Full Length Article

The effect of Al^{3+} co-doping on the structural, magnetic and optical properties of ZnCoO thin films

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A R T I C L E   I N F O

A B S T R A C T

$Zn_{0.99-x}Co_{0.01}Al_xO$ ($x=0$, 0.005, 0.01, 0.02) thin films have been prepared by a sol–gel method. The structural, optical and magnetic properties of the samples were investigated. X-ray diffraction, X-ray photoelectron and UV absorption spectroscopy analyses indicate that Al^{3+} and Co^{2+} substitute Zn^{2+} without changing the wurtzite structure. The (Al, Co) co-doped samples are ferromagnetic at room temperature, and the ferromagnetic moment increased with increasing concentration of Al^{3+}. It was demonstrated experimentally that high-temperature ferromagnetism in Co-doped ZnO thin films can be obtained through increasing the carrier concentration, which was realized by doping a few percent of Al ions using a simple fabrication method.

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1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted a great deal of attention in recent years as enabling materials in the emerging field of "spintronics". However, DMSs usually have low Curie temperature (T_C), which largely hinder their future application. So realizing room temperature ferromagnetic DMSs has become a major issue both in theory and practical applications. According to the previous ab initio studies on the magnetism of diluted magnetic semiconductors, it was expected that room temperature ferromagnetic DMSs can be realized by TM ions doped ZnO [1–4] and a number of experimental results have been reported. Especially for Co doped ZnO, Co is highly soluble in ZnO [5], so it is easy to prepare ZnCoO alloys with different compositions. Many results on Co-doped ZnO with the ferromagnetic properties above room temperature have been reported [6–9]. However, there is no consistent result for observation and the detailed mechanism of room temperature FM Co-doped ZnO

is still not very clear. Recently, it is found that adding Al ions in ZnCoO can realize room temperature FM by increasing carrier concentration using sol–gel method [10]. But if using co-precipitation method to fabricate ZnAlClO, no RM FM can be obtained [11]. These results indicate that the magnetic properties of ZnCoO with the addition of Al are sensitive to the growth methods.

You can add some merits of sol–gel method such as being simple, cheap and so on. In this paper, $Zn_{0.99-x}Co_{0.01}Al_xO$ thin films with different Al contents have been prepared by sol–gel method and the structural, magnetic and optical properties of the samples were investigated. Room temperature FM was observed with the introduction of Al due to the increasing concentration of free carriers. Meanwhile, with increasing Al ions the enhancement of room FM has been obtained.

2. Experimental

The sol was composed of $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and Polyvinyl Pyrrolidone (PVP) in an ethanol solution. The total concentration of metal ions was controlled at 0.1 mol/l. The concentration of Al^{3+} was adjusted to 0.0005, 0.001 and 0.002 mol/l and the

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concentration of Co^{2+} was maintained at 0.001 mol/l. The films were spin-coated on Si (1 0 0) and quartz substrates at 2000 rpm. After the deposition, the substrates were first heated at 100 °C in air for 10 min to evaporate the solvent and then at 350 °C in O_2 for half an hour to eliminate the organic component in the film. This process may be repeated many times to reach the desired thickness. Then thermal annealing was performed for 1 h in an O_2 environment at 700 °C in order to crystallize the film. The thicknesses of all the samples were around 150 nm.

X-ray diffraction (XRD) measurement was taken on a Siemens D500 diffractometer using CuK_α radiation of 1.5418 Å. A UV-360 Spectrophotometer (Shimadzu) was used for the optical characterization. Magnetic characteristics are studied using a vibrating sample magnetometer (VSM, Lake Shore Company) at room temperature. The chemical nature of surfaces was analyzed by X-ray photoelectron spectroscopy (VGESCALAB MK II XPS, VG Co., East Grinstead, UK). The binding energies were calibrated by centering the aliphatic carbon peak at 284.6 eV. Photoluminescence (PL) spectra were measured using the 325 nm line of a He–Cd laser as an excitation source. The electrical properties and Hall data are measured using four probes with Van der Pauw geometry.

3. Results and discussion

X-ray diffraction patterns of $Zn_{0.99-x}Co_{0.01}Al_xO$ are shown in Fig. 1. The diffraction pattern can be identified as that of the wurtzite structure, which indicates that Co and Al co-doping cannot disturb the structure of ZnO. No obvious additional peaks (such as Co, CoO) are observed in $Zn_{0.99-x}Co_{0.01}Al_xO$ indicating that no impurity exists in the films. Furthermore, it should be noted that with
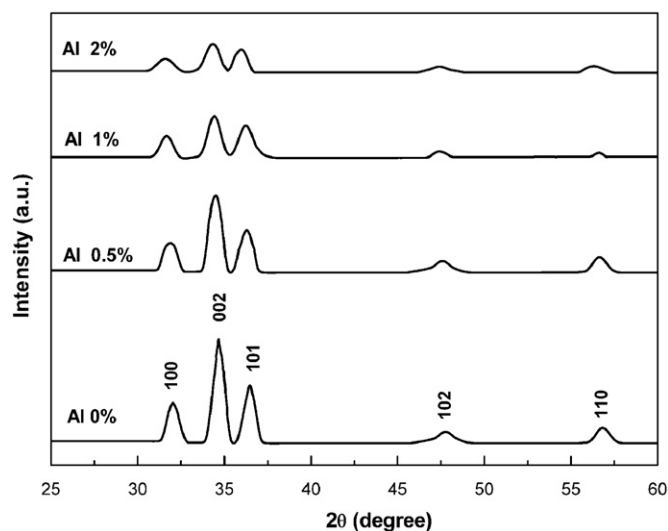

Fig. 1. XRD patterns of $Zn_{0.99-x}Co_{0.01}Al_xO$ thin films with different Al concentrations.
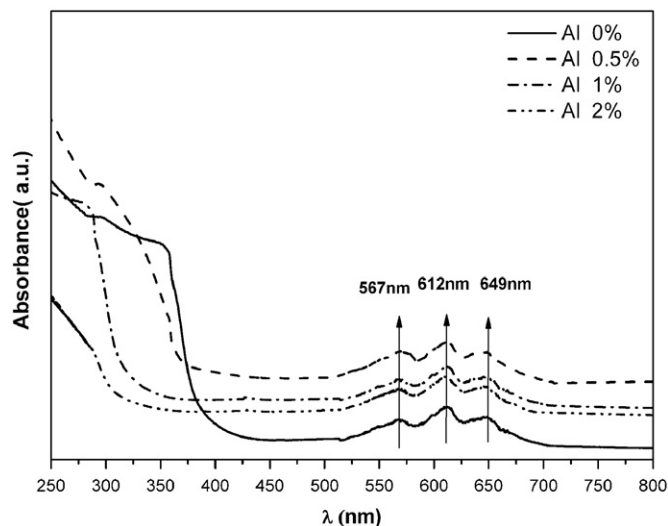

Fig. 2. Room temperature optical spectra of ZnCoO films with different Al concentrations.

increasing doping concentration of Al ions all the diffractive peaks in the XRD patterns shift to the lower angle side gradually as ionic radius of Al^{3+} (0.39 Å) is smaller than that of Zn^{2+} (0.60 Å). This result indicates that Al ions are doped into ZnCoO crystal lattice successfully with substituting positions of Zn ions. Meanwhile, the peak intensity decreases when the Al concentration is increased, which means that the crystalline quality degrades with Al ions doping.

Optical absorption spectra of Al-doped ZnCoO thin films are presented in Fig. 2. The blue-shift of the absorption edges can be seen with increasing Al doping concentration. The optical band gap of the sample obtained from the absorption spectra increased from 3.3 eV (0% Al) to 3.7 eV (2% Al), as a result of the lowest states filling in the conduction band by Al donor electrons—the Burstein–Moss effect [12]. Meanwhile, the absorption peaks at 567, 612 and 649 nm are observed, which should be correlated with the d–d transitions of the tetrahedrally coordinated Co^{2+} ions and attributed to

$^{4}A_2(F) \rightarrow {}^{2}E(G)$, $^{4}A_2(F) \rightarrow {}^{4}T_1(P)$ and $^{4}A_2(F) \rightarrow {}^{2}A_1(G)$, respectively [13], indicating Co^{2+} ions are doped into ZnO crystal lattices successfully.

From Fig. 3, it can be seen that the aluminum 2p peaks show a Al 2p3/2 peak at 74.1 eV, which indicates that the valence state of Al in the films is Al^{3+}. The strong intensity component, with the binding energy of 74.20 eV, is slightly shifted towards a lower binding energy compared to the 74.60 eV peak position in stoichiometric Al_2O_3, an indication of ZnO matrix. The relative quantitative analysis of each element is completed using the XPS peak area data of different elements and their own elemental sensitivity factor. From the former results we conclude that the content ratio of Co is 0.5%. That is, only 0.5% content of Co entered the ZnO lattice and the rest was lost. The content ratio of Al is 0.2%, 0.5% and 1.1%, which was labeled sample A, sample B and sample C, respectively.

Fig. 4 shows the hysteresis behavior of the samples measured at room temperature with a magnetic field
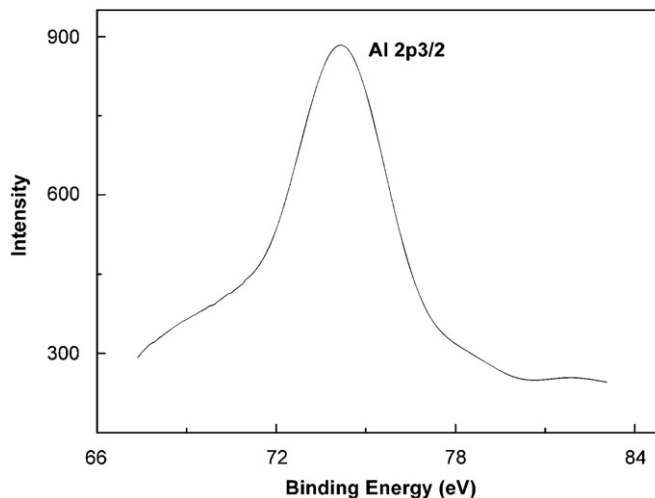

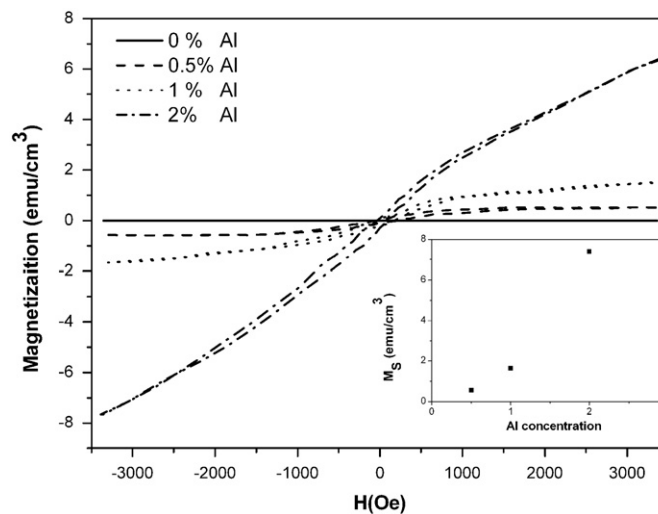Fig. 3. Al 2p spectrum of ZnCoO film with Al doping concentration 2%.

Fig. 4. Room temperature magnetization hysteresis curves of ZnCoO films with different Al concentrations.

perpendicular to the film surface. For the pure ZnCoO sample no FM was detected. But three Al co-doped samples are ferromagnetic at room temperature. The Al content dependence of saturation magnetization M_s is shown in the inset of Fig. 3. It is found that the ferromagnetic moment and M_s increased with increasing concentration of Al^{3+}. Based on the above experiments the ferromagnetic behavior of the samples could not originate from Co nanoclusters because all the samples were grown under the same condition and ZnCoO film does not show FM. Furthermore, there is no diffraction peak associated with Co cluster that can be observed in XRD pattern, as shown in Fig. 1. This result is well in agreement with the XRD patterns. Therefore, the carriers generated by Al doping are considered a main factor to induce the ferromagnetic phenomenon.

In order to confirm the existence and creation of free carriers by the Al doping, the electrical transport properties of the samples are summarized in Table 1. Based on the Hall-effect measurement all the samples are found to show n-type conductivity. The carrier concentrations increase with increasing Al doping concentration from 6.85×10^{14} to 7.71×10^{17} cm^{-3} and the resistivity of the samples decreases with increasing Al doping concentration.

These results indicate that the carrier concentration increased by adding Al ions. The currently accepted picture of DMS's ferromagnetism is that the presence of carriers is essential to mediate the interaction between the magnetic ions. Such n-type ferromagnetism in thin films supports the model of Coey et al. in which the

ferromagnetic exchange is mediated by shallow donor electrons that form bound magnetic polarons, which overlap to create a spin–split impurity band [14]. High Curie temperatures require hybridization and charge transfer from a donor-derived impurity band to unoccupied 3d states at the Fermi level. Consider an interaction of magnetic cations with hydrogenic electrons in the impurity band. The donors tend to form bound magnetic polarons, coupling the 3d moments of the ions within their orbits. From the above electronic measurements, it is found that the carrier concentration increased with the increase of Al doping concentration. The increase of M_s caused possibly due to the increase of electrons, which form bound magnetic polarons inducing more effective ferromagnetic couplings between doped Co^{2+} ions.

Fig. 5 shows room temperature PL spectra of the samples. The UV emissions shift to the high energy side with increasing Al doping concentration , which corresponds to the results of absorption spectra. The UV emission corresponds to the near band edge emission, and the green emission peak is generally referred to as a deep-level or trap-state emission such as those due to O vacancies [15], Zn vacancies and Zn interstitials [16]. When increasing Al doping concentration, the intensity ratio of the visible to UV emission increases, which is attributed to the increase of O vacancies and Zn interstitials relating to a possible source of n-type carriers in ZnO. This trend is well in agreement with the electronic measurement results.

4. Conclusions

In conclusion, the (Al, Co) co-doped ZnO thin films have been prepared by sol–gel method. The XRD, XPS and the optical absorption spectra results indicate that Al and Co ions are doped into ZnO crystal lattice successfully by substituting positions of Zn ions. The electronic measurements confirm that Al ions increase the carrier concentration. Therefore the
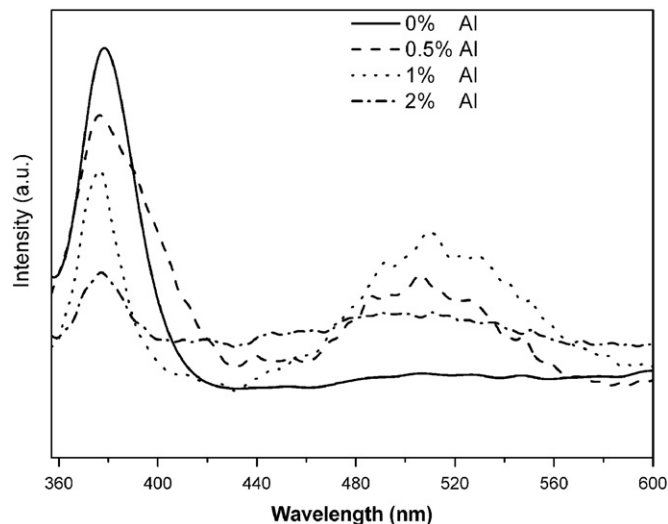
Table 1
Electrical properties of ZnCoO films with different Al concentrations.

Al [%]	Resistivity [Ω cm]	Carrier density [1/cm^3]	Type
0	1.45×10^4	6.85×10^{14}	n
0.5	9.22×10^3	7.68×10^{15}	n
1	7.44×10^3	2.63×10^{16}	n
2	3.26×10^3	7.71×10^{17}	n

Fig. 5. Room temperature PL spectra of ZnCoO films with different Al concentrations.

increase of electrons, which form bound magnetic polarons, induce more effective ferromagnetic couplings between doped Co^{2+} ions. As a result, M_s slightly increases with increasing Al content.

Acknowledgement

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