J Mater Sci (2012) 47:530–533
DOI 10.1007/s10853-011-5830-z

Effects of dopants on magnetic properties of Cu-doped ZnO thin films

**Hailing Yang · Xiaoguang Xu · Shizhe Wu ·
Kai Wu · Chao Ai · Jun Miao · Yong Jiang**

Received: 23 March 2011 / Accepted: 28 July 2011 / Published online: 10 August 2011

Abstract We report the observation of room temperature ferromagnetism (FM) in Cu-doped ZnO (ZnO: Cu) thin films synthesized by sol–gel technique. While donor Al^{3+} cations are introduced into the ZnO: Cu films, the saturation magnetization decreases rapidly. Cu $2p$ core-level X-ray photoelectronic spectra demonstrate that the FM is strongly correlated with Cu^{2+} cations ($3d^9$ configuration). To further study the relationship between the FM and acceptors, Na^+ cations are also introduced into the ZnO: Cu films to increase the saturation magnetization. The enhanced FM in the (Cu, Na)-codoped ZnO is suggested to be due to the hybridization between delocalized holes and spin-split Cu $3d$ states.

Introduction

Diluted magnetic semiconductors (DMSs) have attracted extensive attention for their potential functionalities in spintronics, which allow the control of both the spin and the charge of carriers [1, 2]. Since Dietl et al. [3] have predicted that Mn-doped ZnO could exhibit room temperature ferromagnetism (RTFM), transition metal (TM)-doped ZnO systems have been widely studied. RTFM has been reported in many of these systems, such as Mn- and Co-doped ZnO [4–6]. However, there are a lot of controversies about whether the ferromagnetism (FM) arises from the substituting magnetic cations in ZnO lattices or just from secondary magnetic phases or precipitates. In order to avoid the controversies, the doping of non-magnetic elements in ZnO has been studied [7, 8]. Because neither metallic Cu nor Cu oxide is ferromagnetic and Cu^{2+} is a potential magnetic ion with a total spin of 1/2 according to Hund's rule [9], Cu is an ideal doping element with which one can obtain intrinsic FM [9–11]. However, the carrier type in Cu-doped ZnO (ZnO: Cu) is not clear yet. RTFM has been observed experimentally in both p-type and n-type ZnO: Cu films [9, 12–14]. Therefore, it is important to clarify the effect of carrier types on FM in ZnO: Cu system. In this article, we study the effects of dopants on magnetic properties of a ZnO: Cu system in which Al^{3+} and Na^+ cations serve as the donor and acceptor respectively, in order to check the roles of different carrier types in FM.

Experiments

Cu-doped ZnO, (Cu, Al)-codoped ZnO and (Cu, Na)-codoped ZnO were prepared by sol–gel process, combined with spin-coating technology. The precursor materials used to prepare undoped and doped ZnO films are zinc acetate 2-hydrate $Zn(CH_3COO)_2·2H_2O$, copper acetate 1-hydrate $Cu(CH_3COO)_2·H_2O$, aluminum nitrate 9-hydrate $Al(NO_3)_3·9H_2O$, and sodium acetate 3-hydrate $CH_3COONa·3H_2O$. These materials were dissolved in ethanol and mixed in an appropriate ratio to form precursor solutions. Then, lactic acid was added into the mixture to increase solubility. Finally, different clear solutions were dropped on quartz substrates and spin

---

H. Yang · X. Xu (✉) · S. Wu · K. Wu · C. Ai · J. Miao ·
Y. Jiang (✉)
State Key Laboratory for Advanced Metals and Materials,
School of Materials Science and Engineering, University
of Science and Technology Beijing, Beijing 100083, China
e-mail: xgxu@ustb.edu.cn

Y. Jiang
e-mail: yjiang@ustb.edu.cn

coated. The coating process was repeated 20 times. After each coating process, the precursor films were first dried at 150 °C, and then annealed at 600 °C for 1 h in air.

The crystal structures and phase purity of the annealed films were characterized by X-ray diffraction (XRD) using Cu K_α radiation. Magnetic hysteresis loops were measured by alternating gradient magnetometer (AGM). X-ray photoelectronic spectroscopy (XPS) was employed to study the chemical states of all the films.

Results and discussion

XRD patterns of the Cu-doped and (Cu, Al)-codoped ZnO films are presented in Fig. 1. All the films are in the single phase of ZnO and no secondary phase can be detected. The lattice structure of the films is hexagonal wurtzite with a (002) preferential orientation. In Fig. 1a, compared to the pure ZnO film, the (002) peaks of all the Cu-doped ZnO films show a slight right shift. Since the radii of Cu^+, Cu^{2+}, Zn^{2+} cations in tetrahedral coordination are 0.60, 0.57, and 0.60 Å, respectively [15], the substitution of Cu^{2+} for Zn^{2+} cations will reduce the lattice parameters of ZnO and induce a right shift of the XRD peaks. Therefore, it can be concluded that there must be a number of Cu^{2+} cations in the Cu-doped ZnO films. However, we cannot exclude the possibility of the existence of Cu^+ cations, since the radius of Cu^+ is the same as that of Zn^{2+}.

Figure 2a shows the magnetic hysteresis curves of the $Zn_{1-x}Cu_xO$ films. The saturation magnetization (M_S) reaches the maximum value of 0.01 μ_B/Cu when the Cu content is 1%, and then decreases dramatically with the increasing Cu. When x is larger than 3%, the films are non-magnetic or negligibly ferromagnetic, because enhanced antiferromagnetic (AFM) coupling between Cu–Cu cations overcomes ferromagnetic coupling. The results are in good agreement with pervious reports [16–18].

In order to get a better understanding of the FM in ZnO:Cu system, we have introduced Al cations into the 1 and 2% Cu-doped ZnO films. Figure 2b shows the magnetic

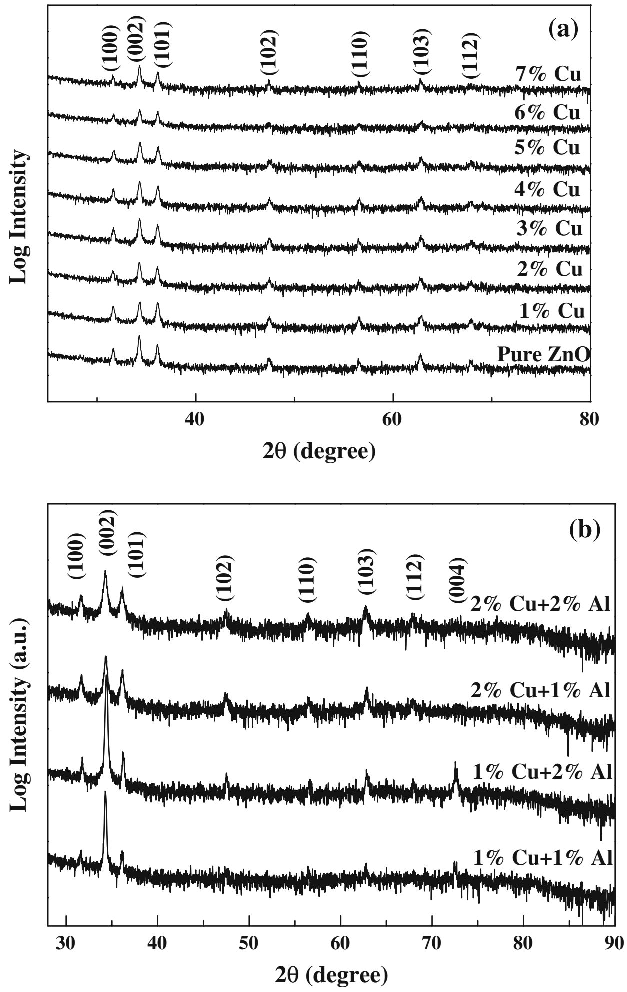

Fig. 1 XRD patterns of **a** $Zn_{1-x}Cu_xO$ ($x = 0.01$–0.07) and **b** $Zn_{1-x-y}Cu_xAl_yO$ ($x = 0.01, 0.02$; $y = 0.01, 0.02$) thin films

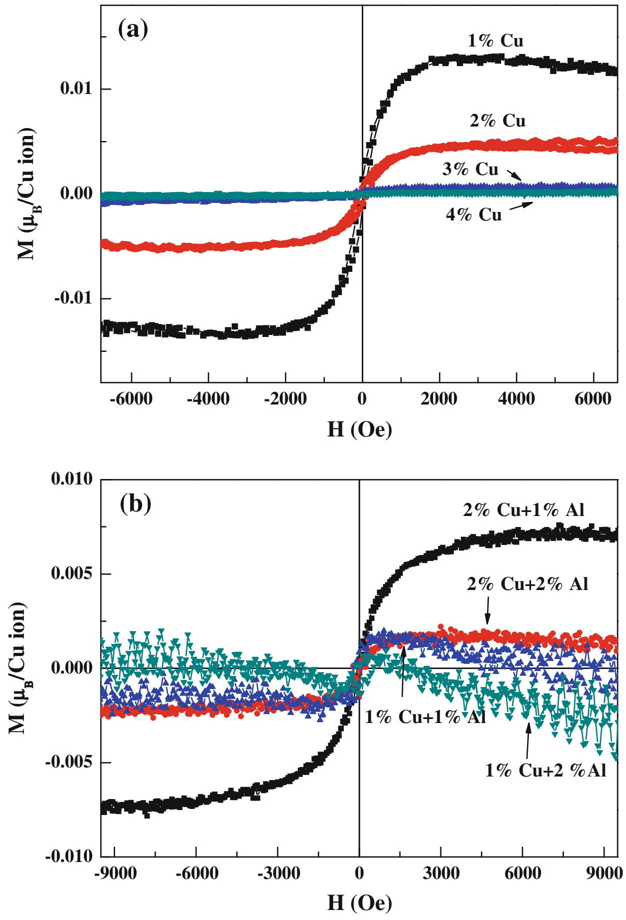

Fig. 2 (Color online) Magnetic hysteresis loops of **a** the $Zn_{1-x}Cu_xO$ ($x = 0.01$–0.04) and **b** $Zn_{1-x-y}Cu_xAl_yO$ ($x = 0.01, 0.02$; $y = 0.01, 0.02$) thin films

hysteresis loops of the (Cu, Al)-codoped ZnO films. From the M-H loops, the $Zn_{0.98}Cu_{0.02}Al_{0.01}O$ film exhibit ferromagnetic property, with a M_S value of 0.007 μ_B/Cu. To rule out the possibility that other factors may bring magnetism into the samples, pure ZnO films, Al-doped ZnO films and quartz substrates were also examined by AGM and no sign of spontaneous magnetization was detected.

XPS was employed to characterize the chemical valence change of Cu cations. Figure 3a shows the full range XPS survey scan for the $Zn_{0.99}Cu_{0.01}O$ and $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ films corrected with C 1s reference (284.8 eV). Figure 3b shows Cu 2*p* core-level XPS spectra. In the XPS spectra, there is no peak from magnetic cations, demonstrating the high purity of the films. The Cu $2p_{3/2}$ and $2p_{1/2}$ core levels of the $Zn_{0.99}Cu_{0.01}O$ film locate at 933.1 and 953.1 eV, respectively, indicating that the Cu cations present a mixed valence state between +2 and +1. For the $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ film, the Cu $2p_{3/2}$ and $2p_{1/2}$ core levels shift to lower energy levels of 932.4 and 952.0 eV, respectively, which are close to those of monovalent Cu. According to the XPS results, the valence state of Cu cations decreases after the Al doping. Therefore, the reason for the valence state change of Cu cations is the increased concentration of Al. As shown in the inset of Fig. 3a, the amplified peak at 74.7 eV derived from Al–O bond reveals that the Al cations are in trivalent state. In the $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ film, one Al^{3+} cation could affect one Cu cation by contributing additional free electrons to Cu 3*d* orbitals. The valence state change of Cu detected by XPS demonstrates the possible charge transfer from Al to Cu cations.

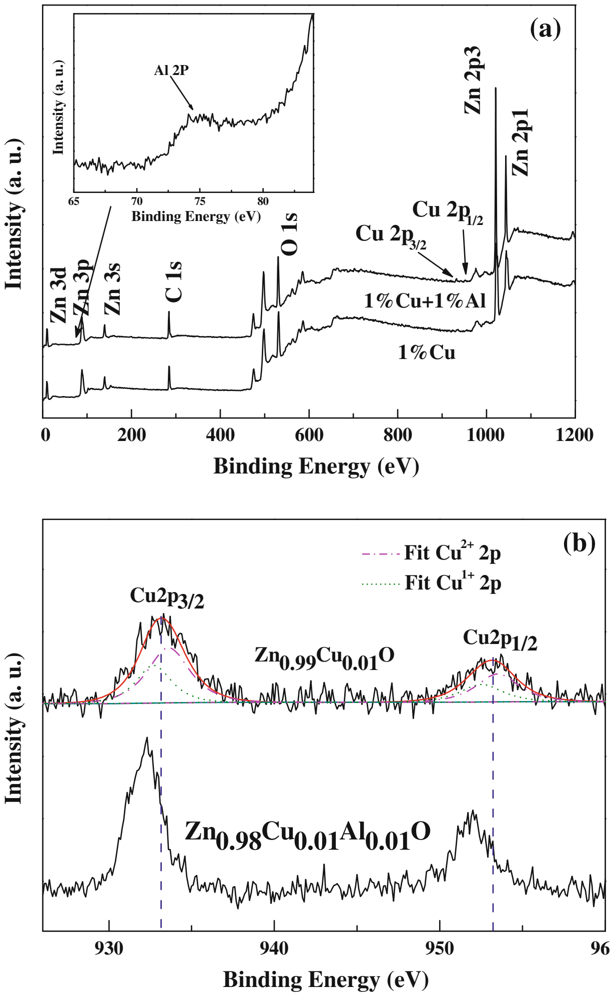

Fig. 3 (Color online) XPS spectra of the $Zn_{0.99}Cu_{0.01}O$ and $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ films. **a** XPS survey scan spectra and **b** narrow scan of binding energy for Cu 2*p*

Cu^+ and Cu^{2+} cations are expected to possess $3d^{10}$ and $3d^9$ configurations, respectively. In the $Zn_{0.99}Cu_{0.01}O$ film, the configuration of Cu^{2+} ($3d^9$) cations provides one unpaired electron and induces FM [13]. Chakraborti et al. [18] suggested that the RTFM in ZnO: Cu^{2+} is caused by the high-spin state of copper. When the Cu^{2+} cations are in tetrahedral coordination, the fivefold degenerate 3*d* orbitals split into t_{2g} and e_g bands, with four electrons in e_g band and five electrons in t_{2g} band, which results in an unpaired electron in t_{2g} band and a high-spin state of Cu^{2+} (1/2 moments per cation). However, in the case of the $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ film, one Al^{3+} cation presents three electrons to oxygen 2*p* orbitals, and Cu appears as nonmagnetic Cu^+ ionization state with a full occupied 3*d* shell. As a result, the $3d^9 \rightarrow 3d^{10}$ transition induced by Al dopant suppresses the ferromagnetic effect of Cu^{2+} cations. It can be seen clearly from Fig. 2b that the FM is significantly weakened in the $Zn_{0.98}Cu_{0.01}Al_{0.01}O$, $Zn_{0.97}Cu_{0.01}Al_{0.02}O$, and $Zn_{0.96}Cu_{0.02}Al_{0.02}O$ films which have Al concentration not less than Cu. In both of the 1 and 2% Cu-doped ZnO films, the ferromagnetic ordering decreases with the increased Al concentration. The 1% Cu-doped ZnO film even shows a diamagnetic property while the Al concentration reaches 2%.

In order to compare with the Al doping, we have introduced Na as acceptor dopants in the ZnO: Cu system. Figure 4 shows the M-H loops measured at room temperature for $Zn_{0.98}Cu_{0.01}Na_{0.01}O$, $Zn_{0.99}Cu_{0.01}O$, and $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ films. It is obvious from the three M-H loops that an appropriate concentration of Na can enhance FM in ZnO: Cu. It is in good agreement with previous theoretical calculations [11]. Na^+ as an acceptor tends to localize electrons around it, which may cause the transition from Cu^+ into Cu^{2+}. Moreover, it has been reported that the p-type behavior in Na-doped ZnO arises from Zn vacancies (V_{Zn}) along with substitutional Na (Na_{Zn}) sites [19]. Our previous work found that V_{Zn} are rather important to the observed FM in boron-doped ZnO [8]. Furthermore, Ogale reported the cation vacancies induced FM in other metal oxides such as CaO and TiO_2 [4]. For the (Na, Cu)-codoped ZnO films in the presence of V_{Zn}, we propose that the

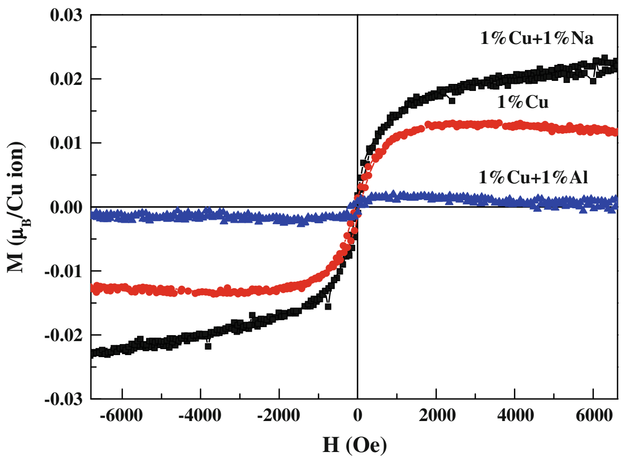

Fig. 4 (Color online) Magnetic hysteresis loops of the $Zn_{0.98}Cu_{0.01}Na_{0.01}O$, $Zn_{0.99}Cu_{0.01}O$, and $Zn_{0.98}Cu_{0.01}Al_{0.01}O$ thin films

enhancement of M_S is due to the formation of Cu_{Zn}–V_{Zn} pairs. In the tetrahedral crystal field, the energy band of Cu 3*d* states splits into t_{2g} and e_g bands [20] and O 2*p* induces delocalized holes. The hybridization between delocalized hole states and Cu 3*d* ones tends to yield bound magnetic polarons (BMPs) [21]. A spin-split acceptor impurity band located at the top of the valence band induces the FM in the $Zn_{0.98}Cu_{0.01}Na_{0.01}O$ film. Accordingly, it can be concluded that holes play an important role in the ferromagnetic exchange interaction of Cu^{2+} cations.

Conclusions

We have studied the doping effect on the FM in the ZnO: Cu system. The RTFM was observed in low concentration Cu-doped ZnO films (1 and 2%). The unpaired electron of Cu^{2+} is responsible for the RTFM. Compared with donor doping, acceptor doping tends to enhance the RTFM in the ZnO: Cu films. Based on the BMPs model, the RTFM in the $Zn_{0.98}Cu_{0.01}Na_{0.01}O$ film is suggested to be due to the hybridization between delocalized holes and spin-split Cu 3*d* states.

Acknowledgements This study was partially supported by the National Natural Science Foundation of China (grant nos. 50831002, 50971025, and 51071022), the National Basic Research Program of China (grant no. 2007CB936202), the Key Grant Project of Chinese Ministry of Education (no. 309006), Beijing Municipal Natural Science Foundation (grant no. 2102032), and the Fundamental Research Funds for the Central Universities.

References

1. Ohno H (1998) Science 281:951
2. Wolf SA, Chtchelkanova AY, Treger DM (2006) IBM J Res Dev 50:101
3. Dietl T, Ohno H, Matsukura F, Cibert J, Ferrand D (2000) Science 287:1019
4. Ogale SB (2010) Adv Mater 22:3125
5. Kundaliya DC, Ogale SB, Lofland SE, Dhar S, Metting CJ, Shinde SR, Ma Z, Varughese B, Ramanujachary KV, Riba LS, Venkatesan T (2004) Nat Mater 3:709
6. Lee HJ, Jeong SY, Cho CR, Park CH (2002) Appl Phys Lett 81:4020
7. Pan H, Yi JB, Shen L, Wu RQ, Yang JH, Lin JY, Feng YP, Ding J, Van LH, Yin JH (2007) Phys Rev Lett 99:127201
8. Xu XG, Yang HL, Wu Y, Zhang DL, Wu SZ, Miao J, Jiang Y, Qin XB, Cao XZ, Wang BY (2010) Appl Phys Lett 97:232502
9. Buchholz DB, Chang RPH, Song JH, Ketterson JB (2005) Appl Phys Lett 87:082504
10. Ye LH, Freeman AJ, Delley B (2006) Phys Rev B 73:033203
11. Huang LM, Rosa AL, Ahuja R (2006) Phys Rev B 74:075206
12. Herng TS, Lau SP, Yu SF, Chen JS, Teng KS (2007) J Magn Magn Mater 315:107
13. Tiwari A, Snure M, Kumar D, Abiade JT (2008) Appl Phys Lett 92:062509
14. Hou DL, Ye XJ, Meng HJ, Zhou HJ, Li XL, Zhen CM, Tang GD (2007) Appl Phys Lett 90:142502
15. Shannon RD (1976) Acta Cryst A 32:751
16. Sharma PK, Dutta RK, Pandey AC (2009) J Magn Magn Mater 321:4001
17. Herng TS, Lau SP, Yu SF, Yang HY, Ji XH, Chen JS, Yasui N, Inaba H (2006) J Appl Phys 99:086101
18. Chakraborti D, Narayan J, Prater JT (2007) Appl Phys Lett 90:062504
19. Lin SS, Lu JG, Ye ZZ, He HP, Gu XQ, Chen LX, Huang JY, Zhao BH (2008) Solid State Commun 148:25
20. Wang XF, Xu JB, Cheung WY, An J, Ke N (2007) Appl Phys Lett 90:212502
21. Coey JMD, Venkatesan M, Fitzgerald CB (2005) Nat Mater 4:173