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Synthesis and Characterization of Cadmium Oxide (Cdo) Deposited by Chemical Bath Deposition Technique

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A B S T R A C T

Thin films of Cadmium Oxide (CdO) have been prepared by Chemical Bath Deposition (CBD) method. The prepared films were annealed at 200^{o}C, 250^{o}C and 300^{o}C. The annealed films were characterized for their Optical and Electrical properties. All the films exhibited their maximum transmittance above 80% (i.e., 84.27%–91.58%) in the VIS and NIR regions of the spectrum and were found to decrease with increasing annealing temperature. The band gap energy (E_g) estimated was in the range of 2.18eV–2.34eV and the refractive index was found to shift towards the higher wavelength region when the annealing temperature increases. The electrical properties of the films reveal an increase in carrier concentration and the conductivity with increase in annealing temperature. The carrier concentration (N) and conductivity (σ) of about 1.245x 10^{22}cm^{-3} and 0.69Ω-m^{-1}were achieved for films annealed at 300^{o}C.

Introduction

Transparent Conducting Oxides (TCOs), in recent years, have attracted the attention of many researchers due to its unique physical properties and wide range of applications in Technology. Metal Oxides such as SnO_2, In_2O_3, CdO and their alloys, because of their transparent conducting property can be used as TCOs. Transparent Conducting Metal Oxides are also referred to as Oxide Semiconductors and their thin films can exhibit various characteristics of Metals, Semiconductors and Insulators with improved electrical and optical properties (Lalithambika *et al.*, 2014). CdO is an n-type Semiconductor with a rock-salt crystal structure (fcc) and possesses a direct band gap between 2.2eV to 2.5eV (Ortega et al, 2000). Its high electrical conductivity (i.e. low electrical resistivity), high carrier concentration, high optical transmittance in the visible region of the spectrum (Manjula and Balu, 2014), and moderate refractive index (Faizullah *et al.*, 2013). Due to these unique properties, CdO has attracted notable attention for various application such as Solar cells and other optoelectronic devices (Veeraputhiran et al, 2015), Photovoltaic devices (Chapness *et al.*, 1985), Photodiodes (Kondo *et al.*, 1971), IR heat mirrors and gas sensors (Mishra *et al.*, 2009), low-

emmisive windows (Gomez- Daza *et al.*, 2001) and thin film resistors (Yan *et al.*, 2001). CdO thin films, both pure and impure have been prepared by various techniques such as Thermal Evaporation (Zein *et al.*, 2013); Chemical Bath Deposition (Lalithambika *et al.*, 2014); Successive Ionic Layer Adsorption and Reaction (Gokul *et al.*, 2013); Pulsed Laser Deposition (Shatha and Azzawi, 2015); Spray Pyrolysis (Sachin *et al.*, 2014); Microwave Synthesis (Veeraputhiran *et al.*, 2015); Solgel Spin Coating (Ilican *et al.*, 2009); Sputtering (Subramanyam *et al.*, 1998); Metal Organic Chemical Vapour Deposition (Ellis and Irvine, 2004) etc.

In this Paper, CdO thin films were deposited on glass substrates using the Chemical Bath Deposition technique. The optical and Electrical Properties of the films were investigated and discussed for different annealing temperatures.

Materials and Method

Cadmium Oxide (CdO) thin films were deposited onto clean glass substrates using the Chemical Bath Deposition (CBD) technique. All chemicals used were of Analytical Grade. Before the deposition, the substrates were rinsed with distilled water, washed with detergent and then rinsed with distilled water. The substrates were again degreased with ethanol, rinsed with distilled water and then dried in an oven. This process was carried out to ensure clean surface essentially for the formation of nucleation centres that is required for thin film deposition. For the deposition, Cadmium Chloride ($CdCl.2H_2O$) was used as precursor for preparation of the CdO thin films as Cd^{2+}ion source. 5ml of $CdCl_2$ was poured into a beaker followed by the gradual introduction of 30% NH_3 with slight shaking which initially turns the solution white and odourless. More quantity of the NH_3 solution was added to about 4ml as demonstrated by Ezekoye *et al.* (2013) and Lalithambika *et al.* (2014). 34ml of double water was added to the mixture which turns the solution fair white. The mixture was kept in an open conical flask in order to acquire sufficient amount of oxygen. The pH of the bath was maintained at 9.5 confirming the alkalinity of the bath.

Thereafter, the solution was transferred back to the beaker ready for deposition process. The cleaned substrates were inserted into the reaction bath and held vertically in a synthetic foam cover which was left for 24 hours for the deposition to complete. The substrates were then withdrawn from the bath and rinsed with distilled water and allowed to dry in air. The samples were then annealed at temperatures of 250^{o}C, 350^{o}C and 450^{o}C for 1 hour each respectively. The thin films were characterised for their optical properties using UV-VIS Spectrophotometer (Perkin Elmer) while, the electrical characterisation of the samples was carried out by considering the transport properties of the thin films which is determined by the Hall effect measurement using the Vander-Paw configuration at room temperature.

Theoretical considerations and calculations

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

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

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

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

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

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

or

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

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

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

or

$$\alpha = \frac{(h\upsilon - E_g)^{1/2}}{h\upsilon} \qquad (5)$$

Where A is the total 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`s 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:

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

For semiconductors (where $K^2 << n^2$) 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.

And the relation between K and α (Pankove, 1971) given by;

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

Also, the relationship existing between R, K and n is given (Islam and Podder, 2009) by;

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

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

Electrical

The relation between resistivity ρ, temperature T and activation energy Ea, is given (Barote and Masumdar, 2014) by;

$$\rho = \rho_o \exp\left(\frac{E_a}{KT}\right) \quad (12)$$

Where, ρ is the resistivity, ρ_o is constant, K is the Boltzmann constant, T is the absolute temperature and Ea is the activation energy. The Hall mobility μ_H and the resistivity ρ are related by the expression given (Hamadi *et al.*, 2010) by;

$$\mu_H = \frac{|R_H|}{\rho} \qquad (13)$$

Where R_H is the Hall coefficient and ρ denotes electrical resistivity. While the carrier mobility due to lattice vibrations is given (Kanjwal *et al.*, 2010) by;

$$\mu_L = A_L m_{eff}^{-5/2} T^{-3/} (14)$$

And the charged ionised centres affect mobility as given (Hamadi *et al.*, 2010) by;

$$\mu_I = A_I m_{eff}^{-1/2} T^{-3/2} (15)$$

Where A_L and A_I are the characteristics parameters, m_{eff} denotes the scalar effective

mass of the charge carriers and T is the absolute temperature.

Results and Discussion

The overall reaction for the deposition can be written as:

$CdCl_2 + NH_3\ H_2O \rightarrow [Cd\ (NH_3)_4]^{2+} + 2OH^- + 2Cl^-$ (16)

$2Cd^{2+} + 2OH^- \rightarrow CdO + H_2O$ (17)

The Cadmium Oxide thin films were deposited when the ionic product (IP) of Cd^{2+} and OH^- exceeds the solubility product (SP) of $Cd\ (OH)_2$.

Optical

Figure 1 depicts the graph of optical transmittance (%) and wavelength (nm) of CdO thin films annealed at different temperatures of 200^o C, 250^o C and 300^o C respectively. The samples recorded maximum high transmittance of 91.58%, 84.78% and 84.27% in the VIS and NIR regions for temperatures of 200^o C, 250^o C and 300^o C respectively. This high transmittance exhibited by all the sample films is an indication of transparency in the VIS and NIR regions which could be attributed to lack of free electrons (i.e. electrons are linked to atoms by covalent bond) because the breaking of electron leakage and moving it to conduction band needs photon with high energy (Reem, 2014). Also, the gradual increase of transmittance with increase in wavelength for all the films with their peaks coinciding to wavelengths between 1500nm and 2000nm and then decrease with increase in wavelength could be attributed to the fact that, the samples absorbed light above these wavelengths which make them transparent to light within the visible region confirming the films as transparent conducting oxides (TCO`s). Hence, the high transmittance exhibited by all the films in the VIS and NIR regions of the spectrum is an indication that the absorbance and reflectance in these regions are very slow.

Figure 2 shows the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$, where α is the optical absorption coefficient and $h\upsilon$ is the energy of the incident photon. The energy gap (E_g) was estimated for a direct transition between the valence and the conduction band. $E_g$is determined by extrapolating the straight line portion of the spectrum to $\alpha = 0$. Based on this, the optical energy gap of E_g = 2.18eV, 2.27eV and 2.34eV were recorded for the films annealed at temperatures of 200^{o}C, 250^o C and 300^o C respectively. The decrease in band gap energy with increase in annealing temperatures is in agreement with the result of Gokul *et al.* (2013) in which he attributed it to increase in carrier concentration and also, quantum confinement.

Figure 3 shows the variation of refractive index with wavelength of the sample films annealed at different temperatures. For the films annealed at 200^o C and 250^o C, their refractive indices increase with increase in wavelength and have their maximum values coinciding at 2.674 around 800nm, then begin to decrease with increase in wavelength of which the two samples (annealed at 200^o C and 250^o C) descends to a minimum values of 1.75 and 1.90 respectively. Thereafter, the refractive indices of the two films begin to increase with increase in wavelength and around 2400nm their peak coincide at the value of 2.685. However, for the film annealed at 300^o C the refractive index increases with increase in wavelength and about 1100nm the refractive index reach a maximum value of 2.689 and then begin to decrease with increase in wavelength until it reach a

minimum value of 1.902 and again continue to increase with increase in wavelength until it reach a maximum value of 2.685 at about 2400nm. The same trend was observed by Gokul *et al.*, 2013 and was attributed to damping of CdO thin films. Also, the observed shift of the refractive index towards higher wavelength region when the annealing temperature increases indicates that, the refractive index of the material can be improved by post annealing process.

Table.1 Transport properties of CdO thin films annealed at different temperatures

S/No.	Annealing Temperature (^oC)	Carrier Concentration (N/CM^{-3})	Mobility (CM^2/NS)	Resistivity $X10^{-3}$ (Ω-M^{-1})	Conductivity Per Ω^{-1}-M^{-1}
1.	200	$0.062X10^{22}$	0.524	18.64	0.53
2.	250	$0.523X10^{22}$	0.401	16.55	0.60
3.	300	$1.245X10^{22}$	0.342	14.72	0.69

Fig.1 Transmittance spectra of CdO thin films annealed at different temperatures

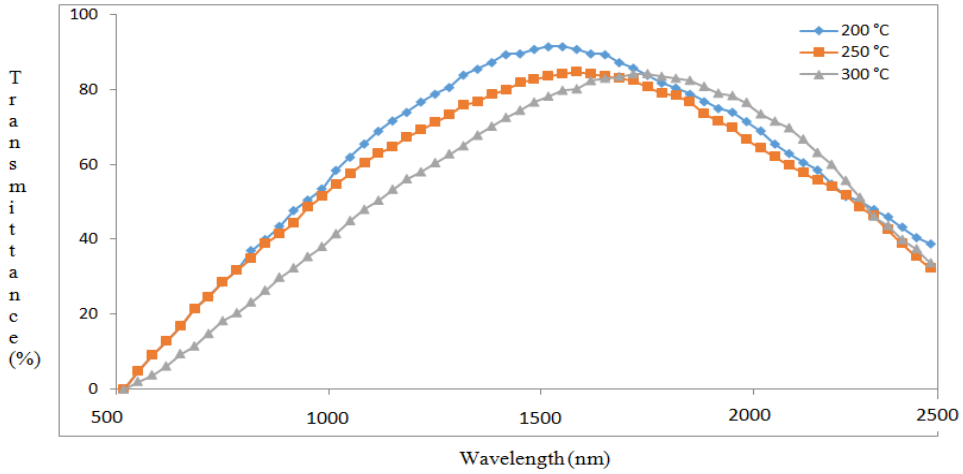


Fig.2 Dependence of band gap of CdO thin films on different annealing temperature

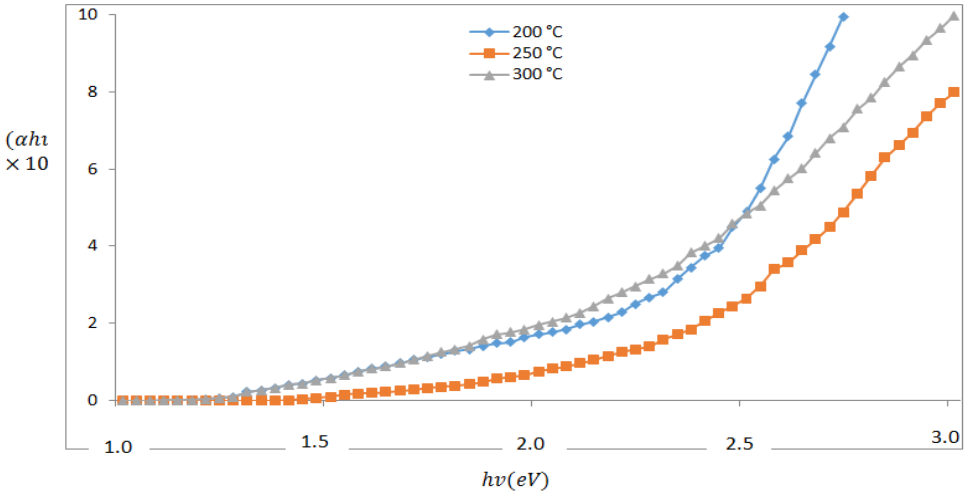
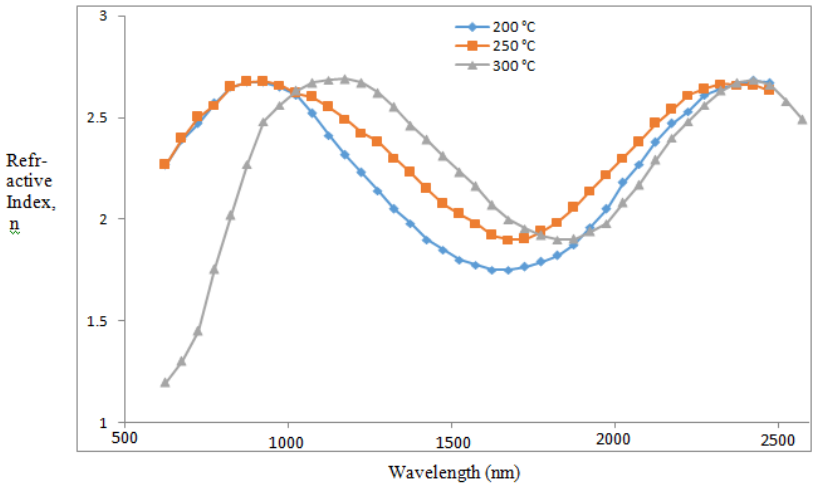


Fig.3 Variation of refractive index with wavelength at different annealing temperatures



Electric transport properties

Table 1 shows the transport properties of the CdO films annealed at different temperatures. The carrier concentration increase with increase in annealing temperature in the order 0.062 x $10^{22}cm^{-3}$, 0.523 x $10^{22}cm^{-3}$ and 1.245 x $10^{22}cm^{-3}$ for sample films annealed at 200^{o} C, 250^{o} C and 300^{o} C respectively and their mobility of the was found to decrease with increase in annealing temperature in the order 0.524cm^2/Vs, 0.401cm^2/Vs and 0.342cm^2/Vs respectively for the above order of annealing temperatures. The same trend of result was reported by Gokul *et al.* (2013) who attributed the higher carrier concentration to the presence of both interstitial and oxygen vacancies which are acting as donors thereby causing scattering of charge carriers.

Although, the mechanism responsible for scattering of charge carriers in thin films is ionized impurity scattering, lattice scattering and grain boundary scattering. But, even when the influence of grain boundary scattering is very little on the mobility and impurity scattering is independent of the temperature, the limiting factor of mobility could emanate from lattice scattering (Yan *et al.*, 2001). However, the resistivity of the sample films decrease with increase in annealing temperature, while the conductivity increase with increase in annealing temperature.

Conclusion

Thin films of CdO were deposited using the Chemical Bath Deposition technique. The films were annealed for temperatures of 200^{o} C, 250^{o} C and 300^{o} C and characterized for their optical and electrical properties. The high transmittance exhibited by all the films in the VIS and NIR regions of the spectrum is an indication that the absorbance and reflectance in these regions are very slow.The optical energy gap of E_g = 2.18eV, 2.27eV and 2.34eV were recorded for the films annealed at temperatures of 200^{o} C, 250^{o} C and 300^{o} C respectively. The carrier concentration increase with increase in annealing temperature in the order 0.062 x $10^{22}cm^{-3}$, 0.523 x $10^{22}cm^{-3}$ and 1.245 x $10^{22}cm^{-3}$ for sample films annealed at 200^{o} C, 250^{o} C and 300^{o} C respectively and their mobility of the was found to decrease with increase in annealing temperature in the order 0.524cm^2/Vs, 0.401cm^2/Vs and

0.342cm^2/Vs respectively for the same temperatures.

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