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Difference in magnetic properties between Co-doped ZnO powder and thin film*

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This paper reports that the $Zn_{0.95}Co_{0.05}O$ polycrystalline powder and thin film were prepared by sol-gel technique under the similar preparation conditions. The former does not show typical ferromagnetic behaviour, while the latter exhibits obvious ferromagnetic properties at 5 K and room temperature. The UV–vis spectra and x-ray absorption spectra show that Co^{2+} ions are homogeneously incorporated into ZnO lattice without forming secondary phases. The distinct difference between film and powder sample is the *c*-axis (002) preferential orientation indicated by the x-ray diffraction pattern and field emission scanning electron microscopy measurement, which may be the reason why $Zn_{0.95}Co_{0.05}O$ film shows ferromagnetic behaviour.

Keywords: ZnO, Co-doped, crystalline orientation, magnetism
PACC: 7550P, 7280E

1. Introduction

Diluted magnetic semiconductors (DMSs) are expected to play an important role in the spintronics because charge and spin of electrons are accommodated into a single matter resulting in interesting magnetic, magneto-optical, magneto-electric properties.[1,2] Compared with conventional semiconductors, the spintronic devices based on DMSs materials have potential advantages of higher speed, lower power consumption, nonvolatility, greater efficiency, better stability and so on.[3] In recent years there is a tremendous research interest in the attainment of ferromagnetic semiconductors to realize new spintronic devices such as spin valve, spin light emitting diodes, spin field emitting transistors, non-volatile memory, optical isolators, ultra-fast optical switches and quantum computation.[4] Among the DMSs, transition metal (TM) doped II–VI and III–V compound semiconductors have been widely studied.[5,6] ZnO, one of the II–VI compounds, is a direct wide-bandgap semiconductor. Especially important, ZnO-based DMSs attracted extensive attentions due to the theoretical prediction by Dietl and Sato who predicted that above room temperature ferromagnetism could be obtained.[7,8]

Several groups have investigated the magnetic properties of Co-doped ZnO powders, films and nanostructural materials. For the powders, paramagnetic or spin-glass behaviour was usually obtained, no matter which method was taken.[9−12] In the case of films, ferromagnetism was usually observed.[13−16] Why are the magnetic properties quite different between the powders and films? Most studies focused on the extrinsic factors such as preparing method, growth conditions, and thermal annealing treatment. But the intrinsic factors such as carrier type and concentration, defects, crystal shape and size, crystalline orientation, are very important in determining the magnetic interactions. In this paper, we investigated the difference in magnetic properties between Co-doped ZnO powder and film. It was demonstrated experimentally that the crystalline orientation might be one of the intrinsic factors which affect the magnetic interactions between doped Co ions.

2. Experimental details

Co-doped ZnO samples were prepared by sol-gel route using $Zn(CH_3COO)_2{\cdot}2H_2O$ (99.9%) and $Co(CH_3COO)_2{\cdot}4H_2O$ (99.9%) as starting precursors. A mixture of 2-methoxyethanol and mo-

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noethanolamine (MEA) were selected as the solvent. The concentration of total metal ions in the solution was 0.75 mol/L with the molar ratio $[Zn^{2+}]$:$[Co^{2+}]$ = 95:5. The molar ratio of MEA to metal ions was kept at 1.0. The resulting solution was stirred at 60 °C for 1 hour to yield a clear and transparent sol. The Si and quartz glass substrates were carefully cleaned. Some sol was dropped on the substrate which was rotating at 3000 r/min for 30 seconds. The film was dried at 300 °C for 15 minutes to evaporate the solvent and remove organic residuals after spin coating. The procedure from spin coating to preheating was repeated 8 times until the thickness reached about 300 nm. The film was then transferred into a furnace and postheated at 700 °C for 1 hour under Ar flow. The Co-doped ZnO powders were prepared under exactly the same conditions except for the case that the sol was transferred into an alumina crucible without spin coating.

The structure and crystalline orientation of Co-doped ZnO samples were performed by x-ray diffraction (XRD, D/MAX-2550V) using monochromic Cu $K\alpha$ radiation operated at 40 kV and 100 mA. The crystal morphology and size were observed by field emission scanning electron microscopy (FESEM, JSM-6700F). Room temperature UV–vis absorbance and transmittance spectra were performed by UV–VIS–NIR spectrophotometer (Cary 500). The film was also characterized by soft x-ray absorption spectroscopy (XAS) using synchrotron radiation from beam line U18 at the National Synchrotron Radiation Laboratory in the University of Science and Technology of China. A quantum design superconducting quantum interference device magnetometer (MPMS XL-7) was used to investigate the magnetic properties. The magnetic field dependence of magnetization was investigated at fixed temperatures of 5 K and 300 K. Temperature dependence of the magnetization was measured with an applied magnetic field of 80 kA/m from low temperature to 375 K.

3. Results and discussion

Figure 1 shows the XRD patterns of $Zn_{0.95}Co_{0.05}O$ powder and film. The reflections exclusively show peaks corresponding to ZnO. No trace of cobalt metal, oxides, or binary zinc cobalt phase was detected. Compared with the powder, the film shows a strong (002) peak, which indicates a more preferential c-axis orientation. The FESEM images of the powder and film are illustrated in Fig.2. The crystal size is about 30 − 40 nm for both film and powder samples. The inset in Fig.2(b) shows the cross-sectional image of the film, which clearly revealed the ⟨001⟩ growth orientation. Pure ZnO powder is white. The $Zn_{0.95}Co_{0.05}O$ powder and film have a slight green colour, which are confirmed by the UV-vis spectra as shown in Fig.3. Comparing with the undoped ZnO, we find that the absorption edge of $Zn_{0.95}Co_{0.05}O$ samples has a red-shift, which is due to sp-d exchange interactions between the band electrons and the localized d electrons of Co^{2+} ions.[11] The characteristic absorption peaks around 650, 610 and 560 nm are correlated with the d-d transitions of the tetrahedrally coordinated Co^{2+} ions and attributed to $^4A_2(F) \rightarrow {}^2E(G)$, $^4A_2(F) \rightarrow {}^4T_1(P)$, and $^4A_2(F) \rightarrow {}^2A_1(G)$. The UV-vis results indicate that Co^{2+} ions substituted for Zn^{2+} ions without changing the wurzite structure. Further information about the cobalt state in the samples comes from the XAS analysis as shown in Fig.4. The Co $L_{2,3}$-edge of $Zn_{0.95}Co_{0.05}O$ film and reference Co metal film were measured by soft XAS at room temperature. Comparing with Co film, we find that the CoL_2 and L_3 edges of $Zn_{0.95}Co_{0.05}O$ film have a slight splitting, which indicates that Co ions are mainly in the +2 state and in a tetrahedral symmetry environment.[17] The UV–vis spectra and XAS analyses exclude the possibility of existing Co-metal clusters in the film.

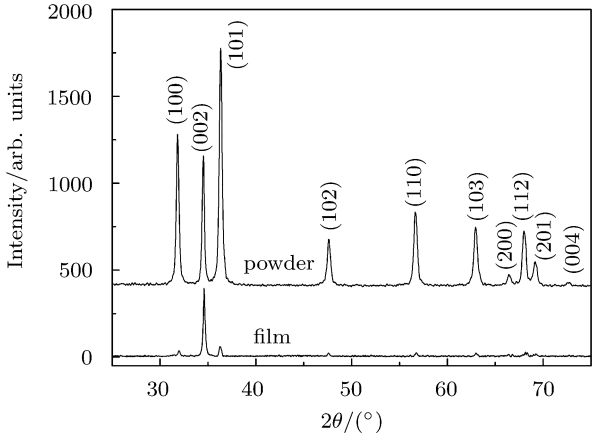


Fig.1. XRD patterns of the $Zn_{0.95}Co_{0.05}O$ powder and film prepared under the same preparation conditions.

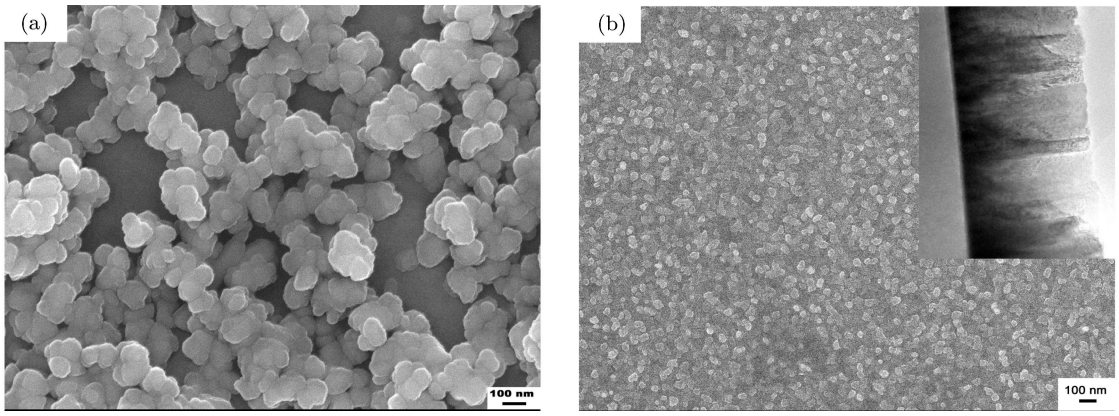


Fig.2. FESEM images of $Zn_{0.95}Co_{0.05}O$ powder (a) and $Zn_{0.95}Co_{0.05}O$ film (b). The inset in (b) shows the cross-sectional view.

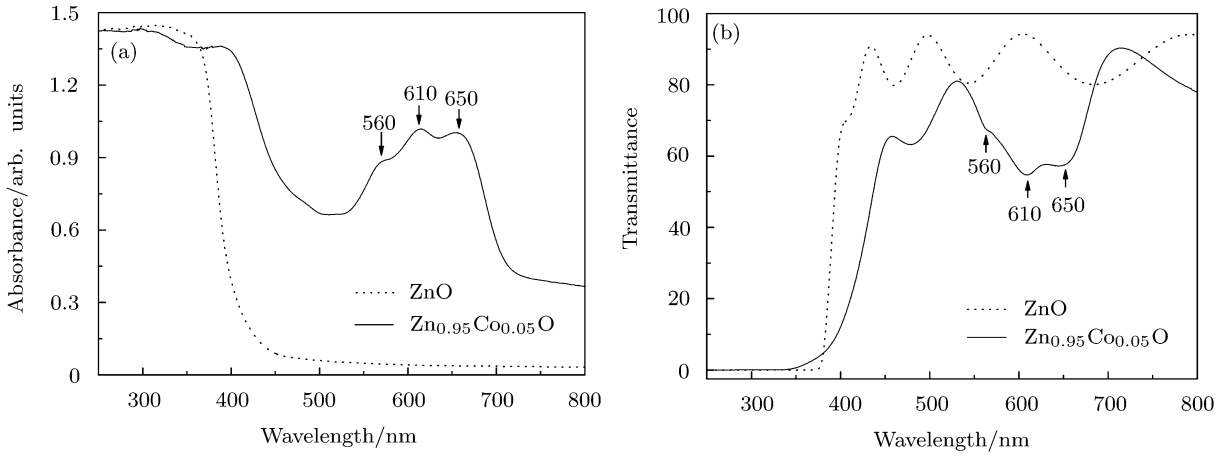


Fig.3. (a) Room temperature UV–Vis absorbance spectra of pure ZnO and $Zn_{0.95}Co_{0.05}O$ powder, (b) Room temperature UV–Vis transmittance spectra of pure ZnO and $Zn_{0.95}Co_{0.05}O$ film.

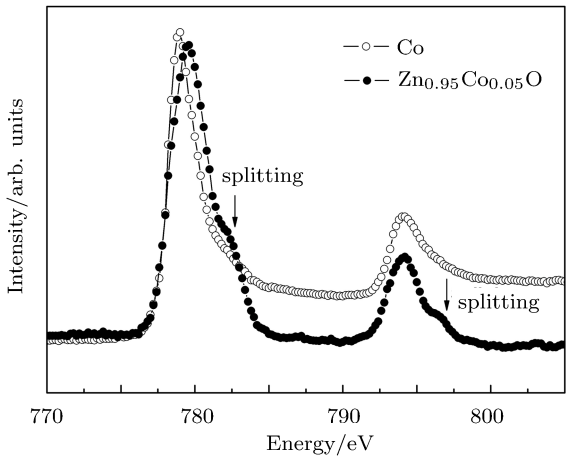


Fig.4. X-ray absorption spectra of Co $L_{2,3}$ edge of $Zn_{0.95}Co_{0.05}O$ and Co film.

Figure 5 shows the magnetic properties of the as-prepared samples. In Fig.5(a), the temperature dependence magnetization ($M-T$) curve was measured from 5 K to 305 K, where a 80 kA/m magnetic field was applied. The magnetization versus magnetic field ($M-H$) curve is given in the insets. The $M-H$ curve exhibits almost linear behaviour except for the samples in the weak fields. The hysteresis loop, with no coercive field (H_c), does not reach saturation magnetization (M_s) even when the applied field increases to 1600 kA/m. Therefore, the dominant interactions between Co^{2+} in the $Zn_{0.95}Co_{0.05}O$ powder are antiferromagnetic coupling.[9−12] It should be emphasized that slight ferromagnetic coupling between some Co^{2+} ions can not be excluded due to the weak field non-linear behaviour. Figures 5(b) and 5(c) show the $M-H$ curves of $Zn_{0.95}Co_{0.05}O$ film at 5 K and 300 K. The contribution from Si substrate as shown in the inset was subtracted from the total magnetization data. The inset in Fig.5(c) displays the $M-T$ curve of $Zn_{0.95}Co_{0.05}O$ film from 5 K to 375 K. Comparing with the powder sample, we can see obvious difference in magnetic properties. $Zn_{0.95}Co_{0.05}O$ film

clearly shows hysteresis loop at 5 K and 300 K, which has the typical ferromagnetic coupling behaviour. The H_c is 12 kA/m at 5 K and it decreases to 4.8 kA/m at room temperature. The $M-T$ curve reveals that the Curie temperature is above 375 K. Recently, Belghazi *et al* found that external pollution was responsible for the observed ferromagnetism in $Zn_{0.9}Co_{0.1}O$ films prepared by sol-gel technique.[18] The external pollution from the substrate or film surface should be excluded. In our experiment, the Si and quartz glass substrates were carefully cleaned. FESEM image does not show any evidence of pollution impurities. Furthermore, energy dispersive x-ray spectroscopy revealed that only Zn, Co and O elements were found in the film (not shown). The films deposited on quartz glass substrates were also found to be ferromagnetic. It can be concluded that the ferromagnetism in $Zn_{0.95}Co_{0.05}O$ film is intrinsic.

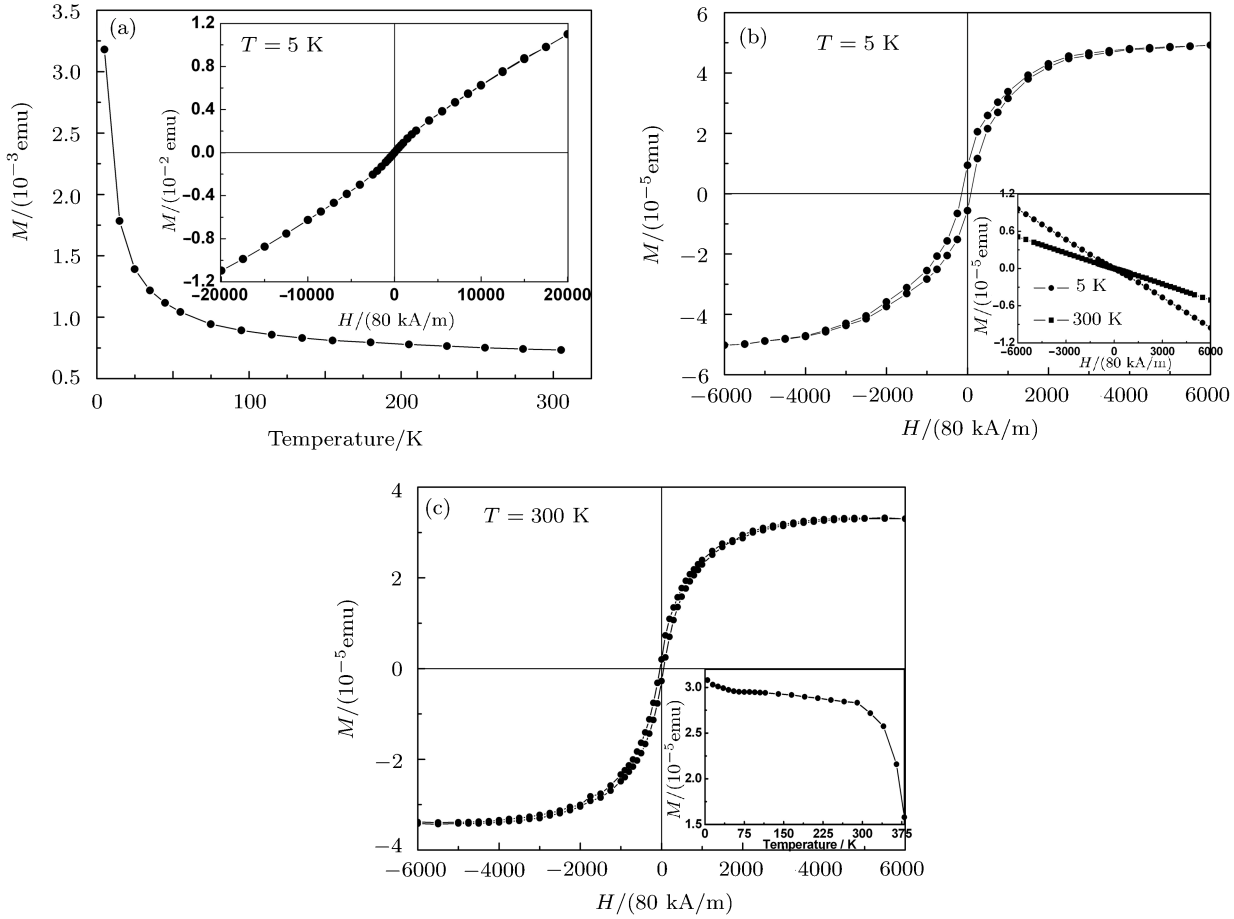


Fig.5. (a) Temperature dependence of magnetization of $Zn_{0.95}Co_{0.05}O$ powder with an applied field of 80 kA/m. The inset shows magnetization hysteresis curve at 5 K. (b) The hysteresis curves of $Zn_{0.95}Co_{0.05}O$ film at 5 K, the inset shows the contribution from Si substrate. (c) The hysteresis curves of $Zn_{0.95}Co_{0.05}O$ at film 300 K, the inset shows the temperature dependence of magnetization with an applied field of 80 kA/m.

Theory predicts that the TM-doped ZnO could obtain ferromagnetism which is mediated by free carriers.[7,8] However, the difference in magnetic properties is obvious between the powder and film in our experiment. It was reported that the intrinsic factors, such as carrier concentration and type, defects, crystal size were critical in determining the interactions between doped TM ions. As discussed above, the same-scale crystal size was observed for the powder and film. The carrier type, doping concentration and defects should be close to each other, since they were prepared under exactly the same conditions. Therefore, the difference in magnetism may come from the crystalline orientation. Sati *et al*[19] reported that the isolated Co^{2+} in ZnO possessed a strong single ion anisotropy which led to an 'easy plane' ferromagnetic state. Rode[13] reported that the out-of-plane was the easy magnetization axis in Co-doped ZnO films. In order

to investigate the role of crystalline orientation, a factor $f_{\rm R} = I_{(002)}/I_{\rm total}$ is defined to describe the (002) preferential orientation, where $I_{(002)}$ is the intensity of the (002) reflection peak, $I_{(\rm total)}$ is the total intensities of all peaks from 25 ° to 75 °. It has been found that the structural orientation plays an important role on the magnetic properties due to the difference in magnetocrystalline anisotropy.[20,21] Crystalline orientation can affect the exchange anisotropy of ferromagnetism/antiferromagnetism (FM/AFM) in the most conventional magnetic materials. Phenomenologically, the magnetic energy of an isolated magnetic domain can be described as

$$E = E_0 + MH\cos\theta,$$

where E_0 is the energy of spontaneous magnetization, which can be described as $E_0 = E_{\rm V} + E_{\rm S}/D + E_{\rm R}/f_{\rm R}$. $E_{\rm V}$, $E_{\rm S}$ and $E_{\rm R}$ are the summed energy contributed from volume, surface and orientation in the spontaneous magnetization respectively, D is the domain size. $MH\cos\theta$ is the energy due to the external magnetic field. M is the magnetization, H is the external field, and θ is the angle of H to spontaneous magnetization direction.[22–24] In our experiment, the $f_{\rm R}$ values are 0.2 and 0.8 for the powder and film respectively. From above equation, we can conclude that the film sample with well orientation tends to minimize the magnetostatic energy in the process of spontaneous magnetization. That means ferromagnetic couplings can be easily realized in the films. The ferromagnetism in DMSs was mediated by enough carriers and doped magnetic ions. It does not mean that the ferromagnetism could be obtained in all the TM-doped ZnO films. In our experiment, all the films are n-type with the electron concentration above $10^{19}{\rm cm}^{-3}$. The crystalline orientation can give some evidences why most Co-doped ZnO powders show absence of ferromagnetism and most corresponding films with (002) preferential orientation ($f_R \approx 1$) exhibit ferromagnetic behaviour. We have prepared $Zn_{1-x}Co_xO$ ($x = 0.05, 0.1, 0.15$) films by using inductively coupled plasma enhanced physical vapour deposition method. The films were deposited on Si (100) substrate by sputtering $Zn_{1-x}Co_xO$ targets which were synthesized by the standard solid-state reaction. The $Zn_{1-x}Co_xO$ targets show paramagnetic behaviour, while the as-deposited films behave ferromagnetism even above room temperature.[25,26] Difference in magnetic properties between bulk and films was also found by other research groups.[11,12,14,15] The dependence of ferromagnetic interaction on crystalline orientation was reported in Mn-doped GaAs.[22,27] It was found that the constructed directions of Mn–Mn pairs had different splitting along different directions and the Mn–Mn interactions are highly anisotropic. Similarly, the ferromagnetic ordering state may induce spin anisotropy with an easy axis along $\langle 001\rangle$ direction in Co-doped ZnO system, which tends to align the doped magnetic moments to minimize magnetostatic energy. A detailed study is in progress.

4. Conclusions

In summary, we have characterized $Zn_{0.95}Co_{0.05}O$ powder and film prepared by sol-gel technique under exactly the same conditions. The analyses of XRD, UV–Vis and XAS indicate that Co^{2+} ions substitute homogeneously for Zn^{2+} ions without changing the wurzite structure. $Zn_{0.95}Co_{0.05}O$ powder does not show typical ferromagnetic behaviour, whereas the corresponding film exhibits ferromagnetic properties at 5 K and room temperature. The remarkable difference in magnetic properties might come from the crystalline orientation, which affects the interactions between doped Co ions.

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