Magnetic properties of ZnO:Cu thin films prepared by RF magnetron sputtering

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Abstract: ZnO films and ZnO:Cu diluted magnetic semiconductor films were prepared by radio frequency magnetron sputtering on Si (111) substrates, with targets of ZnO and $Zn_{0.99}Cu_{0.01}O$, respectively. The plasma emission spectra were analyzed by using a grating monochromator during sputtering. The X-ray photoelectron spectroscopy measurements indicate the existence of Zn_i defect in the films, and the valence state of Cu is 1+. The X-ray diffraction measurements indicate that the thin films have a hexagonal wurtzite structure and have a preferred orientation along the *c*-axis. The vibrating sample magnetometer measurements indicate that the sample is ferromagnetic at room temperature, and the origin of the magnetic behavior of the samples is discussed.

Key words: RF magnetron sputtering; zinc oxide; diluted magnetic semiconductors
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1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted considerable attention because of their potential application in spintronic devices in recent years[1−3]. Through theoretical calculations, Dietl[4] and Sato[5] successfully predicted that ZnO doped with several 3d transition metal ions may exhibit ferromagnetic ordering. A number of groups have, therefore, investigated this material after Hou *et al.*[6] reported that a series of n-type $Zn_{1-x}Cu_xO$ (x = 0.02, 0.06, 0.1, and 0.12) films prepared by direct current reactive magnetron sputtering are ferromagnetic at room temperature. Buchholz *et al.*[7] prepared a series of copper-doped ZnO films grown by pulsed-laser ablation and reported that the location of the copper atoms relative to each other can strongly affect the magnetic properties of the ZnO:Cu (ZCO) system. Although some experiments are successful, the reproducibility is low. Furthermore, the origin of the ferromagnetic order in TM-doped ZnO systems is still under discussion and is not yet completely understood[8−11]. The experiments show that many factors should be considered during the film preparation. In this work, ZnO films and ZnO:Cu diluted magnetic semiconductor films are prepared by RF magnetron sputtering on Si (111) substrates.

2. Experiments

RF magnetron sputtering was used to prepare ZnO and ZnO:Cu films on Si (111) substrates, and the growth parameters are shown in Table 1. The purity of the ZnO target was 99.99%. For the $Zn_{0.99}Cu_{0.01}O$ target, ZnO and CuO powders with purities of 99.99% were mixed with the proper atom ratios for the required compositions. The target-substrate distance was fixed at 75 mm. The substrates were cleaned by an RCA standard technique. The targets were pre-sputtered for 10 min to remove any surface contamination. An MDC-360 film deposition controller (MAXTEK, INC.) was used to monitor the thicknesses of the films. A WDP-500D type grating monochromator (Beijing Modern Rayleigh Ltd. Co.) was used to analyzed the plasma emission spectra during the sputtering, and it was helpful for monitoring the growth. All the spectral data come from Ref. [12].

The crystalline structural properties of the films were characterized by using XD-2 XRD (Cu-Kα, λ = 0.15406 nm), and the results were analyzed by using MDI Jade 5.0. The chemical valence states and composition ratios were measured by using XPS (Al-Kα, E = 1486.6 eV), the results were analyzed by using XPSPEAK 41, and all the binding energies of chemical states and the doublet separation came from the NIST XPS database. The magnetization measurements were performed by using a Lake Shore 7410 VSM magnetometer system at room temperature, and the magnetic field was applied parallel to the thin film surface.

3. Results and discussion

3.1. Plasma emission spectrum

To monitor the condition during the growth, four spectral lines (Zn (472.2, 481.1, 636.2 nm) and Ar (811.5 nm)) were considered, as shown in Fig. 1. The light intensity of Ar 811.5 nm was chosen as a standard[13, 14]; so, all given intensities are relative intensities. RI-A, RI-B, and RI-C in Fig. 1 mean relative intensities of samples A, B, and C, respectively. The emission spectra during the deposition may originate from three areas[15]: the target surface, the plasma areas, and the substrate surface. As shown in Fig. 1, RI-C is larger than RI-B, which indicates the existence of excited Zn atoms on the surface[13]. Comparing to RI-B and RI-C, RI-A is obviously larger, which indicates that more Zn atoms are sputtered into the plasma areas, and a faster deposit rate could be presumed. The growth rates of samples A, B, and C during sputtering are shown in Fig. 2. The figure reveals that the rate of sample A is larger than that of samples B and C, which is in accordance with the above presumption.

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Table 1. Process parameters.

Sample/Targe	Basepressure (Pa)	Substrate	Temperature (°C)	Pressure (Pa)	P_{Ar}/P_{O_2}	Power (W)	Thickness (nm)
A/ZnO	1.0×10^{-3}	Si(111)	400	0.35	5 : 1	130	380
B/$Zn_{0.99}Cu_{0.01}O$	1.0×10^{-3}	Si(111)	400	0.35	5 : 1	120	380
C/$Zn_{0.99}Cu_{0.01}O$	1.0×10^{-3}	Si(111)	450	0.35	5 : 1	120	380

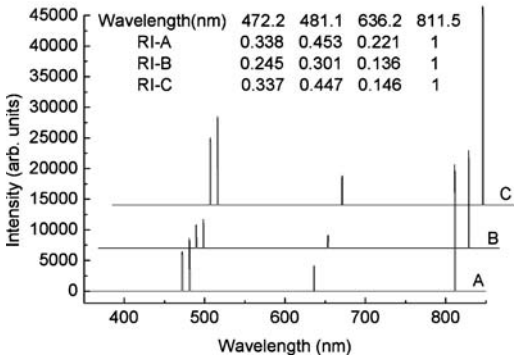

Fig. 1. Plasma emission spectral lines.

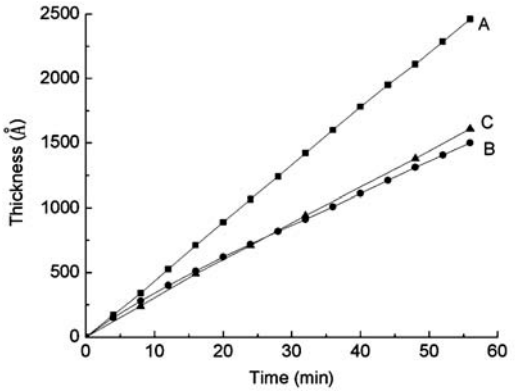

Fig. 2. Growth rates of samples A, B, and C.

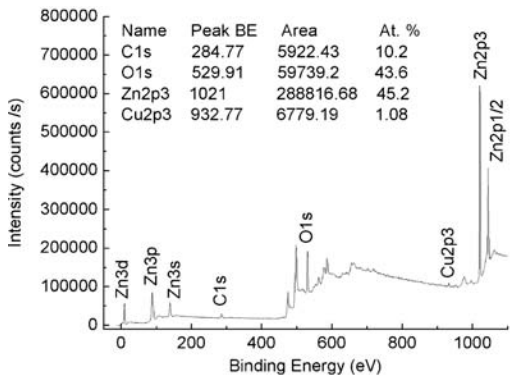

Fig. 3. XPS spectra of sample C.

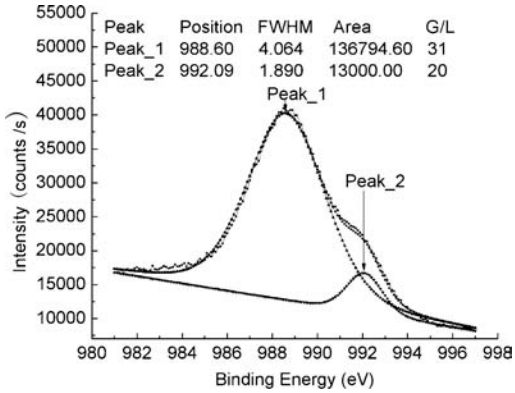

Fig. 4. Auger spectra for ZnLMM.

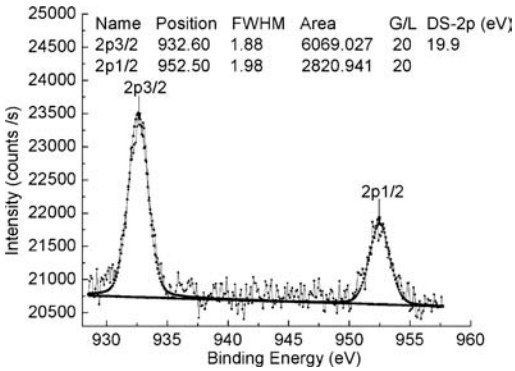

Fig. 5. XPS spectra for Cu2p.

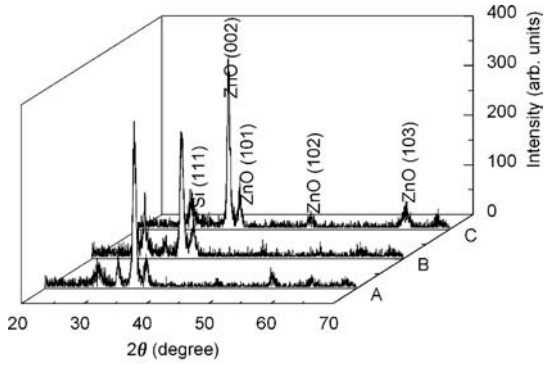

Fig. 6. XRD pattern of samples A, B and C.

3.2. XPS measurements

The element components and valence states of sample C were determined by using XPS. Figure 3 reveals that the percentage of O, Zn and Cu is about equal to that of the target. The existence of C may be caused by organic pollution on the surface. As shown in Fig. 4, the Auger spectra can be fitted by two peaks: 988.6 eV (peak_1) and 992.09 eV (peak_2). The result shows that Zn ions exist mainly in the form of Zn^{2+} and Zn^0. The area of peak_1 is much larger than that of peak_2, which shows that most of the Zn atoms dissolve into the ZnO matrix and others exist in the form of Zn_i. In Fig. 5, no shakeup peak appears between the 2p3/2 peak and the 2p1/2 peak, and the DS-2p (doublet separation) is 19.9 eV, which corresponds to Cu^{1+}.

3.3. Structural properties

The crystalline structural properties of all the films were characterized by using XRD and the results are shown in Fig. 6. The average crystallite size was calculated by using

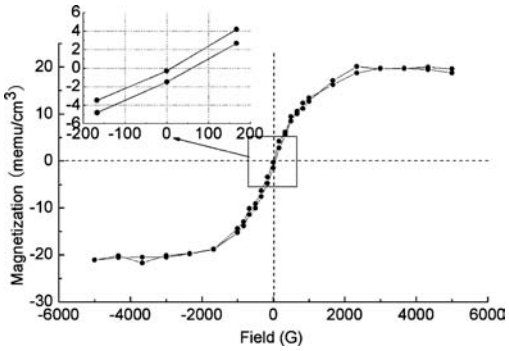

Fig. 7. Room temperature *M–H* curve of sample C. The inset is an expanded view around 0 G.

the Scherrer formula[10]: $D = 0.9\lambda / \rho \cos\theta$, where ρ is the full width at half maximum (FWHM) of 2θ in radians, λ is the wavelength of the X-ray, and θ is the Bragg angle. The thickness D of samples A, B, and C are 16.53, 15.00, and 23.51 nm, respectively.

θ–2θ scans from the three samples show a dominant ZnO (002) diffraction peak and some very low ZnO diffraction peaks. No other peak relating to a Cu metal cluster or a secondary phase is observed. The results indicate that the thin films have a well-ordered wurtzite structure and that the *c*-axis of the crystals is preferentially oriented parallel to the substrate (001) direction. The 2θ positions of the the ZnO (002) diffraction peaks are observed at 34.36 °, 34.32 °, and 34.48 °. The shift of ZnO (002) peak may be caused by the intrinsic Zn_i defects and the doped Cu ions. The radius of Cu^{1+} (0.096 nm) is slightly larger than that of Zn^{2+} (0.074 nm). Cu ions and Zn_i defects in the film will cause structural distortion and disorder; thus, causing the shift of the peak position.

3.4. Magnetic properties

The magnetization-versus-magnetic-field (*M–H*) curve of sample C is shown in Fig. 7. A hysteretic behaviors was observed for the sample at room temperature. The magnetization increases with the magnetic field, and the saturated magnetization (Ms) is 2.0897×10^{-2} emu/cm^3. The inset is an expanded view around the origin of the hysteresis curve. The figure reveals the existence of an exchange bias[16], which is related to the ferromagnetic/antiferromagnetic interface. The exchange bias field H_E is 36 G, and the coercive field H_C is 24 G.

To understand the magnetic behavior of DMSs, Coey *et al.*[17] and Durst *et al.*[18] considered the bound magnetic polarons (BMPs) model. In the BMPs model, an impurity site (donor or acceptor) plays the role of a trap and captures the carrier (electrons or holes) to form a bound polaron. The polarons are surrounded by the magnetic ions. The polaron interaction causes both polarons in the polaron-pair to antialign with the same magnetic ions. Whereas, when the parameters are appropriate, the polarons will align each other in a local space, and the film will exhibit ferromagnetism. Reference [19] reported that the observed strong ferromagnetism in copper-doped ZnO films could be partly associated with Zn-interstitial defects. Considering the sample C,which had Zn_i defects and Cu^{1+} in the ZnO:Cu film. The ferromagnetism observed in the film can be explained by using the BMPs model. The magnetic exchange interaction between Zn_i and Cu^{1+} occupying the same space is aligned with Cu^{1+} spins, forming BMPs. Thus, the sample will exhibit ferromagnetism.

4. Conclusions

High-quality ZnO films and ZnO:Cu DMSs films were prepared on Si (111) substrates by using RF magnetron sputtering. The emission spectra during sputtering have been measured, and are used to monitor the growth condition. XPS measurements supported the existence of Zn_i defects in the films, and the valence state of Cu is found to be 1+. XRD measurements revealed that all the films have a well-ordered wurtzite structure with a preferred orientation along the *c*-axis. Ferromagnetic properties were observed in ZnO:Cu samples, as shown by using VSM measurements at room temperature. The origin of the magnetization was analyzed by using the BMPs model.

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