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OPTICAL PROPERTIES OF COPPER INDIUM DISELENIDE THIN FILMS

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Thin films of Copper Indium diselenide of different thickness have been deposited on well cleaned glass substrates in a vacuum of 10^{-5} Torr. The thickness of the deposited films is measured by employing micro balanced method and confirmed by multiple beam interferometric method. The optical properties have been studied in the range 190 nm to2500 nm. The absorption coefficient has been determined and is found to be of the order of 10^4 cm^-.The band gap of the deposited $CuInSe_2$ films is found to decrease with increase in film thickness and substrate temperature. The refractive index of the $CuInSe_2$ thin films are found to decrease with increase in the incident photon wavelength.

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Keywords: Optical properties, Vacuum deposition, Copper Indium diselenide, Thin films.

1. Introduction

Semiconducting thin films have been extensively studied for a long time due to their significant role in modern science and technology. The reported conversion efficiency (11%) and excellent stability with a(Cd,ZnS/$CuInSe_2$) thin film solar cell[1] has made the ternary thin film polycrystalline semiconductor,$CuInSe_2$ a strong candidate for photovoltaic devices. The optical properties of such films are importance in view of the intensive interest in the optoelectronic properties. Gupta and Isomura [2] have reported the formation of single-phase chalcopyrite films by selenization technique with high absorption coefficient of the order of 10^5 cm^{-1} and an energy gap of 0.99 eV. Padam et al [3] have reported an absorption coefficient of the order of 10^5 cm^{-1} for chemically prepared $CuInSe_2$ thin films. A direct band gap larger than 1.0 eV has been reported for $CuInSe_2$ films by Sahu et al [4]. They have attributed the increase in band gap to quantum size effect, which results due to the small grain size (5nm). Grindly et al [5] have reported a band gap of 1.09 eV for $CuInSe_2$ thin films. They have attributed the deviation of band gap from the accepted value of 1.02 to1.04 eV to the small stoichiometry variations and large number of defects in the layer for small non-parabolicities in the band structure. Aren et al [6] have observed a change in the band gap of $CuInSe_2$ thin films from 1.05 to 1.25 eV when annealed in H_2S atmosphere at 150˚C for 2 hours. They have also observed a slight decrease in refractive index due to annealing. The present work deals with the optical properties of $CuInSe_2$ thin films prepared by single source thermal evaporation.

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2. Experimental

Copper indium diselenide thin films have been deposited on to well cleaned glass substrates in a vaccum of 10^{-5} torr. The weighed high purity elemental copper, indium and selenium are taken in a pure cleaned quartz ampoule of diameter 10 mm and length 65 mm. A pressure of $2x10^{-4}$ Torr is achieved in the ampoule along with the material. The vacuum sealing is done using oxy indane gas.

The sealed ampoule is placed in a rotating furnace and the ampoule is gradually heated at the rate of 100°C/hour step by step up to a temperature of 1100°C. The ampoule is maintained at 1100°C for 24 hours and then cooled slowly to room temperature at a rate of 100°C/hour. The temperature required for synthesisation was determined from the phase diagram of $CuInSe_2$ alloy. During the course of heating and cooling the quartz ampoule is rotated continuously to ensure homogeneity in the molten mixture. After cooling the alloy is taken by breaking the ampoule. The optical transmittance spectra of $CuInSe_2$ films have been recorded from 190nm to 2500nm wavelength using a Jasco UV-VIS-NIR spectrophotometer (Model-V-570) at room temperature using un-polarized lights from deutrium and tungsten lamps which are used at near normal incidence.

3. Results and discussion

3.1 Optical Properties of $CuInSe_2$ Thin Films

The transmittance spectra and band gap plot of $CuInSe_2$ thin films of different thicknesses deposited at three different substrate temperatures 370 K, 523 K and 673 K respectively are shown in Fig. 1-12. All the deposited $CuInSe_2$ thin films show good transparency and exhibit interference pattern in the region of the spectrum where the thin film is transparent. The transmittance spectrum exhibits oscillatory behaviour due to an interference pattern between the wave fronts reflected from the two surfaces of thin film [7].

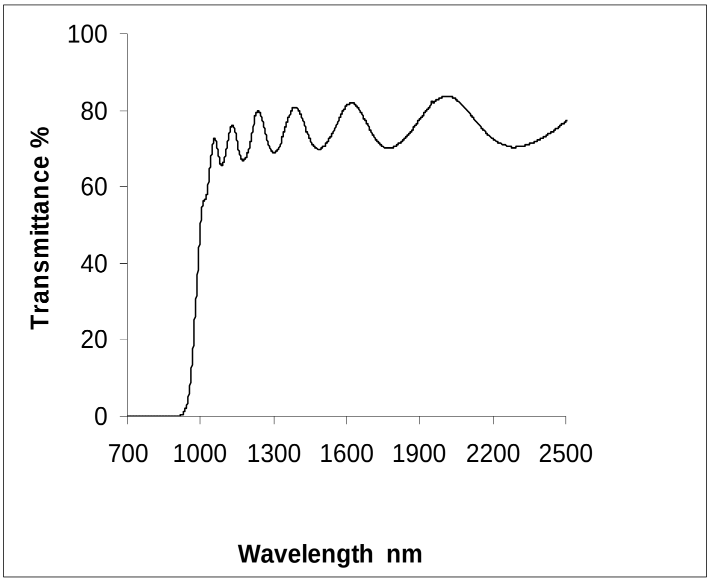

Fig. 1. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 370K with thickness 415nm

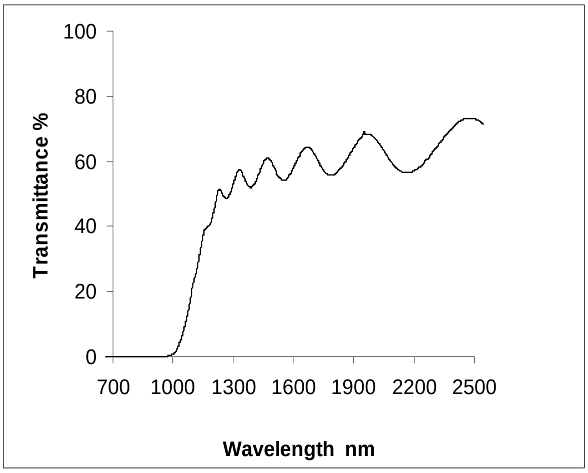

Fig. 2. Transmittance spectra of $CuInSe_2$ thin film deposited at Substrate Temperature 370K with thickness 550 nm

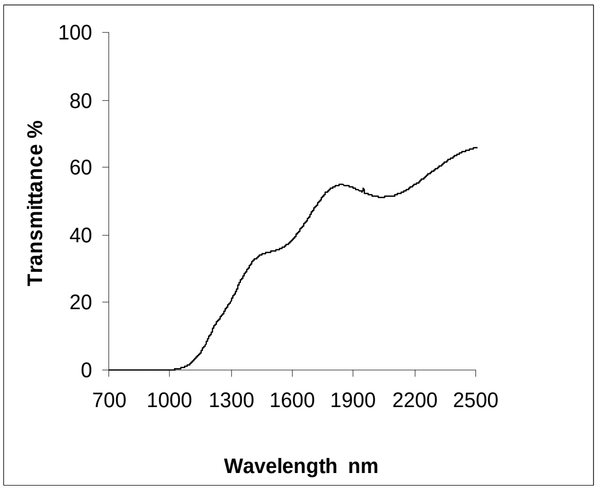

Fig. 3. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 370K with thickness 745 nm

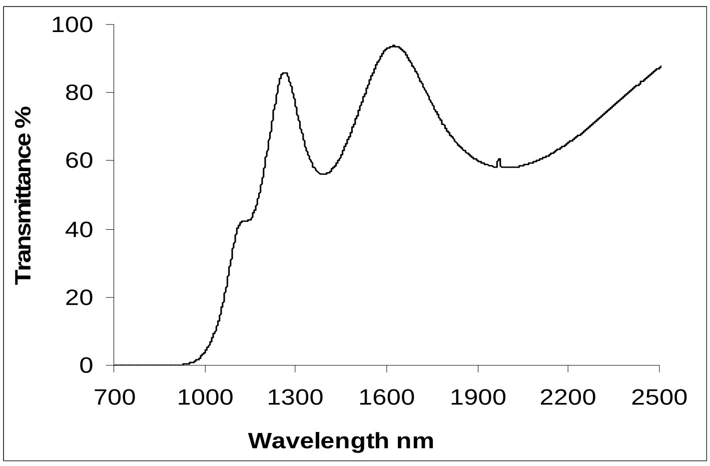

Fig. 4. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 523K with thickness 410 nm

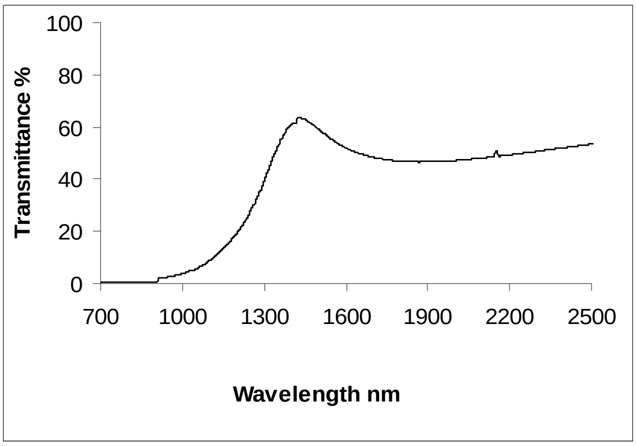

Fig. 5. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 523K with thickness 555 nm

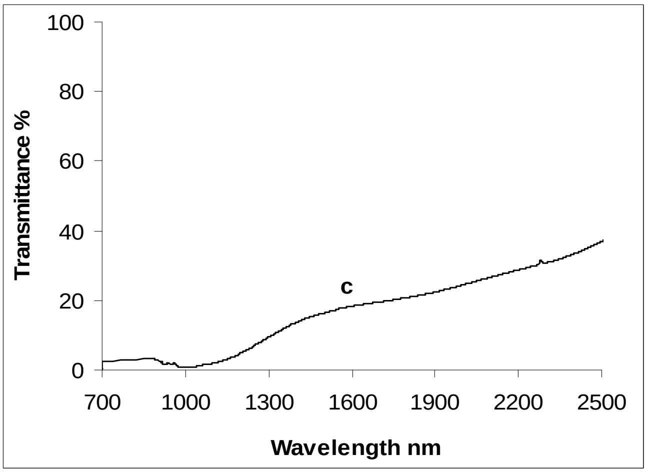

Fig. 6. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 523K with thickness 765nm

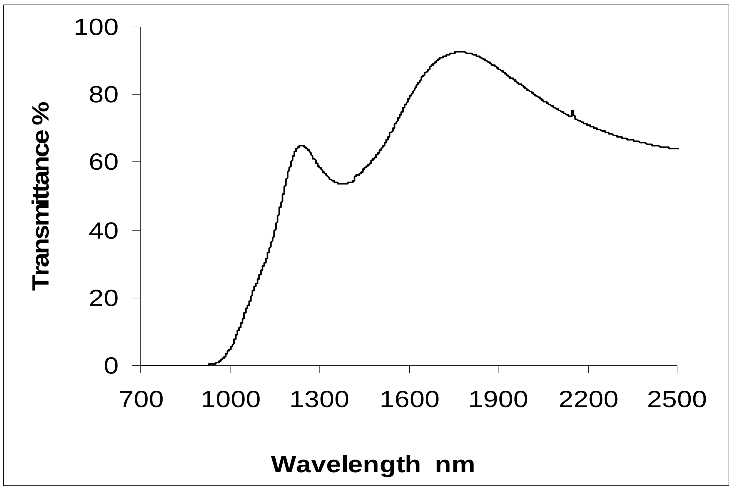

Fig. 7. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 673K with thickness 405nm

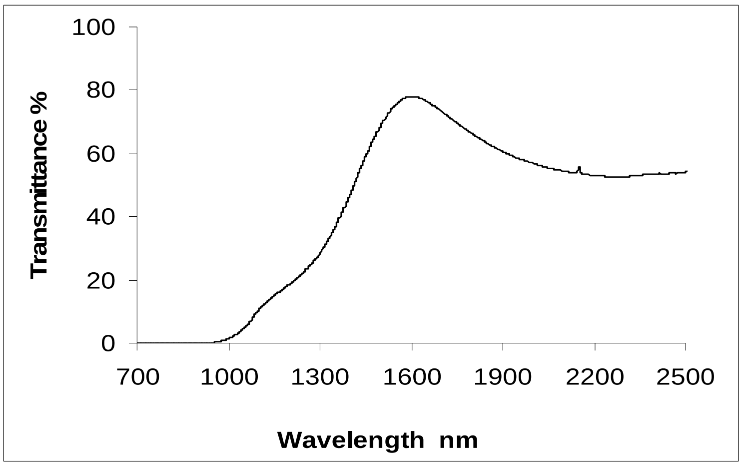

Fig. 8. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 673K with thickness 545nm

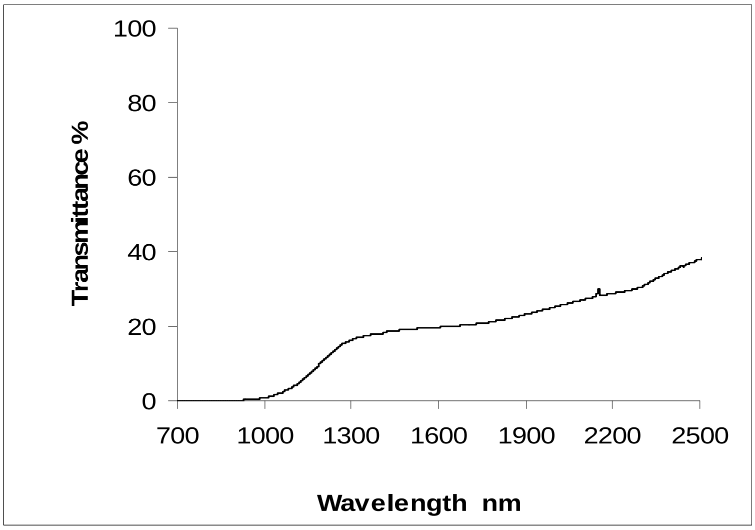

Fig. 9. Transmittance spectra of $CuInSe_2$ thin film deposited at substrate Temperature 673K with thickness 755nm

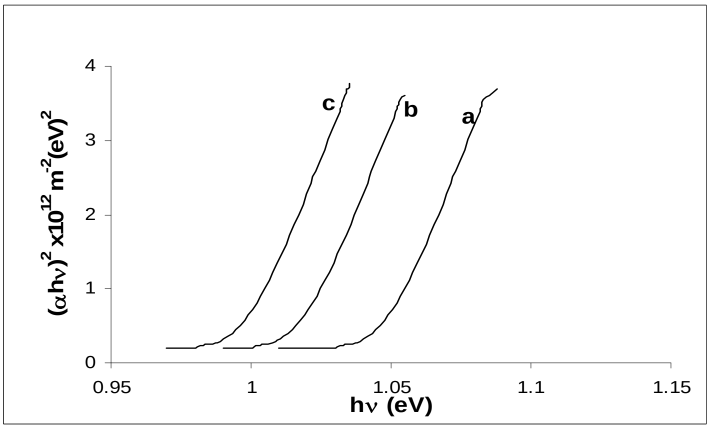

Fig. 10.Band gap plot of $CuInSe_2$ thin films deposited at substrate temperature 370K with thickness a) 415nm b) 550nm c) 745nm

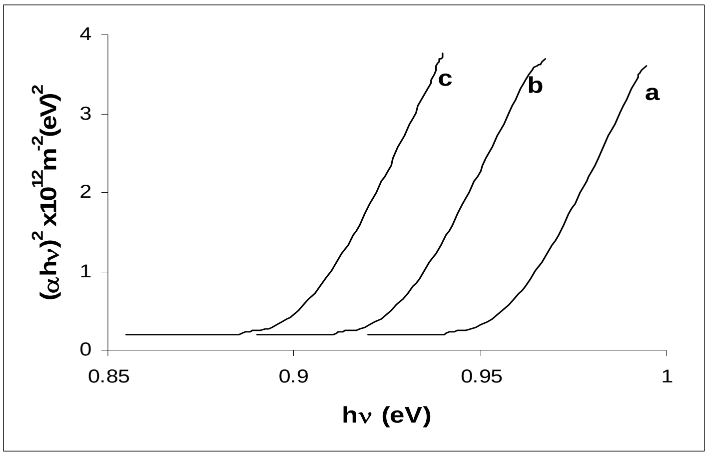

Fig.11. Band gap plot of $CuInSe_2$ thin films deposited at substrate temperature 523K with thickness a) 410nm b) 555nm c) 765nm

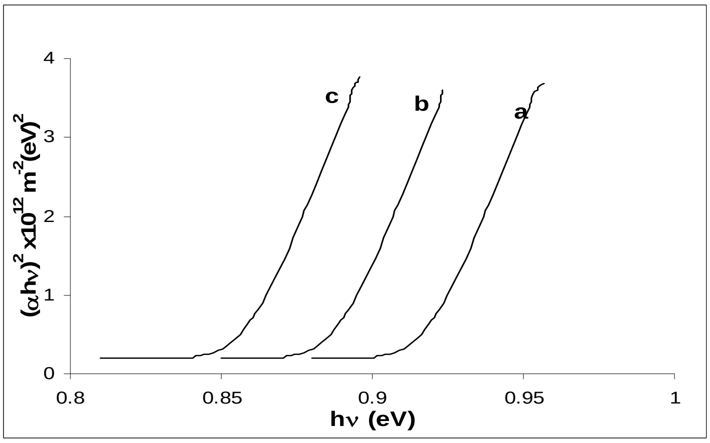

Fig. 12. Band gap plot of $CuInSe_2$ thin films deposited at substrate temperature 673K with thickness a) 405nm b) 545nm c) 755nm

The absorption co-efficient (α) has been determined and is found to be of the order of 10^4 cm^{-1}. This is in good agreement with the values reported by earlier workers [8- 10]. The electronic transition between the valance and conduction band can be direct or indirect. In these two cases, the transition of electron can be allowed as permitted by the transition probability (p) or forbidden where no such probability exists. The transition probability is given by the equation

$$(\alpha h\nu)^p = A(h\nu - E_g) \quad (1)$$

Where E_g denotes the band gap, hν the energy of the incident photon and A is a constant. The exponent p is a number which characterizes the transition process. The nature of transition and band gap E_g is determined by plotting $(\alpha h\nu)^p$ against photon energy hν. For suitable value of p the graph is a straight line and the value of E_g is obtained by extrapolating the linear portion of the graph to intercept the photon energy axis. Since there is no straight line behaviour in the plots for $(\alpha h\nu)^{2/3}$ versus hν (direct forbidden), $(\alpha h\nu)^{1/2}$ versus hν (indirect allowed), $(\alpha h\nu)^{1/3}$ versus hν (indirect forbidden), the type of transition in $CuInSe_2$ thin films is forbidden neither directly nor indirectly. The energy gap of the films has been determined by extrapolating the linear segment of the plots drawn for $(\alpha h\nu)^2$ versus hν to the energy axis. The presence of a single slope in the curves in the plot of $(\alpha h\nu)^2$ versus hν of $CuInSe_2$ thin films suggests that all the films are single phase in nature with direct allowed transition. This type of transition has been reported already by previous researchers on $CuInSe_2$ thin films [11-14].

Table .1. Optical band gap of $CuInSe_2$ Thin films.

Thickness (nm)	Substrate Temperature		
	Band gap(eV)		
	370K	523K	673K
410	1.042	0.958	0.918
550	1.016	0.924	0.886
755	0.998	0.898	0.855

Table 1. give the optical band gap of $CuInSe_2$ thin films of different thicknesses deposited at three different substrate temperatures. The range of optical band gap is found to lie between 0.85 eV and 1.04 eV. The band gap values of $CuInSe_2$ thin films are in good agreement with the band gap values reported by many earlier workers [11, 12, 14-16].

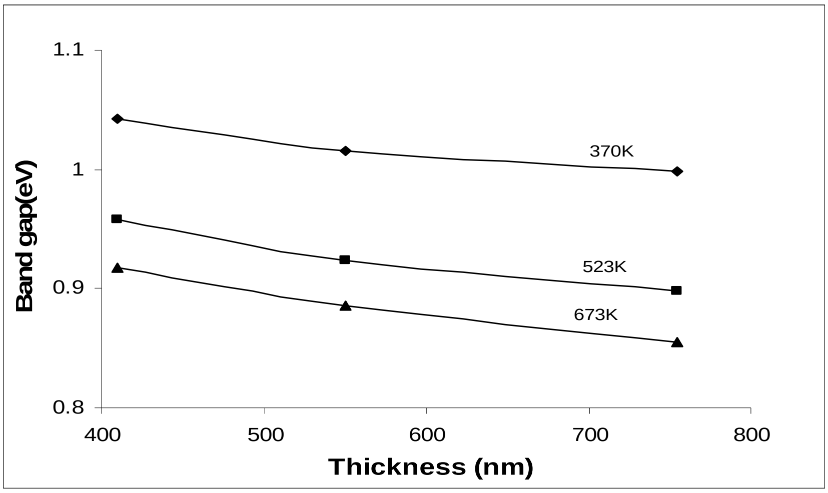

Fig. 13. The dependence of optical band gap of $CuInSe_2$ thin films on Thickness

The Fig. 13 clearly shows that as thickness of the film increases the optical band gap decreases. The decrease in energy band gap with the thickness may be attributed to an increase in particle size and decrease in strain and dislocation density. This can be further explained from the three – dimensional quantum size effect leading to a decrease of band gap with increase of particle size, which is well known for colloidal semiconductors.

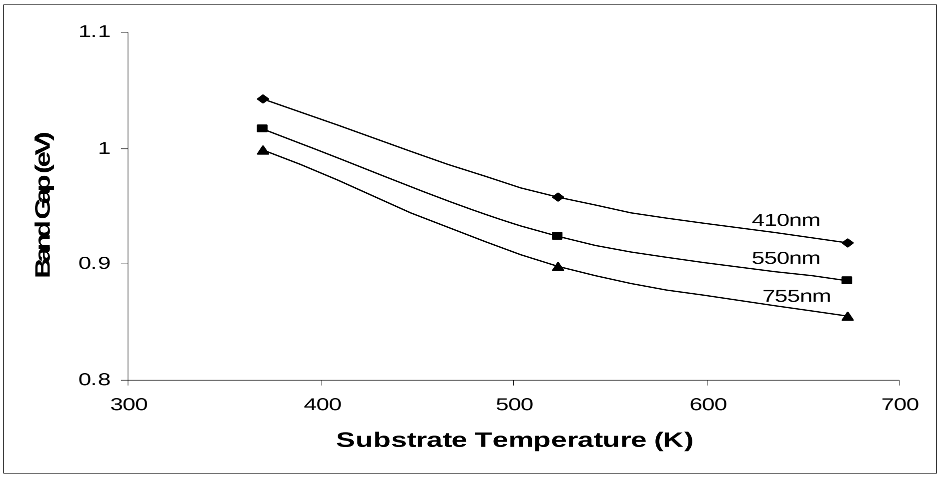

Fig. 14.The dependence of optical band gap of $CuInSe_2$ thin films on substrate temperature

The variation of optical band gap of $CuInSe_2$ thin films with substrate temperature is shown in figure 14. Films deposited at higher substrate temperatures are found to have lower band gap. This may be due to the presence of sharp band edges in the crystalline films. The decrease of band gap with the increase of substrate temperature is likely to be attributed to the increase of particle size and decrease of strain in films deposited at high substrate temperatures.

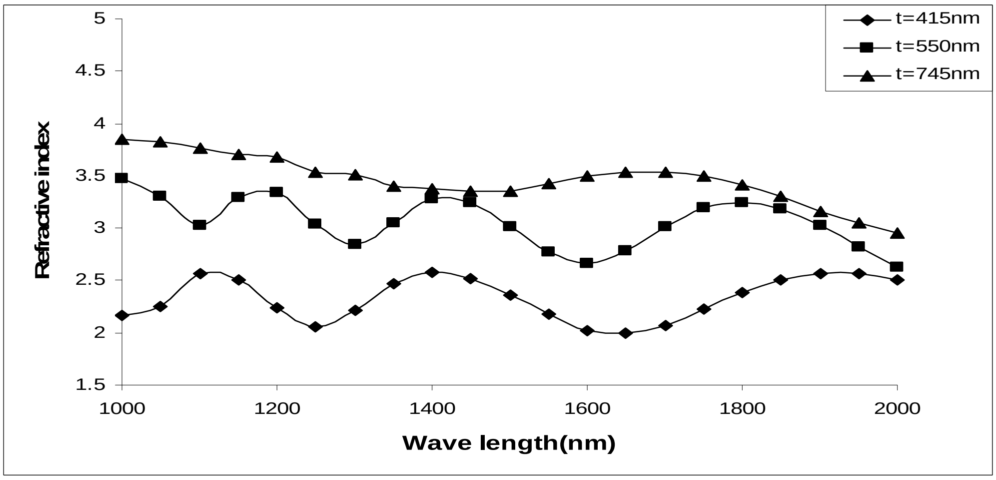

Fig. 15. The variation of refractive index of $CuInSe_2$ thin films of different thickness with the wavelength of the incident photon.

The refractive index n of the films has been determined from the transmittance value T, by fitting the experimental curves by iterative method. The variation of refractive index of the $CuInSe_2$ thin films of different thicknesses with the wavelength of the incident photon is shown in figure 15 since the refractive index of the film is highly dependent on Transmittance of light incident over the film a wavy pattern in the refractive index is observed [17]. The refractive index of the $CuInSe_2$ thin film with the thickness 415 nm is found to lie in the range from 2 to 2.58. This is in good agreement with the reported values of M.Dhanam et al. [6]. The refractive index of $CuInSe_2$ thin film of thickness 745 nm is found to decrease with the increase of incident photon wavelength. Decrease in refractive index is attributed to the strong effect of surface and volume imperfection on microscopic scale [18, 19]. The refractive index of the $CuInSe_2$ thin films is found to increase with the thickness of the film [6].

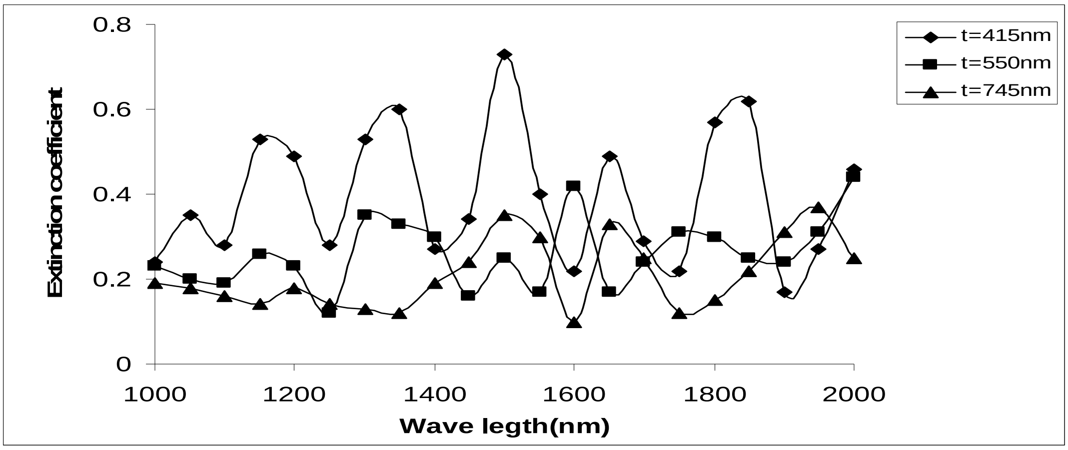

Fig. 16.The dependence of extinction coefficient of $CuInSe_2$ thin films of different thickness with the wavelength of the incident photon

Fig. 16 gives the dependence of extinction coefficient on the wavelength of the incident photon. No monotonic change is observed in the extinction coefficient of hot wall deposited $CuInSe_2$ thin film with the wavelength [17]. It is observed that the extinction coefficient of $CuInSe_2$ thin films is found to decrease with increase in film thickness.

4. Conclusion

The presence of a single slope in the curves of the plot $(\alpha h\nu)^2$ Vs. hν of $CuInSe_2$ thin films suggests that all the films are single phase in nature with direct allowed transition. The absorption coefficient has been determined and is found to be of the order of 10^4 cm^-.The band gap of the deposited $CuInSe_2$ films is found to decrease with increase in film thickness and substrate temperature. The refractive index of the $CuInSe_2$ thin films are found to decrease with increase of the incident photon wavelength.

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