



X-ray diffraction spectroscopy and X-ray photoelectron spectroscopy studies of Cu-doped ZnO films

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ABSTRACT

Cu-doped ZnO films have been prepared using direct current co-reactive magnetron sputtering technique at different oxygen partial pressures. The microstructure and the chemical state of oxygen, copper and zinc in ZnO films was investigated by X-ray diffraction spectroscopy (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The results indicate that ZnO films with moderate Cu doping can obtain wurtzite structure with strong *c*-axis orientation. The crystal quality of the ZnO:Cu films can also be enhanced with moderate enrichment of oxygen in the sputtering process. The XPS spectra of zinc, oxygen and copper results also show that moderate enrichment of oxygen is helpful for the stoichiometry of the ZnO:Cu films, which is consistent with the analysis results of XRD.

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1. Introduction

Nowadays, the semiconductor ZnO has gained substantial interest in the research community for its prospects in short wave optoelectronics applications, owing to its direct wide band gap ($E_g \sim 3.2\text{--}3.4\text{ eV}$ at 300 K [1]) and its large exciton binding energy ($\sim 60\text{ meV}$), which could lead to lasing action based on exciton recombination even above room temperature. ZnO is a self-excitation semiconductor, one of the most important promising materials which have been applied to many fields such as transparent conductive contacts, solar cells, laser diodes, ultra-violet lasers, thin film transistors, optoelectronic and piezoelectric applications, and surface acoustic wave devices [2–7]. ZnO:Cu films have usually been fabricated for their electrical and ferromagnetic properties. In addition, they have potential in surface acoustic wave device applications. Due to its similar electronic shell structure, Cu has many physical and chemical properties similar to those of Zn [8]. Cu doping in ZnO has been reported to be able to change the electrical and optical properties of ZnO thin films. It has also been demonstrated that ZnO films doped with Cu have higher electrical resistance and larger *c*-axis preferentially oriented crystallites [9,10]. However, there is still

debate concerning the mechanism involved in the effects of Cu doping on the properties of ZnO. Furthermore, there have been only a few studies on the effects of the ratio of $\text{O}_2:\text{Ar}$ in the sputtering process on the chemical state of ZnO films in detail.

In this paper, Cu-doped ZnO thin films were prepared on glass substrates by direct current co-reactive magnetron sputtering technique. The effects of Cu doping on the microstructure and the effects of the ratio of $\text{O}_2:\text{Ar}$ in the sputtering process on the chemical state of zinc, oxygen and copper in Cu-doped ZnO films were studied.

2. Experiments

The Cu-doped ZnO films were deposited on glass substrates by direct current co-reactive magnetron sputtering. The glass substrates were ultrasonically cleaned in acetone and rinsed in deionized water. A pure Zn disk of 60 mm in diameter (purity 99.999%, commercially available from General Research Institute for Nonferrous Metals, Beijing, China) was used as target, and the distance between target and substrate was 50 mm. The base pressure in the deposition chamber was $5.0 \times 10^{-4}\text{ Pa}$. During deposition, the reactant pressure was maintained at about 3 Pa, the sputtering current was about 0.1 A, the sputtering voltage was about 400 V, and the substrate temperature was 200 °C. Undoped

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ZnO film was deposited in argon/oxygen mixture atmosphere with the gas flow rate 12 sccm for Ar and 20 sccm for O₂, two Cu-doped ZnO thin films were performed in different argon/oxygen mixture atmosphere with the gas flow rate 12 sccm for Ar and 12 sccm for O₂ and 12 sccm for Ar and 20 sccm for O₂, which were denoted as samples a and b, respectively. To conduct Cu doping, Cu foils (purity ~99.999%, 1 mm in thickness) were pasted to Zn target, with the coverage area of Cu foil about 1.6% of the effective sputtering area. All the films were deposited for 2 h.

The crystal structures were studied using X-ray diffraction (XRD, X'Pert Pro). The chemical state of zinc, oxygen and copper in Cu-doped ZnO films was investigated by X-ray photoelectron spectroscopy (XPS) on ESCA LAB 220-XL photoelectron spectrometer (VG Scientific, USA) using the Mg K α excitation line of 1253.6 eV. The binding energy scale was calibrated by setting the C 1s peak to 284.8 eV and all spectra were taken at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of undoped ZnO film and ZnO:Cu films fabricated at different oxygen partial pressures. As can be seen from the figure, both samples consist of single-phase ZnO with zincite structure. The (100) located at $2\theta = 31.45^\circ$ is only observed in sample a and the two diffraction peaks of ZnO films at $2\theta = 34.15^\circ, 62.95^\circ$ which corresponds to the (002) and (103) planes appeared in all the samples, indicating a polycrystalline but with a preferential orientation along *c*-axis. The intensity of (002) peak increases in the case of Cu doping at the same sputtering condition compared with sample a and undoped ZnO film. Previously, the effect of Cu doping on *c*-orientation of ZnO films has been inconsistently reported. Gonzalez [11] detected a decrease in the extent of *c*-orientation while Lee et al. [10] observed an increase in the extent of *c*-orientation by Cu doping. Lee et al. reported that the increase in the extent of *c*-orientation may be due to the fact that a moderate quantity of Cu atoms exist in the form of sharing the oxygen with Zn atoms and hence improve the (002) orientation. However, the intensity of the (002) peak decreases when the ratio of O₂:Ar decreases, and the (100) peak is observed. The oxygen deficiency in the sputtering process may be responsible for the distortion of crystalline in this case.

From the integral width and peak position of the ZnO (002) peak, the particle sizes of the films were calculated using the Scherrer equation,

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

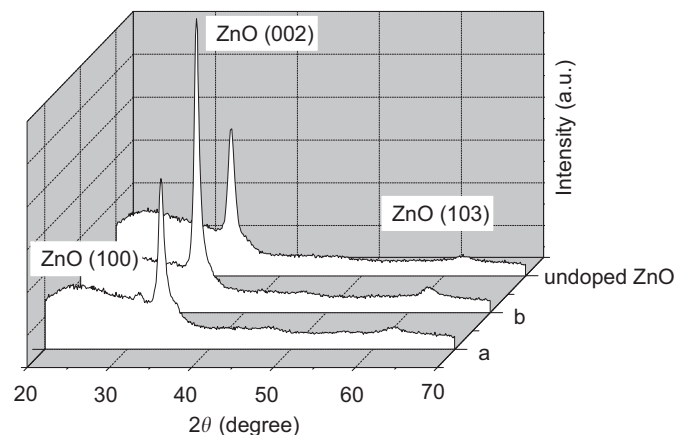


Fig. 1. XRD patterns of the undoped ZnO and Cu-doped ZnO fabricated at different oxygen partial pressure: (a) O₂:Ar = 12:12 (sccm) and (b) O₂:Ar = 20:12 (sccm).

where λ , θ and β are the X-ray wavelength (1.5406 Å), diffraction angle and FWHM of the ZnO (002) peak, respectively. The particle sizes of undoped ZnO, sample a and sample b are 11.3, 9.6 and 11.7 nm, respectively. It is evident that the crystallinity of the films

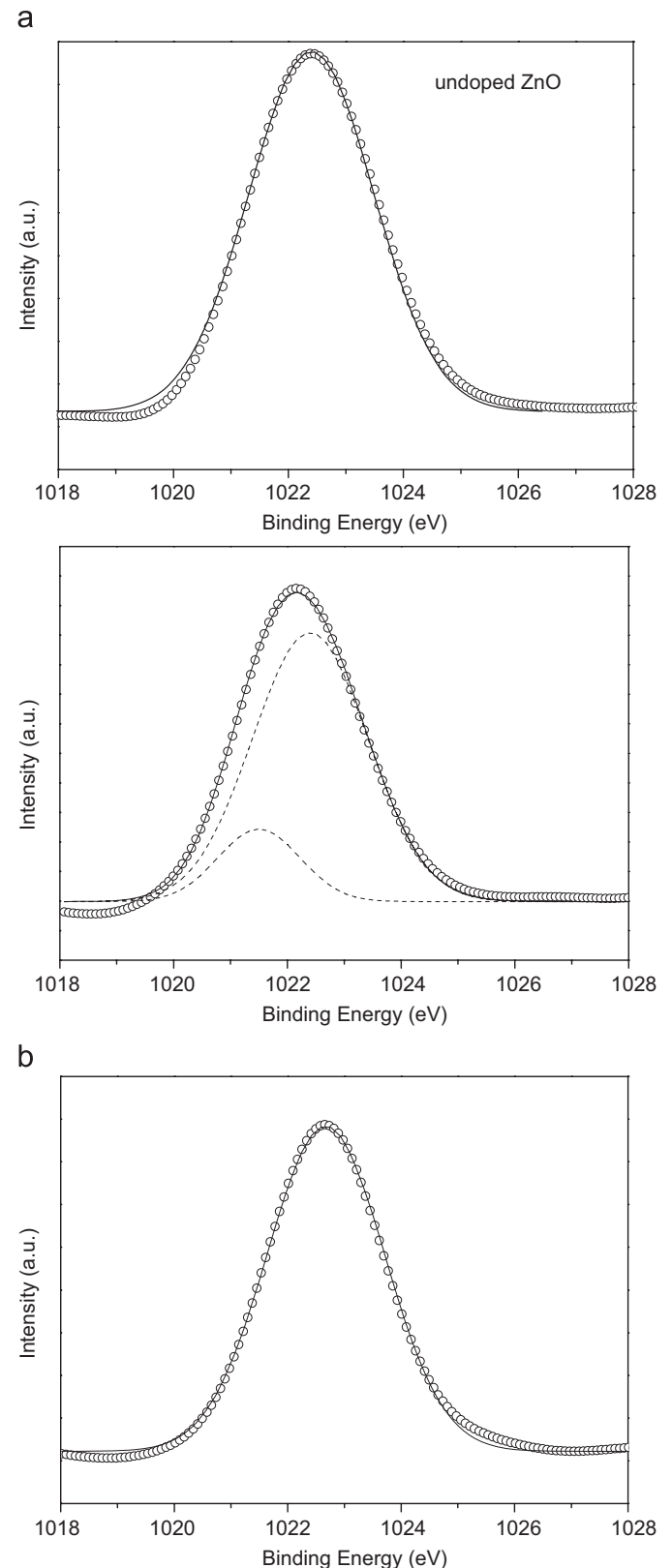


Fig. 2. XPS spectra (open circles) and simulated lines of Zn 2p_{3/2} in the undoped ZnO and Cu-doped ZnO films: (a) O₂:Ar = 12:12 (sccm) and (b) O₂:Ar = 20:12 (sccm).

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