Room-temperature anomalous Hall effect and magnetroresistance in (Ga, Co)-codoped ZnO diluted magnetic semiconductor films*

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This paper reports that the (Ga, Co)-codoped ZnO thin films have been grown by inductively coupled plasma enhanced physical vapour deposition. Room-temperature ferromagnetism is observed for the as-grown thin films. The x-ray absorption fine structure characterization reveals that Co^{2+} and Ga^{3+} ions substitute for Zn^{2+} ions in the ZnO lattice and exclude the possibility of extrinsic ferromagnetism origin. The ferromagnetic (Ga, Co)-codoped ZnO thin films exhibit carrier concentration dependent anomalous Hall effect and positive magnetoresistance at room temperature. The mechanism of anomalous Hall effect and magneto-transport in ferromagnetic ZnO-based diluted magnetic semiconductors is discussed.

Keywords: diluted magnetic semiconductors, (Ga, Co)-codoped ZnO, anomalous Hall effect, magnetroresisance

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1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted great research interest in the past decade. The charge and spin of electrons could be simultaneously manipulated in DMSs, which offers the potential application in spintronic devices combining standard microelectronics with spin-dependent effects.[1,2] Room-temperature ferromagnetic semiconductors are desired for practical devices. Among various types of semiconductors, ZnO is one of the most widely studied host compounds in order to realize intrinsic ferromagnetism with high Curie temperature. It has been theoretically predicted that room-temperature ferromagnetism could be realized in 3d transition-metals (TM) doped ZnO.[2,3] A variety of TM-doped ZnO DMSs such as thin films, nano-materials and single crystals have been reported. Although room-temperature ferromagnetism was observed, the intrinsic ferromagnetism origin still remains an issue.[4−12] The possibility of an extrinsic origin, such as ferromagnetic impurity segregation, could not be ruled out in most cases. This is because the often-performed characterization measurements using a magnetometer are unable to distinguish the intrinsic ferromagnetic signal from an extrinsic one, due to the characteristics of the method to probe all the magnetization from the ferromagnetic sources. It is believed that x-ray absorption fine structure is a spectroscopic tool to provide a 'fingerprint' of electronic states and local structure of incorporated atoms in the host compounds even in a dilute concentrations. Even tiny ferromagnetic impurity could be detected by this technique. However, this could not exclude the possibility of ferromagnetic coupling induced by defects. Bound magnetic polaron (BMP) theory could give a reasonable explanation on defects induced ferromagnetism in oxide-based DMSs, but these materials are not the real DMSs.[13,14] In ideal DMSs, the intrinsic ferromagnetism is caused by spin-polarised carriers that mediated ferromagnetic interaction between distant localized spins of magnetic ions.[15,16] The ferromagnetic response caused by carriers could be a direct manifestation of intrinsic ferromagnetism. A well-known ferromagnetic response of carriers in DMSs is the anomalous Hall effect (AHE).[17] But the AHE can not be regarded as

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the sufficient and necessary condition for demonstrating the intrinsic ferromagnetism in DMSs materials. Therefore, in depth both local structure characterization and AHE measurement will be useful tools for investigating the intrinsic nature of ferromagnetism. In this paper, we investigated the electronic state and local environment of the doped Co and Ga by x-ray absorption fine structure spectroscopy. The AHE and magnetoresistance (MR) measurement was carried out to reveal the spin-dependent transport properties.

2. Experimental details

The (Ga, Co)-codoped ZnO films were grown on Si (100) substrate at 400^{o}C by inductively coupled plasma enhanced physical vapour deposition (ICP-PVD) with magnetic confinement. The sputtering targets were fabricated by a standard solid-state reaction method. [18] A prescribed amount of ZnO (99.99%), CoO (99.99%) and Ga_2O_3 (99.999%) were mixed, sintered at 1000^{o}C for 48 hours in air atmosphere. Mixed plasma of Ar and O_2 was used for sputtering in order to investigate the effect of oxygen pressure on the physical properties. The oxygen pressure was varied at 6.7×10^{-5} Pa, 1.3×10^{-3} Pa and 1.3×10^{-1} Pa and the corresponding (Ga, Co)-codoped ZnO sample was labeled as ZGCO1, ZGCO2 and ZGCO3 in the following descriptions, respectively. The x-ray absorption spectroscopy of near-edge structure (XANES) and extended fine structure (EXFS) measurements were performed on synchrotron radiation from the National Synchrotron Radiation Laboratory (NSRL) in the University of Science and Technology of China. A quantum design superconducting quantum interference device (MPMS XL-7) magnetometer was used to investigate the magnetic properties. The electrical transport and AHE measurement were characterized by a LakeShore Hall measurements system (9700A).

3. Results and discussion

Figure 1(a) shows the room-temperature magnetization versus magnetic field (M–H) curves for (Ga, Co)-codoped ZnO films grown at different oxygen pressures. Typical behaviour of ferromagnetic hysteresis loops is clearly observed with different saturation magnetization (M_s). The sample has the strongest ferromagnetism with an M_s of 75 emu/cm^{-3} and coercive field (H_c) of 120 Oe (1 Oe=79.5775 A/m) when grown at lower oxygen pressure of 6.7×10^{-5} Pa. They decrease to 25 emu/cm^{-3} and 60 Oe, respectively, when the oxygen pressure increases to 1.3×10^{-1} Pa. Room-temperature Hall measurement was carried out and shown in Fig. 1(b). It can be seen that the oxygen pressure has an obvious effect on the electrical properties. The resistivity varies from 8.97×10^{-4} Ω·cm to 5.26×10^{-3} Ω·cm, while the electron density varies from 5.77×10^{20} cm^{-3} to 1.54×10^{20} cm^{-3} with increasing the oxygen pressure from 6.7×10^{-5} Pa to 1.3×10^{-1} Pa. It has been reported that oxygen-rich condition will increase the resistivity and reduce the electron concentration in Ga-doped ZnO films. The possible reason is the formation of compensating-defects such as oxygen interstitials, zinc vancancy and their complexes in oxygen-rich condition[19,20] The variation in the M_s and H_c is attributed to the changes of electrical property caused by the oxygen pressure.

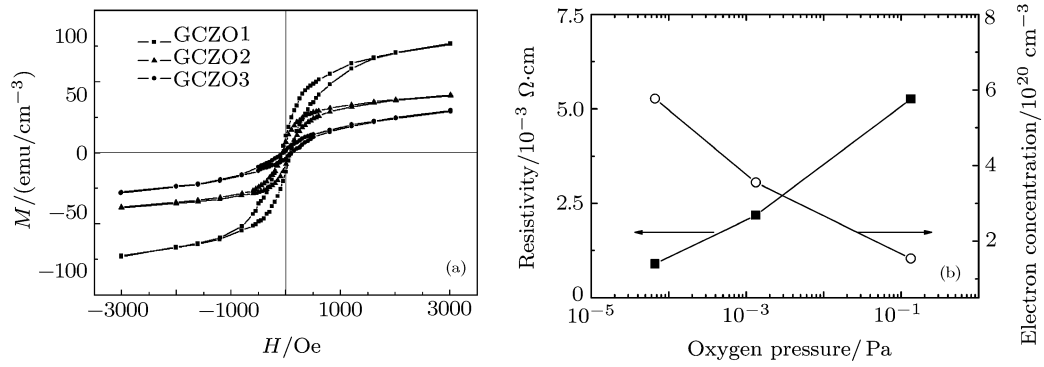


Fig. 1. (a) Magnetization hysteresis curves of (Ga, Co)-codoped ZnO films grown at different oxygen pressure. (b) Room-temperature resistivity and electron concentration of (Ga, Co)-codoped ZnO films grown at different oxygen pressure.

Although room-temperature ferromagnetism is observed in the as-grown thin films, the extrinsic origins from BMP and ferromagnetic impurity segregation could not be excluded. The BMP theory proposed that the ferromagnetism in oxide-based DMSs was induced by defects.[13,14] We have reported that the oxygen vacancy is the main defect in the Co-doped ZnO films grown at high vacuum environment.[21] Therefore, it is quite necessary to elucidate the ferromagnetic origin in our observed samples. If the ferromagnetism is intrinsic, then the ferromagnetic exchange interaction among distant localized spins of magnetic ions should be mediated by spin-polarised carriers. A well-known ferromagnetic response of carriers in ferromagnetic semiconductors is the AHE. In magnetic materials, the Hall resistance has two contributions, the ordinary Hall effect (OHE) arising from the classical Lorenz force and the AHE due to the asymmetric scattering from the spin–orbit interaction between the carrier and the ferromagnetically ordered impurity. The Hall resistance of magnetic material is expressed as

$$R_{\rm Hall} = R_{\rm OHE} + R_{\rm AHE} = R_0 B + R_{\rm S}(\mu_0 M), \quad (1)$$

where R_0 and B are the ordinary Hall coefficient and the magnetic induction respectively, $R_{\rm S}$ and M are the anomalous Hall coefficient and the magnetization, respectively, μ_0 is the free space permeability.

Figure 2 shows the magnetic-field dependence Hall resistivity (ρ_{xy}) for the (Ga, Co)-codoped ZnO films. A Ga-doped ZnO film grown at 6.7×10^{-5} Pa is also included in order to compare the difference between magnetic and non-magnetic films. The magnetic field was applied perpendicularly to the sample's surface. For Ga-doped ZnO sample, ρ_{xy} exhibits linear behaviour with a negative slope in the whole applied magnetic field as shown in Fig. 2(b). This is a typical behaviour of non-ferromagnetic semiconductors with n-type conductivity. All the (Ga, Co)-codoped ZnO films exhibit quite different behaviours. It can be seen that the ρ_{xy} increases up to 0.15 T with increasing magnetic field, and then linearly decreases with further increasing the magnetic field as shown in the insets of Figs. 2(a) and 2(b). This phenomenon reveals that the anomalous part of ρ_{xy} ($\rho_{\rm AHE}$) which is proportional to magnetization, is dominant in low magnetic field, whereas the ordinary part of ρ_{xy} ($\rho_{\rm OHE}$), which is proportional to the inverse of electron yielded negative linear slope, overcomes the $\rho_{\rm AHE}$ and becomes dominant in the high magnetic field, as the magnetization saturates and $\rho_{\rm OHE}$ keeps increasing linearly with increasing magnetic field. Although all (Ga, Co)-codoped ZnO samples show clear AHE, it can be seen that the behaviour depends on electron concentration and ferromagnetic strength. The AHE slightly degrades with the decrease in electron concentration and ferromagnetism. In order to investigate the strength of AHE in (Ga, Co)-codoped ZnO, Hall conductivity was used to explain this, which has been proposed to quantitatively explain the AHE in group III-V ferromagnetic semiconductors.[16,22] In this theory, Hall conductivity is expressed as

$$\sigma_{xy} = \rho_{xy}/(\rho_{xy}^2 + \rho_{xy}^2), \quad (2)$$

which is thought to be an essential measure of AHE strength. It was found that the anomalous part of σ_{xy} strongly depends on carrier density. The calculated σ_{xy} is 0.16, 0.038, and 2.7×10^{-3} $(\Omega\cdot{\rm cm})^{-1}$ for GCZO1, GCZO2 and GCZO3, respectively. The AHE strength of (Ga, Co)-codoped ZnO is in agreement with Co-doped TiO_2 or Cr-doped In_2O_3, but much lower than that in Mn-doped GaAs and InAs.[16,17,22,23]

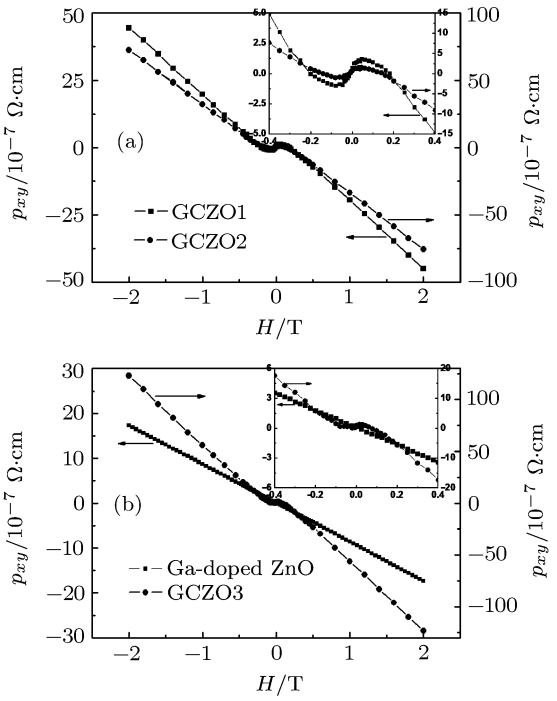


Fig. 2. Anomalous Hall resistivity for (a) sample GCZO1 and GCZO2, (b) sample GCZO3 and Ga-doped ZnO film grown at 6.7×10^{-5} Pa. The insets show the magnification around zero magnetic fields.

It should be mentioned that the AHE should not be considered as the direct evidence of demonstrating

intrinsic ferromagnetism in DMS material since superparamagnetic materials and ferromagnetic particles or films may show such behaviour. However, it is a useful tool for studying the intrinsic nature of ferromagnetic order. The Hall conductivity is used to demonstrate the strength of observed AHE.

The magneto-transport property was also carried out at room temperature using the Hall measurement system. Figure 3 shows the transverse MR,

$$MR = [\rho(H) - \rho(0)]/\rho(0), \tag{3}$$

which is measured at room temperature. All the (Ga, Co)-codoped ZnO films exhibit positive MR of 1.0%, 0.47% and 0.29% for ZGCO1 ZGCO2 and ZGCO3 samples, respectively. Yang *et al.*[24] reported that the MR in Co-doped ZnO thin films was strongly temperature dependent with a positive magnitude from 2 K to 5 K and a negative magnitude above 200 K. However, Wang *et al.*[25] found a large negative MR in Mn-doped ZnO thin film at low temperature (< 5 K) and a large positive MR above 5 K. The positive MR is attributed to a giant spin splitting of band states caused by a sp-d exchange interaction in DMSs,[26−29] while the negative MR is from the third-order sp-d exchange Hamiltonian of the spin scattering.[30,31] In our experiment, the (Ga, Co)-codoped ZnO thin films show room-temperature positive MR and carrier concentration dependent behaviour. The carrier concentration dependence of the MR may be regarded as a sign of intrinsic carrier mediated ferromagnetism. Low temperature MR measurement may provide much more information on the nature of mechanism and the related work is in progress.

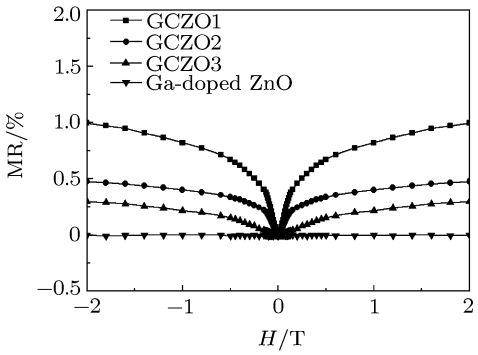


Fig. 3. Magnetic field dependence of magnetoresistance for Ga-doped and (Ga, Co)-codoped ZnO films measured at room temperature.

The x-ray absorption spectroscopy was used to characterise the local electronic structure, since tiny Co clusters or any secondary phase is highly sensitive to this technique.[32,33] Figure 4(a) shows the XANES spectra at Co K-edge as well as those of the Co metal and cobalt oxide for comparison. We also performed Ga K-edge and Zn K-edge x-ray absorption spectra for sample ZCGO3 in order to investigate the Ga position in the Zn–Ga–Co–O system. Both Ga and Zn absorption edges were horizontally transferred in Fig. 4(a). The absorption edge will slightly move for different Co valence state due to the electron transition between different excited states. It can be seen that the absorption edge of Co, CoO and Co_2O_3 moves to higher energy as the effective valence state increases. The Co K-edge of (Ga, Co)-codoped ZnO samples has close proximity to that of CoO, in contrast with those of Co and Co_2O_3. This indicates that the Co ions are in +2 states.[11] However, the oscillations of (Ga, Co)-codoped ZnO films are quite different from CoO in the near edge region due to the completely different coordination. Similar oscillations could be seen for the transferred Ga and Zn absorption edges. This indicates that Co and Ga have the similar coordination as Zn in ZnO lattice. In order to further clarify the local structures around the Co and Ga atoms, EXFS spectra were analyzed as shown in Fig. 4(b). We summarized the radial distribution functions (RDFs) of EXFS spectra at Zn, Co and Ga K-edge for (Ga, Co)-codoped ZnO samples as well as reference samples from Co metal and cobalt oxides. The first and second major peaks correspond to the first nearest-neighbouring anions and second nearest-neighbouring cations from the central scattering atoms. For the Co K-edge of CoO and (Ga, Co)-codoped ZnO samples, they correspond to the nearest oxygen and Zn (Co and Ga) from the central Co atoms. We can clearly see that the oscillation characteristic and the interatomic distance in RDFs is very close to each other except for Co metal and cobalt oxides, which means that Co and Ga ions have similar local structures as Zn ions in ZnO. No existence of tiny secondary phases like Co metal clusters, cobalt oxides or Ga oxides could be observed when the films were grown at different oxygen pressures. The XANES and EXFS results reveal that Co^{2+} and Ga^{3+} ions substituted for Zn^{2+} ions in ZnO lattice rather than being segregated or interstitial.

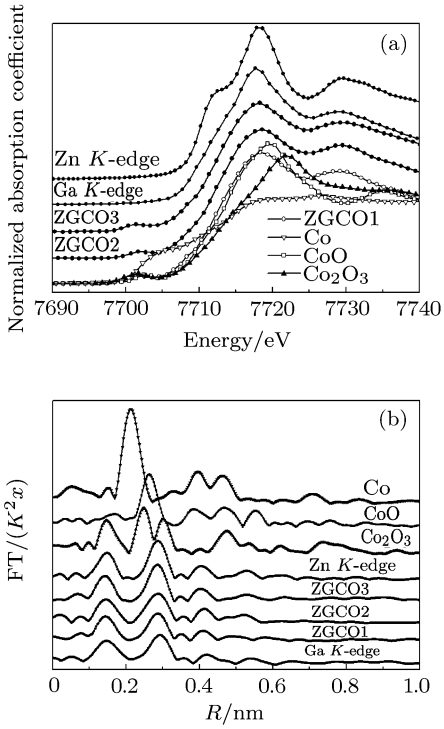


Fig. 4. (a) Normalized x-ray absorption near edge spectra of the (Ga, Co)-codoped ZnO films at Co Ga, and Zn K-edge, and reference samples of Co, CoO and Co_2O_3 at Co K-edge. (b) The RDFs of Co, Ga and Zn from Fourier transformed amplitude of EXFS.

4. Conclusion

In summary, (Ga, Co)-codoped ZnO thin films have been grown by ICP-PVD. Room-temperature ferromagnetism was observed in the as-grown thin films. The local structure characterization revealed that Co^{2+} and Ga^{3+} ions substituted for Zn^{2+} ions in the ZnO lattice and excluded the possibility of extrinsic ferromagnetism from secondary phases. The ferromagnetic (Ga, Co)-codoped ZnO thin films showed obvious carrier concentration dependent AHE and positive MR. The local structure characterization and magneto-transport properties indicated that intrinsic ferromagnetism was obtained in (Ga, Co)-codoped ZnO, which provides not only a useful proof to realize room-temperature ferromagnetic semiconductors but also an important clue towards the realization of spintronic devices based on DMSs materials.

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