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The Effect of Annealing Time on The Structural and Electrical Properties of CdTe Thin Films

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Abstract:

The effect of post annealing of CdTe thin film had been studied, the films were annealed at 400° C for 30, 60, 90 and 120 min, the effect of annealing time on the structure and electrical properties had been done, all the films had a well defined crystal structural. The mean crystallite size had been increased to 26 nm with annealing time up to 60 min at 400° C, after that time the mean crystallite size decreased. The behavior of sheet conductivity also effected to annealing time, and change from (9.33 x 10^{-12} S.□) for the as prepared CdTe thin films to (1.41 x 10^{-11} S. □) for the films annealed for 120 min, and also did the activation energy of these films.

1) Introduction:

CdTe thin films have been interested because of its absorbing characteristic in the visible region, for this reason it become a prime candidate for photovoltaic application [1, 2]. Polycrystalline CdTe is one of the most promising materials for the fabrication of semiconductors devices for gamma and IR detectors, optoelectronics devices, field effect transistors and solar cells [3,4]. Because of its band gap which located at the maximum of the solar energy density incident on the earth's surface makes CdTe very suitable for solar cell applications. The interest in the physical properties of CdTe film grown at low temperatures has been increased in the resent years for solar cells application [5,6]. Solar cells based on polycrystalline CdTe thin films are under intense investigation as potential candidate for low cost, high efficiency photovoltaic application. In the typical cell structure, the active junction is formed at the interface between an n- type CdS layer and a p - type CdTe layer. Most processes for production high efficiency cells involve annealing the structure after the CdTe layer is deposited on CdS, annealing temperature are near 400° C [7, 8]. One of the key steps in optimized the photovoltaic parameters of CdTe solar cells is the post deposition heat treatments of the CdTe films, the effect of post - deposition heat treatment on the structural change of CdTe thin films and its influence on the performance of CdTe - CdS cells were reported [6,7].
The systematic research on these properties in correlation with the film preparation conditions is still necessary for a more comprehensive understanding of this correlation

and for the control of the properties of these films.Doping CdTe with metal such as Ga, Pb, In and Zn produced considerable change in optical and electrical properties[8,9] . Thin films of CdTe have been prepared by various methods. Baker [9] prepared CdTe by thermal evaporation and dope it by Zn, Enriquez and Mathew [6] prepared CdTe thin films by electro deposition. CdTe thin films had been prepared also by sputtering by Marafi et.al. [10].
In this work CdTe thin films had been prepared by thermal evaporation and then annealed at 400° C for 30, 60, 90 and 120 minutes, to study the effect of post annealing time on the structural and electrical properties of the films.

2) Experimental Techniques.

CdTe thin films in this study were prepared by thermal evaporation of high purity CdTe (99.99% from CERAC Inc.), the material was evaporated using Balzers coating unit (model BL 510) at pressure of 2 x 10^{-5} mbar, the substrates were laboratory glass slides which were chemically cleaned and wiped by Alcohol and mounted on a spherical work holder that was rotated at constant speed. The thickness of the deposited films was 250 nm. Thickness was measured using weighing method and obtained at deposition rate of 0.3 $nm.sec^{-1}$.
The films then were annealed in cubic furnace with air atmosphere at (400 ± 2) ° C for 30, 60, 90 and 120 minutes.
X ray diffraction (XRD) technique was used to investigate the film's crystal structures using PHILIPS PW-1050, with Cu - K□ radiation of wavelength 0.154 nm, (V_{max} = 40 kV, I = 20 mA), the diffraction patterns were record with angle (2□□) from 20 to 50°.
The mean crystallite size was calculated from XRD analysis using the method explained by Pielaszek [11, 12], in this method we need to specify two peak width measured at 1/5 and 4/5 of maxima of the diffraction peak (FW1/5M and FW4/5M) respectively. The method takes into account only size - broadening of the diffraction maxima. Therefore the following phenomena are not considered stacking faults, lattice strain, lattice defects and experimental broadening.
For composition analysis we use the Oxford *Twin X,* energy dispersive X-ray fluoresces (EDXRF) with Pd target, maximum voltage was 30 kV, with resolution of 150 eV at 5.9 keV of ^{55}Fe X ray line, the samples for this analysis were deposited on silicon wafer.
After annealing aluminum metal as electrical contacts was deposited in coplanar geometry with space of 3 mm for electrical properties measurement, the resistance of the films were measured as a function of temperature using the Kiethly digital electrometer model 616 with input impedance grater than 10^{14}□□, the temperature range was controlled from 30 up to 150° C (± 2), from the measured resistance of the CdTe thin films (R) and by applying Stuck's low [13]:

$$\sigma = \sigma_o \exp(-\frac{Ea}{K_\beta T}) \qquad \cdots\cdots\cdots\cdots (1)$$

were □□□□is the pre-exponential factor , Ea represents the activation energy (eV) , T the applied temperature (^{o}K) and K□ represents Boltzmann constant. By drawing natural logarithm

of □ as a function of $\frac{1}{K_\beta T}$ we get a straight line which the activation energy is equal to its sloop.

3) Results and Discussion

3.1) The EDXRF studies were made on the CdTe thin films deposited on Si wafers and post deposited annealing at 400º C for 30, 60, 90 and 120 min in order to determine the various elements may be present in the films, in fig (1), the spectrum of the CdTe thin film annealed at 400ºC for 60 min is shown the only elements were found are Cd and Te, the results shows film stoichiometry very closed to ideal one.

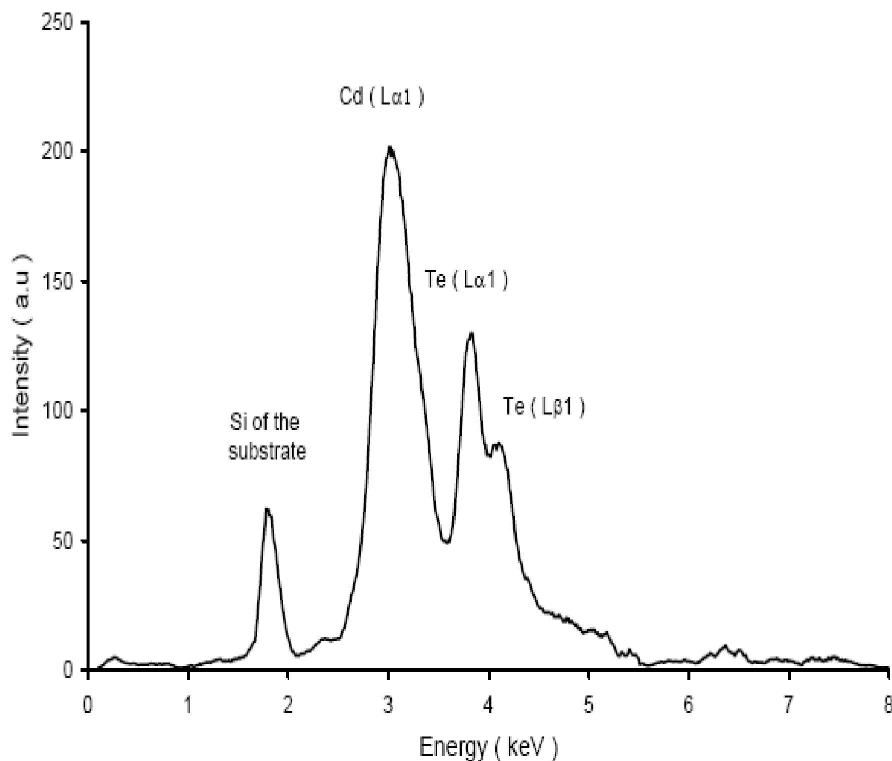

Fig. 1 Represents the EDXRF spectrum of CdTe thin film deposited on Si wafer substrate and annealed

been prepared by thermal evaporation and annealed at 400° C for 30, 60, 90 and 120 minutes, are shown in Fig (2), no diffraction peaks corresponding to metallic Cd or Te were observed. The
[1 1 1] plane of the cubic CdTe structure and this type of textured growth has often been

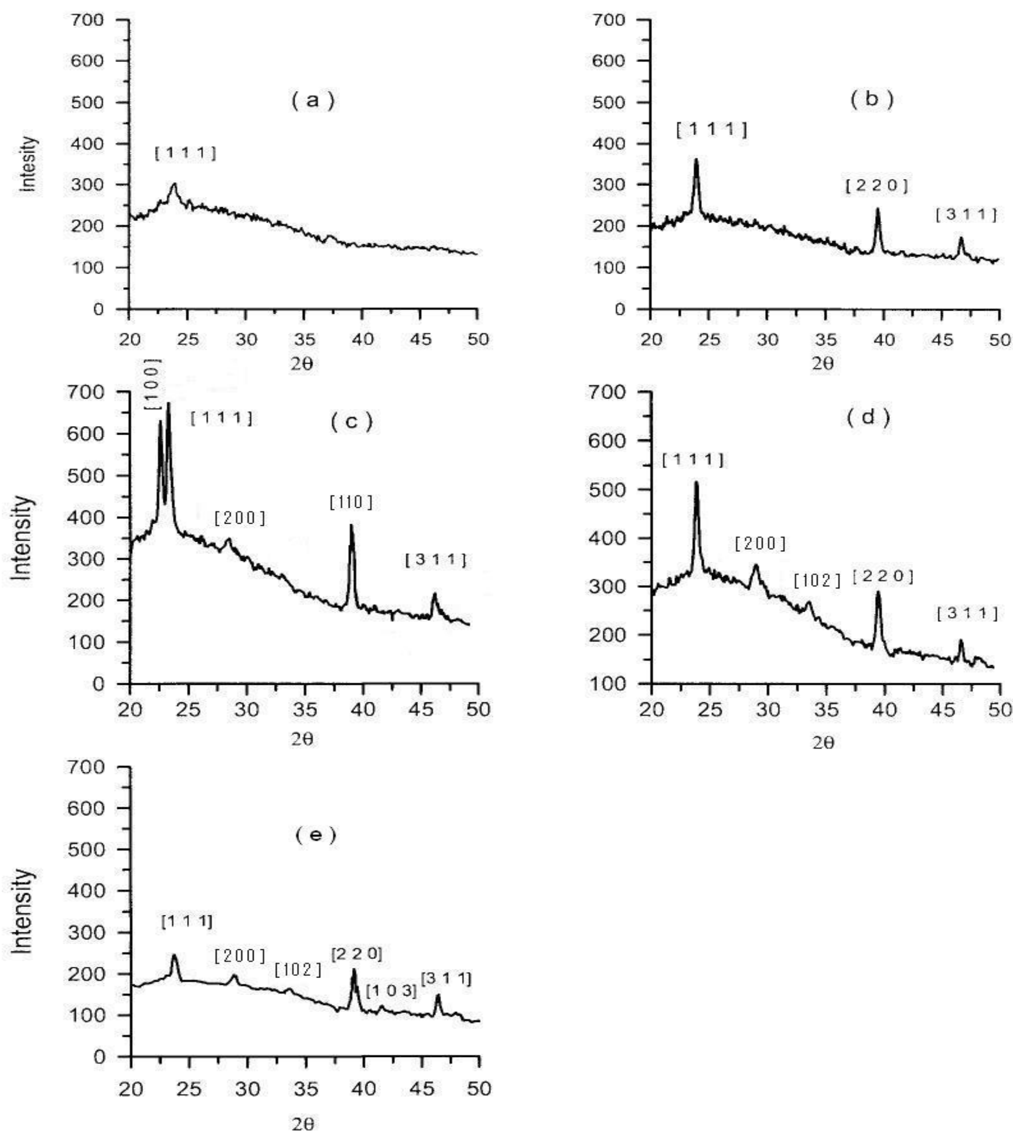

Fig. (2) Represent the XRD patterns of CdTe thin films as a function of annealing time (a) as deposited films, (b) 30 min.,(c) 60 min.,(d) 90 min. and (e) 120 min. (annealed at 400° C)

observed in polycrystalline CdTe films grown on amorphous substrates [7,14]. The influence of the
heat treatment is very clear as it can be seen in Fig.2 (b, c, d, and e). After post - deposition annealing at 400° C for 30 min. (Fig. 2-b) other peaks associated with the cubic phase had been appeared, the first one at 2□ = 39.5° [2 2 0] and the other at 2□ = 47.7° [3 1 1]. The effect of 60 min annealing can be seen in Fig.1-c, in this situation there is a multi phase growth of the CdTe thin film. The first peak at 2□□ = 22.6° [1 0 0] which associated only with the hexagonal phase, the [1 0 0] had been observed by AI-Dafiri [8] after post annealing of CdTe thin film at 500° C for 60 min, which means that we have a mixture of phases when the CdTe thin films has been annealed at 400° C for 60 min.

After annealing of the CdTe thin films at 400° C for 90 min. as shown in Fig. 2-d, the diffraction peak at 2□ = 22.6° [1 0 0], which belongs to the hexagonal phase was disappeared, but there was a growth of the [1 0 2] diffraction peak at 2□ = 33.56° of the same phase [15]. The annealing for 120 min. at the same temperature cause the peaks to became less sharp (Fig. 1-e). AI-Dhafiri [8] had noticed that the CdTe thin films treated thermally at 400° C for 240 min. became amorphous. We had observed that the [0 0 1] peak had disappeared and there is a growth of the [1 0 3] peak at 2□□ = 41.6° of the hexagonal phase [16]. Table (I) summarize the effect of annealing time of the CdTe thin films at 400° C.

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Table I: Shows the variation of structural phase with different annealing time at 400° C

Time (min.)	2θ	d (A°)	hkl	structure
0	23.98	3.71	1 1 1	cubic
	23.93	3.72	1 1 1	cubic
30	39.49	2.28	2 2 0	cubic
	46.70	1.94	3 1 1	cubic
	22.60	3.93	1 0 0	hexagonal
	23.32	3.81	1 1 1	cubic
60	28.56	3.12	2 0 0	cubic
	38.97	2.31	1 1 0	hexagonal
	46.30	1.96	3 1 1	cubic
	23.90	3.72	1 1 1	cubic
	29.10	3.07	2 0 0	cubic
90	33.56	2.67	1 0 2	hexagonal
	39.45	2.28	2 2 0	cubic
	46.40	1.96	3 1 1	cubic
	23.70	3.75	1 1 1	cubic
	28.80	3.10	2 0 0	cubic
120	33.70	2.66	1 0 2	hexagonal
	39.10	2.30	2 2 0	cubic
	41.60	2.17	1 0 3	hexagonal
	46.50	1.95	3 1 1	cubic

Fig.(3) illustrate the effect of post deposition annealing at 400° C for different periods on the mean crystallite size of the CdTe thin films. It's obvious that there is an increase in the mean crystallite size with time reaching the maximum at 60 min., after that there is a decrease in the mean crystallite size of the CdTe films.

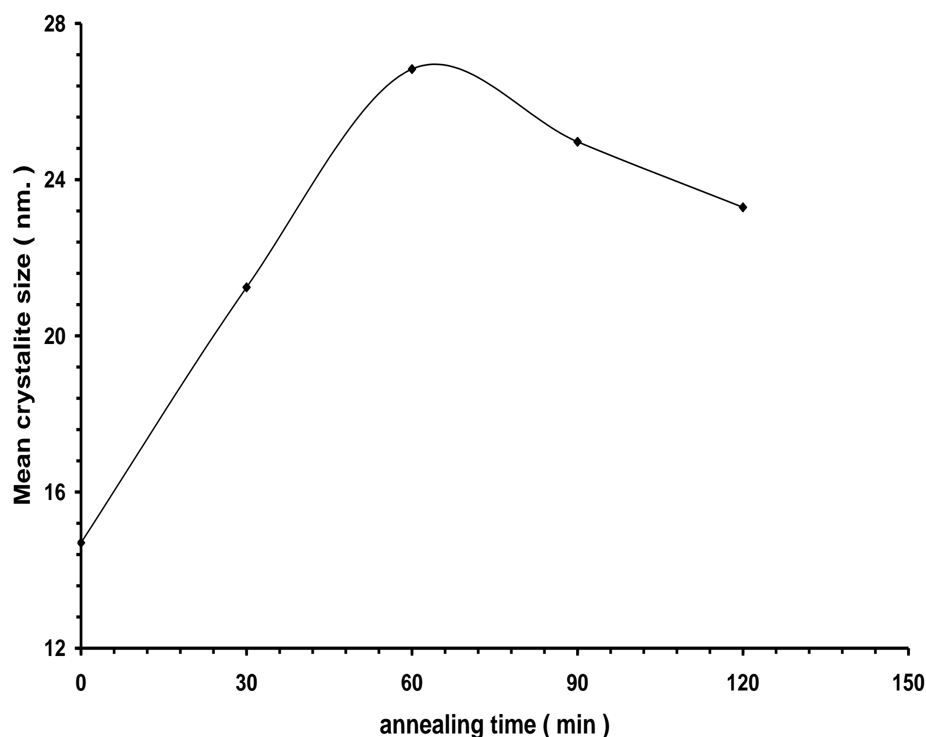
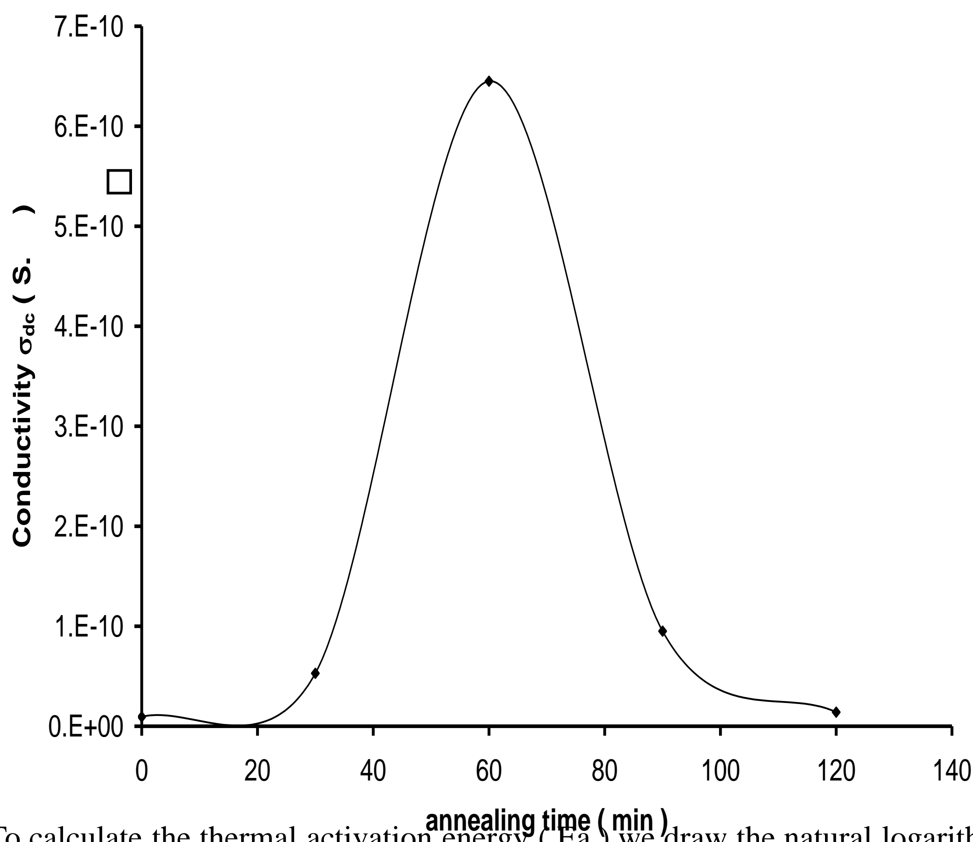


Fig. 3 Represent the effect of annealing time on the mean crystallite size of CdTe thin films annealed at 400°C for 30, 60, 90 and 120 min compared with the as

3.3) The effect of annealing at 400°C for 30, 60, 90 and 120 min on the mechanism of electrical conductivity of CdTe thin films had been studied by measuring the resistance of the films as a function of temperature and applying equation (1) we can estimate the values of Ea for the films as a function of post - annealing temperature, Fig (4) represents the sheet conductivity of the as prepared films with those annealed for 30, 60, 90 and 120 min. It could be noticed that the sheet conductivity of the CdTe film increased with the annealing time reaching the maximum at annealing time of 60 min., after that the sheet conductivity began to decrease with temperature for the films annealed at 400° C for 90 and 120 min.



To calculate the thermal activation energy (Ea) we draw the natural logarithm of the

Fig. 4, Represent the effect of post annealing on the sheet conductivity of CdTe thin films annealed at 400º C for 30 . 60 . 90 . 120 min. compared with the as

Dc conductivity as a function of ($\frac{1}{K_\beta T}$) from the slope of the straight line one can evaluate Ea. Also it was absorved that the mechanism of electrical conductivity was changed with annealing time. For the as prepared film there was only a one activation

energy which became two activation energies with the beginning of heat treatment and for all the rest samples. Fig (5) illustrates this behavior for both as - prepared and annealed at 400° C for 120 min, table II shows the values of the activation energy evaluated by applying equation (1).

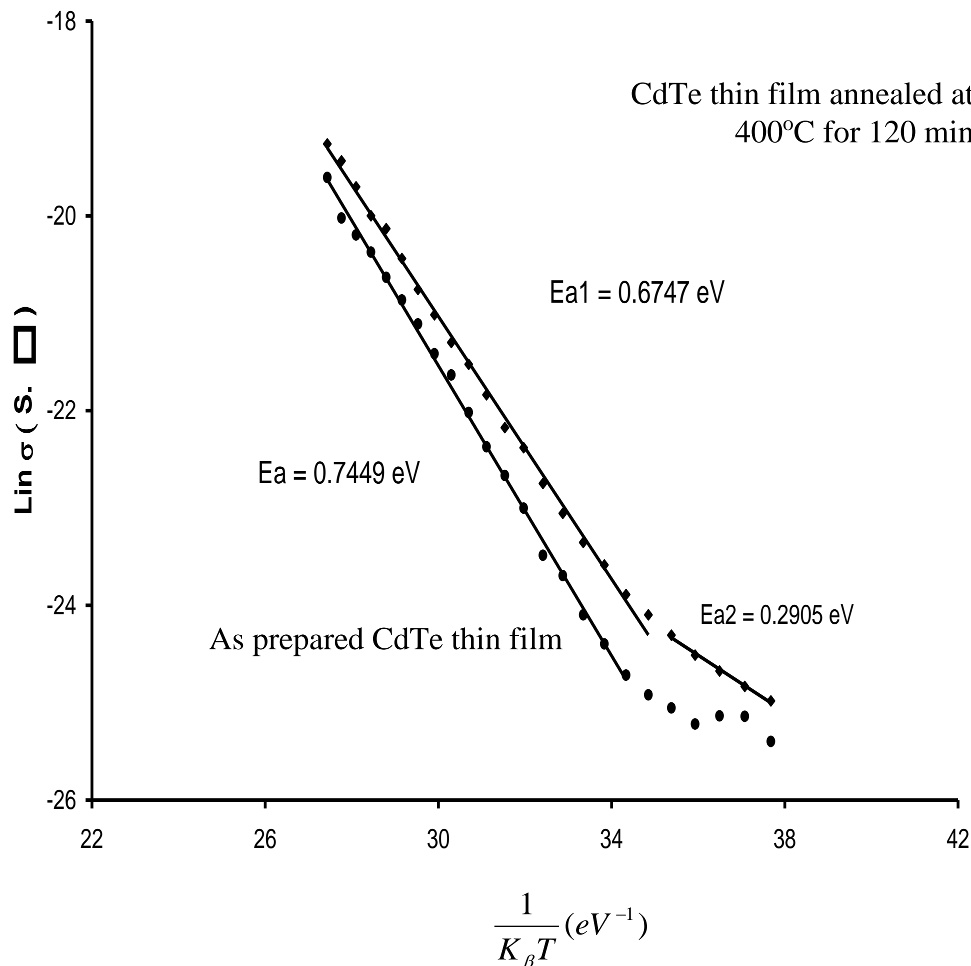


Fig. 5 Represent the activation energy of both as prepared and annealed CdTe thin film at 400° C for 120 min

Table II: The effect of annealing time on the Ea (eV) for CdTe thin films

Time (min)	Ea (eV)
0	0.7449
30	0.8202 2.3735
60	0.7449 1.2821
90	0.6371 1.0927
120	0.6747 0.2905

4) Conclusions

CdTe thin films were prepared by thermal evaporation technique. The obtained data reveal that the structural and the electrical properties of these films are strongly influenced by the post – annealing treatment. It can be concluded that the post – annealing is necessary to produce films with a given properties for specific application, it was noticed that all investigated films have a strong preferred orientation along (1 1 1) direction, but they have a cubic zinc – blend structure for the as deposited films and two phase structure of cubic and hexagonal phases have been formed after post – deposition annealing treatment. From the results of DC conductivity, one may conclude that the calculated values for the thermal activation energy (Ea) are close approximately to the mid gap region of the CdTe material.

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S^*- (o)-converges in Orlicz lattice

تاثير زمن التلدين على الخواص التركيبية والكهربائية لاغشية (كادميوم تيليرايد)

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الخلاصة :

تم دراسة تأثير زمن التلدين لأغشية CdTe المحضرة بطريقة التبخير الحراري بدرجة حرارة (400 ºC) ولفترات زمنية قدرها 30 ، 60 ، 90 و 120 دقيقة على الخواص التركيبية والكهربائية للأغشية المحضرة . أظهرت نتائج تحليلات حيود الأشعة السينية تركيبا بلوريا مميزا لجميع الأغشية المحضرة وأن هناك زيادة في متوسط الحجم الحبيبي للبلورات مع زمن التلدين لغاية 60 دقيقة حيث وصل متوسط الحجم الحبيبي الى 26 نانومتر بعدها يبدأ بالأنخفاض مع زمن التلدين . كذلك الحال مع التوصيلية السطحية للكهربائية المستمرة حيث كانت للغشاء غير الملدن (9.33×10^{-12} S.□)، بينما زادت الى (1.41×10^{-11} S.□) عند زمن التلدين 120 دقيقة ، كذلك فأن طاقة التنشيط هي الأخرى تأثرت بزمن التلدين.