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Room temperature ferromagnetism in sputtered $Zn_{1-x}Cr_xO$ thin films

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ABSTRACT

Cr doped ZnO ($Zn_{1-x}Cr_xO$) thin films with different Cr concentrations (0.4, 1.5, and 8.9 at.%) were deposited on Si substrates using RF magnetron sputtering. Film crystal structure was characterized using X-ray diffraction, and vibrating sample magnetometer measurements were used to investigate their magnetic properties. Unstable ZnO structure is present at low Cr concentrations, while secondary phases appear at higher Cr concentrations. 8.9 at.% $Zn_{1-x}Cr_xO$ film exhibits room temperature ferromagnetism and high 325 K Curie temperature, even after 300 °C annealing for 1 h. This result is promising and demonstrates Cr doped ZnO film's potential use in practical applications.

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1. Introduction

Due to high Curie temperature (TC) and room temperature (RT) ferromagnetism predicted by theoretical calculations [1], diluted magnetic semiconductors (DMS) are regarded as important materials for spintronic and photonic devices. The main efforts in DMS research are focused on doping non-magnetic semiconductors with transition metals (TM) (e.g., Ti, V, Cr, Mn, Fe, Co, Ni and Cu), including TM-doped III–V [2–5], II–VI [6–8] or group IV types [9]. However, most DMSs have low Curie temperature, which limits their practical applications. Dietl et al. [1] theoretically predicted that the Curie temperature of p-type DMSs based on wide-band gap semiconductors, i.e., ZnO could be increased above room temperature with stable ferromagnetism. Sato and Katayama-Yoshida [10] theoretically demonstrated that V, Cr, Fe, Co and Ni doped ZnO exhibits ferromagnetism, which attracted researchers interest to TM-doped ZnO, although some experimental results are quite contradictory. While RT ferromagnetism has been found in TM-doped ZnO systems [11–13], there are some reports indicating no sign of ferromagnetism and high TC [14–17].

Pan et al. summarized the research performed on TM-doped ZnO DMSs in recent years [18]. RT ferromagnetism has been observed in many ZnO-based DMSs despite controversy over its origin. However, very little attention has been paid to Cr-doped ZnO films. Cr-doped ZnO has many advantages, including: (i) the atomic radii of Zn^{2+} (74 pm) and Cr^{2+} (73 pm) are similar, making Cr a favorable dopant; (ii) Cr^{2+} has a large magnetic moment (4 μB); (iii) Cr is anti-ferromagnetic, thus its possible presence in the form of segregated clusters would not result in ferromagnetism. These features make Cr a promising dopant to distinguish intrinsic ferromagnetism from the secondary phases or precipitates in DMSs. The only ferromagnetic Cr oxide is CrO_2 with TC of 386 K [19]. However, compared with the widely studied Co- or Mn-doped ZnO systems, both theoretical and experimental results on Cr-doped ZnO are scarce. Moreover, published experimental results on Cr-doped ZnO are in conflict with each other. Extensive studies carried out by Venkatesan et al. [20] and Ueda et al. [21] did not provide any observation of ferromagnetism in Cr-doped ZnO. Meanwhile, other studies indicate that Cr-doped ZnO films are ferromagnetic at RT [22,23]. This previously conducted research indicates that ferromagnetic ZnO has wurtzite hexagonal structure, although experiments presented in this paper will show otherwise.

2. Experimental

In this study RT ferromagnetism in ZnO ($Zn_{1-x}Cr_xO$) thin films with varying Cr concentration was observed. These films with different crystal structure kept their semiconducting electron transport properties and high Curie temperature. ZnO ($Zn_{1-x}Cr_xO$) thin films with varying Cr concentration (0, 0.4, 1.5, 8.9 at.%) were deposited on Si substrates using RF magnetron sputtering with two different targets of pure Cr (99.99%) and ZnO (99.99%) at RT. Pure Ar (99.999%) was introduced as the working gas via a mass flow controller at a flow rate of 20 standard cubic centimeters per minute. The substrate-target distance was 80 mm. The RF power on the ZnO target was maintained at 200 W, while the power on the Cr target was varied to produce different Cr concentrations. As a result, 200 nm thick films were deposited. The crystal structure of all samples was characterized with X-ray diffraction (XRD) technique using $\theta-2\theta$ scans of Cu-$K\alpha$ radiation ($\lambda_{Cu\text{-}K\alpha 1}=1.5406$ Å). Films were exposed to the X-ray beam at 40 kV and 150 mA in Rigaku D/Max-RB X-ray diffractometer. Films magnetic properties were characterized using a vibrating sample magnetometer, Quantum Design™ VersaLab, which

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allows collecting magnetic moment data as a function of magnetic field (M–H) and temperature (M–T).

3. Results and discussion

XRD patterns obtained from $Zn_{1-x}Cr_xO$ films for x = 0, 0.004, 0.015, 0.089 are shown in Fig. 1. For pure ZnO, i.e. x = 0, two reflections appear at 33.785° and 47.241°, respectively, corresponding to diffraction card 21–1486 [24] and are not indicative of the wurtzite ZnO structure reported by many other researches [18,19,25]. With the chromium concentration increasing to x = 0.015, the films' structure didn't show any obvious changes, but the diffraction intensity decreased. After annealing at 300 °C for 1 h two XRD reflections of x = 0.004 and 0.015 films appear at 34.321° and 46.894°, indicating a wurtzite ZnO structure, which corresponds to diffraction card 36–1451 [24]. With the chromium concentration increasing to x = 0.089, three reflections appear at 34.105°, 35.882° and 48.284°, respectively, originating from $ZnCrO_4$ and ZnO, based on the diffraction card 19–1456 [24]. After annealing x = 0.089 films at 300 °C for 1 h, a new $ZnCrO_4$ reflection appears at 23.570°. The ZnO 47.241° diffraction reflection intensity increased significantly.

Fig. 2 shows magnetization curves of $Zn_{1-x}Cr_xO$ films with different Cr concentrations at room temperature. Pure ZnO films (x = 0) exhibit anti-ferromagnetism. When x = 0.004, a ferromagnetic hysteresis loop was observed. The value of the magnetic moment at 2000 Oe magnetic field is about 9 emu/cm^3. With the Cr concentration increasing to x = 0.015, a large ferromagnetic hysteresis loop was observed with the value of magnetic moment of about 44 emu/cm^3, but for x = 0.089, the value of magnetic moment shows a remarkable decrease to 21 emu/cm^3. The as-deposited samples exhibit good ferromagnetism at room temperature, according to the M–H curves. Fig. 2(b) shows the M–H curve of the x = 0.089 sample before and after annealing. Both samples exhibit room temperature ferromagnetism, but the magnetic moment value decreases after 300 °C annealing for 1 h. The existence of the secondary $ZnCrO_4$ oxide phase affects ferromagnetism. With increasing content of the $ZnCrO_4$ phase, the magnetic moment decreases, but the coercive force shows small increase.

The M–T curves of the sample are shown in Fig. 3. According to Fig. 3, the TC is 325 K, but after annealing, there is no obvious curve

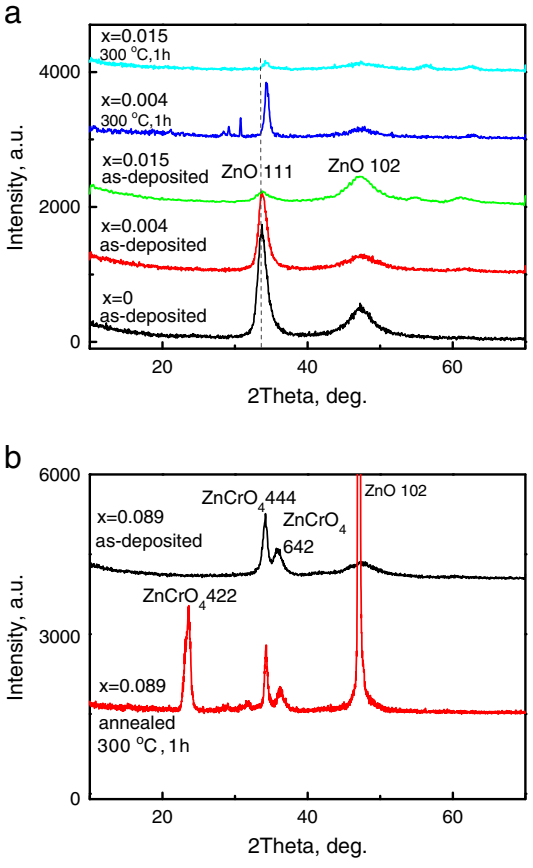

Fig. 1. XRD patterns of $Zn_{1-x}Cr_xO$ with different Cr concentrations and annealing conditions: (a) x = 0, 0.004, 0.015, pre- and after annealing; (b) x = 0.089 pre- and after annealing.

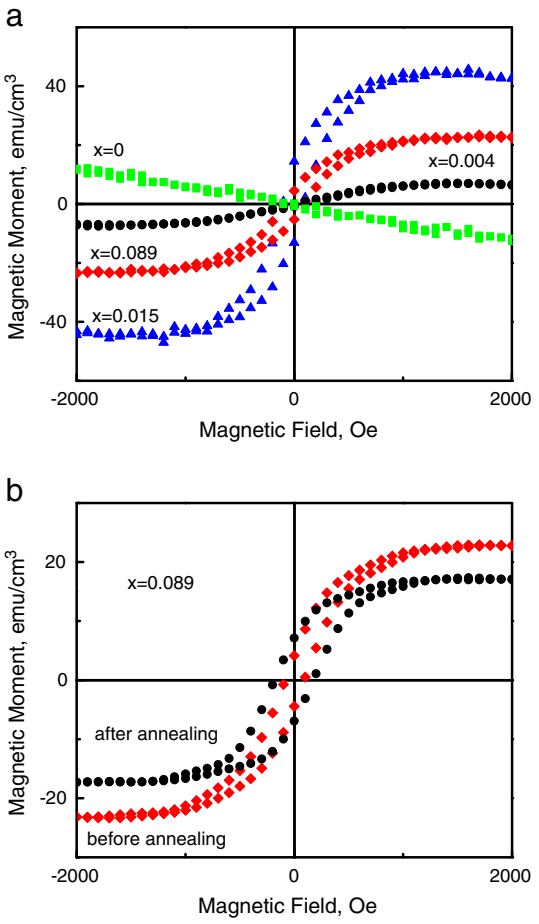

Fig. 2. (a) Magnetic moment dependence on magnetic field for samples with varying Cr concentration before annealing; (b) M–H curves for $Zn_{1-x}Cr_xO$ films (x = 0.089) before and after annealing at 300 °C for 1 h.

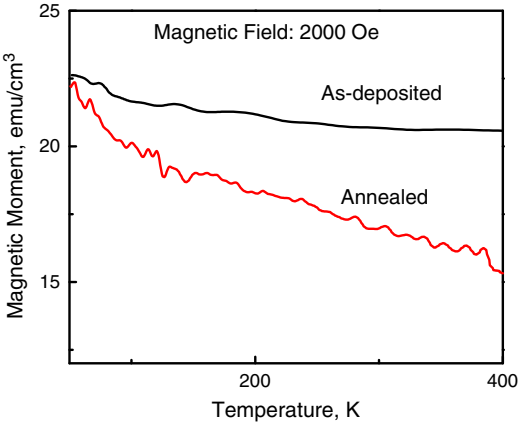

Fig. 3. Magnetic moment temperature dependence of as-deposited x = 0.089 $Zn_{1-x}Cr_xO$ and 300 °C 1 h annealed films.

plateau, which means that the Curie temperature is not in the measured 50–400 K temperature range. According to the M–H curve shown in Fig. 2, the annealed sample exhibits RT ferromagnetism, so its TC is most likely above 400 K.

4. Conclusions

In this letter, ferromagnetism was found in $Zn_{1-x}Cr_xO$ films ($0 \leq x \leq 0.089$) produced by magnetron sputtering at low temperature both in unstable ZnO and c-axis-oriented wurtzite structures. This unstable ZnO structure turns into wurtzite after 300 °C annealing for 1 h with 325 K TC. After annealing, films ferromagnetism changes a little, but the TC is higher than before annealing.

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