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EFFECT OF FILM THICKNESS, ANNEALING AND SUBSTRATE TEMPERATURE ON THE OPTICAL AND ELECTRICAL PROPERTIES OF $CuGa_{0.25}In_{0.75}Se_2$ AMORPHOUS THIN FILMS

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Thin films of $CuGa_{0.25}In_{0.75}Se_2$ of different growth conditions were deposited on glass substrates by thermal evaporation. X-ray diffraction revealed the formation of amorphous films. The effect of thickness (d), heat treatment and substrate temperature (T_s) on the optical energy gap ($E_{opt.}$) and on the activation energy (ΔE) for dc conductivity and the density of localized states at the Fermi level N (E_f) were carried out. For all films deposited at room temperature, the optical transition was found to be indirect. The optical energy gap increase with increasing film thickness and with increasing temperature and time of annealing. The band tail (E_c) obeys Urabach empirical relation. Up to Ts > 500 K, it is obvious that the process of transformation to polycrystalline occurs. As a result, the two direct energy gaps which attributed to the fundamental edge E_{g1} and band splitting Eg_2 are found. The electrical conductivity increases with increasing thickness, with increasing the evaporation conditions (d, Ts, and annealing temperature and time) and exhibits two types of conduction mechanisms. The corresponding band is approximately half the optical energy gaps and the effect is interpreted in term of density of state by Mott and Davis.

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1. Introduction

The measurements of optical absorption and particularly the absorption edge are important especially in connection with the theory of the electronic structure of amorphous materials. In the high absorption region, Tauc et al. [1] and Davis and Mott [2] independently derived an expression relating the absorption coefficient $\alpha(\nu)$, to photon energy, $h\nu$;

$$\alpha(\nu) = \beta(h\nu - E_{opt})^m / h\nu \tag{1}$$

Where β is a constant ($\beta = 4\pi\sigma_o / ncE_c$), c is the speed of light, σ_o is the extrapolated dc conductivity at $T = \infty$, E_c is a measure of the extent band-tailing, n is the refractive index , $E_{opt.}$ is the optical energy gap , and m is a number which characterizes the optical absorption process: m =1/2 for a direct allowed transition, m=3/2 for a direct forbidden transition, m=2 for an indirect allowed transition and m =3 for an indirect forbidden transition.

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Absorption at lower photon energy usually follows the Urbach rule [3], i.e.

$$\alpha(\nu) = \alpha_o \exp h\nu / E_c \qquad (2)$$

where E_c is the Urbach energy which is interoperated as the width of the tails localized states in the band gap.

In the present work was concerned with some experimental observation on effect of film thickness, thermal annealing and substrate temperature on the (i) structure, (ii) optical and electrical conduction of the $CuGa_{0.25}In_{0.75}Se_2$ amorphous thin films.

2. Experimental

$CuGa_{0.25}In_{0.75}Se_2$ thin films were prepared by thermal evaporation in vacuum ($10^{-4}\,Pa$, i.e. about $10^{-6}\,torr$) of synthetic chalcopyrite grown in laboratory. A polycrystalline ingot was prepared from stiochiometric mixture of pure elements (5 N Mathey Chem. Ltd.). The composition and the homogeneity of the alloy were determined by microprobe analysis which was performed at the physical chemistry Institute of Munster University Germany. Excess Se (approximately 3 mol %) was included in the starting composition to compensate for any potential loss of Se vapour during evaporation and to favour p-type electrical conduction in these films. The details of the preparation and evaporation of ingot and thin films are given in Ref. [4] and [5], respectively.

The structure of the as-deposited and the effect of annealed, substrate temperature and film thickness were analyzed using an X-ray diffractmeter (XRD) (Philips PW 1373). The transmission spectra were measured in the wavelength range of 300-2500 nm using a double beam spectrophotometer, model (Shimaza model 3101).

The electrical conductivity, σ was measured by conventional four probe method using specifically constructed sample holder [6], keithly electrometer of type 614 was used for voltage and current measurements. Ohmic contacts were fabricated by use of liquid silver. Each experimental point plotted in the curves of electrical conductivity is the mean value of at least two films having the same thickness and two different successive runs for each thickness.

3. Results and discussion

3.1 X-ray diffraction

Fig.1 show the XRD diagrams corresponding to a powder sample and thin films of different thickness heat treatment for 1 and 2 hour at 373 K and evaporated at different substrate temperature, T_s. It is revealed that the bulk sample has a crystalline structure, while thin films, both as-deposited and different thickness and annealed for 1h and 2h at 373 K, show no evidence of molecular units corresponding to the crystallization, indicating the amorphous nature. The grain size of the film was so small and the disorder within these grains so high that no specific diffraction peaks could be detected. But, the films obtained by evaporation on substrate with temperature ranging from room temperate to $T_s < 473$ K consist mainly of the amorphous phase and the amorphous diminishes with the raise of T_s. Up to $T_s > 523$ K; it is obvious that the process of transformation to polycrystalline occurs.

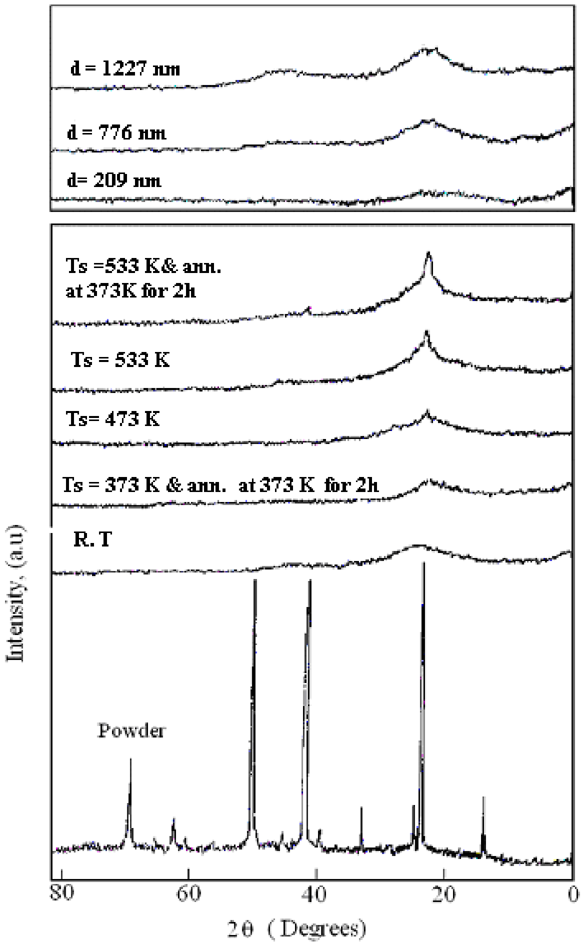


Fig.1 XRD patterns of powder and $CuGa_{0.25}In_{0.75}Se_2$ *thin films at different evaporation conditions.*

3.2 Optical properties

The optical properties were studied by measuring the transmission spectra in the wavelength range of 300-2500 nm. The refractive index was determined using a procedure proposed by Swanepoel [7] which is based on drawing envelope curves through the minima, (T_m) and maxima, (T_M) in the transmission spectrum, the variation in the transmission spectrum is principally due to the interference phenomena. This approach yields

$$\begin{aligned} n_i &= \left[N + (N^2 - n_s^2)^{1/2}\right]^{1/2} \\ N &= 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s + 1}{2} \end{aligned} \tag{3}$$

where n_i is the refractive index of the film, and n_s is the refractive index of the glass substrate (n_s=1.5 in our case). Using Eq.3, n (λ) can be calculated. According to Tauc [8] it is possible to separate three distinct regions in the absorption edge spectrum for amorphous semiconductors; (i) the weak absorption tail, which originate from defects and impurities, (ii) the exponential l randomness of the system, and (iii) the high absorption region which determines the optical energy gap.

On the other hand, thickness of the prepared films has been determined using two different techniques and the results were compared. First it has been calculated from the transmission curves of Fig. 2 using the relation

$$d = \frac{\lambda_1 \lambda_2}{2(n_2 \lambda_1 - n_1 \lambda_2)} \qquad (4)$$

where n_1 and n_2 are the refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2. Second, the multiple beams Fizeau fringes method [9] has been used to determine the film thickness. The values of thickness, d for CuGaInSe thin films determined by different methods were found coincide to within 5 %.

The method used to determine the value of E_{opt} involves plotting a graph of $(\alpha h\nu)^m$ versus $h\nu$. From appropriate value of E_{opt} will be given the interception on the $h\nu$ axis. Different authors have suggested different values of m for different amorphous materials. Davis and Mott [2] obtained m = 2 for most amorphous semiconductors. However, for more complicated materials Fagen and Fritzsche [10] obtained m = 3 and m =1 was obtained by others [11, 12].

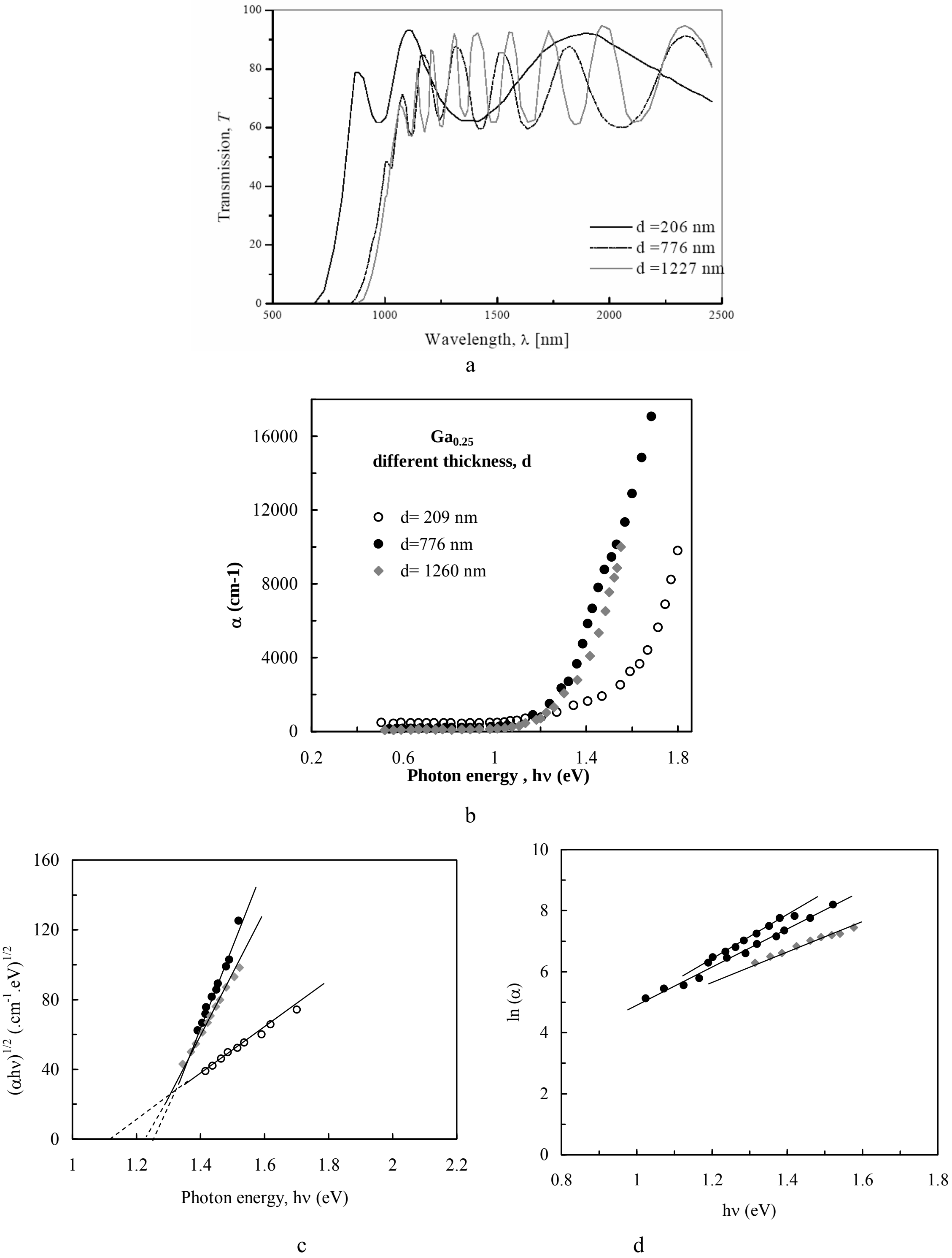
Fig. 2 (a, b, c and d) illustrates the transmission spectra (T-λ), the absorption coefficient, α, $(\alpha h\nu)^{1/2}$ and ln α versus $h\nu$, for all investigated samples deposited at room temperature. The graph of $(\alpha h\nu)^{1/2}$ versus $h\nu$ in Fig. 2c has a well defined linear region thus confirming that Eq.1 holds for m=2 indicating that indirect photon transition are involved and the optical energy gap, E_{opt} was calculated from the curves. Fig.4 (c, d) shows the direct energy gaps for thin films deposited at 533 K and at 533 K and annealed at 373 K for 2h respectively.

3.2. a: Effect of thickness

As shown in Fig.2c and Table 1 the optical energy gap increases with increasing thickness, this can be explained as due to the presence of defects in amorphous materials [13] in terms of elimination of defects in the amorphous structure. The insufficient number of atoms deposited in the amorphous film results in the existence of unsaturated bonds [14]. The unsaturated bonds are responsible for the formation of some defects in the films which produced localized states in amorphous solids [15]. Thicker films are characterized by more homogeneous network, which minimizes the number of defects and localized states, and thus the optical band gap increases. The calculated values of $E_{opt.}$ are listed in Table 1. The values of E_c are very much larges than 0.05 eV and decreases with increasing thickness. The Tauc model [16] based electronic transitions between localized states in the band tails may be valid in our materials, and the extending of deeper band tail in the gap is decrease and led to decrease in the value of E_c and on increase in the value of $E_{opt.}$

Table I Optical parameters.

Thickness (nm)	Subs. Temp (K)	An. Temp. (K)	Time (h)	$E_{gind.}$ (eV)	E_c (eV)	$E_{gdir.}$ (eV)	
						E_{g1}	E_{g2}
208	----	----	----	1.1	0.208	----	----
776	----	-----	----	1.21	0.159	----	----
1227	----	----	----	1.24	0.143	----	----
680	----	----	----	1.185	0.155	----	----
680	----	373	1h	1.21	0.138	----	----
680	----	373	2h	1.23	0.13	----	----
860	----	----	----	1.23	0.15	----	----
860	533	----	----	----	-----	1.14	1.28
860	533	373	2h	----	----	1.11	1.25



a

b

c

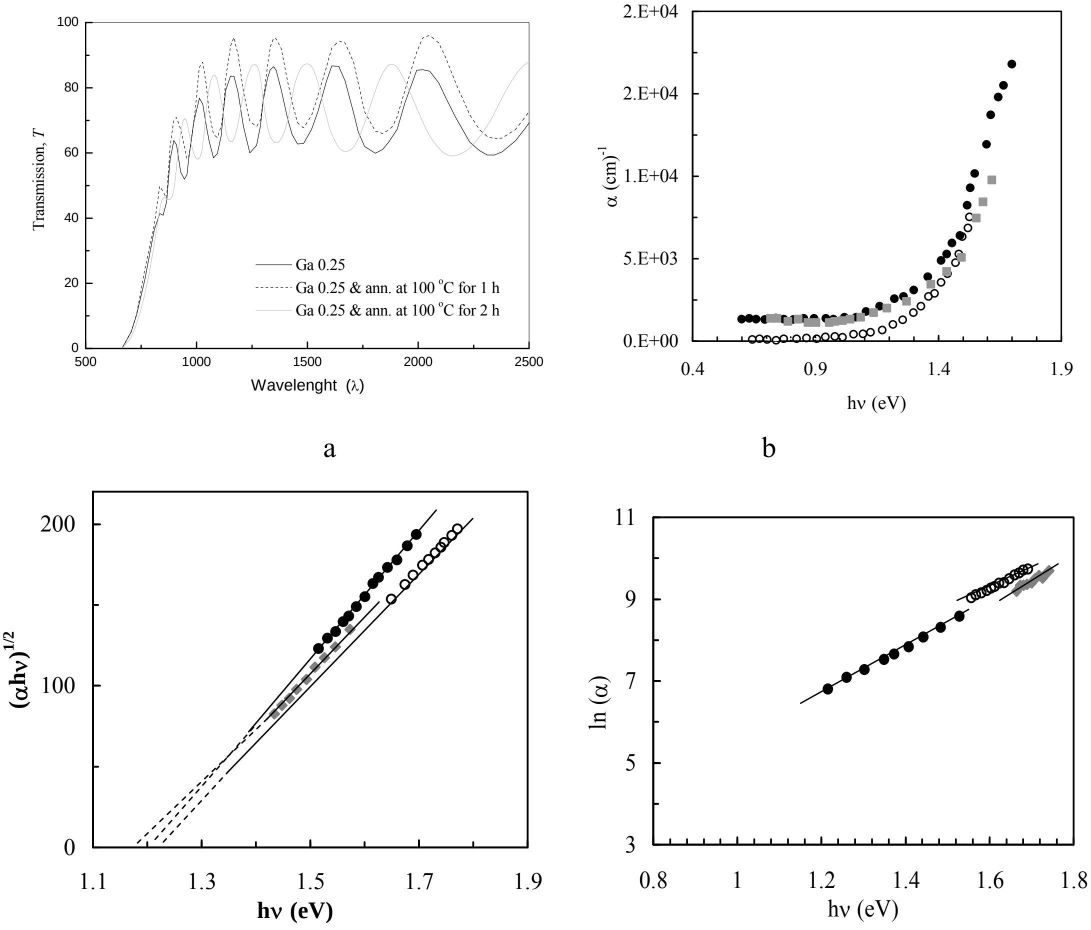
d

Fig.2 Effect thickness on (a) Transmission spectra (b) Absorption coefficient (c) (αhν)$^{1/2}$ vs. (hν) (d) Ln (α) vs. (hν) for CuGa$_{0.25}$In$_{0.75}$Se$_2$ thin films.

3.2. b: Effect of annealing and substrate temperature on the optical band gap

The degree of disorder and defects present in the amorphous structure change due to heat treatment [17]. The decrease in the disorder and defects in the structural bonding is known to increase the optical band gap $E_{opt.}$ Figs. 3(c, d) show $(\alpha h\nu)^{1/2}$ and ln α versus $h\nu$, for the investigated films annealed at 373 K for 1 and 2 h, respectively. The values of E_{opt}. increase as the temperature and time of annealing increase, but the values of E_c decrease. This can be explained by assuming that during the annealing process the films will have time enough for some atomic rearrangement to take place. Some defects will be removed which, reducing the density of dangling bonds, redistribute atomic distances and bond angles and E_{opt}. will then increase.

For substrate temperature Ts = 533 K, and annealed at 373 K for 2h , there are two direct energy gaps Eg_1 = (1.11,1.14) , Eg_2 = (1.25,1.28) shown in Fig. 4 (c, d) due to the existence of polycrystalline phase as a result of amorphous phase transformed to polycrystalline phase Fig.(1). These energies are attributed to the fundamental edge and band splitting. This result is in good agreement with our previous work [5] for polycrystalline $CuGa_xIn_{1-x}Se_2$ deposited at 603 K.



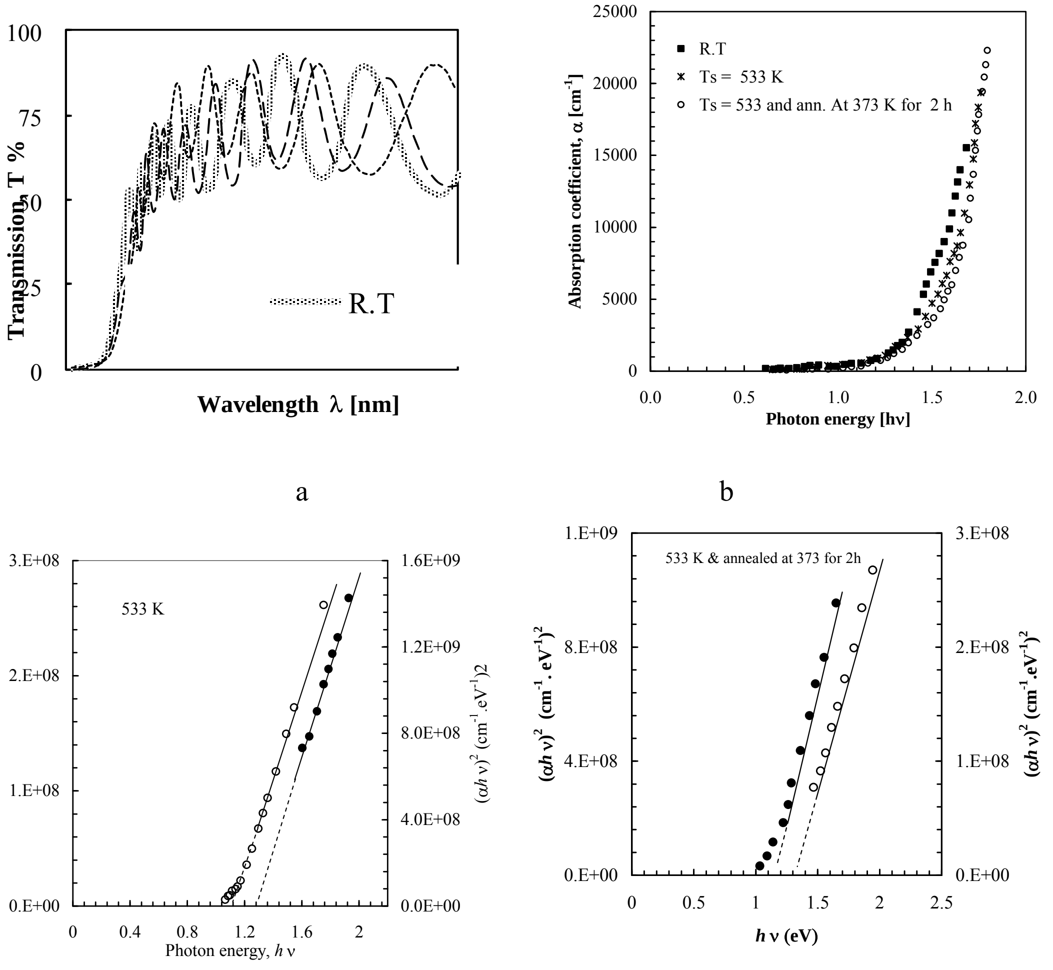
a

b

c

d

Fig. 3 Effect of annealing on (a) Transmission spectra (b) Absorption coefficient (c) $(\alpha h\nu)^{1/2}$ vs. (hν) (d) Ln (α) vs.(hν) for $CuGa_{0.25}In_{0.75}Se_2$.



a b

c d

Fig.4 Effect of substrate temperature on (a) Transmission spectra. (b) Absorption coefficient. (c) $(\alpha hv)^2$ vs. (hv) (d) Effect of substrate and annealing on $(\alpha hv)^2$ vs. (hv) for $CuGa_{0.25}In_{0.75}Se_2$.

3.3 Electrical conductions

The dc electrical conductivity, σ as shown in Fig. 5 was measured as a function of temperature in the range 300-450 K. The general beahviour of $\sigma(T)$ in temperature range 370 K < T < 476 K for all samples was increased exponentially with T and exhibit two types of conduction mechanisms. The activation energy, ΔE can be estimated according Eq.5

$$\sigma = \sigma_o \exp(-\Delta E/kT) \tag{5}$$

where σ_o is the pre-exponential factor and k is the Boltzmann constant and ΔE is the corresponding activation energy, which is a function of the electronic energy levels of the chemically interacting atoms in the glass and hence of the energy gap. The estimated values of ΔE and $\sigma_{R.T}$ (electrical conductivity at room temperature) for all samples are given in Table II. From Table II and Fig.5 it is observed that $\sigma_{R.T}$ and ΔE increase with increasing thickness, annealing and substrate temperature and the value of ΔE is approximately half the optical energy gap show Table I. These results may be due to the enhancement of homogeneity of the films, which contain lower defects [18].

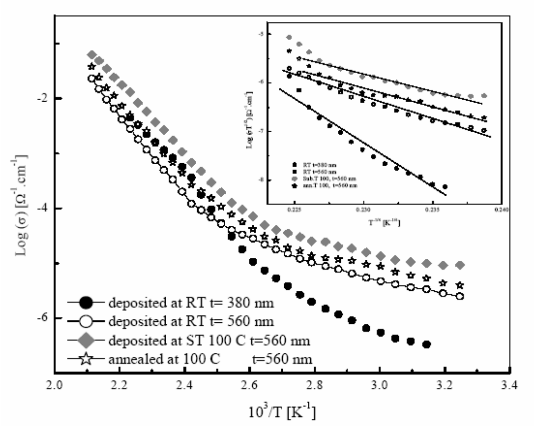


Fig. 5. Temperature dependence of d.c. conductivity for $CuGa_{0.25}In_{0.75}Se_2$ thin films with annealing and substrate temperature. The inset shows the plot of Log $(\sigma T^{1/2})$ versus $T^{-1/4}$ of thin films.

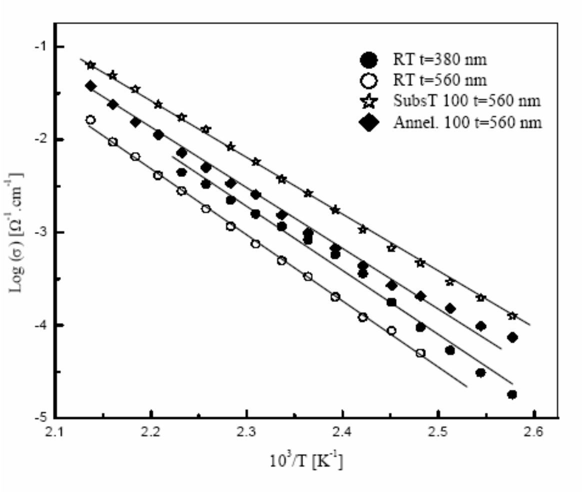


Fig. 6. Temperature dependence of d.c. conductivity for $CuGa_{0.25}In_{0.75}Se_2$ thin films with annealing and substrate temperature. The inset shows the plot of Log $(\sigma T^{1/2})$ versus $T^{-1/4}$ of thin films.

Table II Electrical parameters

Sample	Thickness (nm)	$\sigma_{R.T}$ ($\Omega^{-1}.cm^{-1}$)	A (K^{-1})	T_o (K) ($\times 10^7$)	N(E_f) ($\times 10^{18}$eV cm^{-1})	γ ($\times 10^{-7}cm^{-1}$)	R (cm) ($\times 10^{-7}$)	W	ΔE (eV)
As-dep.	380	3.1×10^{-7}	90.62	6.74	2.94	9.90	8.25	0.143	0.539
As-dep.	560	2.4×10^{-6}	89.58	6.45	3.08	7.31	8.06	0.132	0.544
Ann.100	380	4.5×10^{-6}	92.07	5.11	3.88	2.85	4.74	0.086	0.575
T_s 100	380	9.3×10^{-6}	91.38	5.73	3.46	4.80	5.94	0.12	0.552

In order to interpret the electrical data we shall assume that the model for the electronic density of states in amorphous semiconductors as proposed by Mott et al. [15] is applicable. The essential feature of this model is the existence of narrow tails of localized states at the extremities of the valence and conduction band [15]. The slight increase in $\sigma(T)$ could be explained as follows: the amorphous semiconductor, due to local statisfaction of all valence requirements, exhibits the ability for self-compensation. This self-compensation property of amorphous solid results in an intrinsic σ and well-defined activation energy. Around room temperature up to 330 K region, the electrical conductivity $\sigma(T)$ is insensitive to temperature and corresponding to transport via variable-range hopping of charge carriers in the localized states near the Fermi level, and is characterized by Mott's variable range hopping relation [19]

$$\sigma(T) = (\sigma_o / \sqrt{T})\,[\exp(-T_o/T)^{1/4}] \tag{6}$$

T_o represents the degree of disorder in the material and can be given approximately by:

$$T_o = \frac{18\alpha^3}{kN(E_f)} \tag{7}$$

where $N(E_f)$ the density of localized states at the Fermi level, k is the Boltzman constant and α is the coefficient of the exponential decay of the localized state wave function. A plot of $\ln(\sigma\sqrt{T})$ versus $T^{-1/4}$ for as-prepared films with different thickness and heat treatment is shown in Fig.5. The calculated values of T_o and $N(E_f)$ are given in Table II. It is observed that T_o decreased while $N(E_f)$ increased with increasing thickness and annealing and substrate temperatures. This decrease of T_o results in a decrease in disorder [20]. Two other hopping parameters $R(cm)$ the hopping distance and $W(eV)$ the average hopping energy according to Mott and Davis [21] and Hill [22] are given as

$$\begin{aligned} R &= [9/8\pi\alpha kTN(E_f)]^{1/4} \quad and \\ W &= 3/4\pi R^3 N(E_f) \end{aligned} \tag{8}$$

The calculated values of R and W for thin films are also listed in Table 2.

4. Conclusions

The optical and electrical properties of $CuGa_{0.25}In_{0.75}Se_2$ amorphous films of different growth conditions (thickness, d, substrate temperature T_s and heat treatment) were investigated. The optical transition for all films deposited at room and annealed temperature was found indirect and the band tails E_c obeys Urabach empirical relation. The optical energy gaps E_{opt} increases and E_c decreases with increasing d and with annealing temperature and time, this can attributed to decrease in the degree of disorder. Two direct energy gaps which attributed to the fundamental edge E_{g1} and band splitting E_{g2} are found for films deposited at T_s = 533K as a result of phase transformation from amorphous phase to polycrystalline phase.

The electrical conductivity depends on the thickness and annealing temperature and exhibits two types of conduction mechanisms. The density of localized states at the Fermi level N (E_f) and the activation energy ΔE are increased with evaporation growth and the corresponding band is approximately half the conduction optical energy.

It is reasonable to assume that the observed changes in the optical and electrical properties on annealing and high temperature deposition are a result of microstructural re-arrangement initiated either during deposition or during annealing and the effects are interpreted in terms of density of states model proposed by Mott and Davis.

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