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ARTICLE

Effect of Cu or Sn Doping on Magnetic Properties of $Zn_{0.98}$-$Fe_{0.02}O$ Bulk Samples

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Abstract: Polycrystalline bulk samples $Zn_{0.98}Fe_{0.02}O$ doped with Sn or Cu were prepared at 600 ^oC by a coprecipitation method. The XRD structure analysis shows that all samples are of single phase with the ZnO wurtzite structure. X-ray photoelectron spectroscopy indicates an oxidation state of 4+ for Sn, while a mixed state of 1+ and 2+ for Cu. It is found that $Zn0._{98}Fe_{0.02}O$ without doping shows weak ferromagnetism at room temperature. Cu doping induces an increase of magnetization at low temperature of 10 K, while Sn doping will seriously suppress the ferromagnetism in the whole temperature range from 300 K to 10 K. This result is consistent with bound magnetic polaron model relative to hole carriers.

Key words: diluted magnetic semiconductor; coprecipitation method; ferromagnetism

Diluted magnetic semiconductors (DMSs) have attracted great attention for their potential applications in the field of spin-dependent semiconductor electronics and optoelectronics, or so-called spintronics and optospintronics[1], such as spin light emitting diodes (spin-LEDs),[2-4] spin-polarized solar cells[5] and magneto-optical switches[6] due to the possibility of manipulating charge and spin degrees of freedom in a single material.

Based on the local spin density approximation (LSDA), Dietl et al. suggested that a high Curie temperature (T_C) ferromagnetism (FM) with a large magnetization could be obtained in ZnO if ZnO was doped with Mn along with certain concentration of holes.[7] Simulations of Sato et al. predicated that FM could also be achieved in V, Cr, Fe, Co, and Ni-doped ZnO.[8] Following the original room-temperature ferromagnetism report by Ueda et al. [9], many experiments have been carried out to confirm the theory prediction and the initial result. Some results dealing with magnetic properties of Fe-doped ZnO samples have also been published.[10-17] Room-temperature (RT) ferromagnetism in ZnO doped with Fe has been achieved; however, there remained some questions regarding the origin of the magnetic behavior in Fe-doped ZnO materials. It is deemed that Cu doping is essential to achieve RT FM in Fe-doped ZnO bulk samples.[10] However, Shim et al found that the ferromagnetism in Fe- and Cu-codoped ZnO stemmed from the secondary phase $ZnFe_2O_4$.[12] Recently, Lvill et al. have found that the electron density has a great effect on the magnetism of epitaxial ZnO film codoped with Mn and Sn,[18] and suggested that the magnetism of low-electron density material is consistent with the bound magnetic polaron model, in which bound acceptors mediate the ferromagnetic ordering. Though these experimental results are quite contradictory, most of them show that additional doping, especially carries doping, has a great effect on the magnetic properties of ZnO-based DMS. Thus, a comparative study on magnetism of the samples with different additional carriers doping becomes very essential to ascertain the controversy and understand the origin and mechanism of ferromagnetism in Fe-doped ZnO system.

Most recently, we have reported room-temperature ferromagnetism of $Zn_{0.98}Fe_{0.02}O$ bulk samples doped with Cu and found that the magnetization increased gradually with the increasing of Cu content x from 0.25% to 1%[19]. In the present work, we have introduced Cu or Sn doping in $Zn_{0.98}Fe_{0.02}O$ bulk samples by a coprecipitation method, and

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comparatively studied the effect of different doping on ferromagnetism of $Zn_{0.98}Fe_{0.02}O$ system.

1 Experiment

Bulk samples with nominal components $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ were prepared by a coprecipitation method. $Zn(NO_3)_2$ $6H_2O$, $Cu(NO_3)_2$ $3H_2O$, $SnCl_4$ $5H_2O$ and $Fe(NO_3)_3$ $9H_2O$ high-purity (99.99%) powders were weighed in appropriate proportion and mixed according to the desired stoichiometry, and the mixture was dissolved in distilled water to get homogeneous solution. The mixture was stirred strongly while a proper amount of Na(OH) aqueous solution was poured into it, controlling the pH=7 to deposit all cations of Zn^{2+}, Fe^{3+}, Cu^{2+}, and Sn^{4+} 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 h. The prepared powder was ground, palletized, and sintered at 600 °C for 12 h. To Avoid 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.

2 Results and Discussion

The crystal structure of the samples were characterized by X-ray diffraction using Cu Kα radiation. Data were collected using a step scan of 0.017° in 2θ. Fig.1 presents the typical powder X-ray diffraction patterns for ZnO, $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$. No clear difference in XRD patterns can be found between pure ZnO and doped samples, suggesting that the doping does not change the structure of ZnO. All of 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 is suggested that all samples are of single phase and iron, stannum and copper have been incorporated into the lattice structures, and a solid solution is formed instead of precipitates.

The magnetic properties of $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ were investigated by checking the temperature (T) and magnetic field (H) dependence of the magnetization (M). Fig.2 shows the M as a function of T (M-T) for all samples in an applied field of 0.1 T from 10 K 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 be about 0.74 μ_B/Fe site. The result hints probable low-T 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}. In contrast, $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ exhibits a different magnetization behavior compared with $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, M increases with the decrease of T in the whole T range from 300 to 10 K, and this behavior is very like to a paramagnetic behavior.

The inverse of M as a function of T (M^{-1}-T) for $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ was plotted to understand the magnetism, as shown in Fig.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 Spalek et al.[20], the Curie-Weiss temperature Θ_0 is evaluated to be 140 K for $Zn_{0.98}Fe_{0.02}O$, 90 K for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and –37 K for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$. The positive Θ_0 for $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ suggest that ferromagnetic interaction is dominant in the two samples, which confirms the low-T ferromagnetism in $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ and $Zn_{0.98}Fe_{0.02}O$. While for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$, the Θ_0 is less than zero, which implies the existence of strong antiferromagnetic interaction in this sample. Furthermore, from Fig.3, it can be seen that the M^{-1}-T curve of $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ shows a linear behavior in a quite wide T-range, following the Curie-Weiss law well

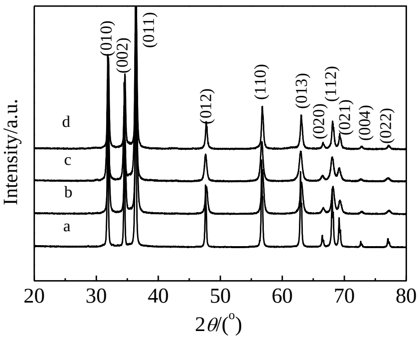

Fig.1 Powder XRD patterns for pure ZnO (a), $Zn_{0.98}Fe_{0.02}O$ (b), $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ (c), and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ (d)

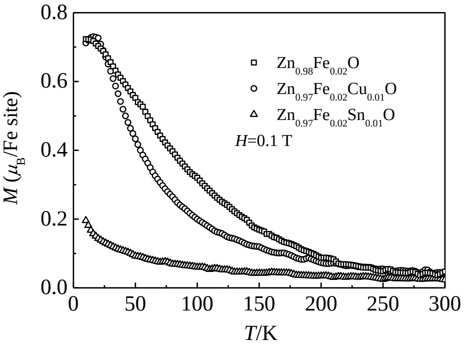

Fig.2 Temperature dependence of magnetization (M-T) for $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ bulk samples in an applied field of 0.1 T

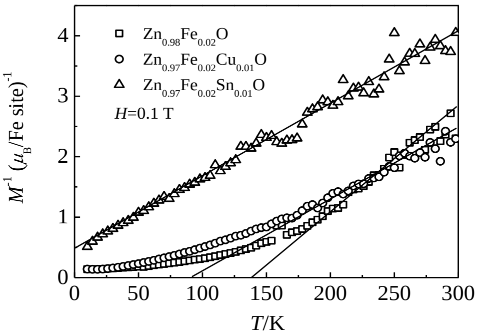

Fig.3 Curie-Weiss plot for $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ bulk samples. The solid line represents the linear extrapolation line fit to the data for 180~300 K

almost in the whole T-range from 300 to 10 K, which suggests that paramagnetic component is dominant in the system.

Fig.4 shows the M-H curves of $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ taken at 300K, and the inset gives a partial enlarged detail. All samples show a room-temperature ferromagnetic behavior with modest hysteresis loops, which suggests that their Curie temperatures (T_C) are higher than RT. This result is consistent to the theoretical predictions[7,8] and essential for practical application in spintronics. From the inset, the Coercive force (H_c) and residual magnetization (M_R) can be estimated to about 0.09 T and 0.005 μ_B/Fe site for $Zn_{0.98}Fe_{0.02}O$, 0.1 T and 0.006 μ_B/Fe site for $Zn_{0.97}Fe_{0.02}$-$Cu_{0.01}O$ and 0.1 T and 0.005 μ_B/Fe site for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$. Simultaneously, the saturation magnetization (M_S) can also be estimated to about 0.08 μ_B/Fe site for $Zn_{0.98}Fe_{0.02}O$, 0.085 μ_B/Fe site for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and 0.055 μ_B/Fe site for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ from Fig.4. From the above, we can see that Sn doping in $Zn_{0.98}Fe_{0.02}O$ causes a clear decrease in M_S, while Cu doping does not induce a remarkable change in magnetic properties at 300 K. This result is very different from the previous results[10], where, a small amount of Cu doping in $Zn_{0.95}Fe_{0.05}O$ bulk sample caused a drastic change in M, the M_S at room temperature of the sample doped with 1% Cu becomes 30 times larger than that of the sample without Cu.

The M-H curves of $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ also have been measured at 10 K, as shown in Fig.5, and 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 M_S of $Zn_{0.98}Fe_{0.02}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ are about 1.5 μ_B/Fe site and 1.85 μ_B/Fe site, respectively. It seems that Cu doping causes an enhancement of ferromagnetism at low temperature of 10 K. However, it is found that the M of $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ shows a behavior similar to linear with the increase of H, very like a paramagnetic behavior. It is clear that Sn doping greatly weakens the ferromagnetism at 10 K.

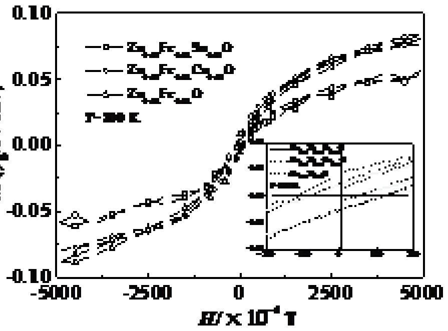

Fig.4 Magnetization as a function of magnetic field (M-H) for $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$, and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ bulk samples at 300 K

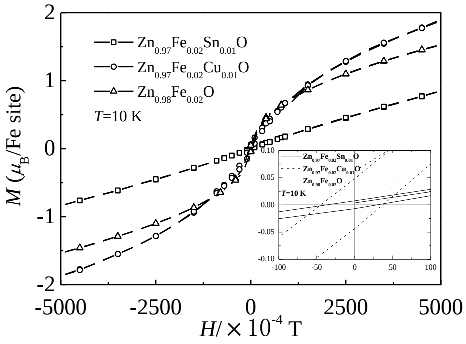

Fig.5 M-H curves of $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ bulk samples at 10 K

Although in some Ⅱ-Ⅵ compound semiconductors, Sn is an amphoteric dopant, substituting on either the Ⅱor Ⅵ site[21,22], many reports on the doping behavior of Sn in ZnO indicate that it introduces a donor state[23-25]. In the present work, the expectation is that Sn will substitute on the Zn site due to a close match in ionic radii between Zn^{2+} (0.074 nm) and Sn^{4+} (0.071 nm). To confirm chemical bonding state of Sn element, the XPS test has been performed. The XPS spectra have been charge-corrected to the adventitious C 1s peak at 284.6 eV and the core state of Sn 3d peaks for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ is presented in Fig.6a. The Sn $3d_{5/2}$ peak occurs at 484.31 eV, suggesting that Sn ions in the sample should be a valence of 4+. So it is clear that Sn doping would increase n-type carrier concentration as a donor in this system. The core state of Cu 2p peaks for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ is also presented in Fig.6b, and the peak of Cu $2p_{3/2}$ is located at 931.8 eV, which is corresponding to Cu^{1+}. Besides this, some satellite peaks are also observed in the figure, which is a typical characteristic of d^9 electron[26,27], indicating the existence of Cu^{2+}. From this result, it is believed that there is coexistence of Cu^{1+} and Cu^{2+} in the sample, the substitution on Zn^{2+} sites of Cu^{1+} would introduce some holes and increase p-type carrier concentration to some extent in the system.

The observation of RT FM in Zn-Fe-O system is consistent with the prediction by theory, and it has been proved that the RT FM in this system is intrinsic, in accordance with the previous work[17]. It should be noted that, Cu doping does not induce obvious change in ferromagnetism of Zn-Fe-O system at 300 K, but rather causes a small increase in *M* only at 10 K. It means that Cu doping has a little effect on ferromagnetism of Zn-Fe-O system, but is not very crucial as mentioned in Ref.[10]. However, Sn doping will induce a great decrease in *M* both at 300 K and 10 K. It is especially interesting that at 10 K the *M-H* curve of $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ shows a paramagnetic-like behavior as shown in Fig.5, ferromagnetism is almost complete disappearance, which suggests that Sn doping has a serious negative impact on ferromagnetism of Zn-Fe-O system.

Although the precise mechanism for ferromagnetic coupling between magnetic ions is still being discussed and debated in the literature for Fe-doped ZnO DMSs, we consider the key factor that affects magnetic properties of Fe-doped ZnO DMSs system and give a reasonable explanation on ferromagnetism observed in the present work according to the above results. As well known, the outermost electron configuration of Sn^{4+} and Cu^{1+} is $3d^{10}4s^24p^0$ and $3d^{10}4s^0$, respectively, all subshells are fully filled and hence Sn^{4+} and Cu^{1+} themselves do not contribute to ferromagnetism. However, if taking the valence states of Sn and Cu ions into account, each Sn^{4+} will offer two additional electrons as a double donor and each Cu^{1+} will offer one additional hole as an acceptor. So it is believed that the variation of magnetic properties observed in the present work should be ascribed to the introduction of additional carriers due to Sn and Cu doping.

So far, the most popular mechanisms relative to carrier proposed to explain ferromagnetic ordering in DMSs are RKKY (Ruderman-Kittel-Kasuya-Yosida) 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 10^6 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 there are not enough free carriers to mediate RKKY-type interaction and/or double-exchange interaction. It seems that the bound magnetic polaron (BMP)[28,29] whereby model is an alternative theory for the FM at RT observed in the present study. For an insulating DMS system with a quite low carrier density to exhibit ferromagnetism, the BMP model provides a mechanism.

Whereby the holes that are located spatially at or near the transition-metal ion are responsible for mediating ferromagnetism.[30] So an appropriate hole concentration is necessary in order to induce ferromagnetic ordering. In the present work, the addition of electrons to the system due to Sn doping will move the Fermi energy level up in the band gap, resulting in the decrease of hole density; as a consequence, the number of BMPs decreases and ferromagnetism weakens. When the number of BMPs decreases to a threshold value below which these BMPs can not overlap each other in whole sample with the decrease of temperature, long-range ferromagnetic ordering breakdowns, and the sample shows a paramagnetic-like behaviour, as shown in Fig.5. On the contrary, 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 Cu doping is quite limited because it is very difficult to realize heavy acceptor doping in ZnO matrix. Therefore, Cu doping induces no significant change in ferromagnetism of $Zn_{0.98}Fe_{0.02}O$, just only at 10 K, causes a light increase of *M*.

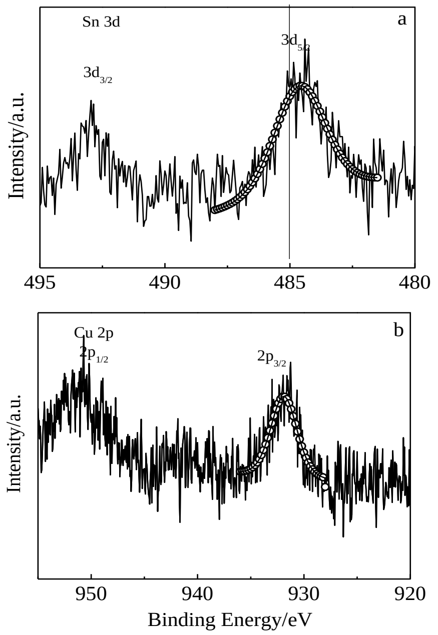

Fig.6 XPS spectra for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ and $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ bulk samples: (a) Sn $3d_{3/2}$ XPS spectrum for $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$; (b) Cu $2p_{3/2}$ XPS spectrum for $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$

3 Conclusions

1) All doping samples are single phase with a wurtzite

structure.

2) A mixed oxidation state is 1+ and 2+ for Cu and 4+ for Sn.

3) Cu doping enhances the ferromagnetism of $Zn_{0.98}Fe_{0.02}O$ at 10 K to some extent, while Sn doping severely suppresses the ferromagnetism in the whole temperature range from 300 K to 10 K. This is consistent with the bound magnetic polaron model relative to hole, in which bound holes mediate the ferromagnetic ordering.

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Sn 和 Cu 掺杂对 $Zn_{0.98}Fe_{0.02}O$ 块体样品磁性的影响

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摘 要：采用共沉淀法在600 ℃制备了Sn和Cu掺杂的$Zn_{0.98}Fe_{0.02}O$多晶块体样品。X射线衍射分析结果显示：所有的样品均为单相，具有ZnO纤锌矿结构。*M-T*曲线显示Sn掺杂在300 K到10 K严重削弱了样品的铁磁性，而Cu掺杂则在10 K增强了样品的铁磁性。这一结果与磁极化子模型一致。额外的Sn掺杂降低了系统中的空穴浓度，冻结了样品中的铁磁耦合作用。

关键词：稀磁半导体；沉淀法；铁磁性

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