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INFLUENCE OF THICKNESS VARIATION ON THE OPTICAL PROPERTIES OF ZnO THIN FILMS PREPARED BY THERMAL EVAPORATION METHOD

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Abstract

ZnO thin films were deposited onto chemically and ultrasonically cleaned glass substrates by thermal evaporation in vacuum (~10^6 mbar). Films of thickness ranging between 50 and 250 nm were prepared at room temperature. The optical properties of the films were ascertained by UV-VIS-NIR spectrophotometry (photon wavelength ranging between 300 and 2500 nm). Influence of thickness of the films on the optical properties was studied keeping other deposition parameters fixed. The optical transmittance spectra reveal a maximum transmittance of 88% around photon wavelength of 2350 nm for the film with thickness of 50 nm. Maximum transmittance decreased with the increase of film thickness in an irregular pattern. Optical transmittance, reflectance and thickness of the films were utilized to compute the absorption coefficient and band gap energy of the films using a computerized iteration process. The nature of the optical transition has been direct allowed with average band gap energies ranging between 3.56 eV and 3.7 eV. The band gap energy has a tendency to decrease with the increase of the film thickness. The extent and nature of transmittance and optimized band gap of the material assure to utilize it for photovoltaic applications.

Keywords: ZnO, thin film, optical transmittance, vacuum evaporation, band gap energy

I. INTRODUCTION

Recently there has been a lot of 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 $CuInSe_2$ and $Cu(In,Ga)Se_2$ solar cells[1-3]. Thin films of transparent conducting oxide (TCO) zinc 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 [4]. Several groups have already done much research on ZnO by use of various film growth techniques, including RF/DC magnetron sputtering [5], chemical bath deposition [6,7], pulsed laser deposition [8], sputtering [9-11] and spray pyrolysis [12]. Thermal evaporation is a useful method for obtaining zinc oxide (ZnO) thin films, because of its ease of operation. Large area surfaces can be coated by using this method. Although lots of works have been done on ZnO, it still requires carrying out intensive research to study its fundamental properties in order to obtain better quality films. Concerning its significant interest in recent research world, our aim is to have a systematic study on ZnO thin film based on vacuum evaporation technique.

In this study, ZnO thin films of different thickness were prepared. Optical properties of the films were investigated by using a ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer. The value of absorption coefficient, 'α' and optical band gap energy (E_g) were obtained from transmittance (T%), reflectance (R%) and thickness of the films. In optoelectronic device applications, knowledge of the optical parameters such as transmittance index and absorption coefficient of semiconductors as well as their electrical properties is necessary for designing appropriate heterostructures.

II. EXPERIMENT

2.1 Growth of the Films

Growth of the Films was carried out by using a high vacuum ($\approx 10^{-6}$ mbar) evaporation pump (Edwards, UK). Films of thicknesses 50 nm, 100 nm, 150 nm, 200 nm and 250 nm were deposited at room temperature onto chemically and ultrasonically cleaned glass substrates. A molybdenum boat was used to evaporate ZnO and placed at a distance of 10 cm from the glass substrate. The thickness of the films was measured in situ by frequency shift of quartz crystal thickness monitor (FTM 5, Edwards, UK). The rate of evaporation was 0.1- 0.2 nm/sec. which was measured in-situ with the same quartz crystal thickness monitor.

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 multiple 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 [13]. Tomlin [14] simplified these expressions for absorbing films on non-absorbing substrates and expressed as

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

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

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 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.

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. $\alpha_1 = 2\pi k_1 d/\lambda, \gamma_1 = 2\pi n_1 d/\lambda$, where d is the thickness of the film and λ is the wavelength of light. This equation has been solved for k_1 using a computer iteration process, $n_2 = 1.45$. Absorption coefficient α was calculated by using the relationship $\alpha = 2\pi kd/\lambda$. The band gap energy has been calculated by using the above mentioned model from the dependence of absorption coefficient, on photon energy.

III. RESULTS AND DISCUSSION

The variations of transmittance of the films with thickness of 50 nm, 100 nm, 150 nm, 200 nm and 200 nm were studied. The films were transparent and uniform to the naked eyes. This is evident from the transmittance curves. The transmittance spectra as a function of photon wavelength ranging between 300 to 2500 nm is represented in Fig. 1 where all sample have the same substrate temperature of 27^{o}C. Transmittance was measured starting from 2500 nm which reaches to a minimum value of around zero at 300 nm of photon wavelength. Maximum transmittance obtained from this study is 88.18% at 2350 nm of photon wavelength for the sample with thickness of 50 nm. In the visible region the transmittance varied between 62.50% to 78.54% for this sample. The transmittance was found to decrease with the increase of film thickness in an irregular manner. Sharp absorption edge was obtained near 500 nm of photon wavelength. The obtained result conforms well with the result of other workers [4]. Maximum transmittance of the films and the corresponding wavelengths are represented in Table (1).

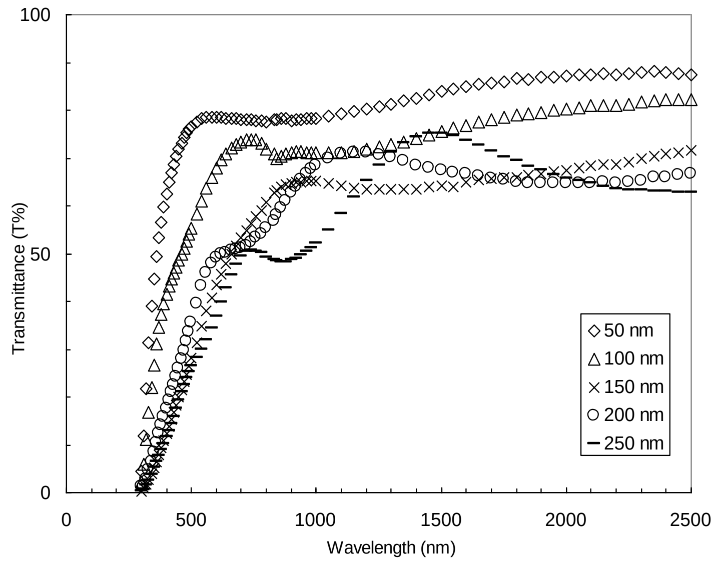

Fig-1: Dependence of optical transmittance on photon wavelength for ZnO thin films having different thickness.

Table: 1 Optical parameters of ZnO thin films.

Thickness (nm)	Wavelength (nm)	Transmittance (T%)	E_g (eV)	A
50	2350	88.18%	3.46	3.8×10^6
100	2500	82.32	3.43	1.65×10^6
150	2500	71.63	3.3	9.6×10^6
200	1150	71.07	3.32	1.1×10^6
250	1450	75.01	3.30	1×10^6

Dependence of absorption coefficient 'α' on photon energy $h\nu$ for ZnO thin films of different thickness is shown in fig. 2. Maximum value of the absorption coefficient 'α' was obtained as 8.1×10^5 cm^{-1} for the sample with thickness 50 nm. Fundamental absorption is steeper for these films. SBG absorption is the lowest for the sample with thickness of 150 nm. Most of the films show tail absorptions. Below the fundamental edge of 1.6 eV the films show absorption coefficient is significantly high (>$10^4 cm^{-1}$). Tail absorption might originate from some gap-states. These gap states occur from the trapping sites located in the grain boundaries [15]. Above the fundamental edge the absorption coefficient is as high as $10^6 cm^{-1}$.

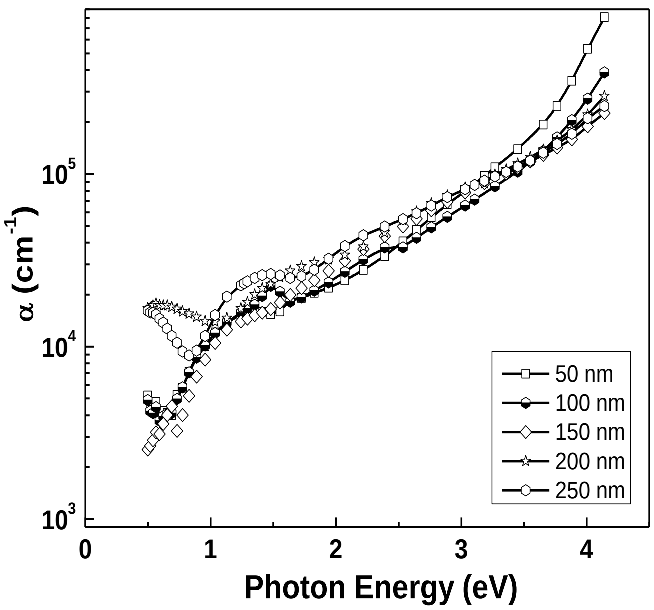

Fig-2: Dependence of absorption coefficient on photon energy for ZnO thin films having different thickness.

The rise of α in the photon energy range 1.8 eV to 4.1 eV follows a relation for an allowed direct interband transition [16], described by

$$\alpha = \frac{A}{h\nu}\left[h\nu - E_g\right]^{1/2} \tag{4}$$

where E_g is the band gap energy of the inter-band transition and A is a parameter that depends on the probability of transition and the refractive index of the material.

The band gap energy E_g and the value of A_1 [Table 1] were extracted from the Tauc's plot of $(\alpha h\nu)^2$ versus $h\nu$ [see Fig.3] in the range $3.2 \le h\nu \le 4.15$ eV.

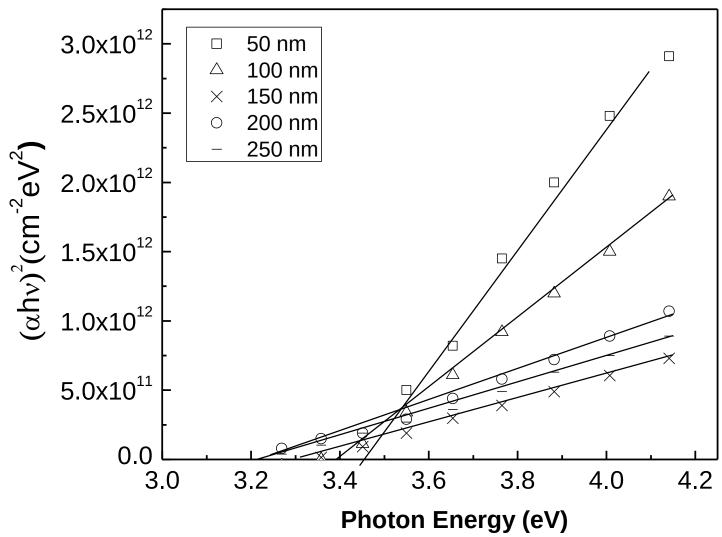

Fig:-3: Variation of $(\alpha h\nu)^2$ vs. photon energy, $h\nu$.

Extrapolation of the linear part of this plot intercepts to the x- axis and gives the value of band gap energy E_g . Energy gap value was found to decrease with the increase of the film thickness (fig. 4).

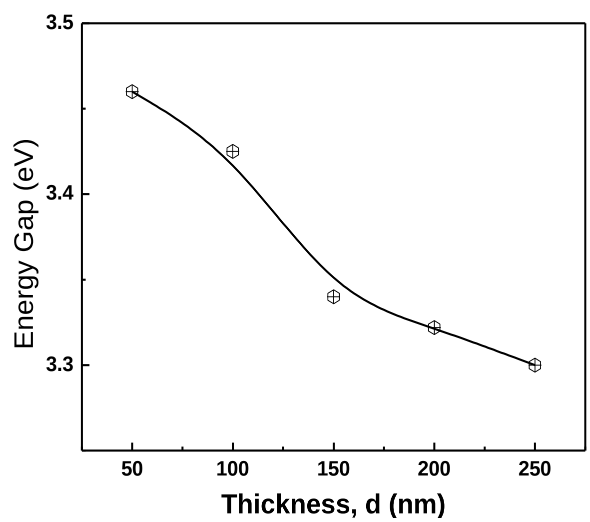

Fig-4: Variation of energy gap as a function of film thickness.

The decrease of direct band gap with the increase of thickness can be attributed to an increase of particle size, decrease of strain and increase of lattice constant [17].

The calculated value of the optical energy gap for five ZnO thin films are given in Table 1.

IV. CONCLUSION

ZnO thin films with high optical transmittance were prepared by thermal evaporation technique. The nature of the optical absorption of ZnO thin films above the fundamental absorption edge is direct allowed optical transition. Optical energy gap decreased with the increase of film thickness. The optical properties of the films could be changed by optimizing the growth parameters which is an important achievement for thin film technology. The results obtained from this study are interesting to be utilized in the field of optoelectronic technology.

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