Electrical Conductivity and Hall Effect Measurements of ($CuInTe_2$) Thin Films

Bushra K. Hassan Al-Maiyaly
Shaymaa K.Abdul-Hassan
Dept. of physics/ College of Edu//cation For Pure Science (Ibn Al-Haitham)/ University of Baghdad.
Falah I. Mustafa
Solar Energy Center/ Renewable Energy Directorate/ Ministry of Higher Education and Scientific Research

Received in:28/February/2016,Accepted in :30/March/2016

Abstract

In this research, the electrical conductivity and Hall effect measurements have been investigated on the $CuInTe_2$ (CIT) thin films prepared by thermal evaporation technique on glass substrate at room temperature as a function of annealing temperature (R.T,473,673)K for different thicknesses (300 and 600) nm. The samples were annealed for one hour.

The electrical conductivity analysis results demonstrated that all samples prepared have two types of transport mechanisms of free carriers with two values of activation energy (Ea_1, Ea_2), and the electrical conductivity increases with the increase of annealing temperature whereas it showed opposite trend with thickness , where the electrical conductivity would decrease as the films thickness increases.

The results of Hall effect measurements of $CuInTe_2$ films show that all films were (p-type) , the carrier concentration and Hall mobility are strongly dependent on the annealing temperature and film thickness.

Key words: $CuInTe_2$, Electrical conductivity, Hall Effect, Thermal Evaporation.

Introduction

The ternary compound I-III-VI_2 chalcopyrite semiconductors thin films (I=Cu,Ag, III=Al,Ga,In, and VI=S,Se,Te) are feasible candidates in recent years due to their potential for application in photovoltaic solar cells and variety of opto-electronic devices such as infrared detectors, light emitting diodes, up converters ,optical parametric oscillators and IR generators also in optical frequency conversion applications in solid state based tunable laser systems [1-7].

$CuInTe_2$ (CIT) crystallizes in the tetragonal chalcopyrite structure [5] has a direct band gap varying between 0.92 eV and 1.04 eV at approximately 300 K and high optical absorption coefficient (10^5 cm^{-1}) which falls in the optimum range to make use of bottom cells for multi-junction (tandem) solar cells [1-7]. This minimizes the requirement for long minority carrier diffusion lengths and needs only a few tenth to a few micron of thickness to make devices, thus minimizing the cost of material [5,8]. Thin films of CIT can be obtained n or p conducting depending on the preparation conditions.[9] Much work on $CuInTe_2$ was done in order to get better understanding of its optical, electronic and electrical properties using several methods of deposition techniques such as electrodeposition [5,10], bridge man technique [2,11], three-source co-evaporation technique [4,7,12], flash evaporation [13] , pulsed laser deposition [14] ,thermal vacuum evaporation [15],etc. In the present work, $CuInTe_2$ films was prepared by thermal evaporation technique, the aim of this research is to collect more information about the electrical properties of these films through the electrical conductivity, and Hall effect measurements.

Experiment

Film Preparation

$CuInTe_2$ (CIT) films were prepared by the alloy which was obtained by mixing of the appropriate quantities of high purity (99.999%) material of copper, indium and tellurium in evacuated fused quartz ampoules , heated at (1473 K) for 12h. The ampoules quenched rapidly in cold water.

$CuInTe_2$(CIT) films were grown onto a glass slide substrate kept at R.T by thermal evaporation technique in a high vacuum system ,the base pressure during the evaporation was ($3x10^{-6}$) Torr using Edward coating unit model (E 306) from molybdenum boat with thickness (300,600) nm. The distance from molybdenum boat to sample holder was about (18 cm), Al electrodes were used as contact material for making the electrical connections. After deposition the samples were annealed at (473, 673) K for one hour.

Characterization of $CuInTe_2$ Thin Films

For D.C. measurement the variation of electric resistance (R) with temperature range (293- 473) K, were measured using Keithly model 616, then calculated the resistivity (ρ) by equation [16]:-

$$\rho=\frac{R\cdot b\cdot t}{L} \quad \text{.......} \quad (1)$$

Where t is film thickness, b is electrodes width; L is distance between two Al electrodes. The resistivity is related to the conductivity (σ) by the formula [16]:-

$$\sigma_{d.c}=\frac{1}{\rho} \quad \text{.......} \quad (2)$$

Hall effect measurements have been carried out to investigate the type of charge carriers, carrier concentrations (n_H) and Hall mobility (μ_H) using the Ecopia HMS-3000 Hall measurement system. The sign of the Hall coefficient (R_H) of semiconductor is determined by the sign of the charge carriers. If the conduction is due to one carrier type , we can measure the carrier concentration according to the relation: [17,18]

$$n_H = \pm 1 / R_H.e \quad \ldots\ldots (3)$$

The mobility is related to the Hall coefficient by equation: [18]

$$\mu_H = \sigma / n_H .e = \sigma . \left| R_H \right| \quad \ldots\ldots (4)$$

Where σ is the conductivity.

The films thickness were measured by using the weighing method according to the following relation[19]:

$$t = m / A .\rho \quad \ldots\ldots (5)$$

Where: t= film thickness, m = mass of film, ρ = density of film, A= films area. Using a sensitive balance whose sensitivity of the order (10^{-4}).

Results and Discussion

Figure (1) shows the variation in the resistivity of $CuInTe_2$ (CIT) films as a function of annealing temperature (R.T,473,673)K for different thicknesses (300 and 600)nm, we can deduct from this Figure that the resistivity values decrease as the annealing temperature increases due to the improvement in the films structure that lead to reduce dangling bonds, defects like vacancy sites, trapping centers of charge carriers and point defect cluster in the films structure[15], this is, perhaps, because of the decreased grain boundary scattering, therefore the number of carriers available for transport increases with the improvement in the electrical conductivity and decreases the resistivity of the films. In addition to that the resistivity values are in good agreement with references [7 and14].

Figure (2) shows a relationship of lnσ of of $CuInTe_2$ (CIT) films versus $10^3/T$ in the temperature range (293- 473) K as a function of annealing temperature (R.T,473,673)K for different thicknesses (300 and 600)nm, it is clear from this figure the general behavior of the films is similar to other semiconductors and the electrical conductivity increases as the annealing temperature increases because of the increase number of carriers available for transport for the same reasons as we mentioned before see Table 1.This figure appears to separate two temperature ranges characterized by different conductivity slopes which means that all (CIT) films have two mechanisms for electrical conductivity and there is two mechanisms of transport of free carriers with two values of activation energy (Ea_1, Ea_2). At higher temperature range (403-473) K, the conduction mechanism is due to carriers excited into extended states beyond the mobility edge and the small values of activation energies at lower temperature range (293- 393) K indicated carriers excited into the localized states at the edge of the band and hopping , such observations were also seen by references.[2,4,2 and21] . Figure (3) and Table 1, show the activation energies varies with increase both the annealing temperature and thickness for CIT films and this may be due to change in crystal structure with these parameter. The values of activation energies are in agreement with those reported by other workers[4].

All CIT films exhibit p-type conductivity, the Hall coefficients for all prepared films are positive, which means that the holes are majority charge carriers in the conduction process and the type of conduction was p-type, this result is in agreement with references [2,4,14,20and22]. The influence of annealing temperature (R.T,473,673)K for different thicknesses (300 and 600)nm on the carrier concentration and Hall mobility are shown in Table 2 and figures (4)and(5) respectively. It can be seen from figure (4) and Table (2) that carrier concentration (n_H) increases some order of magnitude as the annealing temperature increases for different thicknesses, this may be due to the increase of grain size or decreasing of grain boundary scattering and this is because of the improved film structure which increases the number of charge carriers because of the reducing of grain boundary barrier height. Also it shows the carrier concentration values decrease with the increase of film thickness may be due to the increase of the energy gap. In addition to that the carrier concentration and carrier mobility's values are in contrast with the result obtained by references.[2and20]

Conclusion

In the present work, the effect of annealing temperature and thickness on the electrical properties of $CuInTe_2$ (CIT) films prepared by thermal evaporation method are studied in detail, through measurements of conductivity and Hall effect. Throughout our research we showed that the thermal evaporation was a good method to prepare (CIT) film at R.T from alloy, the electrical conductivity and activation energies are strongly dependent on the annealing temperature and film thickness and the CIT films contain two types of transport mechanisms.

We should mention that the resistivity of these films is small; therefore these samples can be used as an absorber layer in the fabrication of solar cell. Hall effect measurements demonstrate that the CIT films were p-type , both the mobility and concentration of the charge carriers are seen to be dependent on the annealing temperature and film thickness.

References

1. Fu,Li. and Guo Yong-Quan, (2014),Synthesis, structure, optical and electric properties of Ce-doped $CuInTe_2$ compound " Chin. Phys.B", 23,12,127801.

2. Mobarak,M.and Shaban, H.T. (2014),Characterization of $CuInTe_2$ crystals," Materials Chemistry and Physics",147, 439-442.

3. Vinothini, C.; Srinivasan, K.and Murali, K.R., (2011), Pulse electrodeposited CuInTe2 films, " The Electrochemical Society", 220th ECS Meeting.

4. Roy,S.; Bhattacharjee,B.; Kundu,S.N.;Chaudhuri,S.and Pal,A.K., (2002), Characterization of $CuInTe_2$ thin film synthesized by three source co-evaporation technique," Materials Chemistry and Physics ", 77, 365-376.

5. Dixit Prasher; Kavita Dhakad; Ashok k. Sharma;Vikas Thakur and Poolla Rajaram, (2014), Electrochemical growth and studies of indium-rich $CuInTe_2$ thin films, " International Journal of Materials Science and Applications", 3, 1, 1 – 5.

6.Cheng,N.; Liu,R.;Bai,S.;Shi,X.;and Chen,L.,(2014),Enhanced thermoelectric performance in Cd doped $CuInTe_2$ compounds," Journal of Applied Physics",115,163705.

7. Takahiro Mise and Tokio Nakada, (2010), Low temperature growth and properties of Cu-In-Te based thin films for narrow bandgap solar cells ,"Thin Solid Films", 518, 5604-5609.

8. Xue, D.;Betzler, K. and Hesse, H., (2000) ,"Dielectric properties of I-III-VI2-type chalcopyrite semiconductors," Physical Review B, 62, 20, 13546 -13551.

9. Bouloufa, A.; Messous, A.;Yakushev, M.V.; Tomlinson, R.D.and Zegadi, A., (2003), Optical Properties of $CuInTe_2$ Single Crystals by Photoacoustic Spectroscopy, "Journal of Electron Devices", 2, 34-39 .

10. Ishizaki, T.; Saito, N. and Fuwa, A., (2004)"Electrodeposition of CuInTe2 film from an acidic solution," Surface and Coating and Technology", 182, 2-3, 156-160.

11. Quintero, M.; Gonzalez, J. and Woolley ,J. C.,(1991) "Optical energy -gap variation and deformation potentials in $CuInTe_2$,' Journal of Applied physics", 70, 3, 1451-1454.

12. Roy, S.; Bhattacharjee, B.; Kundu, S. N.; Chaudhuri, S. and Pal, A.K.,(2003) "Characterization of $CuInTe_2$ thin film synthesized by three source co-evaporation technique," Materials Chemistry and Physics", 77, 2, 365-376.

13. Ananthan, M.R. and Kasiviswanathan, S.,(2009) "Growth and characterization of stepwise flash evaporated CuInTe2 thin films," Solar Energy Materials and Solar Cells", 93, 2, 188-192.

14. Gremenok, V.F.; Victorov, I.A.; Bodnar, I.V.;Hill, A.E.;Pilkington, R. D.; Tomlinson, R.D. and Yakushev, M.V.,(1998), Characterization of $CuInTe_2$ thin films prepared by pulsed laser deposition," Materials Letters", 35, 1-2,130-134.

15. Abo El Soud, A. M.;Hendia, T. A.;Soliman, L.I.; Zayed, H. A. and Kenawy, M. A., (1993), Effect of heat treatment on the structural and optical properties of $CuInTe_2$ thin films," Journal of Materials Science", 28, 5, 1182-1188.
16. Kasap, S.O.,(2002),” Principles of Electronic Materials and Devices”, 2nd edition, Mc Graw Hill.
17. Kazmerski, L. L., (1980), "Polycrystalline and Amorphous Thin Films and Device", Academic Press.
18. William, D. and Callister, Jr, (2003), "Materials Science and Engineering, An Introduction”, 6th edition, John Wiley & Sons, Inc.
19. Donald, A.Neamen ,(2003),"Semiconductor Physics and Devices, basic principles",3th edition, McGraw-Hill Companies,Inc.
20.Dawar,A.L.;Anil Kumar;Mall,R.P, and Mathur,P.C.,(1984),Growth and Electrical Transport Properties of $CuInTe_2$ thin films,"Thin Soild Films",112,107-119.
21.Sridevi,D. and Reddy,K.V.,(1986),Electrical Conductivity and Optical Absorption in Flash Evaporation $CuInTe_2$ thin films, "Thin Soild Films", 141,157-164.
22.Boustani,M.;ElAssali,K.;Bekkay,T. and Dreesen,L.,(1997), Characterization of $CuInTe_2$ thin films prepared by flash evaporation,"Semicond.Sci.Technol.",12,1658-1661.

Table (1): The electrical conductivity and activation energies of CIT films at different annealing temperatures and thicknesses.

Films thickness (nm)	Ta (K)	$\sigma_{R.T}$ $(\Omega.cm)^{-1}$	Ea_1 (eV)	Tem. range (K)	Ea_2 (eV)	Tem. range (K)
300	R.T	19.9005	0.08137	293-393	0.1265	403-473
	473	78.125	0.04827	293-393	0.08935	403-473
	673	278.086	0.03300	293-393	0.03515	403-473
600	R.T	6.313	0.05281	293-383	0.16445	393-473
	473	7.731	0.06911	293-383	0.12018	393-473
	673	41.66	0.06991	293-383	0.02514	393-473

Table (2) Values of Carrier Concentration and Carrier Mobility of CIT films at different annealing temperatures and thicknesses.

Thickness (nm)	Ta (K)	Carrier Concentration n_H (cm^{-3})	Carrier Mobility μ_H (cm^2/v. s.)
300	R.T	5.13 E+15	1.70 E+03
	473	5.45 E+18	4.48E+01
	673	8.28 E+19	1.50E+00
600	R.T	1.55E+12	2.21E+01
	473	3.97E+12	6.23E+00
	673	2.16E+15	1.37E+02

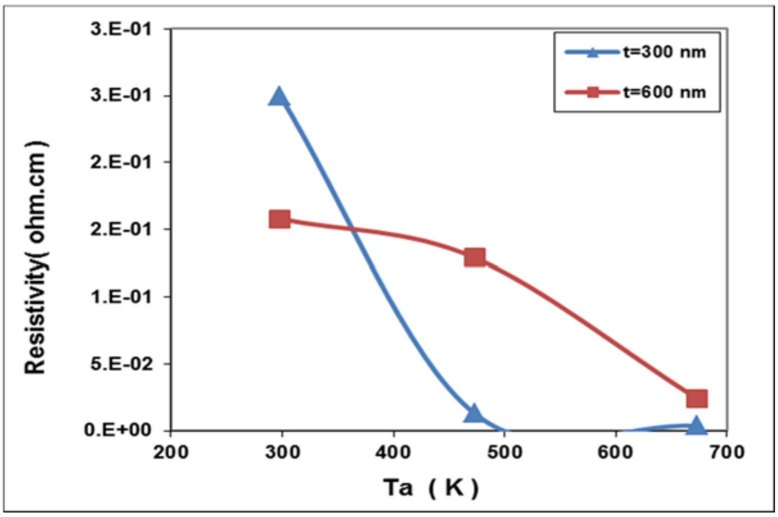
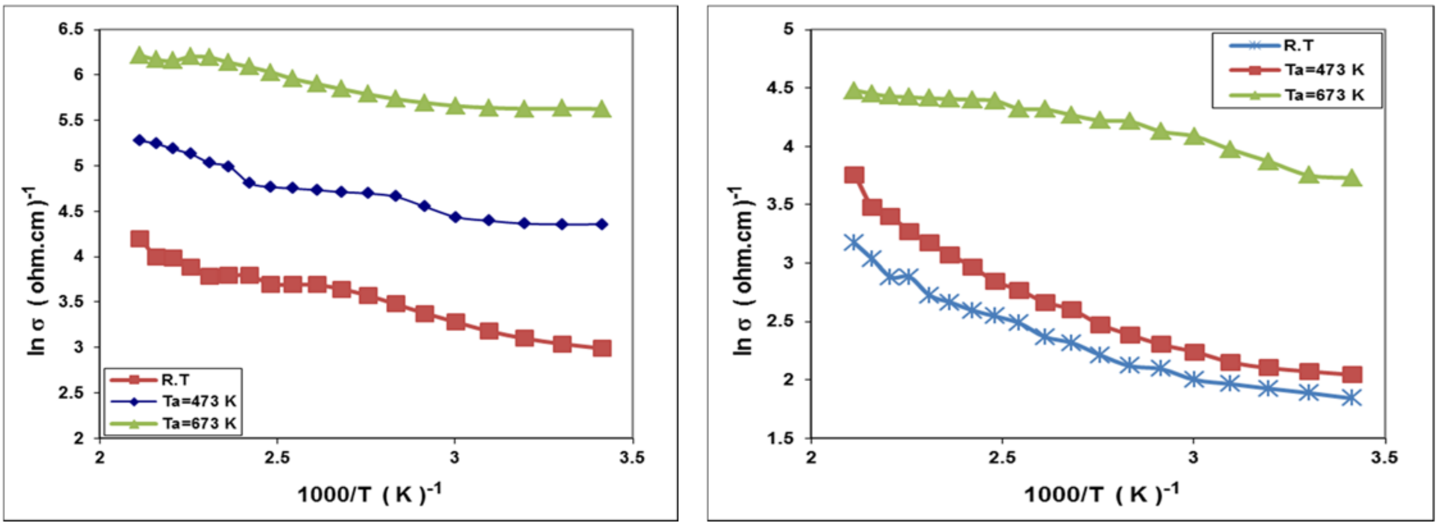


Figure (1): Variation resistivity of CIT films as a function of annealing temperature of different thicknesses.



(a) **(b)**

Figure (2): Variation lnσ versus 10^3/T of CIT films as a function of annealing temperature of different thicknesses. (a) 300nm (b)600 nm

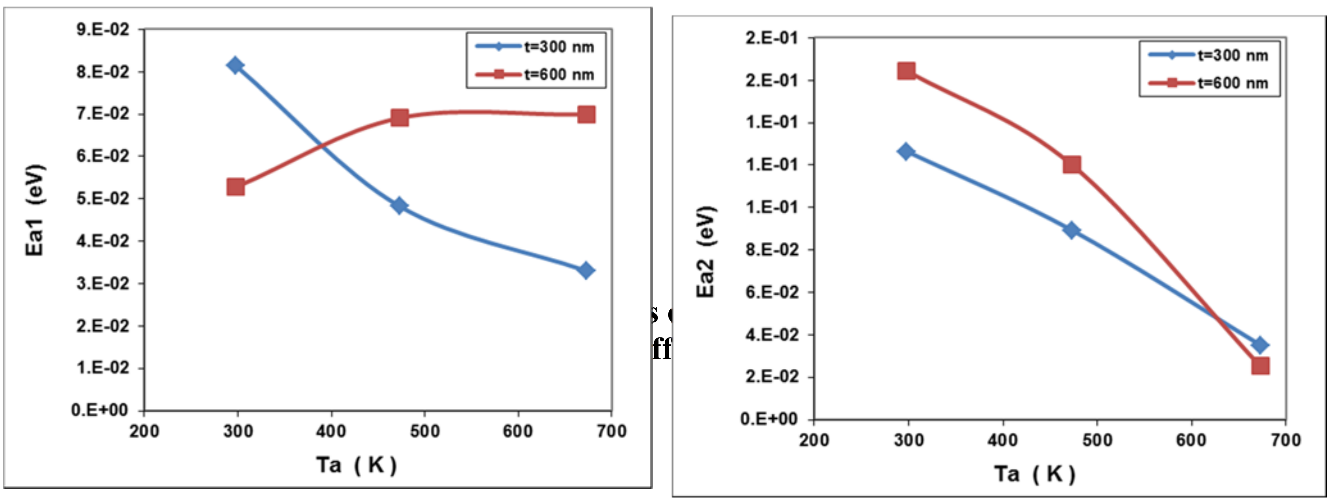


Figure (3): Variation activation energies of (CIT) films as a function of annealing temperature of different thicknesses.

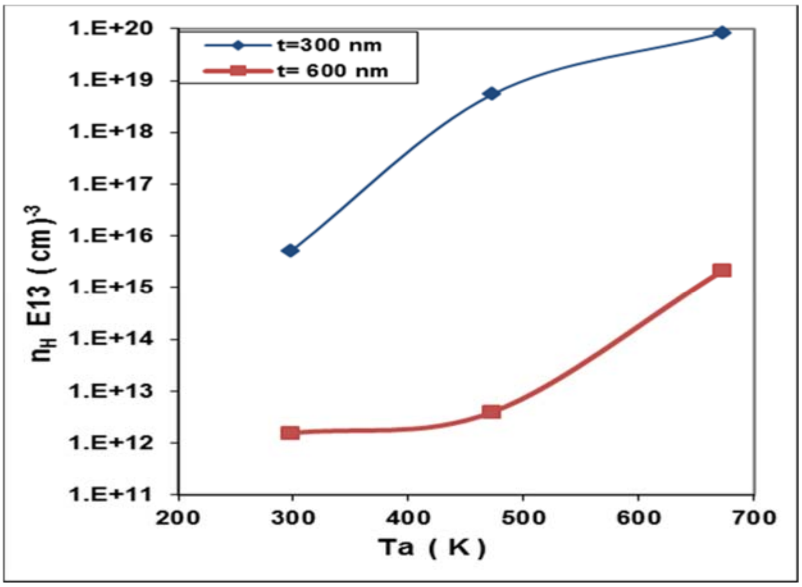


Figure (4): Variation of the charge Carrier's concentration of (CIT) films as a function of annealing temperature of different thicknesses.

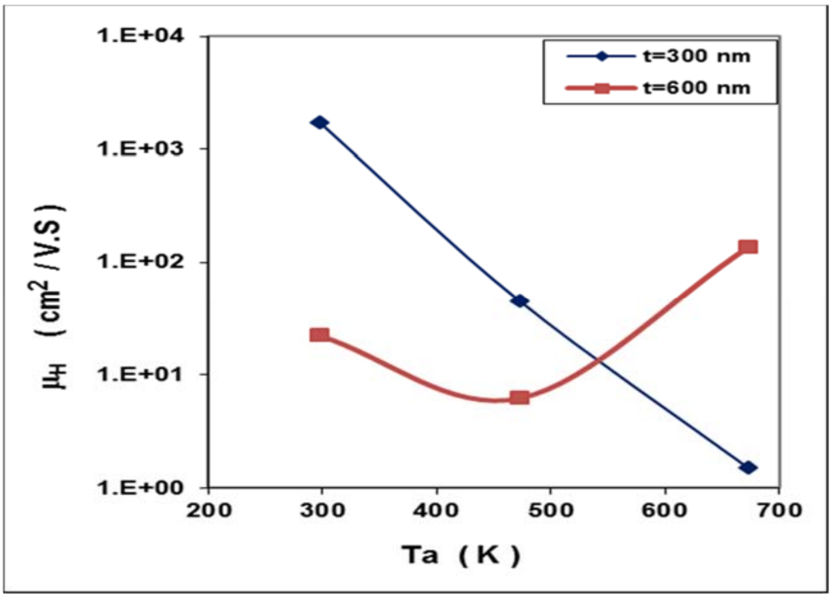


Figure (5): Variation Hall mobility of (CIT) films as a function of annealing temperature of different thicknesses.

التوصيلية الكهربائية وقياسات تأثير هول لأغشية ($CuInTe_2$) الرقيقة

بشرى كاظم حسون الميالي
شيماء قاسم عبد الحسن
قسم علوم الفيزياء / كلية التربية للعلوم الصرفة (ابن الهيثم) / جامعة بغداد
فلاح ابراهيم مصطفى
مركز بحوث الطاقة الشمسية / مديرية الطاقة المتجددة / وزارة التعليم العالي والبحث العلمي

استلم في : 28 /شباط/2016 , قبل في:30/اذار/2016

الخلاصة

تم في هذا البحث حساب التوصيلية الكهربائية وقياسات تأثير هول لأغشية $CuInTe_2$ (CIT) الرقيقة والمحضرة باستعمال تقنية التبخير الحراري على ارضيات من الزجاج عند درجة حرارة الغرفة كدالة لدرجة حرارة التلدين (R.T,473,673)K ولسمك مختلف (300,600)nm ولدنت النماذج لمدة ساعة واحدة.
اوضحت نتائج تحليل التوصيلية الكهربائية ان جميع الاغشية المحضرة تمتلك آليتين للانتقال الالكتروني لحاملات الشحنة وقيمتين لطاقات التنشيط (Ea_1, Ea_2) ولوحظ زيادة التوصيلية الكهربائية مع زيادة درجة حرارة التلدين واظهرت سلوكا معاكسا مع السمك اذ تناقصت قيم التوصيلية الكهربائية مع زيادة سمك الغشاء.
وبينت نتائج قياسات تأثير هول ان جميع أغشية $CuInTe_2$ كانت من نوع (p-type) . واعتمدت قيم كل من تركيز حاملات الشحنة وتحركية هول على درجة حرارة التلدين وسمك الاغشية.

الكلمات المفتاحية :- $CuInTe_2$ ، التوصيلية الكهربائية ، تأثير هول , التبخير الحراري.