

Optical and Electrical Properties of Chemically Deposited ZnO Thin Films.

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ABSTRACT

Good homogenous ZnO thin film was prepared by the chemical bath deposition (CBD) technique using aqueous solution of zinc sulphate ($ZnSO_4$) as a starting material and triethanolamine (TEA) was employed as a complexing agent. The film was characterized for optical and electrical properties. From the results obtained, the film was found to have high transmittance in the wavelength range of 400-1100nm and low transmittance near fundamental absorption. The absorbance of the ZnO film was found to be low in the VIS/NIR regions and high in the UV region. The extinction coefficient of the film suggests that, there is absorption of light at the grain boundary. The X-ray diffraction (XRD) analysis of the film reveals that the ZnO film has hexagonal structure with orientation of C-axis. The Scanning Electron Microscope (SEM) micrograph of the ZnO film illustrates the formation of such-micrometer crystallites over the surface with holes indicating large porosity and agglomeration of small crystallites in certain regions. The decrease in electrical resistance of the ZnO film was found to be related to the increase in Carrier Concentration.

(Keywords: CBD; carrier concentrations, grain boundary, electrical resistance)

INTRODUCTION

Zinc Oxide (ZnO) thin films are one of the most prominent transparent conducting oxides for advanced applications such as window layer in heterojunction solar cells, heat mirrors, piezoelectric devices, multilayer photo-thermal conversion systems, and solid state gas sensors (Elmer, 2000; Krunks and Mellikov, 2007; Aranovich *et al*, 1980; Sahay, 2005; Sahay *et al*, 2005). Zinc Oxide has direct optical energy band gap of 3.3eV which is large enough to transmit most of the useful solar radiation (Sahay *et al*,

2007). However, the abundance of ZnO in nature makes it less expensive and its sharp UV-Cut-off makes it desirable in many applications (Sahay *et al*, 2007).

Though thin films of ZnO have been used, its preparation techniques have been restricted to sputtering, vacuum evaporation, chemical vapor deposition, spray pyrolysis, molecular beam epitaxy, Sol-gel and pulse laser (Ezema, 2004). Many of these techniques are expensive and require high vacuum and controlled formation conditions (Ezema, 2004). Very limited work has been reported on the preparation of ZnO using chemical bath deposition (CBD) technique (Ezema, 2004) though the technique has been extensively used for other materials (Ezema, 2004).

The chemical bath deposition technique (CBD) has several advantages such as simplicity, safety, low cost of both equipments and raw materials. The technique is a promising one and the properties of the deposited material can be varied and controlled by proper optimization of chemical baths and deposition conditions.

In this paper we report the optical and electrical properties of ZnO thin films deposited on glass substrates using chemical bath deposition (CBD) technique.

EXPERIMENTAL DETAILS

The films were deposited on glass slides substrate from aqueous solution of $ZnSO_4$ as starting material at room temperature in a similar way as carried out by Ezema (2004). The reagents used for studies are $ZnSO_4$, concentrated NH_3 ; concentrated TEA; and distilled water. The chemicals were of analytical grade. The bath of desired concentration of various reagents was prepared as follows: 1M of 1ml $ZnSO_4$; 1ml of 100% NH_3 , 1ml of 100% TEA,

and distilled water to make up to 50ml of solutions which were mixed in a beaker. The reaction baths were tested and were found to be purely alkaline medium. The glass slides were previously degreased in NHO_3 for 24 hours, cleaned in cold water with detergent, rinsed with distilled water and drip dried in air. The glass slides were immersed into the bath and were supported vertically to the walls of the beaker, and allowed to stay for 24 hours.

The depositions were done at room temperature ($22^\circ\text{C} - 25^\circ\text{C}$) without stirring. After 24 hours dip time the glass slides were withdrawn, rinsed with distilled water, and drip dried in air. Thin films of ZnO were observed to be deposited on the glass slides.

The film thickness was determined by the gravimetric method using electronic precision balance (Citizen: Y204). The optical transmission of the film was obtained in the UV/VIS/VIR region up to 1100nm using spectrophotometer, at room temperature and normal incidence using uncoated glass slide as reference.

The electrical characterization of the film was carried out using the DC two-probe technique. The variation of electrical resistance (R) as a function of temperature was measured in range 300–500K by means of tube furnace and Keithly system electrometer (N6514). The ohmic contacts were made by silver paste 20mm long, separated by distance of 5mm on the ZnO film. The electrodes width was measured to be 1mm (as was measured by Mondal *et al*, 2008).

The structural and phase identification of the ZnO film was obtained through X-ray diffraction with $\text{CuK}\alpha$ radiation (at $\lambda = 1.54\text{\AA}$) using Philips PW 1830 XRD system.

The surface morphology of the ZnO film was obtained using scanning electron microscope (SEM HITACHI 5.3400N).

THEORETICAL CONSIDERATIONS

Optical: The transmittance (T) can be calculated from the relationship (Pankove, 1971):

$$A = \log \frac{1}{T} \quad (1)$$

where A is the absorbance and T is given (Pankove, 1971) by:

$$T = \frac{1}{10^A} \quad (2)$$

The reflectance (R) is calculated from the relation (Pankove, 1971):

$$A + R + T = 1 \quad (3)$$

Or

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

The absorption coefficient (α) can be calculated from the observed absorbance data using Beer Lamberts formula (Islam and Podder, 2009) given by:

$$\alpha = 2.303 \left(\frac{A}{d} \right) \quad (5)$$

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

The photon energy, E, is given (Pankove, 1971) by:

$$E = h\nu \quad (6)$$

where h is the plank constant and ν is the frequency of the photon.

Similarly,

$$E = \frac{hc}{\lambda} \quad (7)$$

where c is the speed of light and λ is the wavelength. Substituting for constants in equation (7) gives:

$$E = \frac{12,400}{\lambda} eV \quad (8)$$

For semiconductors (where $K^2 \ll n^2$) there exist a relationship between R and n (Janai et al, 1979) given by:

$$R = \frac{(n + 1)^2}{(n - 1)^2} \quad (9)$$

Where R is the reflectance and n is the refractive index.

There exist a relationship between R and α (Pankove, 1971) given by:

$$K = \frac{\alpha\lambda}{4\pi} \quad (10)$$

where R is the extinction coefficient.

The relationship existing between n, R and R is given by (Islam and Podder, 2009) by:

$$n = \left(\frac{1 + R}{1 - R} \right) = \sqrt{\frac{4R}{(1 - R)^2} - K^2} \quad (11)$$

Where n is the refractive index, K is the extinction coefficient and R is the optical reflectance.

Electrical: The electrical resistivity (ρ) can be calculated from the relationship (Mondal *et al*, 2008) as:

$$\rho = \frac{RL}{A} \quad (12)$$

where L is the distance between two electrodes, A is the area of the deposited film (which is the product of length of electrodes and thickness of the film) and R is the electrical resistance.

RESULTS AND DISCUSSIONS

The equation governing the reaction was reported by Cruz – Vazquez *et al*, (2001):

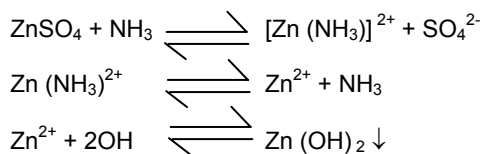


Figure 1 shows the optical transmission spectra of the ZnO film. The transmittance is high between

wavelengths of 400 – 1100nm with drastic fall near the fundamental absorption.

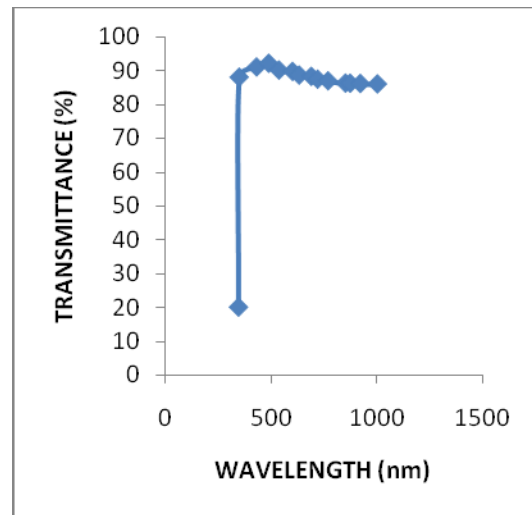


Figure 1: Transmittance of ZnO Film vs. Wavelength.

Figure 2 shows the absorption of the ZnO film. The spectra reveal that the deposited film has low absorbance in the VIS/NIR regions while the absorbance is high in the UV region.

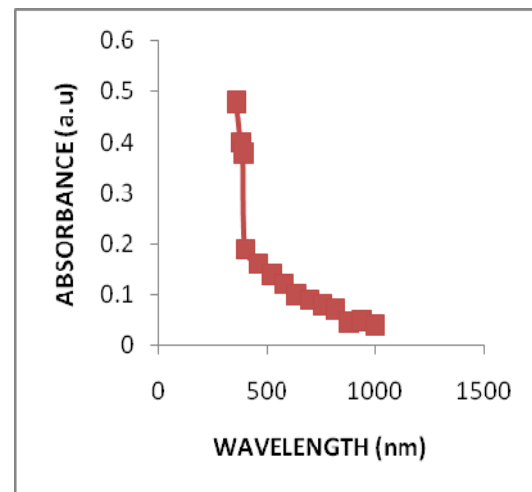


Figure 2: Absorbance vs. Wavelength ZnO Film.

Figure 3 is the extinction coefficient of the ZnO film versus the wavelength. The extinction coefficient is high in the wavelength range of 300 – 400nm and low in the wavelength range of 400

– 1100nm. The rise and fall in the extinction coefficient is directly related to absorption of light (Islam and Podder, 2009). The fall in the extinction coefficient may be due to the absorption of light at the grain boundary (Islam and Podder, 2009).

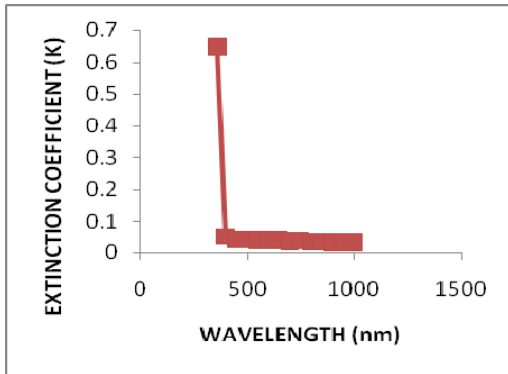


Figure 3: Extinction Coefficient vs. Wavelength of ZnO Film.

Figure 4 shows the plot of refractive index versus wavelength of the ZnO film. From the result, it shows that there is increase in the refractive index in the VIS/NIR regions.

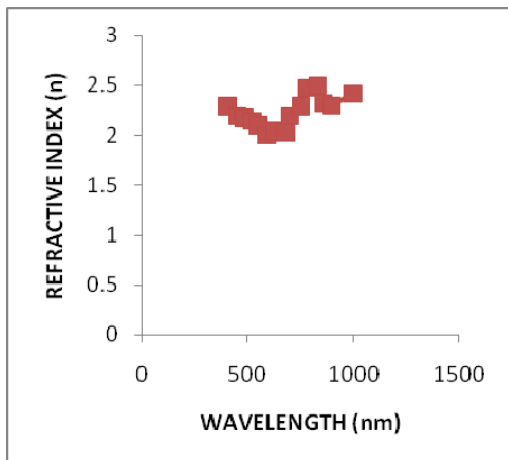


Figure 4: Refractive Index vs. Wavelength of ZnO Film.

X-ray diffraction (XRD) was used for the structural characterization of the ZnO film. The deposited film was annealed at 150°C in an oven before characterization. Figure 5 shows the X-ray pattern of ZnO film, which depicts the intensity (in arbitrary unit) versus 2θ , where θ is the angle of incidence of X-ray beam. From the figure, it is

seen that the maximum intensity from the peak appears at 34.680° . The other peaks appear at 32.25° , 37.23° , 48.25° , and 57.23° and these can be associated with (100), (101), (102), and (110) peaks as is expected for hexagonal ZnO structure (Mondal *et al*, 2008; Mitra and Khan, 2006). From the XRD analysis C – axis orientation is preferred strongly (Mondal *et al*, 2008).

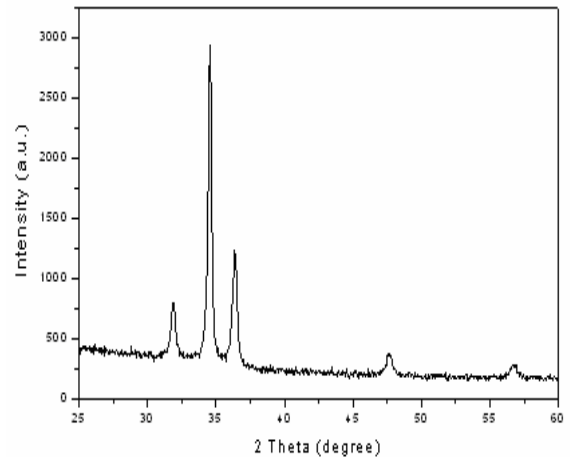


Figure 5: X-ray Diffraction Pattern of ZnO Film.

Figure 6 shows the microstructure of the ZnO film obtained from SEM. The SEM photograph reveals that the chemical bath deposited particles (atoms) are absorbed onto the glass substrate in cluster as primary stage of nucleation, and illustrates the formation of sub-micrometer crystallites distributed more or less uniformly over the surface. However, the low deposition temperature (25°C) in chemical bath deposition (CBD) possibly results in large crystallite (with large particle size). Although no cracks could be detected, there are holes indicating that large porosity is present, and agglomeration of small crystallites also was observed to be present in certain regions on the film surface. Similar observations were taken by Mondal *et al*, (2008).

Figure 7 shows the variation of sheet resistance with temperature. The sheet resistance is found to decrease with increasing temperature. The decrease in resistance is related to the increase in carrier concentration resulting from the activation of deep and shallow donors which may rise due to native defects such as interstitial zinc atoms and oxygen vacancies (Kroger, 1964).

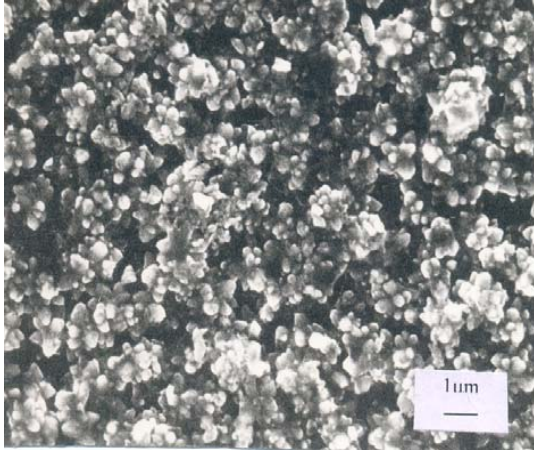


Figure 6: SEM of ZnO Film.

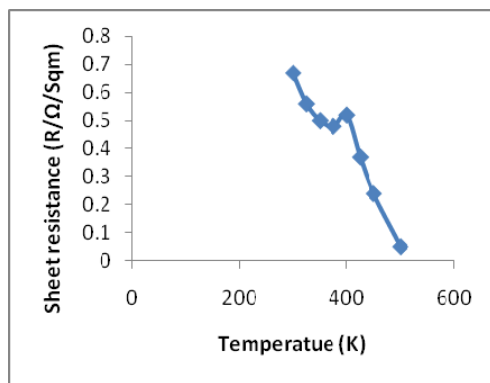


Figure 7: The Sheet Resistance of ZnO Film vs. Temperature.

From the experimental data, the measured resistance is R . the separation between the electrodes L , is 5mm. The area A is the product of length of the electrodes (20mm) and thickness of the film ($4.96\mu\text{m}$). From the calculated results at temperature of 107°C , the sheet resistance is found to be of the order of $10^{12}/\text{cm}^3$ for the ZnO film which is in agreement with the result of Mondal *et al* (2008).

CONCLUSIONS

The deposition of ZnO film was successfully carried out on a glass substrate (glass slide) at room temperature (25°C) using chemical bath deposition (CBD) technique. The film was characterized for optical and electrical properties. From the characterization, the following conclusions were drawn:

1. The optical transmission spectra of the ZnO film are high at wavelengths range of 400 – 1100nm is high and low near the fundamental absorption. The absorption spectra of the film are low in the VIS/NIR regions, and high in the UV region. The extinction coefficient of the film is in the wavelength range of 300 – 400nm and low in the wavelength range of 300 – 400nm and low in the wavelength range of 400 – 1100nm (which is attributed to the absorption of light at the grain boundary).
2. The XRD analysis reveals that the structure of the ZnO film is expected to be hexagonal with preferred C-axis orientation, while the microstructural analysis of the film reveals that the SEM photographs illustrates the formation of Sub-Micron Crystallites distributed more or less uniformly over the surface with holes indicating large porosity and agglomeration of small crystallites present in certain regions on the film surface.
3. The decrease in resistance of the ZnO film was found to be related to the increase in carrier concentration resulting from activation of deep and shallow donors arising due defects such as interstitial zinc atoms and oxygen vacancies, although, the activation barrier is not in anyway affected by the value of the resistance.

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