Effect of Deposition Time on The Optical Properties of Zno Nanocrystalline Films Prepared By Chemical Bath Deposition Method

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Abstract- *Zinc oxide Nanocrystalline thin films were prepared by chemical bath deposition (CBD) method using Zinc Acetate and Sodium Hydroxide as precursors and Ethylene Glycol as capping agent. The effect of different deposition times on the optical properties of the films was investigated. The band gap values were determined from optical absorption spectra. A decrease in band gap with increase in deposition time was observed. The Optical constants like Refractive Index, Extinction Coefficient, Optical Conductivity, Electrical Conductivity, Real and Imaginary Dielectric Constants were determined using absorbance and transmittance data. A rise and fall in the values of all the optical constants with wavelength is observed which can be related directly to the absorption of light .The structure, morphology & elemental composition of prepared zinc oxide nanocrystalline film were studied using XRD, FESEM & EDX spectra .FESEM images confirm the hexagonal nanorod structure of ZnO.The X-Ray diffraction spectrum shows the hexagonal wurtzite structure with maximum intensity for the 100 plane.*

Keywords- Chemical Bath deposition method,Capping agent,Optical Constants,Deposition time.

I. INTRODUCTION

Nanomaterial science is a wide and interdisciplinary area of research and development that has been growing very fast in the last few decades. Materials in the nanoscale show unique optical, magnetic and electrical properties. Zinc oxide (ZnO) nanoparticles have their own importance because of its varied applications in Solar cells,L.E.D's, photocatalyst, protective coating, electrophotography, photoprinting, chemical sensor etc. It is enviroment friendly,easy to synthesize,has low resistivity and high transmittance in the visible solar region[1,2,3]. Zinc Oxide is an interesting material not only because of its physical properties but also due to a wide variety of morphologies. Some of the ZnO nanostructures exhibit various shape such as nanotube, nanowire/nanorod, nanobelt , nanocomb ,nanoflower, nanosheet and tetrapod like structure[3].Due to their high catalytic activity, ZnO has a great advantage to be applied in catalytic reaction process[4]

Many methods have been described in the literature for the production of ZnO nanostructures such as laser ablation [5], hydrothermal methods [6], electrochemical depositions [7], sol–gel method [8], chemical vapor deposition [9], thermal decomposition [10], and combustion method [11,12].recently, ZnO nanoparticles were prepared by ultrasound [13], microwave-assisted combustion method [14], two-step mechanochemical-thermal synthesis [15], anodization [16], co-precipitation [17], and electrophoretic deposition [18]. The chemical bath deposition method(CBD) is one of the most frequently utilised methods for the synthesis of ZnO nanoparticles because of its notable advantages such as its adaptability to large-scale production, low cost, and low synthesis temperature. In the present work, ZnO nanocrystalline films have been synthesized by CBD method and the effect of deposition time on their optical properties have been investigated. The Structural and morphological properties of the films were studied using XRD, FESEM, and EDS techniques

II. EXPERIMENTAL METHOD

2.1 Film Preparation:-

Preparation by CBD method involves precipitation followed by condensation. The precipitates were prepared in 200 ml beakers which were cleaned using HCl, acetone and distilled water. Thin films were deposited on microscopic glass slide (75mm L × 25 mm wide), thickness 1 mm (±0.1 mm). The chemical bath solution was prepared by a solution of 1M Zinc Acetate and 0.5M of Sodium hydroxide added dropwise with continuous stirring for two hours. A white translucent sol is obtained which was filtered and washed with triple distilled water to get a white precipitate. Ethylene glycol was used as a capping agent to form ZnO Nanocrystalline thin film .The solution is stirred in magnetic stirrer for 1 hr and the deposition was made in static condition in the water bath at temperature 60^0C for three different deposition times (3 hrs, 4 hrs & 5 hrs) . At the end of the deposition, white coloured ZnO thin film was formed on the substrates with desired thickness, The films were adherent, homogeneous and without any powder precipitation. The substrates were removed from the chemical bath, rinsed thoroughly in distilled water and dried in the air at room temperature.

2.2 Measuring Instruments :-

The absorbance and transmittance measurements were done using Elico SL 210 UV–Vis Spectrophotometer. The XRD studies were carried out using PAN analytical 3 KW powder X-Ray diffractometer at NIT Raipur. FESEM and EDS studies were done using JSM 7610F Scanning Electron microscope at VNIT Nagpur.

III. RESULTS AND DISCUSSION

3.1 XRD Studies:

The X Ray Diffractogram of the synthesized ZnO nanofilms presented in fig (1) confirms the hexagonal wurtzite structure with predominant orientation along the 100 plane. The assignment of different peaks were made by comparison with JCPDS data(36-1451) and calculation of lattice constants which showed agreement with reported values .The corresponding data are presented in table 1.The average size of the nanoparticles has been calculated for the 100 peak using the Debye-Scherrer formula.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \text{..............................(1)}$$

Where, λ is the x-ray wavelength (1.504 nm), θ is the Bragg diffraction angle, and β is the full width at half maximum. The full width at half maximum was measured using Gaussian curve for the highest peak 100. The average size of nanoparticles was found to be 28.25 nm.

Table 1 : XRD data of ZnO film deposited on glass substrate at 60^0C for 4 hrs

d value (Å)		Relative Intensity		(hkl)	Lattice Constants	
Obs.	Rep.	Obs.	Rep.		Obs	Rep.
2.78	2.4071	100	57	(100)	a=3.25	a=3.249 c=5.206
1.932	1.9113	67	23	(102)	a=3.25 c=5.46	a=3.249 c=5.206
1.58	1.6247	49	32	(110)	a=3.18	a=3.249 c=5.206
1.447	1.4771	37	29	(103)	a=3.25 c=5.12	a=3.249 c=5.206
1.347	1.3582	33	11	(201)	a=3.25 c=5.12	a=3.249 c=5.206

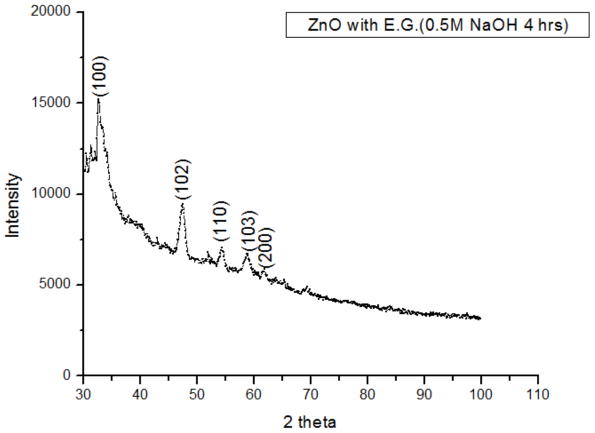


Fig 1 :-X-Ray diffractogram of ZnO Nanocrystalline film prepared by CBD method

3.2 FESEM and EDS Studies :-

The FESEM image of the ZnO film prepared using CBD method with 4 hrs deposition time(magnification-20K) is presented in fig 2(a). A homogenous cluster of hexagonal nanorods can be observed.

EDS analysis is performed to confirm the atomic composition of constituents atoms and foreign impurity atoms. Fig.2(b) shows the EDS spectra of ZnO film prepared using CBD method with 4 hrs deposition time. Zn, O & small percentage of C has been detected from EDS analysis of the films.

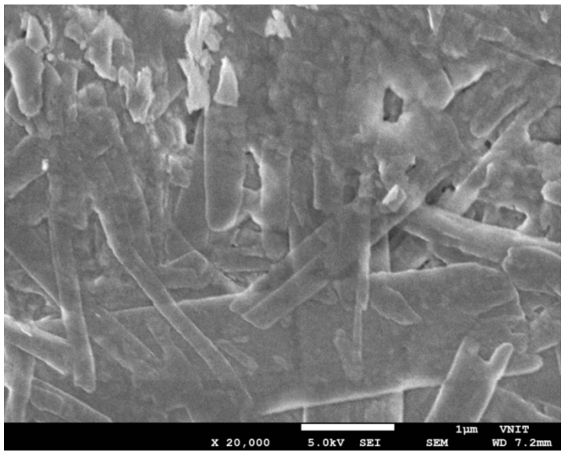


fig 2(a) FESEM image of ZnO Nanocrystalline thin film

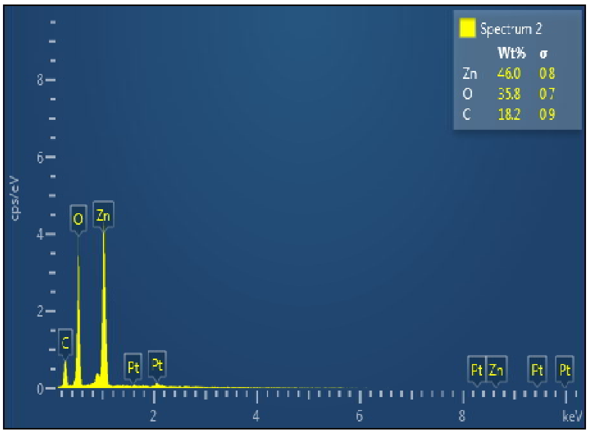


Fig 2(b) EDS Spectra of ZnO

3.3 Absorbance Spectral Studies:-

Fig 3 shows the Optical absorption Spectra of ZnO films prepared by CBD method at three different deposition times. The Optical Absorption Coefficient α and band gap E_g (for direct band gap materials) are represented by the equation

$$\alpha = c(h\upsilon - E_g)^{1/2}/h\upsilon \text{ -----(2)}$$

where, E_g is the optical band gap and c is a constant. Thus a plot between $(\alpha h\upsilon)^2$ vs hυ (Tauc's plot) gives the band gap value E_g of the material. The values of band gap energy obtained from Tauc's plot are presented in table 2 .

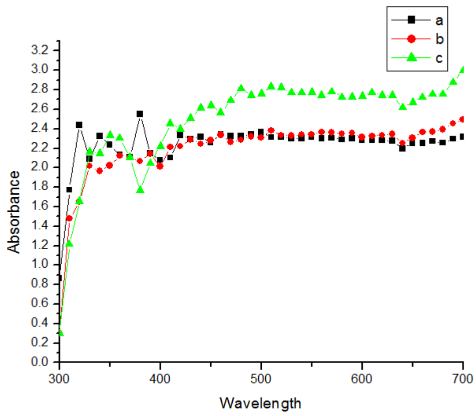


Fig 3 Optical absorption Spectra of ZnO Nanocrystalline thin film with Ethylene Glycol as Capping agent (a) ZnO with 3 hrs D.T. (b) ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.

Table (2) Energy band gap of ZnO with different deposition time

S.No.	Sample name	Energy Band Gap
a.	ZnO with 3 hrs D.T.	3.65
b.	ZnO with 4 hrs D.T.	3.60
c.	ZnO with 5 hrs D.T.	3.40

3.4 Determination of Optical Constants :-

The values of Refractive Index and Extinction Coefficient were calculated from Transmittance spectra. Refractive index (n) is a fundamental property of an optical material as it provide the information about the interaction of light and nanoparticle and hence is of importance to our health and environment [21].Evaluation of the refractive index of these materials is important for application in various integrated optical devices.

In the present work the refractive indices were determined by Envelope method proposed by Swanepoel [22].For energies greater than band gap or for free carrier absorption at higher wavelength, the dispersion of n and k is not very large [23].Using the Envelope method, the refractive index of the film on a transparent substance can be evaluated from the transmittance spectra using the relation[24]

$$n = \sqrt{N + \sqrt{(N^2 - n_s^2)}} \text{ ....(3)}$$

where

$$N = \frac{(n_s^2+1)}{2} + 2n_s \frac{T_M - T_m}{T_M T_m} \text{ ....(4)}$$

and n_s is the refractive index of the substrate (n_s =1.52 for glass)

The extinction coefficient measures the fraction of light lost due to scattering and absorption per unit distance in the participating medium. 'k' can be calculated from the relation

$$k = \alpha\lambda/4\pi \text{ --------------(5)}$$

where α is the absorption coefficient.

Fig 4(a) shows variation of Refractive Index with wavelength of ZnO films prepared with Ethylene glycol capped ZnO films.

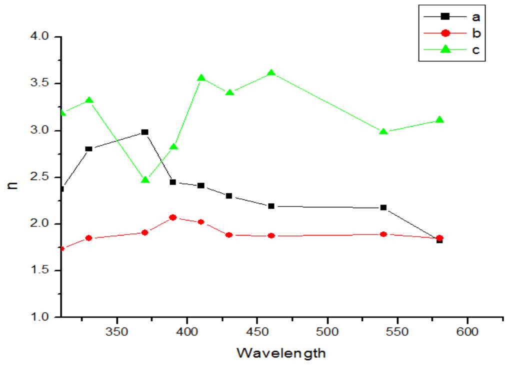
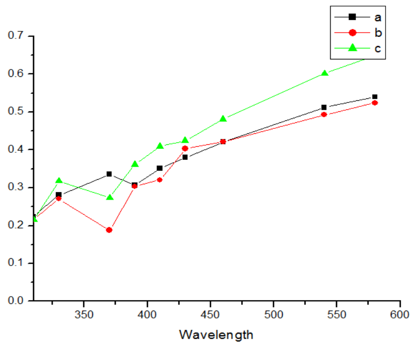


Fig 4(a) Refractive index v/s wavelength of ZnO Nanocrystalline thin film (a)ZnO with 3 hrs D.T. (b) ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.

It can be observed from fig 4 (a) that the values of refractive index reaches a maximum value at around 400nm for films deposited with 3 hrs and 4 hrs deposition time and then decreases with increase in wavelength. However for film deposited with 5 hrs deposition time, the refractive index is high at around 300nm, reaches a low around 350nm and then increases.



4(b) Extinction Coefficient v/s wavelength of ZnO Nanocrystalline thin film (a)ZnO with 3 hrs D.T. (b) ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.

Figures 4(b) show the variation of Extinction Coefficient with wavelength which show a rise and fall which is directly related to the absorption of light. The values of extinction coefficient are lower(between 0.2 and 0.3) in the three cases at lower wavelengths while they increase upto 0.7 at higher wavelength

The optical Conductivity σ_0 was determined by the relation[25]

$$\sigma_0 = \frac{\alpha n c}{4\pi} \quad \text{……………….(6)}$$

The electrical Conductivity was determined by the relation[25]

$$\sigma_e = \frac{2\pi\sigma_0}{\alpha} \quad \text{…………………….(7)}$$

The dielectric constant may be defined as a complex:-

$$\varepsilon = \varepsilon_r + i\varepsilon_0 \quad \text{…………………………………………(8)}$$

$$\text{Thus } \varepsilon_r = n^2 - k^2 \quad \text{…………………………(9)}$$

$$\varepsilon_0 = 2nk \quad \text{……………………………………….(10)}$$

Where ε_r is the real dielectric constant and ε_0 is the imaginary dielectric constant

Figures 4(c),4(d),4(e) &4 (f) show the variation of σ_0 , σ_e, ε_r & ε_0 with wavelength. A similar rise and fall with wavelength is observed in all the cases. The values of , k, σ_0 , σ_e, ε_r & ε_0 at 380nm for the different films are summarized in table 3.

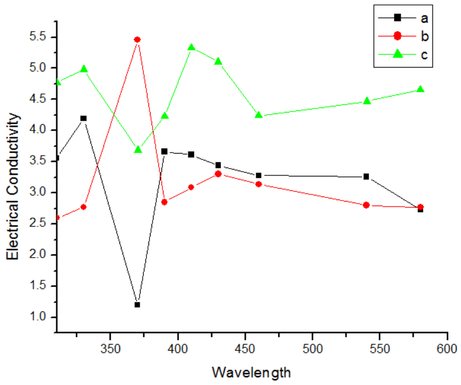
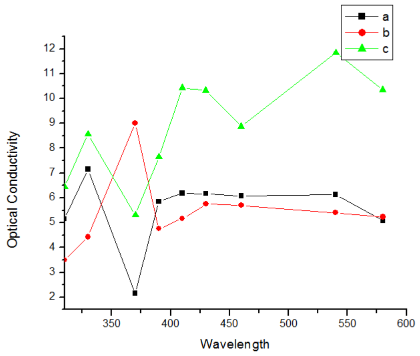
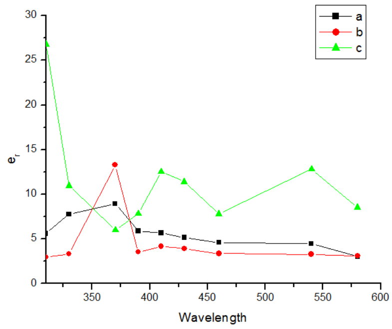


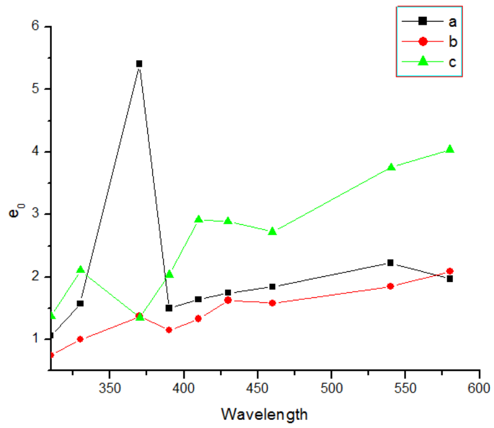
fig 4 (c) Electrical Conductivity v/s Wavelength of ZnO Nanocrystalline film (a)ZnO with 3 hrs D.T. (b)ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.



4 (d) Optical Conductivity v/s wavelength of ZnO Nanocrystalline thin film (a)ZnO with 3 hrs D.T. (b)ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.



4(e) Real Part of Dielectric constant of ZnO Nanocrystalline thin film (a)ZnO with 3 hrs D.T. (b)ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.



4(f) Imaginary part of Dielectric constants of ZnO nanocrystalline thin film (a)ZnO with 3 hrs D.T. (b)ZnO with 4 hrs D.T. (c)ZnO with 5 hrs D.T.

Table 3 Optical constants of ZnO Nanocrystalline thin film

Sample Name	Refractive Index (n)	Extinction Coefficient (k)	Optical Conductivity $\sigma_0 \times 10^{14}$	Dielectric Conductivity $\sigma_e \times 10^7$	Real Part (ϵ_r)	Imaginary Part (ϵ_0)
ZnO 3 hrs D.T.	2.44	0.30	5.85	3.44	5.689	1.64
ZnO 4 hrs D.T.	2.07	0.32	5.17	3.30	3.91	1.62
ZnO 5 hrs D.T.	2.46	0.27	5.32	5.10	7.78	2.72

IV. CONCLUSION

ZnO nanocrystalline films have been synthesized by CBD method on glass substrate at 60^0C for three different deposition times.The effect of deposition time on the optical properties of the films were investigated.The band gap values were in the range of 3.4 to 3.6 eV A decrease in band gap with increase in deposition time was observed. The values of Optical constants like Refractive Index, Extinction Coefficient, Optical Conductivity, Electrical Conductivity, Real and Imaginary Dielectric Constants showed a rise and fall with wavelength which can be related directly to the absorption of light. Hexagonal nanorod structure of ZnO is observed from FESEM images. EDS studies show the presence of Zinc,Oxygen and small percentage of Carbon The XRD studies confirm the hexagonal wurtzite structure with orientation towards 100 plane.

V. ACKNOWLEDGEMENT

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