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Comparative studies on $Zn_{0.95}Co_{0.05}O$ thin films on C- and R-sapphire substrates

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$Zn_{0.95}Co_{0.05}O$ precipitate-free single crystal thin films were synthesized by a dual beam pulsed laser deposition method. The films form a wurtzite structure whose hexagonal axis is perpendicular or parallel to the plane of the surface depending on the C-plane (0001) or R-plane ($11\bar{2}0$) sapphire substrate. Based on the results of high-resolution transmission electron microscopy and x-ray diffraction, C-plane films show larger lattice mismatch. The films exhibit magnetic and semiconductor properties at room temperature. The coercivity of the film is about 8000 A/m at room temperature. They are soft magnetic materials with small remanent squareness S for both crystal orientations. There is no evidence to show that the anisotropy is fixed to the hexagonal axis (C-axis) for the wurtzite structure.

Keywords: Co-doped ZnO thin films, diluted magnetic semiconductor, anisotropy
PACC: 7530G, 6150C, 7360F

1. Introduction

Diluted magnetic semiconductors (DMSs) are potential candidates as new functional materials for future electronics, the so-called 'spintronics'. At the end of the last century, they attracted much interest as materials with both charge and spin degrees of freedom.[1−4] But the applications are feasible only if the materials have ferromagnetic and semiconductor properties at or above room temperature to avoid impractical refrigeration. It is well known that DMSs based on transition metal doped-II–VI semiconductors, such as ZnO based DMSs, are predicted to have Curie temperatures that can be raised above 300 K.[5] Hence, such materials are potential candidates as room temperature ferromagnetic semiconductors for spintronics applications.[6] There have been many studies on this kind of materials since then.[7−9] However, there is no consensus on the origin of magnetism for ZnO-based DMSs, especially for Co-doped ZnO. Understanding the mechanism is one of the most important topics in this area.[10−12,8]

When considering magnetic phenomena in ferromagnetism, behaviours related to ferromagnetic order are generally studied, such as anisotropy and the origin of domain.[13] To study a DMS system, an understanding of magnetic anisotropy is also important.[14] For example, reference [15] studied the influence of magnetic anisotropy to indicate the role of the carrier concentration in the DMS system of (Ga,Mn)As so as to discover the carrier-induced magnetism.

Many techniques have been used to synthesize epitaxial and textured doped ZnO films, including pulsed-laser deposition, molecular beam epitaxy and sputtering. Dual beam pulsed laser deposition (DB-PLD) has also been reported recently as an alternative way for rapid combinatorial study of new material synthesis.[16,17] Based on the orientation of the substrate directly governing the orientation of the easy axis (EA) in films,[18] we fabricated films with the C-axis perpendicular and parallel to the substrate surfaces on different sapphire substrates, and compared the magnetic and electrical properties for the two kinds of thin films. As matching in crystal lattice between the film and the substrate affects the growth behaviours of the films,[19] strains induced in different kinds of films will also be discussed. The purpose of this study is to investigate the effect of orientation and strain in the films on their properties. According to our experimental results, we have verified that there is no evidence to show that the anisotropy is fixed to the hexagonal axis (C-axis) for the wurtzite structure.

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2. Experimental

Co-doped ZnO thin films were grown on (0001) sapphire (C-plane) and (11$\bar{2}$0) sapphire (R-plane) substrates using the DBPLD method. The details of the DBPLD system setup have been reported elsewhere.[17,20,21] A KrF excimer laser (248 nm, 10 Hz) was used in our experiments. Films were grown on sapphire substrates at 650 °C under a pressure of 6.8×10^{-3} Pa. The room temperature M–H curves were obtained by an alternating gradient magnetometer (AGM) (2900 Micromag^{TM}) with the magnetic field applied parallel to and perpendicular to the film planes at room temperature. A Hall effect system (Lakeshore 7500) was used to measure the film conductivity and carrier density with a Van der Pauw configuration at room temperature. To characterize the film composition, x-ray photoelectron spectrometry (XPS) was performed by a Quantum 2000 scanning microprobe system. The sample was analysed by x-ray diffraction (Phylips, X'PERT-MRD) to identify different crystal planes in the film. Detailed lattice structure and possible precipitates were obtained by high-resolution transmission electron microscopy (HRTEM) of the model of JEM 2010F HRTEM.

3. Results and discussion

Figure 1 shows XRD images of the $Zn_{0.95}Co_{0.05}O$ thin films. The film grown on C-plane sapphire substrate is of a wurtzite structure whose C-axis is parallel to that of the substrate (Fig.1(a)). The lattice parameters of the film were determined to be $c = 0.5207$ nm, a little larger than the reported values for ZnO.[22] In contrast, figure 1(b) gives an XRD pattern for the $Zn_{1-x}Co_xO$ ($x = 0.05$) film grown on R-plane substrate. Diffraction peaks corresponding to the (11$\bar{2}$0) plane of $Zn_{1-x}Co_xO$ thin film, and the (10$\bar{1}\bar{2}$), (20$\bar{2}\bar{4}$) and (30$\bar{3}\bar{6}$) planes of Al_2O_3 were clearly observed. No peaks of other planes were detected by XRD. It is shown to be also of wurtzite structure with the film (11$\bar{2}$0) plane aligned with the substrate (10$\bar{1}\bar{2}$) planes. The (11$\bar{2}$0) peak of the $Zn_{1-x}Co_xO$ is located at 56.57°. Insets of Fig.1 show Co 2p3/2 XPS spectra for the films grown on C- and R-plane sapphire substrates. From the shape of the spectra and position of the peaks, in both cases, only Co–O bonding exists in the films. These results suggest that Co has replaced Zn, and Co–O bonding exists in the host lattice. Our HRTEM results also show clearly the lattice of the films without obvious precipitates, which will be discussed later (Fig.3). The detailed crystal structures have also been discussed in our previous paper, Ref.[20]. Based on all these results, it is reasonable to consider that this material is a single compound with the replacement of Zn by Co.

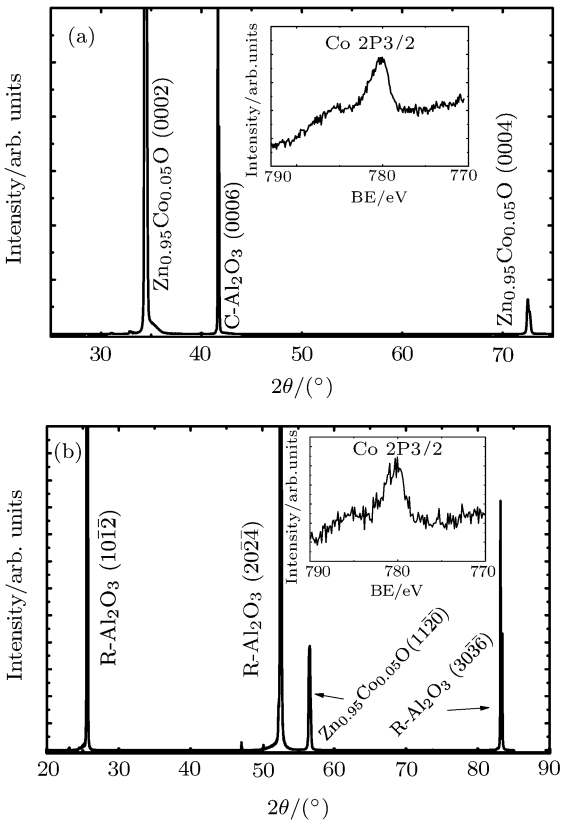


Fig.1. X-ray diffraction patterns of $Zn_{0.95}Co_{0.05}O$ thin films grown on (a) C-plane substrate and (b) R-plane substrate, respectively. Insets show the corresponding XPS spectra of Co 2P3/2.

Figure 2 shows x-ray rocking curves of the thin films. The curves were taken from the diffraction peaks at 34.44° for C-plane and 56.57° for R-plane substrates. The $FWHM$ is 0.18° for C-plane and 0.37° for R-plane sapphire substrates. It indicates that the film grown on C-plane substrate has a more concentrated crystalline orientation. In our view this is due to the higher surface energy of the {0001} facet of ZnO grown on sapphire substrate.

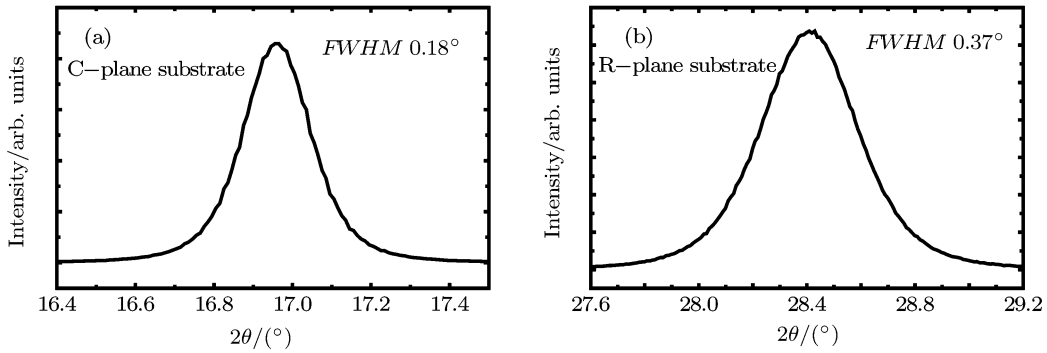


Fig.2. X-ray rocking curves of $Zn_{0.95}Co_{0.05}O$ thin films grown on (a) C-plane substrate and (b) R-plane substrate.

Figure 3 shows HRTEM images of the $Zn_{0.95}Co_{0.05}O$ thin film–substrate interface. In Fig.3(a), the interface between the film and C-plane substrate is found to be smooth and clear. The micrographs show well ordered lattice planes with few defects. There are no precipitates observed. From these images, the epitaxial relationship between the film (f) and substrate (s) was determined to be $(0001)_f//(0001)_s$ and $(10\bar{1}0)_f//(11\bar{2}0)_s$, which agrees well with the XRD results.

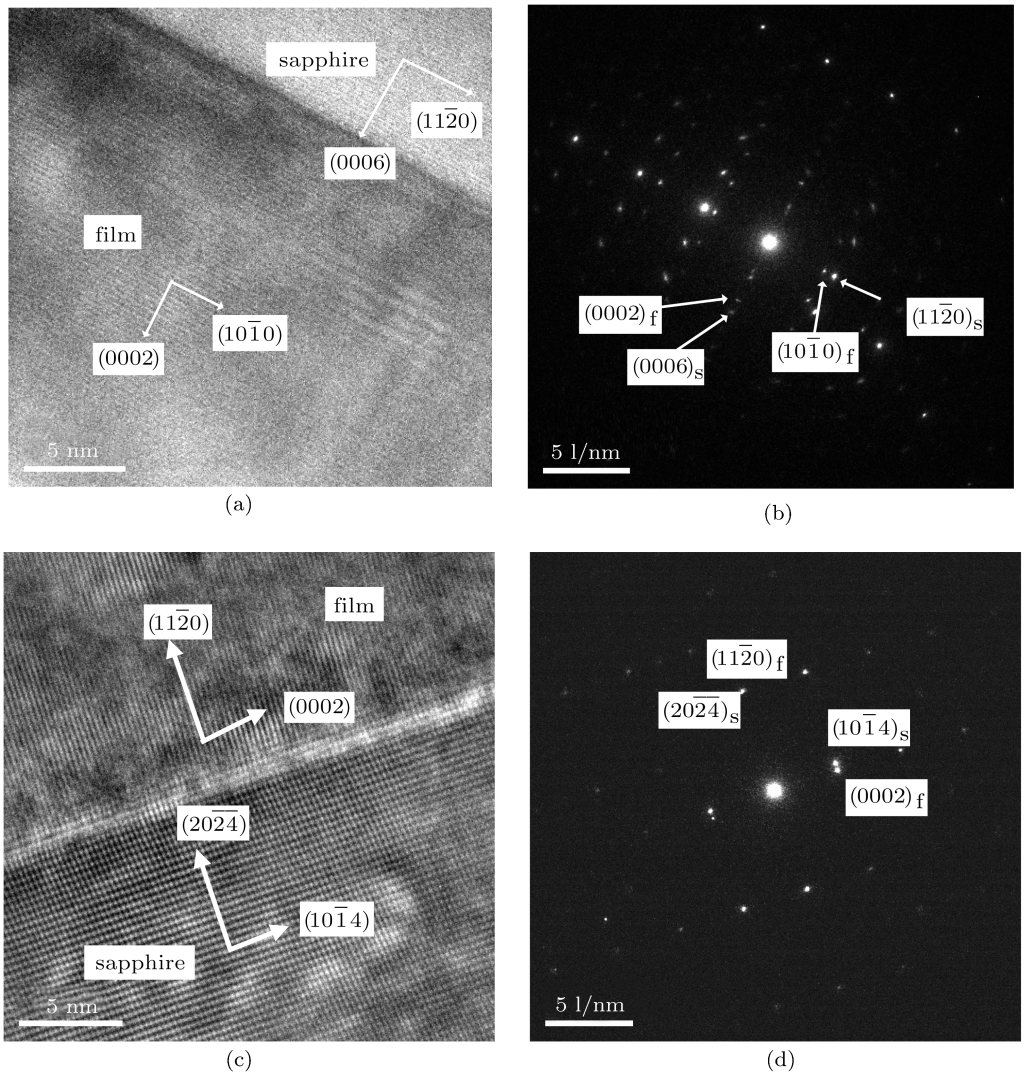


Fig.3. HRTEM images for $Zn_{0.95}Co_{0.05}O$ films on C-plane substrates, (a) showing film, substrate and interface orientations, (b) electron diffraction pattern taken on the interface; R-plane substrates (c) showing film, substrate and interface orientations, (d) electron diffraction pattern taken on the interface.

In Fig.3(c), for those grown on R-plane sapphire substrate, the micrographs also show well ordered lattice planes with few defects. There are also no precipitates observed. Although the interface between the $Zn_{0.95}Co_{0.05}O$ thin film and R-plane sapphire substrate is found to be clear, and the $(11\bar{2}0)$ plane of the film is parallel to the $(10\bar{1}\bar{2})$ plane of the substrate, the lattice (0002) plane of the film is observed to be tilted with respect to the substrate $(10\bar{1}4)$ plane. This tilt can be observed more clearly in Fig.3(d). The tilt angle φ_1 is 6°. From TEM diffractions and imaging studies, the relationship between the film (f) and substrate (s) was determined to be as follows: $(11\bar{2}0)_f//(10\bar{1}\bar{2})_s$, with an angle φ_1 of 6° between $(0002)_f$ and $(10\bar{1}4)_s$. To determine the direction of the C-axis of the $Zn_{0.95}Co_{0.05}O$ relative to the R-plane substrate, we calculate the angle φ_2 by the crystallographic relationship. We have $\cos\varphi_2 = \dfrac{G_{20\bar{2}\bar{4}} \bullet G_{10\bar{1}4}}{|G_{20\bar{2}\bar{4}}|\,|G_{10\bar{1}4}|}$, where G is the reciprocal lattice vector, and φ_2 the angle between $G_{20\bar{2}\bar{4}}$ and $G_{10\bar{1}4}$. Using the lattice parameters of the film and substrate, we have φ_2=84°. Hence the relationship $\varphi_1 + \varphi_2 = 90°$ holds. The C-axis of the film lies in the surface plane. The tilt angle between $(0002)_f$ and $(10\bar{1}4)_s$ results in a larger FWHM of the rocking curves for the $Zn_{0.95}Co_{0.05}O$ thin film grown on R-plane substrate. From the lattice mismatching geometry shown in Fig.3, we calculate the lattice mismatch of the $Zn_{0.95}Co_{0.05}O$ thin films grown on C-plane substrate to be 18%, and on R-plane substrate 5%.

Figure 4 shows the M–H loops of the $Zn_{0.95}Co_{0.05}O$ thin films grown on C- and R-plane sapphire substrates. The coercivity H_c is about 8000 A/m. This result indicates that in both cases they are magnetic at room temperature. However, different M–H loops can be obtained under different experimental conditions, as shown in Fig.4. From Fig.4(a), for the film grown on the C-plane sapphire substrate, remanent squareness S is about 0.056 when the applied magnetic field H is perpendicular to the C-axis of the film, and 0.041 when H is parallel to the C-axis. For the R-plane substrate, S is about 0.107 when H is perpendicular to $[11\bar{2}0]$ of the film and 0.066 in the case with H perpendicular to C-axis. S is small for both R-plane and C-plane substrates. The M–H loops obtained in plane always show more squareness than those obtained out of plane, no matter whether the hexagonal axis is perpendicular or parallel to the film surface. There is no evidence that the anisotropy is fixed to the hexagonal axis (C-axis) for the wurtzite structure.

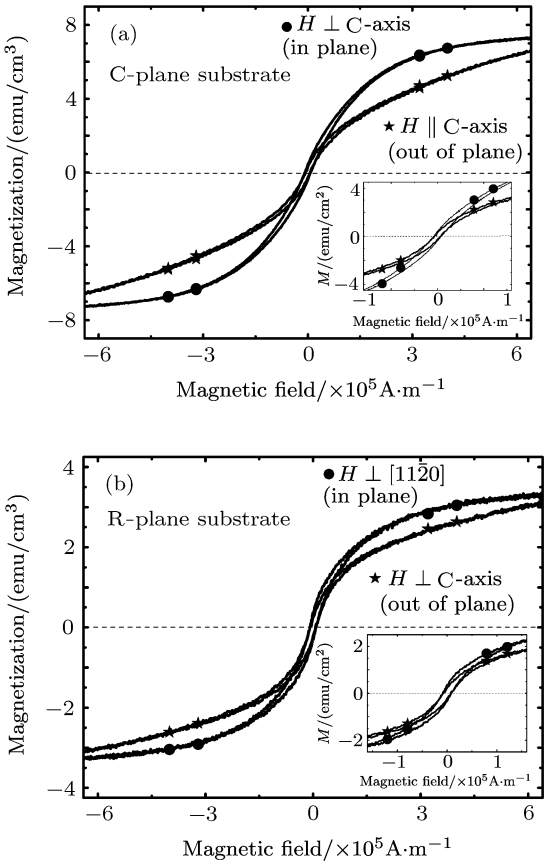


Fig.4. Hysteresis loops for $Zn_{0.95}Co_{0.05}O$ films grown on (a) C-plane and (b) R-plane sapphire substrates. The data are those taken at room temperature with the external field both in plane and out of plane of the films. Insets show enlarged images of the loops.

Electrical transport properties of the $Zn_{0.95}Co_{0.05}O$ thin films grown on C- and R-plane sapphire substrates at room temperature from the Hall measurements are presented in Table 1, from which we can see that both of the films are n-type semiconductors. The carrier concentration is about 6×10^{17} cm^{-3} with a resistivity of 500 mΩ·cm for the films grown on C-plane sapphire substrates; the carrier concentration is about 7×10^{18} cm^{-3} with a resistivity of 100 mΩ·cm for the films grown on R-plane sapphire substrates. The former shows a larger Hall resistivity and a lower carrier density. The different electrical transport properties between the two specimens may be related to the strain in the films.

Table 1. Resistivity and carrier density of the specimens grown on different planes of the substrates.

sample	type	resistivity/mΩ·cm	carrier density/cm^{-3}
C-plane substrate	n	500	6×10^{17}
R-plane substrate	n	100	7×10^{18}

An effect of mechanical stress on the electrical resistance of a conducting crystal has been reported,[23] in which electrical resistance is related to the orientation of the crystal and the strain produced by stress. The change in resistance of the crystals was explained by a theory of the change in resistance produced by stress developed by Bridgman.[23] In his theory the change in resistance due to the strain is related to the stress on the basis of crystal symmetry. Electrical properties is affected by the orientation of the crystal and the strain produced by stress. To our understanding, the different orientations and strains in the films grown on C- and R-plane substrates may also lead to the different Hall resistivities. Under our experimental conditions, the C-axis of the film grown on the C-plane substrate is perpendicular to the surface; while the C-axis of the film grown on R-plane substrate lies in the surface plane. Therefore the Hall current must be associated with electrons jumping in the plane which is perpendicular to the C-axis for the film grown on C-plane sapphire substrate, while they are in the plane in which the C-axis lies for the R-plane substrate. In addition, the mismatch for $Zn_{1-x}Co_xO/Al_2O_3$ in the R-plane sapphire system is smaller than that in the C-plane sapphire system. The higher degree of lattice mismatch may cause the mismatch dislocations, and thus the strain in the film may be partially relaxed, which has been found in p-type (In,Mn)As films.[24] Furthermore, the possible defects involved in the films may also affect the electrical properties. Generally speaking, defects involved in the films will lead to carrier scattering, hence resulting in lower carrier density and higher resistivity. Based on our experimental results, the $Zn_{0.95}Co_{0.05}O$ thin film grown on C-plane sapphire substrate shows higher Hall resistivity though it has a smaller value of $FWHM$ in the x-ray rocking curve, which suggests a better quality of the film compared with that grown on R-plane sapphire substrate.

4. Conclusion

$Zn_{0.95}Co_{0.05}O$ thin films with the C-axis perpendicular to and along the film plane have been fabricated successfully using the DBPLD method. Both types of films have wurtzite single crystal structure. The thin-film C-axis is perpendicular to the film plane for samples grown on C-plane substrates, and lies in the film plane for samples grown on R-plane substrates. The lattice mismatch of the $Zn_{0.95}Co_{0.05}O$ thin films grown on C-plane substrates is larger than that grown on R-plane substrates. The films have magnetic M–H loops and semiconductor properties at room temperature. They are soft magnetic materials with small remanent squareness for both film orientations. There is no evidence that the anisotropy is fixed to the hexagonal axis (C-axis) for the wurtzite structure. They are both n-type semiconductors. Under our experimental conditions, there are some differences between the electrical transport properties for the films grown on C- and R-plane substrates.

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