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Optical Properties of $CdIn_2Se_4$ Thin Films in the Region of the Fundamental Absorption Edge

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Abstract: Thin films of $CdIn_2Se_4$ of different thicknesses were prepared by thermal evaporation technique. Both transmittance (T) and reflectance (R) were measured at normal incidence in the spectral range of 500- 1100 nm. Optical constants (refractive index, n, and absorption index, k) of the prepared films of $CdIn_2Se_4$ have been obtained in the wavelength range 400-1100 nm by using spectrophotometric measurement. The obtained results concerning the absorption index yield the energy gap in addition to the type of the allowed optical transitions (direct or indirect). The dispersion of refractive index is analyzed by using a single oscillator model. Also, Drude model of free carriers contribution have been described for the analysis the dispersion of refractive index for $CdIn_2Se_4$ thin films.

Key words: Optical properties; $CdIn_2Se_4$; thin films.

INTRODUCTION

Cadmium indium selenide ($CdIn_2Se_4$) is a n-type ternary semiconducting compound belongs to vacant diamond like $A^{II}B_2^{III}C_4^{VI}$ type where A = Cd, Zn or Hg, B = In or Ga, and C = S, Se, Te (El-Nahass, M.M., 1991). The cubic nature of $CdIn_2Se_4$ thin films has been confirmed from XRD analysis, also the EDAX studies showed that the material formed is almost stoichiometric (Nikale, V.M., *et al*, 2011). Great intense studies have been made in recent years due to their interesting tailored properties that offer the possibility of implementing innovative applications in many modern applications such as solar energy conversion (Tenne, R., *et al*, 1985), non-linear optics (Marinelli, M., *et al*, 1989) and optoelectronic devices. Ahn, J.H. *et al*, reported 0.42% photoelectrochemical device conversion efficiency for electrochemical synthesis of $CdIn_2Se_4$ thin films at ambient temperature (Ahn, J.H., *et al*, 2007). Recently, Nikale, V.M. *et al*, reported that the Photoelectrochemical performance (PEC) of sprayed n- type $CdIn_2Se_4$ deposited onto the FTO coated glass substrates show best PEC performance (FF = 0.37, η = 1.95%) (Nikale, V.M., *et al*, 2011). Thin films of this material are generally prepared by chemical or physical methods, such as thermal evaporation technique, electrodeposition technique and by slurry pasting technique (Tenne, R., *et al*, 1982). The aim of the present work is to investigate the Optical properties of $CdIn_2Se_4$ thin films in the region of the fundamental absorption edge

2. Experimental Techniques:

The bulk material of $CdIn_2Se_4$ was prepared by using direct fusion of highly pure binary constituents of CdSe & In_2Se_3. Five samples of $CdIn_2Se_4$ were prepared by using a high vacuum coating unit “Edward E306A” under vacuum of 10^{-4} Pa. The films were deposited on fused optically flat glass substrates at room temperature (~ 300 K). The film thickness was controlled during the deposition process, and then measured by Tolansky’s method (Tolansky, S., 1988). The film thickness varies from 69 to 274 nm. The prepared samples were attached to special holder placed in the dark chamber on the spectrophotometer. The structural characterization of the bulk and thin film were carried out by analyzing the XRD pattern using a Philips X-ray diffractometer (model X’ pert) supplied with monochromatic (λ = 1.5405Å for Cu K_α).

For optical measurements, the transmittance, T, and reflectance, R, of the films deposited on glass substrates were determined at normal incidence in the wavelength range 200–1100 nm by means of a double beam spectrophotometer (JASCO 570) to which a specular reflection stage was attached.

The absolute values of measured transmittance and reflection after correcting for the absorbance and reflection of the substrate as follow:

$$I_{ft} = I_o T (1- R_g) (1- A_g) \quad (1)$$

Where I_o is the intensity of incident light. I_{ft} is the intensity light passing through the film substrate system, R_g and A_g are the reflectance and Absorbance of the glass substrate respectively, and:

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$I_g = I_o (1-R_g)^2 (1- A_g)$ (2)

Where I_g is the intensity of light passing through the reference (glass reference). Since the substrate is non absorbing in the measuring spectral range 200 – 1100 nm; i.e $A_g = 0$, then

$T_{exp} = (I_{ft}/ I_g) (1 – R_g)$, (3)

If the intensity of light reflected at normal incidence from the film quartz system is I_{fr} and I_{Al} is the intensity of light reflected from the reference (Al- mirror), then according the reflectance R can be determined by using the following relation by using the following relation (for non absorbing glass substrate):

$R_{exp} = (I_{ft}/I_{Al}) R_{Al} [1 + (1- R_g)^2] – T^2R_g$, (4)

In the present work from the measured T_{exp}, R_{exp} and film thickness, d, the values of the refractive index, n, and the absorption index, k, were computed by a special computer program which overcome the problem produce due to an unvariance search technique when n and k are apparently not highly correlated quantities [15] the modified method is based on minimizing $(\Delta T)^2$ and $(\Delta R)^2$ simultaneously, where

$(\Delta T)^2 = \left| T_{(n, k)} - T_{exp} \right|^2$, (5)
$(\Delta R)^2 = \left| R_{(n, k)} - R_{exp} \right|^2$, (6)

Where T_{exp} and R_{exp} are the experimentally determined absolute values of T and R, respectively, and $T_{(n,k)}$ and $R_{(n,k)}$ are the values of T and R , calculated by using the Murmann's exact equations:

$$R_{(n,k)} = \frac{Ae^{\beta} + Be^{-\beta} + 2C\cos\alpha + 4D\sin\alpha}{Ee^{\beta} + Fe^{-\beta} + 2G\cos\alpha + 4H\sin\alpha} \quad (7)$$

The transimittance $T_{(n,k)}$ can be easily derived to give the following form:

$$T_{(n,k)} = \frac{16 n_o n_q (n^2 + k^2)}{Ee^{\beta} + Fe^{-\beta} + 2G\cos\alpha + 4H\sin\alpha} \quad (8)$$

Where
$A = [(n-n_o)+k^2] [(n-n_q)+k^2]$
$B = [(n-n_q)+k^2] [(n-n_o)+k^2]$
$C = (n^2+k^2) (n_o^2 + n_q^2) - (n^2+k^2)^2 - n_o^2 n_q^2 - 4n_o n_q k^2$
$D = k (n_q-n_o) (n^2+k^2+n_o n_q)$
$E = [(n-n_o)^2+k^2] [(n+n_q)^2+k^2]$
$F = [(n-n_o)^2+k^2] [(n-n_q)^2+k^2]$
$G = (n^2+k^2) (n_o^2 + n_q^2) - (n^2+k^2)^2 - n_o^2 n_q^2 + 4n_o n_q k^2$
$H = k (n_q-n_o) (n^2+k^2- n_o n_q)$

By taking into account the experimental error in measuring the film thickness to be ±2.6% and in T_{exp} and R_{exp} to be ±1%, the errors in the calculated values of n and k were estimated to be ±3%, and ±2.5%, respectively.

RESULTS AND DISCUSSION

Fig. 1. Shows the X-ray diffraction patterns of $CdIn_2Se_4$ in its powder, and the as-deposited film (thickness 453 nm) forms. The powder XRD pattern shows many peaks with different intensities indicating that the material is poly crystalline. JCPDS Card No. 8-267 (1992) was used to index all the diffraction lines, calculate the Miller indices (hkl) and the interplanar spacing (d_{hkl}) value for each diffraction peake . The analysis indicates that $CdIn_2Se_4$ has a tetragonal structure.

X-ray diffraction of the as-deposited film has amorphous structure. The spectral distributions of T(λ) and R(λ) for the as-deposited $CdIn_2Se_4$ thin films of different thicknesses (69 to 274 nm) are illustrated in Fig. 2. At longer wavelength with respect to the absorption edge, T(λ) + R(λ) = 1 indicating that the as-deposited $CdIn_2Se_4$ films become transparent and no light is scattered.

By using transmittance T(λ) and reflectance R(λ) data as well as the film thickness, d; the calculated optical constants were found to be independent on the film thickness in the thickness range mentioned before and within the estimated experimental errors.

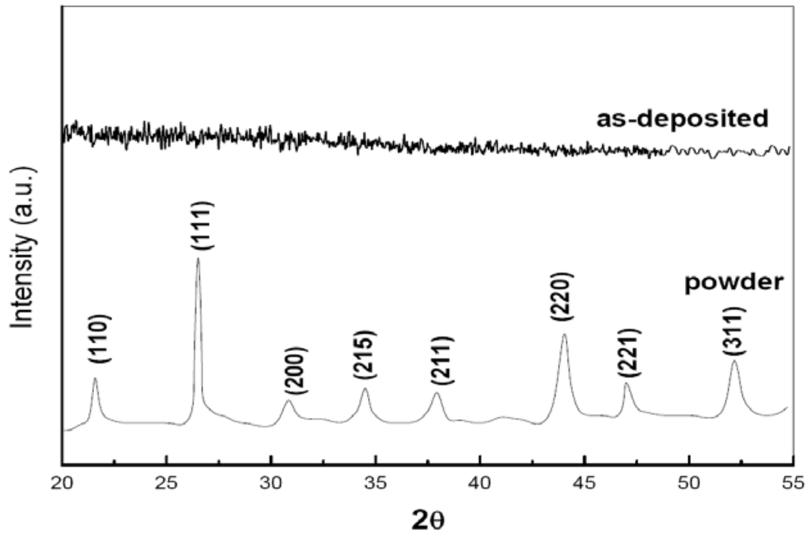


Fig. 1: X-Ray difrection pattern for the powder form and the as-deposited $CdIn_2Se_4$ of thickness 453 nm.

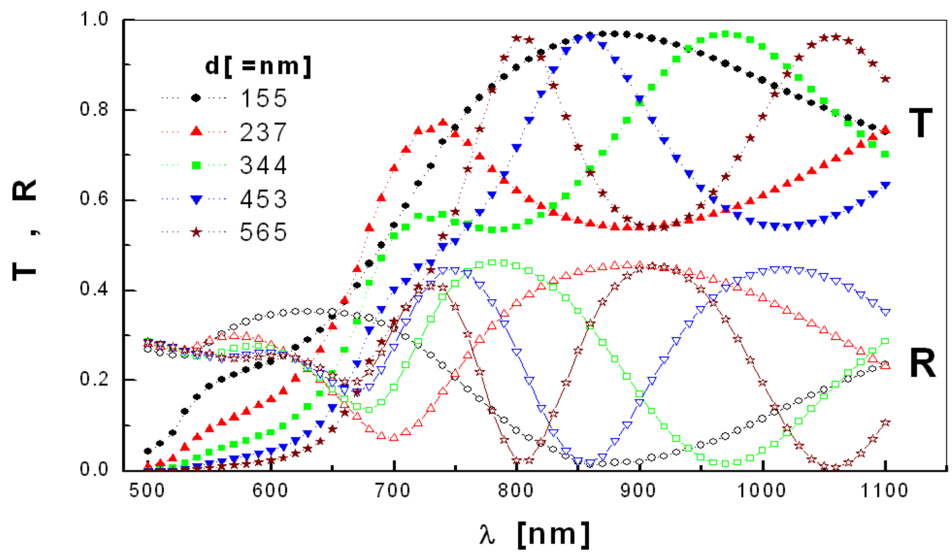


Fig. 2: The spectral dependence of the normal incidence transmittance, T and reflectance, R for the as deposited $CdIn_2Se_4$ thin films with different thicknesses (155–565nm).

Fig. 3 (a&b) shows the mean values of the real, n, and imaginary, k, parts of the indices of refraction for the as-deposited $CdIn_2Se_4$ films.
The absorption coefficient α was calculated from the mean values of the absorption index, k, using the well known relation (El-Nahass, M.M., *et al*, 2010):

$$\alpha = \frac{4\pi k}{\lambda}, \qquad (9)$$

Fig. 4. Shows the absorption spectra for the as-deposited $CdIn_2Se_4$ films.

Fig. 5. Illustrate the dependence of log (αhυ) as a function of log (1/λ) for the as-deposited $CdIn_2Se_4$. As observed, the obtained dependence yields two linear parts indicating the existence of both direct and indirect transitions.

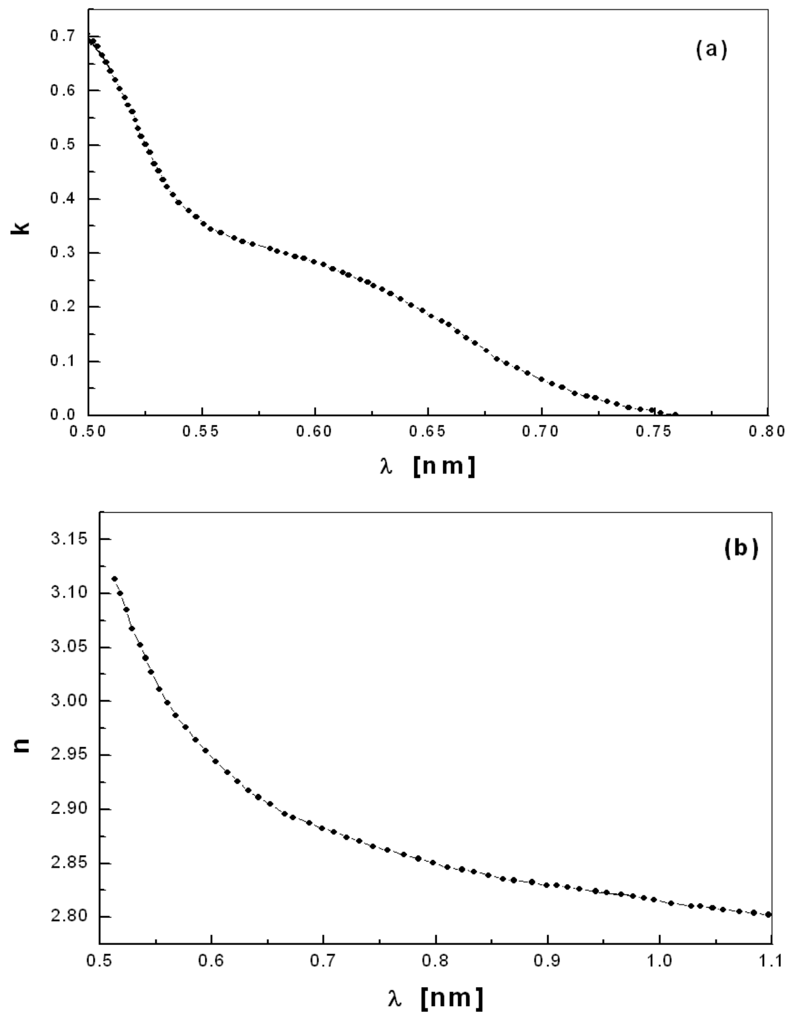


Fig. 3: **(a)** The spectral dependence of the mean values of the real part of refractive index, k(λ), of $CdIn_2Se_4$ films for the as-deposited films.
(b) The spectral dependence of the mean values of the real part of refractive index, n(λ), of $CdIn_2Se_4$ films for the as-deposited films.

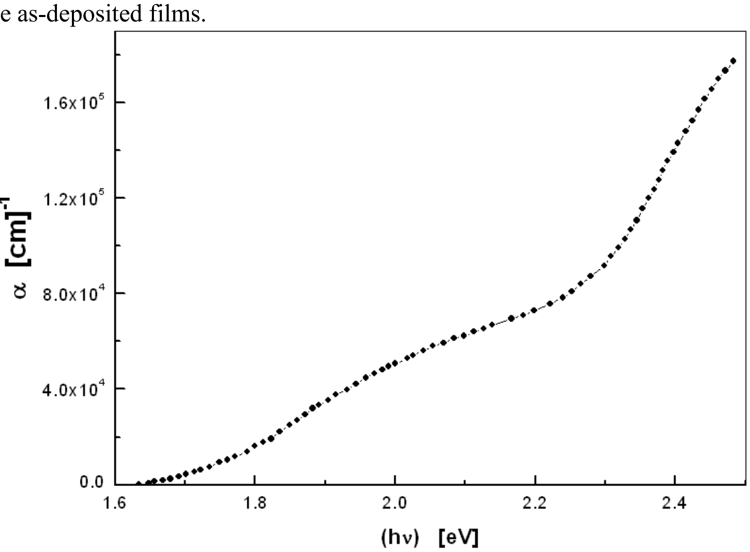


Fig. 4: Spectral behaviour of absorption coefficient, α, for the as deposited $CdIn_2Se_4$ thin films.

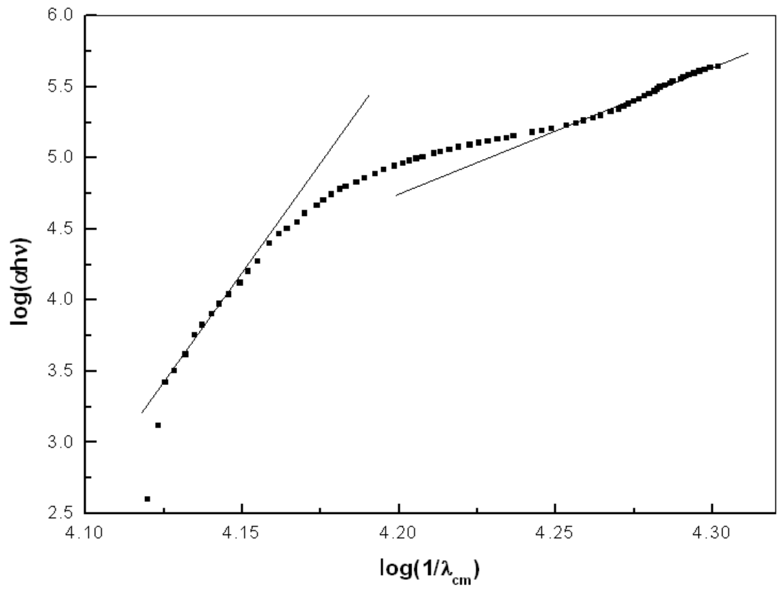


Fig. 5: Plot of log (αhυ) vs 1/λ for the as-deposited $CdIn_2Se_4$ films.

In semiconductor physics, At the absorption edges ($\alpha \geq 10^4$ cm^{-1}), the energy dependences of the inter-band absorption coefficient are given by the following expressions (El-Nahass, M.M., *et al*, 2010):
For indirect allowed transitions

$$\alpha\ (h\upsilon) = A_{ind}\,(h\upsilon - E_g^{ind} \pm E_{ph})^2 \tag{10}$$

For allowed direct transitions

$$\alpha\ (h\upsilon) = A_d\,(h\upsilon - E_g^d)^{1/2} \tag{11}$$

In the above equations, E_g^d and E_g^{ind} represent the band gap energy, and A_d and A_{ind} are characteristic parameters, independent of photon energy, for direct and indirect transitions and E_{ph} is the phonon energy, respectively. The $(\alpha h\upsilon)^{1/2}$ vs (hυ) & $(\alpha h\upsilon)^2$ vs (hυ) plots for the as-deposited $CdIn_2Se_4$ is shown in Fig. 6 (a&b). The indirect band gaps for the as-deposited $CdIn_2Se_4$ are evaluated from the x-axis intercepts and were found to be 1.60 eV and 1.90 eV. Also, the direct band gaps were found to be 1.80 and 2.27 eV.

Wemple and DiDomenico used a single oscillator description of the frequency- dependent dielectric constant to define the dispersion energy parameters E_d and E_o. The relation between the refractive index, n, and the single oscillator strength below the band gap is given by the following expression:

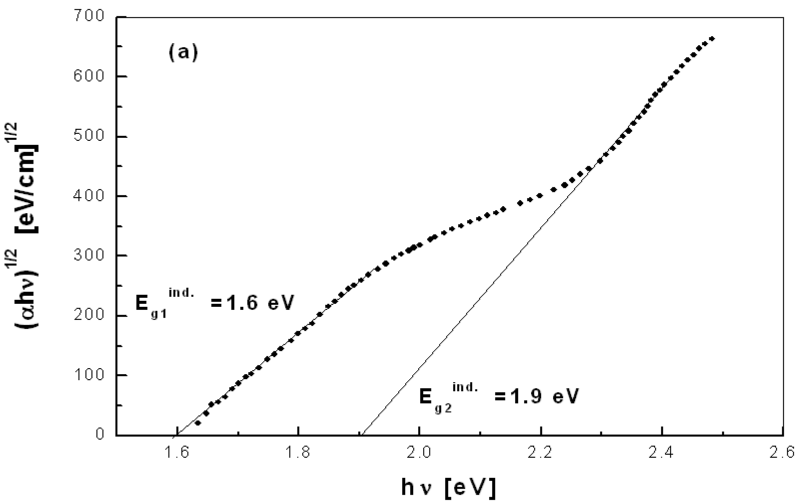
$$\frac{1}{n^2 - 1} = \frac{E_o}{E_d} - \frac{E^2}{E_o E_d}, \tag{12}$$

Where *E (hυ)* is the photon energy, E_o is the single oscillator energy and E_d is the so-called dispersion energy, which measures the average strength of inter-band optical transitions. Experimental verification of the above equation can be obtained by plotting $(n^2\text{-}1)^{-1}$ versus $(h\nu)^2$. The resulting straight line then yields values of the parameters E_o and E_d. Fig. 7. shows the relation between $(n^2\text{-}1)^{-1}$ and $(h\nu)^2$ for the as-deposited $CdIn_2Se_4$ film. The values of E_o and E_d are directly determined from the slope, $(E_oE_d)^{-1}$, and the intercept, (E_o/E_d), on the vertical axis. The calculated values of the dispersion parameter E_o, E_d and ε_∞ were found to be 5.5 eV, 36.4 eV and 7.6.

On the other hand, a significant success of Wemple and DiDomenico model is that it relates the dispersion energy, E_d, to other physical parameter of the material through the following empirical relationship:

$$E_d = \beta\, N_c Z_a N_e \quad \text{(eV)}, \tag{13}$$

where N_c is the coordination number of the cation nearest- neighbour to the anion, Z_a is the formal chemical valency of the anion, N_e is the effective number of valence electrons per anion and β is a constant takes the value (0.37±0.04 eV) for covalently bonded crystalline and amorphous and takes the value (0.26±0.04 eV) for halides and most oxides with a more ionic structure. Taking N_c (Cd) = 2, N_c(In) = 3 and N_c(Se) = 2, we get N_c = 2.53 for the investigated compound $CdIn_2Se_4$ Considering the formal chemical valency of the anion Z_a = 2 and N_e corresponding numbers of valence electrons, i.e. 2, 3, 6], for Cd, In and Se atoms, respectively, we get [N_e = (0.17×2+0.35×3+0.48×6)/0.48 =8.9]. By Talking β = 0.4 eV; the calculated value of E_d for the as deposited films, E_d = 18 eV.



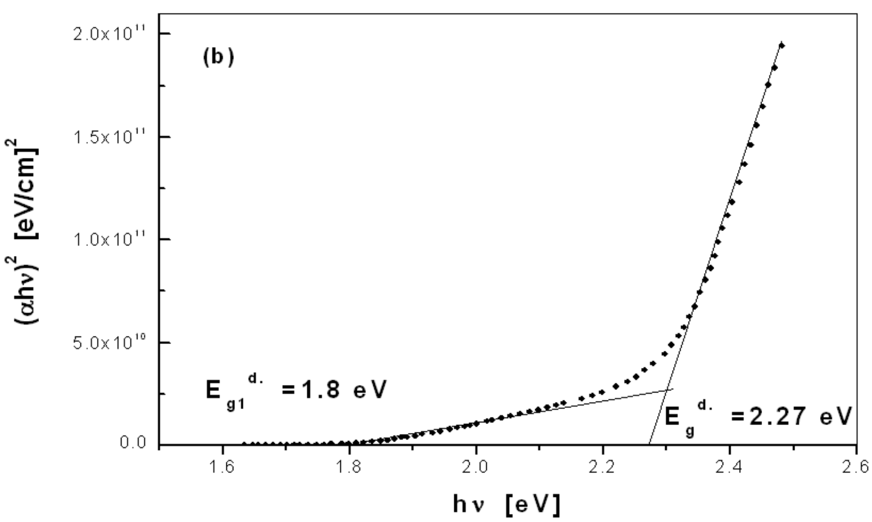


Fig. 6: **(a)**The relation between $(\alpha h\upsilon)^{1/2}$ and photon energy (hυ) for the as-deposited $CdIn_2Se_4$ thin films.
(b) The relation between $(\alpha h\upsilon)^2$ and photon energy (hυ) for the as-deposited $CdIn_2Se_4$ thin films.

In transparent region, the relation between the optical dielectric constant, ε_1, the wavelength, λ, and the refractive index, n, is given by the following equation (Gonzalez-Leal, J.M., *et al*, 1999):

$$\varepsilon_1 = n^2 = \varepsilon_L - D\,\lambda^2, \qquad (14)$$

where ε_1 is the real part of the dielectric constant, ε_L is the lattice dielectric constant or (the high- frequency dielectric constant) and D is a constant depending on the ratio of carrier concentration to the effective mass; $D = \dfrac{e^2 N}{4\pi^2 \varepsilon_o m^* c^2}$, where e is the charge of the electron, N is the free charge carrier concentration, ε_o is the permittivity of free space, m* is the effective mass of the electron and c is the velocity of light (Edward, P.O., 1985).

Fig. 8. shows the relation between n^2 and λ^2 for as-deposited $CdIn_2Se_4$ thin films. It is observed that the dependence ε_1 (= n^2), on λ^2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives the value of $\varepsilon_L = 8.35$ for the as-deposited samples, and from the slope of this linear part we get the constant D, from which the value (N /m*) for the as-deposited thin films is found to be 6.25×10^{48} $cm^{-3}gm^{-1}$.

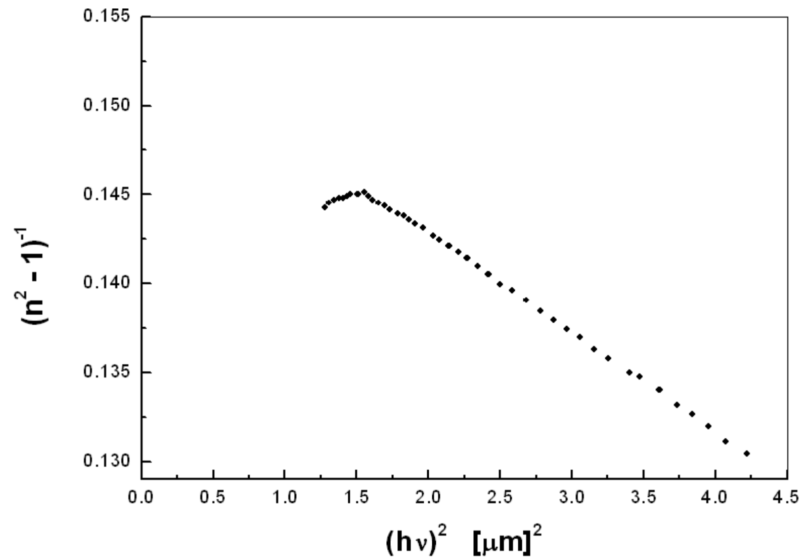


Fig.7. The relation between $(n^2 - 1)^{-1}$ and $(h\upsilon)^2$ for the as-deposited $CdIn_2Se_4$ thin films.

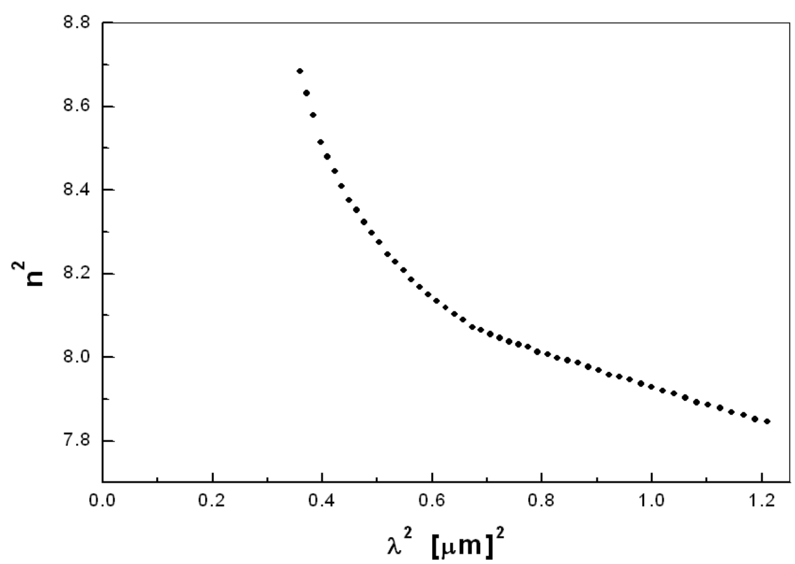


Fig. 8. The relation between n^2 and λ^2 for the as-deposited $CdIn_2Se_4$ thin films.

4. Conclusion:

The optical properties of thermally evaporated $CdIn_2Se_4$ thin films have been characterised by using spectrophotometric measurements of transmittance and reflectance in the spectral range of 500-1100 nm. The optical constants n and k are not affected by film thickness. The optical absorption edge is described using both the direct and indirect transitions. The dispersion parameters such as oscillator energy, dispersion energy and dielectric constant were also estimated.

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