Properties of Nb-doped ZnO transparent conductive thin films deposited by rf magnetron sputtering using a high quality ceramic target

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Abstract. Nb-doped ZnO films with (002) orientation have been grown on glass substrates by rf magnetron sputtering followed by vacuum annealing at 400°C for 3 h. The microstructures and surface figures of the Nb-doped ZnO films were investigated with X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. And its optical and electrical properties were measured at room temperature using a four-point probe technique and 756-type spectrophotometer, respectively. X-ray diffraction (XRD) revealed that the films are highly textured along the c axis and perpendicular to the surface of the substrate. After annealing at 400°C for 180 min under vacuum, transmittance of about 90% in visible region for Nb doped ZnO films was confirmed by the optical transmission spectra, and the low resistivity of $5 \cdot 47 \times 10^{-3}$ $\Omega \cdot$cm was obtained.

Keywords. ZnO films; Nb-doped; magnetron sputtering; optical and electrical properties.

1. Introduction

Transparent conducting oxides (TCOs) have found applications in several optoelectronic devices such as light emitting diodes (LEDs), solar cells, and flat panels as well as flexible displays (Srikant and Clarke 1998; Cui *et al* 2005; Hsieh *et al* 2007). Indium tin oxide (ITO) is the most commonly used TCO for these applications because of its high transmittance in the visible region and a resistivity close to $1 \cdot 0 \times 10^{-4}$ $\Omega \cdot$cm (Paraguay *et al* 1999). However, high cost and scarce resources of In limit its usage in these devices. This has led researchers to explore alternative materials for the TCO applications. Some of the TCOs which have shown transmittance and resistivity values close to those of ITO are ZnO : Al, ZnO : Ga, F : SnO_2, Nb : TiO_2 and so on. Among these, ZnO is the most favourable material because of its benign nature, relatively low cost, good stability in hydrogen plasma process, and non-toxicity (Paraguay *et al* 1999; Joseph *et al* 2001). After doping, ZnO as a semiconductor will become conductive. Therefore, there is a considerable interest in understanding the electrical and transport properties of doped ZnO films, which is critical for further improvement of TCOs characteristics.

Most of the careful doping studies have been performed by the kinds of techniques in order to improve the performance of ZnO films (Srikant *et al* 1995; Tang *et al* 1998; Paraguay *et al* 1999; Minami *et al* 2001; Dang *et al* 2007; Saito *et al* 2007). Doping with Al, Ga, In and so on, has been attempted by many groups, resulting in high-quality, highly conductive *n*-type ZnO films (Cao *et al* 2004; Özgü *et al* 2005). Recently, *n*-type ZnO films doped with other elements such as rare earth, W, Zr and so on has been prepared by different methods (Swanepoel 1983; Sarkar *et al* 1991; Fujimura *et al* 1993). To our knowledge, there is no report for single Nb doped ZnO films. In this paper, we report Nb-doped ZnO films grown on glass substrates at room temperature by rf magnetron sputtering and post vacuum annealing process.

2. Experimental

2.1 *Preparation of ceramic targets*

The raw materials were the commercially available ZnO and Nb_2O_5 (99·95% in purity). Mechanical mixed powders, as the raw materials, were treated by die pressing and normal pressing, and then sintered at 1300°C for 4 h in air. The following compositions were chosen: 98% ZnO + 2% Nb_2O_5 (wt%). The linear shrinkage ratios of the sintered targets reached about 22% and the relative density was about 95%.

2.2 *Preparation of thin films*

Room temperature deposition of high quality transparent conductive thin films is an advantage to industrial production. Nb-doped ZnO thin films were deposited on glass substrates using the ratio frequency (rf) magnetron

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sputtering technique. The glass substrates were thoroughly cleaned ultrasonically using ethanol absolute, acetone and distilled water as solvents and then dried prior to be loaded into deposition chamber. Sputtering was carried out at room temperature with a target–substrate distance of 67 mm and a sputtering gas pressure of 1·6 Pa. The chamber was evacuated to a base pressure of 8×10^{-5} Pa. A sputter-etch of 15 min was used to remove the target surface contamination. Finally, argon gas was introduced, and the gas pressure was adjusted. The substrate temperature was at room temperature. The sputtering power was 110 W. In order to produce more oxygen vacancies, oxygen was not used during the deposition. The samples were annealed at 400°C for 3 h under vacuum ($\sim 10^{-1}$ Pa). The thickness of the films was about 500 nm.

Crystallographic and phase structures of the as-grown Nb-doped ZnO films were determined by X-ray diffraction (XRD) (D8-Advance) with CuKα radiation. The scanning electron microscope (SEM) (JSM-5610LV) was used to investigate the surface morphology and measure the thickness of the films. Optical measurements (absorption and transmission) were made for photon wavelengths ranging from 300–900 nm, using a spectrophotometer (UV-756). During the spectrum testing, as a contrast the absorption spectrum of the bare substrate was already eliminated. The electrical resistivity was measured using a four-point probe technique (RTS-8) at room temperature.

3. Results and discussion

3.1 *Structural studies*

Figure 1 shows the X-ray diffraction (XRD) patterns of the Nb-doped ZnO films prepared at room temperature.
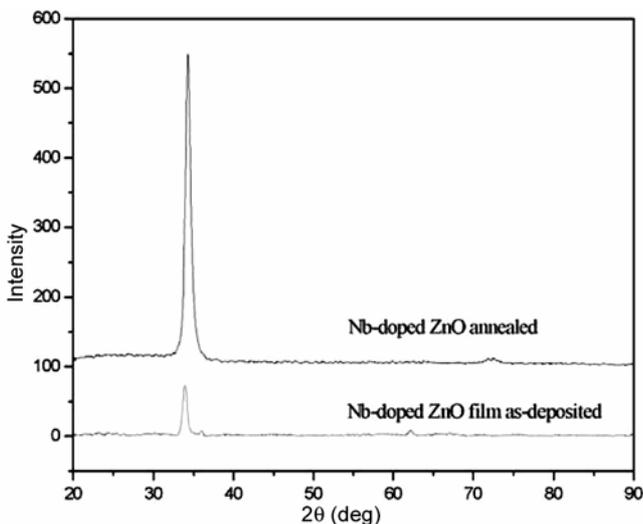

Figure 1. XRD diffraction patterns of Nb-doped ZnO thin films.

The results of these doped thin films are in good agreement with those reported in PDF for ZnO (PDF75-576, $a = 0.324270$ nm, $c = 0.519480$ nm), and the peaks correspond to a hexagonal wurtzite structure. Only the (002) peaks are observed in the XRD patterns, which show that the films are highly textured along the c-axis and perpendicular to the surface of the substrate.
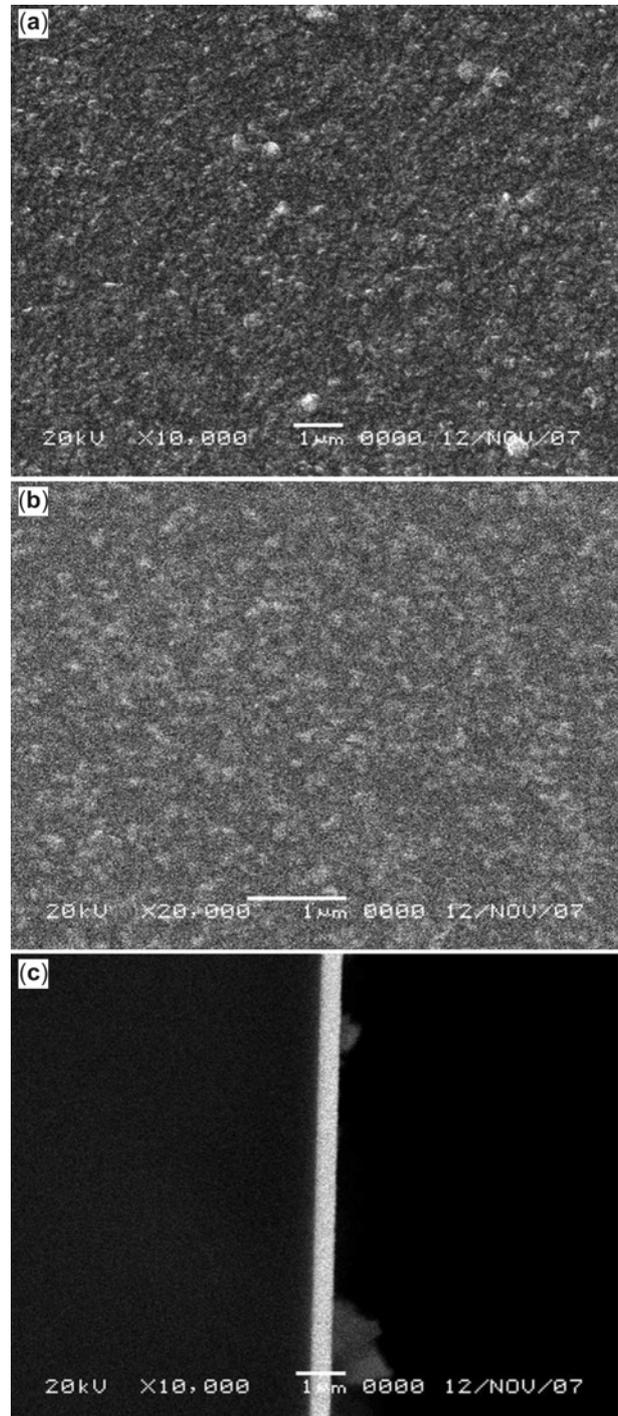

Figure 2. SEM micrographs of Nb-doped ZnO thin films: (**a**) deposited at room temperature; (**b**) annealed at 400°C for 3 h under vacuum and (**c**) the cross-section of the thin film (**a**).

The Nb-doped films obtained exhibited smooth, uniform, and dense surface morphology, as shown in figure 2. In order to calculate the particle size, *g*, of the Nb-doped films we have used the Scherrer formula (Moustaghfir *et al* 2003)

$$g = \frac{0 \cdot 94 \lambda}{B \cos \theta_{\mathrm{B}}}, \tag{1}$$

where λ, θ_{B} and B are the X-ray wavelength (1·54056 Å), Bragg diffraction angle and line width at half maximum. The crystallite size is in the range 15–20 nm.

3.2 *Photoelectric properties*

The transmission spectra of the doped ZnO thin films (with glass substrate) prepared at room temperature is shown in figure 3. In the visible region, all films perform high average transmittances that are more than 90% at wavelengths above 500 nm. The transmission curve for the bare substrate is also shown in figure 3. Evidently, the absorption edge of the bare substrate is away from that of the film, and the absorption edge of the film is within the light-admitting range of the bare substrate. In the visible region, the film annealed shows the average transmittance of the order of 90%, while the film as-deposited was of the order of 95%. It illustrates that the annealing reduces the optical properties. It is caused by diffusing of Nb^{5+} into the ZnO layer to partially substitute Zn^{2+} sites at high annealing temperature and forming of an impurity energy level. So a part of visible light is absorbed by exciting the electrons of the impurity level into conduction band.

Figure 4 shows plot of α^2 as a function of photon energy against $h\nu$ of the Nb doped films. As a direct bandgap semiconductor, the optical bandgap, E_{g}, can be determined by the following equation (Sarkar *et al* 1991)

$$\alpha = A(h\nu - E_{\mathrm{g}})^{1/2}, \tag{2}$$

where A is a constant dependent on the electron–hole mobility, α the absorption coefficient, as a function of the photon energy, $h\nu$. α is given by the formula (Swanepoel 1983)

$$\alpha = (\ln 100/T)/d, \tag{3}$$

where T is the optical transmittance, d the film thickness. The values of the optical energy gap (E_{g}) is determined by extrapolating the linear portion of the curves to $\alpha = 0$. By comparing with pure ZnO (the optical bandgap $\approx 3 \cdot 37$ eV), a shift from 3·37–3·20 and 3·30 eV for the films deposited and annealed, respectively was observed. This is similar to the report of Kim and Park (2002) who observed the bandgap shift from 3·25–3·13 eV for Co doped ZnO film (8% doping concentration), and of Lin *et al* (2008) who observed the bandgap shift from 3·58–3·45 eV for Gd doped ZAO film (1 wt.% Gd doping concentration). There seems to be an increase in refractive index on annealing as seen by the appearance of fringes in figure 3. It is attributed to the amplitude of the oscillations obtained in the envelope of the film at 400°C annealing temperature corresponding to good-quality film, seen from figure 1.

The doped ZnO film shows transition from insulator to metallic behaviour. The low resistivity value of $5 \cdot 47 \times 10^{-3}$ Ω·cm for the Nb-doped ZnO thin film was obtained by an annealing process of 400°C for 3 h. But before annealing, the Nb-doped ZnO film exhibits an insulating property. This indicates that an optimal annealing process will improve the electrical conductivity by increasing
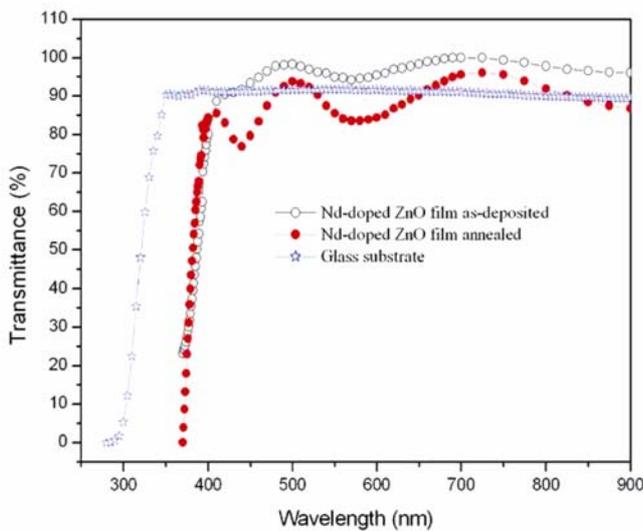

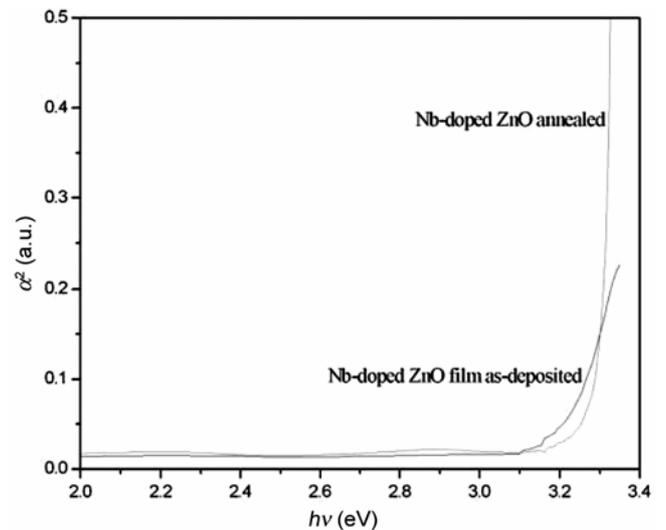**Figure 3.** Optical transmission spectra of Nb-doped ZnO thin films.

Figure 4. Plots of $(\alpha h\nu)^2$ against $h\nu$ for Nb doped ZnO thin films.

the oxygen defects and reducing the grain boundary scattering (Lin *et al* 2008). This result is similar to the argument of Han (2002). For further improvement of properties of the Nb-doped ZnO thin film, increasing sputtering powder and substrate temperature were useful (Cao *et al* 2009).

4. Conclusions

Nb-doped ZnO films were prepared by rf magnetron sputtering on glass substrates at room temperature using Nb-doped ZnO ceramic targets and followed by vacuum annealing at 400°C for 3 h. The structural, optical, and electrical properties of the Nb-doped films were investigated. Results show that the films exhibit hexagonal wurtzite structure with strong orientation along the *c*-axis (002). The Nb-doped ZnO films possessed some excellent properties, such as high transmittance (about 90%) in visible region, the optical bandgap is 3·20 and 3·30 eV for the deposited and annealed films, respectively. And the low resistivity value of 5.47×10^{-3} Ω·cm for the film was obtained by an annealing process of 400°C for 3 h.

Acknowledgement

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