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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 °C 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.

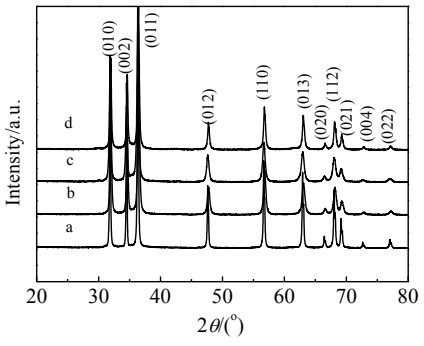

Fig.1 Powder XRD patterns for pure ZnO (a), $Zn_{0.98}Fe_{0.02}O$ (b), $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ (c), and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ (d)

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

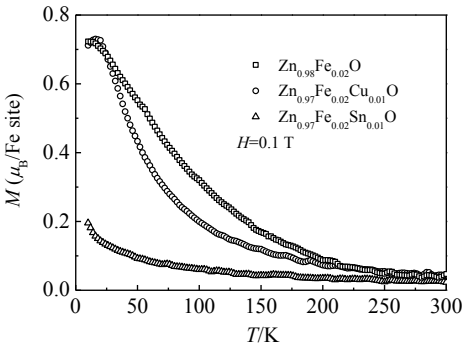

Fig.2 Temperature dependence of magnetization (M-T) for $Zn_{0.98}Fe_{0.02}O$, $Zn_{0.97}Fe_{0.02}Cu_{0.01}O$ and $Zn_{0.97}Fe_{0.02}Sn_{0.01}O$ bulk samples in an applied field of 0.1 T