Annealing Effects on the Structural and Optical Parameters of $Cu_3In_{17}Se_{80}$ Thin Films

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$Cu_3In_{17}Se_{80}$ thin films were prepared by thermal evaporation technique on glass and quartz substrates. X-ray diffraction analysis for the as-deposited and annealed thin films at 423K and 473 K showed that they have amorphous structure nature. The optical constants (refractive index n and absorption index k) of the as-deposited and annealed films for several samples of different thickness (from 11 nm to 61.4 nm) have been calculated from optical transmittance and reflectance data in the wavelength range 400-2500 nm. Analysis of the refractive index, n, yields high frequency dielectric constant of 8.24 for the as-deposited films which increases with annealing. The optical transitions from absorption coefficient (α) analysis are found to be allowed indirect for the as-deposited and annealed films, and the corresponding energy gap is 1.1 eV for the as-deposited films, which increases with increasing annealing temperature.

1. Introduction

In-Se and Se-Te alloys have recently gained much importance as these alloys are found to be more photosensitive, harder, have a higher glass transition and crystallization temperatures and a smaller ageing effect than amorphous Se [1]. The structure of In-Se films with different Se percentage was studied by different authors [2-5]. The structure and physical properties of $In_{20}Se_{80}$ films were studied [1,6]. It was found that $In_{20}Se_{80}$ films have amorphous structure with optical indirect energy gap of 1.76 eV [1]. The direct current conductivity in this material exhibited a transition from ohmic to square law behavior at high voltages. The photoconductivity was studied for the $In_{20}Se_{80}$ films [6] and it was found from the temperature dependence of steady-state photocurrent and dark current that they are thermally activated processes.

The effect of an impurity in an amorphous semiconductor may be widely different, depending on the conduction mechanism and the structure of the material [7]. While in crystalline semiconductors the effect of a suitable impurity is always to provide a new donor or acceptor state, this is not essential in amorphous semiconductors [8]. Several authors have been investigated the effect of impurities of different metals in the physical properties of In-Se in crystalline states [9-15]. No available literature on the effect of Cu doping on amorphous $In_{20}Se_{80}$ films.

In this work the structural and optical parameters of as-deposited and annealed $Cu_3In_{17}Se_{80}$ films were investigated. For this purpose $Cu_3In_{17}Se_{80}$ films of different thicknesses were prepared by thermal evaporation technique. X-ray diffraction and energy dispersive X-ray (EDX) spectroscopy studies have been carried out to get an idea of the structure of as-deposited and annealed films. The optical properties deduced from optical transmittance and reflectance data at room temperature for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films of different thicknesses were studied. The data are analyzed to determine the optical constants (refractive index n, absorption index k and absorption coefficient α). An analysis of the absorption coefficient has been carried out to obtain the optical band gap and determine the nature of the transition involved.

2. Experimental Procedure

$Cu_3In_{17}Se_{80}$ in bulk form were prepared by the melt-quenching method of the constituent elements. $Cu_3In_{17}Se_{80}$ films were obtained by thermal evaporation of powder using a high vacuum plant (Edward type E306 A) on well-cleaned glass and quartz substrates of suitable dimensions from molybdenum boat. The vacuum pressure was maintained at around 10^{-4} Pa. Samples with different thicknesses ranged from 11 nm to 61.4 nm were prepared. The rate of evaporation is kept constant at 6 nms^{-1} during evaporation. The film thickness was measured using thickness monitor (model FTM4 Edwards) during evaporation process and confirmed by interferometric method. The optical transmittance and reflectance of the samples were measured at room temperature using unpolarized light at normal incidence in the wavelength range 400-2500 nm using a dual beam spectrophotometer (UV-3101 PC Shimadzu). Samples were annealed in air at different temperatures of 423 K and 473 K under vacuum =10^{-3} torr. X-ray diffraction characterization of obtained films was carried out using filtered CuK_{α} radiation (Philips PM8203) operated at 40 kV and 25 mA. The chemical composition of the obtained films was checked by energy dispersive X-ray analysis (EDX) using scanning electron microscope (Joel 5400). All measurements reported here were carried out at room temperature.

3. Results and Discussion

Structural properties

Dispersive X-ray analysis (EDX) spectrum was obtained for samples of different thicknesses and the composition was found to be the same for all thicknesses and Fig.(1) represented one of these thicknesses as a representative example. It showed that the composition of the obtained as-deposited films under investigation is approximately $Cu_3In_{17}Se_{80}$ as shown in Table(1). X-ray diffraction pattern obtained for the as-deposited films indicated that it has amorphous structure nature as indicated in Fig.(2). The amorphous structure of the as-deposited films on substrate kept at room temperature is expected because the evaporated molecules precipitate randomly on the surface on the substrate and all the following condensed molecules also adhere randomly leading to disordered films of increased thickness. The loss of adequate kinetic energy for the precipitated molecule keeps them unable to orient themselves to produce the chain structure required for the crystalline structure of $Cu_3In_{17}Se_{80}$. The internal stresses generated in the layers of the film due to the continuous deposition of the hot molecule on the cold predeposited layers increase both the disorder and the degree of randomness which in turn lead to amorphous films whatever is their thickness when formed at room temperature.

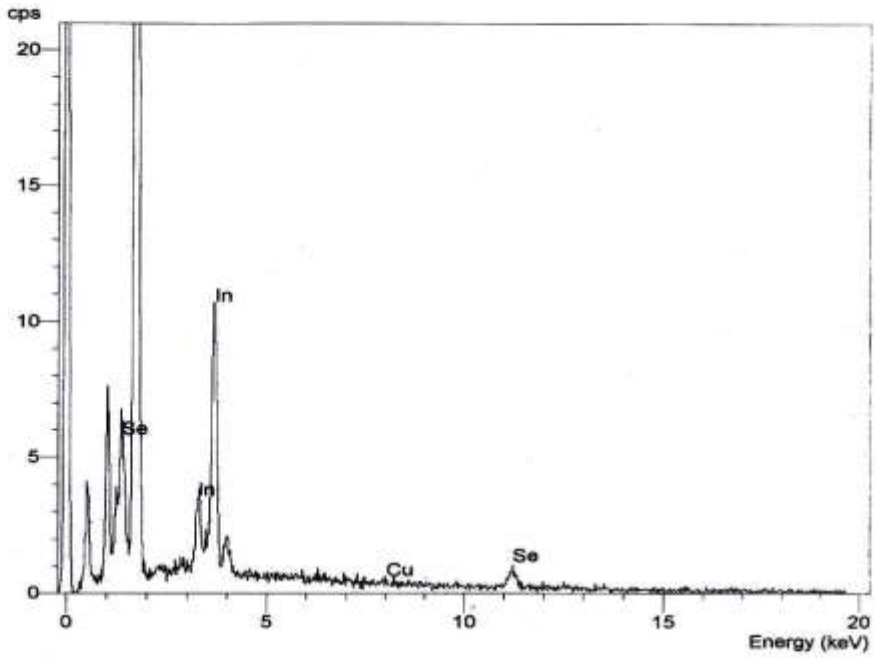

Fig.(1): Energy dispersive X-ray (EDX) spectrum of $Cu_3In_{17}Se_{80}$ film of thickness 61.4 nm (as representative example).

Table(1): EDX spectrum analysis for the investigated films

Element	at %		
	As-deposited	Annealed at 423 K	Annealed at 473 K
Cu	3.05	3.02	2.98
In	17.04	17.04	17.06
Se	79.91	79.94	79.96

To investigate the effect of annealing on the structure $Cu_3In_{17}Se_{80}$ films, samples were annealed for 2h at 423 K and 473 K. EDX spectrum analysis for the annealed samples improve that composition does not practically change with annealing as indicated in Table(1). Fig.(2) shows X-ray diffraction pattern obtained for $Cu_3In_{17}Se_{80}$ films annealed at 423 K and 473 K. It is indicated that films still have amorphous structure nature. Annealing at temperature 473 K leads to change in the shape and thickness of the films due to partial evaporation of films from substrate.

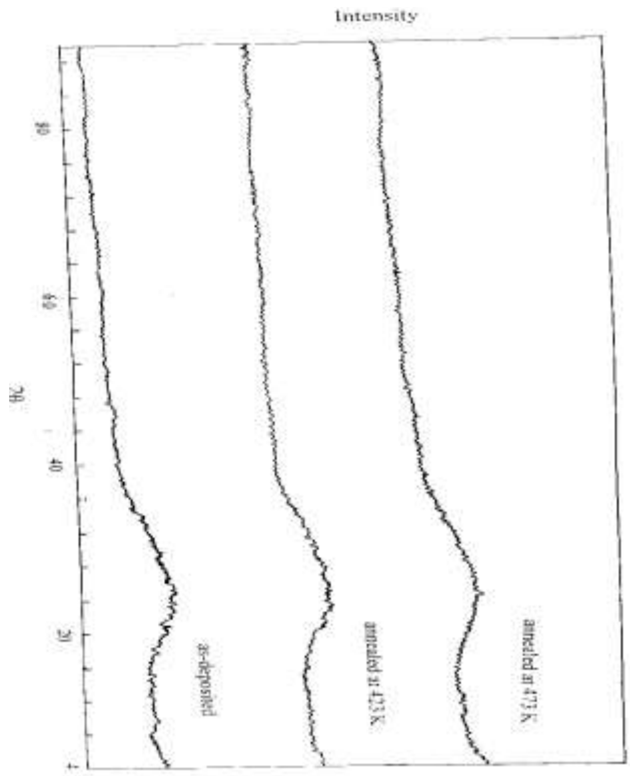

Fig.(2): X-ray diffraction patterns of as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

3.1. Optical properties

3.1.1. Determination of optical constants

Fig.(3,4 and 5) show the spectral distribution of transmittance (T) and reflectance (R) for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films of different thicknesses. It is indicated that at longer wavelengths T+R equals 1 indicating that films are transparent in these ranges and no light is absorbed. It is indicated also that there is a noticeable change in the date of transmittance and reflectance by annealing.

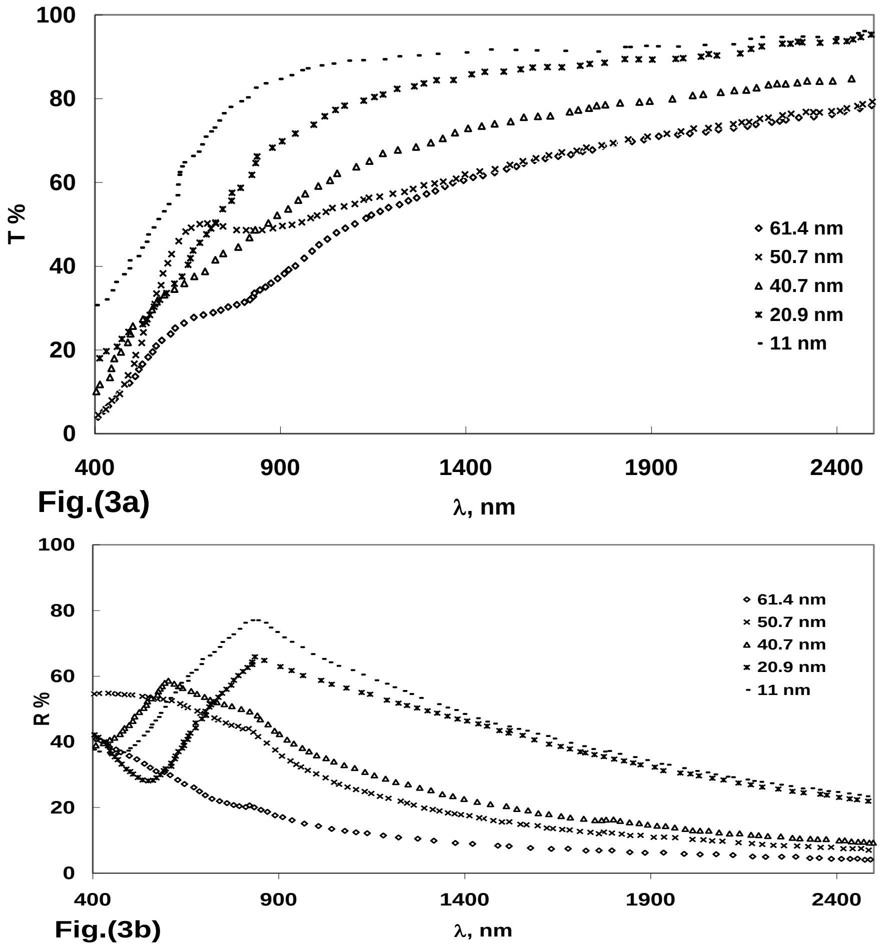

Fig.(3): The spectral distribution of a) transmittance (T) and b) reflectance (R) for as-deposited $Cu_3In_{17}Se_{80}$ films of different thicknesses

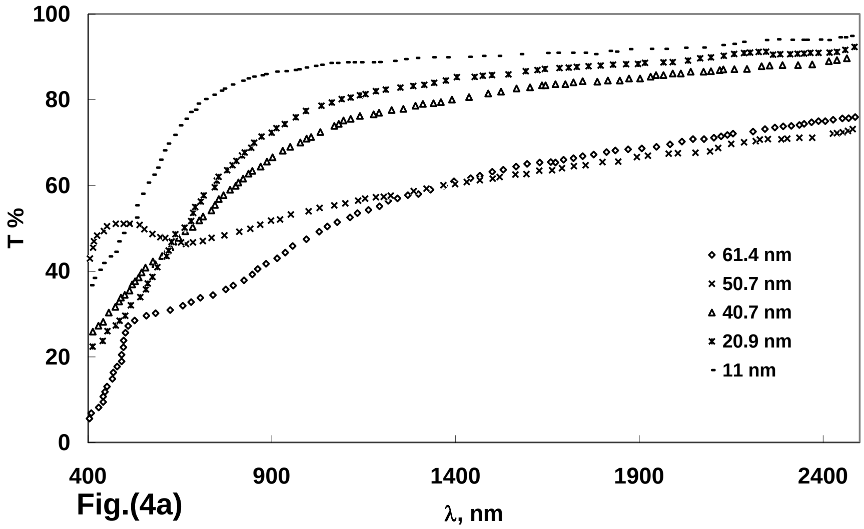

Fig.(4a)

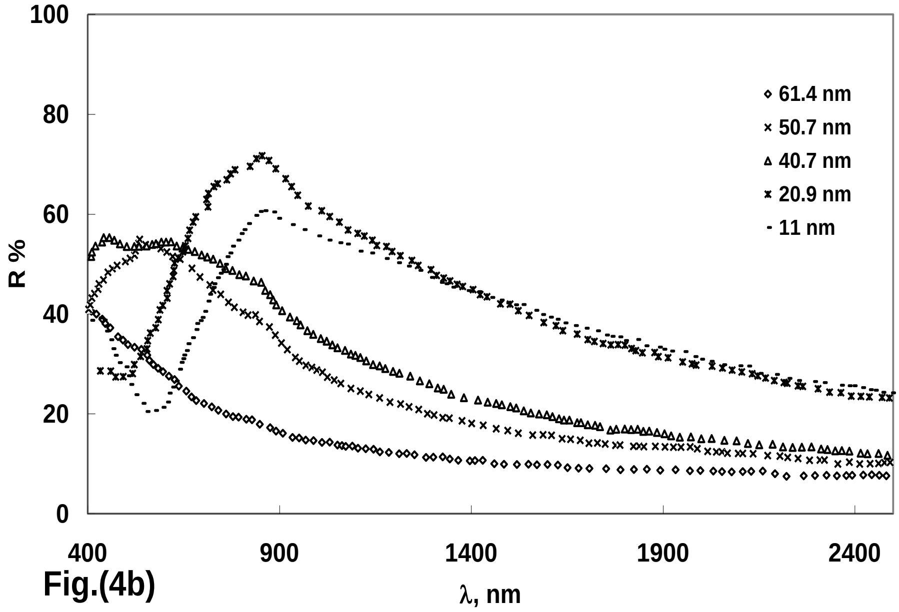

Fig.(4b)

Fig.(4): The spectral distribution of a) transmittance (T) and b) reflectance (R) for $Cu_3In_{17}Se_{80}$ films of different thicknesses annealed at 423 K.

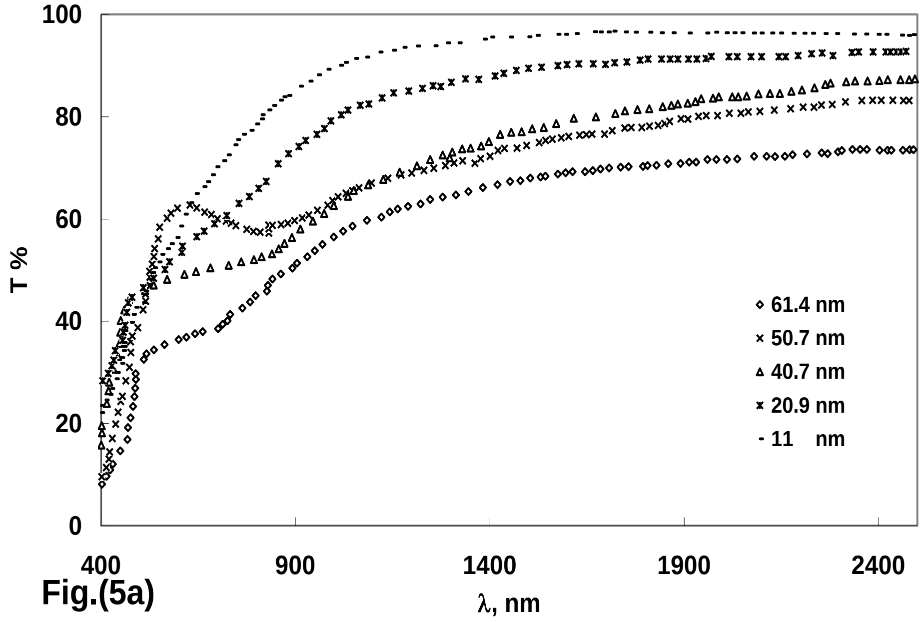

Fig.(5a)

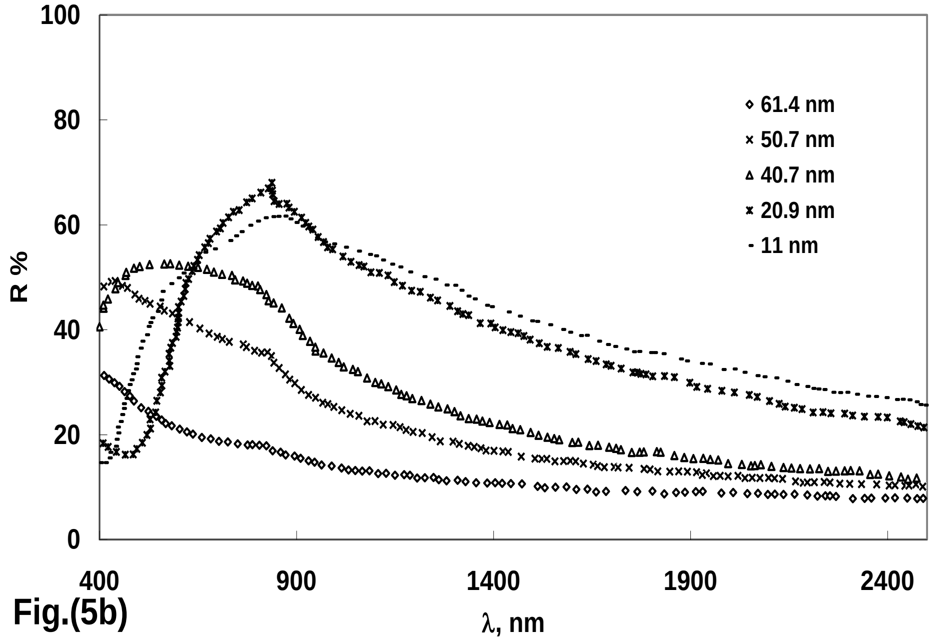

Fig.(5b)

Fig.(5): The spectral distribution of a) transmittance (T) and b) reflectance (R) for $Cu_3In_{17}Se_{80}$ films of different thicknesses annealed at 473 K

In order to obtain accurate values of the optical constants (the refractive index (n) and the absorption index (k)) for the as-deposited and annealed $Cu_3In_{17}Se_{80}$ films, Murmann's exact equations [16] have been applied in conjunction with a special iterative computer program. This method requires approximate values of refractive index (n_a) and absorption index (k_a). Values of n_a and k_a can be obtained using Swanepoel method [17]. Using the experimental values of transmittance (T) and reflectance (R) and the approximate values for n and k, it is easy to solve Murmann's exact equations for transmittance and reflectance simultaneously to obtain the accurate values of n and k.

The spectral distribution of the mean value of both n and k for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films of different thicknesses are given in Fig. (6a,b). The maximum scatter between the data of the films of different thicknesses lies within the range of experimental error ±2.5% for n and ±4.5% for k on average. Accordingly both n and k are practically independent of the film thickness in the range (11 to 61.4 nm). As observed, the refractive index shows anomalous dispersion in the lower wavelength range. For wavelengths greater than 1200 nm the refractive index has normal dispersion.

The real ($\varepsilon_1=n^2-k^2$) and imaginary ($\varepsilon_2=2nk$) parts of dielectric constant were determined at different wavelengths from the obtained data for the refractive index (n) and absorption index (k). Fig. (7) shows the spectral distribution of ε_1 and ε_2 . It is clear that, the values of real part of the dielectric constant for annealed films are higher than that of the as-deposited films and in general the real part values are greater than that of the imaginary part this is most likely due to the reduction spaces between islands.

3.1.2. Analysis of refractive index (n)

The obtained data of refractive index n can be analyzed to obtain the high frequency dielectric constant via two procedures [18]. In the first procedure, the square of refractive index n^2 is plotted versus λ^2 as in the equation: $n^2 = \varepsilon_\infty - (e^2 N / \pi C^2 m^*) \lambda^2$, where e is the charge of electron, N is the free charge carrier concentration, C is the speed of light and m* is the effective mass of electron. This relation is shown in Figures (8a) for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films. It is observed that the dependence of n^2 on λ^2 is linear at longer wavelengths. Extrapolating the linear part of this dependence to zero wavelength gives a value of ε_∞ for the investigated films. These values are given in Table (2). In the second procedure the high frequency dielectric constant can be calculated using the following simple classical dispersion [18]. If n_o is the refractive index of an empty lattice at infinite wavelength, the index will vary as:

$$(n_o^2 - 1)/(n^2 - 1) = 1 - (\lambda_o / \lambda)^2 \qquad (1)$$

where λ_o and n_o are evaluated from plots of $(n^2\text{-}1)^{-1}$against λ^{-2} as shown in Fig. (8b) for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films. Values of $n_o^2 = \varepsilon_\infty$ and λ_o are given also in Table (2). Values of ε_∞ obtained by both procedures are in good agreement with each other as given in Table(2). It is indicated also from the table that ε_∞ increases with annealing.

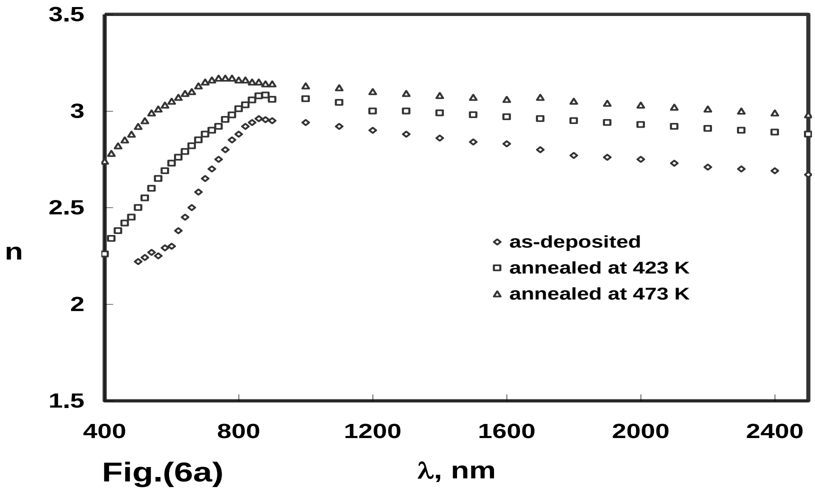

Fig.(6a): Dispersion curves of refractive index (n) for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

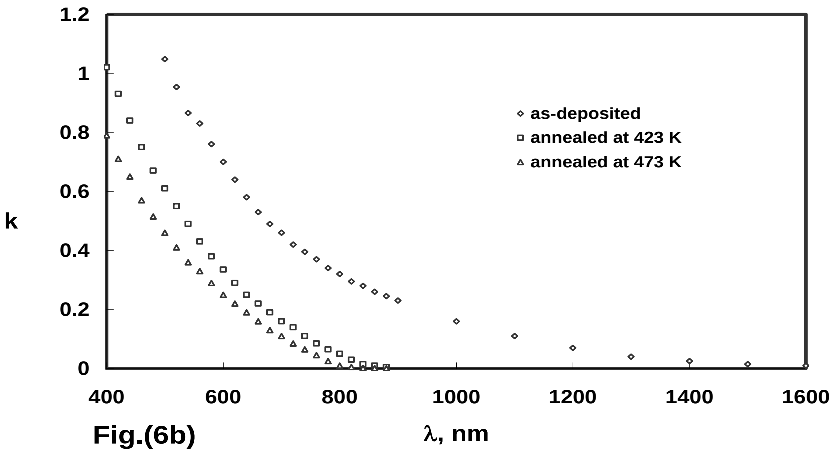

Fig.(6b): Dispersion curves of absorption index (k) for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

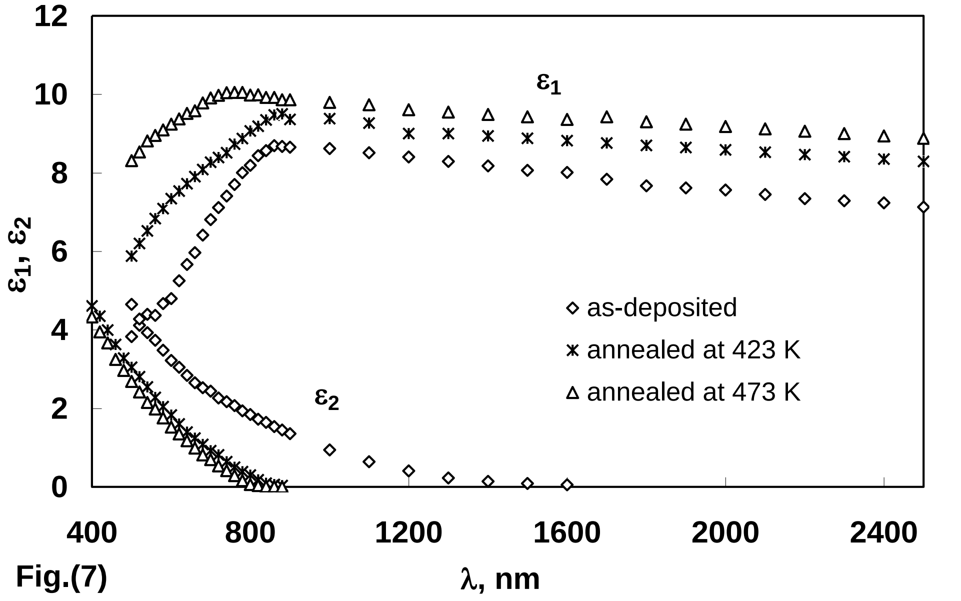

Fig.(7): The spectral distribution of dielectric components for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

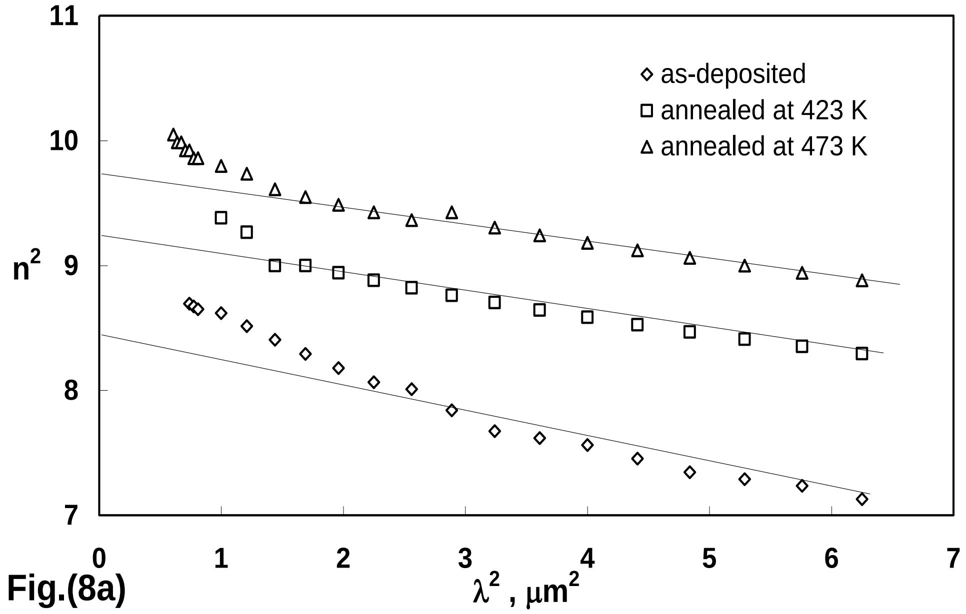

Fig.(8a): The variation of n^2 with λ^2 for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

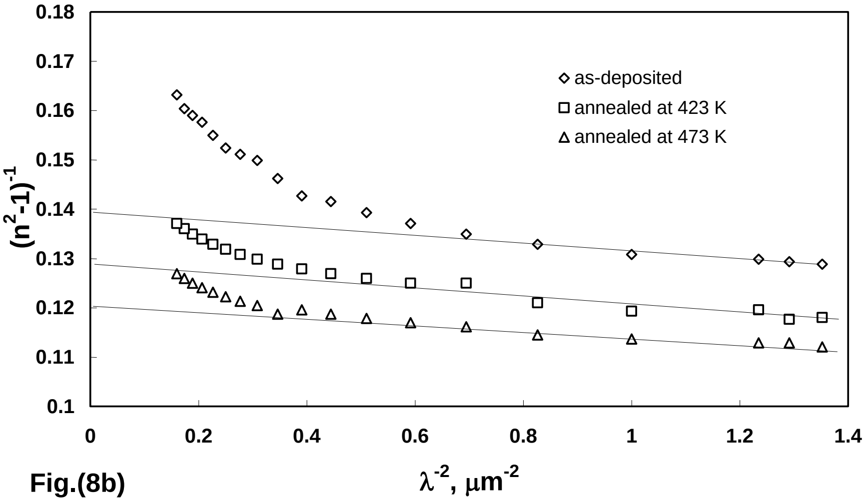

Fig.(8b): The variation of $(n^2-1)^{-1}$ with λ^{-2} for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

Table (2). Parameters derived from refractive index n for $Cu_3In_{17}Se_{80}$ films.

Parameter	As-deposited	Annealed at 423 K	Annealed at 473 K
$\varepsilon_\infty(1)$	8.21	8.90	9.32
$\varepsilon_\infty(2)$	8.19	8.75	9.34
ε_∞(average)	8.24±0.019	8.89±0.017	9.33±0.021
λ_o, nm	281	275	238

3.1.3. Analysis of absorption index (k)

The absorption coefficient (α) of as-deposited and annealed $Cu_3In_{17}Se_{80}$ films can be calculated using the well-known equation $\alpha = 4\,\pi\,k / \lambda$, in which k is substituted by its mean value obtained from Fig. (6b).

The absorption coefficient can be divided into two regions:

(i) for absorption coefficient $\alpha(\nu)$ of less than $\sim 10^4$ cm^{-1} there is usually an Urbach [19] tail where α (ν) depends exponentially on the photon energy ($h\nu$) as:

$$\alpha(\nu) = \alpha_o \exp (h\nu / E_e) \qquad (4)$$

where (ν) is the frequency of the radiation, (α_o) is a constant and (E_e) is often interpreted as the width of the tails of localized states in the gap region and in general represents the degree of disorder in an amorphous semiconductor [20].

Therefore, plotting ln α as a function of hν as shown in Fig.(9), both α_o and E_e can be evaluated. Values of α_o and E_e for the as-deposited and annealed $Cu_3In_{17}Se_{80}$ films are tabulated in Table(3).

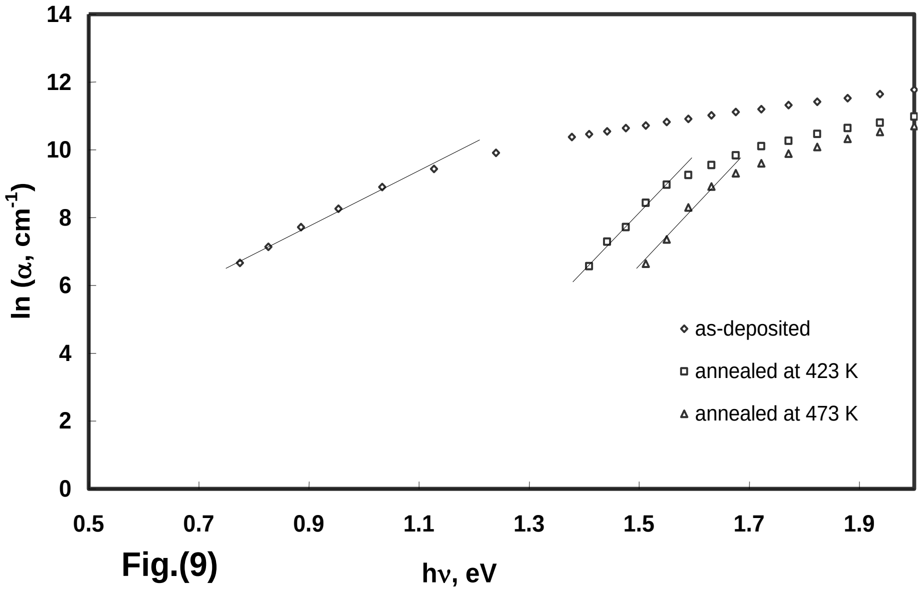

Fig.(9): Plots of log α as a function of hν for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

Table (3): Parameters derived from absorption index k for $Cu_3In_{17}Se_{80}$ films.

Parameter	As-deposited	Annealed at 423 K	Annealed at 473 K
E_e, eV	0.116	0.05۷	0.051
α_o, cm^{-1}	0.99	$1.46x10^{-8}$	$1.25x10^{-10}$
E_g^{opt}, eV Equation (5)	1.1	1.35	1.41
A, $cm^{-1}eV^{-1}$	2.85×10^5	2.89×10^5	2.77×10^5
E_g^{opt}, eV Equation (6)	1.08	1.37	1.41

(ii) For higher values of the absorption coefficient $\alpha(\nu) > 10^4$ cm^{-1}, the absorption coefficient takes the form [21, 22]:

$$\alpha(\nu) = A\,(h\nu - E_g^{opt})^r/h\nu \qquad (5)$$

where A is a constant, E_g^{opt} is the optical energy gap of the material and r is the power which characterizes the transition process, r has the value (1/2) for the direct allowed transition and has the value (2) for the indirect allowed transition (non direct in case of amorphous semiconductor). The usual method for the determination of the value of E_g^{opt} involves plotting a graph of $(\alpha h\nu)^{1/r}$ against hν. Fig.(10) shows that plots of $(\alpha h\nu)^{1/2} = f(h\nu)$ is linear function and $(\alpha h\nu)^2 = f(h\nu)$ is nonlinear for the as-deposited and annealed films. This linearity indicates the existence of the allowed indirect transitions. Values of E_g^{opt} and the constant A for the as-deposited and annealed $Cu_3In_{17}Se_{80}$ films are tabulated also in Table(3). The obtained value of E_g^{opt} for the as-deposited $Cu_3In_{17}Se_{80}$ films is less than the value of energy gap for $In_{20}Se_{80}$ films determined by [1,4]. This means that the 3 at % Cu decreases the optical energy gap. This decrease is considered to be caused by the upward shift of the valence band edge. Cu additive (3 at%) must bring about a compositional change of the host material, i.e. an alloying effect. In this region of Indium content, an increase in the density of charged defects is observed and the increased Cupper content may contribute to an increase in disorder in the atomic bonding between neighbor atoms.

The obtained results for E_g^{opt} can be confirmed by plotting $h\nu\sqrt{\varepsilon_2}$ (ε_2 is the imaginary part of the dielectric constant = 2nk) against hν near the absorption edge as shown in Fig.(11) for the as-deposited and annealed $Cu_3In_{17}Se_{80}$ films. The linear part of this graph is described by the relation:

$$h^2\nu^2\varepsilon_2 \sim (h\nu - E_g^{opt})^2 \qquad (6)$$

This linear part indicates indirect optical transitions [21]. The extrapolation of this linear part yields the value of E_g^{opt}[21]. The obtained values of E_g^{opt} from Fig.(11) are in good agreement with that obtained previously by plotting $(\alpha h\nu)^{1/2}$ against hν for indirect allowed transitions as indicated in Table (3).

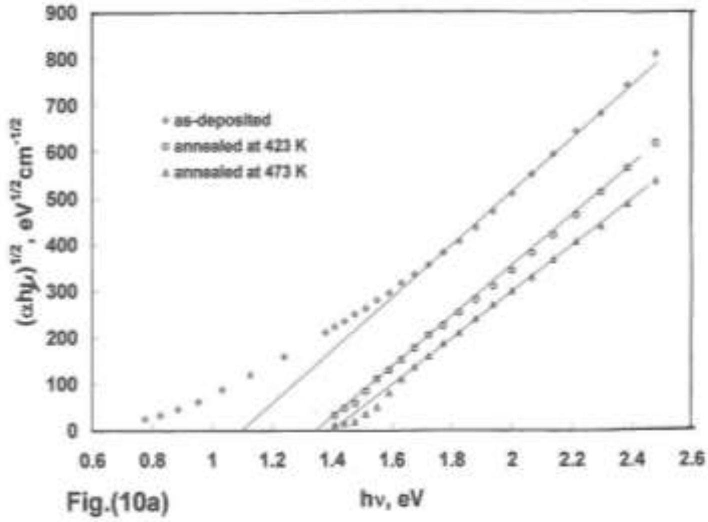

Fig.(10 a): Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy hν for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

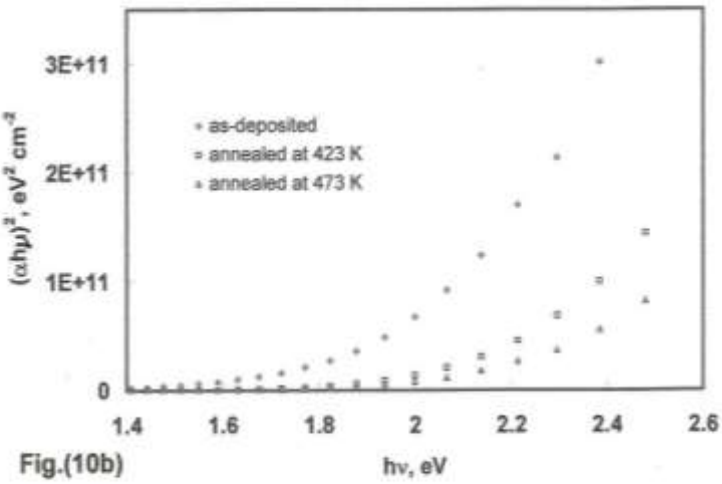

Fig.(10 b): Dependence of $(\alpha h\nu)^2$ on the photon energy hν for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

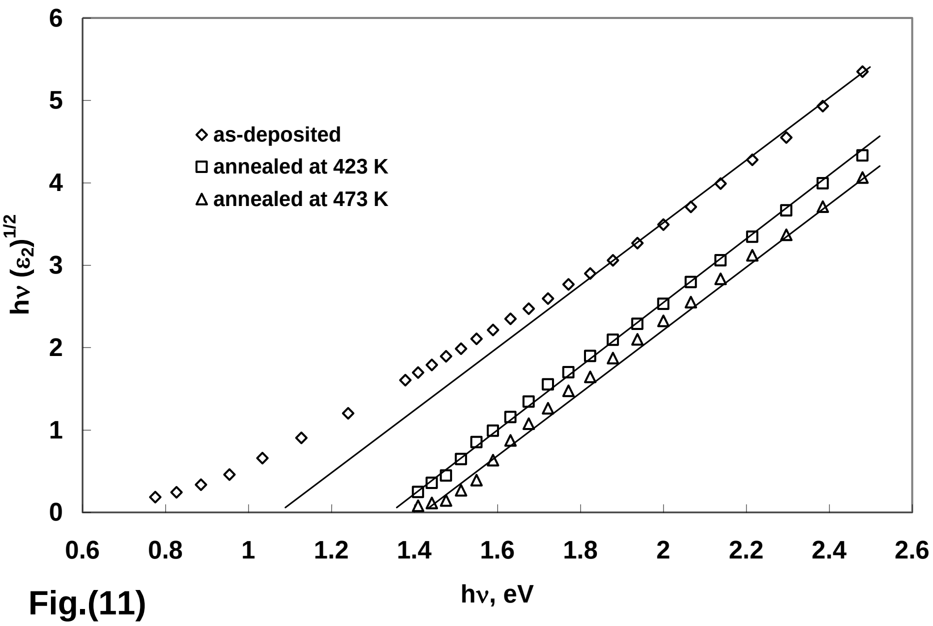

Fig.(11)

Fig.(11): Dependence of hν $\sqrt{\varepsilon_2}$ on the photon energy hν for as-deposited and annealed $Cu_3In_{17}Se_{80}$ films.

From Table (3) it is observed that the optical gap increases, absorption coefficient decreases and the width of Urbach tail decreases with increasing annealing temperature and this is consistent with the initiation of band tailing suppressed to occur of lower values of N(E) on the density of states curves. Since E_e is generally considered to represent the degree of disorder [20], then increasing the annealing temperature leads to a decrease in the disorder of films indicated by decreasing the values of E_e. Now we are trying to explain the effect of annealing process on gap states. The optical energy gaps of amorphous semiconducting films have been successfully analyzed on the basis of the theory proposed by Mott and Davis [23], for the case on non-direct transitions when the k-conservation rule is relaxed. The presence of high concentration of localized states in the band structure is responsible for the low value of E_g^{opt} in case of the as-deposited amorphous films. In the process of annealing, the unsaturated defects are gradually annealed out [24] producing larger number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure and consequently increases the optical gap.

4. Conclusions

$Cu_3In_{17}Se_{80}$ thin films were deposited by thermal evaporation method. X-ray diffraction analysis for the as-deposited films showed that it has amorphous nature. On annealing up to 473 K, films still have amorphous structure. The optical constants n and k of the as-deposited thin films have been determined in the wavelength range 400-2500 nm. Both n and k are practically independent on the film thickness in the range 11-61.4 nm. Analysis of the refractive index n yields a high frequency dielectric constant. The optical absorption measurements indicate that the absorption mechanism is due to allowed indirect transitions, and the corresponding energy gap increases with the increase of the annealing temperature.

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