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# A fabrication and magnetic properties study on Al doped $Zn_{0.99}Co_{0.01}O$ dilution ferromagnetic semiconductors

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This paper reports that a chemical method is employed to synthesize Co and Al co-doped ZnO, namely, $Zn_{0.99-x}Co_{0.01}Al_xO$ dilution semiconductors with the nominal composition of $x = 0$, 0.005 and 0.02. Structural, magnetic and optical properties of the produced samples are studied. The results indicate that samples sintered in air under the temperatures of 500 °C show a single wurtzite ZnO structure and the ferromagnetism decreases with the increase of Al. Photoluminescence spectra of different Al-doped samples indicate that increasing Al concentration in $Zn_{0.99-x}Co_{0.01}Al_xO$ results in a decrease of $Zn_i$, which resembles the trend of the ferromagnetic property of the corresponding samples. Therefore, it is deduced that the ferromagnetism observed in the studied samples originates from the interstitial defect of zinc ($Zn_i$ ) in the lattice of Co-doped ZnO.

**Keywords:** ZnO, DMSs, doping
**PACC:** 7550P, 7280E

## 1. Introduction

Diluted magnetic semiconductors (DMSs) have initiated scientific interest for the last few decades because of their unique spintronic properties with possible technological applications.[1] The ZnO:Co DMSs is particularly interesting due to both theoretical[2] and experimental reports that it could have room temperature (RT) ferromagnetism (FM), which is crucial for application.[3−7]

Several studies on ZnO:Co DMSs suggested that defects, such as zinic interstitial $Zn_i$ and oxygen vacancy $V_O$ could promote FM. Therefore, some work has been contributed with additional dopants to enhance or induce ferromagnetism in ZnO:Co systems. In the case of (Co, Al)- codoped ZnO, for example, Liao *et al*[8] used the water-assistance reactive vapor deposition method and Liu *et al*[9] used a simple sol–gel technique, although completely different methods have been used, all findings indicated that introducing the additional Al dopant played an important role in enhancing the FM of Co-doped ZnO owing to the increase of the free electron carrier density, while Alaria *et al*[10] using the co-precipitation method, confirmed that Al ions increase the free carriers concentration, however, those n-type free carriers are not sufficient to create ferromagnetic interactions. Therefore, the reported findings are controversial and more effort should be made to determine the origin of the RT FM in Co and Al co-doped ZnO.

In this paper, $Zn_{0.99-x}Co_{0.01}Al_xO$ (nominal $x =$ 0, 0.005, and 0.02) were synthesized via the chemical reaction method and finally three kinds of powders, such as $Zn_{0.99}Co_{0.01}O$, $Zn_{0.985}Co_{0.01}Al_{0.005}O$ and $Zn_{0.97}Co_{0.01}Al_{0.02}O$, were obtained. We found that adding the additional Al dopant enhanced the defects of the ZnO crystal, and the FM of the Al-doped samples was decreased in comparison with $Zn_{0.99}Co_{0.01}O$ produced under the same condition.

## 2. Experiments

Samples of $Zn_{0.99-x}Al_xCo_{0.01}O$ ($x = 0$, 0.005, and 0.02) labeled as S1, S2, and S3, were synthesized as follows: Zinc acetate ($Zn(CH_3CO)_2 \cdot 2H_2O$), cobalt acetate ($Co(CH_3CO)_2 \cdot 4H_2O$) and Aluminum chloride ($AlCl_3 \cdot 6H_2O$) with required molar ratios were dissolved in distilled water, and citric acid ($C_6H_8O_7 \cdot H_2O$) was added in 5:1 molar ratio. Then the solution was heated to 75 °C and continuously stirred for about 4 hours, the PH of solution was ad-

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justed to 7–8 by titrating ammonia, at last a thick gel formed. The gel was dried at 150 °C for more than 10 hours and xerogel was obtained. This xerogel was heated in air condition at 500 °C for one hour to remove the carbon, and then the required powders were obtained.

The x-ray diffraction (XRD) measurement was taken with Cu K$\alpha$ incident radiation. The high-resolution transmission electron microscope (HRTEM, JEM-2000) was used to explore the detailed microstructure. The magnetic properties were examined by using a vibrating sample magnetometer (Lake Shore-7407) at RT. Absorbance spectra were obtained (UV–Vis) using a Hitachi U-4100 ultraviolet–visible spectrometer. The photoluminescence (PL) spectra were measured on a Hitachi F-4500 at RT with an excitation wavelength of 325 nm.

## 3. Results and discussion

Figure 1 shows the XRD pattern of a sample of $Zn_{0.97}Co_{0.01}$ $Al_{0.02}O$, confirming that it is of wurtzite structure of ZnO. The inset of Fig.1 shows the fine scanning of XRD patterns of samples with different amounts of Al dopants, demonstrating quite similar patterns for each sample. No traces of impurity peaks other than ZnO were observed.

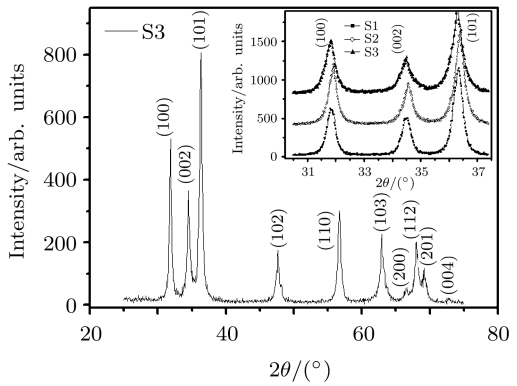



**Fig.1.** The XRD spectra of $Zn_{0.99-x}Co_{0.01}Al_xO$ ($x = 0$, 0.005, and 0.02) samples.

Table 1 shows the hexagonal cell parameters of Co- and (Co, Al)- doped samples. Compared with undoped ZnO, both $a/b$ and $c$ of $Zn_{0.985}Co_{0.01}Al_{0.005}O$ decreased in S1, S2 and S3. The decrease of cell parameters in Co- and (Co, Al)-doped ZnO is owed to the fact that the radii of $Co^{2+}$ and $Al^{3+}$ are smaller than those of $Zn^{2+}$. However, the cell parameters of S3 are larger than those of S1 and S2, which could result in some Al dopants located at the interstitial sizes, leading to its cell volume extension, this is consistent with previous reports.[11,12]

To eliminate the existence of a second phase, an HRTEM image and selected area electron diffraction of S2 was performed and shown in Fig.2. From Fig.2, it can be seen that the sample is polycrystalline, and the selected area electron diffraction (SAED) pattern can be indexed as ZnO crystal planar without any trace of the second phase. The HRTEM indicates that the space between the fringes is 0.261 nm, which agrees with that of the ZnO $c$-axis lattice space and the corresponding fast Fourier transform (FFT) pattern shows a distorted lattice, confirming that the lattice is defective. No trace of any second phase was found, consistent with the results in Fig.1.

**Table 1.** Lattice parameters $a/b$ and $c$ deduced from the x-ray patterns of the samples.

| series | ZnO | S1 | S2 | S3 |
|---|---|---|---|---|
| $a/b$(Å) | 3.250 | 3.2442 | 3.2377 | 3.2447 |
| $c$(Å) | 5.207 | 5.1963 | 5.1886 | 5.1990 |

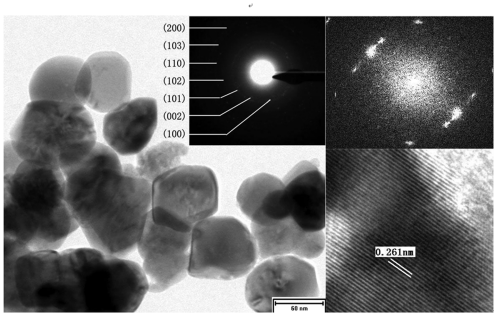



**Fig.2.** TEM image, SAED pattern, HRTEM image and corresponding FFT pattern of $Zn_{0.985}Co_{0.01}Al_{0.005}O$, demonstrating that no second phase was detected in the sample.

Figure 3(a) presents $M$–$H$ loops of S1, S2 and S3 powders measured at RT, indicating that there are ferromagnetic and paramagnetic contributions to all $M$–$H$ loops. Prominent FM was observed in S1, however, reduced gradually in S2 and S3, confirming that increase of Al doping in $Zn_{0.99-x}Co_{0.01}Al_xO$ induces a reduction of the FM. The coercivities ($H_c$) of S1 and S2 are 87.9 and 59.8 Oe (1 Oe = 79.5775 A/m) at RT, respectively. While S3 exhibits nearly zero coercivity ($H_c$) and no remnant magnetization ($M_r$), which is the typical behaviour of paramagnetism. Figure 3(b) presents the $M$–$H$ loops of S1, S2 and S3 after carefully eliminating the contribution of paramagnetism. The inset of Fig.1 shows Al concentration dependent magnetization, from which one can see that the $M_s$ of S1, S2 and S3 are of 0.59, 0.25 and 0.05 $\mu_B$/Co, correspondingly, indicating that the FM in the samples decreased tempestuously with the increase of Al doping concentration.

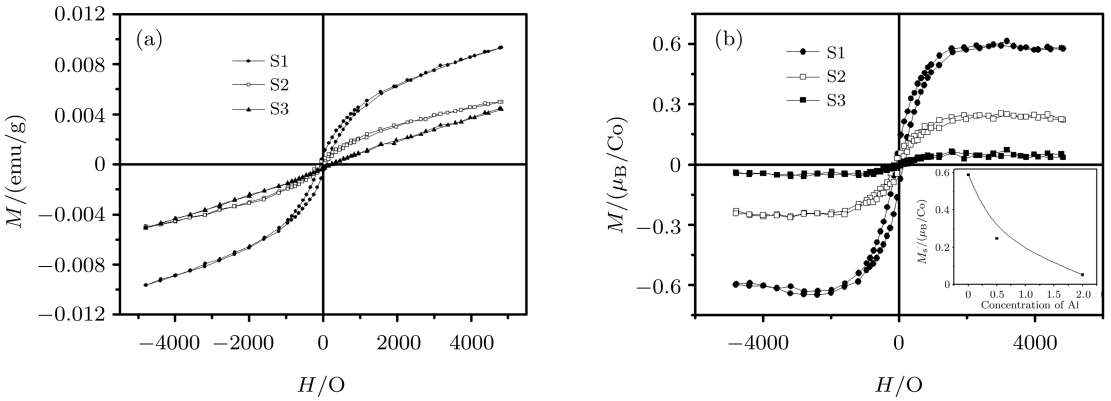



**Fig.3.** (a) $M$–$H$ loops of $Zn_{0.99-x}Co_{0.01}Al_xO$ ($x = 0$, 0.005 and 0.02) samples measured at RT; Fig.3(b) $M$–$H$ loops after carefully eliminating the contribution of paramagnetism in the samples inset is the Al concentration dependent $M_s$.

The FM properties in transition metal Co- or (Co, Al)-doped ZnO have been studied extensively. Intrinsic defects in ZnO crystal are reported crucially on the FM coupling in transition metal doped ZnO. However, the reported evidence is inconsistent.[8−10] In order to explore the mechanism of the origin of the FM in the studied samples, their optical properties were carefully characterized to reveal the defect effect on their FM.

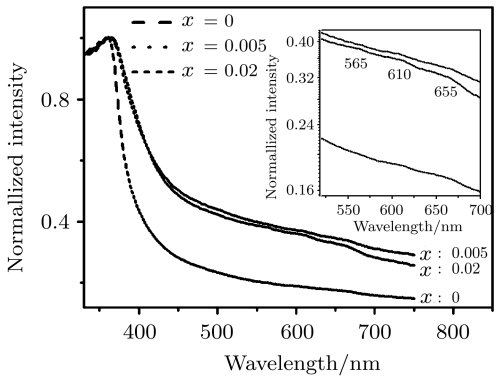



**Fig.4.** Optical absorption spectra of $Zn_{0.99-x}Co_{0.01}Al_xO$ ($x = 0$, 0.005, and 0.02) samples.

Figure 4 shows the RT UV–Vis optical absorption spectra for the samples of S1, S2 and S3. From Fig.3, one can see that the absorption band for S1, S2 and S3 are of 361, 364 and 368 nm, respectively, and is much blue-shifted in comparison with these in a previous report in ZnO.[13] The blue shift of the absorption edge of S1 could result from the small size effect due to the doping of Co in ZnO. With the addition of Al, the red-shift of the absorption edge in S2 and S3 result from the fact that some dopants related impurity band formed in the gap of ZnO.[14−17] The inset of Fig.3 shows three weak absorption peaks at 656, 612 and 564 nm, and these peaks can be assigned as $^4A_2(F) \rightarrow 2E(G)$, $^4A_2(F) \rightarrow {}^4T_1(P)$ and $^4A_2(F) \rightarrow {}^2A_1(G)$ of $Co^{2+}$,[18,19] demonstrating that Co ions are of divalence in the studied samples. Compounding the results shown in Figs.1 and 2, we clearly see that Co is incorporated into the lattice of the ZnO crystal.

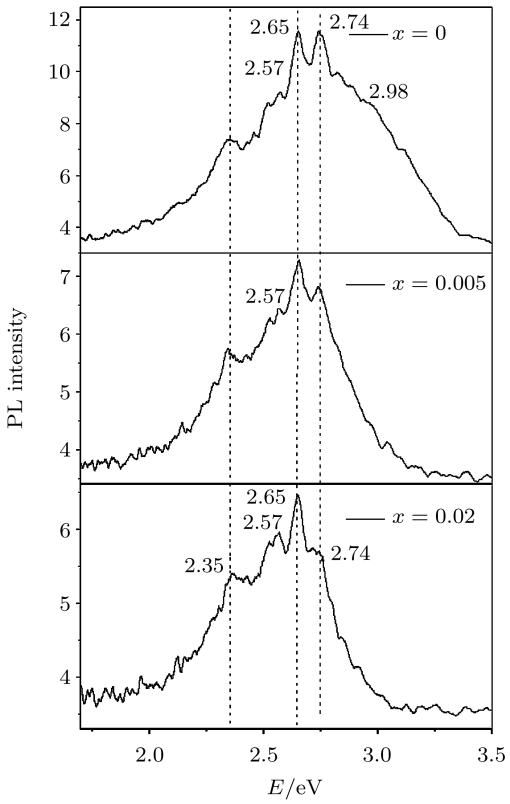



**Fig.5.** PL spectra of $Zn_{0.99-x}Co_{0.01}Al_xO$ ($x = 0$, 0.005, and 0.02) samples.

Figure 5 is RT measured PL spectra of S1, S2 and S3. From Fig.5, one can see that all samples ex-

hibit an intensive PL spectrum in the range from 400 to 600 nm, doping with Al in S2 and S3 suppresses the PL intensity significantly. The ZnO near band edge excitons emission was observed at 2.98 eV in S1 with a relative low intensity, indicating a poor crystal quality of the studied samples.[14,16] Two strong PL peaks at 2.74, 2.65 eV and relatively weak peaks at 2.57 and 2.36 eV were observed in all samples, which can be assigned as ZnO interstitial Zn ($Zn_i$), negative charged zinc vacancy ($V_{zn}^-$), oxygen vacancy and Zn vacancy, respectively.[20] By a careful comparison with the intensity of the PL emission at 2.74, 2.65, 2.57 and 2.35 eV in S1, S2 and S3, one can see that the intensity of the emission at 2.75 eV prominently decreased from S1 to S2, and almost disappeared in S3, while the intensity of 2.57 and 2.35 eV peaks slightly increased from S1 to S3. This result can be understood by seeing that with the addition of the additional Al dopant the $Zn_i$ interstitials are reduced and both O and Zn vacancies are increased.

Based on the above magnetic and optical property measurement results of the studied samples, it is reasonable to deduce that the lower $Zn_i$ concentration sample corresponds to its lower FM, it is consistent with the previous reports;[20,21] consequently, FM in Co doped ZnO should relate mainly to $Zn_i$, and $Zn_i$ plays a crucial role on its FM coupling.

Recently reports demonstrated that the increase of $Zn_i$ defects in Co doped ZnO could enhance its FM coupling.[21,22] Kittilstved *et al* suggested that shallow donors such as $Zn_i$ are energetically aligned with the transition metallic ions ($TM^{2+}$) inducing effective dopant defect hybridization, which could result in FM in TM-doped ZnO.[23] Thus, based on our results, the FM in Co-doped ZnO can be understood by bound magnetic polarons models.[22,23] In our studied samples, Co d-orbital electron hybridizes with Zn interstitial s-orbital electron and results in spin-polarized bands. However, the reduction of Zn interstitial in our studied sample could fail such that s–d orbital hybridization and ferromagnetic coupling between neighbors Co breaks, and finally, the FM in (Co, Al)-doped ZnO reduces.

## 4. Summary

Homogeneous single-phase $Zn_{0.99-x}Al_xCo_{0.01}O$ ($x$ = 0, 0.005, and 0.02) powders were synthesized by a chemical method. The study of magnetic and optical properties suggested that $Zn_i$ interstitial defects in Co-doped ZnO possibly respond to the origin of its room temperature FM.

## References


[1] Ohno H 1998 *Science* **281** 951

[2] Sato K and Katayama-Yoshida H 2000 *Jpn. J. Appl. Phys.* Part 2 **39** L555

[3] Park J H, Kim M G, Jang H M, Ryu S and Kim M 2004 *Appl. Phys. Lett.* **84** 1338

[4] Belghazi Y, Schmerbe G, Colis S, Rehspringer J L, Dinia A and Berrada A 2006 *Appl. Phys. Lett.* **89** 122504

[5] Bouloudenine M, Viart N, Colis S, Kortus J and Dinia A 2005 *Appl. Phys. Lett.* **87** 52501

[6] Duan L B, Rao G H, Yu J and Wang Y C 2008 *Solid State Commun.* **145** 525

[7] Yu Z, Li X, Long X, Cheng X W, Wang J Y, Liu Y, Cao M S and Wang F C 2008 *Acta Phys. Sin.* **57** 4539 (in Chinese)

[8] Liao L, Lu H B, Zhang L, Shuai M, Liu J C, Fu D J and Ren F 2007 *J. Appl. Phys.* **102** 114307

[9] Liu X C, Shi E W, Chen Z Z, Zhang H W, Xiao B and Song L X 2006 *Appl. Phys. Lett.* **88** 252503

[10] Alaria J, Bieber H, Colis S, Schmerber G and Dinia A 2006 *Appl. Phys. Lett.* **88** 112503

[11] Duan L B, Chu W G, Yu J, Wang Y C, Zhang L N, Liu G Y, Liang J K and Rao G H 2008 *J. Mag. Mag. Mater.* **320** 1573

[12] Risbud A S, Spaldin N A, Chen Z Q, Stemmer S and Seshadri R 2003 *Phys. Rev.* B **68** 205202

[13] DjurišićA B and Leung Y H 2006 *Small Journal 2* No.8–9 944

[14] Kim K J and Park Y R 2002 *Appl. Phys. Lett.* **81** 1420

[15] Li X, Zhai F F, Liu Y, Cao M S, Wang F C and Zhang X X 2007 *Chin. Phys.* **16** 2769

[16] Lim J, Shin K, Kim H W and Lee C 2004 *Mater. Sci. Eng.* **107** 301

[17] Ramachandran S, Narayan J and Prater J T 2006 *Appl. Phys. Lett.* **88** 242503

[18] Koidl P 1977 *Phys. Rev.* B **15** 2493

[19] Ueda K J, Tabata H S and Kawai T J 2001 *Appl. Phys. Lett.* **79** 988

[20] Liu H, Zhang X, Li L Y, Wang Y X, Gao K H, Li Z Q, Zheng R K, Ringer S P, Zhang B and Zhang X X 2007 *Appl. Phys. Lett.* **91** 072511

[21] Judith L, Driscoll M M, Khare N, Liu Y L and Vickers M E 2007 *Adv. Mater.* **19** 2925

[22] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nature* **14** 173

[23] Kittilstved K R, Schwartz D A, Tuan A C, Heald S M, Chambers S A and Gamelin D R 2006 *Phys. Rev. Lett.* **97** 037203