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OPTICAL CHARACTERISATION OF THIN FILM CADMIUM OXIDE PREPARED BY A MODIFIED REACTIVE THERMAL EVAPORATION PROCESS

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ABSTRACT

The optical transmission spectra of transparent conducting cadmium oxide (CdO) thin films deposited by a modified reactive evaporation process onto glass substrates have been measured. The interference fringes were used to calculate the refractive index, thickness variation, average thickness and absorption coefficient of the films. The influence of the partial pressure of oxygen (PO_2), during film deposition on the transmittance, optical constants and bandgap of the films is studied. The observation of an optimum value of PO_2 (= 0.040 Pa) at which the transmission is maximum is considered to be a particularly significant result. So, too, is the result that the width of the bandtail has a minimum at the optimum PO_2 value.

Key Words: CdO Films, Optical Transmittance, Evaporation

INTRODUCTION

The development of cadmium oxide thin films for various optoelectronic devices has stimulated great interest in the preparation and characterisation of the material. The optical constants (i.e. the real part of the complex refractive index, $n(\lambda)$ and the absorption coefficient $\alpha(\lambda)$) as well as the thickness d of the films are therefore of utmost importance. The optical properties of thin films have been investigated by several workers using the spectral dependence of optical transmittance $T(\lambda)$ (Hall and Ferguson 1955, Heavens 1965, Lyashenko and Miloslavski 1964, Nowak 1995, Manifacier et al. 1976, Szczyrbowski and Czapla 1977, Swanepoel 1984 and Clark 1968). Heavens (1965), Clark (1968) and Martin et al. (1983) employed the approximation of an infinite substrate. Szczyrbowski and Czapla (1977) studied inhomogeneities in InAs in the form of the surface roughness and it was discovered that surface roughness has a large influence on the calculation of the absorption coefficient $\alpha(\lambda)$. Hall and Ferguson (1955), Lyashenko and Miloslavski (1964) and Manifacier et al. (1976) developed a method using successive approximations and interpolations to calculate the optical constants of semiconducting and dielectric thin films. Of these various methods of analysis, the Swanepoel (1984) method of treatment has proven to be the most effective and most comprehensive analytical technique used to study the optical constants of semiconducting and insulating films (Miotkowski and Miotkowska 1988, Eze 1999).

In this paper, the Swanepoel theory is employed to calculate the thickness variation Δd, average thickness d, and the spectral variation of the refractive index $n(\lambda)$ and absorption coefficient $\alpha(\lambda)$ from the experimental transmission spectra of CdO thin films deposited by a reactive vacuum evaporation process. The effects of the variation in the oxygen partial pressure during deposition on the optical constants and bandgap are also studied.

EXPERIMENTAL DETAILS

Thin films of CdO were prepared using a modified reactive thermal deposition process. A full account of the reactive thermal evaporation method has been given elsewhere (Eze 1998). Here it suffices to say that a specially wound quartz furnace was incorporated in the bell jar vacuum chamber to improve the source-substrate temperature profile. The evaporation unit consisted of an oil diffusion pump backed by a two-stage rotary pump. The chamber was evacuated to 0.00133 Pa. Prior to the film deposition, the quartz glass substrates were cleaned in H_2SO_4/H_2O_2 to remove organic and metallic impurities, followed by cleaning with $NH_4OH/H_2O_2/H_2O$ to remove ionic contaminants and particulates and a 5 min dip in HNO_3 to remove oxidizable inorganic and metallic impurities. To complete the clean-up the substrates were again cleaned with detergent and rinsed in distilled water and then placed in an ultrasonic cleaner. The conditions for the growth of CdO films were obtained for oxygen partial pressures in the range 0.0133 – 0.0533 Pa, substrate temperature of 150°C and incorporated furnace temperature of about 100°C.

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After the deposition, the films were annealed in a tube furnace in an oxygen atmosphere for about 1h at a temperature of about 350°C in order to fully oxidize the films. X-ray diffractometry had earlier been used to assess the quality of CdO films prepared by this method (Eze 1998). The sample prepared in this work were all polycrystalline in nature, with preferred orientation in the (III) plane as ascertained from x-ray diffractometry. Optical transmission measurements were carried out using a dual-beam UV-Visible-Near-IR Spectrophotometer in the wavelength range 300 – 1100 nm. All optical measurements were taken at room temperature.

RESULTS AND DISCUSSION

Transmission Spectra

A typical transmission spectrum shown in Fig. 1 reveals pronounced interference effects for photon energies below the fundamental absorption edge. Such a behaviour of the spectrum is evidence of thickness uniformity of the films. Otherwise, the interference fringes would have been destroyed, resulting in smooth transmission curves. However, certain features of the transmission spectrum suggest that care must be taken in discussing the thickness uniformity of the films. The interference-free transmission of the clean substrate alone was measured, yielding a transmittance, T_s of 0.962. In the case of a uniform film, the departure of the interference maxima from $T_s = 0.962$ corresponds to the onset of absorption. Fig. 1 shows that the spectrum is somewhat 'shrunken', making it difficult to determine where the absorption starts to reduce the transmission. It appears that this behaviour of the transmission spectrum is related to the surface roughness of the films. Such a behaviour had been previously observed for InAs thin films where it was found that the calculated values of the absorption coefficient α decreased considerably when the effects of the surface roughness were taken into account (Szczyrbowski and Czapla 1977).

DETERMINATION OF OPTICAL CONSTANTS FROM TRANSMISSION SPECTRUM

The treatment of experimental data used is presented step-by-step. The envelopes of the spectral dependence of optical transmittance shown in Fig. 1 were determined by employing numerical fitting of the transmittance T in the maxima and minima interference fringes, respectively. Multiple reflections occur at the three interfaces, namely: air-film, film-substrate and substrate-air interfaces. Thus, for normal incidence, the transmittance T is given by (Heavens 1965).

$$T = \frac{Ax}{B - Cx\cos\Psi + Dx^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ 1$$

where

$A = 16n^2 n_s$,
$B = (n+1)^3(n+n_s^2)$,
$C = 2(n^2-1)(n^2-n_s^2)$,
$D = (n-1)^3(n-n_s^2)$,
$\Psi = 4\pi nd/\lambda$, and
$x = \exp(-\alpha\bar{d})$ ……………… 2

In the case of zero absorption the expressions for the envelopes around the maxima and minima interference fringes are, respectively (Swanepoel 1984)

$$T_M = \frac{\lambda}{2\pi n\Delta d}\,\frac{a}{(1-b^2)^{1/2}}\tan^{-1}\left(\frac{1+b}{(1-b^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right) \qquad \ldots\ 3$$

$$T_m = \frac{\lambda}{2\pi n\Delta d}\,\frac{a}{(1-b^2)^{1/2}}\tan^{-1}\left(\frac{1-b}{(1-b^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right) \qquad \ldots\ \ldots\ldots\ldots\ 4$$

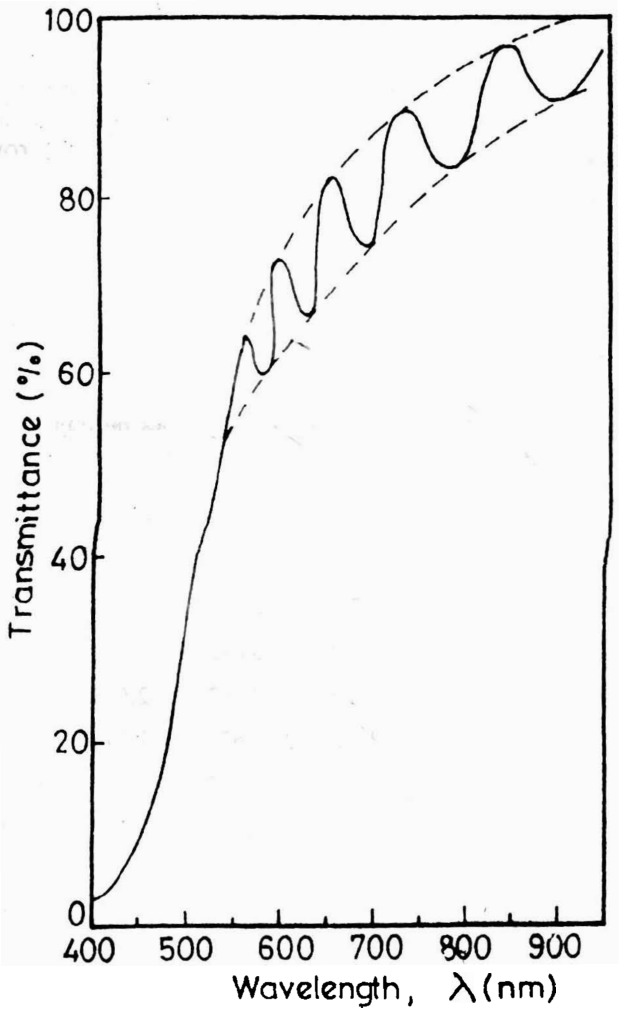

Fig. 1: Typical optical transmission spectrum for a reactively evaporated CdO thin film of thickness 280 nm, annealed in oxygen atmosphere at 350°C for 1h.

where

a = A/(B + D), b = C/(B + D), d is the thickness of the film and n and n_s are the refractive indices of the film and substrate, respectively. The substrate refractive index n_s was assumed to be constant (n_s = 1.515) as no significant variation in the substrate optical transmittance (T_s = 0.962) was observed within the spectral region investigated. It is pertinent to note that T_M approaches T_s only in the long wavelength limit but decreases consistently with decreasing wavelength. Eqns. 3 and 4 represent two independent transcendental equations with only two unknown parameters n and Δd. The equations which are independent of the average film thickness were solved using an IBM-486/PC computer and appropriate programmes written in FORTRAN. Values of the film refractive index and thickness variation are recorded in table 1 as n_1 and Δd, respectively. A comparison of the values of n_1 with true values n_{tr} show that n_1 values agree fairly well with n_{tr} for smaller α but increase sharply for larger values of α.

In the region of weak and medium absorption the absorption coefficient α is non-zero. Thus, eqns. 3 and 4 may now be respectively modified to (Swanepoel 1984):

$$T_{Mx} = \frac{\lambda}{2\pi n\Delta d}\,\frac{a_x}{(1-b_x^2)^{1/2}}\tan^{-1}\left(\frac{1+b_x}{(1-b_x^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right) \qquad \ldots 5$$

$$T_{mx} = \frac{\lambda}{2\pi n\Delta d}\,\frac{a}{(1-b_x^2)^{1/2}}\tan^{-1}\left(\frac{1-b_x}{(1-b_x^2)^{1/2}}\tan\left(\frac{2\pi n\Delta d}{\lambda}\right)\right) \qquad \ldots\ldots\ldots 6$$

Where

$a_x = Ax/(B + Dx^2)$ and $b_x = Cx/(B + Dx^2)$

Eqns. 5 and 6 are two independent equations with two unknowns n and x because Δd has already been calculated from eqns. 3 and 4 in the region of zero absorption. Values of the parameters n and x calculated from eqns. 5 and 6 are recorded in table 1 as n_2 and x. In order to obtain improved values of the refractive index in the strong absorption region values of n_2 were fitted to an equation of the form (Swanepoel 1984):

$$n = \frac{d}{\lambda^2} + C, \qquad \ldots\ldots 7$$

When d and C are Constants.

TABLE 1: Calculated values of Δd, n and α using the values of λ, T_M and T_m from the transmission spectrum shown in Fig. 1

λ (nm)	T_M	T_m	Δd (nm)	n_{tr}	n_1	n_2	α (x 10^6 m^{-1})	x
	0.6446	0.5719	15.26	3.052	3.712	3.050	1.363	0.4923
580	0.7004	0.6008	19.58	2.811	3.58	2.808	1.317	0.5042
595	0.7345	0.6329	22.91	2.739	3.341	2.734	1.203	0.5350
625	0.7853	0.6617	23.77	2.678	3.112	2.690	1.023	0.5875
650	0.8241	0.6926	24.13	2.609	2.903	2.603	0.805	0.6580
685	0.8725	0.7452	25.72	2.542	2.675	2.544	0.706	0.6927
730	0.9052	0.7823	25.95	2.397	2.387	2.401	0.560	0.7474
785	0.9408	0.8317	26.06	2.291	2.063	2.289	0.446	0.7930
835	0.9682	0.8705	26.26	2.081	1.881	2.087	0.323	0.8454
880	0.9850	0.8985	26.37	1.986	1.732	1.979	0.306	0.8529

TABLE 2: Variation of optical properties of CdO films with partial pressure of oxygen during film deposition. The film thickness is 280 nm and the film was annealed in oxygen for 1h at 350°C.

PO_2 (Pa)	Transmittance at λ = 700 nm (%)	Energy Gap, E_g (eV)		Width of Tail States γ^{-1} x 10^{-2} (eV)	Refractive index n at λ = 700 nm
		Direct	Indirect		
0.0133	24.0	2.05	1.65	9.44	3.45
0.0267	64.0	2.36	1.93	7.59	3.03
0.0333	73.0	2.45	2.24	5.46	2.62
0.0400	84.0	2.58	2.40	5.02	2.54
0.0533	71.5	2.42	2.02	6.86	2.37

From table 1 the agreement between n_2 and true values n_{tr} is very good as confirmed from the values reported in the literature. The average film thickness was calculated from the transmission spectra using the relation (Swanepoel 1983):

$$\bar{d} = \lambda_l\lambda_m/2(n_m\lambda_l - n_l\lambda_m) \qquad \ldots\ldots\ldots\ldots 8$$

where n_l and n_m are the refractive indices of two adjacent minima or maxima corresponding to λ_l and λ_m. A value of 280 nm was obtained as the average film thickness. The calculated value of was used to determine the values of α and x from eqn. 2. These values are shown in table 1. The values of x are in good agreement with the values reported for sputtered CdO thin films (Tanaka et al. 1969). The spectral dependence of surface roughness represented by Δd is also shown in table 1. It is observed from the table that in the region of weak and medium absorption the Δd values are low for large α and high for low α values. This is due to the fact that Δd was calculated at zero absorption. A closer look at table 1 shows that

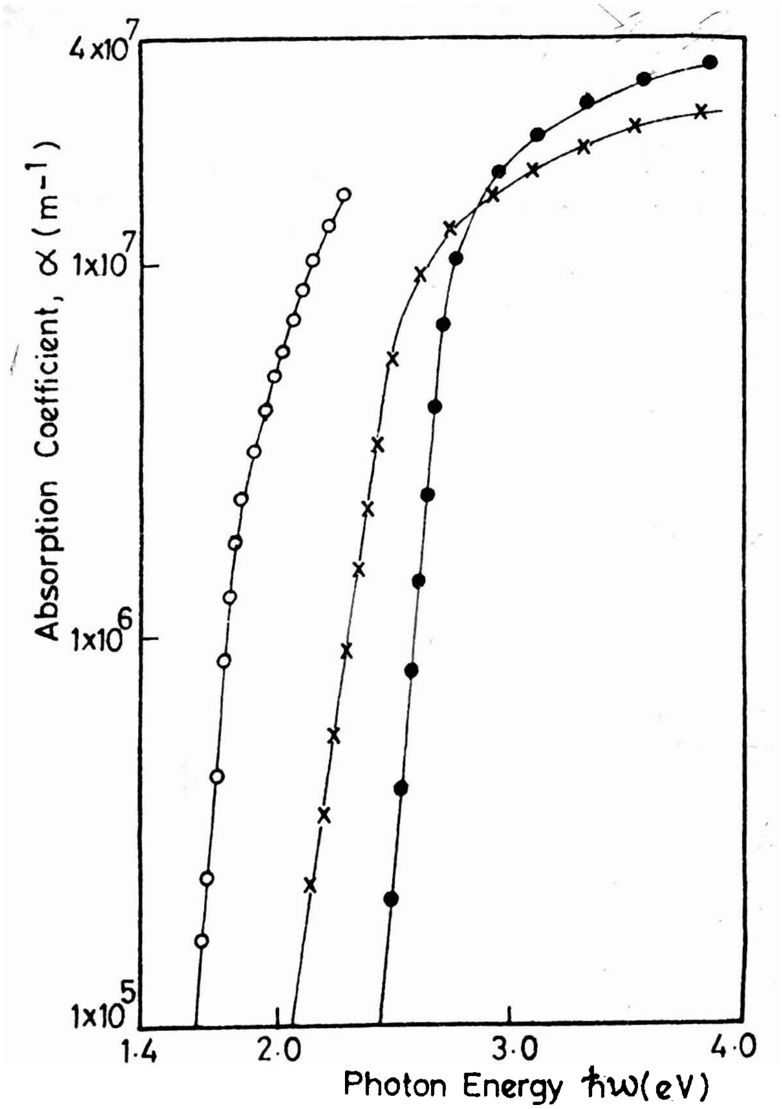

Fig. 2: Semi-logarithmic plots of absorption coefficient α versus photon energy $h\omega$ for CdO films deposited at the indicated oxygen partial pressures: o – 0.0133 Pa; x – 0.0267 Pa; • – 0.040 Pa.

Δd starts to increase when $\alpha \geq 8.05 \times 10^5\ m^{-1}$. The actual value of Δd is obtained by estimating the asymptotic value for very large wavelength. From table 1, $\Delta d \approx 26.1$ nm. The thickness variations Δd were measured independently using a mechanical stylus instrument and the results agreed well with those obtained from the transmission spectra.

The typical transmission spectrum shown in Fig. 1 for a CdO thin film of thickness 280 nm indicates a transmittance of about 65% in the middle of the visible region and much higher (> 90%) in the near infrared regions of the electromagnetic spectrum. However, the optical transmission is found to be dependent on the partial pressure of oxygen during film deposition. This dependence is shown in table 2 and exhibits a maximum at an oxygen partial pressure PO_2 of 0.040 Pa. The decrease in transmittance at PO_2 greater than 0.040 Pa may be attributed to increased light scattering whereas at lower than optimum pressure the film is nonstoichiometric, resulting in a decrease in transmittance.

ABSORPTION COEFFICIENT IN THE STRONG ABSORPTION REGION

It has been observed that for several semiconductors the absorption edge tails well into the forbidden bandgap region and is almost invariably found to obey accurately an Urbach exponential dependence on photon energy in the form (Urbach 1953):

$$\alpha = \alpha_0 \exp[-\gamma(E_0 - h\omega)] \qquad \ldots\ldots\ldots\ldots\ 9$$

where E_c is an energy comparable to E_g, and γ is a constant at room temperature. The inverse of γ is interpreted as the width of the tail of localised states in the bandgap. Typical plots of the absorption coefficient versus photon energy are shown in Fig. 2 for CdO thin films prepared at various oxygen partial pressures. It is evident that the absorption coefficient increases with increasing photon energy in a manner revealing fundamental interband transition. It can be seen that the absorption edge shifts to higher photon energies as PO_2 increases to an optimum value of 0.040 Pa. The slope of the straight line portion of the curve gives γ. The γ^{-1} values obtained are recorded in table 2. The values are in agreement with the values of 4.0 – 10.0 x 10^{-2} eV reported for several semiconductors (Eze 1994). It is noteworthy to mention that films prepared at PO_2 = 0.040 Pa showed the smallest width of the tail states, a result which correlates remarkably well with the previous results on X-ray diffractometry of the films (Eze 1998). The absorption edge arises due to transitions from the top of the valence band to the bottom of the conduction band. The absorption coefficient for band-to-band transitions is given by (Tsidilko 1982):

$$\alpha\hbar\omega = B(\hbar\omega - E_g)^y \qquad \ldots\ldots\ldots\ldots\ldots 10$$

where B is a constant, and y = ½ and 2, for allowed direct and allowed indirect transitions, respectively. Figs. 3 and 4 show typical $(\alpha h\omega)^2$ versus hω and $(\alpha h\omega)^{1/2}$ versus hω plots, respectively for CdO films deposited at various oxygen partial pressures. The plots indicate that both direct and indirect transitions are

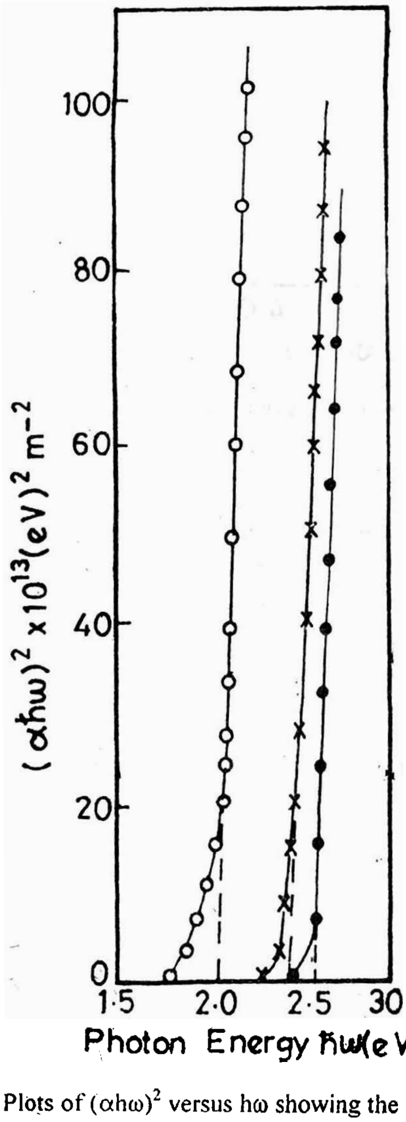

Fig. 3: Plots of $(\alpha h\omega)^2$ versus hω showing the direct bandgap of the CdO films deposited at different partial pressures of oxygen: o – 0.0133 Pa; x – 0.0267 Pa; • – 0.040 Pa.

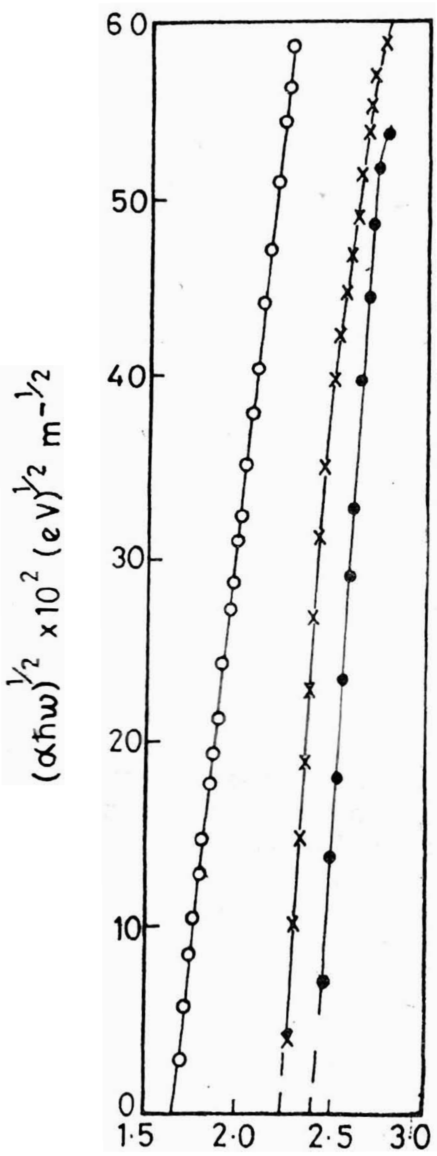

Fig. 4: Plots of $(\alpha h\omega)^{1/2}$ versus hω, showing the indirect bandgap of the CdO films deposited at different partial pressures of oxygen: o – 0.0133 Pa; x – 0.0267 Pa; – 0.040 Pa.

observed. Energy bandgap E_g values deduced from the plots are also shown in table 2. It can be seen that E_g increases with increasing oxygen partial pressure upto 0.040 Pa and decreases thereafter. Direct bandgaps of 2.32 eV (Gurumurugan et al. 1994), 2.40 eV (Chu and Chu 1990), 2.42 eV (Sravani et al. 1991) and 2.50 eV (Lakshmanam 1963) had been reported for films deposited by spray pyrolysis, sputtering and activated reactive evaporation, respectively. A direct bandgap of 1.98 eV has also been reported for spray pyrolysed films (Gurumurugan et al. 1994). Our results are therefore in agreement with the reported values.

The slight differences observed may be attributed to the different deposition techniques employed to prepare the films. It is also pertinent to mention that the partial pressure of oxygen has pronounced effects on the refractive index of the films. The refractive index measured at a wavelength of 700 nm for films deposited at various oxygen partial pressures are recorded in table 2. The refractive index n decreases with increasing PO_2. However, the n value at $PO_2 = 0.040$ Pa agrees with the literature value (Constants and Numerical Data, 1961) indicating that the optimum oxygen partial pressure is 0.040 Pa.

CONCLUSIONS

This work has succeeded in presenting for the first time, the evaluation of optical constants and thickness variation of reactively evaporated CdO thin films in a detailed and comprehensive manner. The refractive index values 1.98 – 3.05 agree remarkably well with the values reported in the literature. The absorption coefficients are higher by about an order of magnitude than those reported for the bulk material. The partial pressure of oxygen (PO_2), during film deposition, was found to have profound effects on the optical transmittance and optical constants, of the films. The optical transmittance increases markedly with increasing PO_2 up to an optimum PO_2 value of 0.040 Pa and decreases thereafter. The refractive index, on the other hand, decreases with increasing PO_2. The tailing of the absorption band edges also decreases with increasing PO_2. The energy gap (E_g) increases with increasing PO_2 and the E_g values deduced are in good agreement with reported values.

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