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Effect of Thickness and Annealing Temperature on Optical Properties of $CuIn_{1-x}Ga_xSe_2$ (CIGS) Thin Films

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ABSTRACT

$CuIn_{1-x}Ga_xSe_2$(CIGS) thin films for x=0.3 with the thickness (500,1000) nm on glass substrate at ambient temperature have been prepared by thermal evaporation technique from four-component semiconductors alloy (CIGS) which obtained by the melt-quenching method. The effects of thickness and annealing temperature on structural and optical properties have been studied. The results showed that as the film thickness increases the crystallinity improves and the more improvement were observed with the increase in annealing temperature. The optical measurements revealed that most of the optical properties were significantly affected by the thickness and annealing temperature, the CIGS thin films conformed that all films have, direct allowed energy gap of (500 and 1000) nm thickness as prepared equal to (1.75 and 2.35) eV respectively. In addition, annealing of the thin films improves their band gap value to 2.59 eV for 500 nm to 2.44 eV for 1000 nm thin films. The values of some important optical parameters of the studied films such as (absorption coefficient, refractive index, extinction coefficient, and dielectric constant (real and imaginary parts) were determined and analyzed.

***Key words**: CIGS, Thermal Evaporation, optical properties, annealing temperature.*

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I. INTRODUCTION

Copper indium gallium dieseline (CIGS) thin films are formed p-type and direct bandgap in the range 1.0-1.4 eV within the family of Cu-chalcopyrite semiconductors, Cu (In, - Ga) Se2 which have light absorption coefficient and high photoelectric conversion efficiency used as an absorber layer in the solar cells[1]. Because of the high absorption coefficient (~105 cm-1) a thin layer of ~2 mm is sufficient to absorb the useful part of the spectrum, they are considered as the most promising material for low cost and high-efficiency solar cells. The higher efficiencies realized in CIGS based devices is due to the fact that the band gap of the material can be adjusted towards the optimum value (1.45 eV) by the partial substitution of gallium for indium [2]. The copper indium gallium dieseline, CuIn1-xGaxSe2 (CIGS), based solar cells have largest efficiencies on the laboratory scale and as well as on the level of large-area modules. In addition CIGS thin-film modules exhibit excellent outdoor stability and radiation hardness. Therefore, this combination of high efficiency coupled with stability and radiation hardness makes CIGS a promising material for the low cost, high efficiency solar cells [3]. CIAS thin films have been prepared by several techniques including CBD [3, 4] co-evaporation [5], RF magnetron sputtering [6], chemical bath deposition (CBD) [7] and sequential deposition methods [8,9]. The aim of the Present work is to study the effect of thickness and annealing temperature on structural and optical properties of CIGS thin films that was prepared by thermal evaporation technique.

II. EXPERIMENTAL PARTS

$CuIn_{0.7}Ga_{0.3}Se_2$ (CIGS) films of different thickness (500 and 1000) nm were prepared by the alloy (CIGS) which obtained by fusing the mixture of the appropriate quantities of the elements Cu, In, Ga and Se of high purity (99.999%) are sealed in vacuum pressure 10^{-4} mbar and heated at the 1373K at a rate of 10 ℃/min for 12 hours. CIGS films were prepared onto a glass slide substrate by thermal evaporation technique in a high vacuum system of ($5x10^{-5}$) mbar using Edward coating unit model (E 306) from molybdenum boat. The distance from molybdenum boat to substrate was about (15 cm), the deposition rate was about (5 nm/s) for all the films on glass substrate as prepared. CIGS thin films of (500 and 1000) nm thickness were annealed at (373, 473,573) K for one hour in air. The structures of the deposited films have been examined by XRD methods using (Shimadzu 6000, Japan) x-ray diffractometer system. The optical parameters, such as the refractive index, real and imaginary parts of dielectric constant, extinction coefficient, and optical energy gap of CuIn1-xGaxSe thin films have been calculated, using the measurement of absorption and transmission as a function of wavelength in range (400-1100) nm, using UV-Visible 1800 spectra photometer.

III. RESULT AND DISCUSSION:

XRD patterns of the CIGS films with different thickness before and after annealing are shown in Fig. 1. All the deposited films are $CuIn_{0.7}Ga_{0.3}Se_2$ polycrystalline tetragonal type structure. The X-ray diffraction patterns have been used to estimate the crystallite size of CIGS thin films by using Scherrer's equation (1)[10] and listed in table (1),

$$D=\frac{k\lambda}{\beta\cos(\theta)} \qquad \text{----------------- (1)}$$

Where'd' is the interplanar spacing and h, k, and l are the Miller indices, D is the mean size of the crystallite, k is a dimensionless factor around 0.9, λ is the X- ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle, the results reveal that the crystalline size increases with thickness and annealing temperature increasing, indicating crystalline quality improvement.

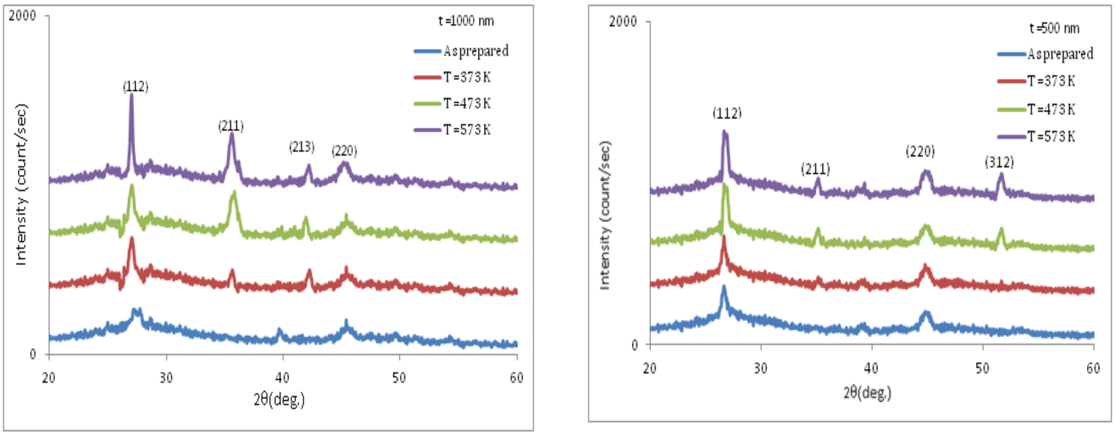


Fig.(1) XRD patterns of the CIGS films with different thickness before and after annealing

Table (1) crystallite size CIGS thin films with different thickness before and after annealing

Sample	Temperature (K)	crystallite size (nm)
Thin film CIGS t=500nm	As-prepared	14.56
	373	20.87
	473	27.34
	573	32.28
Thin film CIGS t=1000nm	As-prepared	10.76
	373	24.79
	473	41.32
	573	56.93

The optical transmission (T) and absorbance (A) spectra of CIGS thin films with varying thicknesses and annealing temperature have been shown in Fig (2) and Fig (3) The transmittance of the films was found to increase and absorbance was found to decrease with increase in wavelength, and transmittance of films with thickness (100nm) higher than that 500 nm may be due to improvement of the crystallinity or indicates a smooth surface and relatively good homogeneity of the films.

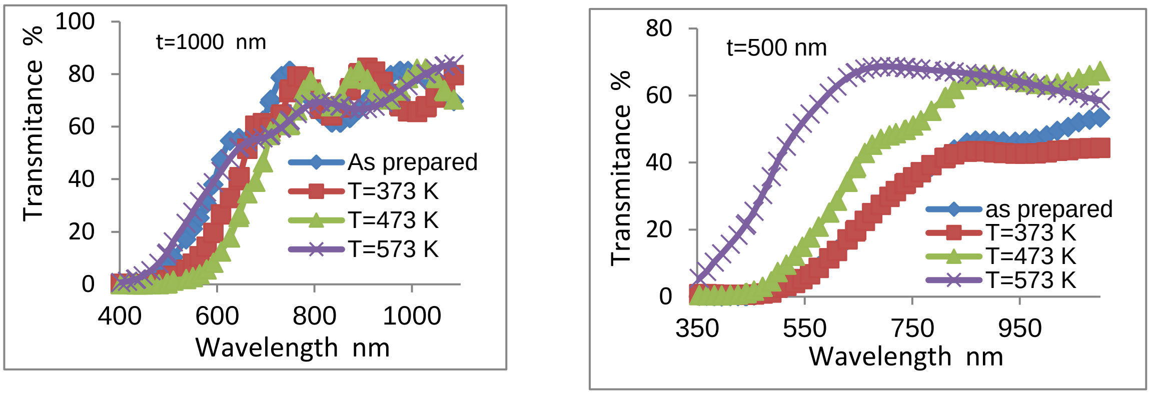


Fig. (2) Transmittance as a function of wavelength of the CIGS films with different thickness before and after annealing

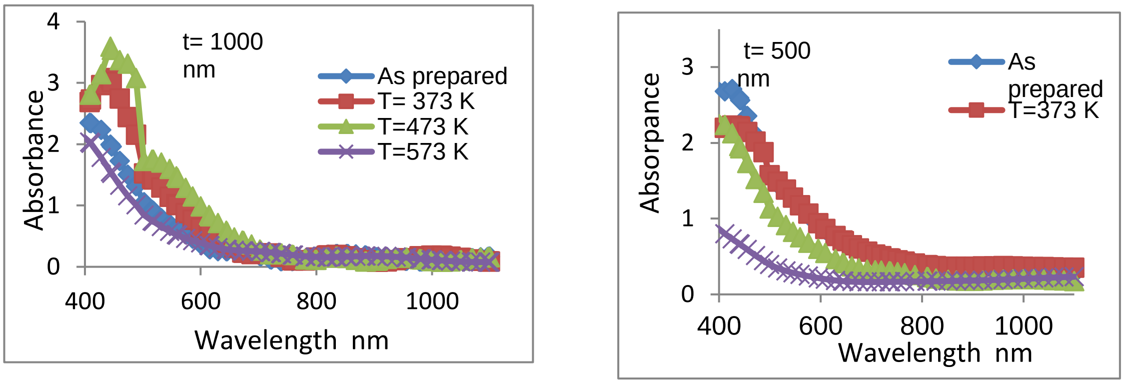


Fig. (3) Absorbance as a function of wavelength of the CIGS films with different thickness before and after annealing

The absorption coefficient α estimated by using following equation [11]:

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad \text{-------------} \quad (2)$$

Where'd' is the thickness of the film.

It is clear from Fig(4) that all values of absorption coefficient higher than 10^4 cm^{-1} this means the direct transition is possible occurs. Also, it can be seen from the figures that the absorption coefficient decrease with increase the thickness and annealing temperature for the film with the thickness 500nm, while for film (1000nm) the absorption coefficient increase with increasing annealing temperature up to 473 K then decreased at 573K, this behavior can be attributed to the density of localize states in energy band gap.

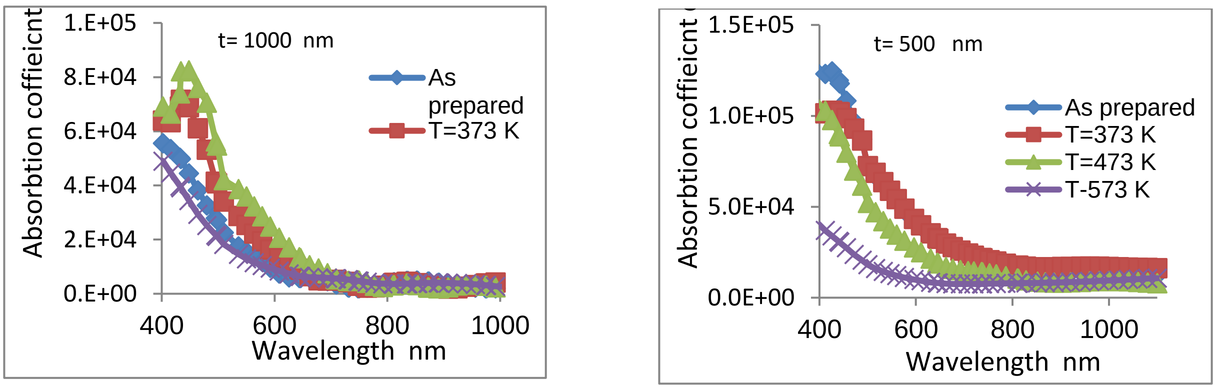
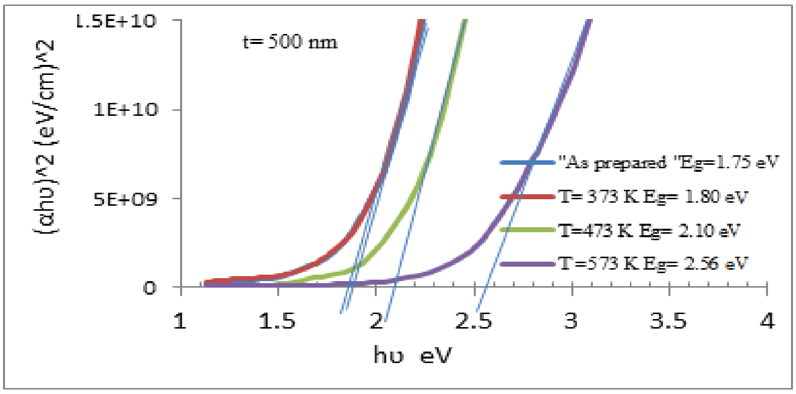


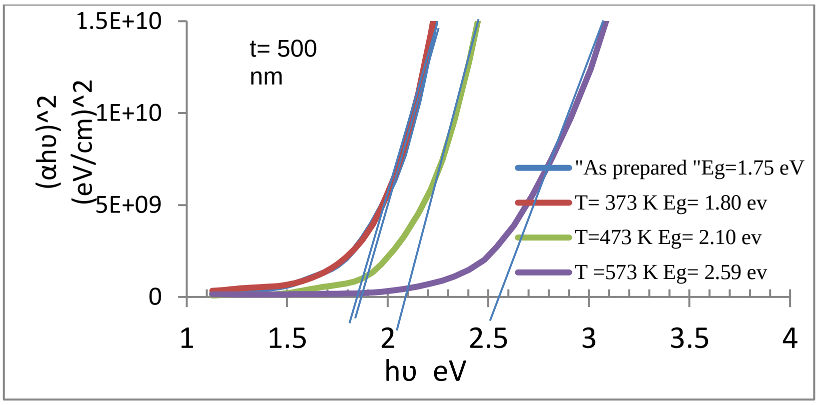
Fig (4) The variation of absorption coefficient as a function of wavelength of the CIGS films with different thickness before and after annealing

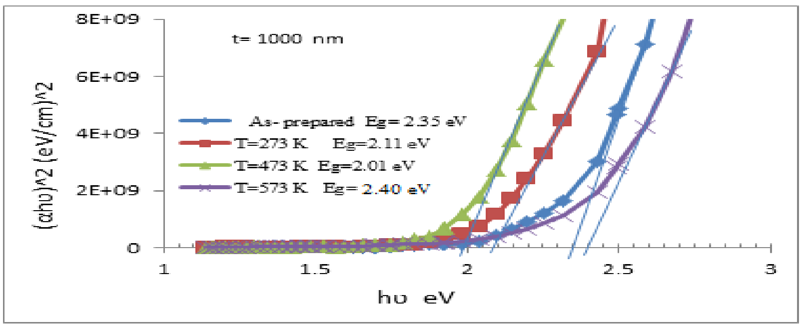
The optical band gap E_g is the calculated by using Tauc formula [11-12]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^{\frac{1}{r}} \qquad \text{------------- (3)}$$

Where B, is a constant, r, is factor depending which depends on the probability of transitions, it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively, $h\upsilon$, photon energy. The optical energy gap Eg thin films was calculated by plotting $(\alpha\, h\upsilon)^2$ versus $(h\upsilon)$ (figure 5a and 5b), then extrapolating the straight-line part of the plot to the photon energy axis. Many authors have reported such a variation in energy band gap with increase in film thickness [11]. However, an increase in band gap of thick CIGS film, with annealing, is consistent with the fact that the crystallinity of the polycrystalline thin film improves on annealing [12]. Table (2) shows the optical band gap of annealed and as-deposited CIGS thin films of different thicknesses. The value of optical band gap energy for increasing film thickness from 500 nm to 1000 nm has been found to be increased from 1.80 to 2.35 eV. In addition, annealing of the thin films improves their band gap value to 2.59 eV for 500 nm to 2.44 eV for 1000 nm thin films. The increasing in the band gap and sharpening of the band edge at the band gap region clearly shows the improvement in the film crystallite after annealing. On the other hand, the density of localized state in the film decreases with the film thickness, which leads to a increase in the energy band gap. Many authors have reported such a variation in energy band gap with increase in film thickness. However, an increase in band gap of thick CIGS film, with annealing, is consistent with the fact that the crystallinity of the polycrystalline thin film improves on annealing [12].







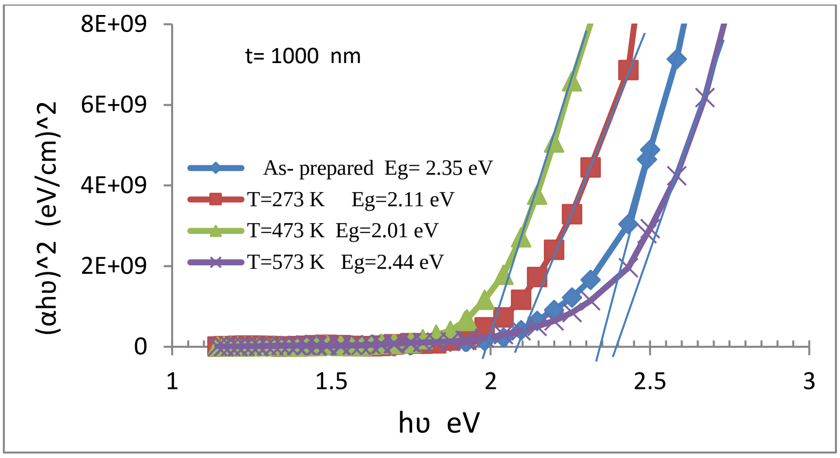
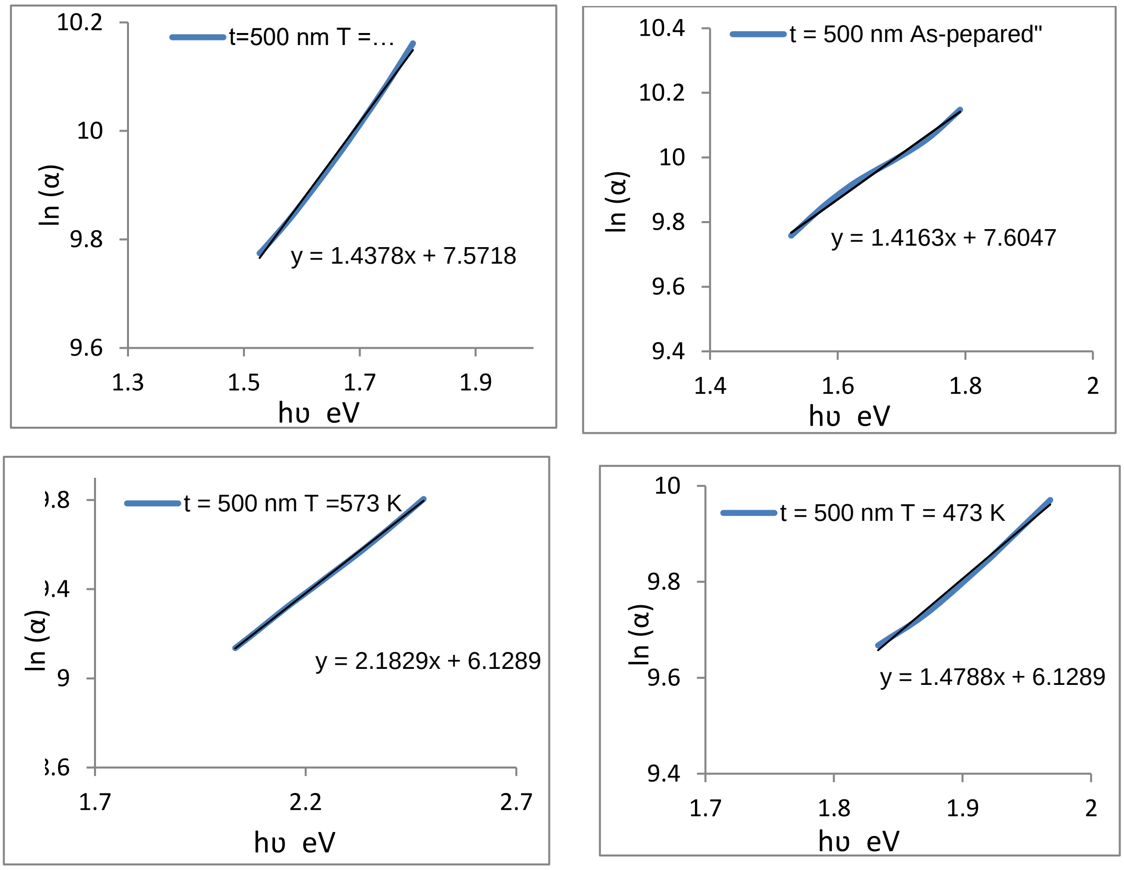


Fig. (5) The paned gap energy of the CIGS films with different Thickness before and after annealing

The width of localized state into energy gap E_u is the calculated by using Urbach formula [13]:

$$\alpha = \alpha_0 \exp\left(\frac{hv}{\Delta Eu}\right) \qquad \text{---------------- (4)}$$

Where α_0 , is a constant, ΔE_u,is the width of localized state into energy gap. Table (2) shows the width of localized state into energy gap of as-prepared and annealed CIGS thin films of different thicknesses. The value of the width of localized state into energy gap for increasing film thickness from (500 to 1000) nm has been found to be decrease from (0.706 to 0.218) eV. In addition, annealing of the thin films decrease their width of localized state into energy gap value to 0.458 eV for 500 nm to 0.205 eV for 1000 nm thin films shows as Fig.(6a and 6b).



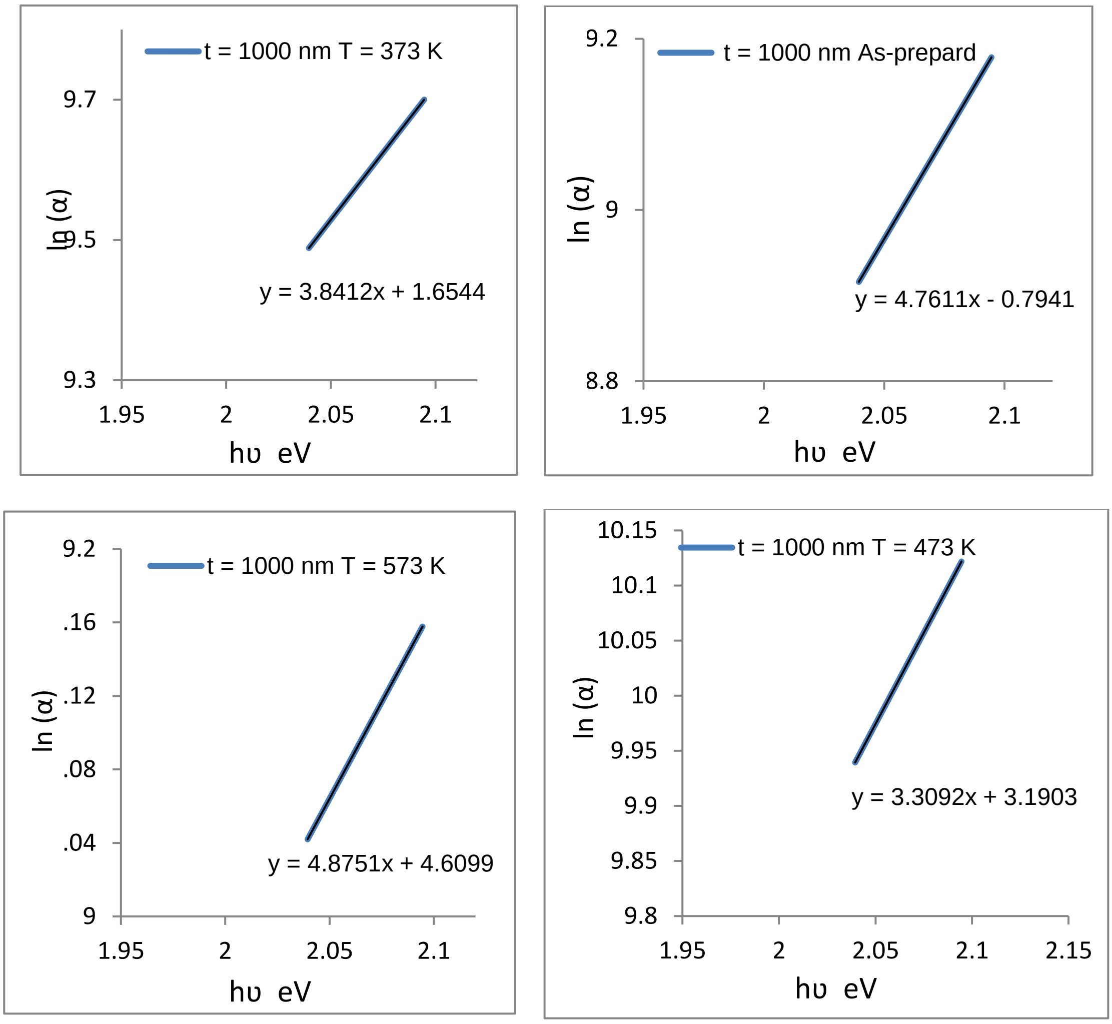


Fig. (6) The variation of paned gap energy of the CIGS films with thickness (t= 1000nm) before and after annealing

Table (2) The optical band gap of CIGS thin films with different thickness before and after annealing

Thickness (nm)	Temperature (K)	Eg (eV)	Eu eV
Thin film CIGS t=500nm	As prepared	1.75	0.706
	373	1.80	0.695
	473	2.10	0.676
	573	2.59	0.458
Thin film CIGS t=1000nm	As prepared	2.35	0.218
	373	2.11	0.276
	473	2.01	0.306
	573	2.44	0.205

. The extinction coefficient (k_o) of CIGS thin films were calculated from [11]:

$$k_o = \frac{\alpha\,\lambda}{4\,\pi} \qquad \text{-------------} \quad (5)$$

Fig(7) shows the extinction coefficient of CIGS thin films with different thickness before and after annealing .It is observed that the extinction coefficient decreases with increase in films thickness and annealing temperature and it behaves the same as absorption.

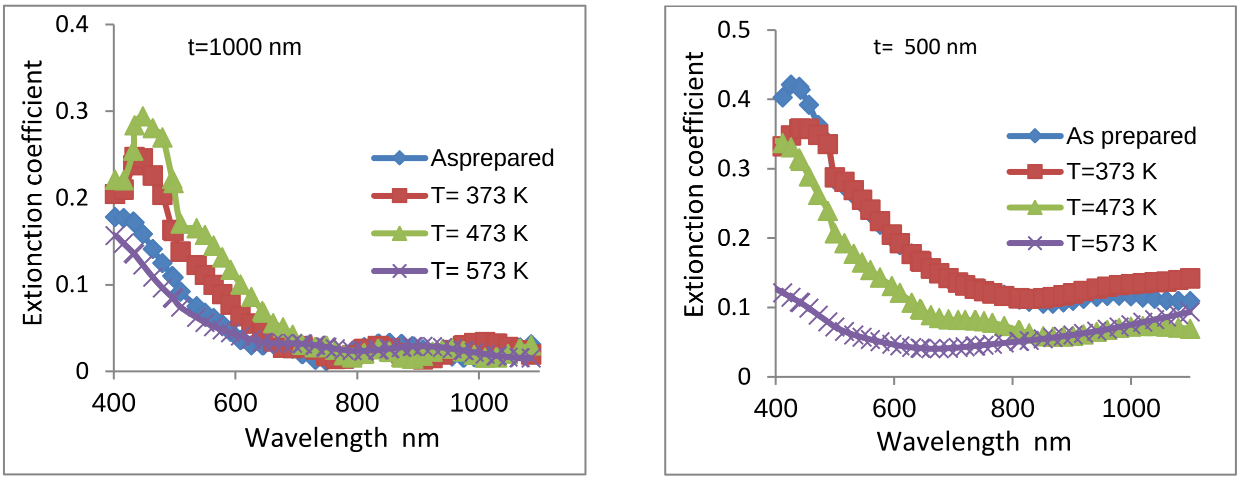


Fig. (7) The variation of extinction coefficient as a function of wavelength of the CIGS films with different thickness before and after annealing

The refraction index (n) value can calculate from the formula [11]:

$n= \{[4R/(R-1)]- k_o^2\}^{1/2} – [(R+1)/(R-1)]$ --------------- (6)

Where, R is the reflectance, the refractive index spectra of CIGS thin films with varying thicknesses and annealing temperature have been shown in Fig.(8) The refractive index decrease with increase in films thickness and annealing temperature probably due to the increase of the compactness of the films after the heat treatment simultaneously with the increase of the crystallite size.

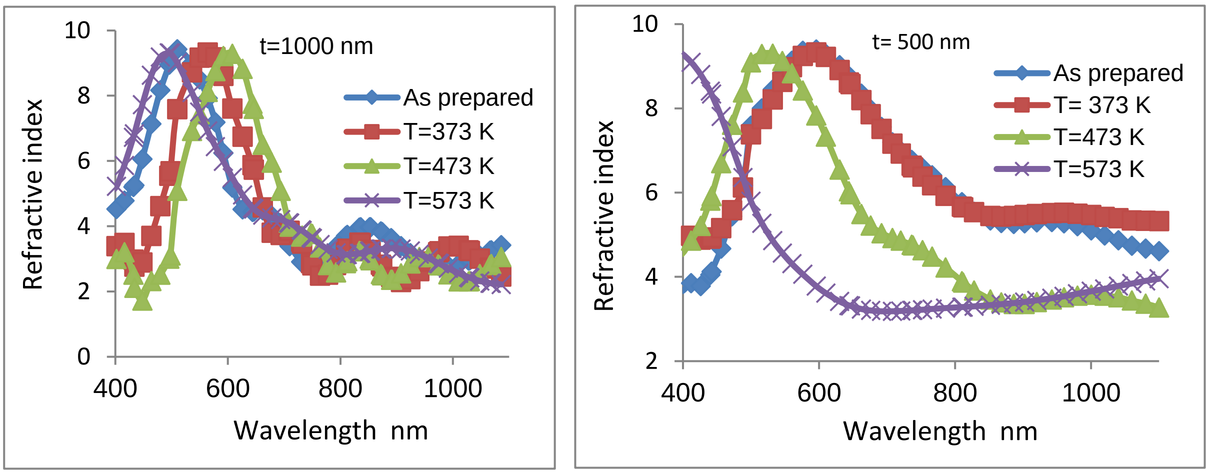


Fig. (8) The variation of refractive index as a function of wavelength of the CIGS films with different thickness before and after annealing.

The dielectric constant can be introduced by [14, 11]:

$\varepsilon = \varepsilon_1 - i\varepsilon_2$ ------------- (7)

Where,

$\varepsilon_1 = n^2 - k_0 2$ -------------- (8)

$\varepsilon_2 = 2nk_0$ -------------- (9)

Fig. (9 and 10) shows the variation of the real ε_1 and imaginary ε_2 parts of the dielectric constant with varying thicknesses and annealing temperature as a function of wavelength. The behavior of ε_1 is similar to refractive index because the smaller value of k_o^2 comparison of n^2, while ε_2 is mainly depends on the k_o values, which are related to the variation of absorption coefficient. It is found that ε_1 and ε_2 decrease with the increase of thicknesses and annealing temperature. The imaginary part represents the absorption associated of radiation by free carriers [15,16].

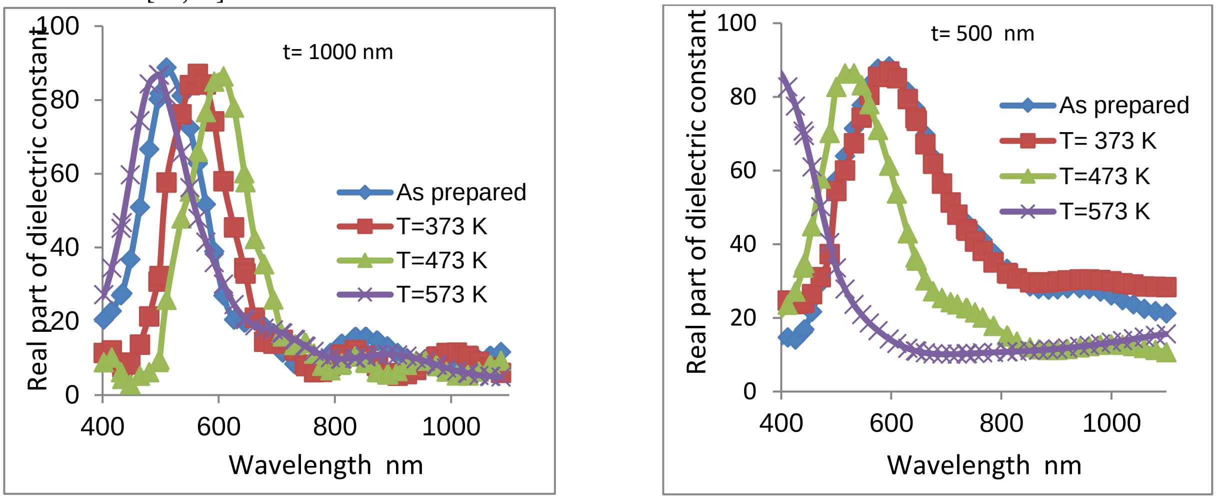


Fig. (9) The variation of real part of dielectric constant as a function of wavelength of the CIGS films with different thickness before and after annealing.

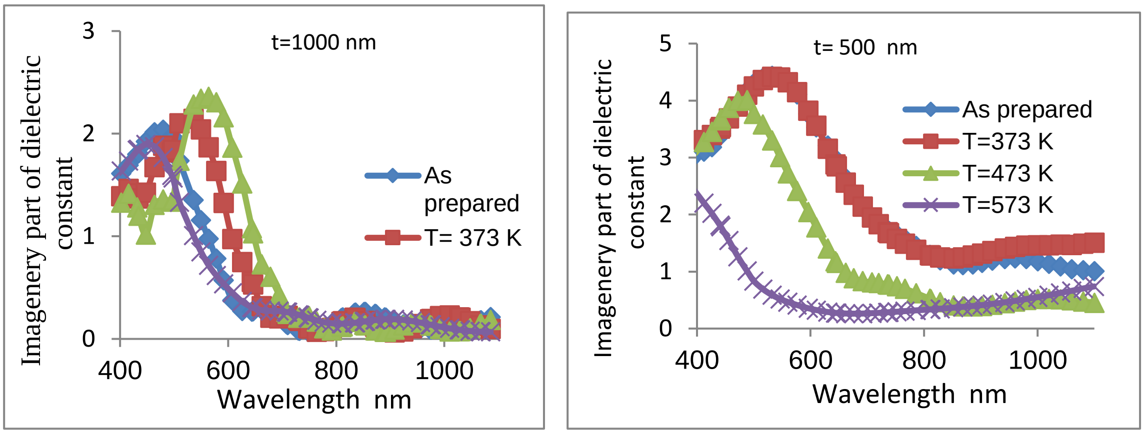


Fig.(10) The variation of imaginary part of dielectric constant as a function of wavelength of the CIGS films with different thickness before and after annealing.

To determine the behavior of the optical constants with different thickness before and after annealing, we selected a specific wavelength near the absorption edge and determined the values of those constants at that wavelength. Values are shown in table (3).

Table (3)the optical constant of the CIGS films with different thickness before and after annealing at wavelength (λ= 630nm).

(CIGS) films Properties		Optical constant at λ=630nm					
Thickness (nm)	Temperature (K)	$\alpha(cm^{-1})$	n	k	ε_r	ε_i	E_g (eV)
t=500	As prepared	35512.1	9.02	0.1779	81.42	3.21	1.75
	373	35338.5	8.91	0.1771	79.41	3.15	1.80
	473	21388.2	6.55	0.1071	42.91	1.40	2.10
	573	8484.7	3.41	0.0485	11.69	0.29	2.59
t=1000	As prepared	6039.2	4.52	0.0300	20.48	0.27	2.35
	373	11115.1	6.74	0.0553	45.51	0.74	2.11
	473	17225.5	8.83	0.0857	77.96	0.51	2.01
	573	7372.6	4.95	0.0367	24.59	0.36	2.44

IV. CONCLUSION

1- The X-ray diffraction observed that all the prepared films were of films have polycrystalline tetragonal type structure of multiphase.
2- crystalline size increases with thickness and annealing temperature increasing
3- The optical energy gap has an allowed direct transition types and it was increase with the increasing of the thickness and annealing temperature.
4- The variation of real and imaginary parts of dielectric constant have similar trends as for refractive index and extinction coefficient respectively

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