

Optical Properties of CdO Thin Films deposited by Chemical Bath Method

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Abstract: There is an ever growing interest in the synthesis of low-cost, non-vacuum transparent conducting oxides (TCOs) with n-type conductivity. In search of such suitable TCOs, it is found that chemical and physical conditions can be conveniently incorporated in the CdO thin films to obtain higher transmission and conductivity. In this work, CdO films have been prepared, using simple Chemical Bath Deposition technique for the molarities 0.05 and 0.1. The prepared films were annealed at a temperature of 100 °C for one hour. Transmission spectra of the films were taken using UV-VIS Double Beam Spectrophotometer in the wavelength range 400-1100 nm. Optical constants such as, band gap, refractive index, extinction coefficient, dielectric constant and Urbach energy were also studied.

Keywords: CdO thin film, optical properties, transparent conducting oxide thin films, extinction coefficient, Urbach energy.

Introduction

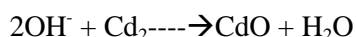
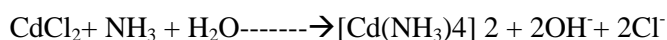
Oxides of many metals such as Tin, Indium, Zinc, Cadmium and their alloys, can be used as TCO's possessing transparent conducting property. Most of the studied transparent conducting metal oxides are anion deficient (i.e., Oxygen deficient) and hence are always n-type conductors[1]. The transparent conducting metal oxides are also referred as oxide semiconductors. Role of metal oxide thin films are very important in the field of science and technology. These films can exhibit various characteristics of metals, semiconductors and insulators with improved electrical and optical properties. So they can be used as electrodes in optoelectronic devices[2], display devices[3] and photovoltaic cells[4]. The n-type CdO thin films exhibit rock salt structure (FCC) with band gap 2.2eV. It also has good optical conductivity and transmission in the visible range [5]. CdO films can be synthesized by various methods such as Spray Pyrolysis[6], Sputtering[7], Sol-gel spin coating[8], Activated reactive evaporation[9], Metal Organic Chemical Vapour deposition (MOCVD)[10], Pulsed laser deposition[11-13]. The main goal of the work is to seek a simple, non-vacuum and economic deposition technique for efficient transparent films. In this study CdO films were synthesized using simple Chemical Bath method at various concentrations with fixed pH value. Optical studies such as transmission, bandgap, refractive index, absorption co-efficient, extinction coefficient, dielectric constant (imaginary and real) and Urbach energy were evaluated.

Experimental Methods

Cadmium Oxide thin films were prepared by CBD method with fixed pH value. Stock solution (5 ml) of CdCl₂ 2H₂O was taken in a beaker followed by the addition of 4 ml of 30% NH₃, with slight shake gave a whitish solution which is odorless. More of 30% NH₃ was poured into the solution until it was clear NH₃.

Double Distilled Water (H₂O, 34 ml) was added to the precursor solution which gave a fair whitish colour. The set-up was kept into an open beaker where a good amount of oxygen was sufficiently supplied to it. Two basic solutions of molar concentration 0.05M, 0.1M film were prepared. The pH of resultant solutions was nearly 10. The glass plates were cleaned well and used in the bath for deposition. Whitish thin films S1 and S2 were deposited on the glass substrates after 24 h, which turned clearly whitish when rinsed with distilled water. Samples were post-treated at 100°C for 1 hour. The films obtained were named as S1(0.05M) and S2(0.1M). After 24 hours all precipitate settled down at the bottom of the bath indicating the completion of the process.

The equations for the chemical reactions are as follows,



Optical studies were carried out with UV-VIS Double Beam Spectrophotometer (PERKIN ELMER Lambda35) for the wavelength region 400 nm to 1100 nm.

Results and Discussion

Thickness of the film

Film thickness (d) was found by Gravimetric Weight Difference Method using high precision electronic balance given by the relation [14]

$$d = M / (\rho * A)$$

where M is the mass of the film deposited on the substrate in gram, ρ the density of the deposited material and A the area of the deposited film. The thickness of the films S1 is 780nm and S2 is 850nm.

Optical studies of the deposited films

Fig. 1 shows the optical transmittance of the films with 0.05M (S1) and 0.1M (S2) with wavelength. The films show high transmission in the visible and near infrared region. It is clear from the transmission spectrum that the transmission of the films increases with the wavelength. Sample S1 exhibits maximum transparency of about 50% and sample S2 slightly less transparency of about 45% in the visible region and it extends up to the near infrared region.

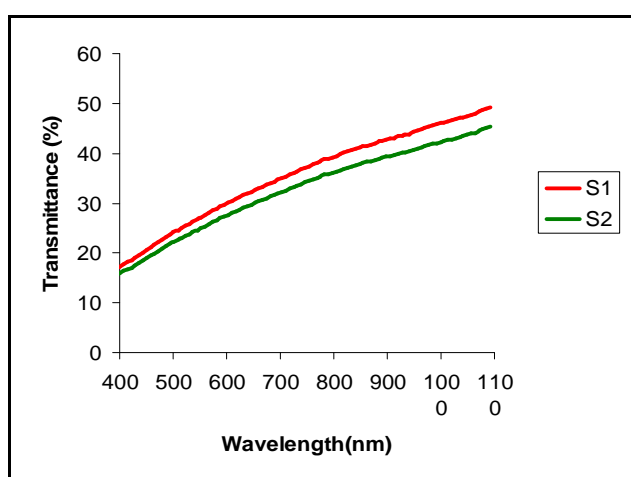


Figure 1. Transmission spectra of CdO films

Figure 2 shows the absorption spectra of CdO. The absorption of CdO films S1 and S2 were studied in the wavelength range 350-1100nm. The optical absorbance of the films decreases with the wavelength. These spectra reveal that as-grown CdO films have more absorbance in the UV region and less absorbance in the visible and high wavelength region.

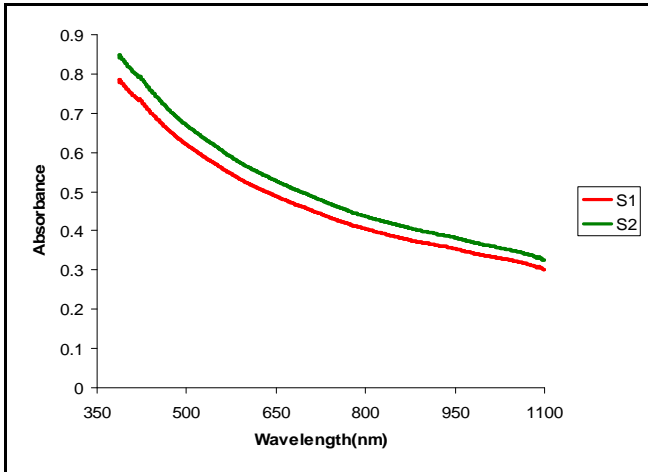


Figure 2. Absorbance spectra of CdO films

The optical band gap of the films S1 and S2 was found using the relation[15]

$$(\alpha h\nu) = A(h\nu - E_g)^m$$

Where, A -energy independent constant, m - constant determining the optical transmission type (for direct allowed $\frac{1}{2}$, indirect allowed 2, direct forbidden $\frac{3}{2}$ and indirect forbidden transition 3) respectively. E_g is the Energy gap. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig 3. CdO is a direct band gap semiconductor. The straight line on the curve in the horizontal axis shows the band gap of the CdO thin films and it is 2.86eV for the film S1 and 2.89eV for the film S2. This change in the band gap may be due to the difference in the deposition method and the parameters used during the process of coating.

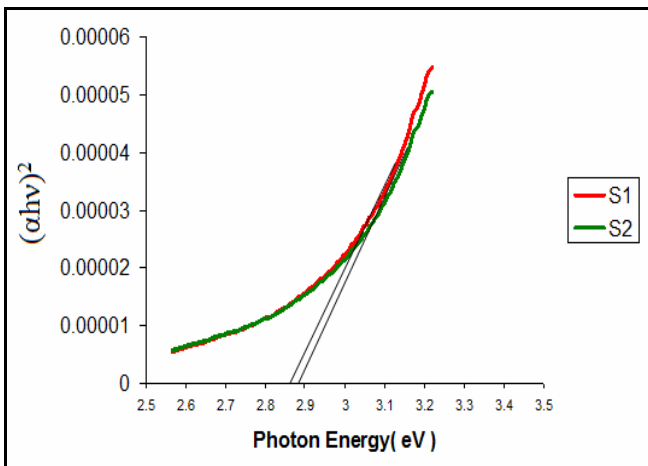


Figure 3. Plot of $(\alpha h\nu)^2$ versus $h\nu$

The measurement of optical constants such as refractive index (n), complex dielectric function (real and imaginary), extinction coefficient (k), are very important to study the optical properties of the solid thin materials. R is the normal incidence reflectivity and is given by-

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

where n is the refractive index and k is the extinction coefficient ($k = \alpha \lambda / 4\pi$) [16]. The values of n and k are calculated using the above equations. The refractive index variation with photon energy is plotted in Fig.4. The film S1 shows refractive index change from 1.91 to 1.94 and S2 from 1.89 to 1.92.

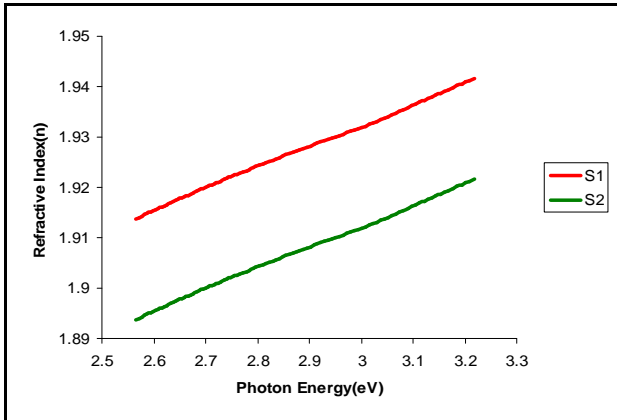


Figure 4. Plot of refractive index (n) vs photon energy(hv)

The extinction coefficient (k) plot against the photon energy in Fig.5 shows that the extinction coefficient (also called the attenuation coefficient) is high for low photon energy and it decreases with increase of photon energy. Stronger absorbing medium shows more extinction coefficient. The energy loss of electromagnetic radiation through that medium is measured by the extinction coefficient of a particular substance. The extinction coefficient is inversely related with the transmittance spectra. The high transmittance shows low extinction coefficient [17] and low transmittance shows high extinction coefficient.

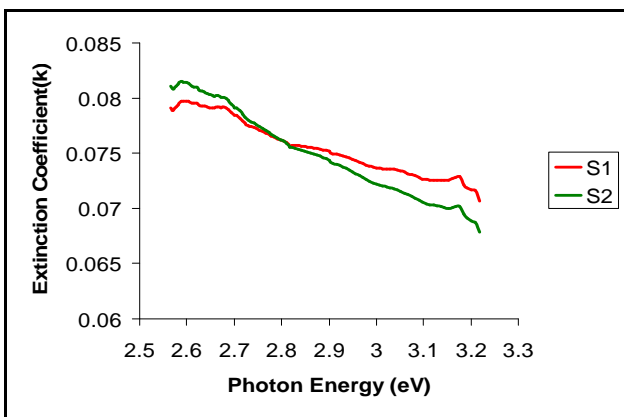


Figure 5. Plot of extinction coefficient (k) vs photon energy(hv)

The optical conductivity is measured using the following formula[18]

$$\sigma = \alpha\lambda/4\pi$$

Optical conductivity of the films S1 and S2 increases with photon energy. The change in the optical conductivity with photon energy is same for both the films (fig-6). The increase of optical conductivity in the high photon energy region is due to the increase in the absorbance of sample thin films.[19] Optical conductivity of S1 is slightly higher than the film S2.

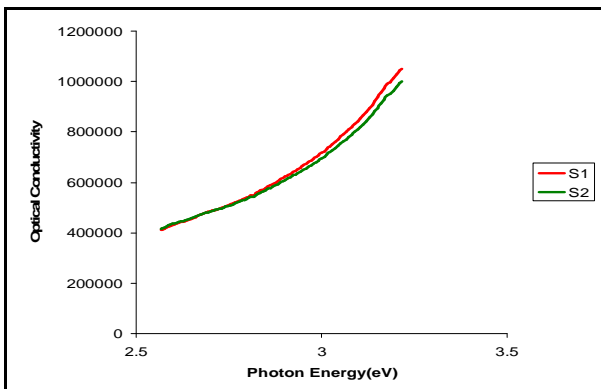


Figure 6. Plot of optical conductivity (σ) vs photon energy(hv)

Real part of the dielectric constant is related to the n value and imaginary part of the dielectric constant to the k value. The values of ϵ_r and ϵ_i were calculated using the relations [20],

$$\epsilon_r = n^2 - k^2$$

$$\epsilon_i = 2nk$$

The imaginary ϵ_i and real ϵ_r parts of the dielectric constants are plotted as a function of photon energy in Fig 7. & Fig 8. The imaginary part shows the absorption of energy of a dielectric material from an electric field due to dipole motion. The imaginary part of dielectric constant decreases with photon energy. Fig-8 shows how much the real dielectric constant will slow down the speed of light in the material. S1 has less value of ϵ_i than S2. Fig-8 shows how much the real dielectric constant will slow down the speed of light in the material. For the film S1 the real part of dielectric constant increases from 3.65 to 3.77 and for S2 from 3.57 to 3.7.

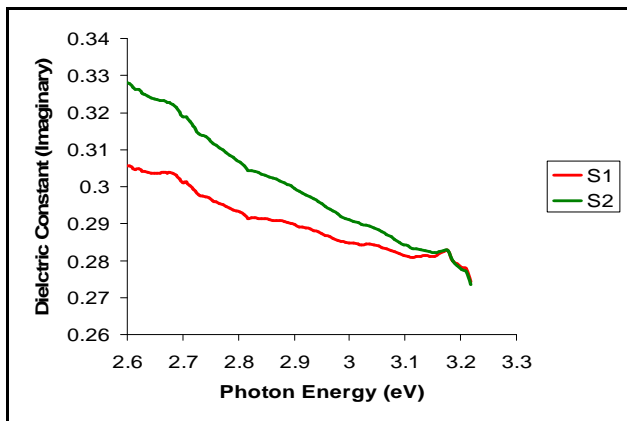


Figure 7. Plot of Dielectric constant (imaginary) vs photon energy(hv)

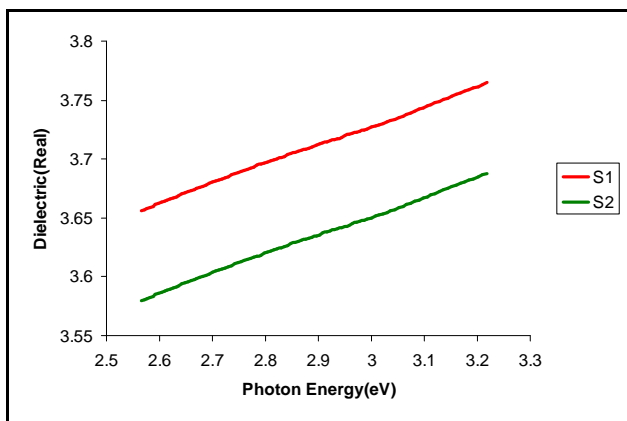


Figure 8. Plot of Dielectric constant (real) vs photon energy(hv)

Plot of $\ln(\alpha)$ with photon energy is depicted in Fig 9. The calculated urbach energy for the film samples are shown in table 1. Lower value of E_u indicates very weak absorption due to minimum level defects and impurities in the system. For the sample S2 E_u is higher than the sample S1.

Table 1. Urbach energy(E_u) of CdO thin films

Sample	Urbach Energy (m eV)
S1	48.14
S2	52.46

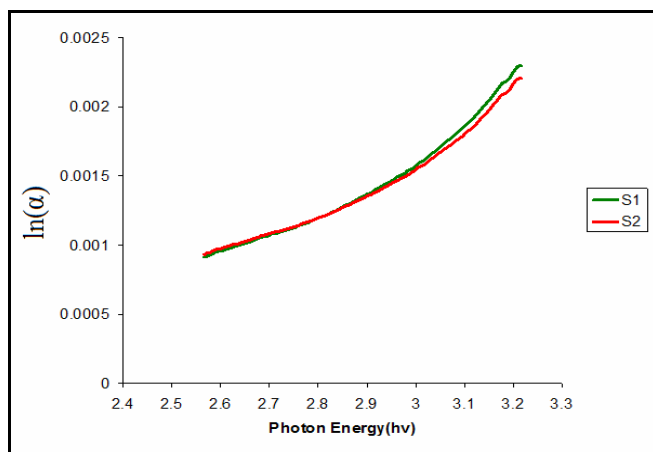


Figure 9. Plot of $\ln(\alpha)$ vs photon energy(hv)

4. Conclusion

CdO thin films are deposited on glass plates using Chemical Bath method after annealing shows film thickness of 780nm and 860nm. The Optical studies show that higher molarity film has less transmittance. The band gap values were found to be 2.86 and 2.89eV. Refractive index increases from 1.91 to 1.94(S1) and 1.89 to 1.92(S2). Optical conductivity increases from 4×10^5 to 10×10^5 with photon energy for the films. The real part of dielectric constant ϵ_r increases with the photon energy and the imaginary part of the dielectric constant ϵ_i decreases with the photon energy. Urbach energy for the samples increases from 0.001 to nearly 0.0025 with photon energy.

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