

Effect of Thickness on the Structure and Electrical Conductivity Properties of CuInSe₂ Thin Films

Iman H. Khudayer¹, Ahmed Z. Obaid²

Associate Professor, Dept. of Physics, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Iraq¹

Ph.D. Student, Dept. of Physics, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Iraq²

ABSTRACT: The influence of different thickness (500, 750, and 1000) nm on the structure properties electrical conductivity and Hall Effect measurements have been investigated on the films of copper indium selenide CuInSe₂ (CIS) the films were prepared by thermal evaporation technique on glass substrates at RT from compound alloy.

The XRD pattern show that the film have poly crystalline structure a, the grain size increasing with as a function the thickness. Electrical conductivity (σ), the activation energies (E_{a1} , E_{a2}), hall mobility and the carrier concentration are investigated as function of thickness. All films contain two types of transport mechanisms of free carriers increase films thickness. The electrical conductivity increase with thickness whereas the activation energy (E_a) decreased.

Hall effect analysis results of CIS films show all films were of (p-type) and both hall mobility and the carries concentration increase with the films thickness, the samples are prepared and annealing with at (600)K.

KEY WORDS: CIS, Electrical conductivity, Hall Effect and Thermal Evaporation method.

I. INTRODUCTION

The ternary compound semiconductor copper indium diselenide (CuInSe₂) has received great attention as photovoltaic absorber material for the fabrication of thin film solar cells due to its high absorption coefficient (10^5 cm^{-1}) and good thermal, environmental and electrical stability

[1]. A variety of deposition techniques have been reported by researchers to prepare CuInSe₂ thin films via, multisource evaporation, flash evaporation, single-source evaporation, RF sputtering[2,3], Spray pyrolysis [4] screen printing etc. For economic reasons and simplicity, low cost deposition methods are under active study. Thermal evaporation of the synthesized CuInSe₂ powder is the simplest of all techniques.

I-III-VI₂ compounds, especially Cu-chalcopyrite thin films have played a major role in thin film photovoltaic technology. Typical Cu-chalcopyrite-based absorber materials are CuInSe₂, CuInS₂,

CuGaSe₂ and their alloys with band gap in the range (1.05-1.7) eV[5].

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

II. EXPERIMENTAL

II-I. CRYSTAL STRUCTURE

Polycrystalline CuInSe₂ (CIS) material alloys was prepared by fusing the mixture of the appropriate quantities of the elements Cu, In and Se of high purity (99.999%) in evacuated fused quartz ampoules.

The compound of CuInSe₂ was synthesized from its constituent elements, i.e., copper (Cu), indium (In), and selenium (Cu, In, and Se) weighed in stoichiometric proportion (1:1:2) were sealed in a quartz ampoule at a base pressure of 10⁻² mbar. The ampoule was placed in an electrical furnace. The temperature of the furnace was raised from room temperature to 1400 K for six hr with rate of 3.88 K/min. The ampoule was then cooled down to room temperature at the rate of 6 K/min.

Thin films of CuInSe₂ (CIS) have been deposited on glass substrate by thermal vacuum evaporation 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 weighing method. All Samples of (CIS) films of deposited with different thicknesses (500, 750 and 1000) nm. All samples are annealed at 600K, with deposition rate about (1.8±0.1) nm/sec. All the deposited CIS films were found to be polycrystalline structure.

The composition as well as structure of the material was established by XRD analysis. It was then used as a source material for deposition (CIS) thin films on cleaned glass substrates by thermal vacuum evaporation.

The crystal structure of these films was checked by X-ray diffraction technique, (XRD) patterns were obtained from a (SHIMADZU Japan-XRD600) automatic Diffractometer using the CuK α radiations ($\lambda=1.54059$ Å) in the range of 2 θ between 10° and 80°.

The lattice parameters (*a*) and (*c*) value for tetragonal crystallographic system was computed from the following equation using hkl parameters and the inter planer spacing (*d*) [6]

$$1/d^2 = h^2/a^2 + k^2/a^2 + l^2/c^2 \dots\dots\dots(1)$$

Crystallite size (*D*) of the as-deposited and annealed films were calculated using the well-known

Scherrer's formula [7]:

$$D = 0.9\lambda/\beta \cos \theta \dots\dots\dots(2)$$

Where λ is the X-ray wavelength used ($\lambda=1.54059$ Å), r (*WFHM*) is the full width at half maximum of diffraction peak measured in radians units, θ is the diffraction angle (Bragg angle), and *k* ($k=0.9$) is the Scherrer's constant of the order unity for usual crystallization.

The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal, has been calculated using the equation [8]:

$$\delta = 1/D^2 \dots\dots\dots(3)$$

The δ -value is criterion of crystallization level

The number of crystallites per unit surface area (*N_s*) of the film was determined using the formula [8]:

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

$$\delta = 1D^2 \dots\dots\dots (3)$$

Where: t is the thickness of the films.

II-II. ELECTRICAL PROPERTIES

The electrical properties of semiconductor are the most important properties that distinguish them from other materials. These properties are affected by difference of preparation conditions and methods of preparation [9].

II-II-I. D.C ELECTRICAL CONDUCTIVITY

Electrical conductivity considered as the most important electrical properties of solids. It consists of two main quantities, the electric charge carriers density and mobility.

The total electrical conductivity of a semiconductor is the sum of conductivity resulting from the negative and positive carriers. Where the resulting current density (J) is equal to the sum of the electrons (J_n) and holes current density (J_p) and holes (J_p) as shown in following equation [10]:

$$J = J_n + J_p \dots\dots\dots (5)$$

Where: J_n, J_p Electrons holes current density respectively.

In the semiconductor, some of atomic vibrations to be energies enough to broken the bond, then electron is liberated will be free to walk around and inside the crystal, it called conduction electron, leaving behind a hole to participate in the conduction process where the hole is going in opposite direction to the movement of electrons and in the same direction of the applied electric field, so, here we will have two types of charge carriers will participate in the conduction process [11, 12].

It can be expressed the electrical conductivity (σ) for semiconductors in following equation [13]:

$$\sigma = J/E = e (n \mu_e + p \mu_h) \dots\dots\dots (6)$$

According Ohm's Law[14]:

$$J = \sigma E \dots\dots\dots (7)$$

Where: J : electric current density, E : electric applied field intensity, e : electron charge, μ_e : electrons mobility, μ_h : holes mobility, n : electrons concentration, p : holes concentration.

This equation shows that the electrical conductivity depends on the concentration of charge carriers and its mobility under the influence of an applied electric field, and these two factors are depends on temperature, doping ratios and preparing conditions [14].

The electrical conductivity (σ_{dc}) is equal to the inverted specific electrical resistivity (ρ) us in the following equation [15]:

$$\sigma_{dc} = 1/\rho \quad (\Omega.cm)^{-1} \dots\dots\dots (8)$$

$$\rho = R/A \cdot L, \text{ where: } \{A=b \cdot t\} \dots\dots (9)$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

Where: R : electrical resistance (Ω), L : distance between the poles of aluminum (cm), A : cross-sectional area the electrons move within, b : Pole width (cm), t : the film thickness (nm) it converts to (cm) Continuous electrical conductivity of semiconductor depends on the temperatures and activation energies. At high temperatures the electrical conductivity achieved by thermal excitation of charge carriers, while at low temperatures the electrical conductivity is achieved by hopping process [16].

II-II-II. HALL EFFECT

This phenomenon was discovered in (1897), and has become one of the important methods in the study of the electrical properties of semiconductors. So by means of this study we can know the type and concentration of charge carriers (n, p) and then finding mobility ($\mu_{n, h}$) of these carries , it was noted that the Hall coefficient (R_H) will have a negative sign for the (n-type) semiconductors and positive for the (p-type) semiconductors is given equations[17,18]:

$$R_H = [+ 1 / nq] \dots \text{for p-type} \dots \dots \dots (10) \quad R_H = [-1 / nq] \dots \text{for n-type} \dots \dots \dots (11)$$

In general, Hall effect is defined as the difference in the current distribution in the slice metal when applying magnetic field in direction perpendicular to the direction of current(I) flow within a conductor, hence a tendency of charge carriers to drift aside causing the generation of a potential difference across the conductor in direction perpendicular to the direction of each of the current and magnetic field, this potential is called the Hall voltage(V_H) ,this voltage also accompanied by emergence of an electric field is called the field of Hall[19].

We can found Hall mobility and mobility by the following equations (12) and (13) respectively [19]:

$$V_H = R_H [\cdot J] \dots \dots \dots (12) \quad \mu_n = \sigma \cdot | R_H | \dots \dots \dots (13)$$

Where: B : magnetic field (Tesla), t : film thickness (nm).

III. RESULTS AND DISCUSSION

Figure (1) depict XRD patterns for samples of different thicknesses grown at room temperature and annealed at 600K. It is revealed that films were characterized by three main crystalline peaks; the first peak appeared at $2\theta \sim 26.488^\circ$ and the second peak appeared at $2\theta \sim 44.112^\circ$ while third peak appeared at $2\theta \sim 52.232^\circ$. On comparing with ICDD (card no. 01-074-7042) and reported values of [4] and [5], the first peak was identified to be belonging to CuInSe_2 structure with the (112) preferred orientation and the second peak designated to (220) orientation, while the third peak designated to (312), all films have poly crystalline structure.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

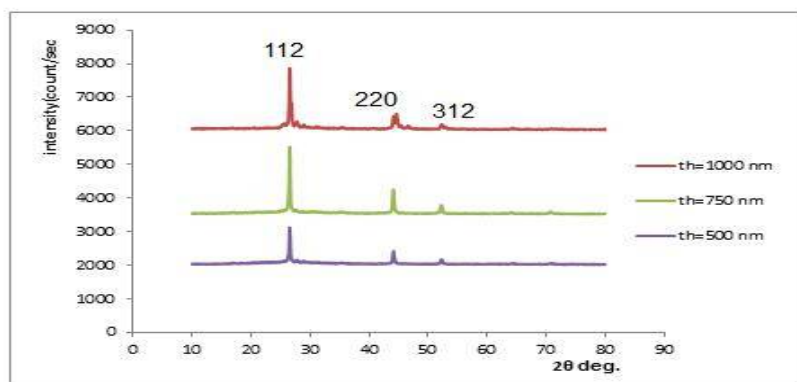


Figure (1).XRD patterns for CIS films for different thicknesses.

The calculated lattice constant for the peaks of (112), (220) and (312) of CIS is averaged to $a=5.78 \text{ \AA}$, $b=11.55$ which is close to the reported value [17]. However, intensity of all peaks rapidly decreases with as shown in Fig. (1), while full width at half maximum ($FWHM$) increases for the films with the 2θ .

It is clear in the figures that, at all thicknesses there is no variation in peak position. On the other hand, the thickness (750) nm have maximum intensity, the peak intensity for 500nm, 750, nm and

1000nm were found to be (663, 1306 and 1216) count/sec respectively, suggesting that the crystallinity of the films is closely related to the film thickness. The low peak intensity observed in a thinner CuInSe_2 film could be associated with an incomplete growth of the crystallites as only few atomic layers of disordered atoms constitute the bulk of the film.

From table No. (1) We notes that the grain size of CIS films increased there would be a large mobility as the thickness increase.

Table No. (1): XRD, results of CIS thin films for the (112) preferred orientation peak.

Thickness (nm)	$2\theta(112)$	$a(\text{\AA})$ observed	$c(\text{\AA})$ observed	$FWHD$ (112)(deg.)	D (nm)	$N_o \cdot 10^{12} (\text{m}^{-3})$	$\delta \cdot 10^{14} (\text{m}^{-2})$
500	26.488	5.69	11.51	0.186	43.51	9.10	5.28
750	26.577	5.75	11.53	0.163	58.41	3.76	2.93
1000	26.607	5.81	11.58	0.137	59.24	3.60	2.84

From table No. (1) The δ -value is criterion of crystallization level. Lower δ -values indicated higher crystallinity levels for the films, since δ is the measure of the amount of defects in a crystal and the value of dislocation density obtained in this work is found to be equal to $5.28 \times 10^{14} \text{ lines/m}^2$ for films. The small value of δ obtained in the present work confirms the good crystallinity of the fabricated CIS film by this method.

From table No. (1) The number of crystallites per unit surface area (N) was found to be equal $9.10 \times 10^{12} / \text{m}^2$ for films. It is decreased with increasing thickness due to increasing of crystallinity. From table No. (2) And figure (2) which include a plot of $\ln \sigma$ of CIS versus $10^3/T$ for different thickness, the activation energy of the electrical conduction can be determined. It is

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

clear that the electrical conductivity increases as a function of the film thickness because of the increasing the number of carriers available for transport. we can notice from table No.(2) and figure (2) that all

(CIS)films have two mechanisms for electrical conductivity which means that there is two mechanism of transport of free carriers with two values of activation energy (E_{a1}, E_{a2}) each one predominating in a different temperature ranges. The electrical conductivity of these films is affected by carriers excited into the localized states at the edge of the band and hopping at other range of temperature (290-415) K, as well as the transport of free carriers in extended states beyond the mobility edge at higher temperature range (450-490) K [16].

Table No. (2): the electrical conductivity and activation energies of CIS films at different thickness at temperature of 600K.

Thickness(nm)	E_{a1} (eV)	Temp. range(K)	E_{a2} (eV)	Temp. range(K)
500	0.019	290-415	0.124	450-490
750	0.018	290-415	0.084	450-490
1000	0.017	290-415	0.101	450-490

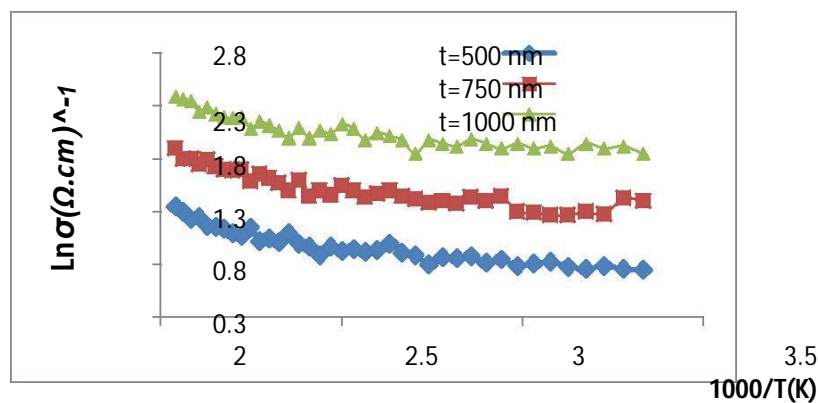


Figure (2): Plots $\ln\sigma$ as a function of $10^3/T$ (K^{-1}) for different thickness CIS films.

As shown in fig. (3) And table (2) the activation energy decreased with increase the thickness because of the improve of crystal linity with the increase of the grain size.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

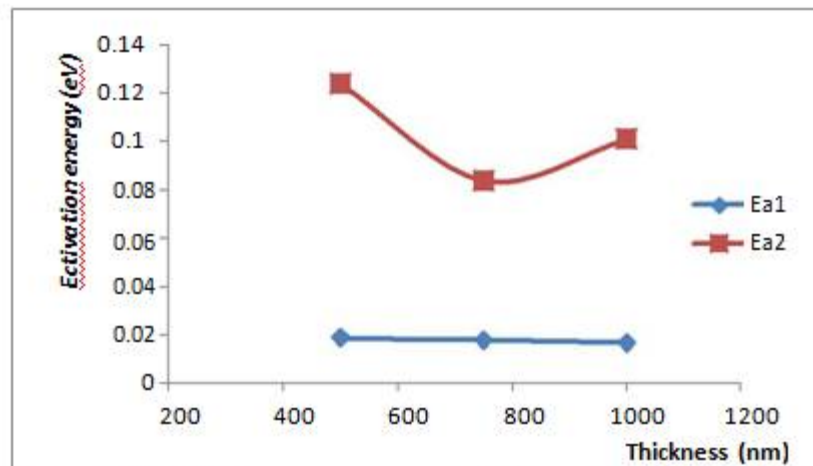


Figure (3): Variation activation energy as a function of thickness for CIS films.

The hall coefficient values (R_H) were calculated for CIS films of different thickness the sign of hall coefficient for all prepared films is positive which means that type of conduction was p-type, i.e. holes are majority charge carriers in the conduction process. In addition to that carrier concentration (n_H) of the order 10^{17} cm^{-3} is in good result, as well as the value of carrier mobility's (μ_H) in contrast which is found in the range $1.047 \text{ cm}^2/\text{V.s}$.

All these parameters are shown in table no. (3) And figure (4). It is clear that both (n_H) and (μ_H) respectively increase as with thickness. This behavior can be attributed to the decrease the trapping centers of charge carriers with the increase of film thickness, this is, **perhaps**, because of the decreased grain boundary scattering which limits the mobility in thinner films and this is because of the improved film structure, reduce native defect centers and grain boundary defects, therefore the carrier mobility improves[10].

Table No. (3): Values of carrier concentration, conductivity, carrier mobility and Hall coefficient

of CIS films for different thickness at temperature 600K.

Thickness(nm)	$\sigma(\Omega.\text{cm})^{-1}$	$R_{(H)}$	$\mu(\text{cm}^2/\text{V.S})$	$n(\text{cm}^{-3})$
500	0.231	3.60	0.831	17.34E+17
750	0.514	2.09	1.074	29.83E+17
1000	0.537	3.155	1.691	19.84E+17

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

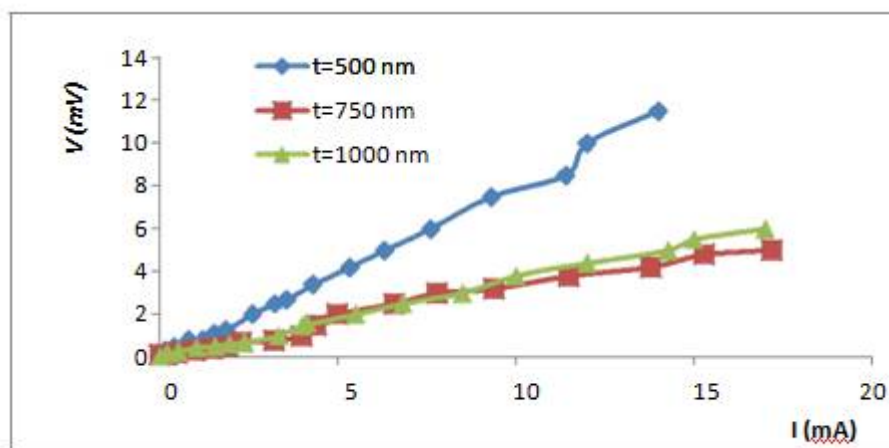


Figure (4): Plots of Hall voltage with current at different values of thickness of CIS films.

IV. CONCLUSION

In research, we have used thermal evaporation method to prepared (CIS) film at R.T. The effect of thickness on structure and the electrical properties of CIS through measurements of XRD diffraction pattern, conductivity and Hall Effect have been studied in work, we conclude the following:

- 1- A thermal evaporation was a suitable method to prepare (CIS) film at R.T from alloy.
- 2-The CIS films have polycrystalline structure, grain size increasing with thickness.
- 3- The electrical conductivity and activation energies of (CIS) films are seen to be dependent on the film thickness, the electrical conductivity shows as a decrease of behavior with an increase of thickness
- 4- The behavior of the electrical conductivity of CIS films as a function of thickness is a result of the community between two mechanisms of transport, hopping charge transport between localized states at the edge of the band at low temperature (290-415) K and charge transport to extended state beyond the mobility gap at higher temperature (450-490) K [16].
- 5- Hall effect measurements confirmed that holes were predominating in the conduction process, both the mobility and concentration of the charge carriers increase with thickness.
- 6- Finally, from the above properties we concluded that (CIS) films may be suitable for solar cells application.

REFERENCES

1. Soon Hyung Kang, Yu-Kyung Kim, Don-Soo Choi, Yung-Eun Sung. "Characterization of electrodeposited CuInSe₂ (CIS) film". Electrochimica Acta, V.(51),pp(4433-4438),(2006).
2. B. Eisener, M. Wagner, D. Wolf and G. Muller, "Study of the Intrinsic Defects in Solution Grown CuInSe₂ Crystals Depending on the Path of Crystallization", Journal of Crystal Growth, Vol. 198-199, p. 321-324,(1999).
3. J.A.M. AbuShama, S. Johnston and R. Noufi, "Bandlike and Localized Defects States in CuInSe₂ Solar Cells", Journal of Physics and Chemistry of Solids, Vol. 66, Issues 11, p. 1855 – 1857, (2005).
4. T. Terasako, Y. Uno, T. Kariya and S. Shirakata, "Structural and Optical Properties of In-rich Cu-In-Se Polycrystalline Thin Films Prepared By Chemical Spray Pyrolysis", Solar Energy Materials and Solar Cells, Vol. 90, Issues 3, p. 262 – 275, (2006).
5. [5]K M A Hussain, J Podder, D K Saha & M Ichimura, "Structural electrical and optical characterization of CuInS₂ thin films deposited by spray pyrolysis", Indian Journal of Pure and Applied Physics, Vol.50,Issues 2,p.117-122, (2012).
6. S. Agilana, D. Mangalarajb., Sa.K. Narayandassb, G. Mohan Raoc, "Effect of thickness and substrate temperature on structure and optical band gap of hot wall-deposited CuInSe₂ polycrystalline thin films",Physica B:Condensed Matter ,Vol.365,Issues 1-4,P.93-101, (2005).
7. N.M. Shah , J.R. Ray , K.J. Patel , V.A. Kheraj , M.S. Desai , C.J. Panchal , Bharti Rehani , "Structural, electrical and optical properties of copper indium diselenide thin film prepared by thermal evaporation method Thin Solid Films", Vol.517,Issucs 13,P.3639-3644, (May 2009).
8. C. Suryanarayana and M.G. Norton, "X-Ray Diffraction: A Practical Approach", Plenum Publishing Corporation, New York (1998).
9. T. L. Floyd, "Electronic Devices, Conventional Current Version", 7th Edition , perason prentice HALL, New York, (2005).

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

10. [10] S . M. Sze , " physics of semiconductors Devices " , Third edition by John Wiley & Sons, Inc. , copyright©2007.
11. J. F. O'Hanlon, " A User's Guide to Vacuum Technology" Book , Third Edition , John Wiley & Sons, Inc. U.S.A (2003).
12. M. S. Shinde, P.B.Ahirrao, I.J.Patil and R.S.Patil " Thickness dependent electrical and optical properties of nanocrystalline copper sulphide thin films grown by simple chemical route ", Indian journal of pure & applied physics , Vol.50, Issucs 9, p.657-660, September (2012).
13. S.L.Kakani, and Amit Kakani, " Material Science" , New Age International Publishers, New Delhi, (2004).
14. K. L. Chopra, "Thin Film Devices Application", Plenum Press, New York, (1983).
15. J. P. Colinge and C. A. Colinge "Physics of Semiconductor Devices", Kluwer Academic Publishers, New York, (2007).
16. S.Agilan, D.Mangalaraj, .K.Narayandass, G.Mohan Rao,S.Velumani, "structure and temperature dependence of conduction mechanisms in hot wall deposited CuInSe₂ thin films and effect of back contact layer in CuInSe₂ based solar cells", International Materials Research Conference (IMRC)Vol.(84), Issucs 10,p.(1220-1225). Cancun, Mexico(2007).
17. [17]S.Agilan, S.Venkatachalam, D. Mangalaraj, Sa.K. Narayandass, S.Velumani, G.Mohan Rao, Vijay p.Singh, "Structure and photoelectrical Characterization of wall deposited CuInSe₂ thin films and the fabrication of CuInSe₂ based solar cells", Materials Characterization, Vol.(58),p.(701-707), (2007).
18. [18]] D. A. Neamen, "Semiconductor Physics and Devices", 3rd Edition, Mc Graw-Hill Com., Inc., University of New Mexico, U.S.A, (2003).
19. [19]L. L. Kazmerski, "Polycrystalline and Amorphous Thin Films and Device", Academic Press. , (1980).