اعتماد الخواص التركيبية والكهربية للشرائح الرقيقة Culnse2 على درجة حرارة التلدن

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الملخص :

أعـــــدّت شرائح رقيقة من Culnse2 بطريقة التبخير للمـــادة المستخدمة تحت التفريغ ، تم المعالجة بالتسخين للشرائح المترسبة من المادة عند درجات حرارة ثابتة (تسمى درجة حرارة التلدن) ومتدرجة في الزيادة حتى درجة حرارة ن 723K . دلت هذه الدراسة باستخدام الأشعة السينية على الشرائح الرقيقة من Culnse2 المعالجة حراريا على كون الشــــرائح متعددة البللــورة (Polycrystalline) ، وتتركب في الطور الرباعي القائم (Tetragonal Phase) . كذلك تناولت دراسة الخواص التركيبية لتغير القيم المحسوبة لمعاملات الشبيكة البللورية (A , C) وتغير متوسط حجم الحبيبات واعتمادهما على درجة حرارة التلدن ، كذلك تناولت الدراسة لمدى اعتماد الخواص الكهربية للشرائح الرقيقة من Culnse2 على درجة حرارة التلدن . ولذا تم قياس الموصلية الكهربية لهذا الشرائح المعالجة عند درجات حرارة تلدن مختلفة كدالة في التغير في درجة الحرارة أثناء القياس , ولقد تم الحصول على منطقتين جوهريتين مختلفتين لطاقة التنشيط ، وكذلك نجد أنه كلما زادت درجة الحــــرارة التلدن فأنه تقل طاقة التنشيط , كما أنه ثبت من الدراسة أن زيادة درجة حرارة التلـــدن تكون مصاحبة بتحسن الخواص الفيزيائية ونوعية الشرائح الناتجة

Annealing temperature Dependence of the Structural and Electrical Properties of Cu In Se_2 Thin Films .

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$CulnSe_2$ thin films were prepared under vacuum by conventional evaporation method .The films were heat treated at different annealing temperatures up to 723 K .X-ray diffraction of the films indicated that films are polycrystalline with tetragonal phase.

The variation of the calculated lattice parameters and mean grain size with annealing temperatures were showed .The electrical properties of $CulnSe_2$ thin films were studied at different annealing temperatures .The dark conductivity of the films was measured as a function of temperature .Two regions were obtained corresponding to two activation energies. The activation energy decreases with increasing the annealing temperature. Increasing the annealing temperature improves the physical properties and quality of the films.

1-INTRODUCION

$C_UI_NS_{e2}$ (CIS) has received considerable attention in the last years because of its potential application for photovoltaic devices (1).*Polycrystalline thin film have been obtained by using different methods, for example spray pyrolysis(2),vacuum evaporation(3),and sputtering(4). Various methods namely R-F-Sputtering(5),*

electro deposition(6),and vacuum deposition(7) techniques have been described to prepare CIS thin films.

In this paper the structure and the effect of the annealing temperature on some physical properties of the films have been investigated.

2.Experimental procedure

<u>2.1-Film preparation:</u>

$CuInse_2$ was prepared from its constituent elements of purity 99.999%. The elements in its stoichiometric proportions were placed in silica tube. 10 gr. of $CuInS_{e2}$ were sealed in a fused silica tube under a vacuum (10^{-4} .Torr) and Kept the ampoule in a rotating oven at sufficiently elevated temperature, at start, slowly to 473 k for 30 minutes and at 573 k for 30 minutes until all the selenium vapor disappeared. This was necessary to avoid explosive reactions, particularly between indium and selenium. As the temperature is raised, selenium vapor becomes visible and it disappears abruptly when the selenium was all reacted .When this has occurred, the furnace temperature was safely raised to 1323 k for 8 hours and at(1073,1023,973,923,873 and 823 k)each for $^1/_2$ hour the constituents became molten; the rocking motion ensures that thorough mixing of the mixture take place. Finally the tube was left to cool to room temperature.

$CuInse_2$ Prepared films deposited by vacuum evaporation in a coating unit model E.306A EDWARD CO.

2.2-measurements :

The thickness of the films determined Using Zeiss leink Micklessin interferometer (8)-X-ray diffraction(XRD) analysis of the as- prepared powder and as- deposited films was carried out using X-ray diffractometer (philips PW1730) with Cu (k_α) radiation ($1.54A^0$) .Scanning Electron microscope model (JOEL JSM-T20) was used to study the surface morphology of the films.

EDAX/unit attached to SEM was used for the elemental analysis of $CuInSe_2$ films (441nm), prepared at two different annealing temperature 573 and 673k.at 30min .Three different points were analyzed along the surface of each film with area ($1mm^2$).

The electrical properties measurements were carried out for $CuInse_2$ thin films in vacuum 10^{-2} Torr at the temperature range from room temperature up to $500k^0$ .Figure (1) shows the schematic representation of $CuInse_2$ thin films and its indium electrodes.

The resistivity ρ of samples was calculated from the formula /9/,

$$\rho = \frac{RS}{L} \ (\Omega\ .Cm) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

S=cross sectional area of the samples***,*** ***L***=distance between the electrodes ,***R***=measured resistance

Figure (2) show the circuit used during the conductivity

Measurement with keithley 616 digital electrometer

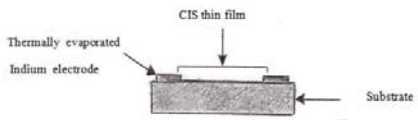


Fig (1) The substrate with its Indium electrode

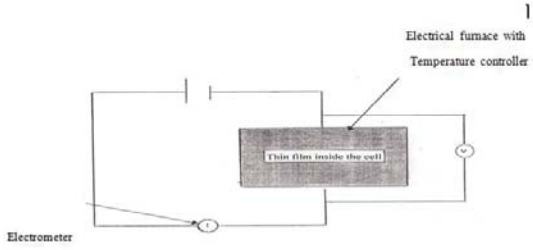


Fig (2) The circuit diagram

3-Results and discussion.

<u>3.1-structural properties and surface morphology</u>

X-ray diffraction patterns were obtained for as-prepared $CuInSe_2$-in powder form and XRD show that $CuInSe_2$ has tetragonal polycrystalline structure with (122)preferred crystal orientation. X-ray pattern for the prepared powder is shown in figure (3) and as indicated from table (1).

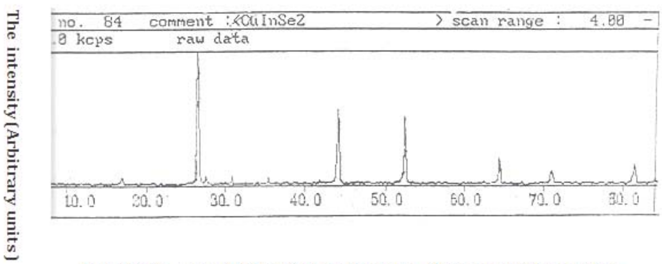


Fig (3) X – ray diffraction pattern for the prepared powder

It is in good agreement with the data reported for $CuInSe_2$.

Table (1) X-ray powder diffraction

Experimental		***JCPDS Card***		
D(A^0)	***I\I$_0$***	***D(A^0)***	***I\I$_0$***	***(hkI)***
3.35	***100***	***3.34***	***100***	***112***

2.05	***59***	***2.04***	***70***	***220,204***
1.75	***46***	***1.743***	***85***	***116,312***
1.44	***28***	***1.446***	***25***	***400***
1.33	***20***	***1.327***	***35***	***316,332***
1.18	***21***	***1.181***	***60***	***424***
1.11	***15***	***1.114***	***25***	***336***

The as-deposited films with the substrate at room temperature appeared to be of a mixed amorphous- microcrystalline nature, as shown in f:g.(4)
The as-deposited films and the heated films under vacuum of 10^{-3} torr for 30 minutes at isochronal annealing temperatures (473, 573, 673 and 723 k are shown in figure (4).

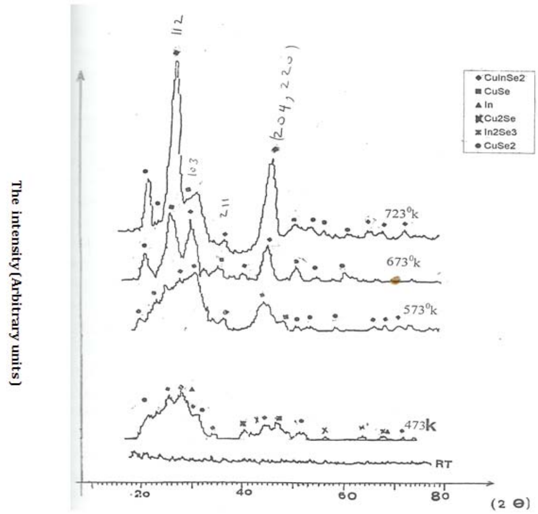


Fig (4) X-ray diffraction pattern for $CuInSe_2$ thin films with thickness (441nm) annealed at different annealing temperatures under vacuum ; a-as deposited, b - annealed at 473, c- annealed at 573K , d-annealed at 673K, e- annealed at 723K

For films annealed at annealing temperature of about 473k ,the XRD pattern (fig .4 b) shows that some peaks start to grow which may be due to the formation of $CuInSe_2$ JCPDS23-0209 , In JCPDS 05-0642, Cu_2 s_e JCPDS 79-1841,$CuSe_2$ JCPDS 71-0046, CuSe JCPDS 20-1020 and In_2Se_3 JCPDS 71-0250. This can be attributed to an early stage of crystallization between RT and 473k . For films annealed at about 573k, the XRD pattern (fig4C) Shows the disappearance of some phases such as In, Cu_2Se and In_2Se_3 and the continuous grows of $CuInSe_2$ on account of them. This finding agrees with

Vikas(10),which had referred to the formation of $CuInSe_2$ phase at about 500k due to the reaction of In with Cu_2Se phase .The other compounds mentioned above still exist. X-ray diffraction was used in identifying the different phases formed .Along with the knowledge of different phases formed at increasing annealing temperatures, it was concluded that $CuInSe_2$ is formed at temperatures as low as 235^0C . the experiments performed show that even at relatively low temperatures $CuSe_2$ is formed . The copper selenite phases changed from Se –rich to Se deficient with increasing temperature.

Increasing the annealing temperature up to 673k ,the XRD pattern (fig.4 d)shows the disappearance of CuSe phase .Many reflections corresponding to $CuInSe_2$ could be seen as in table (2) .Fig (4 c,4d) also shows the transformation of $CuInSe_2$ from random (204 reflex is greater than 112 reflex) to crystallized $CuInSe_2$ phase as reported by vikas(10), at such range of temperature .

Increasing the annealing temperature up to 723k, the XRD pattern (fig.4e) shows that no essential change takes place except that the reflexes of $CuInSe_2$ at (d=3.34 and d=2.04 A^0) becomes larger and the reflex at (d=2.88) becomes very weak .Therefore, one can notice the increase of the preferred crystal orientation (112) shown in fig (4,d and 4e) due to the increase in the annealing temperature .This finding agrees with the reported data (11)

Table (2) XRD of $CuInSe_2$ thin films annealed at different annealing temperatures

JCPDS CARD		***CIS Annealed at (573 k)***	
D(A^0)	***I\I$_0$***	***D(A^0)***	***I\I$_0$***
5.2	***6***	***5.1***	***30***
3.34	***100***	***375***	***50***
3.33	***70***	***3.015***	***100***
2.88	***10***	***2.83***	***56***
2.04	***35***	***1.992***	***53***
1.327	***35***	***1.3***	***26***

Table (2) (a)

JCPDS CARD		***CIS Films Annealed at (623 k)***	
D(A^0)	***I\I$_0$***	***D(A^0)***	***I\I$_0$***

5.2	***6***	***5.36***	***33***
3.34	***100***	***3.35***	***100***
2.52	***15***	***2.46***	***30***
2.15	***6***	***2.34***	***30***
2.04	***70***	***1.9813***	***66***
1.7	***85***	***1.65***	***23***

Table (2) (b)

JCPDS CARD		***CIS Films Annealed(723k)***	
D(A^0)	***I\\I_0***	***D(A^0)***	***I\\I_0***
5.2	***6***	***5.108***	***30***
3.34	***100***	***3.35***	***100***
2.52	***15***	***2.619***	***8***
2.15	***6***	***2.16***	***12***
1.9	***6***	***1.97***	***40***
2.04	***70***	***1.99***	***53***
1.39	***4***	***1.36***	***26***

Table (2) (c)

Therefore, according to the heat treatment, it is seen from the figure (4) ,and from table (2) that as increasing the annealing temperature as the half width of the diffracted peaks is decreasing, as well as increasing the sharpness of the peaks .This decrease in the half- width and the increase in the sharpness of the peaks are associated with the increase of the crystal size and the increase in the crystallinity as indicated from table (2)

This means that increasing the annealing temperature up to 723 k for $CuInSe_2$ thin films cause$_s$ better growth of the films and improves crystal orientation and the crystallinity of the films.

The lattice –parameters a and c of the chalcopyrite $CuInSe_2$ films were calculated according to the following formula (12),

$$1/d^2 =(h^2+k^2)/a^2 +I^2/c^2 \ldots\ldots(2)$$

The lattice parameter values are tabulated in table (3) for $CuInSe_2$ thin films at different annealing temperatures.

The annealing temperature (k)	*A (A^{0})*	*C (A^{0})*
573	*5.73*	*11.16*
673	*6.011*	*11.32*
723	*6.07*	*11.61*

Table (3) the lattice parameters a and c of $CuInSe_2$ thin films at different annealing temperatures.

The Effect of Heat Treatment on Crystallite Size

The peak profile of (112) is used to calculate the approximate crystallite size using the Scherer's formula (13),

$$L=(k\lambda)/(B\cos\theta) \quad \ldots\ldots(3)$$

Where (k) is a constant known as the shape factor factor(k=0.95),λ is the X-ray wavelength(λ=1.541^{0}A), B is the angular half width .And θ is the Bragg's angle.

The crystallite size was determined as a function of the annealing temperature for $CuInSe_2$ thin films with thickness 441nm which annealed at 573 ,673 and 723 k for 30min .The crystal size was found to increase with increasing the annealing temperature .The obtained values of the crystal size are shown in /fig(5) .The increase in the crystal size may be due to the filling of the vacancies. In case of $CuInSe_2$ thin films, the heat treatment produces loss of selenium and the vacancies are nucleated from selenium vacancy clusters, as reported by (14) .Figure(5) shows the variation of the crystal size with the heat treatment for $CuInSe_2$ thin films annealed at 473, 573, 673 and 723 k for 30 min .

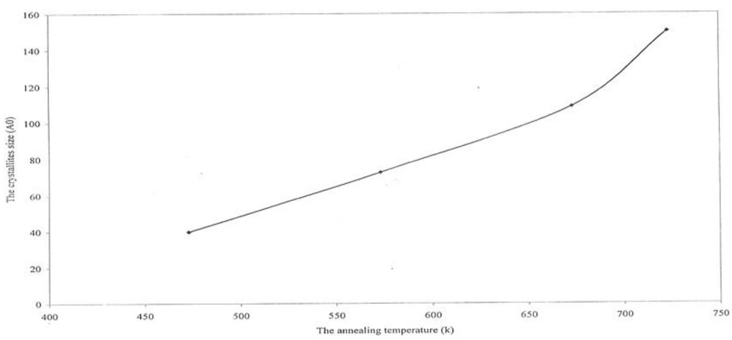


Fig (5) The variation of the crystallites size with annealing for $CulnSe_2$ thin films with thickness (441)nm and annealed (473, 573, 673 and 723 K)

The obtained results for $CnInSe_2$ films annealed at two different annealing temperatures (573 and 673k) are shown in table (4) .

The EDAX data show that the annealing is accompanied by a decrease of the Se concentration in the films. The average change in the composition ratio due to the annealing process was about 4.53%. This shows that at higher annealing temperatures, there is a significant re-evaporation of Se as reported (15).

Sample	Composition At %			Composition Wt %		
	Cu	In	Se	Cu	In	Se
$CuInSe_2$ thin films Annealed at 573 k for 30 min	25.5	20.54	53.96	19.67	28.62	51.71
	27.49	7.13	65.39	22.61	10.59	66.81
	25.57	20.01	54.41	19.77	27.96	52.27
$CuInSe_2$ thin films Annealed at 673k For 30min	24.85	21.52	53.63	19.06	29.83	51.12
	24.46	21.12	54.42	18.78	29.30	51.92
	24.66	23.19	52.15	18.77	31.9	49.33

Table (4) The film composition of $CuInSe_2$ thin films with thickness (441 nm) and annealed at (573 and 673 k) for 30 min .

It is clear from table (4) that there are homogeneity and compositional improvements towards stoichiometry in the films as the annealing temperature rises .

A typical microgragh of CIS thin films are shown in fig. (6a, b and c).

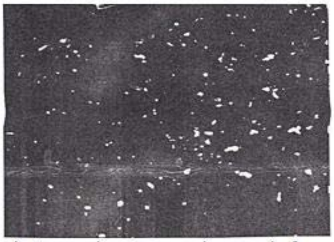
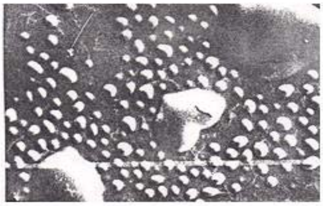


Fig (6,a) Scanning electron microscopy micrograph for as deposited $CuInSe_2$ thin films with thickness 441nm.

Fig (6,b) Scanning electron microscopy micrograph for $CuInSe_2$ thin films with thickness 441 nm and annealed at 573K.



Fig(6,c) Scanning electron microscopy micrograph for $CuInSe_2$ thin films with Thickness 441 nm and annealed at 673 K.

The effects of annealing in CIS thin films surface roughness are clear. The as deposited film contains random distribution of well –defined small crystallites, which formed at certain preferred sites on glass substrate.

The annealed samples showed an enhanced growth of grains which could be attributed to the decreaseof the Se content as a result of vacuum annealing such decrease was reported by many workers (16,17) G.K.Padam (18) Have also reported the decrease in the grain size with increase the Se contents in CIS thin films.

3.2Electrical Properties of CuInSe2 Films

It is found that $CuInSe_2$ thin films obey the Arrehenious equation (19) , which given by

$$\sigma = \sigma_0 e^{(-Ea/kT)} \qquad \text{...(4)}$$

Which in polycrystalline materials is attributable to thermal excitation of the charge carries from grain boundaries to the neutral region of the grain .

The conductivity of $CuInSe_2$ thin films were measured as a function of the temperature . For all films the conductivity is found to increase very slowly with temperature in the lowest temperature range, while in the high temperature region the dark conductivity is found to increase more sharply.

$CuInSe_2$ thin films were subjected to the following annealing temperatures 373k ,473 k and 573k, for 30min . The activation energy was found to decrease with increasing the annealing temperatures.

The obtained values from fig(7) are tabulated in table (5) .The conduction improvement due to heat treatment can be attributed to the improvement of the crystallinity as well as the composition variation which in turn affecting the energy states of the films as reported (20).

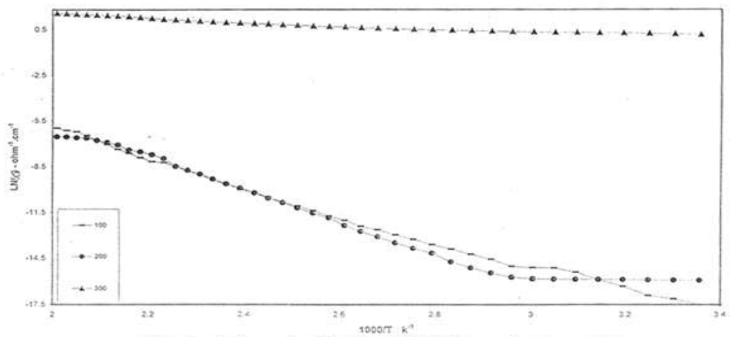


Fig (7) the dark conductivity for different annealing temperatures

Annealing temperature	***Measuring***		***Measuring temp***	
	Temp.(k)	***Activation Energy(eV)***	***Temp.(k)***	***Activation energy(eV)***
373k	***298-423***	***0.063***	***428-498***	***0.908***
473k	***298-358***	***0.021***	***362-498***	***0.832***
600k	***298-338***	***0.014***	***343-498***	***0.153***

Table (5) the activation energy for annealed $CuInSe_2$ thin films with the thickness 441 nm.

Two essential regions ,i.e. two values of E_a , were obtained At high temperatures, the thermal energy is sufficiently great to create vacancies and the activation energy is a sum of the energies required for vacancy generation and the motion of ions into the vacancies(21)

At lower temperatures the thermal energy is only large enough to allow the migration of atoms into vacancies already present in the crystal . The above conclusion indicates why the activation energy at high temperature regions is larger than the activation energy at low temperature regions.

Conclusion

Thin films were deposited in glass substrate by thermal evaporation technique .The $CuInSe_2$ ingot material is to be prepared by direct fusion of stoichiometric proportions of the constituent elements . The film thickness were controlled during the evaporation by a quartz thicknessmonitor. Michleson interferometer were used to determine the film thickness.

Structure characterization is to be undertaken by X-ray diffraction and Scanning electron microscopy. X-ray diffraction studies show that as deposited $CuInSe_2$ in powder form and annealed films has tetragonal polycrystalline structure with (112) preferred crystal orientation .The as deposited films were of mixed amorphous- microcrystalline nature . Annealing the films improves the crystallinity of the films. This behavior is in good agreement with other investigators.

The existence of binary phases with in the film will affect optical and electrical characteristic of the material .Care is therefore required in attributing specific measurement of intrinsic property of "single$CuInSe_2$ phase". We see compositional improvement toward stoichiometric with increasing the annealing temperature .Such approach suggests that the optimization of $CuInSe_2$ thin films by annealing made by grain enhancement. That large grained $CuInSe_2$ aggregate with a minimum of excess minority phases.

SEM shows that the as deposited $CuInSe_2$ films containing substantial numbers of defects within the grains .By annealing $CuInSe_2$ thin films large grain size appear. Accordingly, the influence of the annealing temperature on the surface roughness of $CuInSe_2$ thin films is significant.

The dark conductivity of the films was measured as a function of temperature. It is observed that the conductivity increases with increasing the temperature .Two regions are clearly seen corresponding to two activation energy as shown in table (5) .The activation energy decreases with increasing the annealing temperature.

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