

On the study of optical and structural properties of zinc oxide thin films by sol-gel dip coating technique

Ajayi Jonathan Olanipekun, Oluwatomi Similoluwa and Adedokun Oluwaseun*

Ajayi Jonathan Olanipekun is an Associate Professor in Department of Pure and Applied Physics, LAUTECH, Ogbomosho, Nigeria.

E-mail: joajayi@lautech.edu.ng

Oluwatomi Similoluwa is a graduate of Applied Physics, Department of Pure and Applied Physics, Lautech, Nigeria,

E-mail: deifilius1@gmail.com

Corresponding Author (): Adedokun Oluwaseun is currently Assistant Lecturer in Department of Pure and Applied Physics, LAUTECH, Ogbomosho, Nigeria*

E-mail: oadedokun@lautech.edu.ng

Abstract- This paper reports the study of optical and structural properties of ZnO thin films by sol-gel dip coating technique. ZnO thin films were prepared by sol-gel process using zinc acetate di-hydrate, ethanol and di-ethanolamine as the precursor, solvent and stabilizer, respectively. The dipping time of the substrates and annealing temperature of the thin films were varied. And then structural and optical properties of the as-prepared ZnO thin films were investigated by X-ray diffractometer and UV-Vis spectrophotometer, respectively while the thickness of the as-deposited thin films were determined using a gravimetric method. The structural analysis shows that the films are polycrystalline with a hexagonal wurtzite structure and a preferential c-axis orientation. The films have high transmittance in the VIS/NIR region and low transmittance near the fundamental absorption. The absorbance of the ZnO thin film was observed to be low in the VIS/NIR regions and high in the UV region. From these results, an increase in dipping time, leads to an increase in the thickness of the thin films which also leads to a better uniformly distributed films with smooth absorption spectra of the ZnO thin films. Decrease in the average transmittance of the deposited ZnO thin films was found to be related with increase in annealing temperature of the ZnO thin films.

Index Terms — Absorption coefficient, annealing temperature, dip coating, fundamental absorption, sol-gel, ZnO thin film.

1 INTRODUCTION

Zinc oxide is an important II-VI group semiconductor material, with a hexagonal wurtzite crystal structure ($c = 5.12\text{\AA}$ and 3.25\AA), wide and direct band-gap of 3.3eV (at 300K), large free-exciton binding energy (60meV), strong cohesive energy of 1.89eV , high mechanical and thermal stabilities and radiation hardness [1]. This material is an n-type semiconductor that also belongs to the class of transparent conductive oxides (TCO). Due to its unique properties, zinc oxide has a wide range of applications such as transparent conductors [2], solar cell windows [3], gas sensors [4], surface acoustic wave devices [5], ultraviolet photoconductive detectors [6], ultraviolet light-emitting diodes [7] and so on. So far, ZnO thin films have been prepared by many techniques such as molecular beam epitaxy (MBE), pulsed laser deposition (PLD), metal-organic chemical vapour deposition (MOCVD), magnetron sputtering, electron beam evaporation, spray pyrolysis and sol-gel method [8]. However, the sol-gel process has many advantages such as ease of composition control, low cost and simple deposition equipment, low processing temperature and easy fabrication of large-area films.

In this work, films of ZnO were synthesized using the sol-gel dip coating technique. The structural properties of the

ZnO thin films were examined and effect of dipping time and annealing temperature on some optical properties of the as-prepared films were studied.

2 MATERIALS AND METHODS

2.1 Experimental details

The sol-gel solution was prepared by dissolving 10g of zinc acetate di-hydrate (Zn source) in 25ml of ethanol (solvent) and heated at 100°C for 15 minutes till it became a uniform transparent mixture. 5ml of di-ethanolamine (stabilizer) is added to the mixture and stirred with a magnetic stirrer at 70°C till the solution becomes colourless. This procedure is repeated thrice to get a sol-gel of high volume. Thereafter, the solution is left to age at room temperature for 48 hours before dipping of the substrates. A change in viscosity of the sol-gel after ageing was observed.

In this work, borosilicate glasses were used as substrate. All glass substrates and petri dishes (for keeping samples) were cleansed in deionized water, ethanol and acetone and allowed to dry in air before coating. This was done to remove any impurity or dirt that might have formed on their surfaces which can contaminate the films. Pre cleaned substrates were dipped inside the sol-gel bath for the deposition of ZnO films for a particular time and a known substrate removal rate.

In total, six samples of ZnO thin films were prepared. Similar procedures were followed for substrate removal rate for all the samples. During this dip-coating process, the dipping time of three samples was varied by 2 hours. These samples were labeled as sample 1, 2 and 4 for 2 hours, 4 hours and 6 hours, respectively and were all annealed at 400°C. However, all samples were allowed to dry in air for 30 minutes after removal from the sol-gel solution. Before annealing, all samples were pre-heated in a Genlab vacuum oven at 250°C for 30 minutes. After pre-heating, it was physically evident that ZnO thin films had formed on the glass substrate. And also during the coating process, the dipping time of three samples were kept constant for 6 hours and were labelled as sample 3, 5 and 6 for samples annealed at 500°C, 600°C and 700°C respectively. These ZnO films samples were annealed at various temperatures under inert atmosphere (N₂) for a period of 1hour to study effect of annealing temperature on optical properties of ZnO films.

The substrates were weighed before and after dip-coating with the aid of an analytical weighing balance. The transmittance of the ZnO thin films were obtained at room temperature using Avantes Spectrometer with Avasoft 8.0 in the wavelength range 320-1000nm. The crystal structure of the ZnO thin films was studied with X-ray diffraction (XRD) patterns obtained with a Panalytical Xpert Pro diffractometer with CuKα radiation (λ = 1.54Å) in the range of the scanning angle 10° – 100°.

2.2 Theoretical consideration

The thickness of the thin films was determined using Equation 1

$$t = \frac{M}{A\rho} \quad (1)$$

where $M = M_2 - M_1$ and M_1 is the mass of substrate before deposition; M_2 is the mass of substrate after deposition; A is the area covered by the films; ρ = density of ZnO thin film (5.61 g/cm³).

The absorbance (A) can be calculated from the relationship [9];

$$A = \log \left[\frac{1}{T} \right] \quad (2)$$

where A is the absorbance and T is the transmittance and is given as [9];

$$T = \frac{1}{10^A} \quad (3)$$

The reflectance R is calculated from the relationship [9];

$$A + T + R = 1 \quad (4)$$

Or

$$R = 1 - \{A + T\} \quad (5)$$

The absorption coefficient (α) can be calculated using Beer Lambert's formula [10] given as;

$$\alpha = 2.303 \left(\frac{A}{d} \right) \quad (6)$$

where A is the absorbance and d is thickness of the film.

The photon energy, E is given by [9]:

$$E = h\nu \quad (7)$$

where h is the Planck's constant = 6.63 x 10⁻³⁴ Js and ν is the frequency of the photon.

Similarly,

$$E = \frac{hc}{\lambda} \quad (8)$$

where c is the speed of light = 3.0 x 10⁸ ms⁻¹ and λ is the wavelength.

Likewise,

$$E = \frac{hc}{\lambda e} \quad (eV) \quad (9)$$

where e is the electronic charge = 1.6 x 10⁻¹⁹ C.

The energy band gap, E_g and absorption coefficient, α are related by the equation

$$\alpha = \left(\frac{k}{h\nu} \right) (h\nu - E_g)^\beta \quad (10)$$

where k is a constant; h is the Planck's constant; ν is the frequency of the photon and β is a number which characterizes the nature of electronic transition between valence band and conduction band [12]. For direct allowed transition, β = 1/2 and it is known that ZnO is a direct band gap semiconductor.

Therefore, Equation (10) becomes;

$$\alpha = \left(\frac{k}{h\nu} \right) (h\nu - E_g)^{\frac{1}{2}} \quad (11)$$

Which gives

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (12)$$

where C is a constant. The energy band gap E_g of the samples is obtained from the intercept of the linear portion of the graph of (αhν)² against hν on the x-axis [12].

3 RESULTS AND DISCUSSION

3.1 Structural Analysis of the Polycrystalline Film

Fig. 1 shows XRD pattern of ZnO thin film deposited on glass substrate with a dipping time of 6 hours and annealed at 600°C. It depicts the intensity (in arbitrary unit) against 2θ (diffraction angle). The maximum intensity occurs at 2θ = 30.62° which corresponds to the (002) plane. Other peaks occur at 2θ = 25.73° and 41.81° which correspond to the (100) and (101) planes, respectively. This behavior suggests that the prepared ZnO thin film has a hexagonal structure and is preferentially oriented along the c-axis perpendicular to the substrate surface. The values obtained for the unit cell a = 3.020Å and c = 5.108Å are in good agreement with those reported in the literature [11].

3.2 Effect of Dipping Time on Thickness of ZnO Thin Film

The thickness of the thin film was measured using a gravimetric method as shown in Table 1 and the film thickness was obtained using Equation 1.

The dipping time of three samples (sample 1, 2 and 4) was varied. From Fig. 2, it can be seen that an increase in dipping time results to an increase in film thickness.

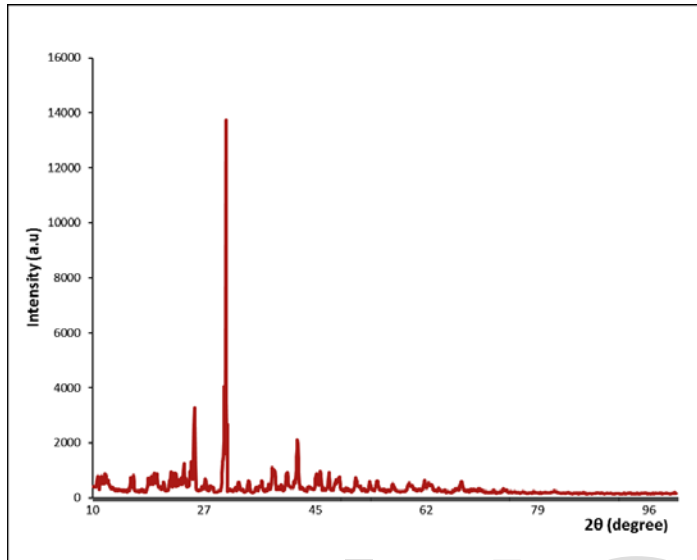


Fig. 1 XRD pattern of ZnO thin film annealed at 600°C.

Table 1: Measurement of mass and film thickness using a Gravimetric method

Sample	Dipping time (hour)	Mass of glass (g) ±0.42	Mass of glass + film (g) ±0.42	Mass difference (g) ±0.02	Area covered by film (cm ²) ±0.05	Thickness of the film (µm) ±0.2
1	2	4.66	4.69	0.035	9.29	6.75
2	4	4.96	5.02	0.058	9.29	11.15
4	6	5.06	5.13	0.069	9.29	13.24

3.3 Effect of Dipping Time on Optical Properties of ZnO Thin Film

Fig. 3 shows the optical transmittance spectra of ZnO thin films with different dipping time. It is clear that all the samples have high transmittance in the visible range. Within the range from 320 – 380nm, dipping time has almost no effect on the transmittance. However, from 400 – 980nm, it is observed that Sample 4 with the highest dipping time has the lowest

average transmittance. It means that as the thickness increases the transmittance decreases.

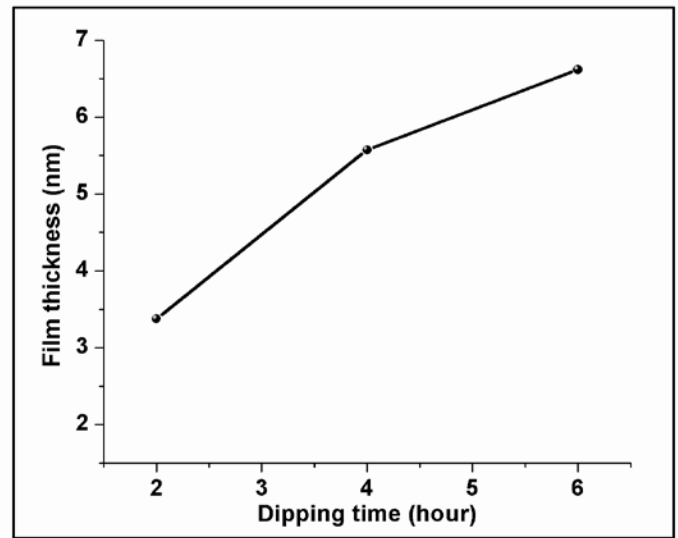


Fig. 2: The effect of dipping time on thickness of deposited ZnO thin films

Fig. 4 shows the optical absorbance spectra of ZnO thin films with different dipping time. The spectra show that the deposited ZnO thin films have low absorbance in the VIS/NIR regions whereas the absorbance is high in the UV region. However, an increase in dipping time corresponds to increase and more uniform absorption spectra of the ZnO thin films.

Fig. 5 shows the absorption coefficient (α) of the deposited ZnO thin films with different dipping time. The results show that an increase in dipping time does not necessarily lead to an increase in the absorption coefficient because the sample with dipping time of 4 hours has the highest values for absorption coefficient curve.

3.4 Effect of Annealing Temperature on Optical Properties of ZnO Thin Film

Fig. 6 shows the optical transmittance spectra of ZnO thin films with different annealing temperature. The transmittance is generally high between 400 – 1000nm with a gradual fall near the fundamental absorption region. It is also evident that increase in annealing temperature leads to a decrease in the uniformity of the transmittance spectra and also a decrease in the average transmittance of the deposited ZnO thin films.

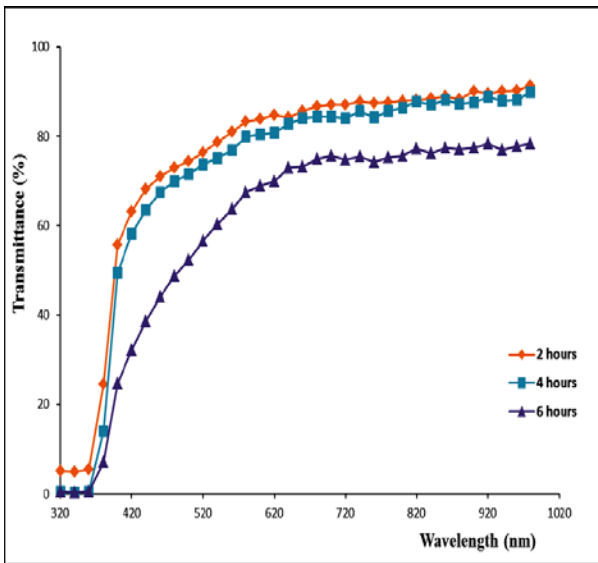


Fig. 3: Transmission spectra of ZnO thin films with different dipping time

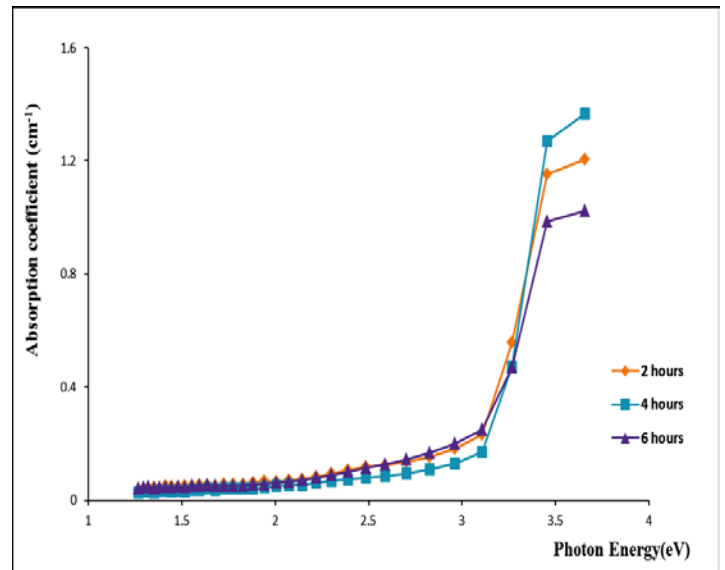


Fig. 5: The variation of absorption coefficient (α) against photon energy (eV) of ZnO thin films with different dipping time

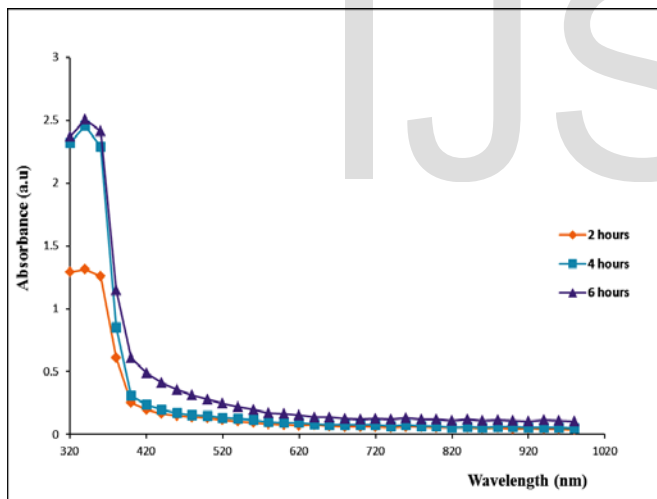


Fig. 4: Absorption spectra of ZnO thin films with different dipping time

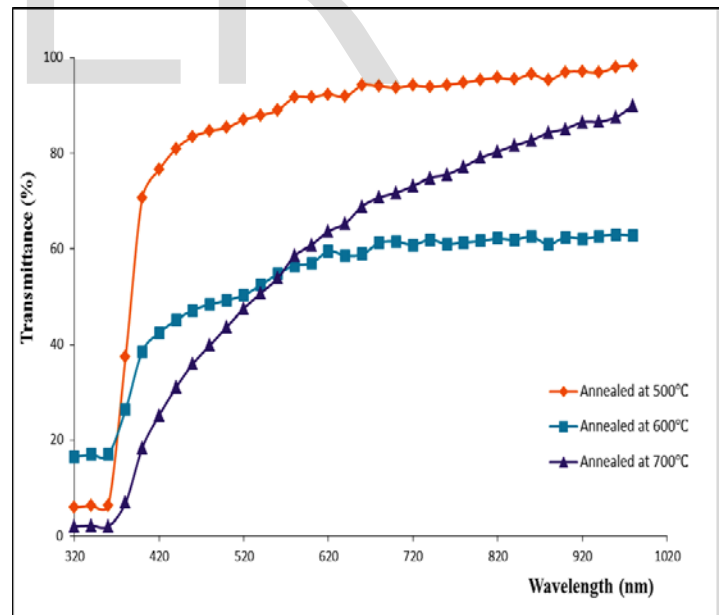


Fig. 6: The transmission spectra of ZnO thin films with different annealing temperature

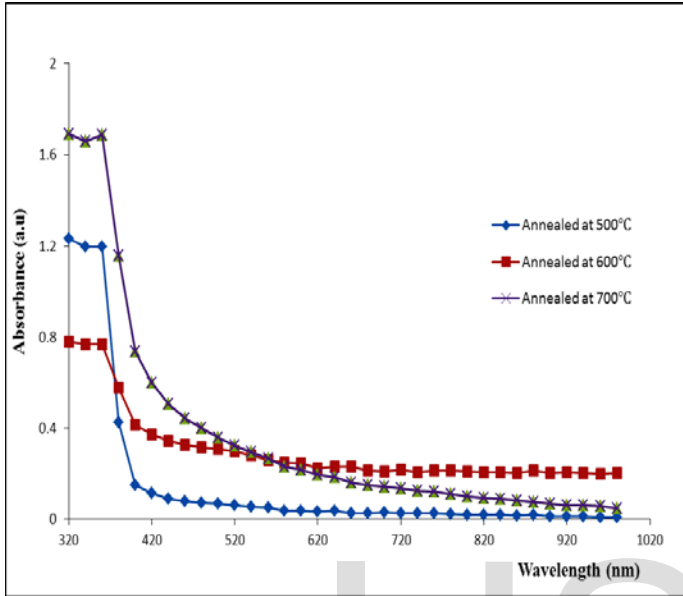


Fig. 7: The absorption spectra of ZnO thin films with different annealing temperature

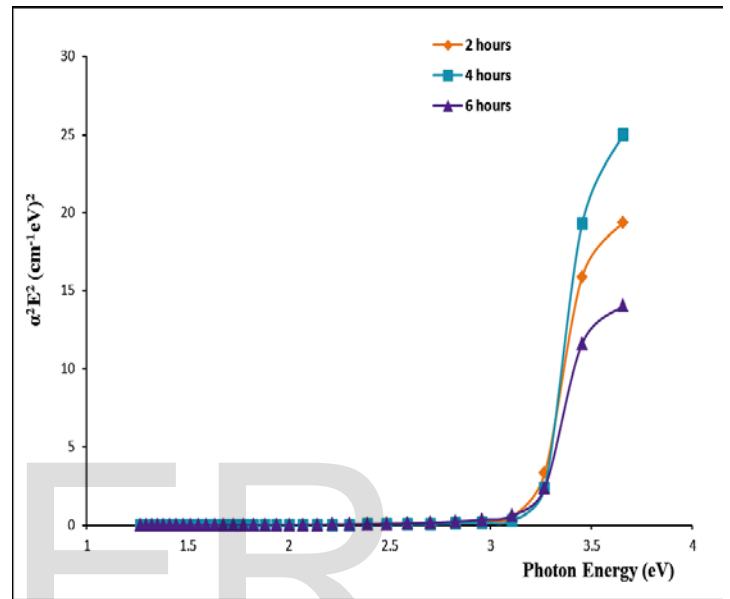


Fig. 9: The graph of $\alpha^2 E^2$ against photon energy (eV) of ZnO thin films with different dipping time

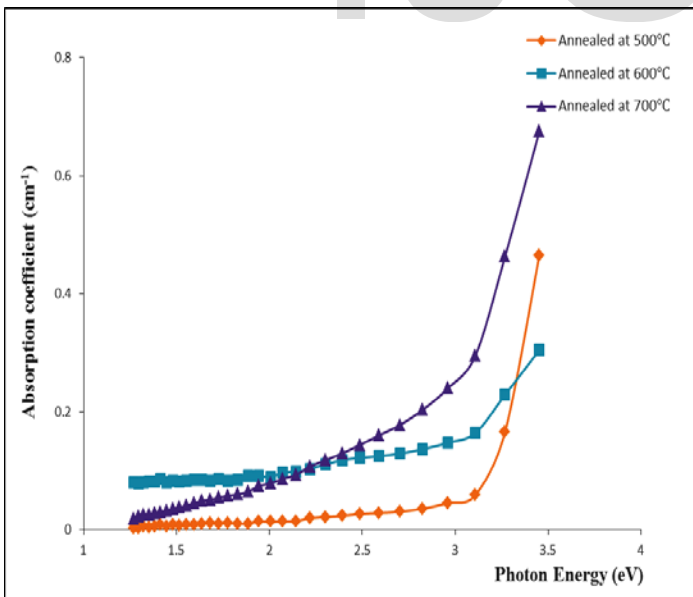


Fig. 8: The variation of absorption coefficient (α) against photon energy (eV) of ZnO thin films with different annealing temperature

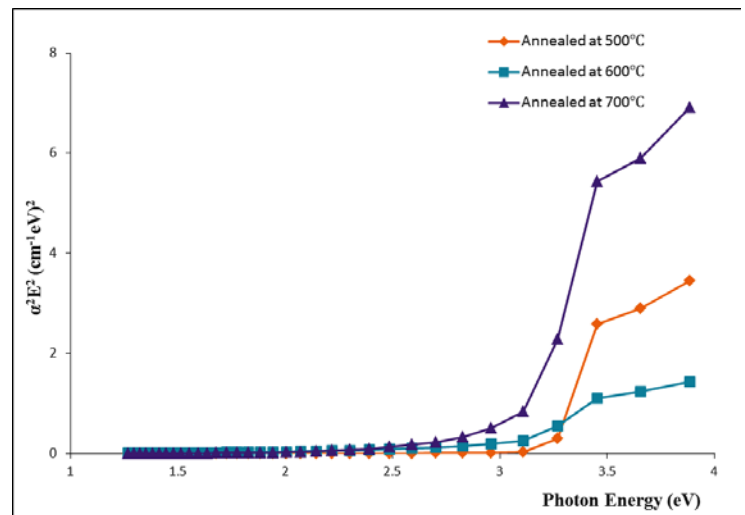


Fig. 10: The graph of $\alpha^2 E^2$ against photon energy (eV) of ZnO thin films with different annealing temperature

Table 2: Energy band gap, E_g of the ZnO films samples

Sample	Dipping time (hour)	Annealing temperature ($^{\circ}$ C)	Band gap, E_g (eV)
1	2	400	3.24
2	4	400	3.24
3	6	500	3.25
4	6	400	3.23
5	6	600	3.12
6	6	700	3.14

3.5 Energy band gap of ZnO Thin Film

Fig. 9 and Fig. 10 show the variation of $\alpha^2 E^2$ versus E (eV) for ZnO thin films with different dipping time and different annealing temperature respectively; where α is the absorption coefficient and E (eV) is the photon energy. According to Equation (12) β is constant for a given transition equal to $\frac{1}{2}$ for allowed direct band gap semiconductor. The band gap was obtained from allowed direct transition by plotting $(\alpha E)^2$ against E and extrapolating the graph to the point where $\alpha = 0$ whose intercept on the energy axis gives the energy band gap, E_g as shown in Fig. 9 and 10.

The energy band gap, E_g for all the samples are presented in Table 1. The results are in agreement to the previous studies of ZnO by Ghodsi et al. [13] with energy band gap of 3.28eV.

4 CONCLUSION

ZnO thin films with various dipping time and annealing temperatures were successfully prepared by the sol-gel dip coating process and the structural and optical properties of the thin films were studied. The structural analysis showed that the prepared ZnO thin films are polycrystalline with a preferred c-axis orientation and peaks corresponding to the (002), (100) and (101) planes. An increase in dipping time corre-

sponds to an increase in ZnO thin film thickness. At the highest dipping time, there is a drastic reduction in the average transmittance of the ZnO thin films while increase in dipping time leads to a better uniformly distributed absorption spectra of the ZnO thin films. However, increase in dipping time does not necessarily lead to an increase in the average absorption coefficient of the deposited ZnO thin films. Increase in annealing temperature leads to a decrease in the uniformity of the transmittance spectra and also a decrease in the average transmittance of the deposited ZnO thin films. It is also evident that increase in annealing temperature does not guarantee an increase in average absorption coefficient of the deposited ZnO thin films. It is strongly believed that the prepared ZnO thin films can be used as transparent electrodes in solar cells; liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs).

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