ISSN 1330–0008
CODEN FIZAE4

STRUCTURAL CHARACTERIZATION AND OPTICAL PROPERTIES OF ANNEALED $CdIn_2Se_4$ THIN FILMS

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Received 24 April 2004; Accepted 20 December 2004
Online 2 February 2005

$CdIn_2Se_4$ chalcogenides thin films were prepared by thermal evaporation process. The effect of thermal annealing in vacuum on the growth characteristics of the deposited films was studied using X-ray and transmission electron microscopy techniques. It was observed that the as deposited films (300 K) were poorly crystalline. The degree of crystallinity increases with increasing the annealing temperature from 300 to 500 K. The compositional elemental analysis of $CdIn_2Se_4$ thin films annealed at 500 K was found to be nearly stoichiometric, however, films annealed in vacuum at 575 K partially dissociated into two binary phases with $CdIn_2Se_4$ as the major phase. The effect of the annealing temperature on the dispersion of the refractive index of the deposited films was investigated and analyzed within the single effective-oscillator approach. Changes of the dispersion parameters were also investigated as a function of the annealing temperature. Analysis of the optical absorption data revealed the existence of allowed direct and indirect optical transitions, and both values of energy gaps decrease with increasing annealing temperature.

PACS numbers: 68.55.-a, 68.60.Dv, 68.90.+g UDC 538.975

Keywords: $CdIn_2Se_4$, thin film, X-ray analysis, TEM, annealing, refractive index, optical absorption

1. *Introduction*

Recently, compounds with the composition II III_2 IV_4 (II= Zn, Cd, Hg; III=In, Ga; IV= S, Se, Te) have been extensively studied, because of their transmission in far infrared, their photoconductivity and their nonlinear optical properties [1−3].

These compounds crystallize with defect chalcopyrite structure, which are derived from that of chalcopyrite by replacing half of A-site cations by vacancies.

Polycrystalline $CdIn_2Se_4$ was first synthesized by Hahn [4] from its binary compounds, CdSe and In_2Se_3, in equivalent amounts and the results of the X-ray analysis indicated that the compound has a tetragonal pseudocubic structure (α modification), with the space group D^1_{2d}–$P\bar{4}2m$. X-ray diffraction studies of $CdIn_2Se_4$ single crystals prepared by chemical transport reaction techniques using iodine as a transport agent [5] revealed two modifications with ordered structure (cubic structure with $a = 0.5815$ nm, α modification) and one with one-dimensional disordering (tetragonal structure with $a = 0.581$ nm and $c = 1.163$ nm, β modification). The optical properties of single crystals of the α and β modifications were studied in the fundamental absorption region using polarized light [6]. The width of the forbidden band gap of β modification exceeds that of the α modification (1.82 eV) by about 0.15 eV. Few reports have been devoted to $CdIn_2Se_4$ thin films prepared by electrodeposition and spray pyrolysis techniques [7, 8]. However, to our knowledge, no extensive work has been published on the effect of annealing temperature on the structural and optical properties of $CdIn_2Se_4$ thin films.

Information about the effect of annealing temperatures on the spectral dependence of optical parameters such as dielectric constants, refractive index and absorption are essential in the characterization of materials that are used in fabrication of opto-electronic devices and also for optimization of the efficiency of the thin-film solar cells.

The aim of the present work is to study the effect of annealing temperatures on the structural and optical properties of $CdIn_2Se_4$ thin films.

2. *Experimental procedure*

$CdIn_2Se_4$ ingot material was prepared by direct fusion of stoichiometric proportions of the constituent elements (99.999 pure) in a vacuum-sealed silica tube (10^{-3} Pa). The tube was heated in a temperature-controlled furnace at 525 K until the Se vapour disappeared; then the tube temperature was raised in successive stages reaching 1300 K, and at this temperature for 2 h with continuous vibrational shaking to ensure homogeneity of the prepared ingot sample. The tube temperature was then lowered slowly and gradually to 773 K and kept at this temperature for 12 h. Finally, the tube temperature was gradually lowered to room temperature.

Thin film samples were prepared from the ingot material by the thermal evaporation technique, using a coating unit (Edwards E 306) and molybdenum boats, with a deposition rate 5 $\mathrm{nm\,s^{-1}}$ on clean glass substrates at 303 K and under vacuum pressure of 1.5×10^{-3} Pa. Quartz crystal thickness monitor was used to control film thickness. The deposited films were annealed in vacuum for 45 min at the annealing temperature in the range 348–573 K.

The structural characteristics of the prepared ingot material and of the deposited films were investigated by means of an X-ray diffractometer (Philips PW 1370, operating at 40 kV) with Ni-filtered CuK_α radiation. The microstructure of the deposited films was studied using a transmission electron microscope (Type EM 10, Zeiss) operating at 60 kV with a stated resolving power 0.4 nm. The identification of the observed phases could be achieved using the attached electron diffraction stage. For this purpose, the thinner deposited films (thickness 115 nm) were floated off the substrate using diluted hydrofluoric acid and placed onto copper grids covered with an evaporated thin carbon film. The chemical composition of the deposited films were investigated using an EDX unit attached to a scanning electron microscope (type Joel, JSM–T 200, Japan) operating at 25 kV.

A double-beam spectrophotometer, with automatic computer data acquisition (type JASCO Corp, V-570 Rerll-00, UV-V-NIR), with photometeric accuracy of ±0.002–0.004 for absorbance and ±0.3 % for transmittance, was employed with normal light incidence to record the optical transmission and reflection spectra of the deposited films over the wavelength range 600 − 2500 nm. Uncoated clean glass substrate, identical to the coated one, was used as a reference to record the absolute transmission of the deposited films. On the other hand, the measurements were performed on various parts of the deposited films, scanning entire sample and a very good reproduction of spectra was generally achieved.

3. *Results and discussion*

3.1. *Structural characterization*

Figure 1 shows an X-ray diffraction pattern of the prepared $CdIn_2Se_4$ in powder form. Analysis of the recorded pattern shows the polycrystalline nature of the tetragonal structure with lattice parameters $\underline{a} = 0.579$ nm and $\underline{c} = 1.161$ nm. The

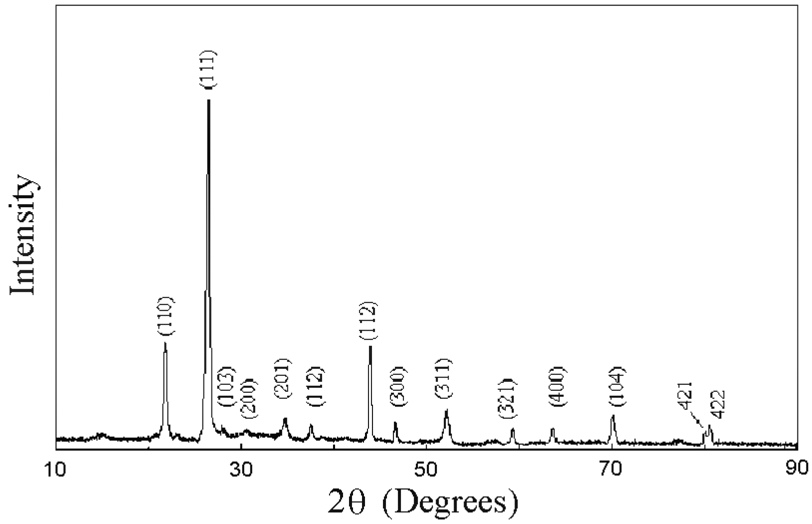

Fig. 1. X-ray powder diffraction pattern of the prepared $CdIn_2Se_4$.

calculated $\underline{d}$ values and the lattice parameters of the recorded pattern are in a good agreement with the standard X-ray diffraction data (JCPDS-card 74-0216). No other observable diffraction peaks corresponding to other binary phases could be detected besides the main $CdIn_2Se_4$ ternary phase. Figure 2 shows typical representative X-ray diffraction patterns of the as-deposited $CdIn_2Se_4$ film (thickness 275 nm) and of other samples of the same film thickness, annealed in vacuum at various temperatures for 45 min. The figure depicts that the as-deposited films are amorphous in nature or poorly crystalline, i.e., the peak intensities are below the detectable limits. The observed peak intensity increased appreciably with increasing annealing temperature. However, for $CdIn_2Se_4$ thin film annealed at 575 K (Fig. 2), minor peaks due to planes (111) at $2\theta = 24.0°$ and (305) at $2\theta = 50.5°$ were observed corresponding to CdSe and In_2Se_3, respectively, indicating the onset of dissociation of the deposited films at this temperature.

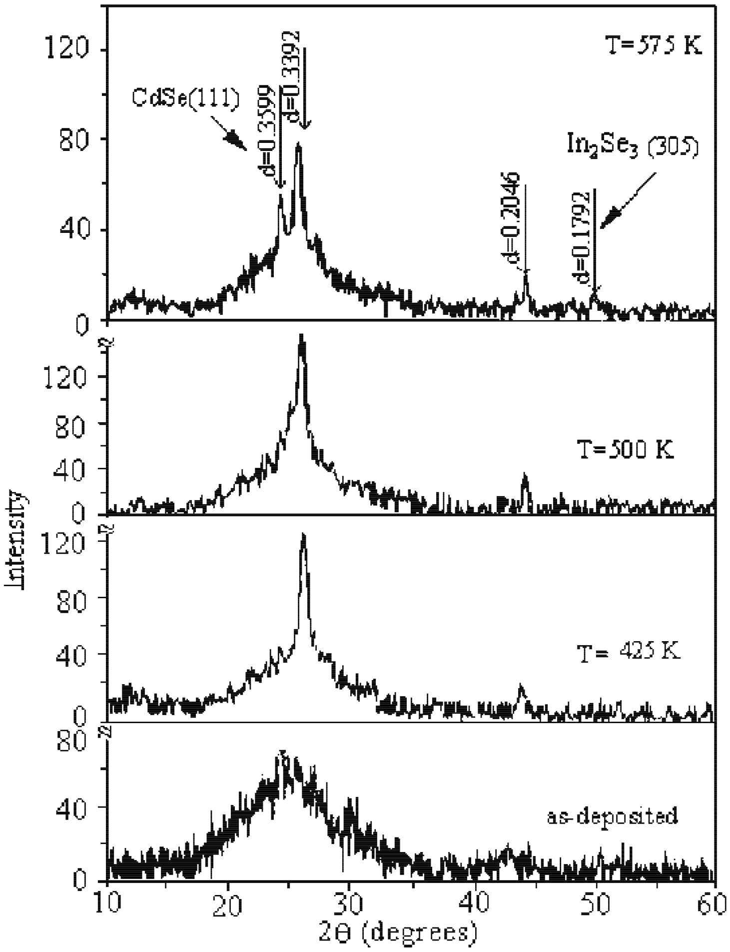

Fig. 2. X-ray diffraction patterns of $CdIn_2Se_4$ *thin films annealed at indicated temperatures.*

Electron diffraction studies of $CdIn_2Se_4$ were performed to check the effect of the annealing temperatures on the crystalline nature of the deposited films. Figure 3 shows typical representative samples of the electron-transmission micrographs and the corresponding electron diffraction patterns for as-deposited $CdIn_2Se_4$ film and those vacuum annealed in the temperature range 500 − 575 K for 45 min. The figures depict that the as-deposited film had a fine-grain structure, as the electron diffraction patterns were slightly diffuse. However, as the annealing temperature increases, the ring patterns become sharper and the grain grew in size and coalesced together,indicating an improvement in the crystallinity of the deposited films with annealing temperature.

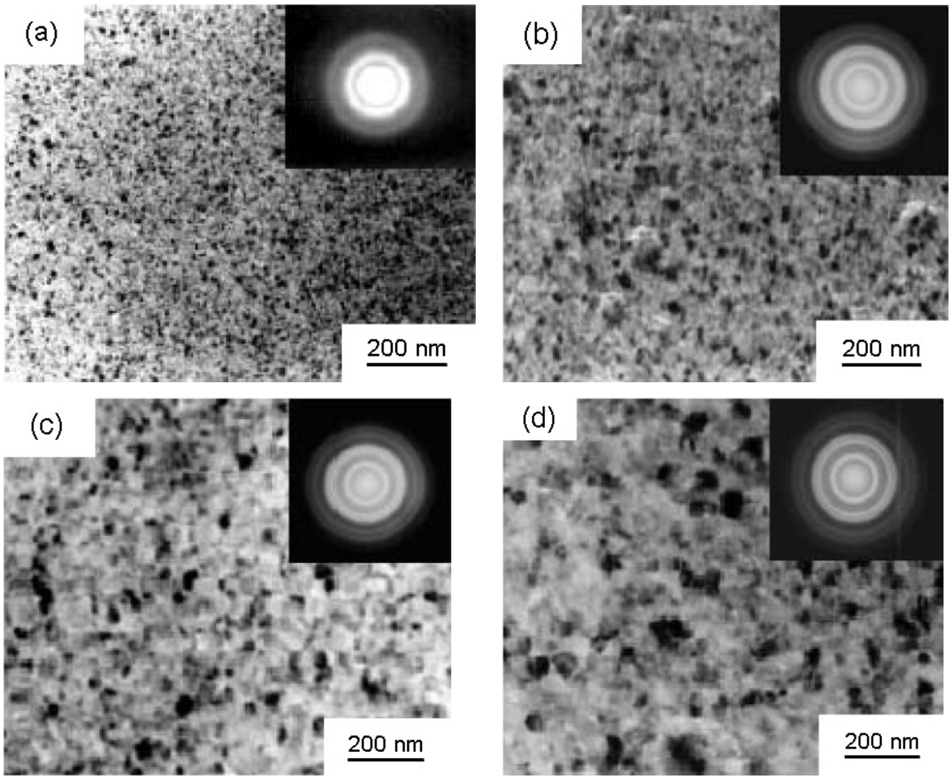

Fig. 3. Transmission electron micrograph and the corresponding electron diffraction patterns of $CdIn_2Se_4$ *thin films (a) as-deposited, and annealed at temperatures of (b) 425* K, *(c) 500* K *and (d) 575* K.

The compositional analysis (EDX) of $CdIn_2Se_4$ thin films annealed at 500 and 575 K for 45 min respectively, is shown in Fig. 4. The results indicated that $CdIn_2Se_4$ thin film annealed at 500 K was found to be nearly stoichiometric ($Cd_{1-x}In_{2(1+3x)}Se_{4(1+2x)}$, where $x = 0.012$). In addition, the EDX of the sample of the same film thickness annealed at 575 K shows an excess in In and Cd with

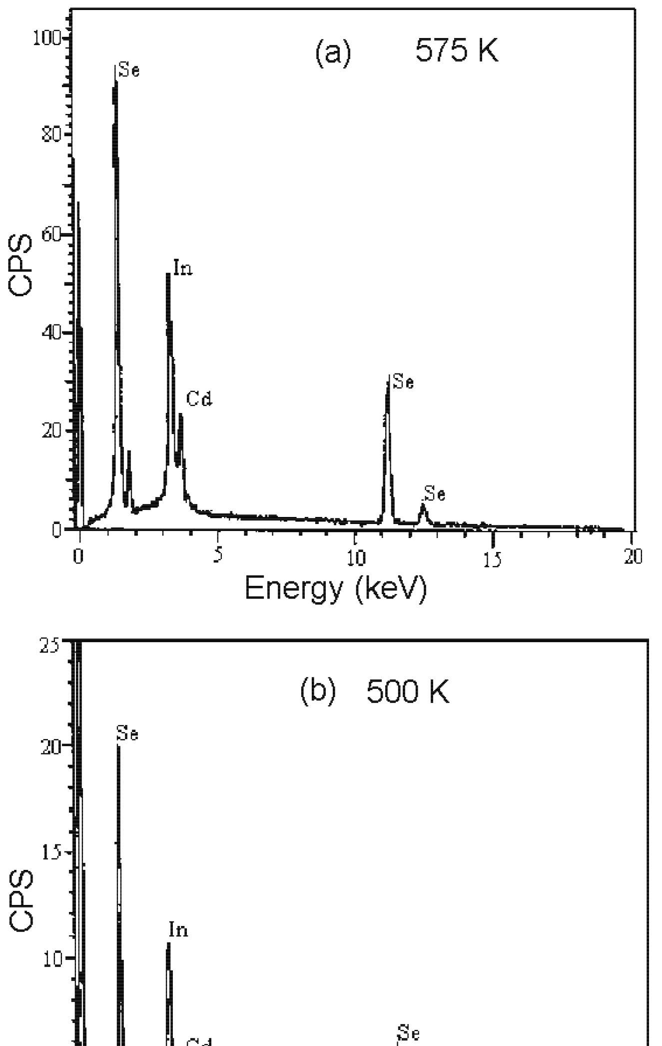

Fig. 4. Elemental analysis (EDX spectra) of $CdIn_2Se_4$ *thin films at annealing temperatures 500 and 575* K.

deficient in Se (composition, Cd : In : Se, 20.04 : 31.60: 46.34 at. %). The deficiency of Se lead to partially dissociation of $CdIn_2Se_4$ film as confirmed throughout X-ray diffraction analysis of the sample annealed at 575 K. Similar results depict the formation of CdSe phase beside $CdIn_2Se_4$ phase during perpetration of $CdIn_2Se_4$ thin film by spray pyrolysis at substrate temperature 553 K [8].

3.2. Optical properties of $CdIn_2Se_4$ thin films

The optical investigations were made with homogeneous and uniform thin films deposited on thick, transparent substrates. The thermally-evaporated film had thickness d and complex refractive index $n_c = n - \mathrm{i}k$, where n is the refractive index and $k = \alpha\lambda/4\pi$ is the extinction coefficient.

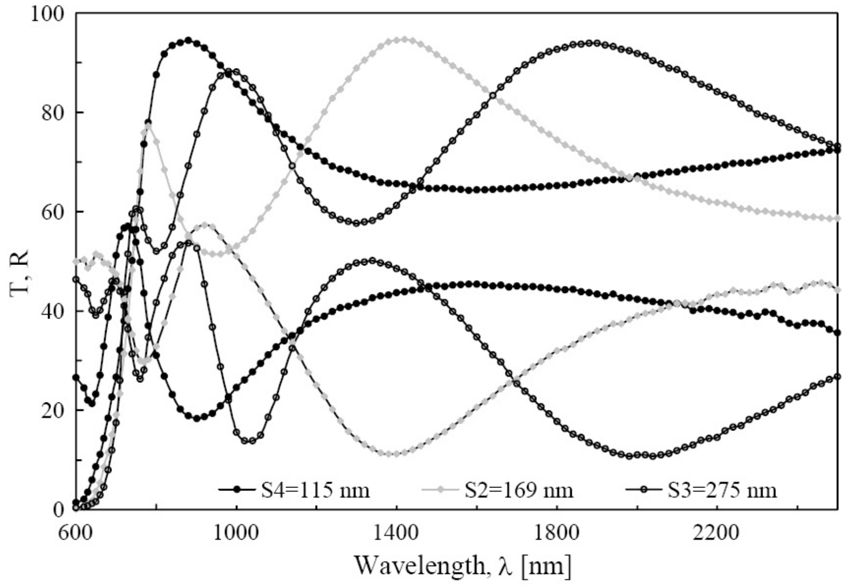

Fig. 5. Transmission, T, and reflection spectra of the as-deposited $CdIn_2Se_4$ *thin films of different film thicknesses.*

Figure 5 shows the spectral behaviour of the transmittance, T, and reflectance, R, spectra at normal light incidence in the wavelength range 600 − 2500 nm for the as-deposited $CdIn_2Se_4$ thin films of different thicknesses. The figure shows that above the absorption edge, the appearance of interference maxima and minima at the same wavelength indicates the optical homogeneity of the deposited films, hence the envelope method [9] can be applied to accurately calculate the film optical constants.

To study the effect of annealing temperature on the optical properties of the deposited films, the dependence of the transmission on the wavelength in the spectral range 600 − 2500 nm was recorded for thicker samples, S_3 (thickness 275 nm), annealed at different temperatures for 45 min. As a typical representative sample, a result is illustrated in Fig. 6.

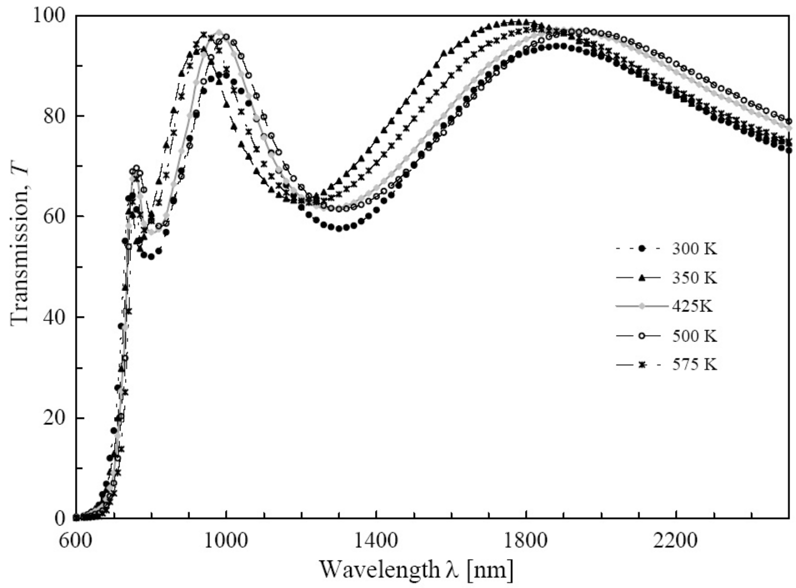

Fig. 6. Transmission spectra of $CdIn_2Se_4$ *thin films as a function of wavelength for a typical representative sample* S_3*, annealed at different temperatures.*

3.2.1. **Refractive index and band gap**

The refractive index and the film thickness are obtained by using only the transmission spectra of the annealed samples, as represented in Fig. 6, using the Swanepoel method [9], which is based on the approach of Manifacier et al. [10] for creating the upper and lower envelopes of the transmission spectrum.

The refractive index in the region where the absorption coefficient, α, is ≈ 0, was calculated using the expression [9]

$$n_i = \sqrt{M + \sqrt{M^2 - s^2}}, \tag{1}$$

where

$$M = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2},$$

s is the refractive index of the substrate, and T_M and T_m are the envelope values at wavelengths at which the upper and lower envelopes and the experimental transmission spectrum are tangent. If n_1 and n_2 are the refractive indices at two adjacent tangent points at wavelengths λ_1 and λ_2, using the basic equation for the interference fringes

$$2nd = m\lambda, \tag{2}$$

where m is an order number, and the film thickness is given by

$$d_i = \frac{\lambda_1 \lambda_2}{4(\lambda_1 n_2 - \lambda_2 n_1)}. \tag{3}$$

Thus solving Eq. (3), a set of values of d_i is obtained for each pair of consecutive tangent points. The mean value of d_i is used together with the first refractive index value, n_i, to determine the order numbers from Eq. (2). More accurately, d values are obtained using n_i and the exact order m. Using the exact m and the mean d_F, final values of the refractive index, n_F, are calculated.

However, in the region of strong absorption ($\alpha \neq 0$), the transmittance decreases drastically due almost exclusively to the influence of the absorption coefficient, α. The refractive index, n can estimated by extrapolating the calculated values of n_F using a reasonable function such as two-term Cauchy dispersion relation ($n = A/\lambda^2 + B$, where A, B are constants).

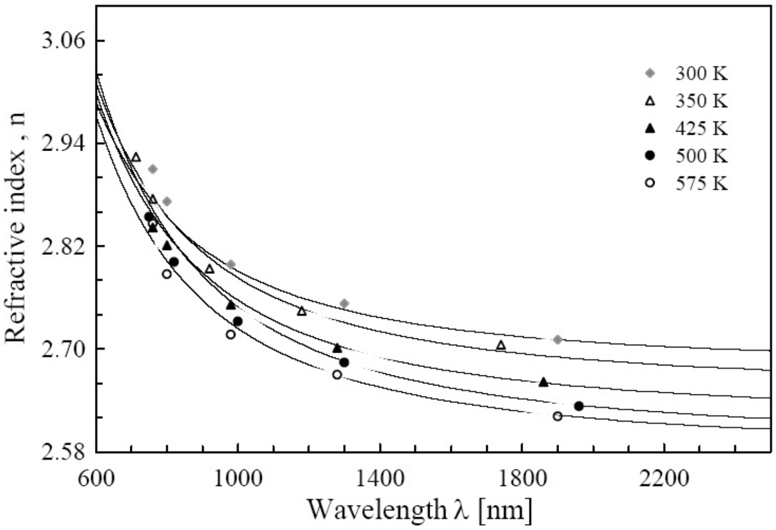

Fig. 7. Refractive index of $CdIn_2Se_4$ *thin films annealed at different temperatures.*

Figure 7 shows the dispersion curves of the calculated refractive index, n along with the experimental calculated values, n_F, for the sample S_3 annealed at various temperatures. The figure depicts that both the experimental and calculated values of the refractive index are extensions to each other. The refractive index at a given wavelength decreases with increasing annealing temperature and tends to be constant at longer wavelengths.

In the high absorption region, the transmittance T, as a function of the absorption coefficient, α, follows the simple relation [11]

$$T = A \exp\{-\alpha d\}, \tag{4}$$

where A is nearly equal to unity at the absorption edge. The absorption coefficient, α, as a function of the photon energy can be expressed as [11]

$$\alpha\hbar\omega = A\big(\hbar\omega - E_{\rm g}\big)^{\gamma}, \tag{5}$$

where $\hbar\omega$ is the photon energy, A is a constant and the exponent γ determines the type of the optical transition. $\gamma = 1/2$ and $\gamma = 2$ for direct and indirect transitions, respectively. Plotting $(\hbar\omega)^2$ and $(\hbar\omega)^{1/2}$ versus photon energy, $\hbar\omega$, (not shown) revealed high-energy threshold in the photon energy range $2.2-1.8$ eV and low energy threshold in the photon energy range $1.8-1.55$ eV, corresponding to direct and indirect optical transitions, respectively. Figure 8 shows the variation of direct and indirect band gaps with the annealing temperatures. The figure depicts that both values decrease with increasing annealing temperatures. However, on increases the annealing temperature to 575 K an abrupt decrease in the direct band gap occurs reaching 1.76 eV. This may attributed to the onset of CdSe (band gap 1.74 eV) and In_2Se_3 phases beside the main $CdIn_2Se_4$ ternary phase.

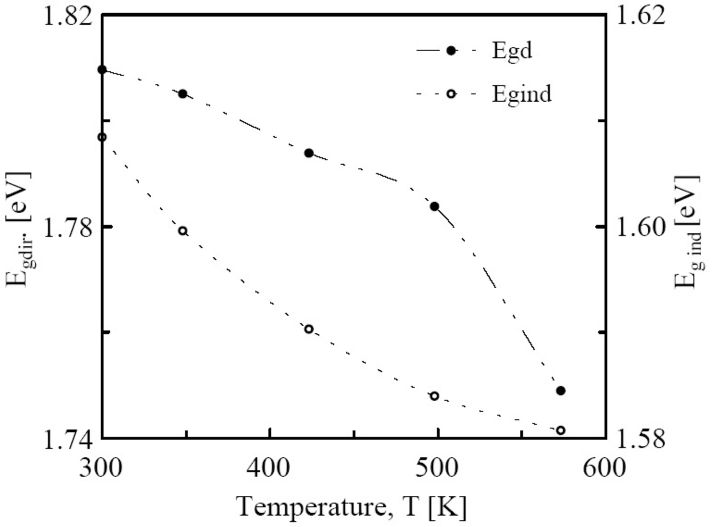

Fig. 8. Variation of both direct and indirect optical band gaps of $CdIn_2Se_4$ *thin films as a function of annealing temperature.*

3.2.2. **Dispersion behaviour of the refractive index**

The values of the refractive index, n, of the annealed samples were analyzed according to the single-effective oscillator model proposed by Wemple and DiDmenico [12]. Those authors investigated dispersion data for more than hundred different materials, both covalent and ionic, and both crystalline and amorphous. They found that the optical data could be described, to a very good approximation, by the following relation

$$n^2(\omega) = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2}, \tag{6}$$

where $\hbar\omega$ is the photon energy, and E_0, E_d are the oscillator and dispersion energy, respectively. Plotting $1/(n^2-1)$ versus $(\hbar\omega)^2$, as shown in Fig. 9, allows one to determine the oscillator parameters by fitting a straight line to the points. The temperature dependence of the single-oscillator parameters of $CdIn_2Se_4$ thin films is presented in Table 1.

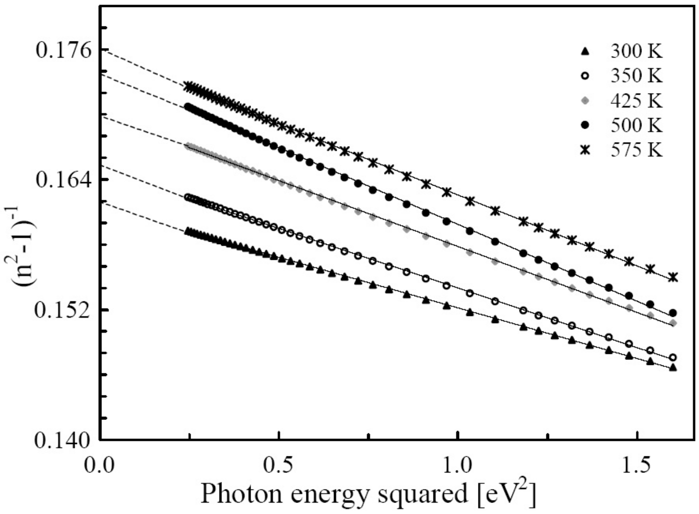

Fig. 9. Plot of $1/(n^2-1)$ *versus photon energy squared* $(\hbar\omega)^2$.

Furthermore, the oscillator energy, E_0, is related empirically to the lowest direct energy gap, E_g, by $E_0 \approx 2E_g$. The static refractive index $n(0)$, at $\hbar\omega \to \infty$. (extrapolating the Wemple and Di Dmenico optical dispersion relationship towards the infrared spectral region, $n(0) = 1 + E_d/E_0$), as well as the high frequency dielectric constant, $\varepsilon_\infty = n^2$, for the samples annealed at different temperatures are also listed in Table 1.

For the dispersion energy, E_d, the empirical relation is established

$$E_d = \beta N_c Z_a N_e, \tag{7}$$

where β is a constant and has the value of 0.37 eV and 0.26 eV for covalent and ionic material, respectively [12], $N_c = 4$ is the coordination number of the cations, $Z_a = 2$ is the formal valency of the anion and $N_e = (2\times1+4\times2+4\times6)/4 = 8.5$ is the effective number of valence electrons per anion. It was found that with increasing annealing temperatures, the covalent nature of structure tends to decrease, which corresponds to a decrease of β values and consequently confirms the onset of the dissociation of the deposited films at annealing temperatures about 575 K.

TABLE 1. Temperature dependence of the single-effective oscillator parameters, static refractive index and high-frequency dielectric constant of $CdIn_2Se_4$ *thin films.*

Annealing temperatures [K]	E_0 [eV]	E_d [eV]	E_g [eV]		$n_0(0)$	ε_∞	E_0/E_g	β
			dir.	indir.				
300	3.92	24.95	1.812	1.610	2.714	7.37	2.16	0.366
350	3.81	23.08	1.805	1.595	2.656	7.05	2.11	0.339
425	3.74	21.88	1.793	1.587	2.617	6.85	2.08	0.322
500	3.65	21.26	1.781	1.581	2.610	6.81	2.05	0.315
575	3.58	20.43	1.749	1.576	2.589	6.70	2.04	0.310

4. *Conclusion*

The room-temperature deposited $CdIn_2Se_4$ thin films are amorphous in nature, and an amorphous-to-crystalline phase transition can be obtained by thermal annealing in vacuum at temperatures in the range 300 – 500 K. The degree of crystallinity increased with increasing annealing temperature. At an annealing temperature of 575 K in vacuum, partial dissociation of the deposited films occured, with $CdIn_2Se_4$ as the main phase.

The effect of the annealing temperature on the refractive index was investigated. It was found that refractive index dispersion data obeyed the single-effective-oscillator model, from which the dispersion parameters, E_0, E_d and high frequency dielectric constant, ε_∞ were determined as a function of the annealing temperature. Analysis of the optical absorption data revealed the existence of both direct and indirect optical band gaps, and their energies decreased with increasing annealing temperature.

Acknowledgements

Authors are very greatful to Dr. M. E. El-Gazzawi Helwan University, Faculty of Science, Cairo, Egypt, for his effort during preparation and EDX analysis of the samples.

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ZNAČAJKE GRAĐE I OPTIČKA SVOJSTAVA OTPUŠTENIH TANKIH SLOJEVA $CdIn_2Se_4$

Isparavanjem u vakuumu pripremali smo tanke slojeve halkogenida $CdIn_2Se_4$. Proučavali smo učinke toplinskog otpuštanja u vakuumu na strukturne značajke naparenih slojeva primjenom difrakcije X-zračenja i prolazne elektronske mikroskopije. Opaža se da su svježe (na 300 K) napareni slojevi slabo kristalinični. Stupanj kristaliničnosti povećava se s povišenjem temperature otpuštanja između 300 i 500 K. Analize elementalnog sastava tankih slojeva $CdIn_2Se_4$ otpuštenih do 500 K pokazale su gotovo točan stoihiometrijski sastav, međutim, slojevi otpušteni na 575 K djelomično se razlažu u dvije binarne faze, dok $CdIn_2Se_4$ ostaje glavna faza. Mjerili smo učinke otpuštanja na disperzivnost indeksa loma naparenih slojeva i analizirali ishode jedno-oscilatornim modelom. Promjene parametara disperzije također smo istraživali u ovisnosti o temperaturi otpuštanja. Analize podataka za optičku apsorpciju ukazuju na postojanje dozvoljenih izravnih i neizravnih optičkih prijelaza s padom širina procijepa za povećane temperature otpuštanja.