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Effects of substrate temperature on the optical properties of vacuum evaporated ZnO thin films

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ZnO thin films were grown onto chemically and ultrasonically cleaned heated and unheated glass substrates in a vacuum of 10^{-6} mbar by using oil diffusion pump. 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. Bang gap and Urbach energy values of the films were calculated. 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 make possible to use it for optoelectronic applications.

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1. Introduction

Zinc oxide (ZnO), is a compound semiconductor of the II–VI family, which crystallizes in hexagonal Wurtzite structure. 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) as 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 [7-12]. In recent years, there is a rapid growth of blue and green light emitting diodes, which are based on GaN [13]. 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 [14]. Several deposition techniques have been used to grow doped and undoped ZnO thin films including chemical vapour deposition [15], sputtering [16], spray pyrolysis [17], magnetron sputtering [18], pulsed laser deposition [19], sol-gel [20] 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). The rate of deposition was 0.1-0.2 nm/sec. During preparation, the thicknesses were measured in situ by frequency shift of FTM5 quartz crystal thickness monitor (Edwards, UK); which also monitors the rate of deposition. Substrate temperature was varied ranging between RT and 145 ^{o}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 dual-beam UV-VIS-NIR recording spectrophotometer (Shimadzu, UV-3100, Japan). 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

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

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 m ultiple reflected systems for transmittance (T %) at normal incidence and reflectance (R %) at near-normal incidence of light on the films have been given by Heavens [21]. Tomlin [22] simplified these expressions for absorbing films on non-absorbing substrates and expressed as

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

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

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 using $\alpha = (4\pi k_1/\lambda)$. 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 condition.

3. Results and discussion

The optical transmittance spectra of ZnO thin films at RT and different substrate temperatures are demonstrated in Fig. 1 (a) which reveals the formation of semiconducting compound. It is observed that the transmittance decreased with the increase of substrate temperature. The mobility of the atoms increases at higher temperatures which causes the increase of grain size [23]. The larger grains might be the reason of 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≤ α ≤2500) transmittance increases with photon energy and another for short wavelengths (300≤ α ≤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 Fig. 1 (b). The films have lower sub-band gap absorption and steeper fundamental absorption region. A significantly high absorption coefficient ($\approx 10^3$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.

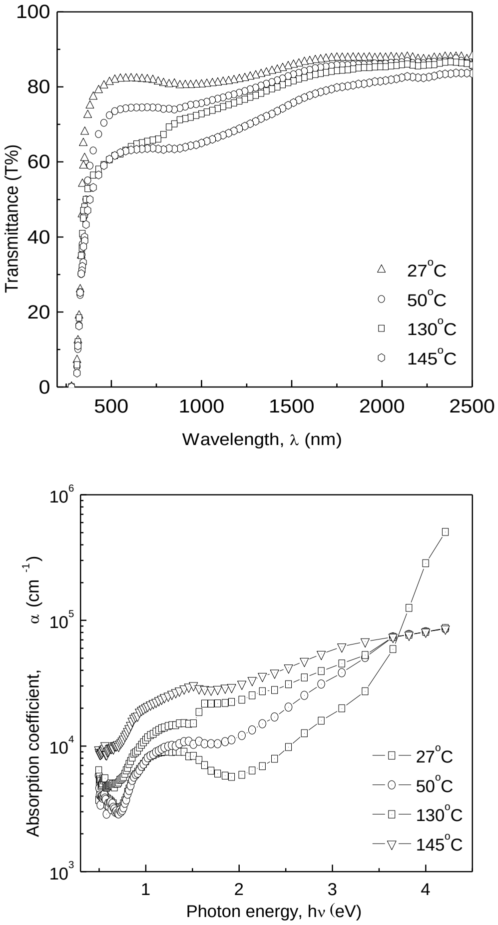


Fig. 1. (a) Optical transmittance (T%) of ZnO thin films as a function of photon wavelength, λ prepared at different substrate temperatures. (b) Dependence of absorption coefficient, α as a function of photon energy, $h\nu$ at different substrate temperatures.

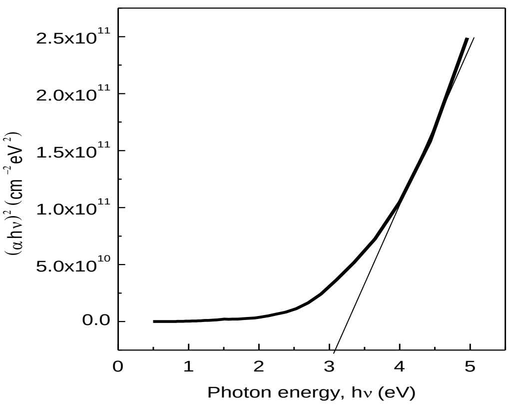


Fig. 2. A typical curve of $(\alpha h\nu)^2$ vs. photon energy, hν of ZnO thin film.

The dependence of the absorption coefficient, α above the fundamental edge follows the relation in the photon energy range 1. 53 ≤ hν ≤ 3.69 eV f for an allowed direct interband transition [24], described by

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

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 $(\alpha h\nu)^2$ vs. photon energy (hν) plot as shown in Fig. 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≤ hν ≤ 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.

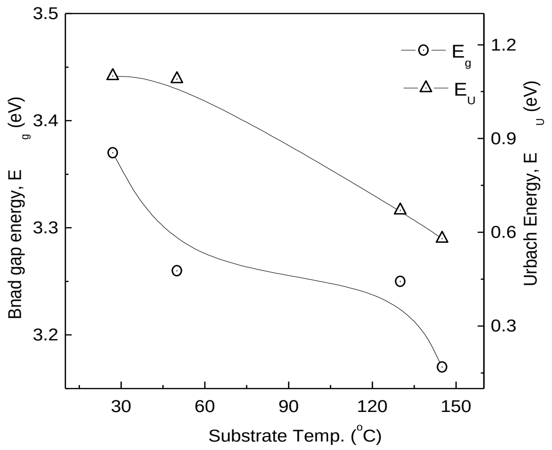


Fig. 3. Band gap energy (E_g) and Urbach energy (E_U) as a function of substrate temperatures.

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 [25]

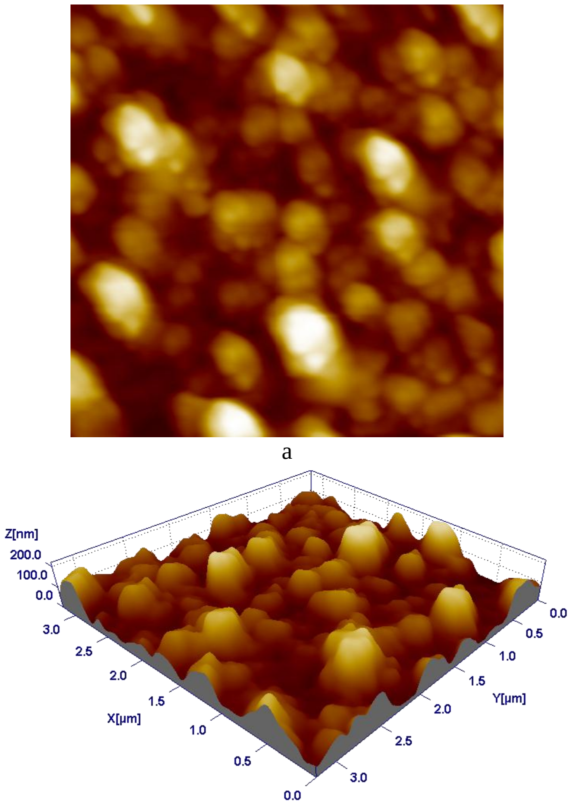
$$\alpha = \alpha_o \exp(h\nu/E_U) \qquad (5)$$

where α_o is a constant and E_U is the Urbach energy which has been derived from the slope of lnα vs. photon energy plot. 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 Fig. 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 Temp. (°C)	Maximum Transmittance (T%)	Energy Gap, Eg (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	$1.\ 52\times10^6$	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 (Fig. 4) for the film with highest transmittance (~88%); which is assigned to be the film possessing best optical quality. The study demonstrates a uniform and densely packed granular arrangement of ZnO film. No defect or void formation are 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.



a

b

Fig. 4. AFM topography on (3.20 × 3.20) μm^2 area of ZnO thin film grown at RT. (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 RT. Bang 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 this film that gives average grain size of 192 nm. The results are important for providing informations on deposition conditions, for the higher quality films and fabrication of the optoelectronic devices.

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