The Effect of Annealing on the Structural, Electrical and Optical Properties of CdTe Thin Films

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Abstract

CdTe Thin films were deposited by thermal evaporation on glass substrates under vacuum of 2×10^{-6}mbar. The annealing has been done under vacuum 10^{-3}mbar at (303,373,423,473) K annealing temperature. The structure was investigated by XRD technique. It is found that the structure for all samples (as-deposited and annealed) is polycrystalline. The d.c. electrical conductivity was investigated and attributed to two mechanisms. The activation energy E_a increases from 0.13 to 0.55eV as annealing temperature increases from 303 to 473K. The a.c. conductivity reveals that the dependence of activation energy E_w on frequency is larger than that on temperature. E_w increases from 0.11 to 0.18eV as annealing temperature increases from 303 to 473K. Optical studies showed that optical energy gap increases with increasing annealing temperature from 1.4eV at 303K to 2.15eVat 473K.

Keyword : CdTe thin films , electrical and optical properties of CdTe thin films.

1. Introduction

Cadmium telluride is one of the most promising polycrystalline materials for thin film solar cells due its physical properties [1]. CdTe has direct band gap in the range (1.4 – 1.5) eV, which is near the maximum solar energy conversion point [2, 3]. CdTe has a high absorption coefficient (larger than 10^5 cm^{-1} at wavelengths around 700 nm), so that only thin film layers (a few microns) are needed for the absorption of the most of the solar spectra photons with energy higher than the band gap. CdTe has the ability to be doped both n- and p- type and the possibility of variety of preparation techniques such as thermal evaporation which often preferred because it offers large possibilities to modify the deposition condition [1, 4, 5].

There are wide applications of CdTe in optoelectronic devices such as detectors for infra-red and X-ray and possible applications in switching and memory devices.

Cadmium telluride can be considered as one of the most promising semiconductor materials for high efficiency thin film photo-voltaic cells as absorbing layer in manufacturing low cost thin film photo – voltaic solar cell [6-8] .

2. Experimental Details

Thin Cadmium Telluride films were prepared by vacuum thermal evaporation on glass substrates of stoichiometric with purity (99.999 %) using an Edward E306 coating unit under pressure $2X10^{-6}$ mbar. Glass substrates were cleaned by a cleaning solution, rinsed in distilled water then pure alcohol in ultrasonic cleaner. The deposition rate was 10nm/min and the thickness of the films was fixed at as 200 nm by using Michlson method.

The annealing was done under vacuum of 10^{-2}mbar and temperatures of 373, 423 and 473K. To investigate the variation of resistivity with temperature we used electrometer from (Kithley 616) and with coplanar configuration. Activation energy was estimated from Stukes equation $\sigma=\sigma_o\exp(-\Delta E/k_BT)$ where σ_o is the minimum metallic conductivity, ΔE is the activation energy k_B is Boltzmann's constant and T is the absolute temperature[9]. For a.c measurements HP-R2C unit model 4274A LCR meter has been used to measure the resistance R with frequencies of 1, 10 and 100 kHz using sandwich configuration.

The optical transmittance and absorbance measurement were taken at room temperature in the range of wavelength (200 – 1100) nm using UV/VIS spectrometer from (Shimadzu UV–160 A). These measurements were achieved to determine the absorption coefficient α by using the relation (α=2.303A/t) where A is the absorbance, and t is the thickness of film [10]. The optical energy gap (E_g) can be estimated using Tauc equation $(\alpha h\nu)=B(h\nu-E_g^{opt})^r$ where υ is the frequency of the incident radiation, B is constant, which depends on density of state (DOS) of conduction and valence bands, r is a constant which depends on the nature of the transition[11,12].

The XRD was carried out using (Shimadzu XRD – 6000) X-ray diffractometer Cu K_α radiation at room temperature which operates at potential difference of 40 KV and a filament current of 20 mA.

3. Results and Discussion

3.1 Structural Measurements

The main purpose of this section is to investigate the structural type of Cadmium Telluride films. Fig.(1) shows the XRD spectrum for as deposited and annealed CdTe films. This figure indicates a polycrystalline structure of all samples before and after annealing. According to the American standard for testing materials (ASTM) cards, the peaks represent a cubic structure having a zinc blend type. In addition to that, there is no separate Cd or Te phase form, which indicates that these films have stoichiometric structure. Point of interest is that the preferential orientation is the [111] direction of the films, this may be due to the layer stability of the {111} planes which reflects the more relaxed bonds with minimum energy, or improvement of crystallinity of the structure which leads to growth in the grain size [13].

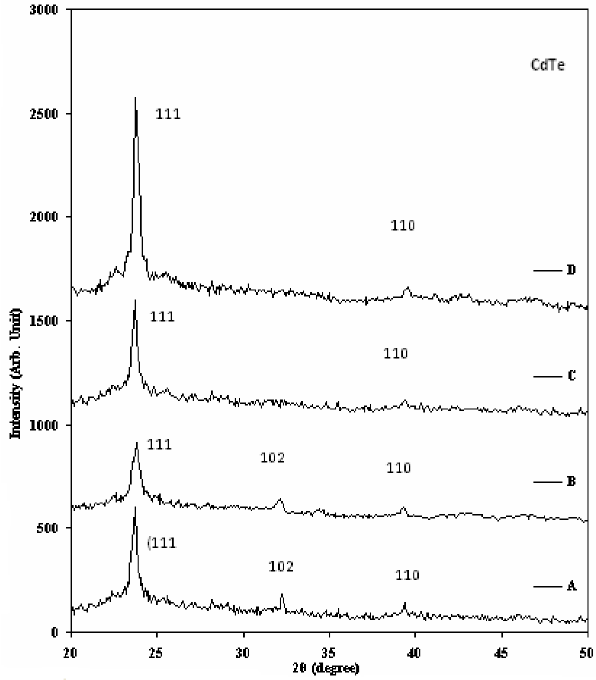

Fig.(1) X-ray diffraction pattern for films (A) as-deposited (B) T_a=373 K C) T_a=423 K (D) T_a=473 K.

All the values of the diffracted angle (2Θ), inter-planer distance (d) and miller indices (hkl) of the peaks of films before and after annealing treatment are shown in Table (1). It can be notice that these values are in agreement with the standard ASTM cards and they are in good agreement with K.N.Shreekanthan et al.[8].

Table (1)
The values of diffracted angle, inter-planer distance, Miller indices and grain size (G.S) for the CdTe films (as-deposited and annealed at 373,423 and 473 K).

T_a (K)	hkl	2Θ (deg.)$_{stan.}$	2Θ (deg.)$_{exp}$	$d_{stan.}$ (A^0)	$d_{exp.}$ (A^0)	FWHM	G.S (A^0)
303	111	23.70	23.68	3.742	3.740	0.420	3.37
	102	32.71	32.19	2.719	2.779	0.366	3.94
	110	39.22	39.39	2.295	2.296	0.40	3.68
373	111	23.70	23.78	3.742	3.737	0.545	2.59
	102	32.71	32.13	2.719	2.784	0.266	5.43
	110	39.22	39.24	2.295	2.298	0.37	3.98
423	111	23.70	23.76	3.742	3.754	0.412	3.43
	110	39.22	39.46	2.295	2.280	0.255	5.77
473	111	23.70	23.82	3.742	3.732	0.373	3.79
	110	39.22	39.59	2.295	2.274	0.315	4.67

3.2. *Electrical Properties*

The temperature dependence of the *d.c* electrical conductivity is shown in Fig.(2). Each graph in this figure can be divided into two distinct regions, which indicates the existence of two activation energies for conduction free charge carriers, one at low range of temperature region E_{a1} where its value was between 0.12-0.27eV and the other at high region of temperature E_{a2} and its value was between 0.13-0.55eV.

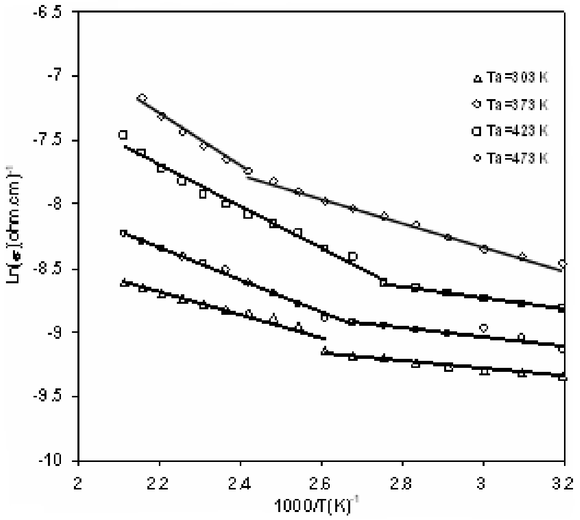

Fig.(2) Dependence of lnσ on temperature for different annealing thin CdTe films.

Fig.(3) shows that the activation energy increases with increasing annealing temperature T_a and this may be attributed to improvement in the structure which leads to reduction of defect state (tail state) in the forbidden gap and this leads to increase in the energy [14]. These results are summarized in Table (2).

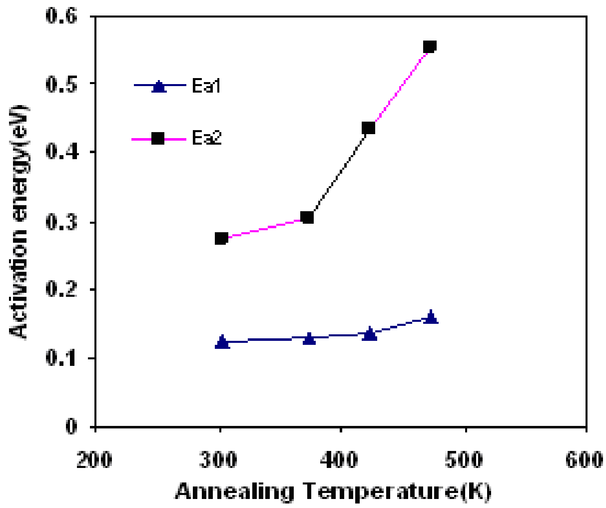

Fig.(3) Variation of activation energy with annealing temperature.

Table (2)
Dc electrical conductivity for CdTe thin films.

T_a (K)	***E_{a1} (eV)***	***Temperature range (K)***	***E_{a2} (eV)***	***Temperature range(K)***	***σ (Ω.cm)$^{-1}$***
303	0.12	303-383	0.13	383-473	9.1*10^{-5}
373	0.27	303-373	0.30	373-473	11.4*10^{-5}
423	0.13	303-363	0.43	363-473	15.2*10^{-5}
473	0.16	303-403	0.55	403-473	29.3*10^{-5}

From Table (2) it is noticed that the activation energy increases with increasing annealing temperature. This can be attributed to the structure arrangement by heat treatment which reduces the defects inside the structure.

Also the activation energy for a.c. conductivity for samples has been evaluated for frequencies (1, 10 and 100kHz), as shown in Fig.(4). It is clear that each sample reveals one activation energy E_w, moreover, we noticed that ac activation energy is smaller than that for dc conductivity because of the dependence of a.c. conductivity on frequency is larger than that of its depend on temperature.

The values of E_w decrease with the increase in annealing temperature as shown in Table (3). This may be due to the increment of CdTe structure with increasing annealing temperature.

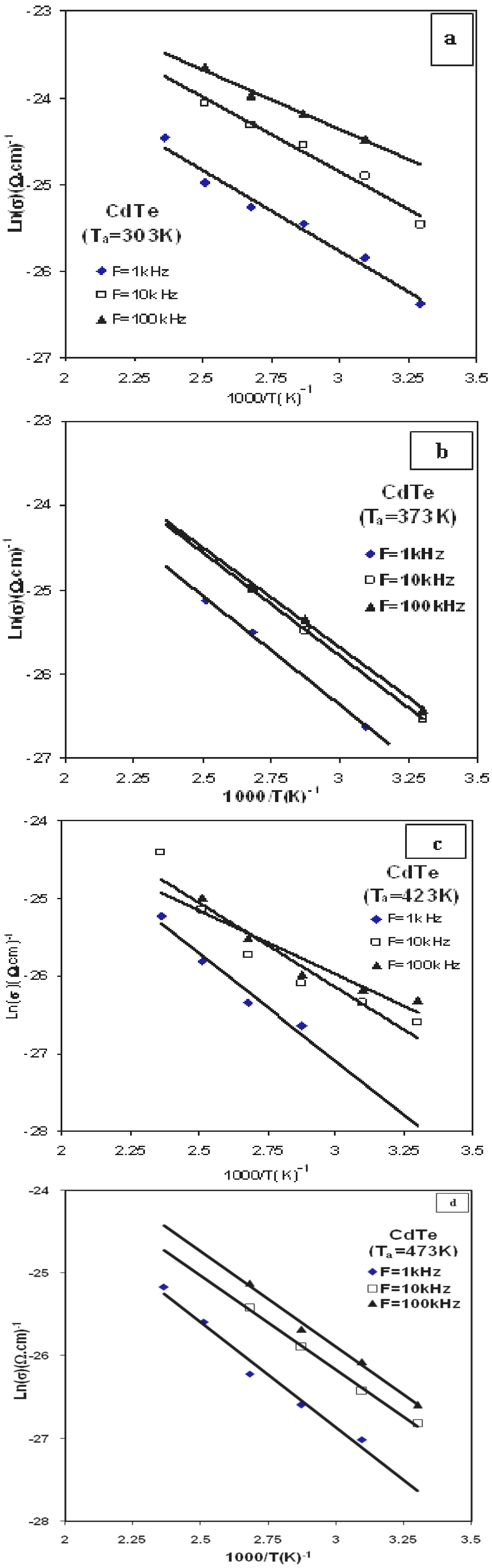

Fig.(4) The relation between Lnσ_{ac} vs.1000/T for as deposited and annealed films.

Table (3)
A.c activation energy E_w for CdTe films at different frequencies and annealing temperatures.

F (kHz)	T_a=303K	T_a=373K	T_a=423K	T_a=473K
	E_w(eV)	E_w(eV)	E_w(eV)	E_w(eV)
1	0.16	0.22	0.24	0.21
10	0.14	0.21	0.18	0.19
100	0.11	0.20	0.14	0.18

3.3 *Optical Properties*

The optical transmittance of CdTe films on glass substrates were measured by UV-VIS spectrophotometer. Fig.(5) shows the transmittance spectra of as deposited and films annealed at (373,423 and 473K). In general we can observe that the transmittance increases with increasing of annealing temperatures. The shifts of transmittance spectrum to shorter wavelengths (higher energies) with the increase of T_a for all samples may be attributed to the crystallization of film structure which is in agreement with our result of *XRD*. These results agree with that of R.A.Abdulah [15].

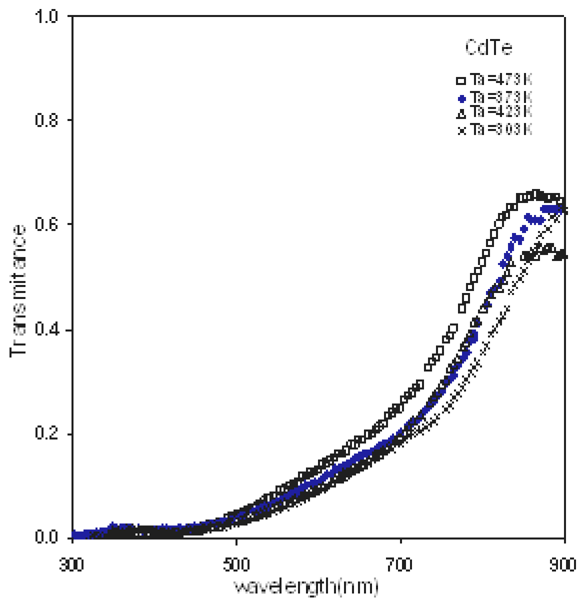

Fig.(5) The transmittance spectra for annealed and un-annealed CdTe thin films.

We noticed that the absorption coefficient of CdTe films is characterized by strong absorption coefficient at the shorter wavelength where the absorption coefficient exhibits high values of α >10^4 which means that there is large probability of the allowed direct transition [16].

By plotting the $(\alpha h\upsilon)^{1/r}$ versus photon energy, it is found that the relation for r=1/2 yields linear dependence. The extrapolation of the figure at $[(\alpha h\upsilon)^2=0]$ is shown in Fig.(6). The value of E_g increases with annealing, this is due to the growth of grain size and the decrease in the number of grain boundaries and these in turn increase the value of E_g (see Table (4)). The increase of E_g with T_a is in agreement with R.A.Abdilah [17]

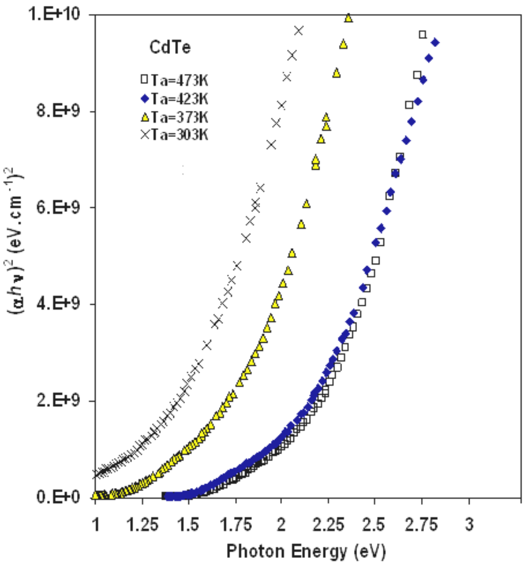

Fig.(6) The relation between $(\alpha h\upsilon)^2$ and photon energy (hυ) for annealed and un-annealed CdTe thin films.

Fig.(7) shows that the energy gap E_g increases with increasing annealing temperature T_a and this may be attributed to improvement in the structure which leads to reduction of defects (tail state) in the forbidden gap and this lead to increase in the energy gap.

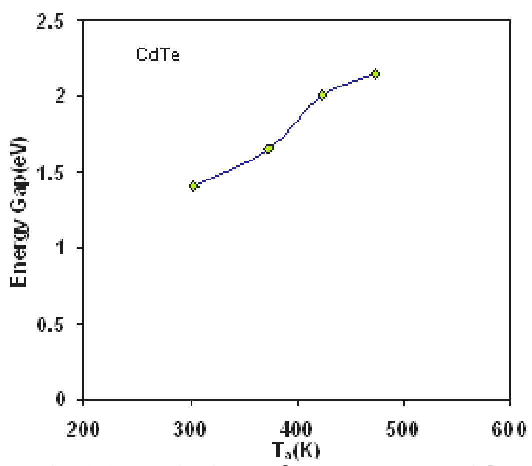

Fig.(7) Variation of energy gap with annealing temperature.

Table (4)
The values of energy gap with annealing temperatures.

$T_a(K)$	T_a=303K	T_a=373K	T_a=423K	T_a=473K
E_g(eV)	1.4	1.65	2.0	2.15

4. Conclusions

X-ray diffraction pattern shows that the structure of samples for different annealing temperature is crystalline and the crystallinity is increasing with increase of annealing temperature. *d.c.* electrical conductivity shows that there are two mechanisms for conductivity and the activation energy increases with increasing annealing temperature, while for ac conductivity there is one mechanism for conductivity, the dependence of activation energy on temperatures decreases with increasing frequencies.

Transmission spectra show that the probability of the allowed transition is the greatest and the optical energy gap increasing with the increase in annealing temperature.

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الخلاصة

تم ترسيب أغشية (CdTe) الرقيقة بطريقة التبخير الحراري للسبيكة على سطوح زجاجية تحت فراغ ٢×١٠^{-٦} mbar. تمت المعالجة التلدينية في الفراغ تحت ضغط $١٠^{-٣}$ mbar عند درجات حرارة (373,423,473) مطلقة.

تم فحص التركيب باستخدام تقنية حيود الأشعة السينية، اذ وجد ان جميع الأغشية المحضرة قبل وبعد التلدين ذات تراكيب متعددة البلورات. ومن خلال دراسة التوصيلية الكهربائية المستمرة لاغشية (CdTe) الرقيقة وجد ان هناك ميكانيكيتان للتوصيل، وطاقة التنشيط تزداد من 0.13 الى 0.55 الكترون فولت عندما تزداد درجة حرارة التلدين من 303 الى 473 درجة مطلقة.أما التوصيلية المتناوبة فأظهرت اعتمادية طاقة التنشيط E_W على التردد اكثر من اعتمادها على درجة الحرارة. E_W تزداد قيمتها من 0.11 الى 0.18 الكترون فولت عندما تزداد درجة حرارة التلدين من 303 الى 473 مطلقة. اظهرت الخواص البصرية أن فجوة الطاقة البصرية تزداد مع زيادة درجة حرارة التلدين حيث تبلغ قيمتها 1.4 الكترون فولت عند درجة حرارة 303 مطلقة بينما تصبح 2.15 الكترون فولت عند درجة حرارة تلدين 473 مطلقة.