IJIRSET

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 5, Issue 6, June 2016**

# Effect Of heat Treatment On The Optical Properties Of $CuInSe_2$ Thin Films

Iman H. Khudayer [1] , Ahmed Z. Obaid [2]

Associate Professor, Dept. of Physics, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Iraq[1]

Ph.D. student, Dept. of Physics, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Iraq[2]

**Abstract:** $CuInSe_2$ (CIS)thin films have been prepared by use vacuum thermal evaporation technique, of 750 nm thickness, with rate of deposition 1.8±0.1 nm/sec on glass substrate at room temperature and pressure ($10^{-5}$) mbar. Heat treatment has been carried out in the range (400-600) K for all samples. The optical properties of the CIS thin films are been studied such as (absorption coefficient, refractive index, extinction coefficient, real and imaginary dielectric constant)by determined using Measurement absorption and transmission spectra. Results showed that through the optical constants we can made to control it is wide applications as an optoelectronic devices and photovoltaic applications.

**Keywords**: $CuInSe_2$ (CIS)thin films, optical properties, the energy gap, vacuum thermal evaporation.

## I. INTRODUCTION

Semiconductor thin films are especially attractive for thin film solar cell applications because of their high optical absorption coefficient and their versatile optical and electrical properties. A copper indium selenium thin film ($CuInSe_2$) is a direct band gap material, a high absorption coefficient, reasonable work function, good stability and largest efficiency[1]. Received considerable attention as one of the most promising materials for the next generation of solar cells. Because of its high conductivity with high transparency in the visible region, it has been used in several applications including optoelectronic devices and photovoltaic applications [2,3].

A copper indium selenium thin film ($CuInSe_2$) is a direct band gap material; it has 1.03 eV in band gap, high optical absorption coefficient ($10^6$ $cm^{-1}$), reasonable work function, good stability and largest efficiency (it achieved an efficiency of 17%) [1,2]. Therefore, these properties make $CuInSe_2$ a promising material for photovoltaic applications[3].It is known that the electrical, optical, morphological and structural properties of this material are strongly influenced by the technique used for the elaboration and by the several experimental parameters.

## II. EXPERIMENTAL DETAILS

From $CuInSe_2$ (CIS) alloy thin films have been deposited on glass substrate by thermal vacuum evaporation technique using (Edwards – Unit 306) system with $2.5x10^{-5}$ mbar at room temperature. The thickness of films were determined with (Precisa-Swiss) microbalance by using the weighing method and found to be about (750∓10) nm, with deposition rate about (1.8∓0.1) nm/sec.

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

The absorption coefficient (α) of a film of thickness (t=750 nm) can be calculated from the transmittance spectrum using the following relation[4]:

$$\alpha = 2.303\,\frac{A}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where: t is the film thickness in nanometer ,A is the absorbance, which is calculated from the relation[4]:

$$A=\log(1/T) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where: (T) is the transparence .

The fundamental absorption, which corresponds to electron excitation from valance band to conduction band, can be used to determine the nature and value of the optical band gap. Which could be calculated using the expression[5]:

$$\alpha h\nu = B(h\nu - Eg)^{n} \ldots\ldots\ldots\ldots\ldots (3)$$

Where: B is constant depending on the type of semiconductor, α($cm^{-1}$) is the absorption coefficient, hν is the photon energy and Eg (eV)is the optical band gap. The parameter (n) is an index related to the nature of the material and which is determined by the optical transition involved in the absorption process, it specifies the allowed direct transition (n = 1/2) and allowed indirect transition (n = 2) in the electronic band structure.

When electromagnetic radiation incident on the surface, part of it reflected and another part is absorbed while the latter part is transmitted. The optical constants fully describe the optical behavior of materials; they are important fundamental properties of matter [6,7]. The optical properties of an evaporated film depend strongly on the technique of evaporation . Optical constants included refractive index (n), extinction coefficient (k), real part ($\varepsilon_1$) and imaginary parts ($\varepsilon_2$) of dielectric constant. The refractive index (n) can be calculated using following equation,[5]:

$$n=\left[\frac{4R}{(R-1)^2} - k^2\right] - \frac{R+1}{R-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where: R is the reflectance and given by the following equation [4]:

$$R + A + T = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The refractive index dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion.

The extinction coefficient( k), (imaginary part of the refractive index), which is related to the exponential decay of the wave as it passes through the medium can be determined by using the following equation[7]:

$$k = \frac{\alpha\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where: λ is the wavelength of the incident radiation.

The fundamental electron excitation spectrum of the films was described by means of a frequency dependent of the complex electronic dielectric constant(ε), and it is defined as [6,8]:

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 5, Issue 6, June 2016**

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

Where: $\varepsilon_1$ is the real of dielectric constant, $\varepsilon_2$ is imaginary dielectric constant ,$\varepsilon_1$ and $\varepsilon_2$ can be calculated by using the equations[5,8].:

$\varepsilon_1 = n^2-k^2$……………….………….(8)

$\varepsilon_2 = 2nk$ ……………………………(9)

## II. RESULTS AND DISCUSSION

Fig.1 shows the optical transmittance spectra as a function of wavelength from 350nm to 1090 nm of the CIS thin film with heat treatment (annealing) that has been carried out in the range(400-600) K for all samples. In generally the optical transmittance increases with the wavelength ,there was an increase annealing temperature which is lead to shift in the wavelength for the region where that the transmittance are increases. We are observe that is the transmittance is very high for all the range of annealing temperature at wavelength longer than (850 nm).

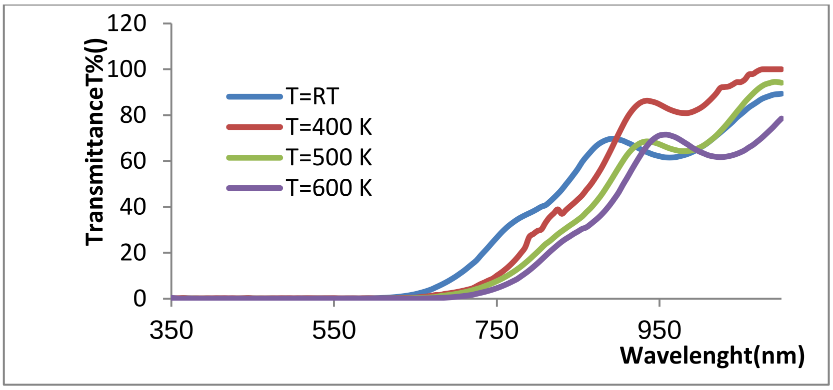


Figure No. (1):Variation the transmittance spectra as a function wavelength of CIS thin films with heat treatment

Absorption spectra of all films are shown in Fig.2. We can observe that the peaks of high absorption shifts to lower wavelength. Increase annealing temperature lead to increase the value of absorption and it change with range of temperature, because heat treatment lead to rearrangement the atoms in the structure .

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

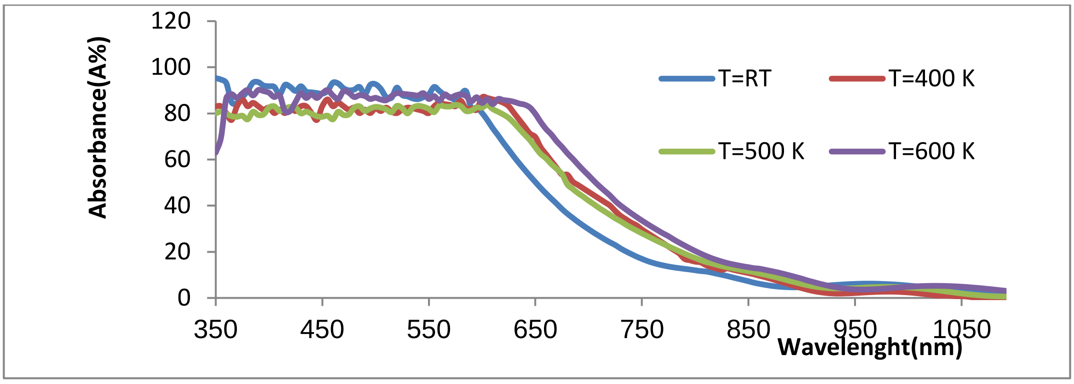


Figure No.(2): Variation the absorption spectra as a function wavelength of CIS thin films with heat treatment

The reflectance spectra of the CIS annealing films are shown in Fig.3. It observed that the average reflectance of $CuInSe_2$ annealing film increased rapidly at region in the range of (500-600) nm compare with room temperature and then increases with the increase of wave length from the range of (600 to 800) nm with the increase the annealing temperature of the CIS films and decrease with wavelength from the range of (800 to 1100) nm. The shift of transmittance and reflectance indicates that these are related to the changes in the film crystalline properties [9].

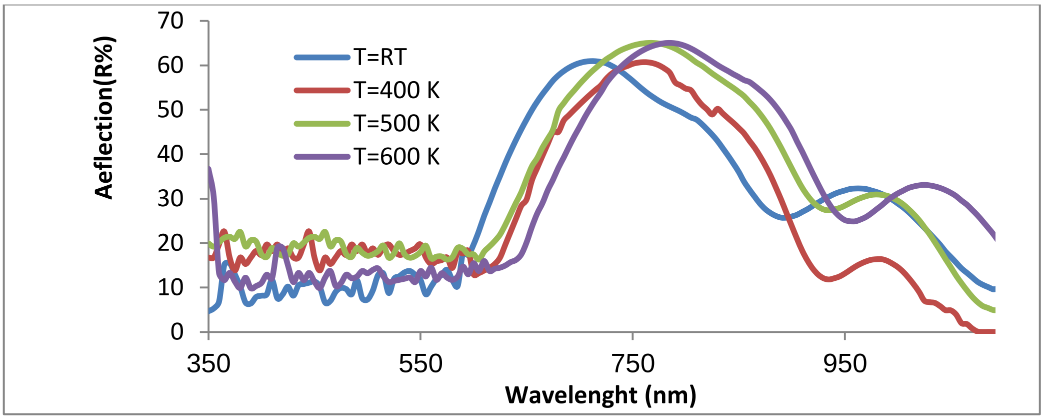


Figure No.(3): Variation of reflectance spectra as a function wavelength of CIS thin films with heat treatment

The ability of a material to absorb light is measured by its absorption coefficient and it is a very strong function of the photon energy and band gap energy [4]. The variation of the optical absorption coefficient with photon energy for the $CuInSe_2$ annealing films is shown in both fig.4and table No.(1).By using equation(1) we can calculated values of absorption coefficient are in the order of $10^4$ $cm^{-1}$.From Fig. 4 it is shown that in the higher photon energies (shorter wavelengths)the absorption coefficient (α) exhibits high value which means that there is a large probability of the allowed direct transition, and then (α) decreases with increase of wavelength. Also, it is shown in table No.(1) that absorbance increases with increase the annealing temperature of the $CuInSe_2$. So, this variation could be related to the variation of the crystallity.

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 5, Issue 6, June 2016**

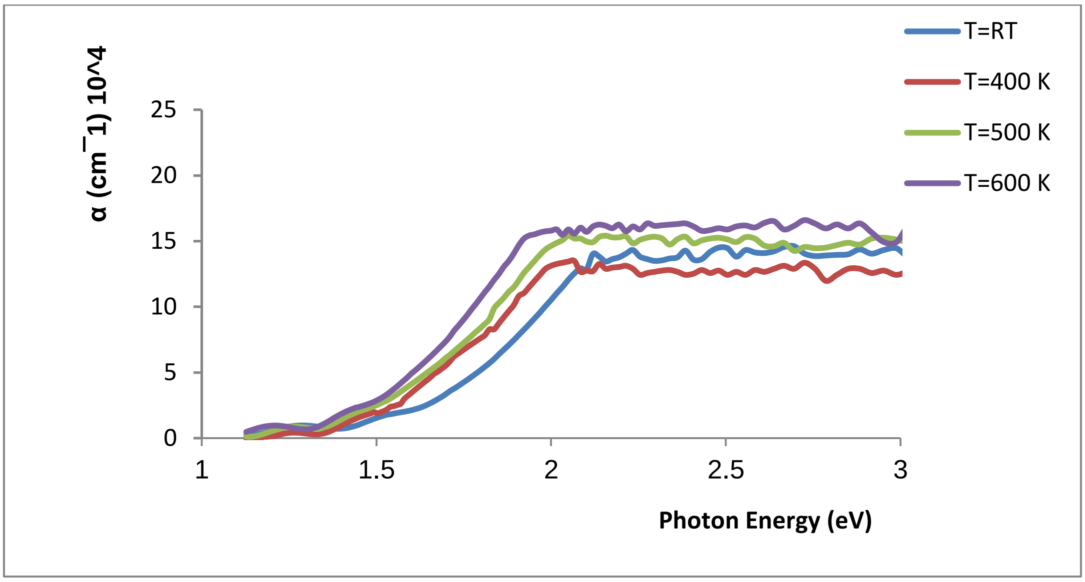


Figure No.(4): Variation of absorption coefficient as a function of photon energy of CIS thin films with heat treatment

Table No.(1) : Variation the optical properties with annealing temperature.

| T( K) | $\alpha$*10$^4$(cm$^{-1}$) | Eg (eV) | *K* | n | ε1 | ε2 |
|---|---|---|---|---|---|---|
| RT | 7.86 | 1.85 | 0.40 | 5.44 | 29.53 | 4.43 |
| 400 | 10.82 | 1.80 | 0.56 | 3.30 | 10.58 | 3.69 |
| 500 | 12.02 | 1.74 | 0.62 | 3.18 | 9.71 | 4.23 |
| 600 | 14.69 | 1.67 | 0.67 | 2.33 | 4.86 | 3.55 |

The optical energy band gap (Eg) was obtained from the intercept on the photon energy axis after extrapolating of the straight line section of the curve of $(\alpha h\nu)^2$ versus (hν) plot as shown in Fig.5. The film has direct band transitions which is an important characteristic for photovoltaic applications. The shift towards higher or to lower energies depends on the method of film preparation [10]. It was found that the annealing temperature of the CIS affects the energy band gap (Eg) shown in both Fig.6 and table No.(1). The energy gap is decrease with increase annealing temperature[1], This can be explained by the rearrangement of atoms in the structure and annealing of some defects. These defects appear as deep and shallow level in the band gap of the elaborated semiconductors material[9].


DOI:10.15680/IJIRSET.2015.0506001

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 5, Issue 6, June 2016**

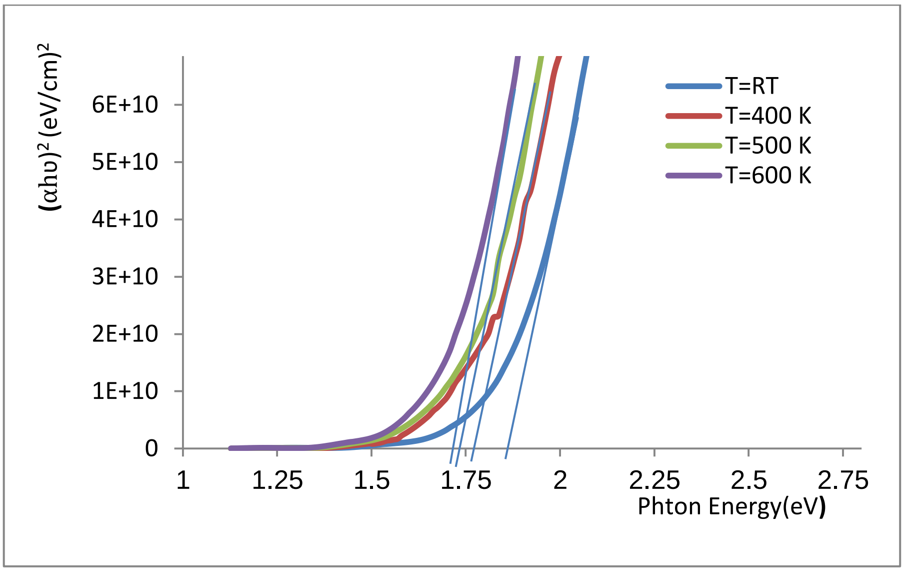


Figure No.(5): Variation of $(\alpha h\upsilon)^2$ with photon energy (hυ)of CIS thin films with heat treatment

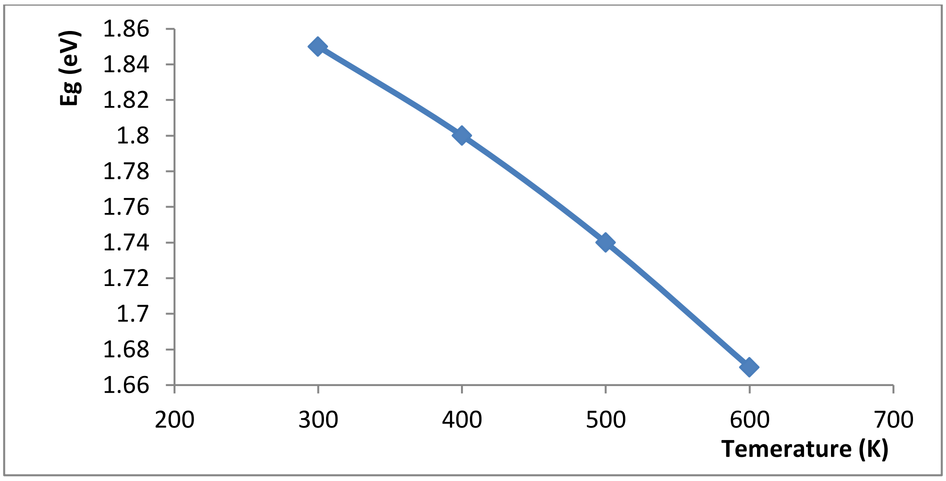


Figure No.(6): Variation of energy gap of CIS thin films as a function of annealing temperature

The refractive index values of the films were calculated using Eq. (4),the behavior of refractive index shown in fig.7.and we can notice that the refractive index increases with the increasing of photon energy (decreases in wavelength) indicating that all the films exhibit a normal dispersion behavior in the range (1.3 - 2) eV corresponding to the wavelength in the range (620-950) nm . From table No.(1) we demonstrated that the annealing films led to decrease the refractive index .

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 5, Issue 6, June 2016**

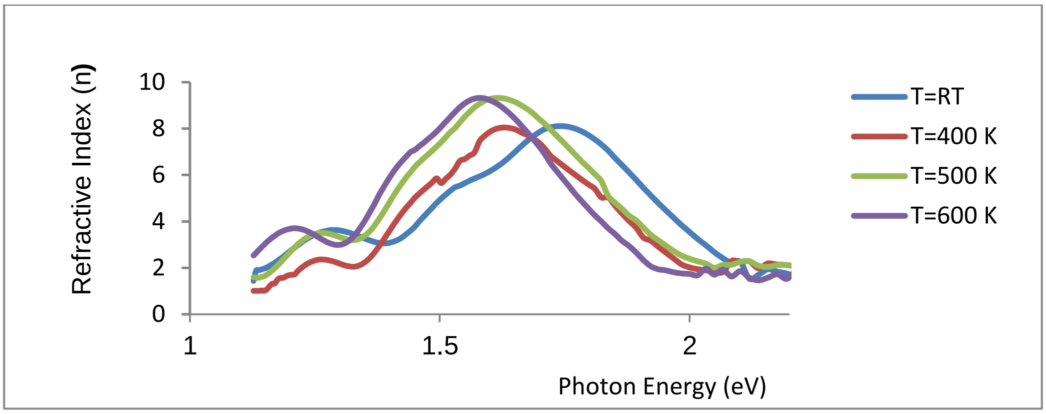


Figure No.(7): Variation of refractive index a function of photon energy of CIS thin films with heat treatment

Fig.8 shows the variation of extinction coefficient (k) as a function of photon energy. The behavior of (k) is nearly similar to the corresponding absorption coefficient (α) because of the extinction coefficient depends mainly on (α) according to the Eq.(5); for this reason, we note the increase of extinction coefficient with the increase of photon energy due to the increase of the absorption coefficient. This means that direct electronic transition happens in these films. From table No.(1) extinction coefficient (k) increase with increase annealing temperature due to change the properties of the film to crystalline structure .

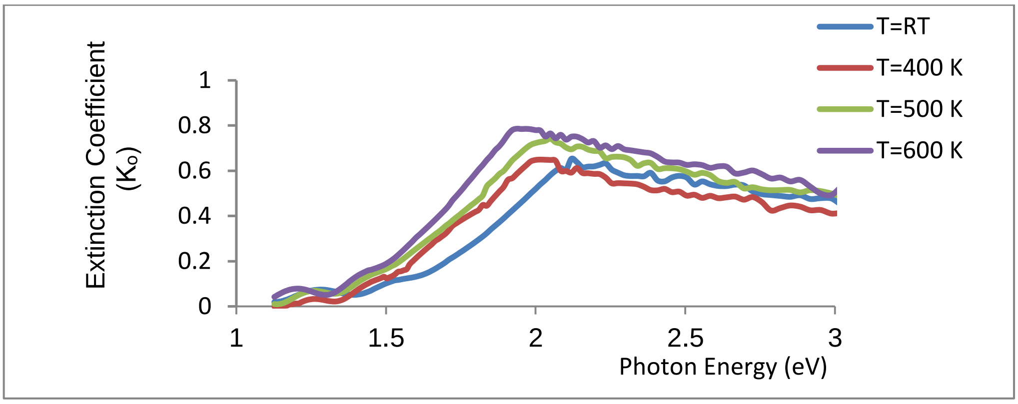


Figure No.(8): Variation of extinction coefficient as a function of photon energy of CIS thin films with heat treatment .

The complex dielectric constant (ε) is a fundamental intrinsic material property. The ($\varepsilon_1$) associated with the term that, how much it will diminution the speed of light in the material and ($\varepsilon_2$) which illustrates how a dielectric absorb energy from electric field due to dipole motion. The normal dielectric constant($\varepsilon_1$) and ($\varepsilon_2$) represents the absorption associated of radiation by free energy [7].

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

It could be from Fig.9 that the behavior of the real dielectric constant ($\varepsilon_1$) is nearly similar to the corresponding refractive index (n) it is clear from Eq.(7) because of the small value of ($k^2$). The value of real dielectric constant ($\varepsilon_1$) increase to maximum peak and then they start decreasing as the photon energy increases. From table No.(1) we note when the annealing temperature increases that is lead to decrease ($\varepsilon_1$) and ($\varepsilon_2$) because the film atoms are rearrangement in it sites and it trend towards crystallization. The behavior of ($\varepsilon_2$) with photon energy is nearly similar to the behavior that of ($\varepsilon_1$) but the value of ($\varepsilon_2$)smaller than ($\varepsilon_1$).

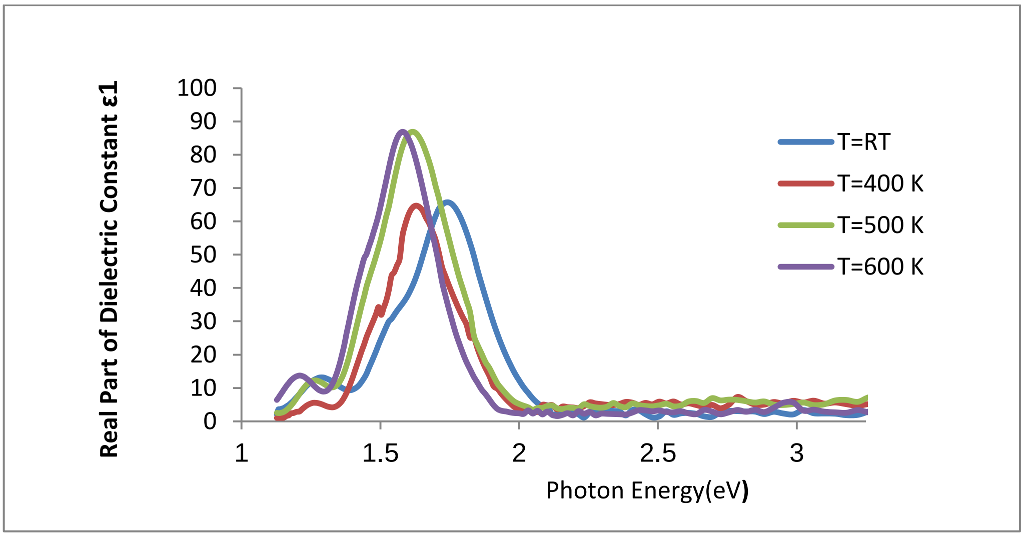


Figure No.(9): Real part of dielectric constant as a function of photon energy of CIS thin films with heat treatment

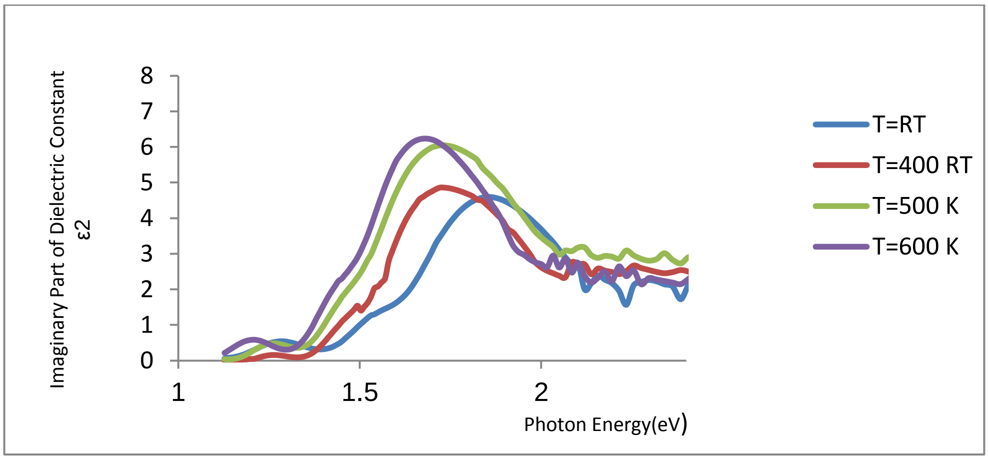


Figure No.(10): Imaginary part of dielectric constant as a function of photon energy of CIS thin films with heat treatment .

ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

*(An ISO 3297: 2007 Certified Organization)*

**Vol. 5, Issue 6, June 2016**

## IV. CONCLUSION

The CIS films were deposited by thermal vacuum evaporation technique. The optical properties of the CIS films were influenced by the heat treatment (annealing) process . It was observed that the absorbance in the visible region is high. Absorption coefficient had been calculated from transmission spectra taken within the wavelength of the range (350 to 1090) nm. The absorption coefficient obtained of the order of $10^4$ $cm^{-1}$ in the energy region value and the rate of absorption is maximum near the region that corresponding the wavelength equal to (350-600) nm. Increase annealing temperature rise the absorbance.

The optical band gap has an allowed direct transition types , it values were found to decrease from (1.85 to 1.67) eV with increasing of annealing temperature. The optical constants of the films had been investigated in this work , and they depend on the annealing temperature.

Finally, from the above properties we concluded that CIS films may be suitable for application in various optoelectronic devices and photovoltaic applications.

## V. REFERENCES

1. O.Meglali,A.Bouraiou and N.Attaf,"Characterization of CuInSe2 thin films elaborated by electrochemical deposition", Vol.11 No.1 p.19-24, (2008).

2. Soon Hyung Kang, Yu-Kyung Kim, Don-Soo Choi, Yung-Eun Sung,"(2006). Characterization of electrodeposited CuInSe2 (CIS) film", Revue des Energies Renouvelables, Vol. 11 No.1 p. 19 – 24,(2008).

3. S. Agilan , S.Venkatachalam , D.Mangalaraj, Sa.K.Narayandass , S. Velumani , G.Mohan Rao , Vijay P.Singh, "Structural and photoelectrical characterization of hot wall deposited CuInSe2 thin films and the fabrication of CuInSe2 based solar cells. International Materials Research Congress,Vol.58 p.701-707, (2006).

4. Donald, A. Neamen, Semiconductor physics and devices. Bi-Company, Inc. university of New Mexico, USA. ,(1992).

5. Sze, S. M. and Kwok, K. ,"Physics of Semiconductor Devices", John Wiley & Sons, Inc. New York, (2007).

6. . Bertie,J.E., "Handbook of Vibrational Spectroscopy",Copyright©2006 John Wily & Sons, Ltd. (2001).

7. Pankove, J.I. "Optical Processes in Semiconductors", Prentice–Hall , Inc., Englewood cliffs, New Jersy. (1971).

8. Clark, A. H.,"Polycrystalline and Amorphous Thin Films and Devices", Academic Press, p. 135. Article, New York. (1980)

9. A.Bouraiou, M.S.Aida, A.Mosbah, N.Attaf, "Annealing time effect on the properties of $CuInSe_2$ grown by electrodeposition using two electrodes system", Brazillin Journal of Physics Vol.39 No.3,(2009).

10. Sangha You, Kwangjoon Hong, Bongju Lee and Jin Ju Bang, "Optical and Structural Properties for CuInSe2 Epilayers Grown by Using Hot Wall Epitaxy",Vol.50 No.6 P.1784-1788,(2007).


DOI:10.15680/IJIRSET.2015.0506001