Structural and magnetic properties of insulating $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films

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Cobalt-doped ZnO ($\text{Zn}_{1-x}\text{Co}_x\text{O}$) thin films were fabricated by reactive magnetron cosputtering. The processing conditions were carefully designed to avoid the occurrence of Co precipitations. The films are *c*-axis oriented, and the solubility limit of Co in ZnO is less than 17%, determined by x-ray diffraction. X-ray photoemission spectroscopy measurements show Co ions have a chemical valance of 2+. In this paper, hysteresis loops were clearly observed for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films at room temperature. The coercive field, as well as saturation magnetization per Co atom, decreases with increasing Co content, within the range of $0.07 < x < 0.17$. Most intriguing, the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films are nonconductive as *x* is no more than 17%. Our results clearly demonstrate that ferromagnetism can be realized in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ without carrier incorporation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1756212]

I. INTRODUCTION

There has been both fundamental and technological interest in diluted magnetic semiconductors (DMSs), since the discovery¹ of ferromagnetism in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ with Curie temperature $T_c = 110$ K. DMSs exploit both the spin and the charge of the carriers and, hence, raise the possibility of spintronic applications. In the very recent years, 3*d* transition metal (TM)-doped zinc oxide (ZnO) has been receiving remarkable attention. ZnO is transparent to visible light, and has a higher TM solubility compared to its III–V counterparts; therefore, it is promising for potential use in magneto-optical devices.² Dietl *et al.*³ first predicted room temperature ferromagnetism for ZnO containing 5% of Mn and a high hole concentration ($3.5 \times 10^{19} \text{ cm}^{-3}$). Numerous reports on the ferromagnetism of TM-doped ZnO have emerged ever since. Norton *et al.*⁴ observed ferromagnetism with a T_c up to 250 K in Mn-implanted ZnO:Sn, which is *n* type. This results is in contradiction with the above prediction. Sato² and co-workers performed band structure calculations in the framework of the local density approximation (LDA), and suggested that for V, Cr, Fe, Co, and Ni dopants, ferromagnetic ordering in ZnO is favored without additional charge carriers. For films doped with 3–25 at % Ni, ferromagnetism was observed at 2 K.⁵ Ferromagnetic behavior with T_c higher than 350 K was found in V-doped ZnO films fabricated by pulsed laser deposition.⁶ As to Co-doped ZnO, a few papers appeared recently,^{7–11} but the results are controversial. Ueda *et al.*⁷ reported T_c above 280 K for Co-doped ZnO, but the reproducibility was less than 10%. Prelrier *et al.*⁸ observed ferromagnetism with T_c close to room temperature in 5% Co-doped ZnO. Ferromagnetism with T_c above 350 K was found in films fabricated by the sol-gel method.⁹ However, Jin *et al.*¹⁰ detected no indication of fer-

romagnetism for TM-doped ZnO down to 3 K. Some authors believed that the observed ferromagnetism might be ascribed to Co precipitates.¹¹ So, it is still a key issue to elucidate the origin of ferromagnetism in Co-doped ZnO.

Oxygen vacancies may lead to the formation of Co clusters;¹¹ therefore, the avoidance of oxygen vacancies is a way to eliminate the contribution of Co precipitations to the ferromagnetism in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloy. In this paper, we report the growth and magnetic properties of insulating $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films. The insulating nature of these films indicates the occurrence of oxygen vacancies was effectively avoided; thus, the presence of Co clusters was impossible. In this work, ferromagnetic behaviors were clearly observed at room temperature, which firmly shows that ferromagnetism can be realized in Co-doped ZnO without carrier incorporation. Examination of these films is of value for further understanding the ferromagnetic mechanism in Co-doped ZnO.

II. EXPERIMENTAL PROCEDURE

The (Zn,Co)O films were grown on $20 \times 20 \text{ mm}^2$ Si(001) substrates at 350 °C by reactive magnetron cosputtering. Zn (99.999%) and Co (99.99%) of 8 cm diameter were used as targets. The magnetron sources are tilted 45° away from the substrate normal. Current-regulated dc power was applied to the magnetron with Zn target, and the magnetron with Co target was run at rf power. In this work, Zn target was positioned 11 cm away from the substrate for all sample preparations, and the dc power was fixed at 40 W. But then, the rf power, the distance between the Co target and the substrate, were changeable in order to get specimens with different ratio of Zn to Co. Prior to deposition, the Si substrate was cleaned and degreased by successive rinses in ultrasonic baths of acetone, ethanol, and deionized water, followed by HF solution to remove the contaminants and the native SiO_2 layer on the surface. After insertion into the growth chamber, the surface of the substrate was further cleaned by heating it to 800 °C for 15 min. The base pressure was approximately 8.0×10^{-5} Pa. The sputtering gas was a mixture of Ar

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FIG. 1. 2θ - θ XRD patterns of Co-doped ZnO for different Co content x (a) $x=0$; (b) $x=0.07$; (c) $x=0.11$; (d) $x=0.17$; and (e) $x=0.22$. The data are shown in a logarithmic scale.

(99.999%) and O_2 (99.999%) with a ratio of 1:4, at a total pressure of 1.0 Pa. Presputtering of 15 min was performed to purify the targets. All films in the present work grew for 3.5 h, and the growth rate is rather low, between 0.5–1.0 nm/min. For the purpose of growing films of homogeneous thickness, the substrate holder, motivated by a motor, kept rotating during sputtering. To improve the crystallinity of the films, *in situ* annealing was performed at 600 °C for 15 min, in a flowing oxygen atmosphere of 1.0 Pa.

Structural properties of the samples were determined with 2θ - θ x-ray diffraction (XRD, Mac Science M18XHF-SRA) using $Cu K\alpha$ radiation. The film thickness was measured by a profilometer. The surface morphology was studied with atomic force microscopy (AFM). Surface composition of the $Zn_{1-x}Co_xO$ films was measured by PHI-610/SAM Auger electron spectroscopy (AES). The chemical valence of Co atoms was characterized by x-ray photoemission spectroscopy (XPS) using $Mg K\alpha$ radiation. Room temperature magnetic properties were examined using a model 2900 Micromag™ alternating gradient magnetometer (AGM) with the magnetic field applied parallel to the film plane.

III. RESULTS AND DISCUSSION

XRD patterns of $Zn_{1-x}Co_xO$ films deposited on Si (001) substrates are shown in Fig. 1, for $x=0, 0.07, 0.11, 0.17$, and 0.22 . It is evident that the films have single-phase structure and c -axis preferred orientation when the Co doping concentration $x < 17\%$. The ZnO (002) peak is significantly broadened as Co is incorporated into ZnO. These results indicate that Co atoms systematically substituted for Zn positions in the films without changing their wurtzite structure. For $x=0.17$, the ZnO (002) peak strikingly bulges at $\sim 36^\circ$, which is an indication of phase separation. As x exceeds 0.17, a peak is clearly observed at $\sim 36.1^\circ$. We assign the corre-

sponding parasitic phase to be CoO, which has a preferential (111) alignment in the ZnO host matrix. The occurrence of phase separation means the solubility limit of Co in ZnO is less than 17%. No Co phase was detected by XRD. It is noticeable that CoO, rather than Co_2O_3 or Co_3O_4 , appears in Fig. 1(e), under the aforementioned growth process. In fact, when Co concentration further increases, occurrence of Co_3O_4 is found. Detailed information about the films with Co content higher than the solubility limit will be presented elsewhere.

AFM images with scanning area of $5 \times 5 \mu m$ are shown in Fig. 2. The films consist of sizable close-packed tetragonal columns (about 400 nm in dimension), which is quite different from the hexagon-like patterns in Ref. 12. We think this may be related to the difference of the substrates. The films exhibit rather rough surfaces with rms (root-mean-square) surface roughness of 4–9 nm, and each column consists of strip-like microcrystals, indicating strong recrystallization during the annealing treatment.

Typical Co $2p$ core level XP spectrum is presented in Fig. 3, for $x=0.11$. The charge-shifted spectrum was corrected using the maximum of the adventitious C $1s$ signal at 284.6 eV. The Co $2p_{3/2}$ peak occurs at 780.7 eV, while the Co $2p_{1/2}$ peak is located at 796.2 eV, showing large chemical shifts compared to that of pure Co metal.¹³ The difference between Co $2p_{1/2}$ and Co $2p_{3/2}$ is 15.5 eV. These results indicate that Co ions have a valence of $2+$ in a rather high probability.¹³ Satellite peaks appeared at about 786.2 and 803.2 eV, respectively. The very intense satellite structure results from the charge-transfer band structure characteristic of the late $3d$ transition metal monoxides.¹⁴ The differences between the main peaks and the corresponding satellites are close to that of CoO in the literature.¹⁵ These results may further prove that Co ions are surrounded by oxygen atoms and have a chemical valence of $2+$.

Figure 4(a) presents the M - H curves (field dependence of magnetization) of $Zn_{1-x}Co_xO$ films measured at room temperature, for $x=0.07, 0.11$, and 0.17 . The diamagnetic contributions from the substrate have been subtracted out of the data. Hysteresis loops were clearly observed for the films. The coercive field (H_c) is less than $150 O_e$, indicating the soft nature of the films. It is evident from Fig. 4(b) that H_c shows nearly linear reduction with increasing Co concentration, within the range of $0.07 < x < 0.17$. The value of H_c is merely $59 O_e$ for $Zn_{0.83}Co_{0.17}O$. Assuming the lattice constants of $Zn_{1-x}Co_xO$ are the same as in pure ZnO, the cobalt number per square centimeter is estimated from the film thickness and concentration. The resulting saturation magnetization (M_s) per Co atom also decreases with increasing x , which is of the same order of magnitude as the results of Ref. 9.¹⁶ The decrease of M_s with increasing Co content may be caused by the enhanced antiferromagnetic coupling between Co ions.

It seems plausible to assign the magnetic behavior to Co precipitations, but it is not the case in the present experiment. The measurements of XRD and XPS show no evidence of Co precipitations, although these two instruments may be inadequate to provide information to the degree needed here. In addition, as formerly mentioned, the film growth process

FIG. 2. Surface morphology of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ grown on Si(001) substrate (a) $x=0.07$; (b) $x=0.11$; and (c) $x=0.17$.

in this experiment was carefully designed to avoid the presence of Co clusters. It is well known that ZnO is commonly n -type, which originates from O vacancies or Zn interstitials,^{17,18} namely the lack of oxygen atoms. Stoichiometric ZnO is insulating, as a result of its wide band gap (3.35 eV at room temperature). Co^{2+} forms deep levels⁹ in the band gap and, therefore, $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films of stoichiometry are expected to be nonconductive. Under very low

FIG. 3. X-ray photoemission data of Co 2p core levels for film of $\text{Zn}_{0.89}\text{Co}_{0.11}\text{O}$. "S" denotes satellite peaks, and the solid line shows a smooth to the data.

growth rate and oxygen-rich sputtering gas of 1.0 Pa, the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films grown in this work are indeed insulating ($>10^6 \Omega\text{cm}$) as x is no more than 17%. This indicates the oxygen supply is adequate and Co, Zn atoms are fully oxi-

(a)

(b)

FIG. 4. (a) In-plane $M-H$ curves of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films measured at room temperature, and (b) variation of H_c , M_s as the function of Co content x . The calculation of M_s is based on the assumption that the lattice constants are invariable for different x .

dized. Therefore, the appearance of Co particles can be ruled out. Furthermore, even if Co precipitations account for the origin of the observed ferromagnetism, the diameter of which should be above 5 nm, because Co particles smaller than that size are superparamagnetic at room temperature.¹⁹ In any case, the appearance of Co clusters with diameter larger than 5 nm is beyond belief under the aforementioned growth process. Further studies such as magneto-optical spectrum²⁰ measurement are planned to obtain more convincing evidence.

As above, the observed ferromagnetism definitely originates from the Co substitution for Zn in ZnO. It is clear that the nonconductive character makes the RKKY-type mechanism rather unlikely in the present case. LDA computations^{2,21,22} show a large number of delocalized Co-3d electrons near the Fermi level, and thus the double-exchange mechanism is relevant. However, the insulating nature of the films suggests the weight of Co-3d electrons near the Fermi level was overestimated and the proposed mechanism is impossible. Resonant photoemission spectroscopy is powerful for providing information on the electronic structures, which it is programmed to do for the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films. Litvinov and Dugayev suggested²³ that ferromagnetic spin-spin interaction could originate from virtual excitations between the acceptor-like impurity level and the valence band. The theory^{24,25} based on the interaction between bound magnetic polarons (BMP) is another possible candidate. Disorder^{26–28} effects may also be important for ferromagnetism in $\text{Zn}_{1-x}\text{Co}_x\text{O}$. Calculations²⁹ based on LDA suggested that formation of nanoclusters (just a few magnetic atoms in dimension) is energetically favorable. We also note the recent experimental results³⁰ realizing ferromagnetism in insulating Co, Mn, and Cr doped AlN.

IV. CONCLUSIONS

Insulating $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films were fabricated by reactive magnetron cosputtering. The films show ferromagnetic ordering at room temperature, as evidenced by the presence of hysteresis in M versus H loops. The coercive field, as well as magnetization saturation per Co atom, decreases with increasing Co concentration, in the region of $0.07 < x < 0.17$. The contribution of Co precipitations is precluded. Due to the insulating nature of the films, conventional carrier-mediated ferromagnetism may not be the mechanism account for the observed magnetic properties. The relevant mechanism needs further investigation.

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