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STRUCTURAL AND OPTICAL PROPERTIES OF CdO THIN FILMS PREPARED BY CHEMICAL METHOD

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Abstract: *CdO thin films of different thicknesses were prepared by a simple chemical technique called Successive Ionic Layer Adsorption & Reaction (SILAR) technique onto well cleaned substrates and the thicknesses of the deposited films were determined by gravimetric technique. Uniform and adherent CdO thin films are prepared and annealed at different temperatures of 100℃, 200℃ and 300℃ respectively. The films are investigated with X-ray diffraction, EDAX and optical spectroscopy. The structural characterization was carried out by X-ray diffraction which confirms the polycrystalline nature of the films with a cubic structure. EDAX analysis conforms the presence of the constituents Cd and O and the weight percentage is presented . From the transmittance spectra the type of transition, band gaps of the films, refractive index of the films were estimated. From the results of the structural and optical analysis, CdO has been identified as an alternate window /n-type conductor for fabricating solar cells.*

Keywords: *CdO, TCO, SILAR, XRD, EDAX, BANDGAP*

1. Introduction

Transparent conductive oxide (TCO) films have been extensively studied because of their use in semiconductor device technology [1–3]. Particularly, II–VI compound semi- conductor 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[4]. These oxide materials have attracted significant attention due to their potential applications in optoelectronics, ultraviolet light emitting devices, laserdiodes, solarcells and optical communications [5,6]. However, among these compounds, cadmiumoxide (CdO) films received less attention mainly due to their narrow band gap energies compared to other wide band gap oxides [7–9]. 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 [10]. CdO films can be synthesized by various methods such as Spray Pyrolysis[11], Sputtering[12], Sol-gel spin coating[13],Activated reactive evaporation[14], Metal Organic Chemical Vapour deposition (MOCVD)[15], Pulsed laser deposition[16-18]. The main goal of the work is to seek a simple, non-vaccum and economic deposition technique for efficient transparent films. In this study CdO thin films were prepared using simple Chemical Method Successive Ionic Layer Adsorption and Reaction (SILAR) technique, because this method has received immense advantages such as low cost, high growth rate at low temperature and control shape and size of thin films. CdO thin films have prepared at fixed deposition parameters such as concentration, pH value and temperature and annealed at different temperatures. Further, the structural and composition characteristic of annealed CdO thin films are discussed in detail. Optical studies such as transmission, bandgap, refractive index, absorption co-efficient, extinction coefficient, dielectric constant (imaginary and real) were evaluated.

2. Experimental Methods

Cadmium Oxide (CdO) thin films were deposited onto clean glass substrates using the Successive Ionic Layer Adsorption & Reaction (SILAR) 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 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. In SILAR technique, the depositions of CdO thin films were carried out from solutions containing Cadmium nitrate as cationic precursor (3.08gm) and H_2O_2 (40ml) as anionic precursor. The deposition was carried out at a temperature of 70°C. The deposition cycle was varied from 30 to 100 cycles to obtain films of different thicknesses. It has been found that uniform films can be prepared if the deposition cycle range is 30–60 cycles. While varying the pH of the bath, it is found that the solution having pH value 12 gives uniform films. The deposition process is as follows:

1. Well-cleaned substrates was immersed into the cationic precursor for 20 s and then rinsed with deionized water for 30 s to remove unattached ions.

2. Then the substrates were immersed into anionic precursor solution for 18 s and then rinsed with deionized water for 30 s to remove unattached ions.

3. The above cycle was repeated and the optimized dippings were 40 dipping times to get enough film thickness.

Thus, deposition parameters such as temperature, concentration of ions in the bath and dipping cycle have been optimized and then the films were taken out and dried naturally. The thicknesses of the prepared films determined by the gravimetric technique and CdO thin films were annealed at 100°C , 200°C, 300°C for one hour and then used for the analysis. Structural characterization of these films was carried out by using Shimadzhu (Lab X-6000) x-ray diffractometer with Cu Kα (λ = 1.5406 Å) line in 2θ range from 20 to 80 degrees. A JASCO (V570: UV-vis-NIR) double beam spectrophotometer was used for optical studies in the wavelength range 400–2500 nm. Energy dispersive x-ray analysis (Thermo SuperDry II) is used to carry out semi - quantitative elemental analysis of the annealed thin film samples.

3. Results and discussion

3.1 Compositional Analysis

Fig. 1 shows the EDAX spectra of representative CdO thin film prepared by SILAR technique and the spectrum shows the presence of the chemical constituents (Cd and O) of CdO thin films. EDAX quantitative results confirm the atomic percentage of constituents in the prepared films [Table 1].

3.2 XRD analysis of CdO thin films

Fig 2 shows the x ray diffractograms of CdO thin films prepared at 70°C containing cadmium nitrate, H_2O_2 and deionized water in same molar concentrations. Uniform and adherent CdO thin films are prepared and annealed at different temperatures of 100°C, 200°C and 300°C respectively and then used for structural analysis.

From the XRD profiles, the interplanar spacing d_{hkl} was calculated using the Bragg's relation, [19]

$$d = \frac{n\lambda}{2\sin\theta} \qquad \text{………. (1)}$$

The crystallite size (D) was calculated using the formula from the full width at half maximum (FWHM) [19].

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad \text{………. (2)}$$

where the constant K is the shape factor ≈ 0.98, 'λ' is the wavelength of the x-rays (1.5406Å for Cu K_α), 'θ' is the Bragg's angle and 'β' is the FWHM.

The dislocation density (δ) can be evaluated from the crystallite size (D) by the following relation.

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

The origin of the microstrain is related to the lattice misfit, which in turn depends upon the deposition conditions. The micro strain (ε) can be calculated from the following relation.

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

From (hkl) planes, the lattice constant can be evaluated using the relation

$$\frac{1}{d^2} = \frac{4}{3}\left\{\frac{h^2 + hk + k^2}{a^2}\right\} + \frac{l^2}{c^2} \qquad \text{---------------- (5)}$$

All the films shows polycrystalline nature containing cubic structure of pure CdO phase. The lattice spacing 'd' has been determined and it has been found that it is in well agreement with ASTM DATA (75-0594), earlier researchers [20] and are presented in Table 2. The predominant peaks (111) and (200) and weak intense peak at (220) plane were observed, when annealing temperature increases from 100°C to 200°C, 300°C, but for 100°C sample only the predominant peak (111) with less intense is observed. This may be due to the less concentration of the constituents. The crystallite size also increases from 5.49nm to 5.79 nm for the sample annealed from 100 to 300°C. The intensity of the diffraction peak were also found to increase with increase in annealing temperature and get sharper with decreasing full width half maximum(FWHM). This can be attributed to the improvement in crystallinity of CdO thin films. The structural parameters of CdO thin films are given in table 2.

Lattice constant (a) is found to be 0.461nm, 0.462 nm and 0.464 nm for the films annealed at 100°C, 200°C and 300°C, respectively. However a shift in lattice constant towards its standard value (0.4695 nm) is observed when the films annealed from 100°C to 300°C. From Table 2, it is evident that the post annealing process improves the quality of the crystalline thin films.

The individual crystalline size (D_C) in the films of different thicknesses have been estimated equation [2] are in the range of 520 – 650 nm and in very good agreement with the reported values [21-23]. Using the size of the crystallites, the dislocation density, the number of crystallites per units surface area, volume and strain have been determined equation [2-5] and presented in Table 2. From the table 3 it is observed that both dislocation density and strain decrease with increasing annealing temperature. This can be attributed to the improvement in crystallinity due to the regular arrangements of atoms in the crystal lattice [24].

Linear increase in texture coefficient is observed for all thin films with increase in annealing temperature. For a preferential orientation, the texture coefficient should be greater than unity [25]. It observed that the texture coefficient for (111) plane is greater than unity and increases with increase in annealing temperature.

3.3 Optical analysis of CdO thin films

Absorption coefficient was calculated using the transmittance (T) value measured for a particular wavelength and the film thickness (t) using the relation,

$$\alpha = \frac{-\ln(T)}{t} \quad \text{.................. (6)}$$

The absorption index or the extinction coefficient (k), which is the attenuation per unit radian, may be written as

$$k = \frac{\alpha\lambda}{4\pi} \quad \text{.................. (7)}$$

where λ is the wavelength of the monochromatic light.

The optical transmittance spectra of CdO thin films of different annealing temperatures are shown in Fig 3. All the films show transmittance above 80% in the IR region. The film annealed at 300°C exhibited maximum transmittance and minimum transmittance for 100°C. The absorption edge is found to shift towards longer wavelength as a function of annealing temperature [26].

Important optical parameters such as type of transition, band gap etc. can be satisfactory analyzed on the basis of formulae derived for 3D and 2D models [27]. By 3D crystal model, nature of transition in film composition can be obtained by plotting $(\alpha h\nu)^{1/2}$ versus (hν) for various values of r [α is the absorption coefficient, hν is the photon energy and exponent r determines the type of transition and dimensionality of the bands]. ν has values ½ (direct allowed), 3/2 (indirect allowed), 2 (direct forbidden). Extrapolation of straight-line portion of $(\alpha h\nu)^{1/2}$ versus (hν) plot at (hν > Eg; Eg = direct band gap) to zero absorption (hν-axis) gave the value of energy gap.

Plot of $(\propto h\nu)^2$ versus (hν) (Figure 4) for all CdO thin films were plotted and the straight line portion is extrapolated to cut the x axis which gives the band gap. The estimated band gaps are found to be 2.2eV, 2.06eV and 1.86eV for the films annealed at 100°C, 200°C and 300°C respectively (Table 4). It was observed that the band gap decreases with increase in the annealing temperatures and in agreement with the earlier researchers [28-29]. The decrease in optical band gap energy with increasing annealing temperature may be due to the increase in the carrier concentration and also may be due to its quantum confinement effect since the crystallite size is found to be very small [30].

Plot of (hν) versus $(\propto h\nu)^{1/2}$, $(\propto h\nu)^{1/3}$ and $(\propto h\nu)^{2/3}$ reveals that CdO films did not have line above hν>Eg. Since extrapolation of it did not touch the zero absorption axis which confirms the fact that CdO phase do not have indirect allowed, direct forbidden and indirect forbidden transitions.

The optical parameters such as absorption coefficient, extinction coefficient, reflectance, refractive index, band gap and dielectric constant are estimated and are presented in Table 4.

Refractive index of CdO thin films has been calculated using the relation [31],

$$n = 1+R/1-R \qquad \ldots\ldots\ldots\ldots\ldots (8)$$

Fig 5 shows the wavelength dependence on refractive index at different annealing temperatures. Refractive index of the CdO films increased from 1 to 2.2 with increase in temperature from 100 to 300℃ in the wave length region of 300 to 600 nm. Thereafter, refractive index of the CdO films annealed at 100 and 200℃ has a constant refractive value in the wavelength region of 600 to 1200 nm, but the refractive index of the film annealed at 300℃ decreases in the same wavelength region. This unusual increase and decrease in the refractive index as a function of wavelength may be due to the damping of CdO thin films [28] [Table 4].

Reflectance of CdO thin films has been calculated using the relation [31],

$$R=1-(A+T) \qquad \ldots\ldots\ldots\ldots\ldots (9)$$

Fig 6 shows the wavelength dependence on percentage of reflectance at different annealing temperatures. Film annealed at 300℃ shows the reflectance of the film increases as wavelength increases with highest reflectance upto 900 nm. The higher reflectance exhibited by this material makes it useful in the manufacture of highly reflectance mirrors commonly found in desktop scanners, photocopy machines, car head lamps and halogen lamps [32]. But the films annealed at 100 and 200℃ shows the minimum reflectance in the same wavelength region [Table 4].

4. Conclusion

CdO Thin Films are prepared by Successive Ionic Layer Adsorption and Reaction method. Thickness of the prepared films are calculated by Gravimetric Method. Structure of the prepared films has been analyzed by XRD. It reveals that the prepared films are polycrystalline in nature with cubic structure. The characteristics peaks are identified and the structure parameters are calculated and presented. EDAX analysis conforms the presence of the constituents Cd and O and the wavelength percentage is presented. The type of transition and band gap has been estimated from optical analysis. The band gap is found to be in the range 2.2 to 1.8 eV respectively. Then optical parameters such as absorption coefficient, extinction coefficient, reflectance, refractive index are calculated and presented.

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Table 1 Elemental composition of CdO thin films

Annealing Temperature : 100°C and Film Thickness : 530 nm	
Element	Atomic %
O K Cd L	32.06 67.10

Table 2 XRD data of CdO thin films

Annealing Temperature (°C)	**Film thickness (nm)**	**hkl plane**	**2θ (Degree) Observed**	**d spacing (Å) Observed**
100	530	111	33.45	2.67
200	620	111 200 220	33.48 48.52 57.39	2.65 2.25 1.69
300	650	111 200 220	33.64 48.17 57.74	2.68 2.41 1.59

Table 3 Structural parameters of CdO thin films

Annealing temperature (°C)	**Film thickness (nm)**	**Lattice constant** a (nm) Observed	**Lattice constant** a (nm) ASTM	**Volume** **(Å)^3**	**Crystalline size D(nm)**	**Dislocation density**(δ) **(10^{15}/lines/m^2)**	**Number of crystallite per unit area (10^{15} m^{-2})**	**Strain**(ε) **(10^{-3})**	**Textured Coefficient**
100	530	0.461		0.097	5.495	67.251	4.41	6.725	0.539
200	610	0.462	0.465	0.098	5.606	31.819	3.03	6.387	0.587
300	650	0.464		0.099	5.797	29.757	1.16	5.385	2.78

Table 4 Optical parameters of CdO thin films prepared and annealed at different temperatures

Annealing Temperature °C	**Film Thickness (nm)**	**α (10^6 m^{-1}) [λ = 1000 nm]**	**Reflectance R**	**Refractive index n λ=1000 nm**	**K [λ=1000 nm]**	**Eg (eV)**
100	530	1.31	1.053	1.186	0.817	2.38
200	610	1.17	1.403	1.485	0.0923	2.12
300	650	1.02	1.784	1.505	0.0923	2

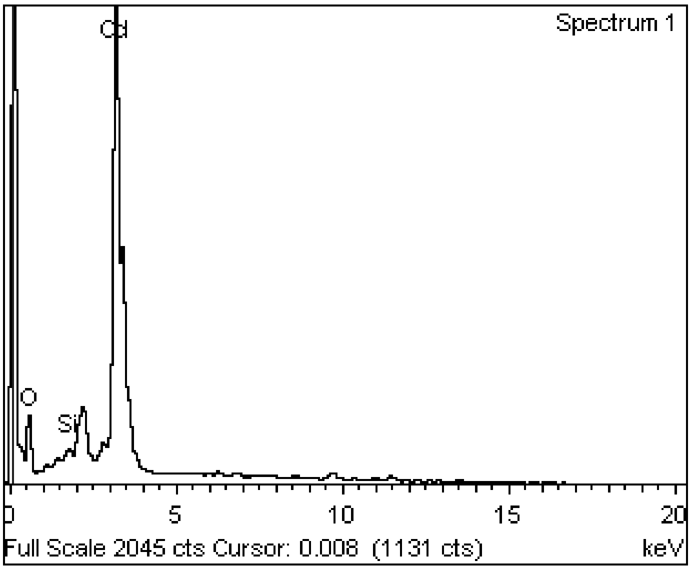
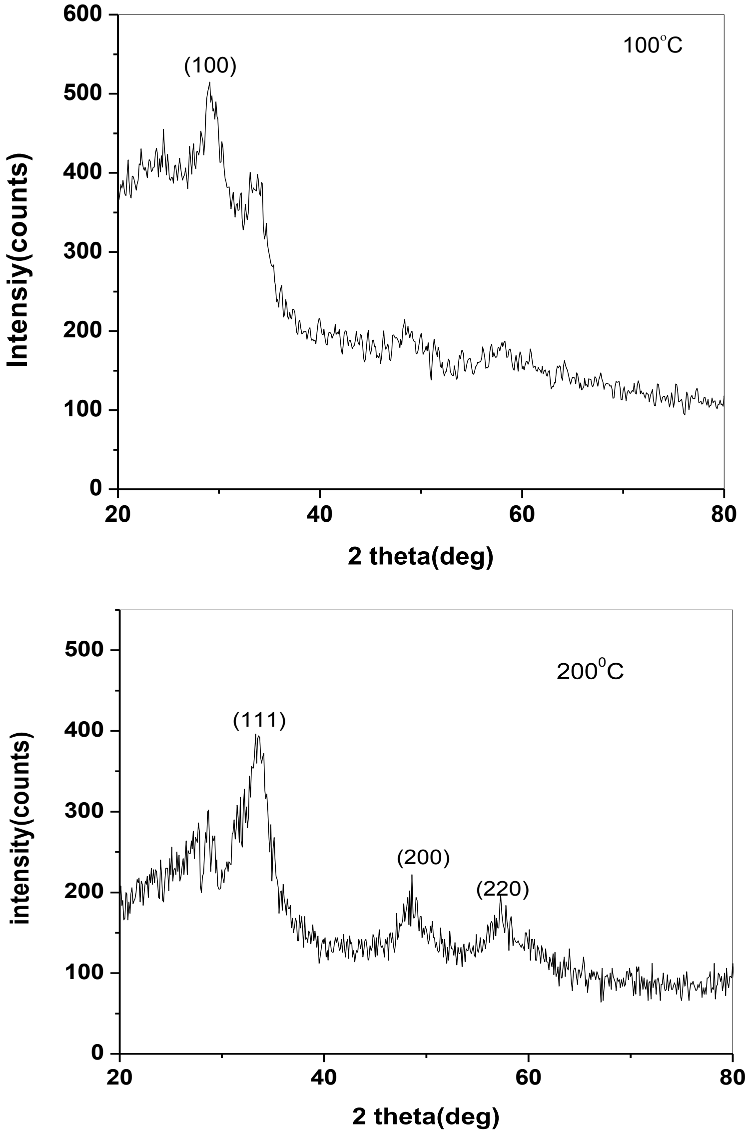


Fig.1 Representative EDAX spectra of CdO thin film.



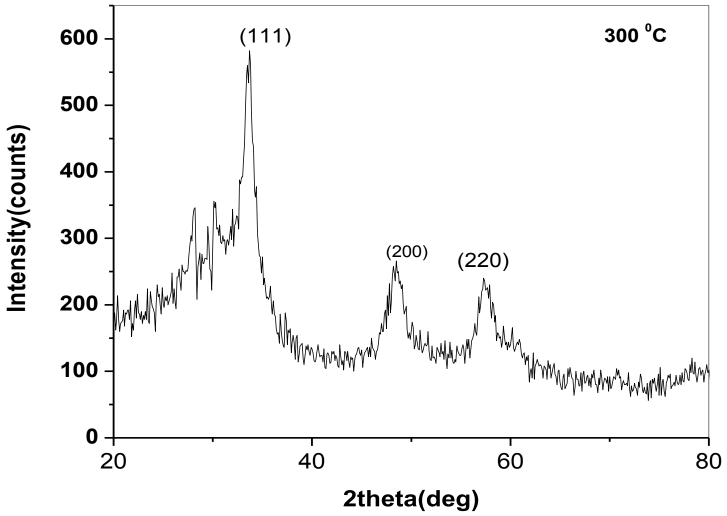


Fig 2. X-ray diffractograms of CdO thin films.

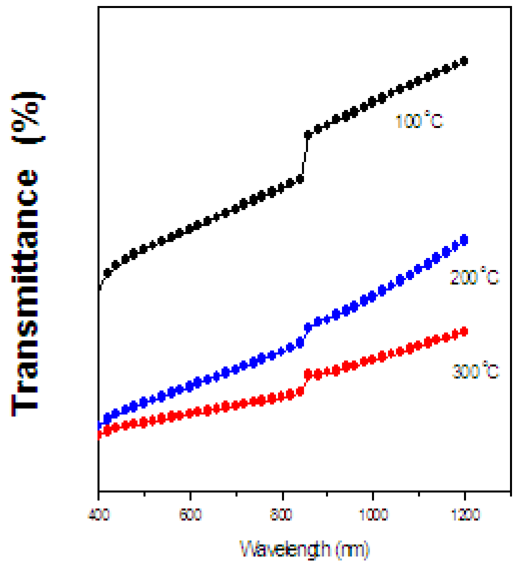


Fig. 3 Transmittance spectra of CdO thin films prepared and annealed at different temperatures.

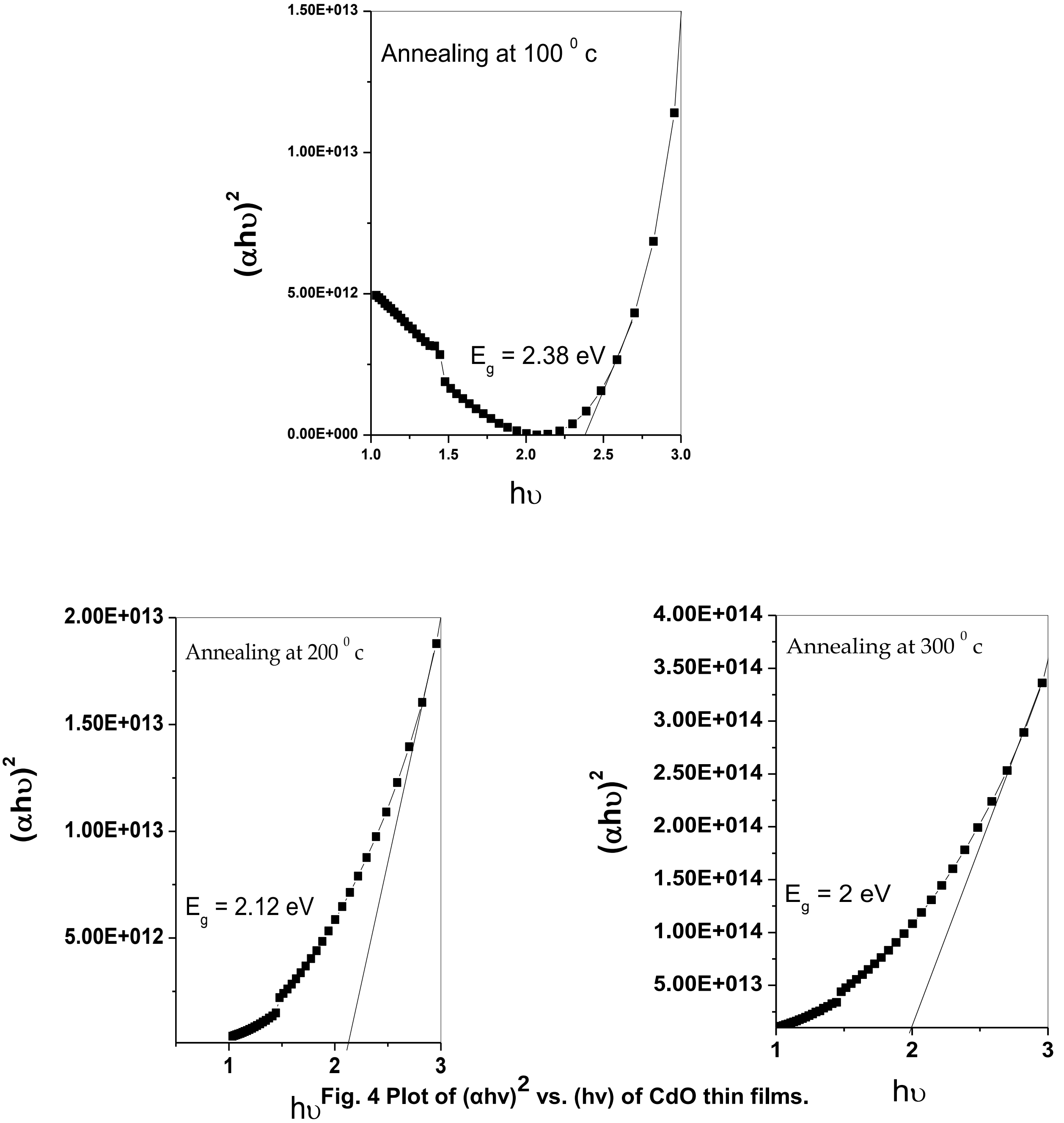


Fig. 4 Plot of $(\alpha hv)^2$ vs. (hv) of CdO thin films.

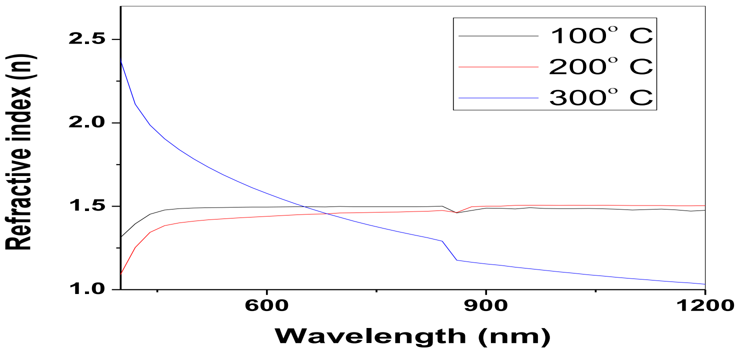


Fig. 5 Plot of Wavelength vs Refractive index of CdO thin films.

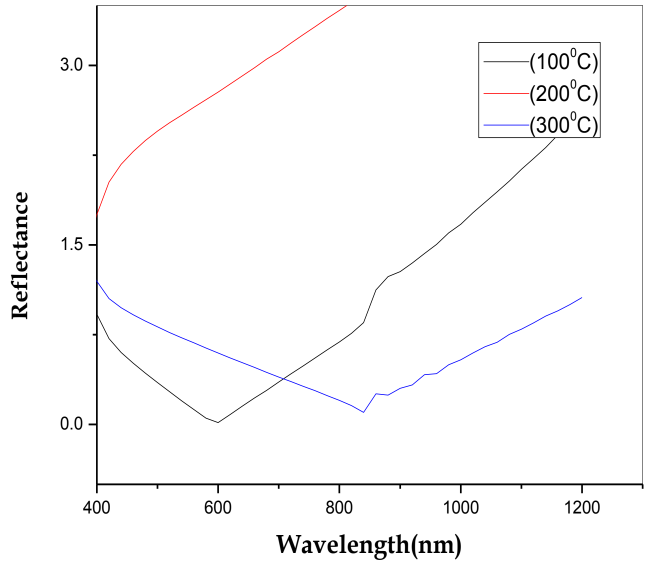


Fig. 6 Plot of Wavelength vs Reflectance of CdO thin films.