Ferromagnetism studies of Cu-doped and (Cu, Al) co-doped ZnO thin films

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Abstract. We have studied the room temperature ferromagnetism (FM) in Cu-doped and (Cu, Al) co-doped ZnO thin films which were grown on quartz substrates by chemical method based on a sol-gel process combining with spin-coating technology. X-ray diffraction (XRD) patterns demonstrate that both the Cu-doped and (Cu, Al) co-doped ZnO films have the hexagonal wurtzite structure with c-axis orientation. Alternating Gradient Magnetometer (AGM) measurements confirm that all the doped ZnO samples are ferromagnetic at room temperature. When the doped Cu content is 1 %, the Cu-doped ZnO film has the strongest FM. The FM significantly decreases in the (Cu, Al) co-doped ZnO films. The doping of Al ions suppresses the FM induced by the doped Cu ions.

1. Introduction

Integrating magnetic properties into semiconductor materials is a pivotal mission for practical application. [1] Recently diluted magnetic semiconductors (DMSs) have attracted much attention because of their potential applications in spintronic devices, which exploit the spin in magnetic materials along with the charge of electrons in semiconductors. Dietl et al [2] predicted that wide band gap materials such as ZnO should be a promising candidate for room temperature DMS with hole doping. Sato and Katayama-Yoshida [3] reported theoretically that not only the hole doped ZnO but also the other transition metal (TM) doped ZnO show room temperature ferromagnetism (FM). After that, TM-doped ZnO such as Co-doped ZnO, Fe-doped ZnO and Mn-doped ZnO [4-6] with FM above room temperature have been reported. But the origin of FM in TM-doped ZnO is controversial because the FM is possibly caused by a secondary phase or external pollution. [7, 8] In order to avoid the controversies, non-magnetic elements doped ZnO have been studied. [9-11] Cu is also an ideal doping element because it is a potential magnetic ion with a total spin of 1/2 by Hund’s rule and the Cu-related secondary phases such as CuO and Cu₂O are non-ferromagnetic. [12-16] Therefore Cu-doped ZnO has the potential of exhibiting FM only due to the substitution of Cu on Zn sites. Meanwhile, many co-doped DMS materials have been studied. For instance, Zn doping can affect the concentration of Fe and optical properties in (Zn, Fe) co-doped CdS films. [17] Duan et al. [18] reported that (Co, Mn) co-doped Zn thin films synthesized by an autocombustion method show room
temperature FM. These results demonstrate that the co-doping may lead to remarkable change in the properties of DMS.

In this letter, we have studied the magnetic properties of Cu-doped and (Cu, Al) co-doped ZnO thin films which were prepared by sol-gel process combining with spin-coating technology. The study of the (Cu, Al) co-doped ZnO is helpful to figure out the origin of FM in Cu-doped ZnO samples.

2. Experimental details
In our experiment, we used zinc acetate 2-hydrate Zn(CH₃COO)₂·2H₂O, copper acetate 1-hydrate Cu(CH₃COO)₂·H₂O, aluminum nitrate 9-hydrate Al(NO₃)₃·9H₂O, lactic acid and ethanol to synthesize the coating solution. All these reagents are of analytical grade and were directly used without special treatment.

The coating solution was prepared by a simple sol-gel process. Zn(CH₃COO)₂·2H₂O, Cu(CH₃COO)₂·H₂O and/or Al(NO₃)₃·9H₂O were used as the raw materials and dissolved in the ethanol. The lactic acid was used as the stabilizer. The total metal ion concentration was 0.4 mol/L. Having been sufficient mixed, the coating solution formed crystal and symmetrical sol.

The coating solution was then dropped on quartz substructure and spin coated with 2000 r/m for 20s in air. This process made a precursor film on the substrate. Then the precursor film was dried at 150 °C in air for 10 min. This spin-coating process was repeated 20 times on each substrate. Then, the precursor films were annealed in air at 600 °C for 1 h with a calefactive speed of 1.8 °C /min.

We have synthesized Cu-doped ZnO thin films (Zn₁₋ₓCuₓO, 1% <Cu< 7%) and (Cu, Al) codoped ZnO thin films (Zn₀.⁹⁸Cu₀.⁰₁Al₀.⁰₁O, Zn₀.⁹⁷Cu₀.⁰₁Al₀.⁰₂O, Zn₀.⁹⁶Cu₀.⁰₂Al₀.⁰₂O and Zn₀.⁹⁷Cu₀.⁰₂Al₀.⁰₁O) by this method. In order to make a comparison, we also prepared pure ZnO and Al-doped ZnO thin films.

3. Results and discussion
XRD patterns of the Zn₁₋ₓCuₓO and pure ZnO films are shown in figure 1, the XRD patterns of the Zn₁₋ₓ₋ₓAlₓO films are shown in figure 2. XRD patterns show that the wide peaks at the positions which are high agree with the PDF pattern of ZnO (JCPDS 36-1451). The XRD patterns demonstrate that nearly all the Cu-doped, Al-doped and (Cu, Al) co-doped ZnO films exhibit hexagonal wurtzite structure while no other phase exists. All of these XRD patterns show that the peaks at 34.4° are much stronger than others, indicating that all these films have a strong c-axis orientation.

Compare with the pure ZnO samples, all the (002) peaks in the doped ZnO are slightly right shifted which illustrates the incorporation of Cu or Al ions into ZnO lattices. As we know, the radius of Cu⁺, Cu²⁺, Zn²⁺ ions in tetrahedral coordination are 0.60, 0.57, and 0.60 Å, respectively. [19] For the Cu-doped ZnO, because the Cu⁺ and Zn²⁺ ions have the same radius, the doping of Cu⁺ should not cause much change of the lattice parameters. In other words, the doping of Cu⁺ ions will not affect the XRD pattern of ZnO. On the other hand, the substitution of Cu²⁺ for Zn²⁺ ions should reduce the lattice parameter of ZnO and make the ZnO peaks right shift. According to the XRD results, the (002) peak in the doped ZnO has a slight right shift which indicates the existence of Cu²⁺ ions. However, since the doping of Cu⁺ ions will not affect the XRD pattern of ZnO, we can not demonstrate whether there exist Cu⁺ ions.

Figure 3 shows the room temperature M-H loops for the pure and Cu-doped ZnO films. The pure ZnO film is superparamagnetic while all the Cu-doped ZnO films are ferromagnetic. The saturation magnetization (Mₛ) of the Cu-doped ZnO films decreases with the increasing content of Cu ions. The results are similar to the ones reported by several other groups. [12-15] The FM is induced by the p-d hybridization between 3d of Cu²⁺ and ZnO valence bands (O-p bands), which forms a magnetic moment. On the other hand, the increased antiferromagnetic interaction in Cu-Cu ions reduces the FM in the higher Cu doping films.
Figure 1. X-ray diffraction patterns of Cu-doped ZnO and pure ZnO films.

Figure 2. X-ray diffraction patterns of (Cu, Al) codoped ZnO films.

Figure 3. Room-temperature M-H loops of Cu-doped ZnO and pure ZnO films.
To further study the origin of FM, we measured the hysteresis loops for the (Cu, Al) co-doped ZnO films, as shown in figure 4. All the (Cu, Al) co-doped ZnO samples are ferromagnetic. Figure 5 gives the variation of $M_S$ with the doped Cu/Al ratio. Comparing with the Cu-doped ZnO, the FM is significantly weakened in $\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Al}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Al}_{0.02}\text{O}$ and $\text{Zn}_{0.96}\text{Cu}_{0.02}\text{Al}_{0.02}\text{O}$ films which have Al ions not less than Cu ions. The $M_S$ of $\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Al}_{0.02}\text{O}$ film is slightly lower than that of $\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Al}_{0.01}\text{O}$ film. Our result demonstrates that in the ratio of nearly 1:1 the doping of Al ions significantly suppresses the FM originating from the doping of Cu ions. Moreover, the $M_S$ of $\text{Zn}_{0.97}\text{Cu}_{0.02}\text{Al}_{0.01}\text{O}$ film is nearly the same as that of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$. Although several groups [20, 21] observed room temperature FM in Al-doped ZnO, we have not observed FM in our Al-doped ZnO. We therefore infer that Al doping decreases FM by suppressing the effect of Cu ions. One $\text{Al}^{3+}$ ion can only affect one Cu ion because one $\text{Al}^{3+}$ offers one free electron in ZnO lattices. According to the carrier-mediated mechanism theory, the free electrons of $\text{Al}^{3+}$ in ZnO lattices should suppress the p-d hybridization between 3d of $\text{Cu}^{2+}$ and ZnO valence bands (which is the origin of FM) because these free electrons may capture the 3d electrons of $\text{Cu}^{2+}$.

![Figure 4](image1.png)

**Figure 4.** Room-temperature M-H loops of (Cu, Al) codoped ZnO films.

![Figure 5](image2.png)

**Figure 5.** Room-temperature $M_S$ of (Cu, Al) codoped ZnO films.
4. Conclusions
The Cu-doped and (Cu, Al) co-doped ZnO thin films which were grown on quartz substrates have been studied. We have observed room temperature FM in the Zn_{1-x}Cu_{x}O and Zn_{1-x-y}Cu_{x}Al_{y}O films. The experimental data show that the doped Cu ions are the primary reason for the FM. The FM has been significantly weakened in the (Cu, Al) co-doped ZnO films. The doped Al ions suppress the FM induced by the doped Cu ions, which can be understood by the carrier-mediated mechanism theory.

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References
[1] Gary A Prinz 1998 Science 282 1660
[2] T dietl, H Ohino, F Matsukura, J Cibert and D Ferrand 2000 Science 287 1019
[3] K Sato and H Katayama-Yoshida 2000 Jpn. J. Appl. Phys. Part 2 39 L555
[4] K Ueda, H Tabata and T Kawai 2001 Appl. Phys. Lett. 79 988
[5] S D Yoon, Y Chen, D Heiman, A Yang, N Sun, C Vittoria, and V G. Harris 2006 J. Appl. Phys. 99 08M109
[6] P Sharma, A Gupita, K V Rao, F J Owens, R Sharma, R Ahuja, J M Osorio Guillen, B Johansson and A A Gehring 2003 Nat. Mater. 2 673
[7] C Sudakar, J S Thakur, G Lawes, R Naik, and V M Naik 2007 Phys. Rev. B. 75 054423
[8] Y Belghazi, G Schmerber, S Colis, J L Rehspringer, and A Dinia 2006 Appl. Phys. Lett. 89 122504
[9] H Pan, J B Yi, L Shen, R Q Wu, J H Yang, J Y Lin, Y P Feng, J Ding, L H Van, and J H Yin 2007 Phys. Rev. Lett. 99 127201
[10] Santa Chawla, K Jayanthi, and R K Kotnala 2009 Phys. Rev. B. 79 125204
[11] X G Xu, H L Yang, Y Wu, D L Zhang, S Z Wu, J Miao and Y Jiang arXiv 1003.4423.
[12] T S Herng, S P Lau, S F Yu, H Y Yang, X H Ji, J S Chen, N Yasui and H Inaba 2006 J. Appl. Phys. 99 086101
[13] D Chakraborti, J Narayan and J T Prater 2007 Appl. Phys. Lett. 90 062504
[14] Xiao Li Li, Xiao Hong Xu, Zhi Yong Quan, Jun Feng Guo. Hai Shun Wu, and G A Gehring 2009 J. Appl. Phys. 105 103914
[15] Prashant K Sharma, Ranu K Dutta and Avinash C Pandey 2009 J. Magn. Magn. Mater. 321 4001-4005
[16] M Wei, N Braddon, D Zhi, P A Midgley, S K Chen, M G Blamire, and J L MacManus Driscoll 2005 Appl. Phys. Lett. 86 072514
[17] K Liu, J Y Zhang, X Wu, B Li, Y Lu, X Fan, and D Shen 2007 Physica B (Amsterdam) 389 248
[18] L B Duan, G H Rao, Y C Wang, J Yu and T Wang 2008 J. Appl. Phys. 104 013909
[19] R D Shannon 1976 Acta Crystallogr., Sect. A: Cryst. Phys., Diffrr., Theor. Gen. Crystallogr. 32 751
[20] S J Chen, K Suzuki, and J S Garitaonandia 2009 Appl. Phys. Lett. 95 172507
[21] Y W Ma, J Ding, J B Yi, H T Zhang and C M Ng 2009 J. Appl. Phys. 105 07C503