RESEARCH ARTICLE

DISPERSIVE OPTICAL CONSTANTS OF AMORPHOUS SE$_{90}$IN$_{9.3}$CU$_{0.7}$ THIN FILMS.

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Manuscript Info	*Abstract*
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Manuscript History Received: 12 June 2016 Final Accepted: 19 July 2016 Published: August 2016 *Key words:* Se-In-Cu, alloy film system, Optical constant, Optical band gap, Single-oscillator model.	Thin film of chalcogenide glassy alloy Se$_{90}$In$_{9.3}$Cu$_{0.7}$ was deposited glass on substrate at room temperature (300k) by thermal evaporation technique. The refractive index(n) is determined by using the optical transmission spectrum. The absorption coefficient (α) and the refractive index (n) are determined from the reflectivity and transitivity spectrum in the range of 500-2500nm.The dielectric behavior is discussed by calculating and drawing the real (ε_r) and the imaginary (ε_i) parts of the dielectric constant versus the photon energy (hυ). The oscillator energy (E$_o$), dispersion energy (E$_d$) and other parameters are determined.

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Introduction:

Chalcogenide glasses have received much attention due to their potential use in various solid state devices. Due to their technological importance, the optical properties of chalcogenide films have been the subject of numerous studies Cu In Se in a semi-conducting compound belongs to the I-III-VI chalcopyrite family [1]. It is convenient to regard the chalcopyrite structure in terms of two interpenetrating sub-lattices. I-III atoms act as cations rest on one sub-lattice and the group VI atoms act as anions rest on the other sub-lattice [2]. Cu In Se is a direct band gap [3] material with band gap ~ 1.0eV. Further its band structure can be doped to make both n and p type within a wide range of resistively [4], makes it a candidate for photovoltaic devices. It has an absorption coefficient ~ 10^5 cm^{-1} in thin films form [5]. Accurate knowledge of the optical functions of these materials is very important for many applications. This work studies the optical properties of Se$_{90}$In$_{9.3}$Cu$_{0.7}$ thin films using transmittance and reflectance spectra over the wavelength 400-2500nm. Also, the oscillator energy (E$_0$) and dispersion energy(E$_d$) will be under test.

Theoretical Background:

From the optical transmission, T, and reflection, R, spectra for amorphous semiconductor thin films, the absorption coefficient α can be calculated from the relation [6];

$$T/(1-R)^2 = e^{-\alpha d}$$
$$\ln[T/(1-R)^2] = -\alpha d$$
$$\alpha = (-1/d)\ln[T/(1-R)^2] \qquad (1)$$

Where, d is the thickness of the thin films. However, the absorption is due to only the difference in the film thickness and the reflection is at the film-substrate interface (with neglecting interference).
The variation of the optical absorption near the fundamental absorption edge has allowed us to determine the optical energy gap. In the absorption process, a photon exits an electron from a lower to a higher energy state which is

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called an absorption edge. In the region of the fundamental absorption edge, the optical absorption dependence of photon energy is expressed as follows [7];

$$(\alpha h\upsilon) = B\,(h\upsilon - E_{opt})^2 \quad (2)$$

where, B is constant which include band properties and E_{opt} is the optical band situated between the localized state near the mobility edges according to the model density of states presented by Mott and Davis [8,9].

According to Swanepoel´s method [10] which is based on the approach of Manifacier et al [11] of creating the upper and lower envelope of the transmission spectrum, the refractive index in the region where the absorption coefficient (α) is~zero, can be obtained from the expression [10];

$$n = [N + (n^2 - s^2)^{1/2}]^{1/2} \quad (3)$$

Where;

$$N = 2s\,[(T_{max} - T_{min})/T_{max}T_{min}] + [(S^2 + 1)/2] \qquad (4)$$

Where, S is the refractive index of the substrate, T_{max} and T_{min} are the envelope values at the wavelengths in which the upper and lower envelops of the experimental transmission spectrum are tangent, respectively.

Wemple and DiDomenico [12, 13] proposed a formula, according to the single-effective-oscillator model, for the dispersion of the refractive index as follow;

$$n^2(h\nu) = 1 + \{E_d E_o / [E^2_o - (h\nu)^2]\} \qquad (5)$$

Where, $h\upsilon$ is the photon energy, E_o is the oscillator energy and E_d is the oscillator strength or the dispersion energy.

There are other formulas for the absorption coefficient, α, using the refractive index, n, are giving by;
a-For the case of the strong absorption region, the absorption coefficient, α is;

$$\alpha = (1/d)\ln\{16n^2 S/[(n+1)^3(n+s^2)T_o]\} \qquad (6)$$

Where, T_o is the measured transmission.

b- In spectral region of medium absorption, where interference fringes appear distinctly in the transmission spectrum, α is giving by [14];

$$\alpha = (1/d)\ln\{(n-1)^3(n-s^2)/[F - [F^2 - (n^2+1)^3(n^2 - S^4)]^{1/2}\} \qquad (7)$$

Where, $F = 8n^2 S/T_i$, with $T_i = 2T_{max}T_{min}/(T_{max} + T_{min})$.
The spectral variation of the extinction coefficient is giving by;

$$k = \alpha\lambda/4\,\pi \quad (8)$$

The spectral response of the real and the imaginary parts of the complex dielectric constant can be calculated from the values of the refractive index and the extinction coefficient using the following relations;

$$\varepsilon_r = n^2 - k^2 \;,\; \varepsilon_i = 2nk \qquad (9)$$

Experimental Procedure:

Polycrystalline ingots of $Se_{90}In_{9.3}Cu_{0.7}$ were prepared by fusion of constituent elements in the stoichiometric ratio in sealed evacuated silica tubes (10^{-3} Pa) which left at 1200^oC for 10 hours, then quenched in iced water at 1000^oC. Thin films of these composition are deposited by thermal evaporation technique onto a quartz substrate at room temperature (300K) using a high vacuum coating unit (Edwards E30Ga) with resistively heated molybdenum boat. The working vacuum is kept at about ~ 6×10^{-4} Pa during deposition. The film thickness is 940 nm which is determined by quartz crystal-thickness manometer (FTM4) and interferometrically.
X-ray diffraction patterns of amorphous $Se_{90}In_{9.3}Cu_{0.7}$ thin films are recorded using an X-ray diffractometer (Shimadzu X D-3) as deposited and after annealing at 375 and 425K for 1h in vacuum ~ 10^{-2}Pa. The patterns were run with Cu as a target and Ni as filters.

The transmittance, T, and reflectance, R, of a-$Se_{90}In_{9.3}Cu_{0.7}$ thin films as deposited and annealed are recorded by double beam spectrophotometer (type JASCO Crop, Model V-570) at normal incidence of light in the wavelength 400-2500 nm.

Table 1 X-raycrystallographic data of annealed a- $Se_{90}In_{9.3}Cu_{0.7}$ thin film at two different temperatures in vacuum for 1 hour.

Temperature of annealing T(K)		Experimental		ASTM cards			
		2θ	d(A$^\circ$)	Crystal phase	d A$^\circ$	(hkI)	
375	a	23.6	3.765	Se	3.779	310	Monoclinic
	b	29.5	3.024	In_6Se_7	3.026	114	------------
	c	41	2.199	Cu_5Se_4	2.200	042	Orthorhomic
425	a	23.2	3.89	Se	3.89	-112	Monoclinic
	b	29.5	3.024	Cu_6Se_7	3.026	114	------------
	c	41.0	2.199	Cu_5Se_4	2.20	042	Orthorhomic
	d	43.4	2.08	Cu_2Se	2.06	404	Tetragonal
	e	51.5	1.772	Cu_2Se	1.76	533	Tetragonal
	f	65.2	1.429	Cu_2Se	1.440	800	Tetragonal

Results and Discussions:

The X-ray diffraction of amorphous and thermally annealed samples $Se_{90}In_{9.3}Cu_{0.7}$ at each of 375K & 425K for one hour, for each separately, were recorded in Figure 1. This figure shows that; the as prepared sample was amorphous. The annealed samples show the detection of the crystalline phases Se, In_6Se_7, Cu_5Se_4 and Cu_2Se. The X-ray energy dispersive confirm the presences of Se, In and Cu with the same of initial ratio, without impurities, figure (2).
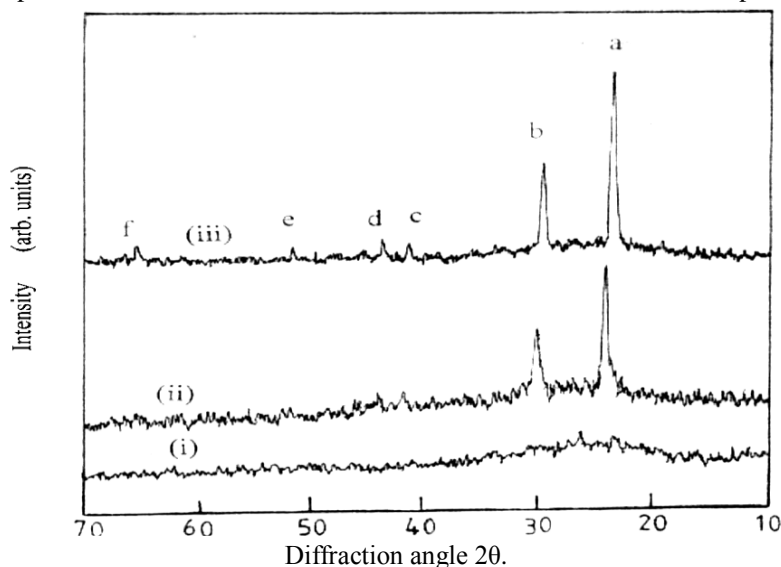

Figure 1: X-ray diffraction of a- $Se_{90}In_{9.3}Cu_{0.7}$ thin film.
1. a-deposited (300 K).
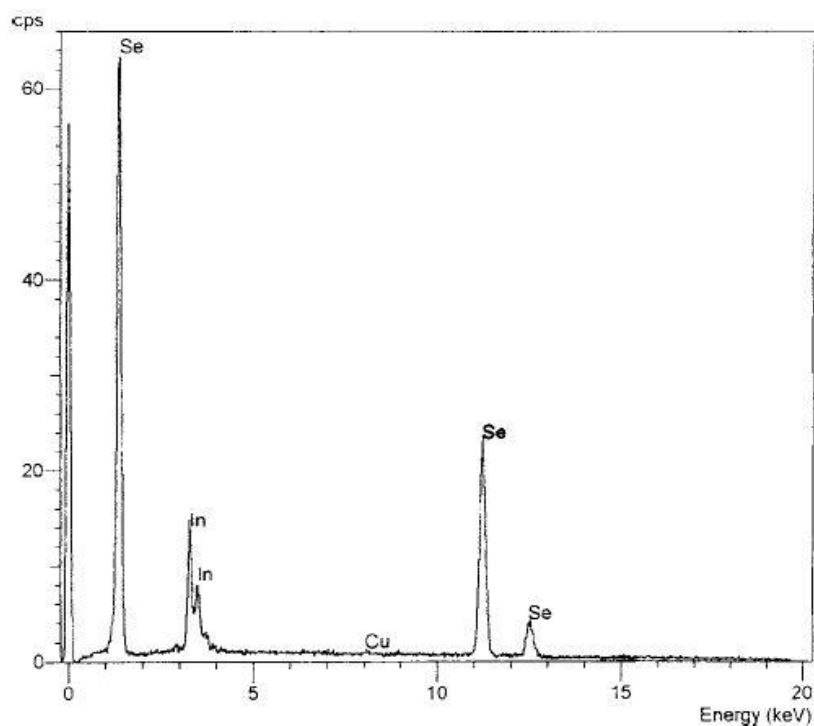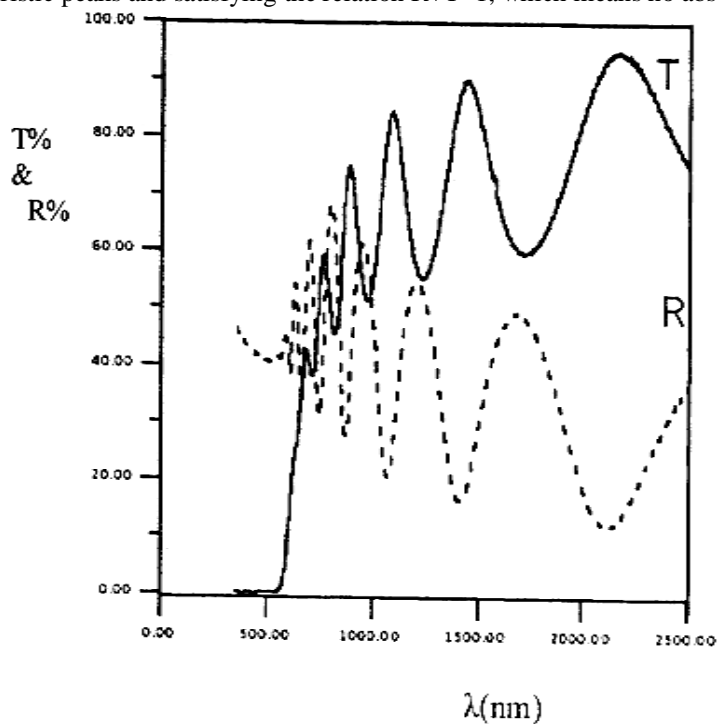2. annealed at 375K.
3. annealed at 425 K for 1h.

Figure 2:- Energy dispersion X-ray diffraction (EDAX) of a-$Se_{90}In_{9.3}Cu_{0.7}$ alloy [17].

The optical transmission (T), and reflectance (R), for both green and thermally annealed samples were recorded in the spectral wavelength rang of 400 – 2500 nm, figure (3). It is clear that, for all samples the spectra of T & R have the same characteristic peaks and satisfying the relation R+T=1, which means no absorption [15, 16].

$$\lambda(nm)$$

Figures 3: Transmission (T) and reflection(R) versus wavelength.

The results, of T_{max} and T_{min}, from Figure (3) with use of equation (3), the values of refractive indices were deduced and redrawn as a function of wavelength, figure (4). Figure (4), illustrate that n is decreased as the wavelength increase and reach minimum saturation value at $\lambda \geq 1600$ nm.
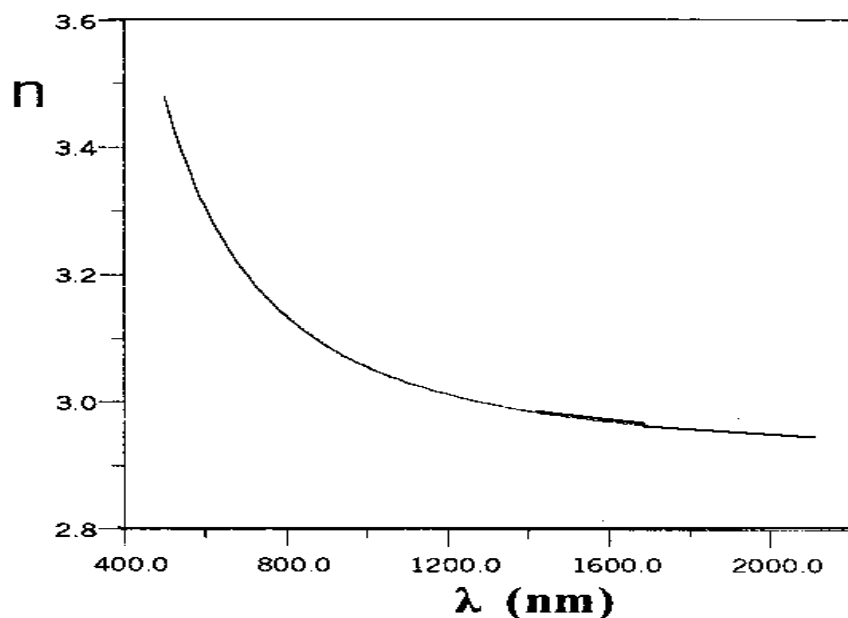

Figure 4: The relation of refractive index (n) and wavelength (nm).

To obtain the oscillator energy E_o and the oscillator strength E_d, the Wemple and DiDomenico, relation was employed by the relation $1/(n^2-1)$ against $(h\upsilon)^2$ in Figure (5). The obtained values of each of E_o and E_d were 3.9eV and 29.5eV respectively.
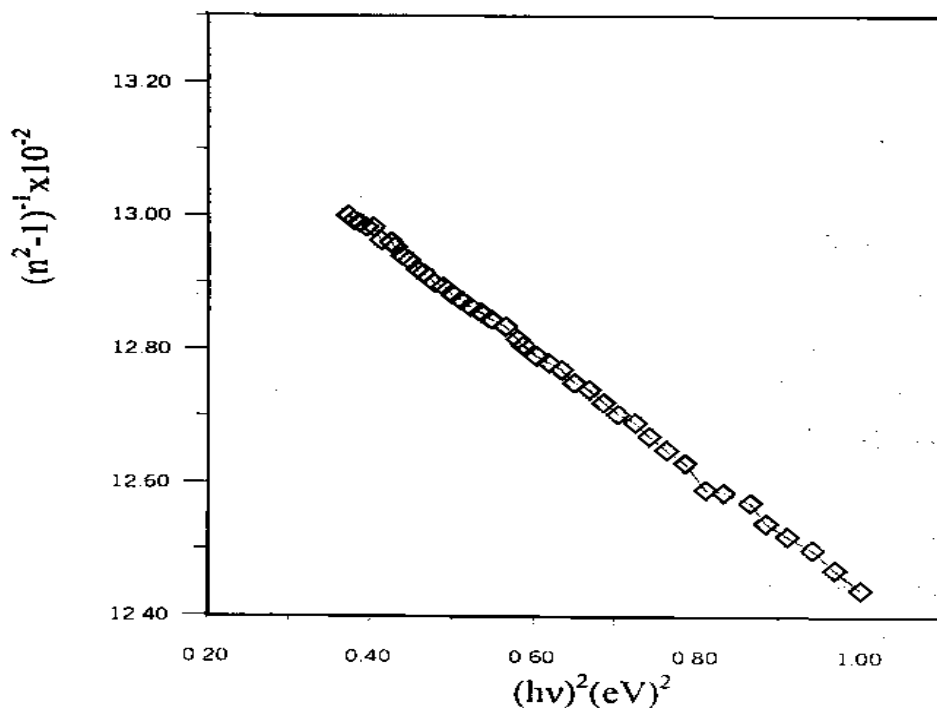

Figure 5: The relation between $(n^2-1)^{-1}$ and $(h\upsilon)^2 (eV)^2$ for a-$Se_{90}In_{9.3}Cu_{0.7}$ thin film

The relation between (αhυ)1/2 and (hυ) is plotted in Figure 6. However, it is cleared that   (αhυ)1/2 varies linearly with hv which has the best agreement with the classical theory of the band transition. From Equation (2), Eg is obtained (Eg=1.96eV) which gives good agreement compared with the previous result (since the optical energy gap Eg, as an average value, is half the oscillator energy E_o).
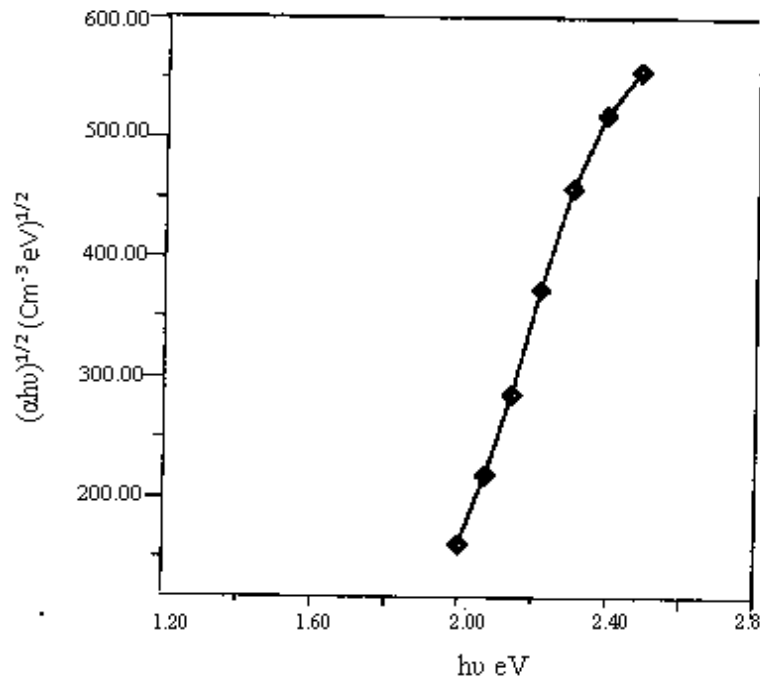

Figure 6: The relation between $(\alpha h \upsilon)^{1/2}$ and (hυ) (eV).

The extinction coefficient characterized by high value at higher photon energy. This clear from figure (7), which illustrate the decrease of k as the wavelength λ increase to reach minimum value.
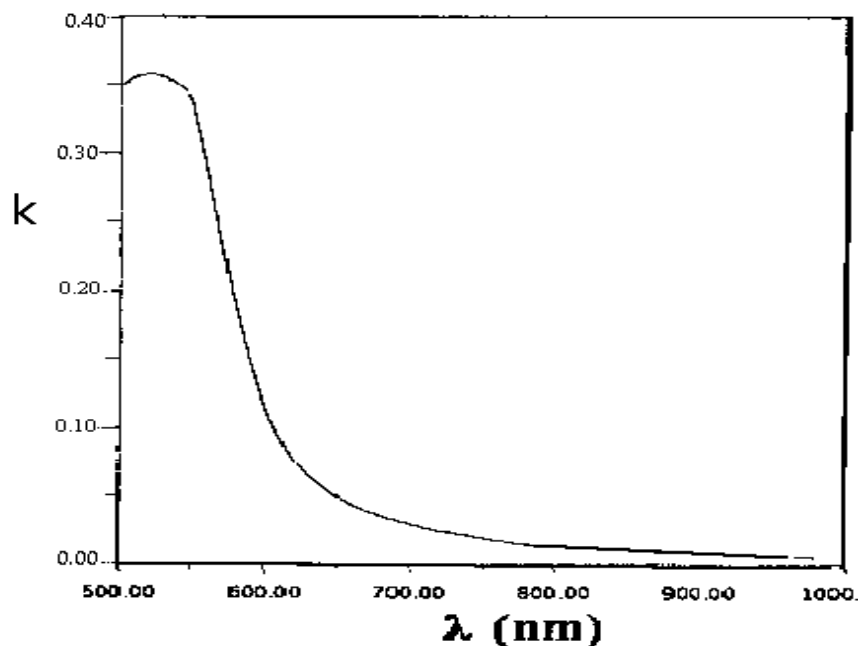

Figure 7: The relation of extinction coefficient (k) and wavelength (nm)

The components of the dielectric constant(ε) were calculated using equation (9). The redrawn of each part against, the photon energy show, the increase of each of them as the photon energy increase. This means that, the material is a good insulating material in all possible energy range, figures (8&9).
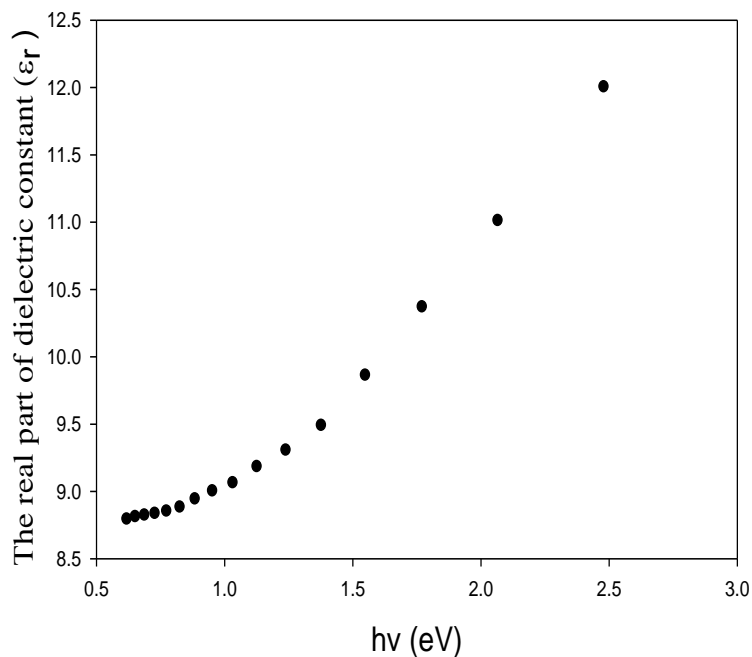

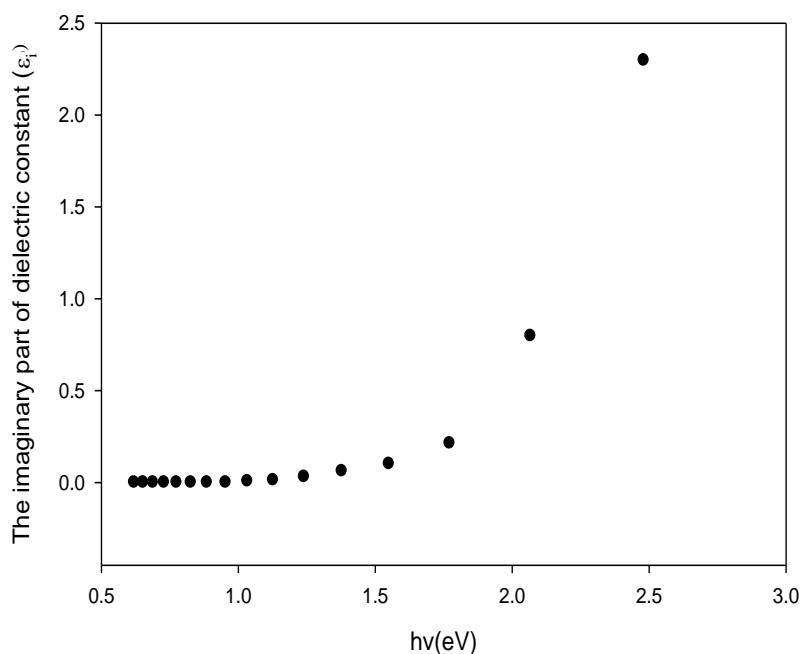**Figure 8:** The real part of dielectric constant versus the photon energy hυ(eV).

Figure 9: The imaginary part of dielectric constant versus the photon energy hυ(eV).

Conclusions:

The relations T, R, n and K are nonlinear relations in the wavelength range 400-2500 nm. The amorphous phase of this material was crystallized as it thermally annealed at each of 375K &425K.

The detected crystalline phases were increased as the annealing temperature increase from 375K to 485K.

The components of the dielectric constant were increase as a function of the photon energy, which mean thin material is a perfect insulating on all over the given photon energy range.

References:

1. Feng, Wanxiang, et al, Phys Rev. Lett. 106(2011)0031-9007.
2. V.K. Gandotra, et al., Phys. Stat. Sol. (A) 98 (1986) 595.
3. Jonathan J. S. Scragg, et al, Phys. Status Solidi B 253, 2(2016)247–254
4. B. Tell and H.M. Kasper, Phys. Rev. B4 (1971) 4455.
5. K. Konan, et al., J. Appl. Sci. (2007)2646-2650.
6. EL-H. Kadouri, et al., Phys. Stat. Sol. (A) 176 (1999) 1071.
7. N. F. Mott, E. A. Davs, Elect. Proc. In Non-Cryst. Mat., 2nded. Oxford: Charendon Press, (1979).
8. N.F. Mott, F. A. Davis, Electr. Proc. In Non-Cryst. Mat., M, (1971) 389.
9. J. Tauc, Amorphous and Liquid Semiconductors, (1974) M ed., New York: Plenum.
10. R. Swanepoel, J. Phys. E 16 (1983) 1214.
11. J.C. Manifacier, et al. J Phys. E 9 (1976) 1002.
12. S.H. Wemple, M. DiDomeninco, M. Phys. Rev. B 3 (1971) 1338.
13. S.H. Wemple, Phys. Rev. B7 (1973) 3767.
14. K.L. Bhatia, et al., J. Thin Solid Films, 293 (1997) 303-309.
15. M. M. El-Nahass and M. B. El-Den, J. Optics and Laser Tech., 33(2001)31-35.
16. J. M. Gonzalez-Leal, et al., Applied Optics, 4134 (2002) 7300.