The Role of Annealing Temperature on the Optical Properties of Thermally Deposited CdTe Films

M. F.A. Alias[(1)], M. A. Razooqi[(2)], R. A. Al_ Matooq[(2)], A.A.Al-Douri[(3)] and A.A. Alnajjar[(3)]

[(1)]Dept. of Physics, College of Science, University of Baghdad. Jadiriyah, P.O.Box 47162, Baghdad, Iraq
[(2)]Dept. of Physics, College of Science, University of Tikreet- Iraq.
[(3)]Applied Physics Department, Science College, University of Sharjah, P.O.Box 27272, Sharjah, UAE

Abstract

A polycrystalline CdTe film has been prepared by thermal evaporation technique on glass substrate at substrate temperature 423 K with 1.0 µm thicknesses. The film was heated at various annealing temperature under vacuum (T_a =473, 523 and K). Some of physical properties of prepared films such as structural and optical properties were investigated. The patterns of X-ray diffraction analysis showed that the structure of CdTe powder and all films were polycrystalline and consist of a mixture of cubic and hexagonal phases and preferred orientation at (111) direction.

The optical measurements showed that un annealed and annealed CdTe films had direct energy gap (E_g). The E_g increased with increasing T_a. The refractive index and the real part of dielectric constant for films were observed to decrease with increasing T_a, while the extinction and the imaginary part of dielectric were increased. Our result is good candidate for manufacturing optoelectronic device such as solar cells.

دور درجة حرارة التلدين على الخصائص البصرية لاغشية CdTe المرسبة حراريا

ميسون فيصل الياس[(١)] و محمد عبدالوهاب[(٢)] و رشا عباس[(٢)] و علاء احمد جمعة[(٣)] و عبدالله عبدالعزيز النجار[(٣)]

[(١)]قسم الفيزياء ـ كلية العلوم ـ جامعة بغداد
[(٢)]قسم الفيزياء ـ كلية العلوم ـ جامعة تكريت
[(٣)]قسم الفيزياء ـ كلية العلوم ـ جامعة الشارقة

الخلاصة:

حضرت أغشية CdTe متعددة التبلور بتقنية التفريغ الحراري على قواعد زجاجية بدرجة حرارة اساس ٤٢٣كلفن وبسمك واحد مايكروميتر. لدنت الاغشية بدرجات حرارة تلدين مختلفة وتحت الفراغ (573 & 523 ,473= T_a) كلفن. درست بعض الخصائص الفيزيائية لاغشية CdTe المحضرة كالخصائص التركيبية والبصرية. أظهرت نتائج حيود الاشعة السينية بان تركيب المسحوق والاغشية المحضرة ذات تركيب متعدد التبلور متضمنا خليطا من الاطوار السداسية والمكعبة باتجاه (١١١). بينت الخصائص البصرية امتلاك الاغشية الغير ملدنة والملدنة فجوة طاقة مباشرة.تزداد فجوة الطاقة بزيادة درجة حرارة التلدين.لوحظ بان معامل الانكسار وثابت العزل الحقيقي يقل بزيادة درجة حرارة التلدين بينما يزداد معامل الخمود والجزء الخيالي لثابت العزل. أظهرت النتائج ملائمة هذه الاغشية لصناعة النبائط الالكتروبصرية كالخلايا الشمسية.

Introduction

Cadmium telluride (CdTe) is unique among II-VI series of semiconductor compounds, as it exhibits both n- and p-types conductivity, this permits the fabrication both homojunction and heterojunction configuration [1]. Cadmium telluride has been identified as a potential material for low cost terrestrial photovoltaic energy conversion. *CdTe* is a direct band gap semiconductor about 1.45 eV, and it is a good absorber for sunlight with high optical absorption coefficient ($\alpha > 10^4 cm^{-1}$ i.e., less than the optical absorption edge) [2, 3]. It can easily be prepared in polycrystalline film using a variety of inexpensive cost by effective deposition methods. It has also better radiation tolerance, which makes it suitable for space application [4]. The purpose of this paper is studying the role of annealing temperature on the structural and optical properties of CdTe thin film.

Experimental Work

We used corning glass slides substrates which are cleaned [5]. The weighting method is one of several methods that can be used for measuring the thickness of prepared films. This method gives an approximate deposited film thickness (t), which is determined by the relation:

$$t = \frac{m}{2\pi\rho.R^2} \qquad (1)$$

where m and ρ are the material mass and density respectively, *R* is the distance between the substrate and the boat. A polycrystalline *CdTe* were prepared by thermal evaporation technique using *CdTe* of 99.999% purity under pressure nearly 10^{-6} mbar and at substrate temperature (T_s) of 423K.Thedistance between the molybdenum boat and the substrate was 20 cm. The deposition rate of *CdTe* films was 1.6 Å/sec. The samples have been annealed in vacuum oven at different annealing temperatures (473, 523 and 573 K).

The structure of *CdTe* film which prepared at T_s of 423 K and of 1.0 μm thickness and annealed at 473, 523 and 573 K for 60 min under vacuum have been examined by X-ray diffraction (XRD) with Cuk$_\alpha$ wavelength 1.5405 Å, the scanning angle has varied in the range (20-60) with speed 2 cm/min, current 25 mA and voltage 40 kV. The inter planer distance $d_{(hkl)}$ can be determined from Bragg's law [6,7].

$$2d_{(hkl)} \sin\theta = m'\lambda \qquad (2)$$

where θ is the angle between X-ray beam and reflecting planes, $m'\lambda$ is path difference. By comparing this $d_{(hkl)}$ value with ASTM card for *CdTe* has been examined the structure of their alloys and films. The grain size dimensions of these compounds (D) are calculated from Scherrer relation [8].

$$D = \frac{K\lambda}{B'\cos\theta} \qquad (3)$$

where K is the shape factor, which is approximately 0.9 and B' is the line broadening of pure diffraction profile on 2θ scale in radius and equal to:

$$B'^2 = (FWHM)^2 - b^2 \qquad (4)$$

where FWHM is full width at half maximum intensity of the peak, and b is the instrument effect estimated from the broadening of the substrate diffraction line, and will take equal to zero, then last equation becomes:

$$D = \frac{0.9\lambda}{B'\cos\theta} \qquad (5)$$

Results and Discussion

The X-Ray diffraction spectra for *CdTe* powder material and films annealed at different annealing temperature (room temperature (RT), 473,523 and 573 K) are illustrated in Fig.(1). The spectrum of the *CdTe* powder and films have been compared with ASTM cards of *CdTe* structure which gives a polycrystalline structure containing a mixture of hexagonal (wurtizite structure) and cubic (zinc blend structure) phases, similar data have been also obtained by other researchers, Heiba [9], Shalimova *et al.*

[10], Myers *et al*. [11], Arizpe *et al*. [12], Pandey *et al*. [13], Lee *et al*. [14], and Al-Dhafiri *et al*. [15]. The presence of mixed hexagonal and cubic phases cannot be ruled out [1]. The spectrum of the *CdTe* powder has shown sharp peaks at reflection surfaces (111), (110), (311) and (400), as shown in Fig. (1a).

For the as prepared *CdTe* films by thermal evaporation technique at 423 K as shown in Fig. (1b), he XRD pattern displays strong reflections at (111) direction as well as the low intensity peaks at (102), (110) and (311). One can observe that the reflection from (400) plane has disappeared at all other annealed films. Also the poor intensity (102) hexagonal plane at RT has appeared while this peak has disappeared at the other annealed films.

(a)

(b)
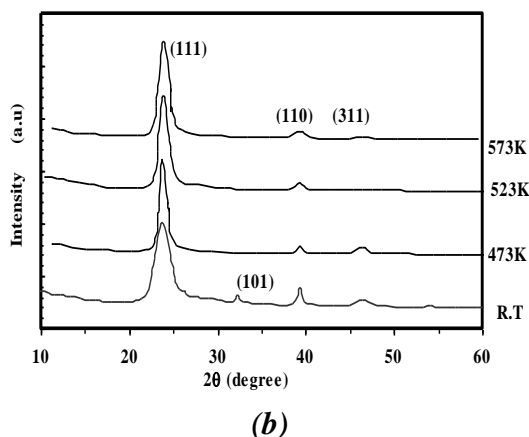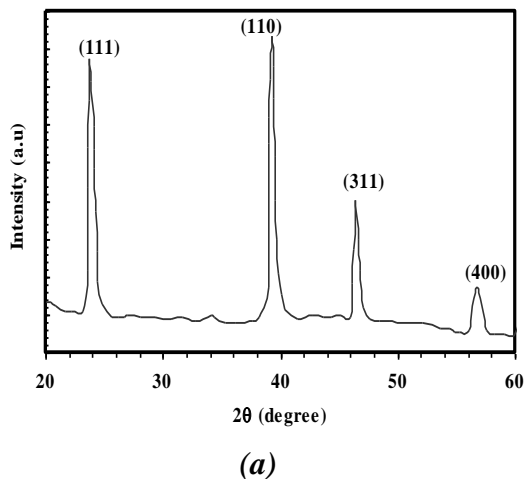
Fig. (1) XRD spectra for CdTe (a) powder (b) Films annealed at RT,473, 523 and 573 K.

The XRD pattern has shown crytallinity improvement for the sample annealing at 473 K, the intensity of (111) plane has increased and the intensities of (110) and (311) planes have decreased. More crystal structure improvement has been occurred after annealing for the sample at 523 and 573K by increasing the intensity of (111) plan and decreasing the intensities of both planes (110) and (311). The improvement in crystal structure with the annealing cloud be attributed to an improvement by rearrangement of *Cd* and *Te* atoms in the film crystallites ,and this is in good agreement with Al-Dhafiri [15], Table (1) shows the variation of the grain size for (111) plane with the annealing temperature. The XRD spectra also shows a little shifting towards higher diffraction angle for (111) plane after annealing at 523, 573 K comparing with as-prepared and annealed films at 473 K, these results have been shown in Table (1). It may be attributed to the dependence on composition [9], which includes the stoichiometry of *CdTe* compounds [10]. The lattice constant (a) of *CdTe* powder was 6.486Å.Our result is in good agreement with those results of researchers Rami *et al* [16] and Pandey *et al* [13].

Table (1) The structural parameters of CdTe powder and films annealed at various T_a.

	hkl	2θ	$(I/I_0)_{Stan.}$	$d_{Stan.}$ (Å)	$(I/I_0)_{Exp.}$	$d_{Exp.}$ (Å)	structure	Grain size (μm)
CdTe Powder	111	23.7	100	3.742	93.27	3.751	Cubic	
	110	39.2	60	2.295	100.00	2.296	hexagonal	
	311	46.4	30	1.954	48.17	1.955	Cubic	
	400	56.7	6	1.619	20.93	1.622	Cubic	
Film at R.T	111	23.7	100	3.742	86.17	3.751	Cubic	0. 489
	102	32.2	30	2.735	12.76	2.777	hexagonal	
	110	39.2	60	2.295	21.27	2.296	hexagonal	
	311	46.4	30	1.954	07.87	1.955	Cubic	
Film at T_a=473 K	111	23.7	100	3.742	97.87	3.751	Cubic	0. 601
	110	39.2	60	2.295	10.63	2.296	hexagonal	
	311	46.4	30	1.954	07.44	1.955	Cubic	
Film at T_a=523 K	111	23.8	100	3.742	97.87	3.735	Cubic	0. 731
	110	39.2	60	2.295	09.57	2.296	hexagonal	
	311	46.4	30	1.954	03.05	1.955	Cubic	
Film at T_a=573 K	111	23.8	100	3.742	100.00	3.735	Cubic	0. 902
	110	39.2	60	2.295	09.20	2.296	hexagonal	
	311	46.4	30	1.954	02.76	1.955	Cubic	

The optical properties of *CdTe* films of 1μm thickness at different annealing temperatures RT, 473, 523 and 573 K have been determined using UV-VIS-NIR transmittance spectrum in the region 0.2-1.1 μm.

The transmittance and absorbance spectra of *CdTe* films for as prepared and the annealed films are shown in Figs. (2 & 3) respectively. From these figures, in general, it can be observed that the peak of transmittance spectra of both *CdTe* films shift toward the shorter wavelengths with increasing the annealing temperatures compared with the as deposited films. While Heo *et al.* [2], Rami *et al.* [16] and Pandey *et al.* [13] have also found that the transmittance spectra shifting of *CdTe* toward the shorter wavelengths. This shifting is due to the structural improvement that is represented by increasing the crystallites size. This results consolidated by XRD of our prepared films .The trend of absorbtance spectra of CdTe films are opposite behavior that seen for transmittance as illustrated in Fig.(3) . The absorption coefficient of *CdTe* films for the as prepared and annealed films at 473, 523 and 573 K are illustrated in Fig. (4). From this figure the absorption coefficient of *CdTe* films are characterized by strong absorption at short wavelength region within the range 0.3-0.76μm with a sharp edge at the long wavelength side within the range 0.78-1μm. In the shorter wavelength region, α takes higher value within the range 1.374-1.408 x10^{4}cm^{-1}, when $\alpha > 10^4$cm^{-1}, the probability of the allowed direct transition is the greatest, beyond this region α decreased sharply for the whole wavelength range. The values of α are nearly in agreement with those of Myeres *et al.* [11] and Albin *et al.* [17].
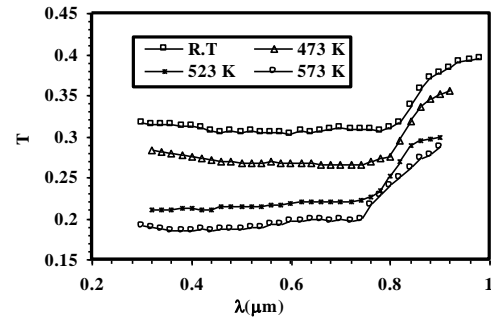

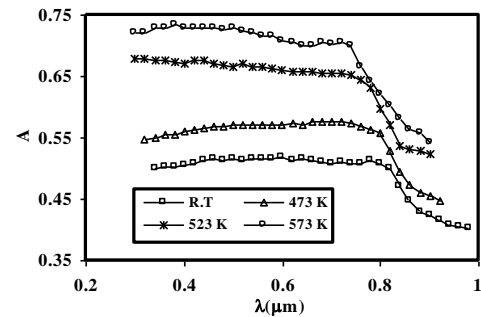*Fig. (2) The transmittance spectrum forCdTe films annealed at different T_a.*

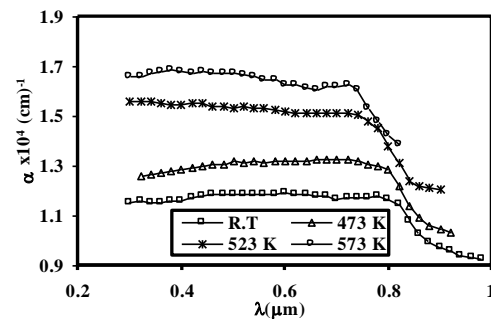*Fig. (3) The absorbance spectrum for CdTe films annealed at different T_a.*

Fig. (4) The absorption coefficient spectra for CdTe films annealed at different T_a.

The value of α for *CdTe* films at 0.84 μm wavelength is tabulated in Table (2).It can be observed that the films, the absorption coefficient increases with increasing the annealing temperatures by factor of 1.24[from (1.085 to 1.340) ×10^{4}cm^{-1}], this behavior may be due to reduce the recombination process and improvement in the crystalinity of films then reduce the density of localized states inside the energy gap by increasing the

annealing temperatures [17] which coincides with the XRD results.

The direct optical energy gaps of *CdTe* films were estimated lie in the range 1.32-1.56 eV, and it is slightly increased with increasing T_a by factor of 1.18 when varying T_a from R.T to 573 K. The variation of E_g with T_a is tabulated in Table (2) and illustrated in Fig. (5). Our results nearly agree with those of Cruz and de Avillez [3], Myeres *et al.* [11], Pandy *et al.* [13] and Al Asadi [18]. The increasing of E_g is in agreement with observed increase in the crystallite size as T_a increases, which further consolidates the suggestion that T_a enhances the crystallinity improvement [12]. This result is consolidated by the XRD results of *CdTe* films.
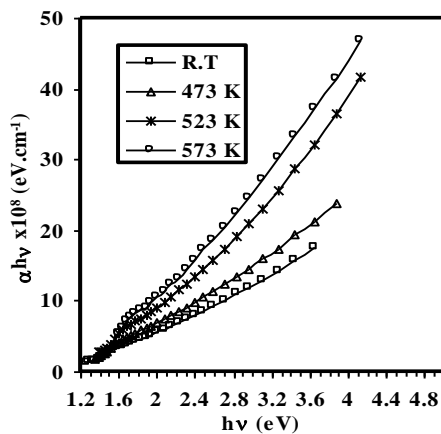

Fig. (5) The plot of $(\alpha h \nu)^2$ vs. $h\nu$ for CdTe films annealed at various T_a.

The coefficient **B** (Tauc's slope in Tauc equation) has been obtained from the root square of the straight line slope of Fig. (5). From Table (2), one can observe that **B** increases with increasing T_a. **B** is inversely proportional to amorphosity and the width of the band tails [19]. A larger **B** value means a smaller amorphosity and the increasing of **B** with increasing T_a for *CdTe* films suggests an increase of film crystallinity .These results also consolidate the XRD results.

The values of refractive index (n) for *CdTe* films at 0.84 μm wavelength with different T_a have tabulated in Table (2). It can be observed that n has decreased with increasing T_a from 2.551 to 2.303. This result is in agreement with that of Ray [1] and Meyers *et al.* [11], due to increase in the E_g which causes the lattice expand and the grain size to grow then to decrease the defect states [20].

The behavior of extinction coefficient is nearly similar to the corresponding absorption coefficient, as shown in Fig. (6) for *CdTe* and films at different annealing temperatures. From this figure and Table (2), we can observe that the extinction coefficient for *CdTe* films at 0.84 μm increases with increasing the annealing temperature by the factor of 1.22.
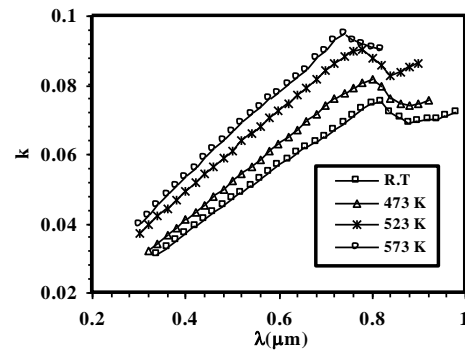

Fig (6)The extinction coefficient spectra for CdTe films at different T_a.

Table (2) shows the variation of real and imaginary part of dielectric constant for *CdTe* films at different annealing temperatures. The behavior of ε_r is similar to refractive index because of the smaller value of k^2 comparison to n^2, while ε_i depends mainly on the k values, which is related to the variation of absorption coefficient. For *CdTe* films ε_r decreased with increasing T_a from R.T to 573 K, within the range 6.504 to 5.294, such results have been pointed out by Meyers *et al.* [11] and Al Asadi [18]. While ε_i increased with increasing T_a from RT to 573 K, from 0.369 to 0.413, which is nearly agreement with Meyers *et al.* [11].

Table (2) The optical parameters of CdTe films annealed at different T_a

T_a (K)	$\alpha \times 10^4$ (cm^{-1}) at 0.84 μm	E_g (eV)	$B \times 10^9$ (eV/cm^2)	E_u (eV)
RT	1.085	1.32	0.72466	0.254
473	1.143	1.38	0.92835	0.233
523	1.239	1.43	1.4106	0.174
573	1.340	1.56	1.7776	0.065
T_a (K)	n at 0.84 μm	K at 0.84 μm	ε_r at 0.84 μm	ε_i at 0.84 μm
RT	2.551	0.073	6.504	0.369
473	2.506	0.076	6.273	0.383
523	2.416	0.083	5.829	0.400
573	2.303	0.089	5.294	0.413

Conclusions

• The XRD testes of *CdTe* films at different annealing temperatures showed polycrystalline structure consists of a mixture of hexagonal and cubic phases. The crystalline orientation and relative intensity were affected by heat treatment process from 573 K and which resulted in a strong peak at (111) direction.

• The transmittance spectra for *CdTe* films found to shift the peak of the transmittance spectrum to the shorter wavelength compared to the as prepared films for all films with increasing T_a.

• The absorption coefficient of *CdTe* films increases with increasing T_a.

• The optical energy gap has direct transitions with (r) equal to (½) for both films.

• The E_g for *CdTe* films increased with increasing T_a, The refractive index and the real part of the dielectric constant, for *CdTe* films was decreased with increasing T_a, while extinction coefficient and the imaginary part of the dielectric constant was increased with increasing T_a.

References

[1] B.Ray :*II-VI Compounds* (1969)1st .ed.

[2] J.Heo, H. Thn, R.Lee, Y.Han and D. Kim:Solar Energy Materials and Solar Cells 75, (2003) p.193.

[3] L.R.Cruz, R.R.de Avillez,:de Superficies Y de Vacio 9(1999), p.92.

[4] V.Ramanathan, L.A.russel, C.H. Liu and P.V.Lueyers, :J.solar Cells 28 (1990)p.129.

[5] H. Metİn and R.Esen:*Erciyes Üniversitesi Fen Bilimleri Entitüsü Dergisi* 19 (2003)1-2, p.96.

[6] D. Holliday, R.Rsnick and K.S.Krane: *Physics* (John Wiley and Sons Inc)2(2002) 5th ed.

[7] M.A.Omar :*Elementary Solid State Physics*(Wesley Publishing Co.Inc)(1975).

[8] J.P. Enriquez and X. Mathew :Solar Energy and Solar Cells 81(2004)p. 363.

[9] Z.K.Heiba :Crys. Res. Technol. 38 (2003) p.488.

[10]V. Shalimova, O.S.Bulatov, E.N. Vorankov and V.A. Dimitreiv :*Soviet Physics Crystallography*" 11(1966) 3 ,p.431.

[11]T.H. Mayers, H.W. Edwards and J.F. Schetzina:J Appl.Phys." 52 (1981)6.

[12] H. Arízpe- Chävez, R. Ramírez-Bon, F.J.Epinoza-Beltrán and O.Zelaya-Angel :*Superficies Vacio*8 (1999) p.120.

[13] S.K.Pandey, U.Tiwari, R.Raman, C.Prakash, V.Krishna,V.Dutta and K.Zimik :Thin Solid films 473 (2005)p.54.

[14] Jae. Hyeong Lee, Dong-Gun Lim and Jun-Sin Yi :Solar Energy Materials and Solar Cells, 75(2003) p.235.

[15] A.M. Al Dhafiri :*Crys. Res. Techno*.37 (2001)9 p.950.

[16] M.Rami, E.Benamar, M.Fahoume, F.Charabi and A.Ennaoui :M.J. Condensed Matter 3(2000)1 p.66.

[17]D.Albin, D.Rose, R.Dahere, D.Levi, L.Woods, A.Swartzlander and P.Sheldon: *Comparison of CSS and CBD CdS Films Effects of CdTe Solar Cells*, Proc. 26th IEEE PVSC. California (1997).

[18] I. Al Asaadi: M.Sc Thesis, University of Baghdad, Baghdad, Iraq(1998).

[19] N. Mott and E. Davis :*Electronic Process in Non-Crystalline Materials*, (Oxford University Press) (1980)2nd ed..

[20] E.Al Fawade,PhD.Thesis, Baghdad University, Baghdad, Iraq (2005).