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The origin of room temperature ferromagnetism in cobalt-doped zinc oxide thin films fabricated by PLD

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Abstract

We have fabricated $Zn_{0.75}Co_{0.25}O$ thin films on sapphire (0001) substrates at different substrate temperatures (400–700 °C) in a fixed O_2 pressure of 1×10^{-5} Torr using pulsed laser deposition technique and investigated their structural and magnetic properties in relation to the growth conditions. X-ray diffraction and transmission electron microscopy observations have revealed that hexagonal Co clusters are present in the films grown at 700 °C. At relatively low temperatures (400–600 °C), homogeneous alloy films of wurtzite structure are formed with an epitaxial relationship of $(0001)_{ZnCoO}||(0001)_{sap}$ and $[01\bar{1}0]_{ZnCoO}||[\bar{1}2\bar{1}0]_{sap}$, which is the same as that for ZnO grown on (0001) sapphire. Observed results of the structural and magnetic properties collectively imply that the presence of the ferromagnetic Co clusters leads to ferromagnetism in Co-doped ZnO films.

Keywords: Electron microscopy; Films; Magnetic properties; X-ray methods; ZnO

1. Introduction

Diluted magnetic semiconductors (DMSs), referred to semiconductor alloys in which magnetic atoms are introduced in the lattice, have attracted considerable recent attention as promising materials in the rapidly evolving area of spintronics since they have charge and spin degree of freedom in a single substance.[1] Most recent efforts have focused on III–Mn–V compound semiconductors such as $Ga_{1-x}Mn_xAs$ (Ref. 1) and $In_{1-x}Mn_xAs$,[2] which are *p*-type and exhibit ferromagnetic ordering. However, their low Curie temperatures, whose reported maximum is 110 K for $x=0.053$ in $Ga_{1-x}Mn_xAs$, have hindered practical applications using DMSs. Although ferromagnetic ordering in these materials is commonly believed to be induced by carrier-mediated interactions between the magnetic atoms, the precise underlying mechanism is still to be clarified.[3–5]

Currently, in the oxide-DMS family, ZnO-based DMSs have been of great interest because of some theoretical predictions of room temperature ferromagnetism.[4,5] Fukumura et al.[6] reported the first successful growth of a ZnO-based DMS by pulsed laser deposition (PLD) technique, namely $Zn_{1-x}Mn_xO$, which was found to exhibit no ferromagnetic ordering.[7,8] While Jin et al.[8] detected no indication of ferromagnetism in $Zn_{1-x}Co_xO$ films, Ueda et al.[9] observed ferromagnetic features with a Curie temperature as high as 300 K in some of pulsed laser-deposited $Zn_{1-x}Co_xO$ films, although the reproducibility was less than 10%. These controversial results raise questions about the origin and the intrinsic nature of ferromagnetism in Co-doped ZnO. In this work, we examine structural and magnetic properties of pulsed laser-deposited $Zn_{0.75}Co_{0.25}O$ films to suggest that the presence of ferromagnetic hexagonal Co clusters leads to room temperature ferromagnetism in Co-doped ZnO.

2. Experimental

$Zn_{1-x}Co_xO$ (ZnCoO) thin films with $x=0.25$ and the thickness of ~200 nm were fabricated by pulsed laser deposition (PLD) on sapphire (0001) substrates at various substrate temperatures (400–700 °C) in an oxygen gas pressure of 1×10^{-5} Torr, using sintered targets synthesized by standard solid-state reaction method. No intentional carrier doping was used. The chamber was evacuated by a turbomolecular pump to a base pressure 1×10^{-6} Torr. The targets were ablated by KrF excimer laser pulses ($\lambda=248$ nm, 5 Hz) with a laser energy

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density of 1.5 J/cm^2. The target-substrate distance was fixed at 4 cm.

The Co concentration in the films was determined by electron-probe microanalysis. The crystalline structure and the microstructural morphology were examined by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The conventional θ–2θ scan was conducted on a Rigaku X-ray diffractometer using Cu K_α radiation. The X-ray rocking curve was measured on a high resolution X-ray diffractometer. Thin specimens for conventional TEM and high resolution TEM investigations were obtained by mechanically polishing, dimple grinding, and ion milling. Conventional TEM observations were performed with a Philips CM20 and high resolution TEM observations were carried out using a F20 Technai equipped with field emission gun. Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) with the magnetic field applied parallel to the film surface.

3. Results and discussion

Fig. 1 shows the XRD θ–2θ angular scans of the $Zn_{0.75}Co_{0.25}O$ films fabricated on sapphire (0001) substrates at different substrate temperatures (400–700 °C) in a fixed O_2 pressure of 1×10^{-5} Torr. All the intense peaks are indexed assuming the same hexagonal wurtzite structure as pure ZnO without Co impurities. As seen in Fig. 1, homogeneous alloy ZnCoO films are grown for relatively low substrate temperatures ($\leqslant$600 °C), whereas heterogeneous structures with wurtzite ZnCoO plus rock-salt CoO plus hexagonal Co are formed when the substrate temperature is relatively high. This result illustrates that the solubility of Co ions in ZnO depends on the growth condition. The XRD patterns clearly shows only {000l} family of planes of wurtzite ZnCoO and sapphire, indicating a high degree of texturing along [0001] normal to the substrate, i.e. $(0001)_{ZnCoO}||(0001)_{sap}$.

The mosaicity of the films was determined by XRD rocking curve measurements on the (0002) ZnCoO peak. The obtained result for the variation of the XRD rocking-curve full width at half maximum (FWHM) with the substrate temperature in a fixed O_2 pressure of 1×10^{-5} Torr was plotted in Fig. 2, along with that for d-spacing of $(0002)_{ZnCoO}$. It can be seen that the FWHM for the $Zn_{0.75}Co_{0.25}O$ films is weakly dependent on the substrate temperature in the range of 400–600 °C and is lower than 0.15°, implying the high crystallinity of the laser-deposited ZnCoO films, while it is worse ($\sim$0.33) for the film grown at an substrate temperature of 700 °C. The best rocking-curve FWHM was 0.035° for the $Zn_{0.75}Co_{0.25}O$ film grown at 600 °C, almost half of that (0.069)[10] for the best ZnO film deposited by PLD. The (0002) d-spacing decreases slightly with the increase of substrate temperature up to 600 °C and rapidly drop at a substrate temperature of 700 °C. We attribute this sudden drop in (0002) d-spacing to the reduction of the Co concentration in the wurtzite ZnCoO phase due to the Co cluster formation and the segregation of CoO in the film, as shown in Fig. 1. A linear increase of the (0002) d-spacing for ZnCoO with the increase of the Co concentration was previously observed.[9] We relate the slight decrease in the (0002) d-spacing observed in the homogeneous growth region to the improvement of crystalline quality with the increase of the substrate temperature. The films deposited at 300 °C showed large hexagonal shaped flakes on the surface and those grown at 700 °C exhibited very porous and rough surface, according to SEM observations of the film microstructure.

To determine the in-plane epitaxy, pole figures were registered for the ZnCoO (10$\bar{1}$1) directions along with ϕ

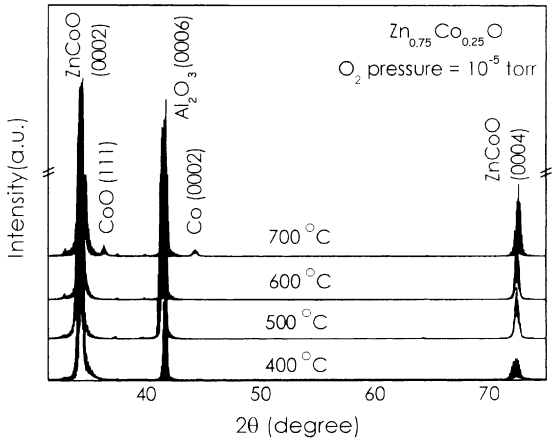

Fig. 1. X-ray diffraction θ–2θ scans of pulsed laser-deposited $Zn_{0.75}Co_{0.25}O$ films at different substrate temperatures (400–700 °C) in a fixed O_2 pressure of 1×10^{-5} Torr.

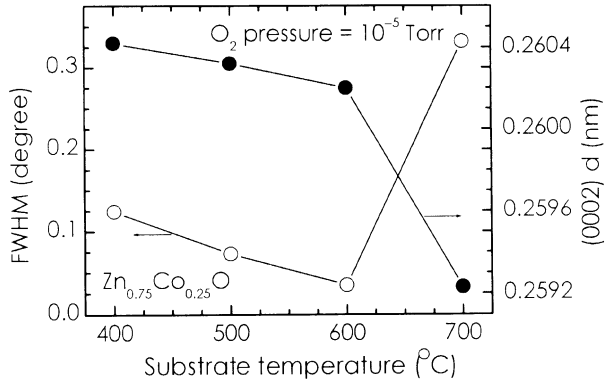

Fig. 2. Variations of the d-spacing and the full width at half maximum (FWHM) of the X-ray rocking curve of the wurtzite (0002) plane for laser-deposited $Zn_{0.75}Co_{0.25}O$ with the substrate temperature.

scans of $\{10\bar{1}1\}$ peaks with ϕ rotation axis parallel to the c-axis of the film and TEM investigations of the ZnCoO/sapphire interface. A ZnCoO $(10\bar{1}1)$ pole figure of the $Zn_{0.75}Co_{0.25}O$ film grown at 600 °C in an O_2 pressure of 1×10^{-5} Torr is shown in Fig. 3. It can be seen that the films are characterized by an expected six-fold symmetry of an epitaxial hexagonal layer. Only six peaks with a 60° separation were also observed in the ϕ scans of $\{10\bar{1}1\}$ peaks.

Fig. 4 shows a cross-sectional high-resolution TEM lattice image of a $Zn_{0.75}Co_{0.25}O$/sapphire interface in ZnCoO $[1\bar{1}00]$ zone with the $Zn_{0.75}Co_{0.25}O$ film grown at 600 °C. The selected area diffraction (SAD) pattern from an area containing both the film and substrate is also shown in Fig. 4. It is clear from Fig. 4 that the $Zn_{0.75}Co_{0.25}O$/sapphire interface is quite sharp without any indication of interdiffusion. From the SAD pattern, the epitaxial relationship between the film and the substrate was found to be $(0001)_{ZnCoO}||\ (0001)_{sap}$, $[\bar{1}2\bar{1}0]_{ZnCoO}||\ [01\bar{1}0]_{sap}$, $[01\bar{1}0]_{ZnCoO}||\ [12\bar{1}0]_{sap}$. This relationship corresponds to a 30° in-plane rotation of the ZnCoO basal planes with respect to the sapphire substrate in (0001) plane, which is the same as the epitaxial growth characteristics of ZnO and group III-nitrides on sapphire (0001) substrates.[11,12]

A cross-sectional TEM image taken from a heterogeneous $Zn_{0.75}Co_{0.25}O$ film grown at a substrate temperature of 700 °C is shown in Fig. 5(a). High-resolution image of a Co particle in ZnCoO near the film surface is presented in Fig. 5(b). The TEM image in Fig. 5(a) demonstrates threading dislocations almost perpendicular to the interface between the film and the sapphire substrate. The film surface is seen to be quite rough. TEM energy-dispersive spectrometer (EDS) analysis presented in Fig. 5(a) obviously illustrates a higher Co concentration on the interface and the film surface compared to the middle area of the film.

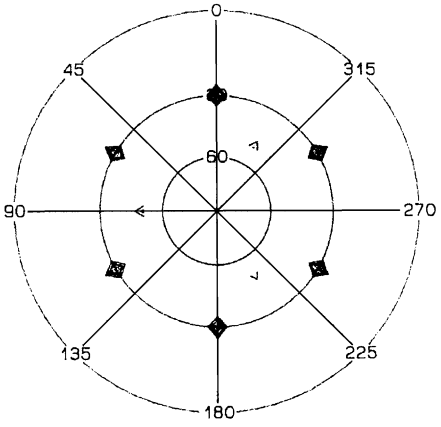

Fig. 3. ZnCoO $(10\bar{1}1)$ pole figure of a $Zn_{0.75}Co_{0.25}O$ film laser-deposited on sapphire (0001) at a substrate temperature of 600 °C in an O_2 pressure of 1×10^{-5} Torr.

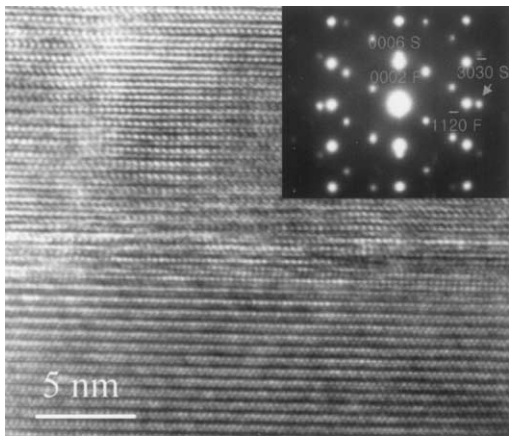

Fig. 4. High resolution TEM cross-sectional image of a $Zn_{0.75}Co_{0.25}O$ near the film/sapphire substrate interface in ZnCoO $[1\bar{1}00]$ zone. The $Zn_{0.75}Co_{0.25}O$ film was grown at a substrate temperature of 600 °C in an O_2 pressure of 1×10^{-5} Torr. Inset: Selected area diffraction (SAD) pattern from an area containing both the film (F) and sapphire substrate (S).

Especially, the Co content near the film surface is found to be much higher than that of ceramic target, in which the ratio of Zn and Co is 75:25. It is thus concluded in combination with XRD results that Co clustering and CoO segregation in heterogeneous ZnCoO film occurs mainly near the film surface and the film/substrate interface. The size of the observed Co clusters was several tens of nanometer, as seen in Fig. 5(b).

We now discuss the magnetic properties of the homogeneous ZnCoO films and the heterogeneous films. Typical magnetization (M) versus temperature (T) curves for the homogeneous and heterogeneous $Zn_{0.75}Co_{0.25}O$ films are presented in Fig. 6(a) and Fig. 6(b), respectively. The M–T curves were recorded during cooling from 300 K in a field of 10 kOe with the diamagnetic contribution of the sapphire substrate subtracted. The magnetization for the homogeneous film in Fig. 6(a) exhibits a slight increase from 300 to 100 K, followed by a steep increase below 50 K, corresponding to a typical paramagnetic (PM) behavior. In contrast, the magnetization curve for the inhomogeneous film in Fig. 6(b) can be well understood by a superimposed curve of the contributions from the PM ZnCoO matrix and the ferromagnetic Co precipitates, as in the case of $Zn_{1-x}Mn_xAs_2$ DMS containing ferromagnetic MnAs clusters.[13] We note the difference in the scale of magnetization in Figs. 6(a) and (b). A sizable magnetization for the heterogeneous film, exhibiting little T-dependence up to 300 K, is attributed to the Co clusters, while a slight increase in M below 50 K is due to the minor contribution from the PM ZnCoO phase. The Curie temperature of the hexagonal Co is known to be as high as 1304 K.[14] The above discussion points out that the presence of the Co clusters leads to room temperature ferromagnetism in ZnCoO.

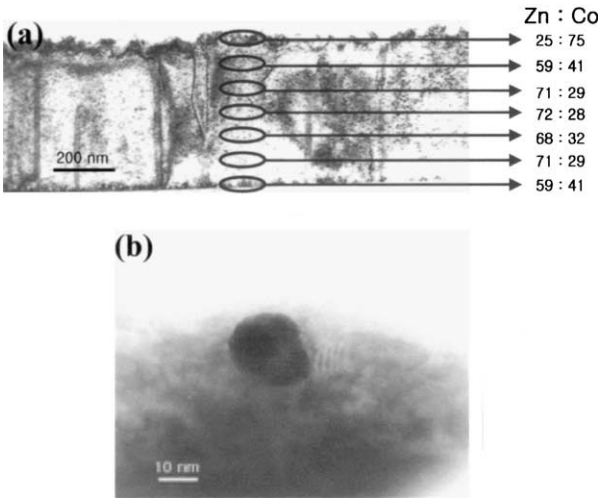

Fig. 5. (a) Cross-sectional TEM image of a $Zn_{0.75}Co_{0.25}O$ film laser-deposited on sapphire (0001) at a substrate temperature of 700 °C in an O_2 pressure of 1×10^{-5} Torr. The arrows indicate the composition ratio of Zn and Co analyzed by EDS at different points. (b) High resolution TEM image near the film surface, showing a Co cluster.

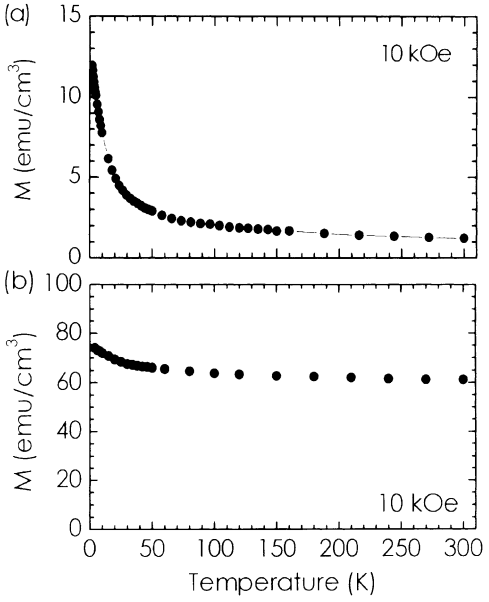

Fig. 6. Magnetization versus temperature curves for laser-deposited $Zn_{0.75}Co_{0.25}O$ films at substrate temperatures of 600 °C (a) and 700 °C (b) in an O_2 pressure of 1×10^{-5} Torr.

4. Conclusion

We have examined the structural and magnetic properties of the pulsed laser-deposited $Zn_{0.75}Co_{0.25}O$ films to elucidate the origin and the nature of ferromagnetism in Co-doped ZnO. The solubility of the Co ions in ZnO depends on the growth condition. For a fixed O_2 pressure of 1×10^{-5} Torr, homogeneous alloy ZnCoO films are grown at low temperatures ($\leqslant$600 °C), while heterogeneous structures with wurtzite ZnCoO containing Co clusters are formed at 700 °C. The structural and magnetic measurements for these films collectively give sufficient evidence that the ferromagnetism in the ZnCoO system originates from the presence of the ferromagnetic clusters and ZnCoO is intrinsically paramagnetic. We consider that our results raise some interesting questions about the origin and the nature of magnetism in ZnO-based DMS.

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