Paramagnetism in Cu-doped ZnO*

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$Zn_{0.98}Cu_{0.02}O$ powders are prepared by the sol–gel method. A small number of CuO impurity phases are observed by the x-ray diffraction, indicating the solubility of Cu in ZnO is less than 2 at.%. The $Zn_{0.98}Cu_{0.02}O$ powders exhibit diamagnetism at 300 K and paramagnetism at 5 K. After subtracting the diamagnetic contribution of ZnO bulk and the paramagnetic contribution of defects, Cu ions exhibit weak paramagnetism. By codoping Cu with Co or Mn in ZnO, only paramagnetism is observed at room temperature.

Keywords: diluted magnetic semiconductors, ZnO, paramagnetism, defects
PACC: 7550P, 7280E, 7850G, 7155G

1. Introduction

By alloying nonmagnetic semiconductor and magnetic elements, diluted magnetic semiconductors (DMS) are considered to have potential important applications in future spintronics.[1] The 3*d* transition metal (TM) doped ZnO attracted much attention after the theoretical prediction of room temperature ferromagnetism in 3*d* TM doped ZnO.[2,3] Following these theoretical predictions, many experimental studies revealed the room temperature ferromagnetism in magnetic 3*d* TM doped ZnO.[4−10] However, due to the weak ferromagnetic signal, the intrinsic nature of the observed ferromagnetism was always doubted.[11] Ferromagnetic impurities accounting for the previously reported room temperature ferromagnetism were always reported in magnetic doped ZnO.[12]

Room temperature ferromagnetism is also observed in non-magnetic ion doped ZnO, for example, Cu-doped ZnO films.[13,14] The ferromagnetic contribution from the ferromagnetic impurities formed by doping ions can be excluded. However, conflicting results were also reported on the magnetic properties of Cu-doped ZnO. In contrast to the reported ferromagnetism,[13,14] we previously observed only paramagnetism in Cu-doped ZnO films prepared by pulsed laser deposition.[15] One of the main obstacles to understand the role of Cu in ZnO is the magnetic contribution from defects. For example, ferromagnetism has been reported in pure ZnO due to defects.[15,16] In the present paper, we reveal the weak paramagnetic contribution of doped Cu ions by subtracting the magnetic contribution from ZnO bulk and defects and the paramagnetism at room temperature in Cu doped and Mn or Co codoped ZnO.

2. Experimental details

$Zn_{0.98}Cu_{0.02}O$ powders were prepared by the sol–gel method. An amount of $Zn(NO_3)_2{\cdot}6H_2O$ (AR) and $Cu(NO_3)_2{\cdot}3H_2O$ (AR) were dissolved in de-ionized water. Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$, AR) and ethylene glycol ($HOCH_2CH_2OH$, AR) were added into the solution. The obtained solution was dried at 80 °C, then calcined at 300 °C for 24 h. After that, the obtained powders were sintered at 700 °C without touching any ferromagnetic tool to prevent any ferromagnetic contamination from being invaded. The structure was studied by x-ray diffraction (XRD) measurements with $\theta - 2\theta$ scans using a Cu Kα source. The magnetic properties were measured by a vibrating sample magnetometer (VSM) integrated in a physical property measurement system (PPMS-9, Quantum Design). The valence state of Cu in ZnO was studied by x-ray photoelectron spectroscopy (XPS) analysis. To study the codoping effect of Cu, $Zn_{0.96}Cu_{0.02}Mn_{0.02}O$ and $Zn_{0.96}Cu_{0.02}Co_{0.02}O$ powders were prepared in the same way as $Zn_{0.98}Cu_{0.02}O$

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powders.

3. Results and discussion

Figure 1 shows the XRD pattern of $Zn_{0.98}Cu_{0.02}O$ powders. The diffraction peaks can be indexed to the wurtzite ZnO. A small impurity peak marked by star can be observed, which is indexed to CuO (111). We also prepared $Zn_{0.98}Cu_{0.02}O$ powders at other temperatures (300 °C, 400 °C, 500 °C, 900 °C), and the CuO (111) impurity phase peak can be observed in all the samples. It is noted that for the $Zn_{0.96}Cu_{0.02}Mn_{0.02}O$ and $Zn_{0.96}Cu_{0.02}Co_{0.02}O$ powders, the CuO impurity peak can also be observed from the XRD patterns. Thus the solubility of Cu in ZnO is less than 2 at.%.

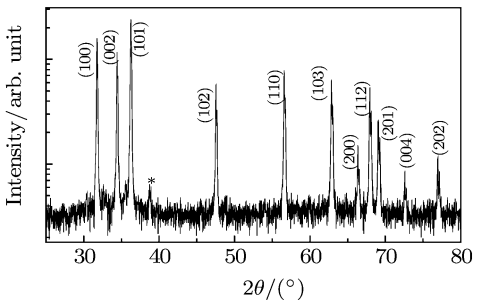


Fig. 1. The XRD pattern of $Zn_{0.98}Cu_{0.92}O$ powders sintered at 700 °C, where star (*) marks CuO (111).

Figure 2 shows the field dependent magnetizations of $Zn_{0.98}Cu_{0.02}O$ powders measured at 300 K and 5 K (dash curves), separately. In contrast to other reports of the ferromagnetism in Cu-doped ZnO,[13,14,17,18] the sample exhibits diamagnetism at 300 K and paramagnetism at 5 K. To understand the complicated magnetic properties, we must take into account all the possible magnetic contributions since the magnetization measurement is a bulk effect. Bulk ZnO is diamagnetic with a susceptibility of -2.65×10^{-7} emu/Oe·g.[19] (1 Oe=79.5775 A/m) In our previous study on the ZnO powders Zn vacancy defects exhibited paramagnetism.[20] To understand the magnetic contribution from doped Cu ions, the diamagnetic contribution from the ZnO bulk and the paramagnetic contribution from the defects should be subtracted. As the $Zn_{0.98}Cu_{0.02}O$ powders were prepared under the same conditions as ZnO, it is assumed that there exist the same types of defects and concentrations in $Zn_{0.98}Cu_{0.02}O$ powders. The Zn vacancy defect density is 0.45% ($Zn_{1-x}O$) with 1.55 μ_B per vacancy.[20] By subtracting the magnetic contributions from ZnO bulk and Zn vacancies, a weak paramagnetism is observed for the doped Cu ions at 300 K (Fig. 2(a), solid curve), which can be seen clearly in the enlarged M–H curve as shown in the inset of Fig. 2(a). A small ferromagnetic hysteresis loop is observed whose signal is about 10^{-5} emu and close to the sensitivity limit of VSM. Such a kind of signal can arise from extrinsic sources very easily.[21] Thus this weak ferromagnetism cannot be conclusively attributed to the $Zn_{0.98}Cu_{0.02}O$ nanopowders. At 5 K, after subtracting the paramagnetic contribution from Zn vacancies, the magnetization is one order smaller (Fig. 2(b) and the inset).

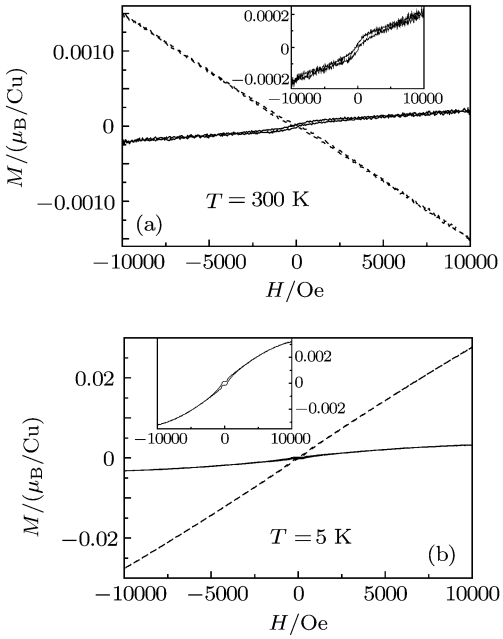


Fig. 2. The M–H curves of $Zn_{0.98}Cu_{0.02}O$ at (a) 300 K and (b) 5 K, before (dash curve and after (solid curve, and the enlarged view shown in the insets) subtracting the magnetic contributions from ZnO bulk and defects.

Figure 3 shows the zero-field cooling (ZFC) and field cooling (FC) magnetizations of $Zn_{0.98}Cu_{0.02}O$ powders. Before subtracting the magnetic contributions from ZnO bulk and Zn vacancies, both ZFC and FC magnetizations decrease rapidly with temperature increasing from 5 K, and change into negative values at around 120 K. After subtracting the magnetic contributions from ZnO bulk and Zn vacancies, both ZFC and FC magnetizations are positive from 5 K to 300 K, confirming the paramagnetic contribution of the doped Cu ions. However, as can be seen, the magnetization from doped Cu ions is very small, only about 0.003 μ_B/Cu at 5 K under 1 T.

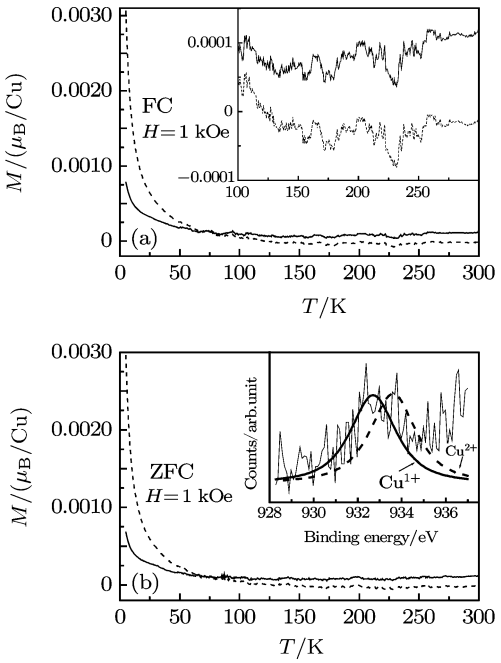


Fig. 3. (a) FC and (b) ZFC magnetizations of $Zn_{0.98}Cu_{0.02}O$ before (dash curve) and after (solid curve) substracting the magnetic contributions from ZnO bulk and defects. The insets show the enlarged FC magnetization (a) and the Cu $2p_{3/2}$ XPS spectra (b), which are fitted to thicker curve (Cu^{1+}) and dash curve (Cu^{2+}).

To understand the origin of quenched magnetization of Cu ions, the valence state of Cu ions was studied by XPS. The $2p_{3/2}$ peaks of Cu and Cu^{1+} appear both at about 932.7 eV, and $2p_{3/2}$ peak of Cu^{2+} is at 933.6 eV.[17] Owing to too low concentration of Cu in ZnO which is close to the detection limit of XPS, the XPS spectrum of Cu ions is very noisy. Thus we can only roughly fit the spectrum by using Gaussian fitting with fixing peak position at 933.6 eV (Cu^{2+}) or 932.7 eV (Cu^{1+}). The fitting of Cu^{1+} is much better than that of Cu^{2+}, indicating that the doped Cu ions are mainly in a valence state +1. The concentration of impurity CuO might be below the detecting limit of XPS, thus Cu^{2+} cannot be clearly resolved from the noisy XPS spectrum. Since the outer shell of Cu^{1+} is $3d^{10}$, there is no net spin of electrons. Thus no magnetic contribution is expected from Cu^{1+} ions.

Cu ions were always considered as an acceptor dopant.[22−24] Cao *et al.* reported on the room temperature ferromagnetism in ZnCoO doped with Cu^{1+}.[22] In contrast to their results, only paramagnetism has been observed in both $Zn_{0.96}Co_{0.02}Cu_{0.02}O$ and $Zn_{0.96}Mn_{0.02}Cu_{0.02}O$ at 300 K (Fig. 4), though Cu ions are in +1 valence state. Thus, consistent with Hong *et al.*'s conclusion,[24] Cu ions are not very crucial in determining the ferromagnetism, but the defects of ZnO due to the growth conditions might play a crucial role in determining the magnetic properties of ZnO. The understanding of the defect types and their magnetic contributions to ZnO is important for the realization of room temperature ferromagnetism in ZnO-base DMS.

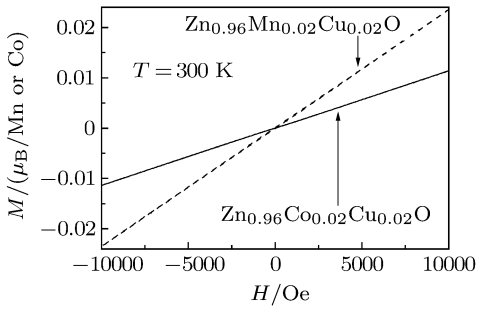


Fig. 4. The M–H curves of $Zn_{0.96}Mn_{0.02}O$ (dash curve) and $Zn_{0.96}Co_{0.02}Cu_{0.02}O$ (solid curve powders at 300 K on the assumption that the depoed Cu ions make on contribution to the magnetization.

4. Conclusions

$Zn_{0.98}Cu_{0.02}O$ powders are prepared by the sol–gel method. A small number of CuO impurity phases are observed from the x-ray diffraction, indicating the solubility of Cu in ZnO is less than 2 at.%. Diamagnetism at room temperature and paramagnetism at 5 K are observed. By subtracting the diamagnetic contribution of ZnO bulk and the paramagnetic contribution of defects, Cu ions exhibit weak paramagnetism. From the XPS measurement, the doped Cu ions are determined to be in a +1 valence state. By codoping Cu with Co or Mn in ZnO, only paramagnetism is observed at room temperature. The clear understanding of defect types and their magnetic roles is important for the realization of room temperature ferromagnetism in ZnO-based DMS.

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