



## Effect of heat treatment on the structural and optical properties of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}$ thin films

**I.H.Khudayer**

Associate Professor, Department of Physics, College of Education for Pure Science/ Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

**Bushra. K.H.al-Maiyaly**

Associate Professor, Department of Physics, College of Education for Pure Science/ Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

**Ali Hussein abd al razak**

Researcher, Department of Physics, College of Education for Pure Science/ Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

### ABSTRACT

The structural, optical properties of copper indium gallium selenite ( $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}$ ) have been studied.  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}$  thin films for  $x=0.6$  have been prepared by thermal evaporation technique, of  $2000 \pm 20$  nm thickness, with rate of deposition  $2 \pm 0.1$  nm/sec, on glass substrate at room temperature. Heat treatment has been carried out in the range (373-773) K for 1 hour. It demonstrated from the XRD method that all the as-deposited and annealed films have polycrystalline structure of multiphase. The optical measurement of the CIGS thin films conformed that they have, direct allowed energy gap equal to 1.7 eV. The values of some important optical parameters of the studied films such as (absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant) were determined using absorption and transmission spectra.

### KEYWORDS

CIGS thin films, optical properties, XRD, structural properties

### 1.INTRODUCTION:

Thin layers of  $\text{CuInSe}_2$  (CIS) and  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) and  $\text{CdTe}$  compound semiconductors are important for terrestrial applications because of their high efficiency, long-term stable performance and potential for low-cost production. Because of the high absorption coefficient ( $\sim 10^5 \text{ cm}^{-1}$ ) a thin layer of  $\sim 2$   $\mu\text{m}$  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, because of their high absorptivity ( $> 10^5 \text{ cm}^{-1}$ ) and stability against photo-degradation. Solar cells based on  $\text{CuInSe}_2$  (CIS) and  $\text{Cu(In,Ga)Se}_2$  (CIGS) have reached conversion efficiencies as high as 18.8% and 19.5%. Several methods for preparation CIS (CIGS) absorber films have been reported, such as co-evaporation, sputtering and selenization, and electrodeposition[1,2], sequential evaporation, closed space vapor transport, spray pyrolysis[3].

Within the family of Cu-chalcopyrite semiconductors,  $\text{Cu(In,Ga)Se}_2$  is of considerable interest for photovoltaic applications because of its desirable direct band gap in the range 1.0-1.4 eV, high optical absorption coefficient, a moderate surface recombination velocity and radiation resistance. These properties give an opportunity for the fabrication of low cost, stable and high efficiency thin film solar cells [4, 5].

The copper indium gallium diselenide,  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS), based solar cells have largest efficiencies on the laboratory scale and as well as on the level of large-area modules. In addition to high efficiencies, 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 [6].

X-ray Diffraction (XRD), was used to the position and intensity of diffracted intensity spectra versus Bragg's angle,

gives information on the crystal structure such as phase crystalline, polycrystalline, amorphous, grain size, and lattice parameter.

**The inter planer distance  $d$  (hkl) for different planes was measured by Bragg's law[7]:**

$$2d \sin \theta = n \lambda \quad \text{-----} (1)$$

Where  $n$  is the reflection order.

**The optical absorption spectrum used to determine the optical energy gap and the absorption coefficient. We employed Tauc formula equation[6]:**

$$\alpha h\nu = B (h\nu - E_g^{\text{opt}})^{1/r} \quad \text{-----} (2)$$

Where,  $B$  is a constant inversely proportional to amorphousity,  $h\nu$  is the photon energy (eV),  $E_g^{\text{opt}}$  is the optical energy gap (eV), and  $r$  is constant and may take values 2, 3, 1/2, 3/2 depending on the material and the type of the optical transition. There are two types of the optical transitions, direct and indirect transition, according to the type of materials and the optical transition.

The optical behavior of a material is generally utilized to determine its optical constant [refractive index ( $n$ ), extinction coefficient ( $k$ ) and, real ( $\epsilon_1$ ) and imaginary parts ( $\epsilon_2$ ) of dielectric constant].

**The refraction index value can calculate from the formula [8]:**

$$n = \{ [4R/(R-1)] - k^2 \}^{1/2} - [(R+1)/(R-1)] \quad \text{-----} (3)$$

Where,  $R$  is the reflectance, and  $k$  is the extinction coefficient.

**The absorption coefficient is related to  $k$  by:**

$$\alpha = 4\pi k / \lambda \quad \text{-----} (4)$$

Where,  $\lambda$  is the wavelength of the light.

**The dielectric constant can be introduced by [9]:**

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \quad (5)$$

$$\text{Where, } \varepsilon_1 = n^2 - k^2 \quad (6)$$

$$\varepsilon_2 = 2nk \quad (7)$$

Where,  $\varepsilon_1$ ,  $\varepsilon_2$  are the real and imaginary parts of dielectric constant respectively.

## II. EXPERIMENTAL PARTS

The  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}$  thin films have been prepared by using thermal evaporation method at pressure about  $2 \times 10^{-6}$  mbar in vacuum, with rate of deposition  $2 \pm 0.1$  nm/sec, using Coating unit (Edward-320E),

Annealing heat treatment have been done for the various degree of temperature from (373, 473, 573, 673, and 773) K, with furnace of (Annealing oven Victoreen 187) type. 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  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}$  thin films have been calculated, using the measurement of absorption and transmission as a function of wave length in range (400-1100) nm, using UV-Visible 1800 spectra photometer.

## III. RESULTS AND DISCUSSION:

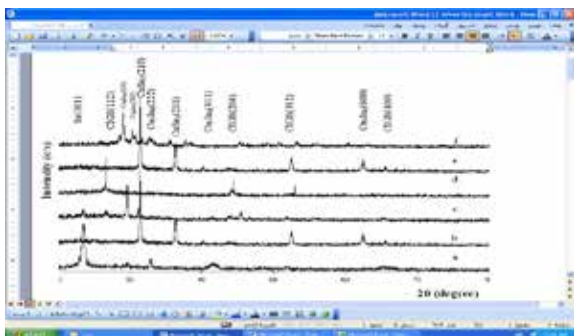
### 1-Structural properties:

The as-deposited and all annealed samples of CIGS thin films were analyzed structurally for the identification of different phases.

The XRD patterns of all CIGS samples are shown in Fig. (1). The reflecting planes and the corresponding phases of CIGS are indicated in these patterns

It is obvious from these patterns that the samples contained a mixture of the following phases; Se exhibits only one peak corresponding to (101) orientation in the case of as deposited films,  $\text{Cu}_3\text{In}_4$  in (220,300,411,600) direction,  $\text{CuSe}_2$  in (210, 211) direction, which was found to be necessary for the incorporation of S into the partly selenized alloy in order to form good quality of absorber layer [3], and CIGS along certain crystallographic planes such as (112, 204,312,400) direction for all other samples.

This results show that there was phase separation for as-deposited films, and this phenomena disappear in the annealing condition indicating continuous growth and improved structural formation of binary  $\text{CuSe}_2$  and quaternary CIGS compounds.



**Fig.(1) XRD pattern for CIGS thin films for different values of annealing temperature within the range (373-673) K, (a) at R.T(300K) , (b) at 373 K, (c) at 473 K, (d) at 573 K, (e) at 673 K and (f) at 773 K.**

### 2-Optical properties:

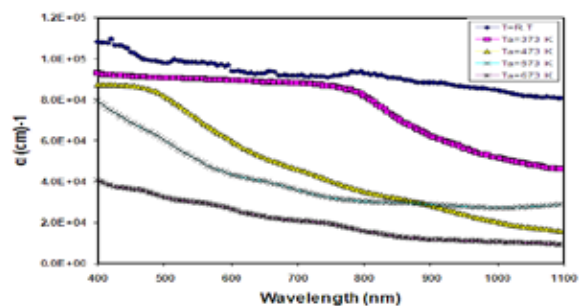
Optical experiments provide a good way of examining the properties of semiconductors. Particularly measuring the absorption coefficient for various energies gives information about the band gaps of the material. Knowledge of these band gaps is extremely important for understanding the electrical properties of a semiconductor, and is therefore of great practical interest.

This mechanism of the absorption of light mainly depends on the relation between the band gap energy and the photon energy of light. The optical characteristic of CIGS thin films in this experiment is measured as a function of wavelength of the spectrum of light. The absorptivity is characteristic of photon absorption by generated electron-hole pairs or generated of carrier charge [10].

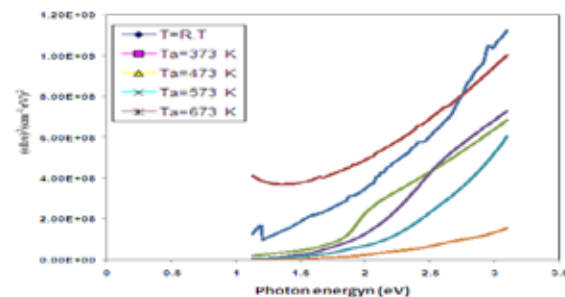
Fig.(2) The variation of absorption coefficient as a function of wavelength at different annealing temperature within the range (373-673) K, the diagram shows that for the low values of wavelength i.e. high energies there is no transmission because all the light is absorbed. For low energies however there are no appropriate electronic transitions possible so transmission is very high in this range. It is not 100% however, because of reflection. There is a relatively sharp delimitation between the areas of high and low absorption.

The measurement results of absorption coefficient as a function of photon energy for the interval of 1100-800 nm is very low. Since, there is a minimum creation of carrier in the conduction band to valence band. That's mean the carrier will be generated in the first interval in the stable condition, because the carrier generate only in the interband transition. In the second interval, the value about 800 to 700 nm, the absorption coefficients shown significantly increase with exponentially which indicating the starting of the transitions processes of electrons and holes to be generated a carrier. This carrier could be applied in the current carrying charge on the sensor and solar cell application.

Then, less than 700 nm, the absorption coefficient is become stable again, because the generation of carrier approximately constant. That implied the carrier concentration is saturated and has reached the optimum value of optical absorption.



**Fig.(2) The variation of absorption coefficient as a function of wavelength at different annealing temperature (373-673) K.**



**Fig.(3) The variation of  $(\alpha h\nu)^2$  as a function of photon energy at different annealing temperature (373-673) K.**

The optical energy gap was found to increases after heat treatment, this increasing is attributed to existence of a tails below the fundamental absorption edge (near the bands) which observed in the absorption coefficient Fig.(2), which is a characteristic of most of the optical data on polycrystalline semiconductors which is considered to be determined mainly to the structural disorder existing at the grain boundaries, these tails decreased after heat treatment due to the increasing in crystallite size and the grain boundaries became more ordered than in as- deposited films [11].

The increase of energy gap with annealing temperature is due to decrease the absorption coefficient as shown in table (1).

The decrease of absorption coefficient caused by the magnitude of the photon energy at almost equal to the energy gap and reduction factor as a function of annealing temperature.

The dispersion is a measure of the change of the refractive index with wavelength.

Dispersion can be explained by applying the electromagnetic theory to the molecular structure of matter. If an electromagnetic wave impinges on an atom or a molecule the bound charges vibrate at the frequency of the incident wave [11].

Fig.(4) represent the variation of the refractive index as a function of wavelength at different annealing temperature within the range (373-673) K. It can be seen that in the main spectral transmission region the refractive index increases towards shorter wavelength. Additionally the dotted line shows the absorption coefficient as a function of the wavelength.

The refractive index depends also on the density of the measured sample, which is affected by its temperature. Typically, refractive index decreases with the decreasing density (increasing temperature). The measurement of a refractive index is therefore reported together with the temperature and the wavelength of light used [12].

The refractive index increases after the heat treatment probably due to the increase of the compactness of the films after the heat treatment simultaneously with the increase of the crystallite size [11].

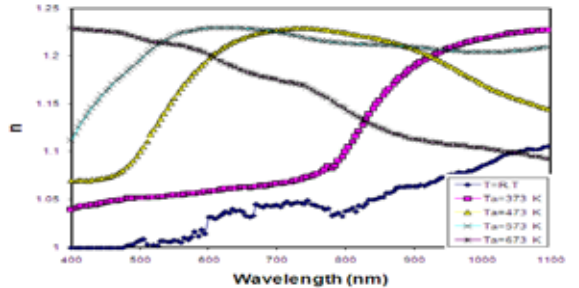


Fig.(4) The variation of refractive index as a function of wavelength At different annealing temperature (373-673) K.

From this figure it is found that the extinction coefficient (k) takes the similar behavior of the corresponding absorption coefficient.

One can deduce from this figure that the extinction coefficient increased with decreasing the photon energy up to  $\approx 3.647\text{eV}$  due to the high values of the absorption coefficient at this range of wavelength, after that the extinction coefficient increased very slightly which is associated with the increasing of the transmittance in this region and the large decreasing of the absorption coefficient at this wavelength.

The extinction coefficient is affected by heat treatment, which is decreased after annealing process. This behavior of the extinction coefficients values similar to that of the absorption co-

efficients for the same reasons as mentioned before.

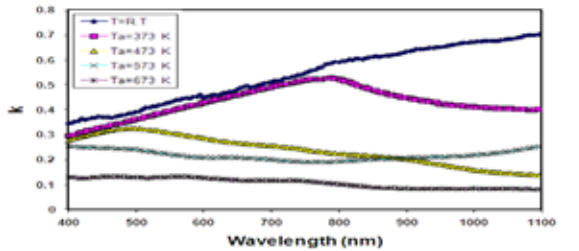


Fig.(5) The variation of extinction coefficient as a function of wavelength at different annealing temperature (373-673) K.

Figures (6 and 7) shows the variation of ( $\epsilon_1$  and  $\epsilon_2$ ) which is calculated from equation 6&7 respectively with different annealing temperatures as a function of wavelength. The behavior of  $\epsilon_1$  is similar to refractive index because the smaller value of  $k^2$  comparison of  $n^2$ , while  $\epsilon_2$  is mainly depends on the k values, which are related to the variation of absorption coefficient. It is found that  $\epsilon_1$  and  $\epsilon_2$  decrease with the increase of Ta.

The imaginary part represents the absorption associated of radiation by free carriers [13,14]. Table (1) gives values of the real and imaginary parts of the dielectric constant at wavelength equal to 750 nm.

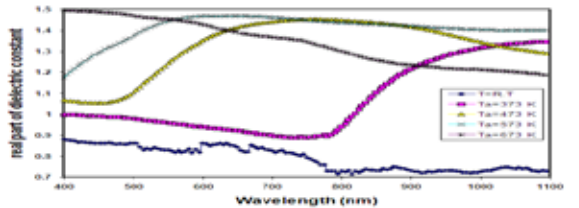


Fig.(6) The variation of real dielectric constant as a function of wavelength at different annealing temperature (373-673) K.

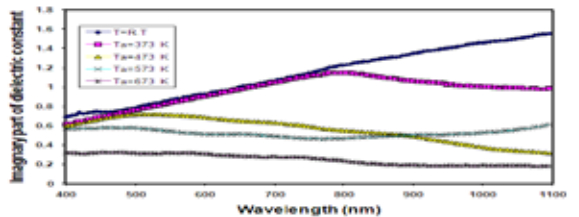


Fig.(7) The variation of imaginary dielectric constant as a function of wavelength at different annealing temperature (373-673) K.

Table (1) the optical parameters  $E_g(\text{eV})$ ,  $\alpha(\text{cm}^{-1})$ , k, n,  $\epsilon_1$ ,  $\epsilon_2$  for CIGS thin films for different annealing temperature.

T(K)	$E_g(\text{eV})$	$\alpha(\text{cm}^{-1})$	K	n	$\epsilon_1$	$\epsilon_2$
300	0.8	91630	0.55	1.05	0.79	1.14
373	1.35	86477	0.52	1.07	0.88	1.11
473	1.7	40302	0.24	1.22	1.34	0.59
573	1.85	32011	0.19	1.22	1.45	0.47
673	1.88	19114	0.11	1.17	1.45	0.26

## VI.CONCLUSIONS

- 1- The X-ray diffraction observed that all the prepared films were of poly crystalline structure.
- 2- The optical energy gap have an allowed direct transition types and it was increase with the increasing of the annealing temperature.
- 3- The variation of real and imaginary parts of dielectric constant have similar trends as for refractive index and extinction coefficient respectively according to Maxwell's equations

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