

Morphological and optical properties of vacuum evaporated ZnO thin films

Farzana CHOWDHURY¹, S. M. Firoz HASAN¹ and M. Sahabul ALAM^{2,3}

¹*Experimental Physics Division, Atomic Energy Centre, Bangladesh Atomic Energy Commission, 4, Kazi Nazrul Islam Avenue, Dhaka-1000, BANGLADESH*
e-mail: farzana1311@yahoo.com

²*Department of Physics, University of Dhaka, Ramna, Dhaka-1000, BANGLADESH*

³*Department of Physics, University of Erlangen-Nuremberg, Erwin-Rommel Strasse 1, D-91058 Erlangen-GERMANY*

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Abstract

ZnO thin films were deposited onto chemically and ultrasonically cleaned glass substrates by thermal evaporation in vacuum ($\sim 10^{-6}$ mbar). The thickness of the films was measured by frequency shift of quartz crystal. The optical properties of the films have been ascertained by UV-VIS-NIR spectrophotometry in the photon wavelength range of 300–2500 nm. The effect of substrate temperature on the optical properties of the films has been investigated, where all film thickness was kept fixed at 100 ± 10 nm. The optical transmittance spectra reveal a maximum transmittance of 88% at room temperature around photon wavelength of 2350 nm. Band gap and Urbach energy values of the films were calculated. The nature of the optical transition has been direct allowed. Surface topography studied by Atomic Force Microscopy (AFM) measurements showed a uniform film texture. The extent and nature of transmittance and optimized band gap of the material assure to utilize it for optoelectronic applications.

Key Words: ZnO thin film, vacuum evaporation, optical properties, urbach energy

1. Introduction

There has been much recent research on ZnO in thin film form for its possible applications in UV light emitters, gas sensors, transparent electronics, liquid crystal displays and as transparent contact in CuInSe₂ and Cu(In,Ga)Se₂ solar cells [1, 2].

ZnO is a widely used functional material with wide and direct band gap of 3.37 eV at room temperature (RT), large exciton binding energy (60 meV) compared with 24 meV for GaN, and excellent chemical and thermal stability, high optical transparency in the visible and near-infrared region [1–6].

There has been ongoing research on ZnO especially, in thin film form owing to its potential applications in optoelectronic devices such as in solar cells, optical wave guide, light emitting diodes (LED), flat-panel displays,

ferroelectric memories, gas sensors and biosensors, thin film transistors etc. [7–11]. Thin films of transparent conducting oxide ZnO is one of materials which attract much interest because of typical properties such as high optical transparency in the visible and near-infrared region.

In recent years, there has been rapid growth of blue and green light emitting diodes, which are based on GaN [12]. Zinc oxide thin film has near-perfect lattice match to gallium nitride (GaN) and its structure is isomorphic. As a result ZnO can be used as an alternative to GaN as a high energy light emitter and, thereby, reducing the cost [13]. Several deposition techniques have been used to grow doped and undoped ZnO thin films including chemical vapour deposition [14], sputtering [15], spray pyrolysis [16], magnetron sputtering [17], pulsed laser deposition [18], sol-gel [2] and so on.

An ultra high vacuum is necessary to grow device quality films with uniform morphology and free from contamination. Films were prepared employing thermal evaporation technique in vacuum in this study. This technique is simple and can be employed to coat large area surfaces and is, therefore, economically advantageous. The films prepared by vacuum evaporation have a very smooth surface and highly adherent to the surface of the substrate. The investigations on the effects of substrate temperature on the optical properties of ZnO thin films have been addressed.

2. Experimental

2.1. Growth of the films

Growth of ZnO films onto glass substrates was carried out by using an oil diffusion pump (E 306A, Edwards, UK) in vacuum ($\sim 10^{-6}$ mbar). ZnO powder (99.99% pure, USA) was used as a source material. During preparation, the thicknesses and the rate of deposition were measured in situ by frequency shift using an Edwards FTM5 quartz crystal thickness monitor, which also monitors the rate of deposition. The rate of deposition was 0.1–0.2 nm/sec. Substrate temperature was varied ranging between RT and 145 °C.

2.2. Optical measurements

2.2.1. Transmittance, reflectance and thickness.

Optical transmittance T and absolute specular reflectance R of the films with wavelength of light incident on them were measured using a Shimadzu UV-3100 dual-beam UV-VIS-NIR recording spectrophotometer. Light signals coming from the samples were detected by an integrating sphere. The thickness of the composite films was verified by the infrared interference method using the spectrophotometer. It depends on the reflectance characteristics of the films. In this method the thickness of a film is given by

$$d = \frac{\Delta m}{2\sqrt{n_1^2 - \sin^2 \theta}} \frac{1}{(1/\lambda_1) - (1/\lambda_2)}, \quad (1)$$

where n_1 is the refractive index of the film, θ is the incident angle of light to the sample, λ_1 and λ_2 are the peak or valley wavelengths in the reflectance spectrum and Δm is the number of peaks or valleys between λ_1 and λ_2 , where $\lambda_2 > \lambda_1$. The thickness was calculated using a fixed value of n_1 (here, $n_1 = 1.98$). The obtained thickness of the films was 100 ± 10 nm which conforms with the measuring value of thickness monitor as was controlled during experiment.

2.2.2. Absorption coefficient and band gap energy.

Expressions for the multiple reflected systems for transmittance T (in %) at normal incidence and reflectance R (in %) at near-normal incidence of light on the films have been given by Heavens [19]. Tomlin [20] simplified these expressions for absorbing films on non-absorbing substrates and expressed as

$$\frac{1-R}{T} = \frac{1}{2n_2(n_1^2 + k_1^2)} \times \left[\begin{array}{l} n_1 \{ (n_1^2 + n_2^2 + k_1^2) \sinh 2\alpha_1 + 2n_1n_2 \cosh 2\alpha_1 \} \\ + k_1 \{ (n_1^2 - n_2^2 + k_1^2) \sin 2\gamma_1 + 2n_2k_1 \cosh 2\gamma_1 \} \end{array} \right] \quad (2)$$

$$\frac{1+R}{T} = \frac{1}{4n_2(n_1^2 + k_1^2)} \times \left[\begin{array}{l} (1 + n_1^2 + k_1^2) \{ (n_1^2 + n_2^2 + k_1^2) \cosh 2\alpha_1 + 2n_1n_2 \sinh 2\alpha_1 \} \\ + (1 - n_1^2 - k_1^2) \{ (n_1^2 - n_2^2 + k_1^2) \cos 2\gamma_1 - 2n_2k_1 \sinh 2\gamma_1 \} \end{array} \right], \quad (3)$$

where n_1 and n_2 are the refractive indices of the film and substrate, respectively; k_1 is the extinction-coefficient of the film; $n_2 = 1.45$; $\alpha_1 = (2\pi k_1 d / \lambda)$ and $\gamma_1 = (2\pi n_1 d / \lambda)$, where λ is the wavelength of light and d is the thickness of the film. Equations (2) and (3) have been solved for k_1 and n_1 using a computerized iteration process. The absorption coefficient α was then calculated via the relation $\alpha = (4\pi k_1 / \lambda)$. The dependence of α on photon energy has been analyzed with the models discussed in equation (4) to find the nature of the band gap energy.

2.3. Atomic Force Microscopy (AFM) measurements

The surface topography of the investigated sample was studied by Atomic Force Microscopy technique. All AFM images were recorded using a NT-MDT instrument operating in non-contact mode. Resolution for topography measurements was 256×256 points. The experiment was carried out under ambient conditions.

3. Results and discussion

The optical transmittance spectra of ZnO thin films at RT and different substrate temperatures are shown in Figure 1(a), revealing the formation of the semiconducting compound. It is observed that the transmittance decreased with increase of substrate temperature. The mobility of the atoms increases at higher temperatures, which causes the increase in grain size [21]. The larger grains might explain the lower transmittance. The average transmittance reached above 80%. Maximum transmittance of 88.16% was achieved at 2500 nm of photon wavelength for the sample which was developed at RT, i.e. no substrate temperature. These spectrums show two distinct regions: one for long wavelengths ($750 \leq \alpha \leq 2500$), in which transmittance increases with photon energy; and another for short wavelengths ($300 \leq \alpha \leq 750$), where transmittance decreases abruptly down to almost zero. Dependence of absorption coefficient on photon energy for ZnO thin films having different substrate temperatures is shown in Figure 1(b). The films have lower sub-band gap absorption and steeper fundamental absorption region. A significantly high absorption coefficient ($\approx 10^3 \text{ cm}^{-1}$) below 1.53 eV, the fundamental edge is found for these films. The figure reveals the presence of tail absorption in the films. The departure of the lattice from perfect periodicity and unexpected localized states within the band gap cause tail absorption. The width of the localized states is calculated later in this paper.

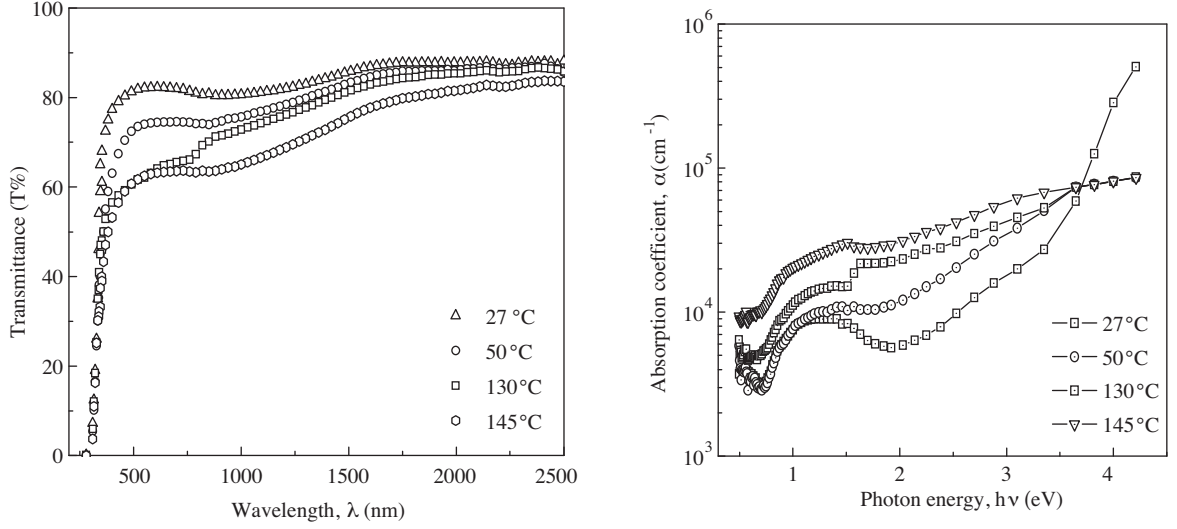


Figure 1. (a) Optical transmittance T (in %) of ZnO thin films as a function of photon wavelength λ , prepared at different substrate temperatures. (b) Dependence of absorption coefficient α as a function of photon energy, $h\nu$, at different substrate temperatures.

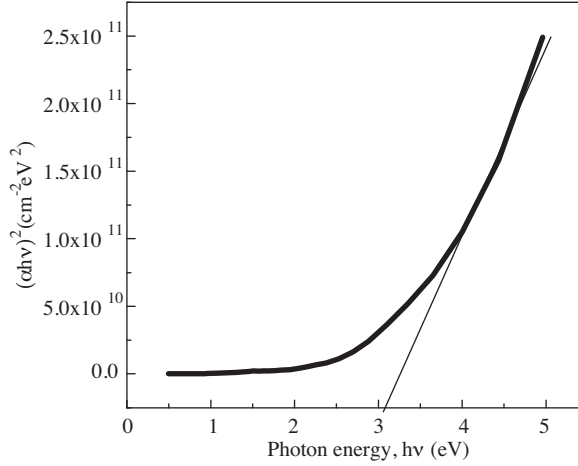


Figure 2. A typical curve of $(\alpha h\nu)^2$ vs. photon energy $h\nu$ for ZnO thin film.

The dependence of the absorption coefficient α above the fundamental edge follows the relation in the photon energy range $1.53 \leq h\nu \leq 3.69$ eV for an allowed direct interband transition [22], described by the relation

$$\alpha = \frac{A_1}{h\nu} [h\nu - E_{g1}]^{1/2} \quad (4)$$

Here, E_{g1} is the band gap energy of the interband transition and A_1 is a parameter that depends on the probability of transition and the refractive index of the material. The energy gap value was determined from a plot of $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, as shown in Figure 2. The linear portion of this plot intercepts to the x-axis giving the value of direct energy gap in the photon energy range $3.17 \leq h\nu \leq 3.37$ eV. The band gap energy increased as the substrate temperature decreased from RT to 145 °C. At RT, the

obtained direct optical energy gap (3.37 eV) of ZnO film conforms with the reported value [3]. The calculated energy gap values E_g and the values of A_1 are given in Table 1.

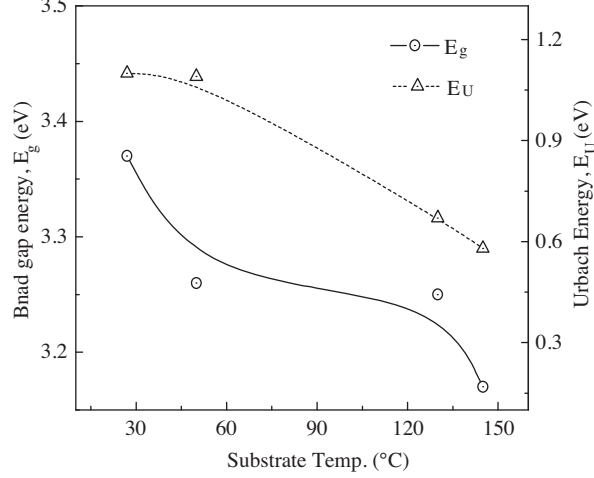


Figure 3. Band gap energy E_g and Urbach energy E_U as a function of substrate temperatures.

Width of the tails of the localized state associated with the amorphous state in the forbidden band can be determined by the following relation described by Urbach [23]

$$\alpha = \alpha_o \exp(h\nu/E_U),$$

where α_o is a constant and E_U is the Urbach energy which has been derived from the slope of $\ln(\alpha)$ plotted as a function of photon energy. Calculated values of E_U are shown in Table 1. Band gap energy and Urbach energy as a function of substrate temperatures are shown in Figure 3. It is shown that band gap energy has a correlation with Urbach energy, as both decreases with the increase of substrate temperatures.

Table 1. Optical parameters of ZnO thin films.

Substrate Temperature °C	Maximum Transmittance T (in %)	Energy Gap E_g (eV)	A_1	Urbach Energy E_U (eV)
Room Temperature	88.16	3.37	1.65×10^6	1.10
50	87.60	3.26	1.52×10^6	1.09
130	86.66	3.25	1.60×10^6	0.67
145	83.75	3.17	1.74×10^6	0.58

Studies on surface morphology were performed by AFM measurements (Figure 4 for an image sample) for the film with highest transmittance ($\sim 88\%$); this is the film possessing the best optical quality. The study demonstrates a uniform and densely packed granular arrangement of ZnO film. No defect or void formation is present on the surface of the film. The average grain size was determined as 192 nm. The root mean square value of surface roughness was estimated to be 43 nm.

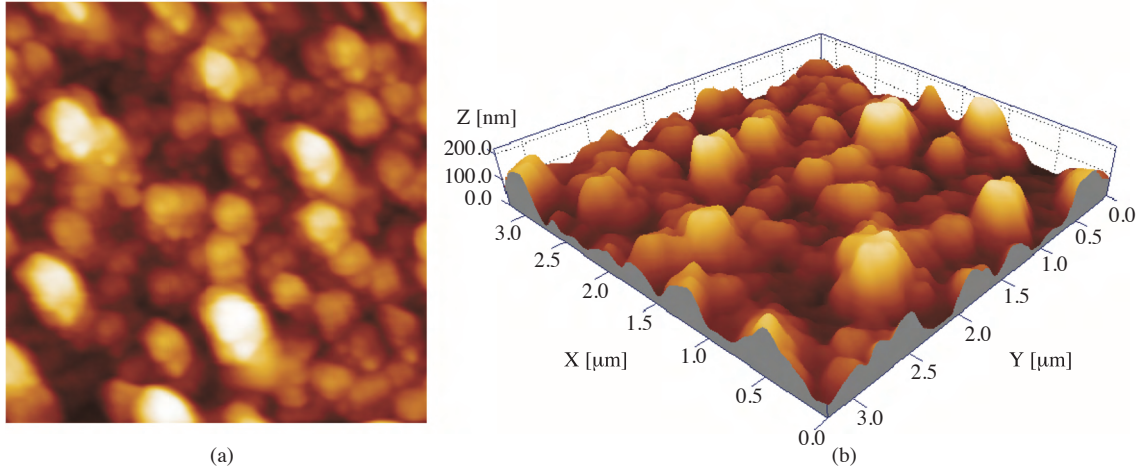


Figure 4. An image sample showing AFM topography on $3.20 \times 3.20 \mu\text{m}^2$ area of ZnO thin film grown at room temperature. (a) 2-D image. (b) 3-D image.

4. Conclusions

ZnO thin films of uniform surface and high optical transmittance were prepared. Maximum transmittance of 88.16% was found for ZnO films developed at room temperature. Band gap energy was found to be direct allowed and varied between 3.17 and 3.37 eV depending on the substrate temperatures. The RT band gap value agrees with the reported value of ZnO. Urbach energy has a value of 1.1 eV for the film with highest transmittance which is grown at RT. Band gap energy shows a correlation with Urbach energy for the studied ZnO films. The AFM study shows a compact granular nature of the film possessing highest transmittance shows average grain size of 192 nm. The results are important for providing information on deposition conditions, for the higher quality ZnO films and fabrication of the optoelectronic devices.

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