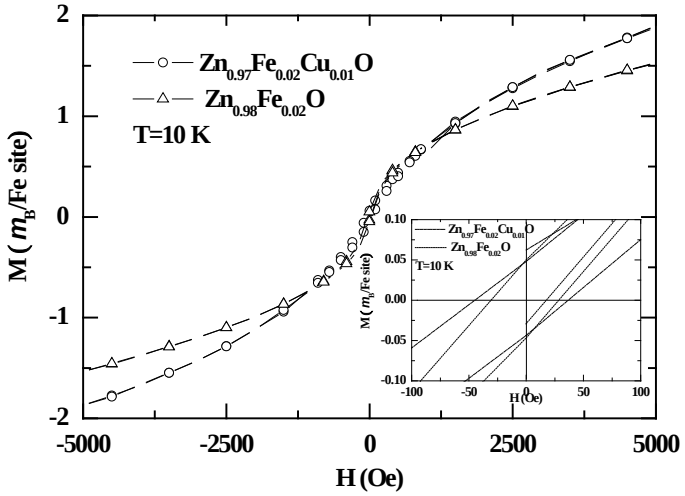

Figure 5. The *M-H* curves of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ bulk samples at 10 K.

that the RT FM in this system is intrinsic, in accordance with the previous work [7]. It should be noted that, additional Cu doping has not induced obvious change in ferromagnetism of Zn-Fe-O system at 300 K, but rather caused a small increase in M only at 10 K. It means that additional Cu doping has a little effect on ferromagnetism of Zn-Fe-O system, but not very crucial as mentioned in [4].

The most popular mechanisms relative to carrier proposed to explain ferromagnetic ordering in DMSs are RKKY interaction, double-exchange mechanism, and the bound magnetic polaron (BMP) model. A quantitative calculation of the carrier concentration is very helpful to understand this issue by measuring the Hall effect of these samples, but we have failed to obtain the carrier concentration due to the considerable Hall voltage created by the large bulk resistivity higher than 106 Ω·cm at room temperature. Nevertheless, from this we can conclude that most of carriers are localized in these samples and these samples are insulating. So both RKKY-type and double-exchange mechanism can be eliminated because that there are not enough free carriers to mediate RKKY-type interaction and/or double-exchange interaction. It seems that the bound magnetic polaron (BMP) [8] [9] model is an alternative theory for the FM at RT observed in this study. For an insulating DMS system with a quite low carrier density to exhibit ferromagnetism, the BMP model provides a mechanism whereby holes that are located spatially at or near the transition-metal ion are responsible for mediating ferromagnetism [10]. So appropriate hole concentration is necessary in order to induce ferromagnetic ordering. Additional Cu doping will

increase the hole density of the system, thus increases the number of BMPs, and then results in an enhanced ferromagnetism. However, the increase of hole density caused by additional Cu doping is quite limited because it is very difficult to realize heavy acceptor doping in ZnO matrix. Therefore, additional Cu doping has induced no significant change in ferromagnetism of $Zn_{0.98}Fe_{0.02}O$, just only at 10 K, caused a light increase of M.

4. Conclusion

In conclusion, the magnetic properties of Fe-doped ZnO bulk samples doped with additional Cu were comparatively investigated. All doping samples are single phase with a wurtzite structure characterized by XRD. The results of magnetic measurement suggest that Cu doping has enhanced the ferromagnetism of $Zn_{0.98}Fe_{0.02}O$ at 10 K to some extent. This is consistent with the bound magnetic polaron model relative to hole, in which bound holes mediate the ferromagnetic ordering.

Acknowledgements

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