Cadmium Oxide Thin Films Deposited by a Simplified Spray Pyrolysis Technique for Optoelectronic Applications

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Abstract

Cadmium oxide thin films were fabricated on glass substrates by a simplified and low cost spray pyrolysis technique at different substrate temperatures. The X-ray diffraction study showed that irrespective of substrate temperature all the films exhibits a preferential orientation along the (1 1 1) plane. The values of crystallite size were found to be in the range 20.72 – 29.6 nm. The percentage transmittance and the optical band gap values are found to be in the range of 78 – 89 % and 2.38 – 2.55 eV respectively. The optical transmittance is found to increase gradually with increase in substrate temperature. Urbach energy decreases with increase in substrate temperature. Optical parameters such as refractive index and packing density were calculated. The dispersion parameters of the as-deposited CdO films were calculated to analyze their choice in designing optical devices. PL studies confirm that the films exhibit strong luminescent properties. The value of ρ decreases with increase in substrate temperature and attains a minimum value of 0.26 x 10^{-6} ohm-m for the film coated at 375ºC which has the least thickness.

Key words: *Optical materials, Oxides, X-ray diffraction, Crystal structure, Electrical resistivity, Figure of merit.*

Introduction

Transparent conducting oxides (TCOs) are critical components as transparent electrodes in flat-panel displays, solar cells, gas sensors, and smart windows [1– 3]. Applications of TCOs emerge from their electrical conductivity, which enables their use as current collectors in solar cells and transparent electrodes for charging and discharging of electrochromic smart windows [4]. Amongst these TCOs, CdO films are of great interest due to their metal like charge transport behaviour with an exceptionally large carrier mobility and good optical transparency in the visible and near IR spectral regions [5, 6]. CdO films have n-type semiconducting properties with an electrical resistivity of 10−2

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to 10⁻4ohm-cm and a band gap between 2.2 and 2.7 eV [7]. CdO films show very high electrical conductivity even without doping due to the existence of shallow donors caused by intrinsic interstitial cadmium atoms and oxygen vacancies [8]. Thin films of CdO have been prepared by various physical and chemical deposition techniques such as activated reactive evaporation [9], ion beam sputtering [10], reactive dc magnetron sputtering [11], sol-gel [12], spray pyrolysis [13], chemical vapour deposition [14]. Among the chemical methods, spray pyrolysis technique is suitable for large area deposition of many binary and ternary semiconducting thin films. Film growth can easily be controlled by preparative parameters such as spray rate, substrate temperature, concentration of solution, nozzle frequency, etc [15]. Even though the conventional spray pyrolysis technique is simple, it requires high substrate temperature and compressed carrier gas. Considering these factors, a further simplified spray procedure using perfume atomizer is employed in the present work to deposit CdO films. The use of perfume atomizer has some specific advantages over the conventional spray technique which uses spray gun assembly [16, 17]: low cost, no need for carrier gas, fine atomization, improved wettability between the sprayed micro particles and loss of the precursor to the surroundings is almost nil.

It is well known that the electrical properties of undoped CdO films can be improved by the movement of interstitial cadmium atoms and oxygen vacancies [8]. Lokhande et al. [18] obtained a low resistivity value of 10-4 ohm-m for the CdO films fabricated by spray pyrolysis technique at 400ºC. They observed that the low resistivity value is due to higher growth temperature which results in the increment of oxygen vacancies. Even though, the effect of substrate temperature resulted in desirable effects on the electrical and optical properties of undoped CdO films, no report is evident on very low resistivity value (10-6 ohm-m) for undoped CdO films fabricated by spray pyrolysis technique at growth temperature less than 400ºC. Also the report on the substrate temperature effect on the luminescent properties of spray deposited CdO films is very scarce in the literature. Hence in the present study, the effect of substrate temperature on the physical properties of sprayed CdO films is performed systematically. Moreover, for the first time to the best of our knowledge, a simplified spray technique using perfume atomizer is employed for the fabrication of CdO films.

Experimental

Preparation of CdO Thin Films

Cadmium oxide thin films were fabricated using an aqueous solution (60 ml in volume) of 0.1M cadmium acetate at four different substrate temperatures (225, 275, 325 and 375ºC) on glass substrates with dimensions 76mm x 25mm x 1.4mm cleaned thoroughly

with organic solvents using an ultrasonic agitator. The precursor solution is sprayed intermittently on preheated substrates using perfume atomizer. The intermittent spray procedure employed in this study consists of two steps viz. a spray and a 5 sec interval so that the desired temperature is maintained throughout the deposition process. Aqueous solution of cadmium acetate, when sprayed over the hot substrates, pyrolytic decomposition of the solution takes place and orange colored films of CdO are formed.

Characterization of CdO Thin Films

X-ray diffraction patterns, SEM images, optical transmission and electrical resistivity values of the films were obtained using X-ray diffractometer (PANalytical – PW 340/60 X'pert PRO), Scanning electron microscope (HITACHI S-3000H), PerkinElmer UV-Vis-NIR double beam spectrophotometer (LAMBDA–35), and four point probe apparatus respectively. X-ray diffractometer was operated at 40 kV and 30 mA with CuKα radiation of wavelength 1.54060 Å. Transmission spectra were recorded in the range 300 – 1100 nm. The thicknesses of the films were measured by means of weight gain method.

Results and Discussion

Structural Studies

Figure 1 depicts the X-ray diffraction patterns of CdO films fabricated by the simplified spray technique at various substrate temperatures.
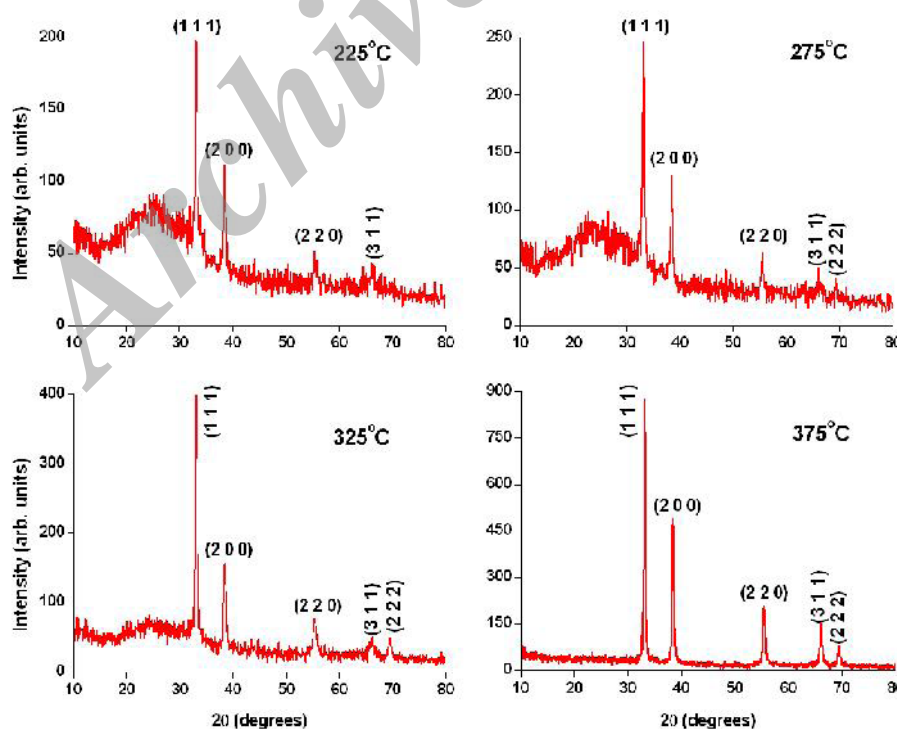

Figure 1. XRD patterns of CdO films fabricated by the simplified spray technique.

The presence of many peaks indicates the polycrystalline structure of the films. X-ray diffraction patterns indicate the presence of (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes for cubic CdO [19]. The crystallites in a polycrystalline material normally have a crystallographic orientation different from that of its neighbours. This orientation of the crystallites, called the preferential orientation, may be randomly distributed with respect to some selected frame of reference. The calculated values of preferential orientation factor f(h k l) of the peaks ((1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2)) presented in Table 1 shows that the value of f(1 1 1) irrespective of the substrate temperature is large compared to that of f(h k l) of other peaks indicating a strong orientational growth along that plane. This result on preferential orientation is well agreed with several earlier reports [13, 20].

Table 1. Calculated preferential orientation factor f(h k l) of the CdO films.

Substrate temperature (ºC)	f(h k l)				
	f(1 1 1)	f(2 0 0)	f(2 2 0)	f(3 1 1)	f(2 2 2)
225	0.525	0.198	0.071	----	----
275	0.571	0.222	0.089	0.026	0.044
325	0.581	0.267	0.113	0.032	0.051
375	0.647	0.330	0.137	0.058	0.036

The variation of f(1 1 1) with substrate temperature is shown in Figure 2. The value of f (1 1 1) increases with substrate temperature indicating an improvement of crystallinity as temperature increases.
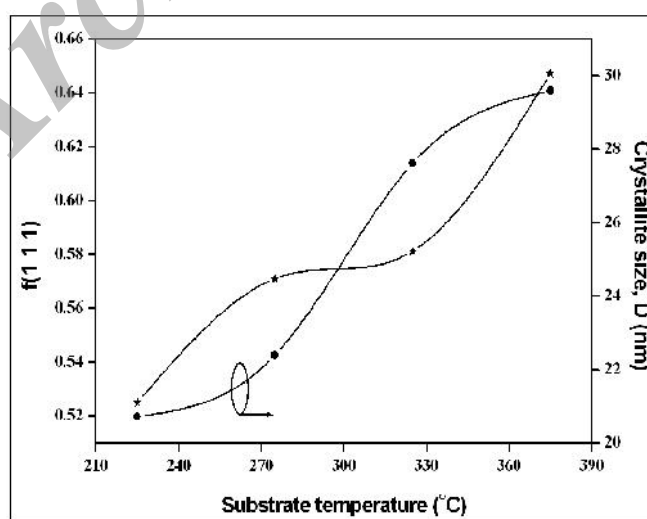

Figure 2. Variation of f(1 1 1) and crystallite size with substrate temperature of CdO films.

Crystallite size of the films was calculated from the (1 1 1) peak at 2θ = 33º using the Debye- Scherrer formula, $D = \dfrac{0.94\lambda}{\beta \cos\theta}$ where, λ is the wavelength of X-rays (CuKα line), β is the full width at half maximum (radians) and θ is the Bragg's angle. The crystallite size of the films lies between 20.72 and 29.6 nm. The variation of crystallite size of the CdO samples deposited at different substrate temperatures is depicted in Figure 2. It is evident from the figure that the crystallite size increases with substrate temperature confirming the fact that crystallization improves as substrate temperature increases; this result agrees with the XRD pattern. At low substrate temperature when the solution droplets containing cadmium acetate reaches the substrate, evaporation of the solvent occurs thereby forming a solid phase which decomposes thermally to form CdO thin films. As substrate temperature increases, the solvent evaporates before the droplets reach the substrate and only solid precursor reaches the substrate where complete decomposition takes place to form better layers of CdO. At 375ºC, evaporation of solvent and subsequent decomposition of solid precursor occurs in the gas phase and only porous, hollow crust of former droplets reaches the substrate, leading to coarser CdO layers [21]. Hence, the films deposited at 375ºC have better crystallinity and larger crystallite size. The above mentioned dependence of crystallite size with increase in substrate temperature is strongly supported by the reported results of Gurumurugan et al. [22].

The lattice constant 'a' of the cubic CdO films is calculated using the following formula:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad (1)$$

The calculated lattice constant values are presented in Table 2. The value of 'a' increases with substrate temperature. The increase of lattice parameter with substrate temperature suggests that the grains were strained in the as-deposited films possibly due to the appreciable concentration of the native imperfections [23]. Such behaviour can be attributed to the change of nature, deposition conditions and the concentration of the native imperfections developed in thin films. This results in the elongation or compression of the lattice and the structural parameters. The density of the film is therefore found to change considerably in accordance with the variations observed with the lattice constant values. The lattice parameter value obtained for the film coated at 375ºC closely matches with the bulk CdO lattice parameter value (4.690 Å) in ASTM data profiles [19]. This indicates that the film coated at 375ºC has less strain. The structural parameters such as strain (ε), dislocation density (δ) and the number of crystallites (N) per unit area were calculated using the relation [24]:

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (2)$$

$$\delta = \frac{1}{D^2} \qquad (3)$$

$$N = \frac{t}{D^3} \qquad (4)$$

The calculated structural parameters for CdO thin films deposited at different substrate temperatures are presented in Table 2.

Table 2. Structural parameters of CdO films fabricated by the simplified spray technique.

Substrate temperature (ºC)	Thickness, t (nm)	Lattice constant, 'a' (Å)	Strain, ε x 10^{-3}	Dislocation density, δ x 10^{15} lines/m^2	Number of crystallites, N x 10^{16}
225	298	4.675	5.862	2.329	3.350
275	157	4.677	5.424	1.993	1.397
325	105	4.679	4.38	1.310	0.498
375	62	4.681	4.11	1.141	0.239

The number of crystallites per unit surface area and the dislocation density are found to be lower for the film coated at 375ºC. As dislocation density is the measure of the defects in crystalline structure, the smaller value of δ obtained for the film coated at 375ºC showed that the film has comparatively better degree of crystallinity due to reduced internal stress. The micro strain variation exhibits a slow decreasing trend with increase in substrate temperature. Singh et al [25] reported that the reduction in the strain and dislocation density of the ZnSe films with substrate temperature may be due to the reduction in the concentration of lattice imperfections. The decreasing trend of strain and dislocation density with substrate temperature obtained here strongly favors the reduction in the concentration of lattice imperfection which

takes place due to the movement of interstitial cadmium atoms from the bulk of the grain to its boundary region which dissipates to larger area and this might be the reason for the low resistivity value obtained for the CdO films coated at 375ºC (Section 3.2).

Electrical Studies

CdO film is an n-type semiconductor which has good electrical conductivity even without any extrinsic doping. The factors that influence the resistivity of chemically sprayed CdO films are i) oxygen vacancies and ii) interstitial incorporation of cadmium [8]. The resistivity of the as deposited CdO thin films was determined by the four point probe method. The variation of film thickness (t), and resistivity (ρ) of the CdO films with substrate temperature is shown in Figure 3.
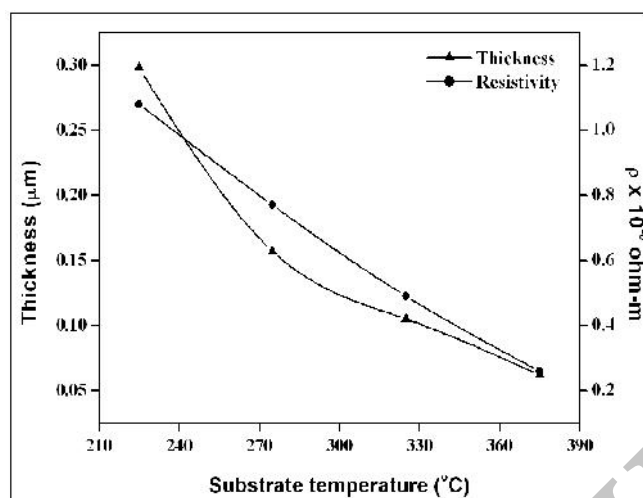
Figure 3. Variation of film thickness and resistivity of CdO films with substrate temperature.

A high resistivity (1.08 x 10^{-6} ohm-m) is observed for the film coated at 225ºC which has the highest thickness. At lower substrate temperature, chemisorption of oxygen takes place on the film surface and in pores which act as an acceptor to accept an electron from the occupied conduction band resulting in high surface resistivity [26]. The value of ρ decreases with increase in substrate temperature and attains a minimum value of 0.26 x 10^{-6} ohm-m for the film coated at 375ºC which has the least thickness. This may be due to the reduced concentration of lattice imperfections which takes place due to the movement of interstitial cadmium atoms from the bulk of the grain to its boundary region. The above discussion is strongly favored by the low value of strain and dislocation

density obtained for the film coated at 375ºC. The very low value of resistivity obtained for all the films in this work exactly matches with the values obtained for the CdO films fabricated by activated reactive evaporation [27] and dc reactive magnetron sputtering [28]. It is important to point out, even when more sophisticated techniques have been used; this value is within the lowest resistivity value range reported in the literature that too obtained at a comparatively lesser substrate temperature.

Surface Morphological Studies
Figure 4 (a–d) shows the SEM images of CdO thin films fabricated by the simplified spray technique at different substrate temperatures.
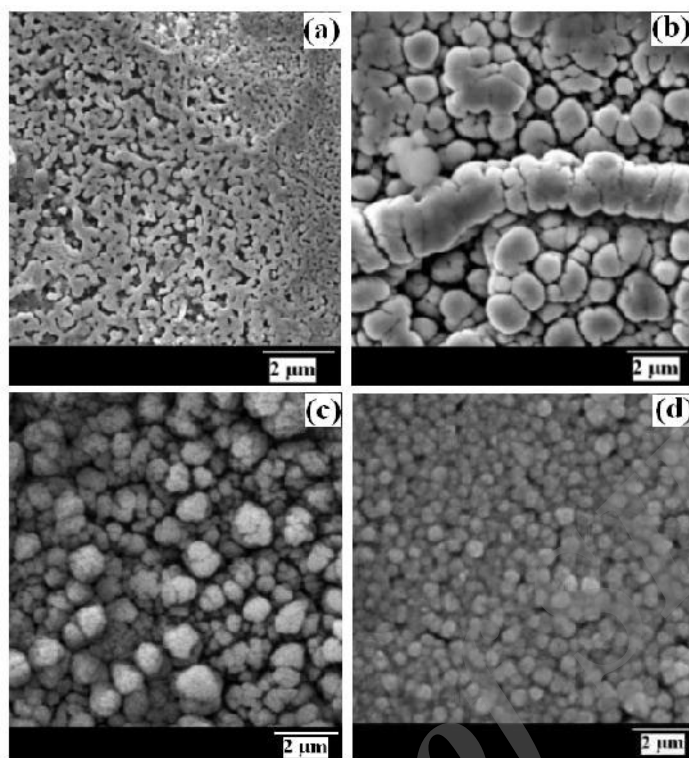
Fig. 4

Figure 4. SEM images of CdO films fabricated at different substrate temperatures.

Film coated at 225ºC (Figure 4(a)) consists of clusters interconnected. As substrate temperature increases, cluster formation is minimized and interconnected spherical grains with porous space in between are observed for the film coated at 275ºC (Figure 4(b)). At 325ºC (Figure 4(c)), no cluster formation is observed and the film surface appears to be uniform with well-defined grain boundaries. Mixture of multi-sized grains was observed throughout the substrate surface with an average grain size equal to 66 nm. For the film coated at 375ºC, equally sized grains with a size of 54 nm were found to be distributed throughout the substrate surface (Figure 4(d)). The grains are tightly packed and consequently the surface of the film looks more continuous without any cracks or holes which is an identification of improved crystallinity as evident from the structural parameter values obtained (Table 2). Thus with increasing substrate temperature, a gradual change in the growth of crystallites from clusters to densely packed nature takes place with reduced gaps between the grains. Poor crystallinity (cluster formation) in the layers grown at low substrate temperatures is probably due to lack of thermal energy for nucleation of deposited atoms and coalescence of grains [29].

Optical Studies

Optical properties of CdO films were studied

by recording the transmittance and absorption spectra in the wavelength range 300 – 1200 nm. Figure 5 shows the variation of absorbance with wavelength of CdO films fabricated by the simplified spray technique at different substrate temperatures.
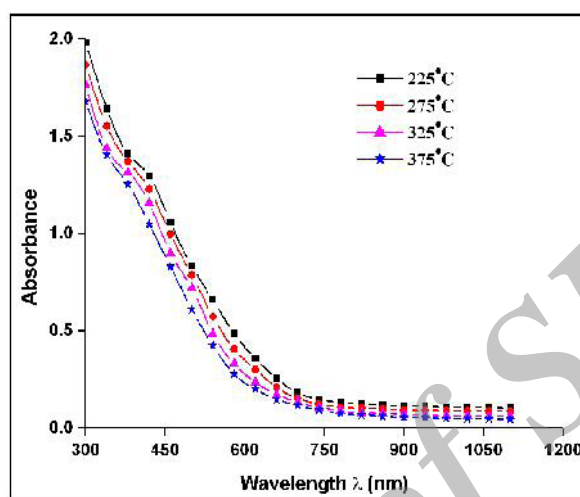

Figure 5. Absorption spectra of CdO films fabricated by the simplified spray technique.

The spectra show two regions, one for higher wavelength showing practically negligible absorption and other for lower wavelength in which absorption increases rapidly for all the samples. The linear rise in the absorption curve below 600 nm confirms the highly crystalline and monophase nature of the deposited films. The optical absorption coefficient (α) can be deduced from the absorption spectra using the relation:

$$\alpha = \frac{2.303A}{t} \qquad (5)$$

where t is the thickness of the as deposited films. The absorption coefficient values calculated from the transmittance data are about $10^4 \, cm^{-1}$ near the absorption edge as well as in the visible region. The optical band gap E_g was determined by analyzing the optical data with the expression for the absorption coefficient (α) and the photon energy (hγ) using Tauc formula for direct band gap semiconductor [30]:

$$(\alpha h\gamma)^2 = A(h\gamma - E_g) \qquad (6)$$

where A is a constant which depends on the transition probability, E_g is the optical gap energy, γ is the frequency of the incident photon and h is the Planck's constant. The energy band gap was estimated from the straight line of the plot $(\alpha h\gamma)^2$ versus photon energy for CdO films shown in Figure 6.
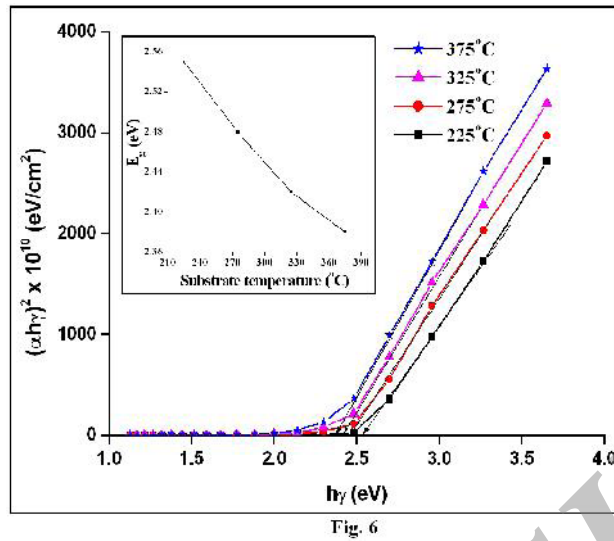
Figure 6. Variation of $(\alpha h\gamma)^2$ vs photon energy and graph of E_g versus substrate temperature for CdO films.

Extrapolation of linear portion of the graph to the energy axis at $\alpha = 0$ gives the band gap energy of the CdO films. The direct band gap values of the films vary between 2.38 and 2.55 eV (inset plot of Figure 6). The band gap value obtained exactly matches with the values reported earlier [31]. It can be found from the inset of Figure 6 that the band gap value decreases with increase in substrate temperature which in turn depends on the increase in crystallite size of the films with increasing substrate temperature (Figure 2). The low value of E_g obtained for the film coated at 375ºC might be due to the removal of defect levels from the film as confirmed from the low value of dislocation density obtained for that film. In the exponential edge region the absorption coefficient $\alpha(h\gamma)$ is well described by the exponential law

$$\alpha = \alpha_0 \exp\left(\frac{h\gamma}{E_u}\right) \quad (7)$$

known as Urbach law [32]. Here α_0 is a constant, $h\gamma$ is the incident photon energy, and E_u is called Urbach energy, which characterizes the slope of the exponential edge region and is width of the band tails of the localized states. The Urbach tail of the absorption edge is usually ascribed to the optical electronic transitions between the excited sates and the near edge localized states. The formation of localized states with energies at the boundaries of the energy gap is one of the effects of the structural disorder on the electronic structure of amorphous materials. This is the reason why the Urbach energy is frequently used as a measure of the degree of structural disorder. E_u is given by the relation:

$$E_u = \left[\frac{d(\ln(\alpha))}{d(h\gamma)}\right]^{-1} \quad (8)$$

The graph of $\ln(\alpha)$ versus $h\gamma$ is given in Figure 7 and the variation of Eu with substrate temperature of the CdO films is shown in the inset of Figure 7.
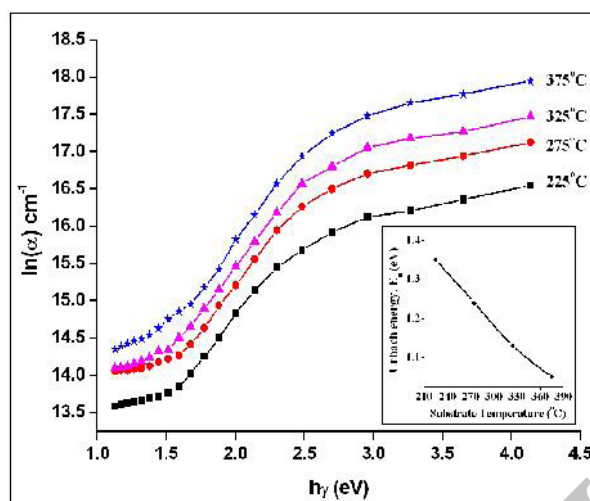
Fig. 7

Figure 7. Variation of ln(α) versus photon energy and graph of E_u versus substrate temperature of CdO films.

It is observed that Urbach energy decreases with increase in substrate temperature. The high value of E_u obtained for the film coated at 225ºC indicates that there is deviation of its bond length and angle from the standard value. As substrate temperature increases, the value of E_u decreases suggesting that there is a reduction in the disorder of the film. The percentage transmittance of the films increases from 78 % to 89 % with increase in substrate temperature (Figure 8). The low transmission at 225ºC is due to non-stoichiometric CdO films probably due to the presence of unreacted metallic cadmium as revealed from the XRD data. As substrate temperature increases, the stoichiometry of the films improves which might be due to the decrease in density of defect centers. As the density of defect centers decreases the light loss by scattering of defect centers decreases which results in the increase of transmission for the films coated at higher temperature. Optical reflectance spectra of CdO thin films are depicted in Fig. 8. The overall specular reflectance for the CdO films is very low. The high transmittance and low reflectance values obtained for the films makes them suitable as antireflecting coating materials for thin films solar cells.
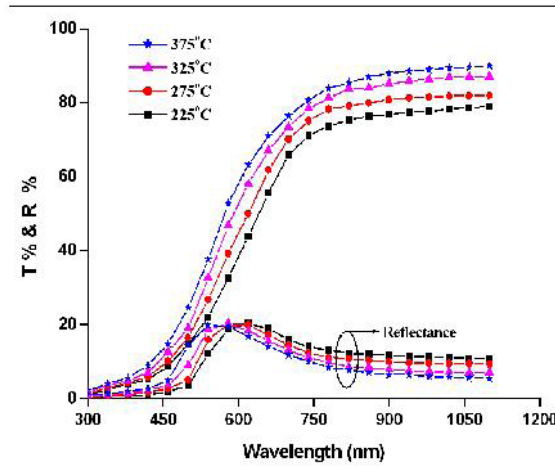
Fig. 8

Figure 8. Reflectance spectra of CdO films fabricated by the simplified spray technique.

Refractive index is one of the fundamental properties for an optical material because it is closely related to the electronic polarization of the ions and the local field inside materials. The complex optical constant (refractive index, (n)) of the as-deposited samples has been calculated using the relation [33]:

$$n = \frac{1+R}{1-R} \pm \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (9)$$

where $k = \frac{\alpha\lambda}{4\pi}$ is the extinction coefficient. From the refractive index data, the packing density which is defined as the ratio of the solid volume to the total volume of the film is estimated using the relation [34]:

$$n = n_s p + (1 - p) n_v \quad (10)$$

where n is the refractive index of the film, ns is the refractive index of the bulk material and n_v is the refractive index of voids, which are generally filled with ambient, i.e. air.

The variation of the refractive index (n) and packing density (p) as a function of the substrate temperature is shown in Figure 9.
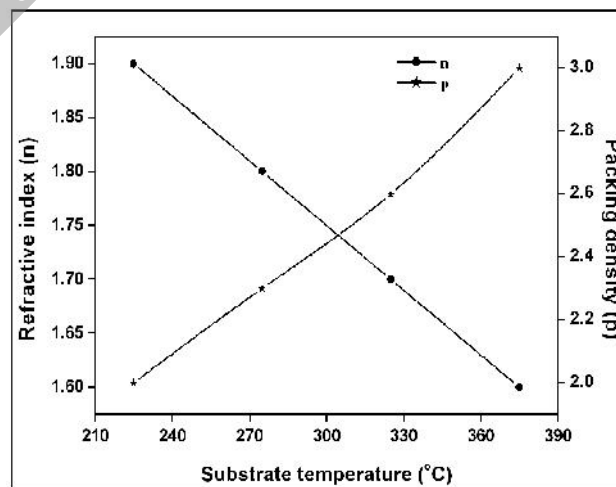

Fig. 9

Figure 9. Refractive index and packing density variation with substrate temperature for CdO films.

The obtained value of n exactly matches with the results obtained earlier [35]. It is observed from Figure 9, that the refractive index value decreases with increase in substrate temperature. The high value of n obtained for the film coated at 225ºC can be attributed to an increase of its surface roughness which acts to decrease the effective mean free path through increased surface scattering [36] and this fact strongly favours the reason for the reduction of its transparency. Packing density increases with increase in substrate temperature. The high value of packing density obtained for the film coated at 375ºC indicates good crystallinity of the film.

Refractive index dispersion plays an important role particularly in designing optical devices. The dispersion parameters of the as-deposited CdO films were calculated to analyze their choice in designing optical devices. According to the Wemple-DiDomenico single oscillator model, the refractive index (n) of a dielectric medium in the region of low absorption is given by [37]:

$$\left(n^2 - 1\right)^{-1} = \frac{E_o}{E_d} - \frac{1}{E_o E_d}\left(h\gamma\right)^2 \quad (11)$$

where n is the refractive index, h is the Planck's constant, γ is the frequency, $h\gamma$ is the photon energy, E_o is the average excitation energy for electronic transitions (single oscillator energy) and E_d is the dispersion energy parameter, which is a measure of the strength of an interband optical transition. From the $(n2-1)^{-1}$ versus $(h\gamma)^2$ graph (Figure 10), Ed and Eo can be directly determined from the slope $(E_d E_o)^{-1}$ and intercept E_o/E_d at the vertical axis.
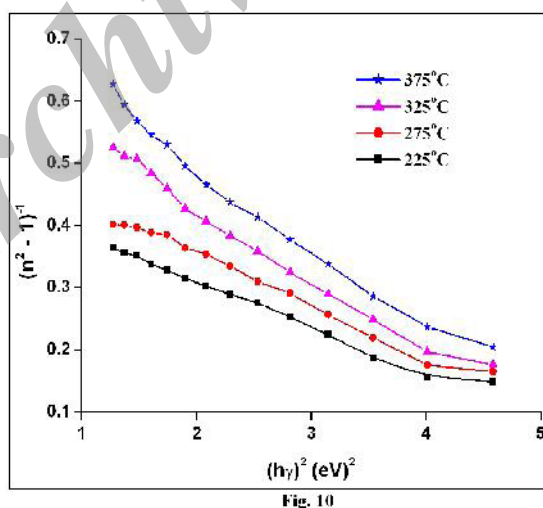

Figure 10. $(n^2-1)^{-1}$ vs $(h\gamma)^2$ graph of CdO films.

The obtained values of E_o and E_d are presented in Table 3. The values of E_o and Ed decreases with increase in substrate temperature. The high value of E_o and E_d obtained for the film coated at 225ºC can be attributed to an increase in the number of scattering centers

which results in the decreased effective mean free path for charge carriers and this is the

reason for the high absorbance value obtained for that film.

Table 3. Dispersion parameters of CdO films prepared at different substrate temperatures.

Substrate temperature (°C)	E_d (eV)	E_o (eV)	E_g (eV)	E_o / E_g
225	8.8112	3.3923	2.55	1.33
275	5.501	2.530	2.48	1.02
325	4.7150	2.428	2.42	1.0
375	4.0424	2.405	2.38	1.01

The obtained values of E_o and E_d suggest that the single-oscillator model is valid for the coated CdO films and they can be used in optical device applications. For efficient use of TCOs in solar cells and other optoelectronic applications, both electrical conductivity and optical transmittance should be as high as possible. The films fabricated in this work satisfy both criteria and hence they are desirable for solar cell and other optoelectronic applications.

Photoluminescence Studies

Photoluminescence (PL) spectroscopy in the band edge emission region is one of the versatile techniques to study the lattice defects in thin film samples. When samples are excited by radiation, characteristic broad luminescence bands are observed with peaks corresponding to the F and V centers. PL spectra of CdO thin films fabricated by the simplified spray technique at different substrate temperatures under excitation wavelength of 350 nm are shown in Figure 11.
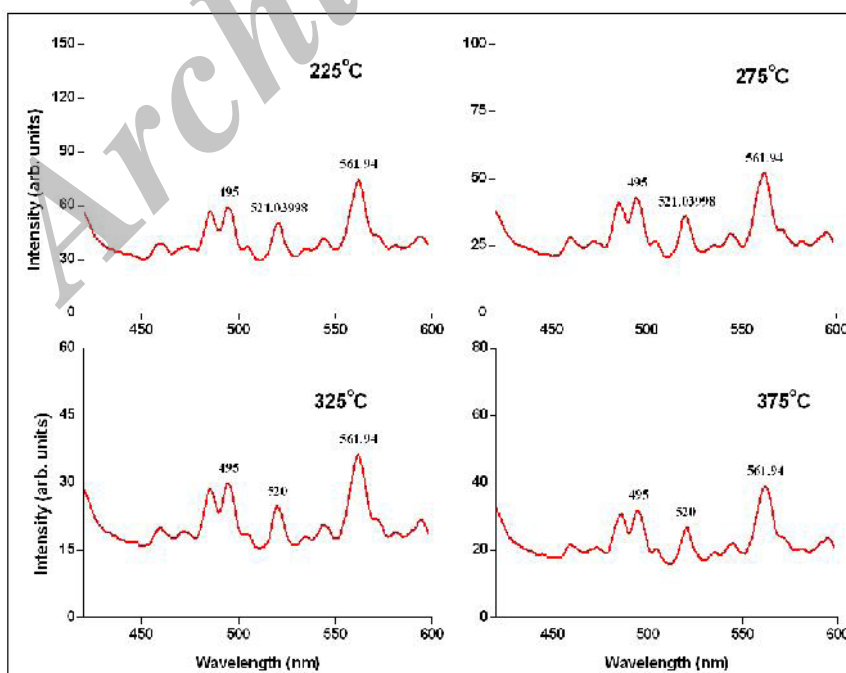

Fig. 11

Figure 11. PL spectra of CdO films fabricated by the simplified spray technique at different substrate temperatures.

Clearly it could be seen that there are emission peaks at about 495 nm (blue), 521 nm (green) and 561 nm (green) for all the samples. The peak located at 495 nm (2.51 eV) may be attributed to the excitonic transitions which are size-dependent and the peak at 521 nm (2.38 eV) can be ascribed to the deep trap emission and surface-state emission that is less size dependent [38]. The peak at 521 nm may be assigned to the self-activated (SA) luminescence band whose positions is in good agreement with SA – centre $[V_{zn}^{-} + D^{+}]^{o}$ energy [39]. This peak confirms the quantum confinement effect of the as-deposited samples which is ascribed to the near-band-edge (NBE) emission of CdO [40]. The peak at 561 nm (2.21 eV) arises from the oxygen vacancies of CdO films because of recombination of photo generated holes in the valence band with electrons in the conduction band [41]. The peaks observed at 521 and 561 nm shows that the CdO films fabricated using this simplified spray technique have strong PL in the blue region. The small width peaks at about 460, 485 and 540 nm could not be assigned to any emission process but may be regarded as noise [42]. These PL observations confirm that CdO films deposited here can be used for developing luminescent devices.

Conclusion

CdO thin films were grown by simplified spray technique on glass substrates at different substrate temperatures. The effect of substrate temperature on the crystal structure, morphology, optical band gap and electrical resistivity of the as-deposited films has been investigated. XRD pattern suggested that the films were polycrystalline in nature with cubic crystal structure. It was observed that the crystalline nature improves with increase in substrate temperature. The high transmittance and low reflectance values obtained for the films makes them suitable as antireflecting coating materials for thin film solar cells. Electrical resistivity was found to be in the range $1.08 \times 10^{-6} – 0.26 \times 10^{-6}$ ohm-m. The films were found to have good physical properties desirable for solar cell and other optoelectronic applications. PL studies confirm that the films fabricated by this simplified spray technique exhibits strong photoluminescence in the blue region.

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