N-doping-related room temperature ferromagnetism of electrodeposited ZnCoO films

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Abstract

A series of Co-doped ZnO films were fabricated by an electrodeposition method. The X-ray diffraction results and absorption spectra show Co ions have been doped successfully into the ZnO crystal lattices. The as-grown samples have no ferromagnetism at room temperature. However, after plasma treatment used ammonia as reactive gas, the room temperature ferromagnetism was detected in ZnCoO samples. The Hall measurement reveals the resistivity of samples was increased by two orders of magnitude after the treatment. Although the aspect conductivity is an n type, some holes generated by N doping still play an important role to induce the room temperature ferromagnetic properties for Co-doped ZnO samples.
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1. Introduction

Recently, diluted magnetic semiconductors (DMSs) have attracted much attention because of their potential technological applications on optoelectronic, magnetoelectronic, and microwave devices [1]. Since Dietl predicted the Curie temperature (T_c) of Mn-doped ZnO could be realized upon room temperature in 2000 [2], many efforts were made to dope transition metal ions into ZnO materials [3–5]. Some theoretic works showed that carriers played an important role to induce the ferromagnetic state of ZnMO (M = Mn, Co) through hybridization, super exchange, or double exchange [1,6,7]. But other scientists revealed that the ferromagnetism (FM) could be obtained on ZnO doped with V, Cr, Fe, Co and Ni without any doping treatment [8].

As Co is highly soluble in ZnO [9], Co-doped ZnO has been studied widely [3–6]. But the experimental results of FM properties of ZnCoO were complicated. There have only been few reports about the ferromagnetic properties of ZnCoO thin films above room temperature [4,5], while a recent result showed that pure $Zn_{1-x}Co_xO$ was found to be no FM at room temperature with x value up to 0.1 [6]. The microstructure in ZnCoO nanostructure, fabricated by different growth conditions, was another important point to affect the room temperature FM [10]. And for high-doped ZnCoO, Co metal cluster was considered to be the origin of FM at room temperature [11]. Moreover, the FM in ZnCoO could also be achieved by co-doping with Cu or H [12,13]. By now, a clear correlation between nitrogen addition (p type doping) and strong 300 K FM in Mn:ZnO is observed [7,14], which shows that Mn:ZnO has strong ferromagnetism when nitrogen was introduced during materials preparation. An inverse result was also reported for Co:ZnO, which showed no ferromagnetism at room

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temperature with nitrogen co-doping Co:ZnO [15,16]. However, another experiment demonstrates that room temperature ferromagnetism arose in Co:ZnO through hole doping with Li [6].

In order to understand the effect of carrier type on ferromagnetism of Co:ZnO, nitrogen-doped Co:ZnO samples with different Co concentrations were fabricated, as well known, nitrogen is a preferred hole dopant in ZnO. N-doped ZnO thin films could be fabricated by using NO and N_2O source with the radio frequency plasma [17,18]. P-ZnO with N doping have been realized by several methods [18,19]. In this paper, ZnCoO films were prepared by electrodeposition method. Then plasma created in plasma-enhanced chemical vapor deposition (PECVD), in which the ammonia was used as reactive gas, was used to treat the samples to realize the N doping in the film. It was found that only after the treatments the series of samples revealed FM at room temperature. The relationship between N and ZnCoO is discussed.

2. Experiments

Experimentally, zinc nitrate hydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 10 mmol], hexamethylenetetramine [$C_6H_{12}N_4$, 10 mmol], and cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$] taken in required molar ratios (corresponding to 2, 5, and 7% Co) were dissolved in 200 ml deionized water to grow $Zn_{1-x}Co_xO$ and the samples were labeled as A, B and C, respectively, corresponding to the increasing concentration of Co. The n-type Si (1 0 0) wafers were used as the substrates, which were etched with dilute HF (5%) for 5 min before the deposition. The deposition was carried out at a constant potential of −0.8 V for 1 h at 65 °C.

X-ray diffraction (XRD) measurement was taken on a Siemens D500 diffractometer using CuK_α radiation of 1.5418 Å. Magnetic characteristics are studied using a vibrating sample magnetometer (VSM) (Lake Shore Company) at room temperature. X-ray photoelectron spectroscopy (XPS) characterization was carried out on VGESCALAB MKII instrument from English VG Company. The electrical properties and Hall data are measured using four probes with Van der Pauw geometry.

3. Results and discussion

For the as-grown samples, the XRD spectra for $Zn_{1-x}Co_xO$ samples are shown in Fig. 1. The XRD patterns showed that $Zn_{1-x}Co_xO$ had the hexongal wurtzite structure. No additional impurity phases could be detected by XRD under the chosen measurement conditions. And due to the Co^{2+} ionic radius (0.58 Å) is close to the value of Zn^{2+} ion (0.60 Å), the calculated lattice parameters are very similar to the pure ZnO ones. And the thicknesses of the samples were all near 200 nm obtained by SEM. In order to confirm the real concentrations of Co ions in the samples, the typical Co 2p XPS measures were also performed. The relative quantitative
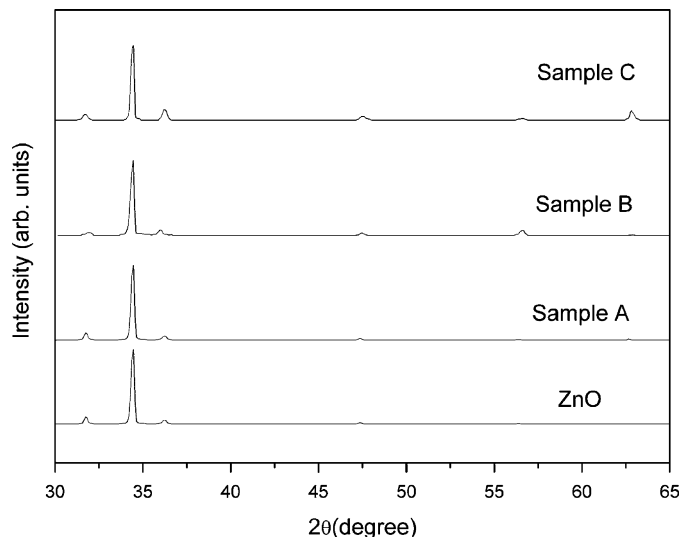

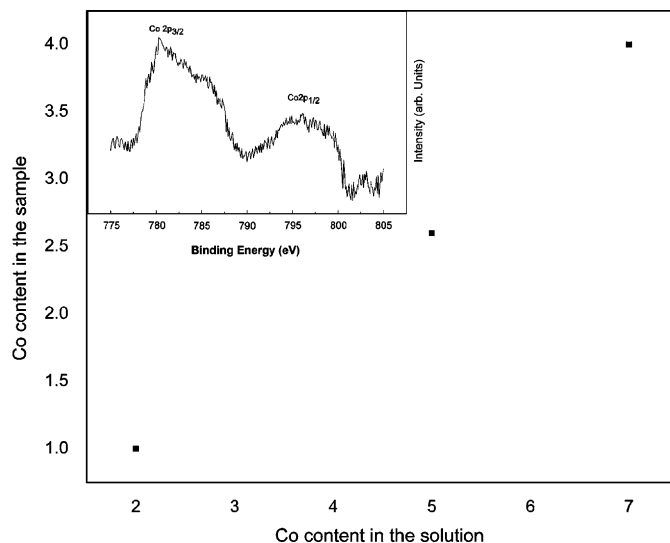Fig. 1. The XRD spectra of pure ZnO and Co-doped ZnO samples.

Fig. 2. The relation of Co content in sample and Co content in solution. The inset shows the Co 2p XP spectrum of sample C.

analysis of each element is completed using the XPS peak area data of different elements and their own elemental sensitivity factor. The Co 2p spectrum of sample C is shown in the inset of Fig. 2. From the results, the Co concentrations in the samples are calculated with 1%, 2.6% and 4% in the samples A, B and C, respectively, which are indicated in Fig. 2. And the rest is lost in the solution, not participating in the reaction.

The optical absorption spectra of the Co-doped ZnO samples were measured at room temperature and the band gap of different samples were calculated based on them. The shifts of band edge with different Co composition are shown in Fig. 3. The band gap transition for the pure ZnO is observed at 3.26 eV. Compared with pure ZnO, the absorption edges of Co-doped ZnO samples shift to low-energy side and the calculated band gap of Co-doped ZnO
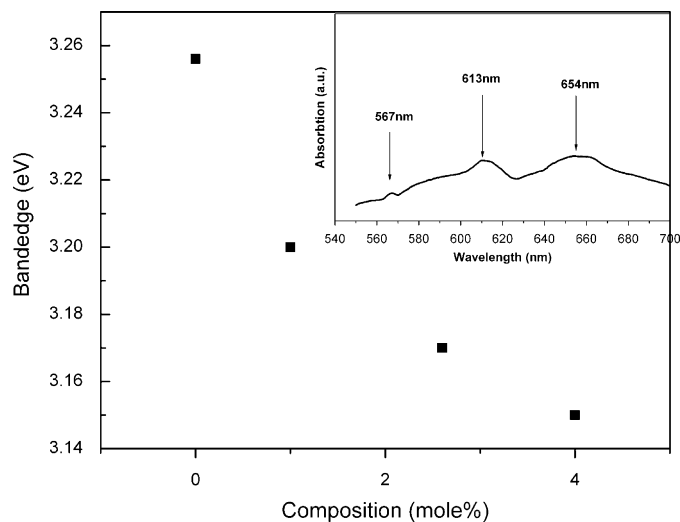
Fig. 3. Shift of band edge in Co-doped ZnO nanoparticles with composition. The inset shows the absorption spectrum of Co^{2+}.

Table 1
Electrical properties of samples before-and-aftertreatment by plasma

Sample		Sample A	Sample B	Sample C
Resistivity (Ωcm)	As grown	1.4×10^{-4}	6.2×10^{-4}	3.9×10^{-4}
	After treatment	2.1×10^{-2}	1.5×10^{-2}	3.4×10^{-2}

Fig. 4. N1s XPS spectrum of the sample after plasma treatment.

decreases with increasing Co concentration. This change of band gap is attributed to sp–d exchange interactions between the band electrons and the localized d electrons of the Co^{2+} ions substituting Zn ions [20–22]. The s–d and p–d exchange interactions give rise to a negative and a positive correction to the conduction-band and valence-band edges, respectively, leading to a band gap narrowing [23]. It can be seen from Fig. 3(inset) that the absorption peaks are observed in the case of sample C. These absorption bands are at 567, 613 and 654 nm, respectively, due to the transitions of Co^{2+}. From the above analyses, Co^{2+} ions were confirmed to be doped successfully into the ZnO crystal lattices.

For the ferromagnetic properties, no FM was found for the as-grown samples detected by VSM measurements at room temperature. In order to obtain the FM at room temperature for Co-doped ZnO samples and understand the relationship of FM properties with carrier type, we introduced N in the ZnCoO samples with treatment by plasma-enhanced chemical vapor deposition. The treatment was carried out for 1 h under a power of 10 W, which the ammonia was used as reactive gas in the treatment. After the treatment the electrical properties of the samples were changed dramatically. Table 1 shows the electrical properties measured by Hall-effect measurement using a four-probe van der Pauw method. It can be found that the resistivity increase by two orders of magnitude after the treatment. The increase in resistivity may result from the Co:ZnO surface defects passivated by nitrogen atoms. And some nitrogen atoms could be incorporated into ZnCoO samples during the treatment process to occupy oxygen positions, and the presence of N in the crystal lattice is partly compensating some donors originated from non-stoichiometric composition [19].

N element could also be detected by XPS spectrum for the treated samples (shown in Fig. 4). The binding energy of N1s located at 399.4 eV could be attributed to N–H

bonds [19]. In the present paper, the nitrogen source was NH_3, and a part of N binds strongly with H to form NH pairs because the formation energy of this defect is lower than 'pure' N_O (N-on-O substitution) defects. In this case, the N_O acceptor defects are electrically inactive because of hydrogen passivation [24]. Due to this effect the effective acceptors are not enough to compensate donors, leading to the ZnCoO samples still presents n-type conductivity. That is to say, in this case, two carriers (hole and electron) are coexisted in ZnCoO samples with different carrier densities.

Fig. 5 shows the hysteresis behavior of the treated samples measured with the magnetic field perpendicular to the film surface. All three samples are ferromagnetic at room temperature, and the ferromagnetic moment increased with increasing concentration of Co. The Co content dependence of saturation magnetization M_s is shown in the inset of Fig. 5. The M_s slightly increases with increasing Co content. However, it is smaller than that of Co^{2+} in a tetrahedral crystal field ($3.0\mu_B$/Co). The results show that the plasma treatment is very important for the ferromagnetism to ZnCoO samples. As the as-grown samples are only electron conductivity (table I), we consider the above phenomenon could be explained by the hole-mediated exchange interactions [2]. In our experiments, although the measured Hall conduction is n type, there are some holes in the crystal generated by plasma treatment. Under this theory, a bound magnetic polarons (BMPs) could be formed with the introduction of
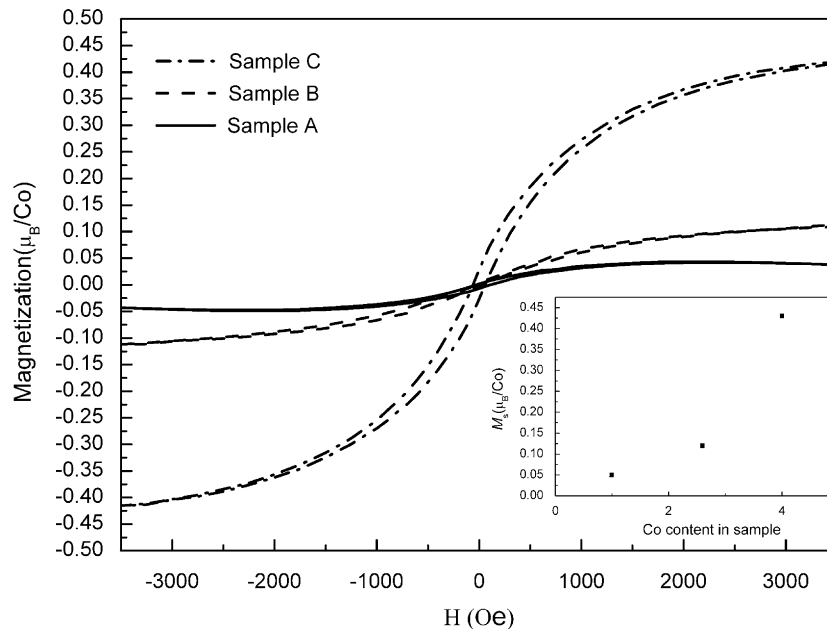
Fig. 5. Hysteresis loop at 300 K for ZnCoO samples after treated by plasma. The inset shows the Co content dependence of saturation magnetization.

p-type dopants. Magnetic exchange interactions between defect-bound valence band holes and Co^{2+} ions occupying the same space are proposed to align Co^{2+} spins with respect to one another, forming a BMP [14].The hole-induced FM in ZnCoO has already been observed by Li doping [6]. And the author also theoretically argued that Co has the best potential as a Zn substitutional dopant in ZnO for producing DMS when combined with hole dopants [6].

4. Conclusion

In conclusion, the electrodeposited Co-doped ZnO thin films have been fabricated. According to the XRD and absorption spectra, we can confirm that the Co^{2+} ions have been doped in the ZnO crystal lattice successfully. The as-grown samples were no FM property at room temperature. However, after the plasma treatment, the series of ZnCoO samples show FM at room temperature. The origination of FM is thought due to be the mediation though the p–d exchange interactions between holes and Co atoms.

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