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THE EFFECT OF DEPOSITION TIME ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS BY AQUEOUS CHEMICAL GROWTH TECHNIQUE

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We achieved the deposition of highly crystalline zinc oxide thin films by aqueous chemical growth process at 95°C. The precursor solution used in the deposition include $Zn(NO_3)_2.6H_2O$ and $C_6H_{12}N_4$. Two different samples were grown on glass substrates at 5 hours and 12 hours deposition time. These were characterized by means of x-ray diffraction, scanning electron microscope, and spectrophotometer at normal incidence of light. X-ray diffraction results show that highly crystalline ZnO thin film can be achieved at a longer deposition time. Besides, the increase in the deposition time leads to a red shift in the band gap energy of the films.

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Keywords: Aqueous chemical growth, thin film, optical properties, band gap shift

1. Introduction

Nanostructured thin films are very important in modern technology. Zinc oxide, a wide band gap semiconductor, has attracted more and more interest in recent years because of variety of interesting applications. Examples included ZnO transparent film materials as transparent electrodes for solar cells [1], nanometer ZnO particles as sensors for gas – detector, electrode and piezoelectric devices etc [2 - 4]. The interest in zinc oxide has lead to the synthesis of a variety of zinc oxide nanostuctures through different deposition techniques. The reported zinc oxide nanostructure include zinc oxide nanorods via aqueous chemical growth [5], sol-gel technique [6] and metal organic chemical vapour technique [7]; zinc oxide nanowires synthesized through pulsed laser deposition system [8]; zinc oxide nanoplates through micro-jet under electron-beam techniques [9]; zinc oxide nanoblade by ultrasonic spray pyrolysis technique [10]; Cu doped zinc oxide nanoneedle via thermal evaporation technique [11]; zinc oxide nanoparticles synthesized by aqueous chemical growth technique [12], zinc oxide nanobelts via metal oxide chemical vapour technique [13], etc.

Aqueous chemical growth is advantageous synthesis technique of thin films over many other techniques because it requires non-expensive equipment and non-toxic reagents. Literature survey shows that the size and shape of the structures grown by this technique can be controlled by adjusting the growth parameters such as concentration of solution, reagent stoichiometry, pH and temperature [14 - 16].

In this work, we report on the effect of deposition time on the structure, morphology, optical and solid state properties of zinc oxide thin films synthesized via the well-known aqueous chemical growth technique. Possible application area is considered.

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2. Experimental details

In this work, aqueous chemical growth (ACG) technique was used for the growth of zinc oxide thin films. The glass substrates used for the deposition were degreased in HCl (20%) solution for 10 minutes, thoroughly washed in detergent water and rinsed several time with distilled water.

Zinc oxide thin films were grown on the glass substrates using an equimolar 0.1M aqueous solution of $Zn(NO_3)_2.6H_2O$ and $C_6H_{12}N_4$ as precursors. The solution and the substrates were placed in pyrex glass bottles with sealed caps and heated at 95°C for 5 and 12hours. After each time, the substrates were removed from the bottles and thoroughly rinsed with distilled water to eliminate residual salts or amino complexes, and dried in air at the room temperature. The residue was filtered and dried in oven as powder.

Thin films of zinc oxide successfully grown by aqueous chemical growth were characterized to obtain the structural and morphological properties using x-ray diffractometer and scanning electron microscope (SEM) respectively. By convention, the radiation used for the structural characterization is the Cukα X-rays, selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15sec. Phase identification was then made from an analysis of intensity of peak versus 2θ. The composition of the films was determined by Rutherford back scattering (RBS) and energy dispersive X-ray analysis (EDX). The absorption coefficient (α) and the band gap of the films were determined by using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 300-900 nm.

3. Results and discussion

We achieved the deposition of zinc oxide thin films at two different deposition times, viz. 5 hours (sample C5) and 12 hours (sample C12). The deposited zinc oxide samples were white in colour over the whole area of the substrate, for all deposition conditions. Moreover, sample grown for longer deposition time appeared to have better adhesion.

Fig. 1 shows the result of the compositional analysis of ZnO thin film deposited in 5 hrs. The compositional study was achieved by using Rutherford backscattering (RBS). The RBS analysis was carried out using 2.20 MeV, $4He^+$ ions and 5.00μc at 16.80nA. From the film's composition presented in Table 1, we observe that sample C5 has no impurity content and Zn to O ratio is approximately 1:1. The result from RBS also shows that the thickness of the deposited film on glass substrate was 100nm. Similarly, the composition of the sample deposited at 12hrs was determined by using energy dispersive X-ray analysis (EDX) with the use of Jeol JSM5600 equipment. The EDX scans results shown in fig. 2 confirmed the result from RBS. In addition, Ge appeared in the EDX figure, which is possibly a component of the glass substrate used for the deposition of the films

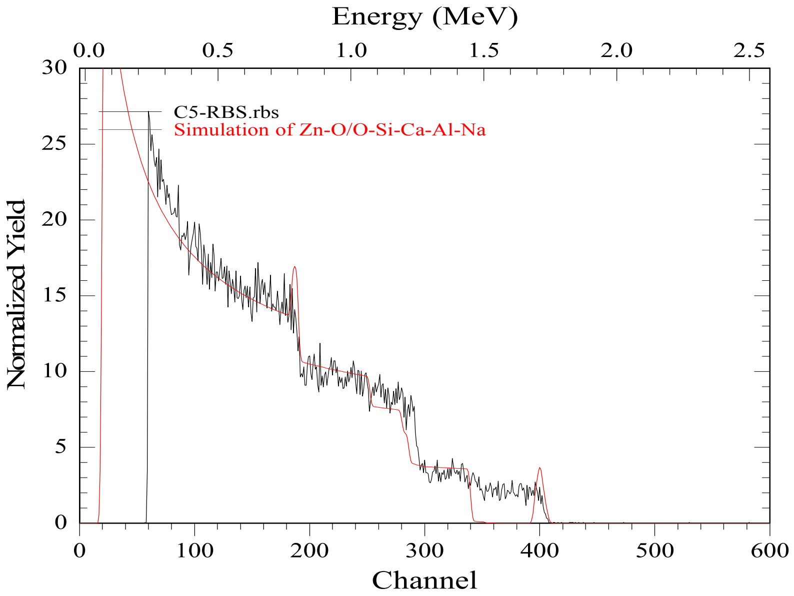


Fig.1: RBS spectrum of zinc oxide thin film deposited in 5 hours

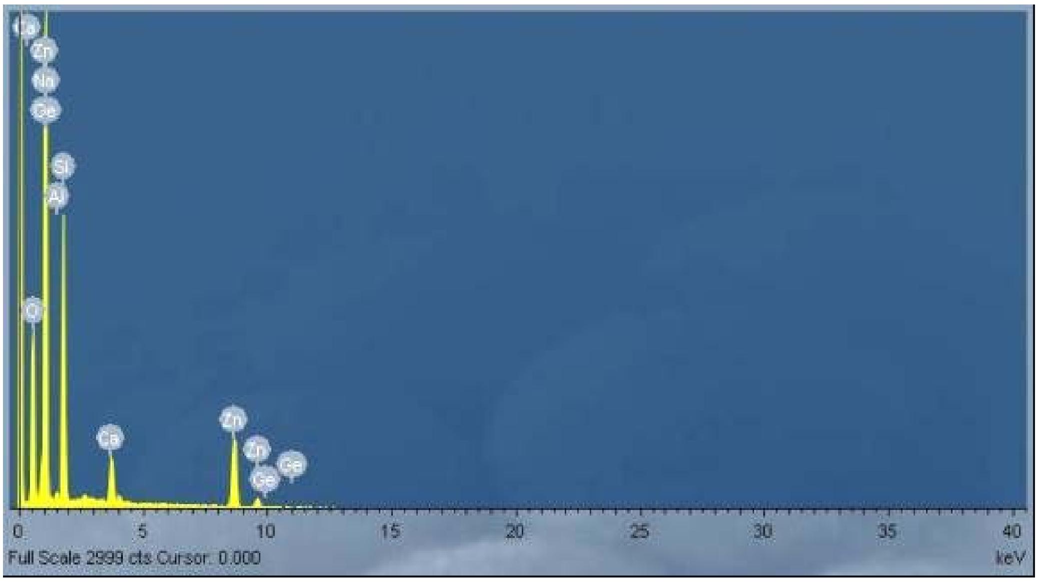


Fig. 2 EDX spectrum of ZnO thin film deposited in 5 hrs.

Table 1: The composition of substrate and ZnO film from RBS analysis.

	Zinc	Oxygen	Silicon	Calcium	Aluminum	Sodium
ZnO thin film	0.45	0.55	-	-	-	-
Glass substrate	-	0.50	0.12	0.10	0.10	0.18

Fig. 3 shows the XRD patterns of ZnO thin films deposited on glass substrate in 5 and 12 hrs. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films. The patterns exhibit the characteristics peaks of the wurtzite ZnO hexagonal structure, in accordance with the JCPDS card file No. 36-1451. A comparison between the spectra of the two films in (a) and (b) show that there is more crystallization and more orientation of the crystal growth in the case of the film deposited within 12 hrs. The lines are stronger with slight preferential orientation at 2θ values of 34.42°, 36.25°, 47.53°, 56.60°, 62.86° and 66.38° corresponding to (002), (100), (102), (110), (103) and (200) planes respectively (JCPDS 36-1451). The XRD pattern (not shown here) from powdered residue gave poor result, indicating that the residues were mainly from un-reacted precursor components or over-growth during the deposition process.

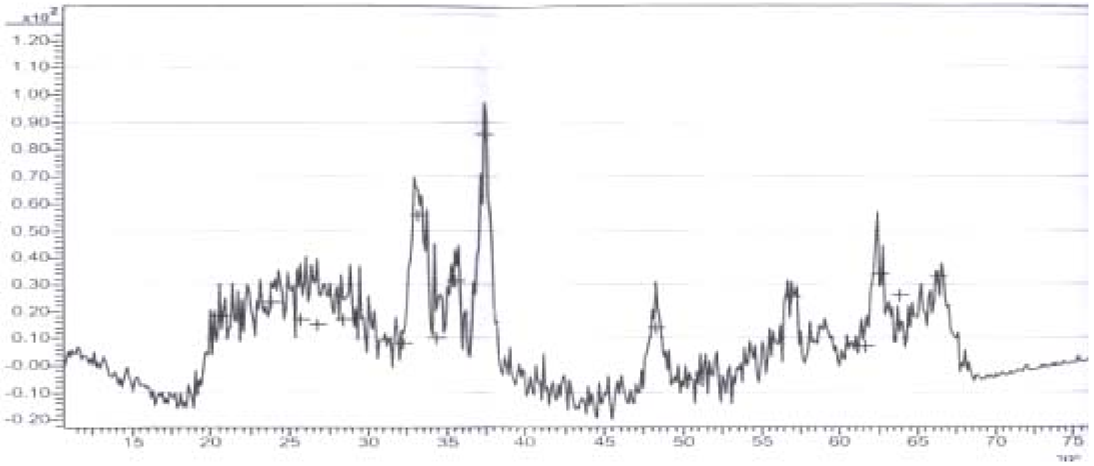


Fig. 3a: XRD pattern of ZnO thin film deposited in 5 hrs.

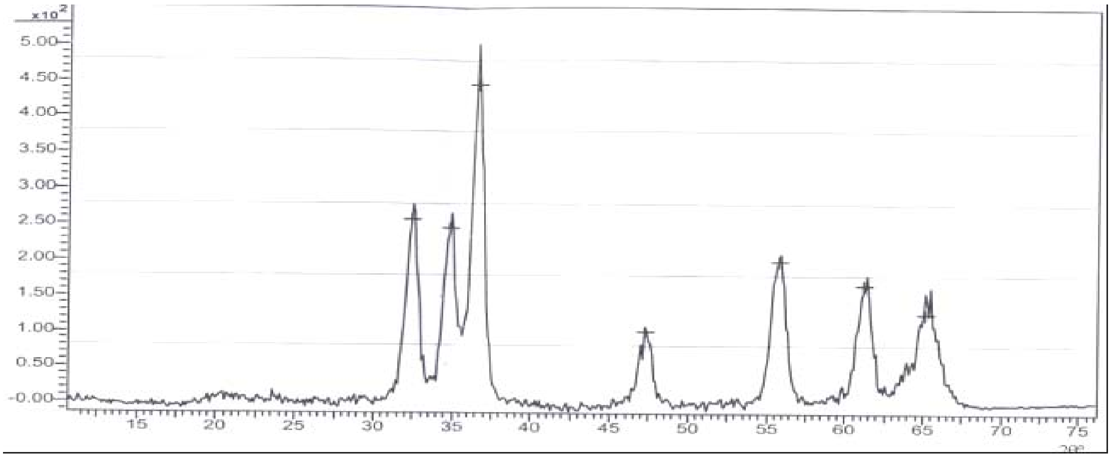
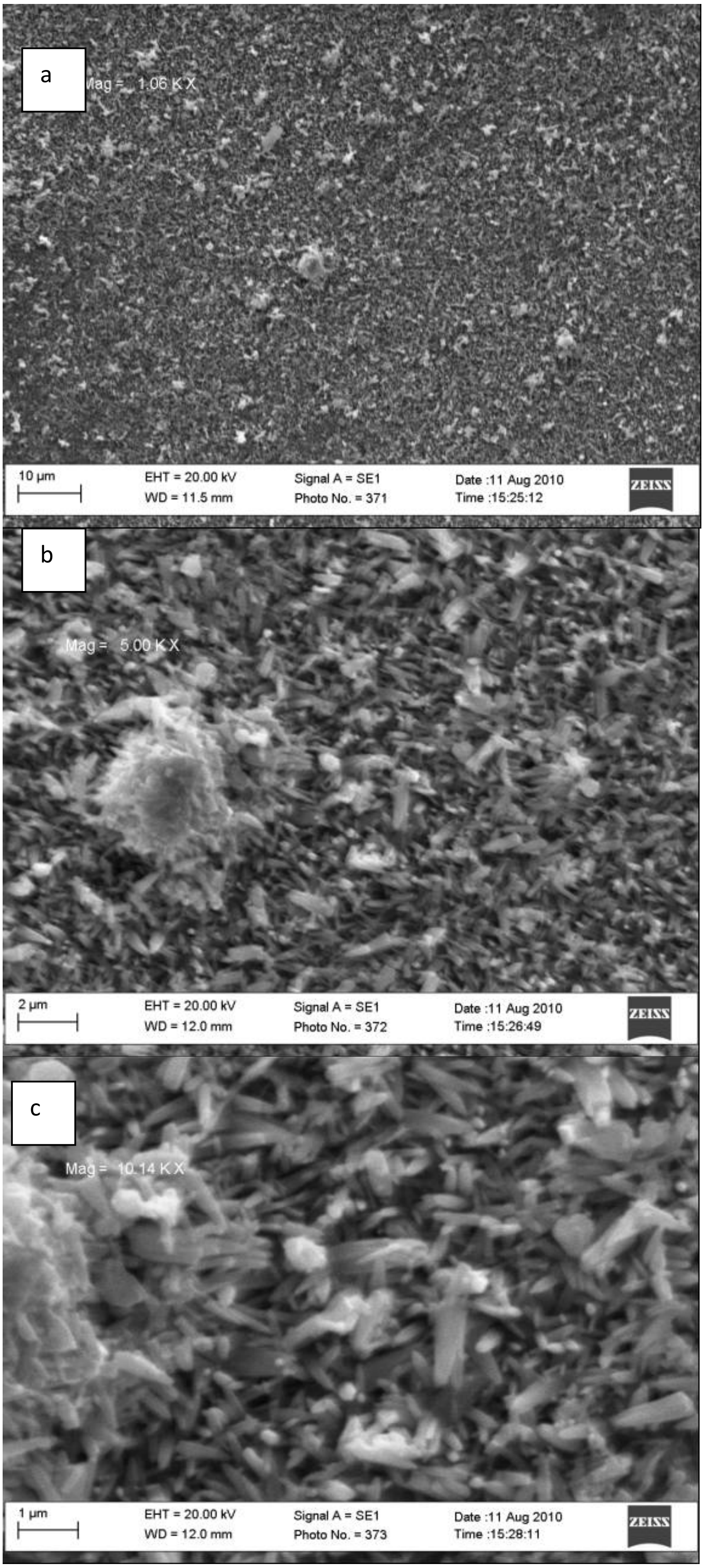


Fig. 3b: XRD pattern of ZnO thin film deposited in 12 hrs.

The surface microstructure of the film coated on the transparent glass slide was obtained with the aid of scanning electron microscope. The scanning electron micrograph of the film deposited in 12 hrs is displayed in fig. 4a-c, at different magnification. The SEM picture shows that the ZnO films have a rod-like structure. The films appear dense and uniform over the entire glass substrate, with small over-growth appearing at some spots.


a
Mag = 1.06 K X
10 µm
EHT = 20.00 kV
WD = 11.5 mm
Signal A = SE1
Photo No. = 371
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b
Mag = 5.00 K X
2 µm
EHT = 20.00 kV
WD = 12.0 mm
Signal A = SE1
Photo No. = 372
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c
Mag = 10.14 K X
1 µm
EHT = 20.00 kV
WD = 12.0 mm
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Fig.4: SEM of ZnO deposited in 12 hrs. at different magnifications

Accurate knowledge of optical parameters, such as absorption coefficient, optical transmittance, refractive index and optical band gap of semiconductors is indispensable for the design and analysis of various optical and optoelectronic devices. In this regards, we measured directly, from spectrophotometer, the absorbance and transmittance of the films and used appropriate equations to calculate other important parameters.

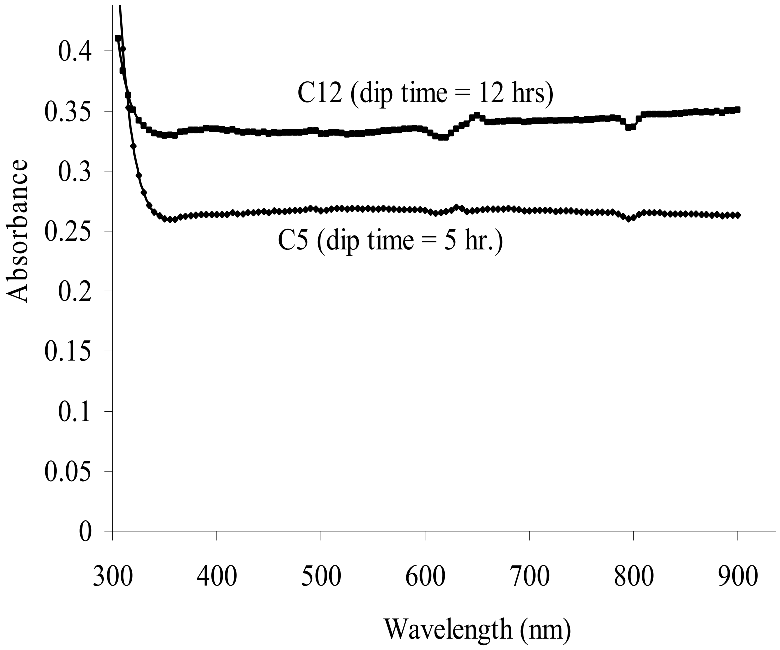

Fig. 5: Spectral absorbance of ZnO thin films grown at two different dip times

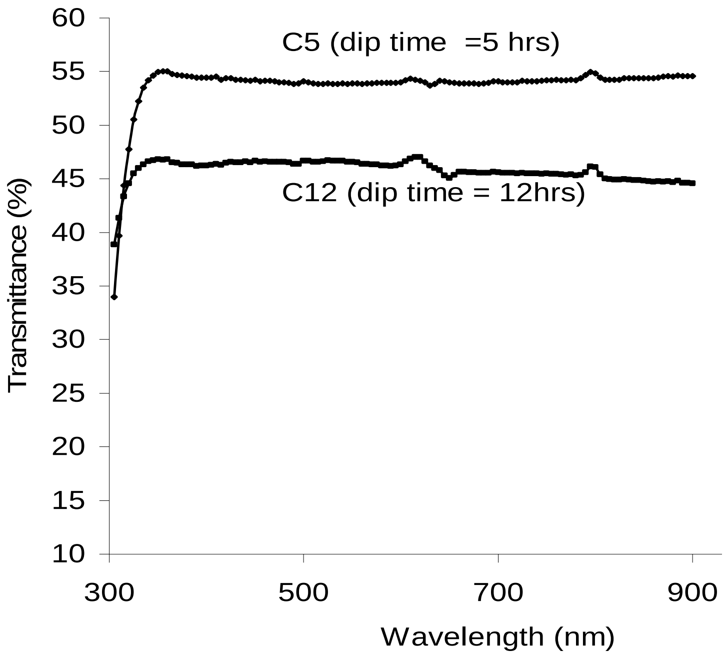

Fig. 6: Spectral transmittance of ZnO thin films grown at two different dip times.

The optical absorption spectra of ZnO thin films deposited on a glass substrate were studies at room temperature in the range of wavelengths 300 – 900nm. The variation of absorbance and transmittance with wavelength are shown in figs. 5 and 6 respectively. The films show an increase in absorbance and a decrease in transmittance at longer deposition time. The details of the mathematical determination of the absorption coefficient could be found in literature [17–19], while the plots of absorption coefficient against photon energy is shown in fig.7. These absorption spectra, which are the most direct and perhaps simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap (E_g).

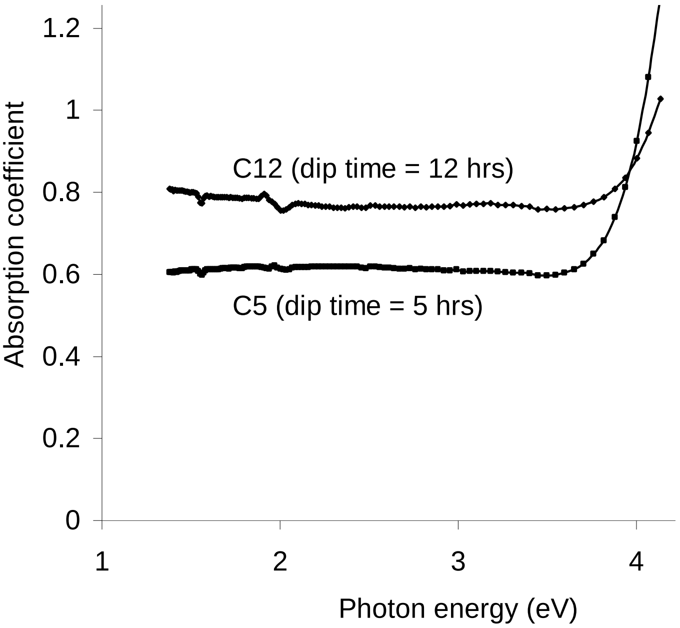

Fig.7: Plot of absorption coefficient against photon energy for ZnO thin films

The band gap energy was determined using the following relation [19, 20]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \tag{1}$$

where A is a constant, E_g is the band gap of the material and the exponent n is equal to ½ for direct band gap semiconductors. The estimated band gaps from the plots of $(\alpha h\nu)^2$ versus hν are shown in fig.8. The linear nature of the plot indicates the direct nature of the transition. The band gap was determined by extrapolating the straight portion of the energy axis at α = 0. It was found to lie in the range of 3.70 – 3.98 eV for ZnO thin films.

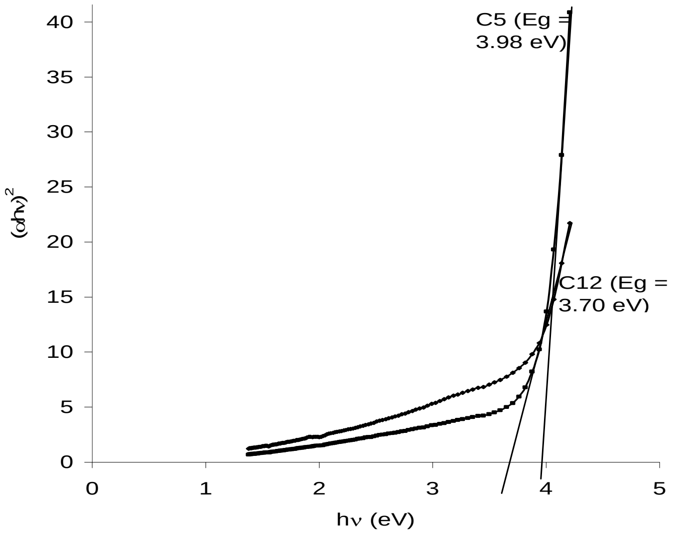

Fig. 8: Direct band gap plot for ZnO thin films.

The value of band gap energy reported here for ACG ZnO thin films is very high at lower deposition time. The blue shift in the band gap energy from that of bulk ZnO (3.3 eV) towards 3.98eV is an indication that the films grown by ACG technique were deposited at much smaller crystallite size. Similarly, the decrease in the band gap energy (a red shift of 0.28 eV) with the deposition time is likely to be attributed to an increase of crystallite size and a modification of the grain boundary configuration during growth. The range of band gap energy reported here are in close agreement with the values 2.8 – 4.0 eV [21], we reported earlier for CBD ZnO. The band gap values reported by other authors for ZnO include 3.12 – 3.28 eV, by SILAR method [22], 3.2 – 3.7 eV by CBD technique [23], 3.21 – 3.26 eV, deposited via ultrasonic spray pyrolysis [24]. These results by other authors show that high band gap ZnO thin film could be achieved by adopting the method employed in this work and optimising the deposition time.

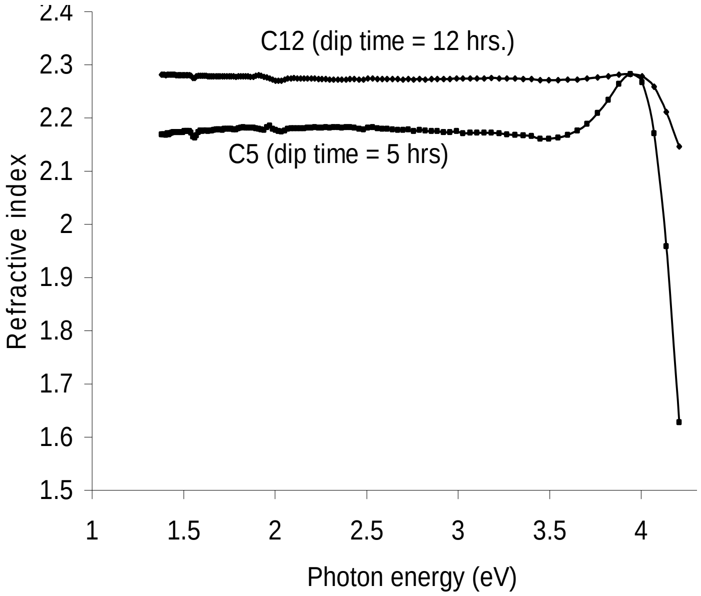

Fig. 9: The plot of refractive index against photon energy for ZnO thin films

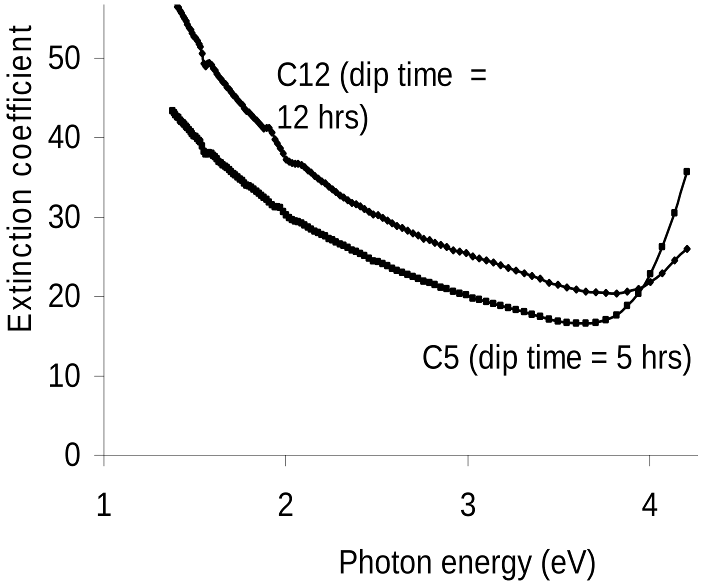

Fig.10: The plot of extinction coefficient against photon energy for ZnO thin films

The reflectivity (R) of materials of refractive index (n) and extinction coefficient (k) is given by [17, 25].

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \qquad (2)$$

The optical transmittance (T) is related to the absorption coefficient (α) and the refractive index (n) by the relation [26]:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{(1-R^2)\exp(-2\alpha d)} \qquad (3)$$

The extinction coefficient (k) is related to α by the relation [17, 26]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

By these relations, k and n can be defined from the measurements of R and T. Hence, the equation above was used to determine the extinction coefficient. The plots of n, the refractive index and k, the extinction coefficient against photon energy are given in figs. 9 and 10 respectively. We observe an increase in the extinction coefficient of the films with the deposition time. The films exhibited high refractive index of more that 2.1 in almost all the wavelengths under study.

4. Conclusions

This research focuses on the synthesis of zinc oxide thin films through aqueous chemical growth technique and the characterization of the resulting thin films. Within the limit of the instrument errors, we have been able to show that the films deposited consists of elemental Zn and O in the ratio of 1:1, by means of RBS and EDX. The effect of the deposition times was seen in both the structure, morphology, optical and solid-state properties of ZnO thin films deposited at 5 and 12 hrs. The large band gap energy exhibited by the film suggests that the films could be used as window material in solar cell application.

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