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Temperature Effect on Optical and Electrical Properties of ZnO Films†

S.C. HER* and T.C. CHI*

Department of Mechanical Engineering, Yuan Ze University, Chung-Li, Taiwan

*Corresponding author: Tel: +886 3 4638800; E-mail: mesch@saturn.yzu.edu.tw

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Zinc oxide thin films were deposited on a glass substrate by Radio frequency magnetron sputtering. The effect of substrate temperature on the microstructure, optical and electrical properties was investigated. Crystal structure and surface morphology of the films were examined by X-ray diffraction and atomic force microscopy. XRD patterns and AFM images show that the crystallinity and grain size are increasing with the increase of substrate temperature. Electrical properties of the films were evaluated by Hall effect measurements. Experimental results indicate a decrease of film resistivity with the increase of substrate temperature. Zinc oxide films exhibit high transmittance of 84 % in the visible wavelength range 400-800 nm and is independent on the substrate temperature. Present work shows that the enhancement of the ZnO film performance with high transparency and low resistivity can be achieved by increasing the substrate temperature.

Keywords: Zinc oxide film, Substrate temperature, Transmittance, Resistivity.

INTRODUCTION

Since ZnO film is a wide band gap (3.37 eV) semiconductor with a relatively large excitation binding energy (60 meV). It exhibits several advantages with respect to other materials, including low resistivity, high transparency, wide band gap, high thermal and chemical stability, low cost and nontoxicity. Zinc oxide has many potential applications such as field-effect transistors[1], photodiodes[2], chemical and biological sensors[3] and solar cells[4]. In solar cell device technology, it is commonly used as transparent conducting layer because of its transparent in the visible region and electrically conductive. To obtain high quality ZnO films, a variety of preparation techniques can be used such as reactive evaporation, chemical vapor deposition (CVD), sputtering, pulsed laser deposition (PLD) and sol-gel spin coating. Magnetron sputtering with high deposition rate, high reliability and good control of the film properties is the most attractive and common use technique. Tsoutsouva *et al.*[5] examined the effect of oxygen pressure on the structural, electrical and optical properties of ZnO thin films, prepared by pulsed laser deposition. Lin and Kim[6] studied the influence of annealing temperature on tribological behavoiur of ZnO films deposited by Sol-gel method. Kumeta *et al.*[7] investigated the dependence of gas flow ratio and bias voltage on the formation of ZnO nanostructures by radio frequency magnetron sputtering. Dagamseh *et al.*[8] studied the effects of sputtering deposition parameters such as power and working pressure on the crystallite size of Al-doped ZnO films.

In this study, the effect of substrate temperature on the surface morphology, optical and electrical properties of ZnO films was investigated.

EXPERIMENTAL

The surface morphology and roughness of ZnO films were observed using atomic force microscopy (AFM). The grain size of ZnO films was calculated from the X-Ray diffraction (XRD) spectra using the Scherrer equation. Optical transmittance was measured using a spectrometer Lambda 750 from Perkin Elmer. Electrical properties were investigated using the Hall measurement.

Film preparation: A series of ZnO films were prepared by radio frequency magnetron sputtering system (ULVAC MB06-4703) on Corning 2000 glass substrate at different temperatures. Prior to deposition, the substrate was cleaned in soap solution, submerged in acetone solution and in an ultrasound bath for 15 min after rinsing with distilled water. Then the substrate was dried in an oven at the temperature of 50 ºC for 0.5 h before the application of deposition. The chamber is equipped with a rotary vane pump and a root pump. After a pumping time of 1 h, the chamber was evacuated down to a base pressure of 1.2×10^{-3} Pa. Highly pure (99.999 %) argon

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was used as the sputtering gas with the flow rate of 10 sccm. Before the application of deposition, the target and substrate were sputter-cleaned by Ar plasma for 10 min to remove the oxide and contaminant. Zinc oxide films were deposited at an operation pressure of 2×10^{-1} Pa with the duration of 1 h for all the prepared samples. In this way, four sets of ZnO thin films were prepared by varying the substrate temperatures (25, 100, 200 and 275 ºC). The effect of deposition temperature on the microstructure, optical and electrical properties of the ZnO film was investigated. The thicknesses of ZnO films prepared at substrate temperatures of 25, 100, 200 and 275 ºC are 409, 424, 505 and 567 nm, respectively. It shows that the film thickness is increasing with the increase of substrate temperature. This is probably due to the higher kinetic energy of the ad-atoms deposited to the glass substrate with increasing substrate temperature.

Surface topography: The microstructure and surface topography of ZnO films were examined using atomic force microscopy (Seiko Instruments Inc. SPA 400). Fig. 1 shows the AFM images of the surface topography of ZnO films prepared at different substrate temperatures [9]. The surface roughness (root mean square RMS) of ZnO films deposited at temperatures of 25, 100, 200 and 275 ºC are 3.45, 2.73, 5.16 and 5.03 nm, respectively. The increase of substrate temperature leads to an increase in the RMS roughness of the ZnO films. The films exhibit fine polycrystalline grains with uniformly distributed round clusters. It reveals that the films are highly dense and compact in nature. More energy is supplied to the deposition particles at higher temperatures resulting in the higher migration mobility, which in turn increases the surface roughness.

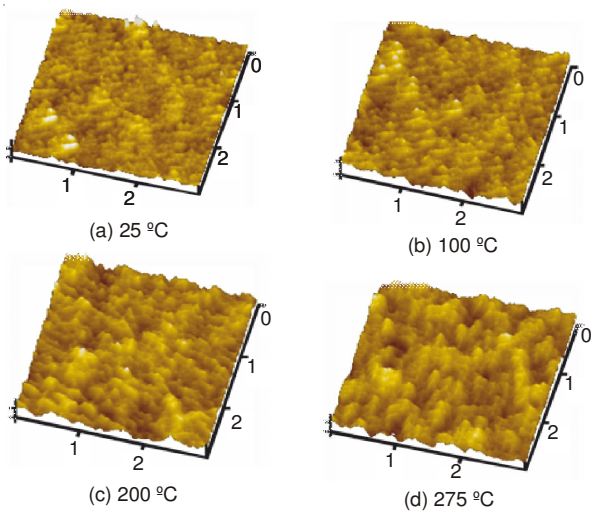

Fig. 1. Surface topography of ZnO film prepared at different substrate temperatures

The crystalline structure and preferential orientation of ZnO films was examined by X-ray diffraction (XRD) using Shimadzu LabX XRD-6000 with CuK_α radiation (λ = 0.154 nm) and scanned from 20-80º at a rate of 2º/min. A typical XRD pattern of ZnO film deposited at substrate temperature of 25 °C is shown in Fig. 2. All of the films show strong peaks in (002) direction, implying a polycrystalline hexagonal wurtzite crystal structure with a preferred c-axis orientation.

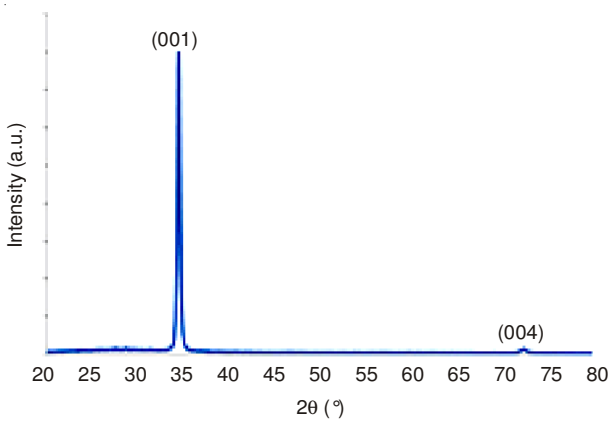

Fig. 2. XRD pattern of ZnO film prepared at substrate temperature 25 ºC

In the case of polycrystalline hexagonal structure, the most closely packed and with the lowest free surface energy is the (002) plane, which will favour the grain growth in this direction[10]. The increase of substrate temperature is found to enhance the ZnO (002) diffraction peak intensity. It is assumed that the temperature increase accelerates the mobility of the ad-atoms to energy favourable position resulting in an enhancement of the crystallinity of ZnO films[5]. Other low intensity peaks corresponding to (004) direction are also observed indicating that the films have a preferred orientation with c-axis perpendicular to the substrate.

The grain size (D) of ZnO films can be determined from the XRD spectrum using Scherrer equation[6] as follow.

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where λ, B and θ are X-ray wavelength (0.15406 nm), full width at half minimum (FWHW) of (002) peak and Bragg diffraction angle, respectively.

Substituting the values of FWHW and Bragg diffraction angle evaluated from the XRD spectrum into Scherrer eqn. 1, the grain sizes of ZnO films deposited at substrate temperatures of 25, 100, 200 and 275 ºC are 23.08, 23.36, 26.81 and 27.54 nm, respectively. This indicates that the grain size of the ZnO film is increasing with the increase of substrate temperature. The increases of diffraction intensity and narrowing of FWHW result in the enhanced crystallinity and increased grain size.

Optical properties: In this work, the transmittance spectra measurement was performed with the double beam spectrometer Lambda 750 from Perkin Elmer. Fig. 3 shows the optical transmittance spectrum in the wavelength range 300-1200 nm for ZnO films deposited at various substrate temperatures. No apparent changes of the average transmittance are observed for ZnO films deposited in the studied temperature range. The films have 75 % of average transmittance in the wavelength range 300-1200 nm and increase transmittance values up to 84 % in the visible wavelength range 400-800 nm.

The optical direct and indirect bandgap energy of thin films can be calculated using the following equations[11]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where α is absorption coefficient, $h\nu$ is photon energy, E_g is the bandgap energy, A is a constant independent on the photon energy and n is a constant depending on the nature of electronic

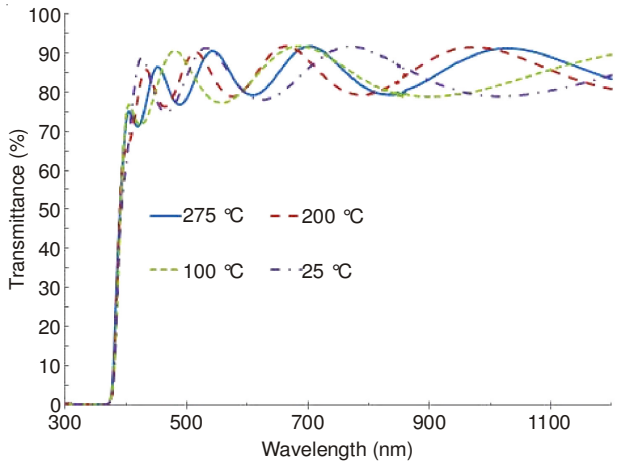

Fig. 3. Transmittance spectra of the ZnO films deposited at different substrate temperatures

transition. For the direct allowed transition, has a value of 1/2 while for indirect allowed transition, n = 2. ZnO crystals are characterized by direct allowed interband transition. Substituting n = 1/2 into eqn. 2, leads to

$$(\alpha h\nu)^2 = A^2(h\nu - E_g) \quad (3)$$

For a transparent thin film, the absorption coefficient α can be determined from its transmittance T as follow[12]

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (4)$$

where d is the film thickness.

By plotting the dependence of $(\alpha h\nu)^2$ *versus* hν, the bandgap energy E_g can be determined by extrapolating the linear portion of this plot to $(\alpha h\nu)^2 = 0$. The intercept on the x-axis gives the value of the bandgap energy E_g. A typical plot for ZnO films deposited at substrate temperature of 25 ºC is presented in Fig. 4. The bandgap energy of ZnO films increases from 3.248 to 3.276 eV while the substrate temperature is increasing from 25 to 275 ºC. These results show that the bandgap energy shifts to higher energy value for ZnO film deposited at higher substrate temperature. The wide bandgap shifts the absorption edge to a shorter wavelength as shown in Fig. 3 due to the Burstein-Moss effect. The blue shift of the absorption edge is attributed to the increasing crystallinity quality of the ZnO films deposited at higher temperature.

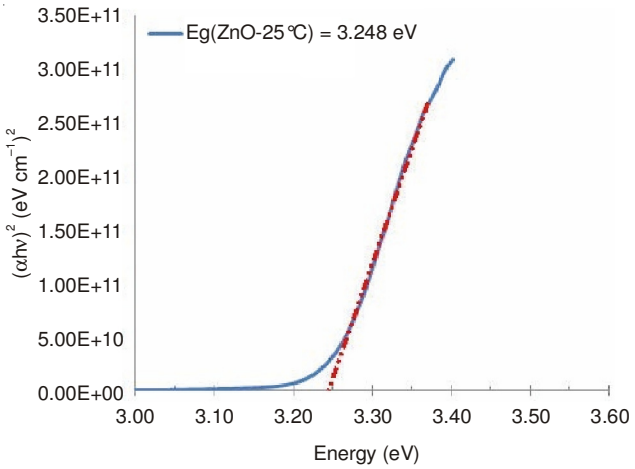

Fig. 4. Plot of $(\alpha h\nu)^2$ *versus* hν for ZnO film deposited at substrate temperature 25 ºC

Electrical properties: Room temperature Hall and resistivity measurements were conducted to characterize the electrical properties using an Ecopia HMS-300 system. The Hall measurements were repeated several times for each sample. The resistivities of the films deposited at substrate temperatures of 200 and 275 ºC are 1.26×10^{-2} Ωcm and 5.84×10^{-2} Ωcm, respectively. However, the resistivities of the films deposited at substrate temperatures of 25 and 100 ºC are too high to be detected by the Hall measurement. The Hall mobility increases from 4.05 to 7.67 cm^2/Vs as the substrate temperature increases from 200 to 275 ºC. The decrease of the resistivity as the substrate temperature increasing is attributed to the increase in the extent of the crystallization and orientation, which cause an increase of the mobility[13,14]. The carrier concentration increases from 1.23×10^{19} to 1.33×10^{19} cm^{-3} as the substrate temperature increases from 200 to 275 ºC.

Conclusion

Zinc oxide films were prepared on a glass substrate by radio frequency magnetron sputtering at different substrate temperatures ranging from 25-275 ºC. The effect of substrate temperature on the microstructure, optical and electrical properties was investigated. The AFM measurements show that the surface roughness increases with the increase of the substrate temperature. The electrical resistivity decreases and the mobility increases as the substrate temperature increases. High optical transmittance of 84 % in the visible range was achieved. The increase of the substrate temperature enhances the performance of ZnO films with a lower resistivity and a wider optical bandgap.

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