تأثير درجة حرارة التلدين وسماكة الغشاء علي الخواص البصرية لأغشية الأفلام CuInSe2 الرقيقة

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الملخص العربي :

في هدا البحث أعدت أغشية CuInSe2 بطريقة التبخير التقليدية تحت التفريغ . كما أعدت الأفلام الرقيقة بسمك مختلف ودرجات حرارة تلدين مختلفة. يشير حيود الأشعة السينية إلى أن الكتل والأغشية المحضرة كانا عبارة عن خط متعدد البلورات مع طور رباعي الزوايا . أجريت الدراسة في درجات حرارة تلدين مختلفة وسمك غشاء مختلف علي الخواص البصرية لأغشية CuInSe2 الرقيقة. تظهر الثوابت البصرية (معامل التوهين ومعامل الانكسار للأغشية واعتمادها على درجة حرارة التلدين وسماكة الفيلم) كما تم الكشف عن الانتقال المباشر وغير المباشر في الأغشية المحضرة كان حوالي واحد الكترون فولت ولم يحدث تغير ملحوظ في فجوة الطاقة مع تباين الأفلام.

Effect of Annealing Temperature and Film Thickness on the Optical properties of CuInSe2Thin Films .

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Abstract

The researcher prepared CuInSe2 thin films by conventional evaporation method under vacuum . And he also prepared films at different film thickness and different annealing temperatures. X-ray diffraction indicates that the prepared bulk and films both were polycrystalline line with tetragonal phase. The study conducted at different annealing temperatures and different film thicknesses on the optical properties of CuInSe2 thin films. The Optical constants (the attenuation coefficient and the refractive index of the films and their dependence on the annealing temperature and film thickness show Direct and indirect transition. Markedly change occurred in

the energy gap due to transition detected in the prepared films that was around 1eV.No with the variation of the films.

1-Introduction

Thin films of the chalcopyrite compound CuInSe2 are promising candidates for new solar cells. The heterojunction cell with CdS shows a high efficiency of more than 10%. And excellent stabilitiy (1,2) .Several preparation methods have been proposed to obtain proper films for solar cells :Vacuum evaporation (2-4) , sputter-ing (5), spray pyrolysis(6-8), selenization of metallic film(9), electrode position (10)etc.

In the present paper ,we report the preparation of CuInSe2 films by vacuum evaporation of :its bulk crystal, synthesized from its constituent elements. The effect of the annealing temperature and the film thickness on the optical properties of CuInSe2 thin films have been investigated.

2-Experimental details

2-1.Film preparation:

CuInSe2 was prepared from its constituent elements of purity 99.999% .The elements in its stoichiometric proportions were placed in silica tube.10 gr. Of CuInSe2 were sealed in a fused silica tube under a vacuum (10-4 .Torr) and kept the ampoule in a rotating oven at sufficiently elevated temperature, at first , slowly to 473 k for 30 minutes and at 573k for 30 minutes until all the selenium vapor disappeared .This was necessary to avoid explosive reactions, particularly between indium and selenium. As the temperature is raised , selenium vapor becomes visible and it disappears abruptly when the selenium was all reacted. When this has occurred, the furnace temperature was safely raised to 1323 k for 8 hours and at (1073, 1023 ,973 ,923, 873 and 823 k) each for $^1/_2$ hour the constituents became molten; the rocking motion ensures that thorough mixing of the mixture take place. Finally the tube wasleft to cool to room temperature.

Prepared CuInse2 films deposited by vacuum evaporation in a coating unit model E.306A EDWARD CO.

2.2-Measurements :

Thethickness of thefilms determined using Zeiss leinkmicklessoninterferometer (11) and was found to be (107-254-688-749-1118) nm.

X-ray diffraction(XRD) analysis of the as- prepared powder and as- deposited films was carried out using X-ray diflractometer (Philips PW1730) with Cu(kα) radiation,($1.54A^0$)

The reflection and the transmission of the films was measured at room temperature using (jassco) spectrophotometer in the wave length range (2500-190 nm).

3-Results and discussion.

X-ray diffraction patterns were obtained for as-prepared $CuInSe_2$in powder form and XRD show that $CuInSe_2$ has tetragonal polycrystalline structure with (122)preferred crystal orientation. X-ray pattern for the prepared powder is shown in Figure (1a). The as deposited films with the substrate at room temperature appeared to be of a mixed amorphous-microcrystalline nature. Figure (1.b) and figure (1.c) show XRD pattern of deposited $CuInSe_2$ films at room temperature, and annealed at 723k respectively.

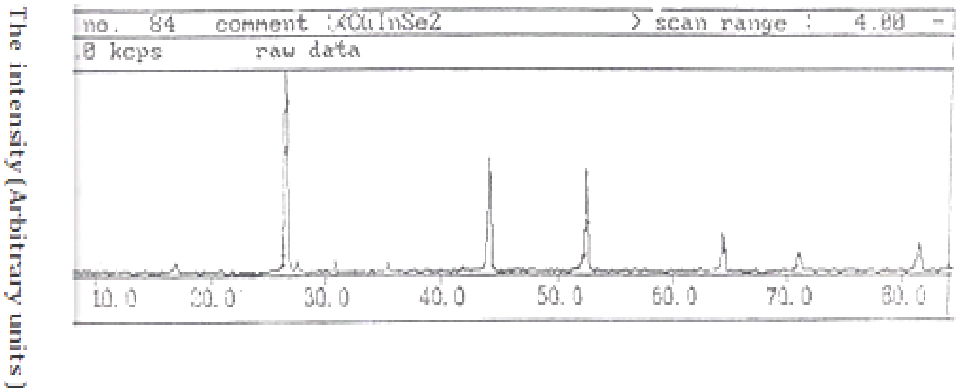

Fig (1-a) X – ray diffraction pattern for the prepared powder

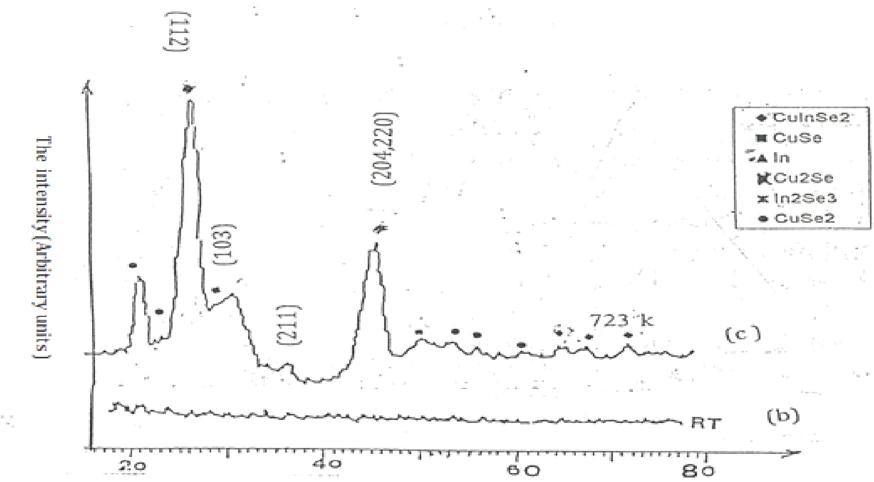

Fig (b, c) x- ray diffraction pattern for $CuInSe_{2\,thin}$ films with thickness (441nm) annealed

(a)- As deposited, (b-) annealed at 723k.

3.1-Optical properties:

Figures (2,3) show the reflection (R) versus wavelength (λ) for $CuInSe_2$thin films with different film thickness (188,352,419 and 526 nm)and at different annealing temperatures (473,573,673 and 723k) respectively.

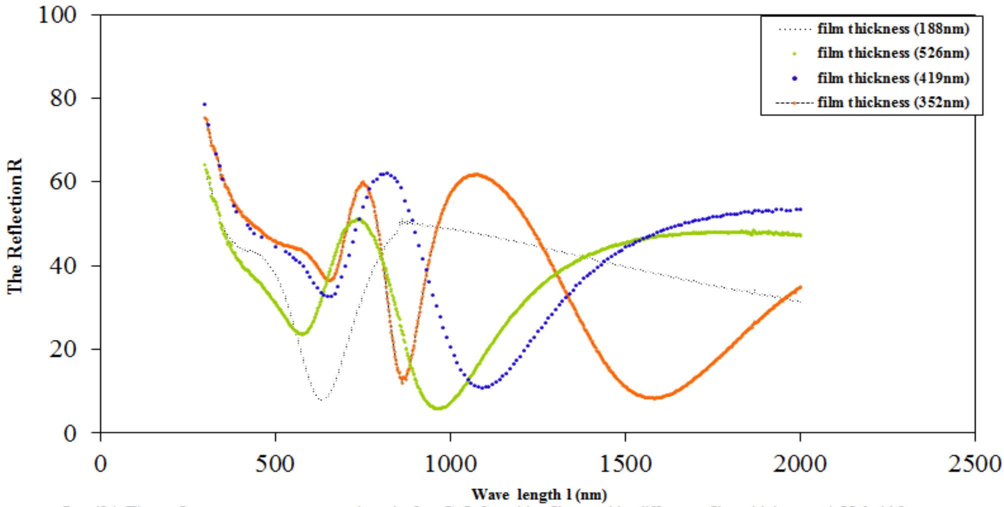

fig. (2) The reflectance versus wave length for $CuInSe_2$ thin films with different film thickness (526-419-352 and 188nm)

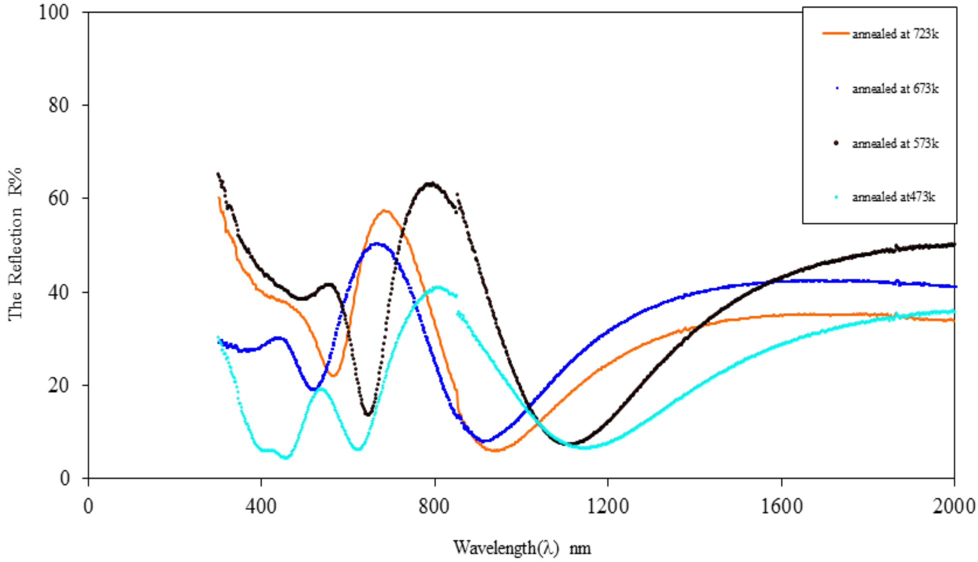

fig.(3) The reflection of $CuInSe_2$ thin films with thickness 577nm at different annealing temperatures(723-673-573-473k)

Figure (4) shows thetransmission (T) versus wavelength (λ) for different film thickness (188,352,419 and 526 nm)and it is clear that the transmission decreases with the increase of the film thickness.Figure (5) show the transmission versus wavelength at different annealing temperatures (473,600,673 and 723k).After annealing, the optical transmission for all the films increases . The increase of the annealing temperature makes the band edge more sharp and shifts it toward long wavelength. This is due to the improved crystallinity of the films.

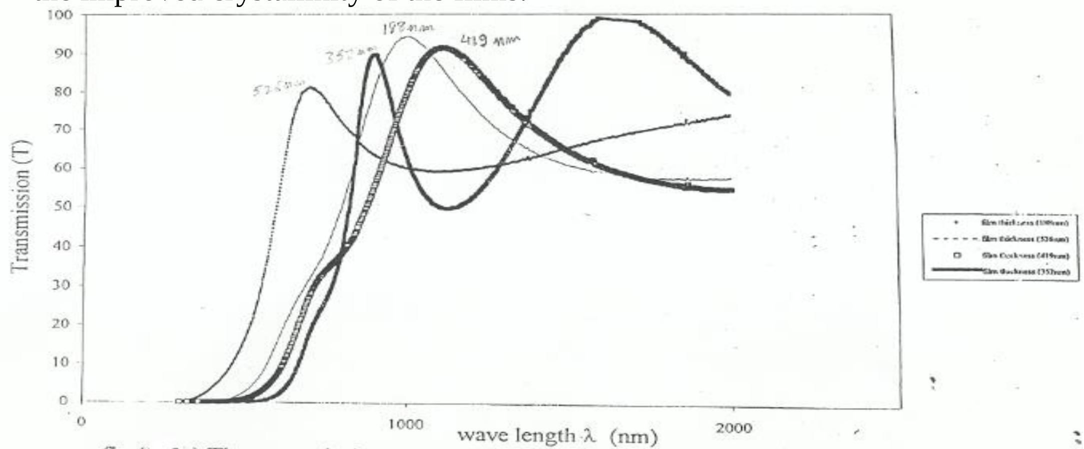

fig.(4) The transmission versus wave length for CuInSe2 thin films with different film thickness (526-419- 352 and 188nm)

3.2-Optical Transition in CIS films

The absorption coefficient(α) has been calculated from the thickness of the film and the transmission curve ,using the following equation as reported(12),

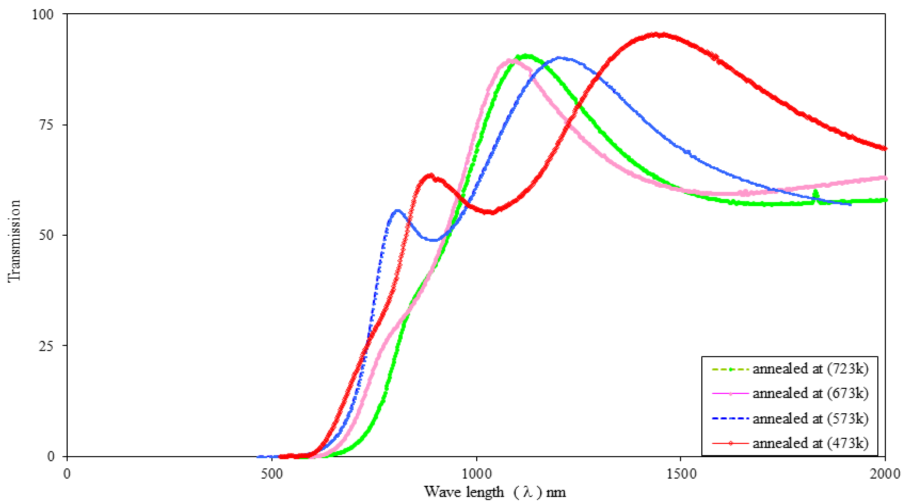

fig.(5) The transmission versus wavelength for $CuInSe_2$ thin films with thickness 577nm and annealed at (723,673,573 and 473k)

$$\alpha=\frac{\ln\frac{I_0}{I}}{t} \qquad (1)$$

Where I_0 and I are the intensities of the incident and the transmitted radiation respectively,(t) is the film thickness.

The interband absorption theory shows that near the optical absorption band edges, the absorption coefficient satisfies the relation:

$$\alpha h\upsilon=A_r(h\upsilon-Eg)^r \qquad (2)$$

A_r is a constant and Eg is the energy gap for direct transition ($r={}^1/_2$) and in this case Eg is the energy of the optical direct gap .For the indirect allowed transition (r=2) and where Eg now will be the energy of the indirect gap.

The experimental curve linearity:

$$(\alpha h\upsilon)2 =A^2_{1/2}\ (h\upsilon-Eg)\mathbf{(3)}$$

The absorption coefficient α_d due to the direct transition is calculated from equation (3)

The values of α_d (The absorption coefficient in the direct transition) is differ greatly fromα calculated from equation (1) .This difference can be explained by another contribution .The plot of the relation

$$(\alpha h\upsilon)^{1/2} = A_2^{1/2}(h\upsilon - Eg) \qquad (4)$$

Gives the value of Eg ,the indirect gap in the indirect transition . α_i the absorption coefficient in the indirect transition is now computed from the relation (4) .

The total absorption coefficient is given by the relation(5),as reported(13),

$$\alpha_t = \alpha_d + \alpha_i \quad (5)$$

Figures (6) showsIn (α) versusln ($h\upsilon$) for $CuInSe_2$ thin films annealed at 723k thin films respectively. The graph indicates the existence of more than one type of optical transitions ,and fits the absorption coefficient given by the equation (1) ,indicating a contribution of both direct and indirect transitions(12,14) .

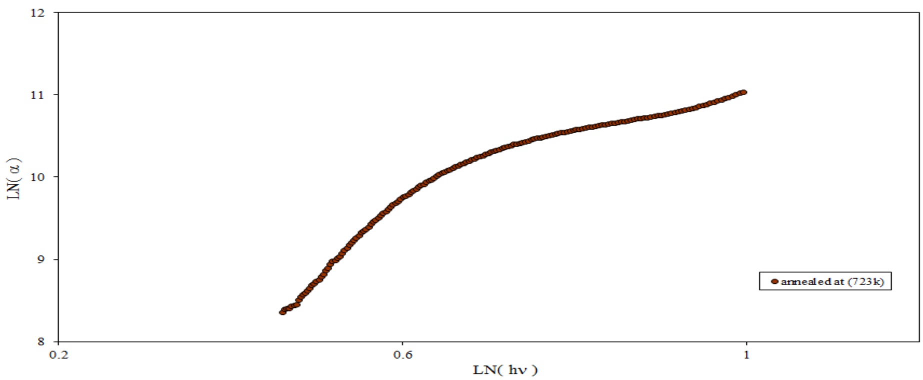

fig.(6) The plot of LN(α) versus LN($h\nu$) for $CuInSe_2$ thin films with thickness (577nm) and annealed at (723k)

The direct energy gap can be calculated using equation (3).Therefore, The direct and indirect energy gap studied for $CuInSe_2$ with thickness577 nm and annealed at different annealing temperatures473,600,673 and 723. The direct and indirect energy gap for as deposited $CuInSe_2$ thin films with thickness (188,352,419,577 nm) were also studied. The plot of $(\alpha h\upsilon)^2$ against $h\upsilon$ is found to have linear region and extrapolation of the straight line region to (α=0), gives E_g ,as shown in figures(7,8).

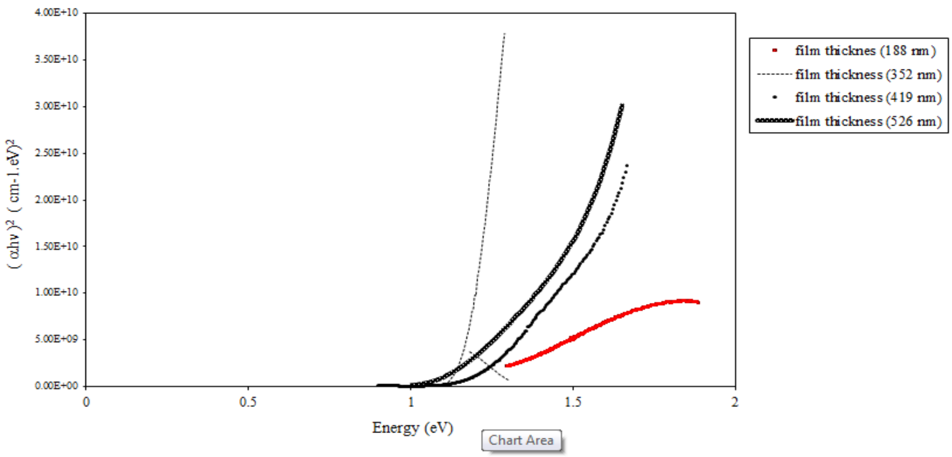

fig.(7) The variation of (αhν)^2 with energy for $CuInSe_2$ thin films with different film thickness

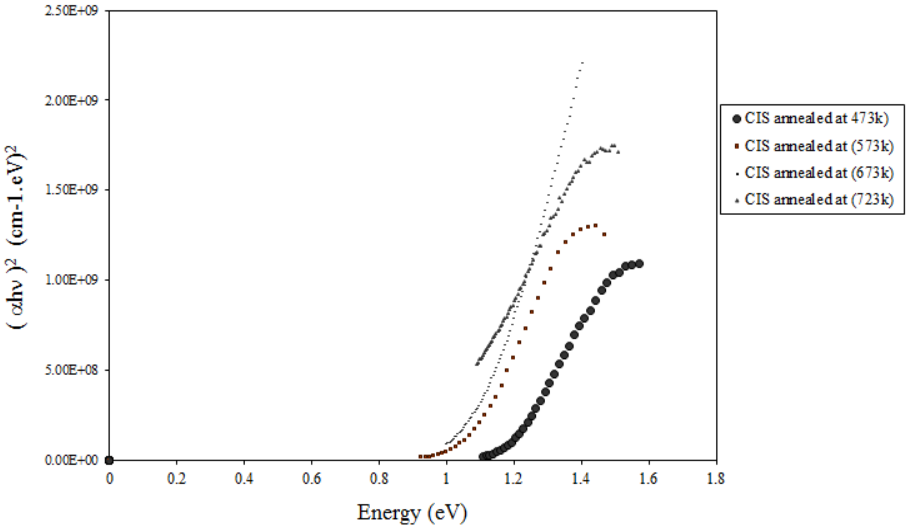

fig.(8) The variation of (αhν)^2 with energy for $CuInSe_2$ thin films having thickness (577 nm) and annealed at (473,573,673 and 723k)

The indirect energy gap can be calculated using equation (4).The plot of $(\alpha h\upsilon)^{1/2}$ against hυ is found to have linear region and extrapolation of the straight line region to (α=0) gives Eg, as shown in figures (9,10).

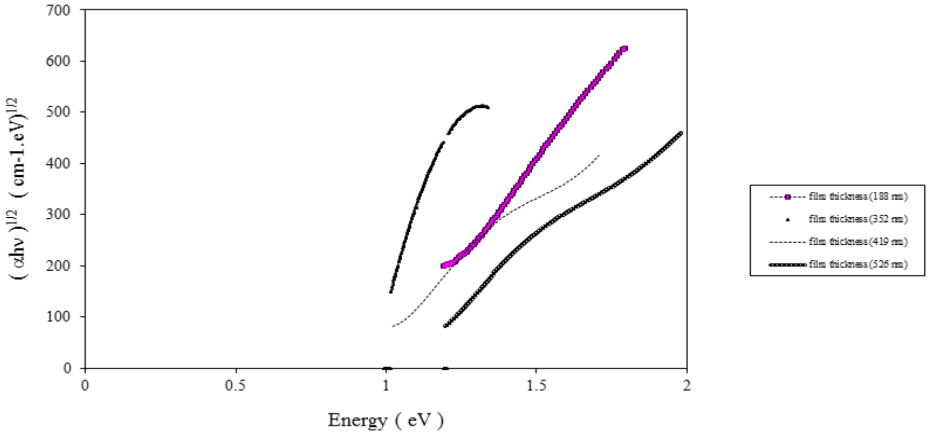

fig.(9) The variation of ($\alpha h\nu$)$^{1/2}$ with energy for $CuInSe_2$ thin films with different film thickness

A decrease of the band gap was observed for annealed films as reported by others(15) .This may be due to electron –electron and electron-impurity interaction.The energy gap has been calculated and tabulated in table (1) and table (2).

The annealing temperature (k)	***Direct(*Eg*)* *(e v)***	***Indirect(*Eg*)* *(e V)***
473	***1.18***	***1.02***
600	***1.06***	***0.96***
673	***1.03***	***0.93***
723	***0.98***	***0.84***

Table (1) the values of direct and indirect energy gap for annealed CuInSe2 thin films with thickness (577 nm), at different annealing temperatures.

The film thickness (nm)	***Direct(*Eg*)* *(e v)***	***Indirect(*Eg*)* *(e V)***
188	***1.24***	***0.97***
352	***1.23***	***0.97***
441	***1.24***	***0.98***
749	***1.24***	***1.03***

Table (2) the values of direct and indirect energy gap for as deposited CuInSe2 thin films with different film thickness.

The tables show the values of direct and indirect energy gap for CuInSe2 thin films. From the results, one notice that no detectable change in the values of direct and indirect energy gap for CuInSe2 thin films with different film thickness .This means that, the energy gap is independent on the film thickness. On the other hand, increasing the annealing temperature for CuInSe2 thin films with thickness (577 nm) and annealed at 473,600,673 and 723 k, both direct and indirect energy gap decrease . This behavior could be attributed to the improvement of the film structure by increasing the annealing temperature.

3.3-**Optical Constants of CuInSe2 Thin Films.**

The values of the transmittance,T, and reflectance, R, together with film thickness, t, were used to determine the components of the complex refractive index. A computer program, utilizing an iteration method, was used in calculating n(λ) and k(λ).Figure (11) represents the spectral dependence of n(λ) for CuInSe2 thin films with different film thickness (577,419,352 ,and 188 nm). The dispersion curve is flat above (1200 nm), normal dispersion and shows anomalous dispersion towards the shorter wavelength.

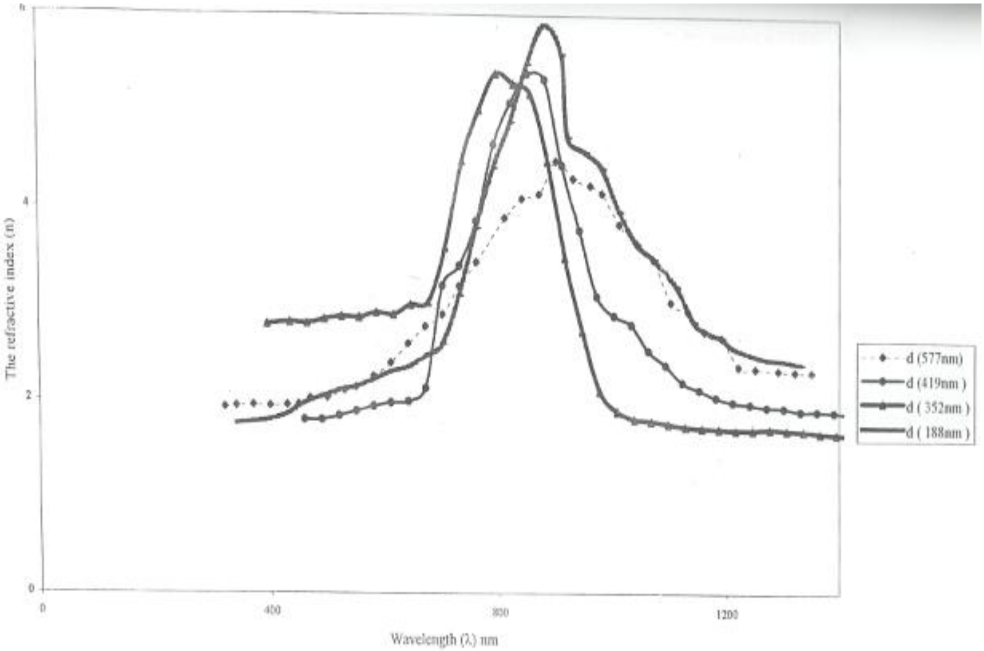

fig.(**11**) The variation of the refractive index with wavelength for as deposited $CuInSe_2$ thin films with different film thickness

Figure (12) shows the variation of the refractive index(n) , with the wavelength , λ, in spectral range 350 to 1600 nm for CuInSe2 thin films with thickness 577 nm, and annealed at different annealing temperatures (473k, 600k,673k and 723 k) respectively . It Is observed that the dispersion curves of (n) for allsamples have the same behavior.

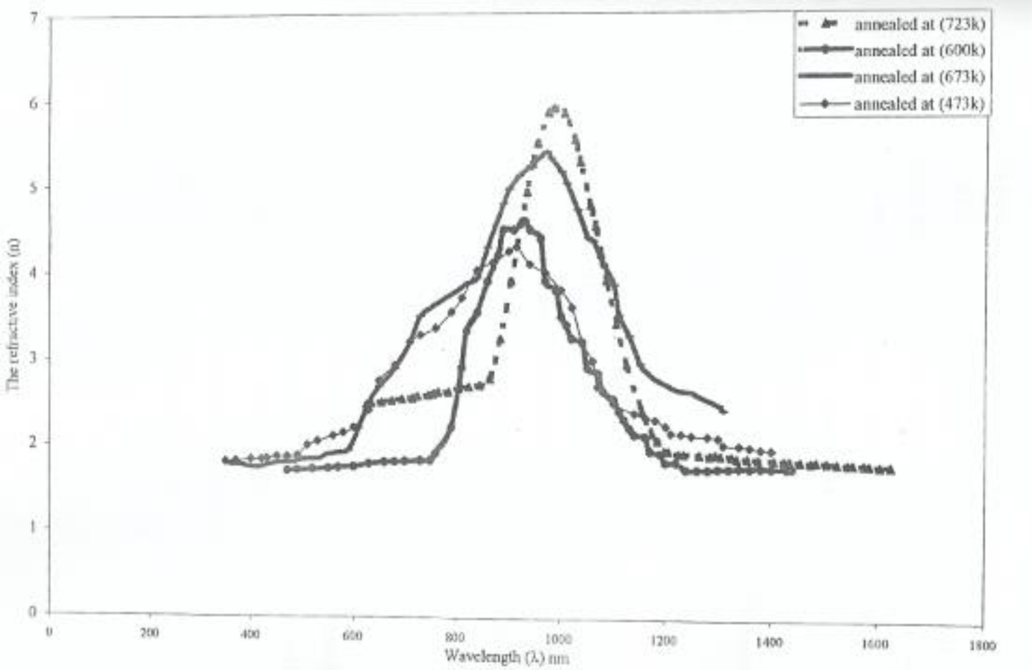

fig.(**12**) The variation of the refractive index with wavelength for CuInSe2 thin films with thickness (577nm) at different annealing temperature

The peak that appears in the spectral distribution of the refractive index is due to the rapid increase in the absorption mechanism in the fundamental absorption edge. The results shows that for each sample the refractive index attains a peak value at wavelength,λpeak , which shifts towards longer wavelengths as the annealed temperature increase.

At longer wavelength λ> 1200 nm all the curves reach to normal dispersion.

The absorption coefficient (α) for the medium is defined by the condition that energy in the wave falls to (1/e) in a distance α. The attenuation coefficient (k) obtained from the absorption coefficient (α) as reported (16),

$\alpha=(4\pi\ k)/\lambda$ (6)

Where λ is the wavelength in free space. Measurements of the transmission through CuInSe2 thin films used to determine (α) and k. For all the films , it is found that the attenuation coefficient decrease with increasing the wavelength.

Figures (13,14) show the variation of the absorption index with wavelength for both as deposited CuInSe2 thin films at differekt film thickness and annealed CuInSe2 thin films at different annealing temperatures respectively.

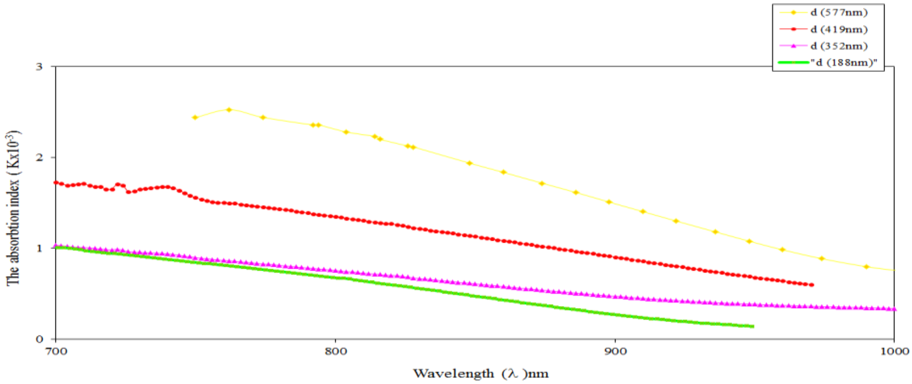

fig.(13) The variation of the absorbtion index with the wavelength for as deposited $CuInSe_2$ thin films with different film thickness

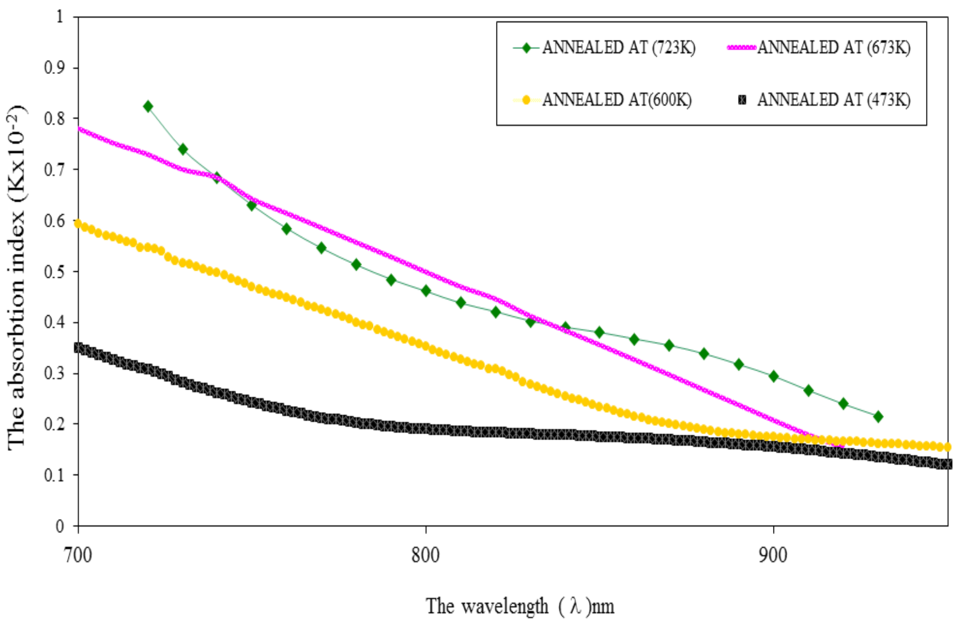

fig.(14) The variation of the absorbtion index with wavelength for $CuInSe_2$ thin films with thickness 577nm annealed at (723,673,600 and 473k)

The refractiveindex(n) shown in figure(13)was found from the reflectivity of the material and the attenuation (extinction)coefficient using the relation (7) as reported by Tembhurkaretal(12).

$$R=\frac{(n-1)2+k^2}{(n+1)2+k^2} \qquad (7)$$

From the [illegible]n coefficient and the refractive index, ε^- and $\varepsilon^=$ [illegible]uced (15) .

$$\varepsilon^- = n^2 - k^2 \qquad (8)$$

$$\varepsilon^= = 2nk \qquad (9)$$

Conclusion

The optical properties have been studied in relation with the annealing temperature and film thickness. X-ray diffraction patterns were obtained for as-prepared $CuInSe_2$in powder form and XRD show that $CuInSe_2$ has tetragonal polycrystalline structure with (122)preferred crystal orientation. The thetransmission (T) versus wavelength (λ) for different film thickness (188,352,419 and 526 nm) decreases with the increase of the film thickness. The increase of the annealing temperature makes the band edge more sharp and shifts it toward long wavelength. This is due to the improved crystallinity of the films.

The optical constants (refractive index, and distinction coefficient),were obtained from reflection and transmission measurements in the range (350-1600 nm).

A graphical representation of In (α) Vs In (hυ) indicate the existence of both direct and indirect transition .Direct and indirect transition were detected in the prepared films. It was around 1 eV . The observed absorption coefficient variation is due to direct transition with an energy gap in the range 0.97-1.26 eV , and an additional indirect transition with an energy in the range 0.84-1.03 eV . The deduced values are in good agreement with the values reported for CuInSe2 thin films (17) .No markedly change occur in the energy gap with the variation of the film thickness. On the other hand a decrease in the energy gap occur with increasing the annealing temperature.

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