The Effect of CdCl$_2$ and annealing treatments on structural properties of CdS/CdTe heterojunction

M.F.A.Alias* Muhammad A. Razooqi** , Zaid G. Al_Mashhadani***
and Rasha A. Abdullah**

*Department of Physics. College of Sciences, University of Baghdad

Email: may_roza@yahoo.com

**Department of Physics. College of Sciences, University of Tikreet

***Material Branch Department of Practical Sciences, University of Technology

Abstract

CdS and *CdTe* thin films were thermally deposited onto glass substrate. The *CdCl$_2$* layer was deposited onto CdS surface. These followed by annealing for different duration times to modify the surface and interface of the junction. The diffraction patterns showed that the intensity of the peaks increased with the *CdCl$_2$*/annealed treatment, and the grain sizes are increased after *CdCl$_2$*/annealed treatment.

دراسة تأثير طبقة ثنائي كلوريد الكادميوم و تغير الفترة الزمنية للتلدين على الخواص التركيبية للمفرق ألهجيني CdS/CdTe

ميسون فيصل أحمد الياس*، محمد عبد الوهاب رزوقي**، زيد غانم المشهداني*** و رشا عباس عبد الله**
*قسم الفيزياء- كلية العلوم – جامعة بغداد
**قسم الفيزياء- كلية العلوم– جامعة تكريت
***فرع المواد – قسم العلوم التطبيقية – الجامعة التكنولوجية

الخلاصة :

أغشية كبريتيد الكـادميوم و الكـادميوم تيلورايد الرقيقة رسبت حراريا بواسطة التبخير الحـراري علـى شـرائح زجاجية لتكوين المفرق الهجيني CdS/CdTe. و تم ترسيب مادة ثنائي كلوريد الكادميوم على سطح المفرق، ثم تبع العملية عملية تلدين في ازمنة مختلفة لترتيب السطح العلوي و السطح الفاصل للمفرق. نماذج حيود الاشعة السينية توضح بان شدة القمم تزداد مع ترسيب طبقة ثنائي كلوريد الكادميومو مع زيادة زمن التلدين و كذلك الحجم الحبيبي.

Introduction

II-VI semiconductors compounds are potentially important because of their low cost, high efficiency and stable performance. II-VI semiconductors compounds of considerable interest because of their extensive use in the fabrication of transistors, heterojunction diodes, space charge limited diodes, photovoltaic devices, photoconductors, IR detectors and solar cells [1, 2]. Cadmium telluride (CdTe) is one of the few II-VI compounds CdTe which is a very promising material for use in thin film devices spatially for solar cells [3]. Its optimum band gap energy is 1.45 eV, which corresponds closely to sunlight spectrum and suitable for the efficient photo conversion. CdTe has a direct transition type band structure, so the absorption coefficient is larger for light with wavelength below the absorption edge, so that it is used as absorber for solar cells and successful development of high efficiency solar cells and modules [4, 5]. The calculated theoretical efficiency for CdTe solar cells has been estimated at

around 29% but in practicality efficiency has only reached 16.5% [3, 6]. On the other hand, cadmium sulphide (CdS), is known to act as a very suitable window layer for $CuInSe_2$ and CdTe based solar cells [4]. The band gap energy of CdS films exists near the photon energy of maximum solar radiation spectrum; however, the CdS films are prepared as thin as possible to avoid optical transmission losses [4]. The quality is improved by increasing the degree of crystallinity and reducing dislocation effects through annealing. The $CdCl_2$ heat treatment can be improved over all performance of the devices [3]. Treatment with $CdCl_2$ during annealing of CdTe/CdS heterojunctions, after deposition and the effects on the structure and composition of the cells has been the subject of various studies. Yet, no conclusive picture of the role of Cl or of the extent to which *S* and Te interdiffuse has been obtained. a mechanism for the recrystallization *of* CdTe, which involves the formation of a liquid Te-Cl phase during annealing [4]. properties of the films after being subjected to chemical treatment in saturated solution of $CdCl_2$ in the methanol followed by thermal annealing between 400°C and 500°C for 30 min. The exact mechanism for the improvement in efficiencies after treatment is still under investigation, but some of the observed effects are: inter-diffusion of S and Te in the junction, forming $CdS_xTe_{(1-x)}$ decrease in the interface state density and grain growth and the passivation of the grain boundaries [4].

Experimental Work

A polycrystalline CdTe thin film about 800 nm thick have prepared by thermal evaporation technique by using the Edward E306A coating system (in thin films laboratory - college of science - university of Baghdad), the chamber was evacuated to a pressure of about 10^{-5} mbar on 7059 corning glass slides from *CdTe* powder of 99.999% purity, the substrate

temperature kept at 373 K and the distance between the substrate and the molybdenum boat (source) was kept at 20 cm. CdS thin films of 100nm thick have deposited on the CdTe thin film by thermal evaporation technique by using the same coating system from CdS powder of 99.999% purity. The prepared heterojunction have divided into two groups; the first annealed at 523 K for different duration times of annealing 60 and 120 min's, under vacuum of 30 mbar by using Memert oven. The second heat treated in presence of $CdCl_2$ thin films (which prepared at the same condition that of CdTe and CdS thin films) of 100 nm thickness and also annealed at 523 K for different duration times of annealing 60 and 120 min's.

X-ray diffraction technique was used to investigate the heterojunction structures. The experiments were carried out using Cu K_α radiation of average wavelength 1.54056 Å. It was operated with a target current and voltage of 25mA and 40 kV respectively. The diffraction pattern was recorded between $2\theta=(10°-60°)$. By comparing the interplaner distance for different planes (d_{hkl}) value with ASTM card for CdTe and CdS have been examined the structure. The grain size (D) was calculated using XRD analysis from Scherrer relation [7]

$$D = 0.9\lambda / \beta \cos\theta$$

Where λ is X-ray wavelength, β is the angular width at half maximum intensity (full width at half maximum intensity (FWHM)) and θ is the diffraction angle (Bragg angle). The grain size was calculated using FWHM of (111) plane.

Results and Discussion

The diffraction pattern spectra of CdS/CdTe heterojunction annealed under vacuum at 523 K for different duration times of annealing without and with $CdCl_2$ heat treatment are illustrated in Figures 1 and 2 respectively.

Fig.(1) XRD spectra for CdS/CdTe heterojunctio without CdCl$_2$ heat treatment for different duration times of annealing.

Fig.(2) XRD spectra for CdS/CdTe heterojunction with CdCl$_2$ heat treatment for different duration of annealing.
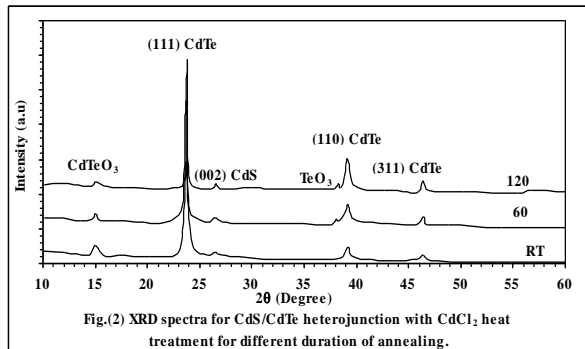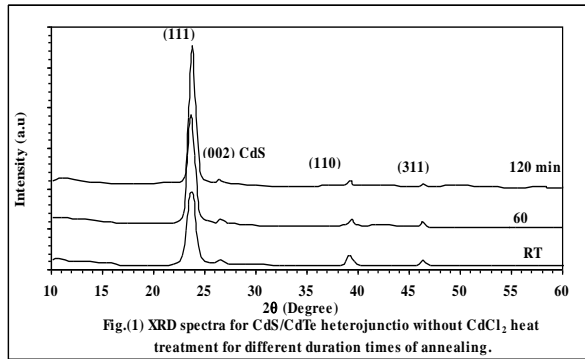
The spectra of the as prepared and annealed CdS/CdTe heterojunction have a polycrystalline structure consist of cubic (zinc blend structure) and hexagonal (wurtizite structure) phases, these figures show a good agreement with ASTM cards. Similar results have been observed by many researches which have prepared CdS/CdTe heterojunction with different preparation methods and conditions, Heiba [2], Al Dhafiri [7], Enriques and Mathew [8], Myeres *et al* [5], Lee et al [6], Nakamura *et al* [7], Mountinho *et al* [8], Bayhan and Erçelebi [9], Shalimova *et al* [10], Pandey *et al* [11], Arizp-Cháves *et al* [12], Latitha *et al* [13], Chandra *et al* [14] and Romeo *et al* [15].The XRD parameters of CdS/CdTe heterojunction annealed under vacuum at 523 K for different duration times of annealing without and with CdCl$_2$ heat treatment are tabulated in Table 1.

1. The effect of variation duration times of annealing

The as prepared and annealed CdS/CdTe heterojunctions without and with CdCl$_2$

heat treatment as it shown in figure 1and 2 respectively, exhibit a strong preferred orientation of CdTe along the (111) planes parallel to substrate, as well as the weak reflections at (002) of CdS, (110) and (311) planes of CdTe, but the XRD spectra CdS/CdTe heterojunctions with CdCl$_2$ heat treatment annealed at different duration times of annealing (60 and 120 min's) have shown that the formation of oxide of CdTe as CdTe$_y$O$_x$ is evident at 15.1° correspond to *CdTe*O$_3$, and the thermally grown oxides begin to decrease, as we can see from the spectra in figure 2. The formation of oxide Te as TeO$_x$ observed at 38.2° corresponds to TeO$_2$ is appeared at CdS/CdTe heterojunctions with CdCl$_2$ heat treatment annealed at 60 and 120 min's.

The XRD spectra for the annealed at 523 K for different duration times of annealing (60 and 120 min's) show crystallinity improvement, the intensity of CdTe (111) cubic plane and CdS (002) hexagonal plane have been increased, indicating that the degree of preferential orientation toward this directions increased, and the intensities of CdTe (110) and (311) planes have been decreased, the FWHM of the peak decreased, such crystallinity improvements with increasing the time of annealing have observed by Al-Dhafiri [7] and Enriques and Mathew [8]. There is slight shift in peak position was observed in (111) plane towards the higher diffraction angle (smaller lattice parameter), due to thermal stress [15], it may be attributed to the dependence on composition which includes the stochiometry of *CdTe* compound [9, 10]. The crystal structure improvement is due to rearrangement in the CdS/CdTe crystallites [7, 16]. The increase in intensity with increasing the duration times of annealing may be permitting better grain growth by maintaining the preference for the (111) plane [8]. While The XRD spectra for the annealed at 523 K for different duration times of annealing (60 and 120 min's) with CdCl$_2$ heat treatment show crystallinity

improvement, the intensity of CdTe (111), (110) and (311) planes and CdS (002) hexagonal plane have been increased, the FWHM of the peak decreased, there is slight shift in peak position was observed in (111) plane towards the higher diffraction angle (smaller lattice parameter). CdTe grains mixed with oxygen atoms (CdTeO$_3$) crystallite grains in a strongly stressed environment [8]. Oxygen diffusion into II-VI semiconductors up on annealing was assumed by many authors Sundri et al [1], Heiba [2], Enriques and Mathew [8], Raturi et al [17] and Pérez et al [18]. The incorporation of oxygen into the CdTe lattice site has no preferential substitution for Cd or Te atoms, as the radius of oxygen atom of 65×10^{-12} m is smaller than Cd atom of 97×10^{-12} m or Te atoms of 207×10^{-12} m [2, 12, 19], substitutional oxygen atoms may shrink the lattice which finally becomes distortioned [12]. The high reactivity of oxygen to *Te* atoms leads to formation TeO$_2$. Heating CdTe is accompanied by losses in weight which is attributed to the evaporation of the highly volatie Te, then The vacancies have created in the lattice and provide possible way for oxygen to diffuse into the lattice [2].

2. The effect of CdCl$_2$ heat treatment on CdS/CdTe heterojunction

The XRD spectra are presented in figures 3, 4 and 5 showing the influence of CdCl$_2$ heat treatment on CdS/CdTe heterojunctions for 523 K at various duration times of annealing (60 and 120 min's). The as prepared CdTe thin film heat treated with CdCl$_2$ has (111) preferred orientation, but loss in orientation at 120 min. Generally as comparing the structural properties of CdS/CdTe heterojunctions without and with *CdCl$_2$* heat treatment, the intensities have increased and the FWHM of peaks have decreased considerably after CdCl$_2$ heat treatment, this results show that this heat treatment enhance the

recrystallization of films, it can be observed the values of grain size of (111) planes for CdTe without and with heat treatment. The CdCl$_2$ heat treatment causes chloride ion *(Cl$^-$)* moves via grain boundaries diffusion through the CdTe site which is due to the fact that Cl$^-$ atomic radius 97×10^{-12} m is expected to substitute over telluride atoms 207×10^{-12} m or cadmium atom 169×10^{-12} m [11, 19].
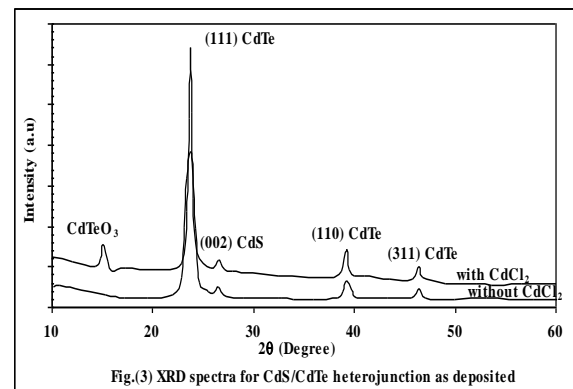

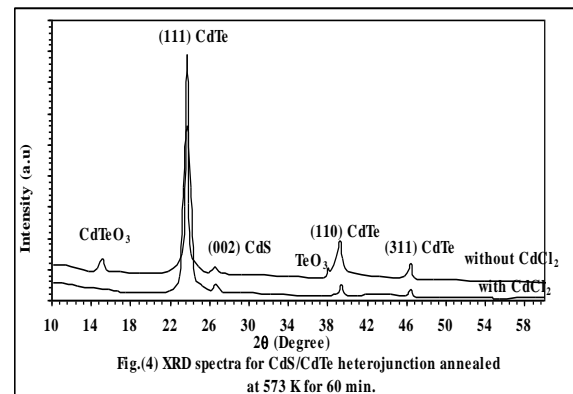Fig.(3) XRD spectra for CdS/CdTe heterojunction as deposited

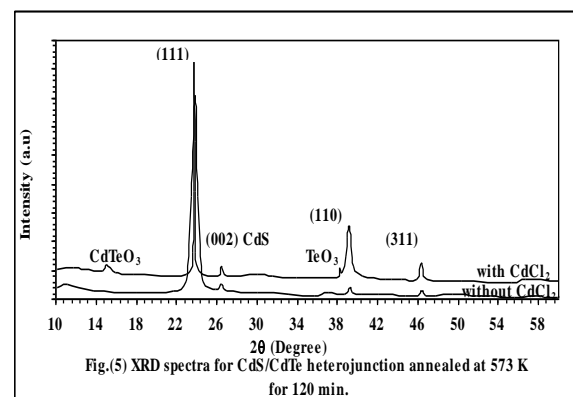Fig.(4) XRD spectra for CdS/CdTe heterojunction annealed at 573 K for 60 min.

Fig.(5) XRD spectra for CdS/CdTe heterojunction annealed at 573 K for 120 min.

The crystallinity will in turn affect the defect density [20], this means that the

presence of $CdCl_2$ eliminates the effect of the defect density [20, 21]. The presence of *CdCl2* enhances recrystallization and grain growth due to decrease the inter grain pore size and increase in the grain size causes widening of grain boundaries [19, 22].

The grain size results show that a small fluctuation in this values were noted as the duration times of annealing was increased as shown in figure 6 and tabulated in Table 1. In the other hand our results show a significant increase of grain size was obtained for heat treated CdTe with $CdCl_2$, hence the $CdCl_2$ acts like a

Conclusions

The CdS/CdTe heterojunctions with $CdCl_2$ heat treatment show better crystal structure by increasing the average grain size from 1.66 Å to 8.29 Å and affecting the preferred orientation of the (111) CdTe layers. The recrystallization of films enhanced thermally.

sintering flux as small grain grow and coalesce of grain boundaries [12, 23], such structural improvement and increasing the grain size after $CdCl_2$ heat treatment and annealing were observed by Romio et al [23], Romio et al [24] and Rami et al [4].

The d_{hkl} spacing is shown in Table 1 for CdTe and CdS without and with $CdCl_2$ heat treatment. As comparing the experimental values with the standard, these values are good agreement with the values presented by ASTM cards. There is no significant change observed in d_{hkl} values after annealing.

Fig.(6) The variation of grian size of (111) plane of CdTe versus duration times of annealing
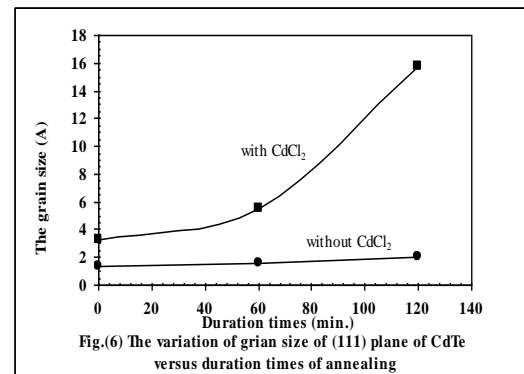
Table -1-The XRD parameters for CdS/CdTe heterojunctions without and with CdCl₂ heat treatment heat treatment for the as prepared and annealed films at 523K for different duration times of annealing

	hkl	2θ	$(I/I_0)_{stan.}$	$d_{stan.}$(Å)	$(I/I_0)_{exp.}$	$d_{exp.}$(Å)	structure	Material	D(111)Å
CdS/CdTe heterojunction without CdCl₂ heat treatment									
Film R.T	111	23.7	100	3.747	44.6	3.751	cub.	CdTe	1.3754
	002	26.5	91	3.36	1.942	3.361	hex.	CdS	
	110	39.2	60	2.287	5.547	2.296	hex.	CdTe	
	311	46.4	30	1.928	2.988	1.955	cub.	CdTe	
film at t_a=60 min.	111	23.77	100	3.747	66.23	3.74	cub.	CdTe	1.5742
	002	26.5	91	3.36	2.017	2.296	hex.	CdS	
	110	39.2	60	2.287	4.16	2.296	hex.	CdTe	
	311	46.4	30	1.928	2.584	1.955	cub.	CdTe	
film at ta=120 min.	111	23.8	100	3.747	81.4	3.735	cub.	CdTe	2.0241
	002	26.5	91	3.36	2.295	3.361	hex.	CdS	-
	110	39.2	60	2.287	3.164	2.296	hex.	CdTe	-
	311	46.4	30	1.928	1.904	1.955	cub.	CdTe	-
CdS/CdTe heterojunction with CdCl₂ heat treatment									
	hkl	2θ	$(I/I_0)_{stan.}$	$d_{stan.}$(Å)	$(I/I_0)_{exp.}$	$d_{exp.}$(Å)	structure	Material	D(111)Å
Film R.T	-	15.1	-	-	6.884	-	-	CdTeO₃	-
	111	23.72	100	3.747	68.33	3.748	cub.	CdTe	3.2198
	002	26.5	91	3.36	2.269	3.361	hex.	CdS	
	110	39.2	60	2.287	8.396	2.296	hex.	CdTe	
	311	46.4	30	1.928	3.631	1.955	cub.	CdTe	
film at t_a=60 min.	-	15.1	-	-	4.249	-	-	CdTeO₃	
	111	23.72	100	3.747	88.17	3.748	cub.	CdTe	5.9029
	002	26.5	91	3.36	2.622	3.361	hex.	CdS	
	-	38.2	-	-	0.996	-	-	TeO₃	
	110	39.2	60	2.287	12.48	2.296	hex.	CdTe	
	311	46.4	30	1.928	5.245	1.955	cub.	CdTe	
film at ta=120 min.	-	15.1	-	-	3.24	-	-	CdTeO₃	
	111	23.77	100	3.747	100	5.862	cub.	CdTe	15.742
	002	26.5	91	3.36	4.034	1.955	hex.	CdS	-
	-	38.2	-	-	2.131	-	-	TeO₃	-
	110	39.2	60	2.287	19.78	2.296	hex.	CdTe	-
	311	46.4	30	1.928	7.237	1.955	cub.	CdTe	-

References

[1] S. T. Sundari, V. Swaminthan, A. K. Tyagi and T. Mahalingam :Phys. Stat. Sol. (a), 177, 495 (2000), 495-502.

[2] Z.K.Heiba :Crys. Res. Technol., 38, (2003), 488-49.

[3] H.R. Moutinho, M.M. Al-Jassim, F.A. Abulfotuh, D.H. Levi, P.C. Dippo, R.G. Dhere, and L.L. Kazmerski : The 26th IEEE Photovoltaic Specialists Conference, September 29– October 3, 1997, Anaheim, California National Renewable.

[4]   M. Rami, E. Benamar, M. Fahoume, F. Chraibi, and A. Ennaoui: M.J. Condensed Matter, 3 (1), July (2000), 66-70.

[5]   Xavier Mathew, J. Pantoja Enriquez, Alessandro Romeo, Ayodhya N. Tiwari: Solar Energy, 77 (2004) 831–838.

[6]   H. Bayhan :Turk. J. Phys., 30 (2006), 109 (114).

[7]   A.M. Al Dhafiri: Crys. Res. Techno., 37(9), (2001), 950-957

[8]   J.P. Enriquez and X. Mathew :Solar Energy & Solar Cells, 81(2004),. 363-369.

[9]   H.Bayhan and Ç. Erçelebi :Tr. J. of Phys., 22, (1998), 441-451.

[10] K.V.Shalimova, O.S.Bulatov, E.N.Vorankov and V.A.Dimitreiv: Soviet Physics Crystallography, 11(3), (1966), 431-432.

[11] S.K.Pandey, U.Tiwari, R.Raman, C.Prakash, V.Krishna, V.Dutta and K.Zimik :Thin Solid films, 473, (2005), 54-57.

[12] H. Arízpe- Chävez, R. Ramírez-Bon, F.J.Epinoza-Beltrán and O.Zelaya-Angel: Superficies Vacio, 8 (1999) S120-124.

[13] S. Lalitha, R.Sathyamoorthy, S.Senthilargsu, A. Subbarayan and K. Natarajan :Solar Energy Materials & Solar celles, 28 (2004) 187.

[14] S. Chandra, S.T. Sundri, G. Reghavan and A.K. Tayaji :J. Phys. D: Appl. Phys.,36 (2003) 2121.

[15] A. Romeo "Growth and Characterization of High Efficiency CdTe/CdS Solar Cells", Ph.D Thesis, Swiss Federal Institute of Technology, Zürich, 2002.

[16] G.G. Rusu and M. Rush : Solid State Communication, 116 (2000) 363.

[17] A. K. Raturi, R. Thangara, A. K. Sharma, B.B. Tripathi and O.P. Agninotri : Thin Solid Films, 91 (1982) 55.

[18] B. Bartóo- Pérez, M.H. Farias, R.Castro- Rodrigues, J.L. Peňa, F. Caballero- Briones and W.Cauich: Superficies Y Vacio, 12 (2001) 8-11.

[19] B.L.Bätzner, A.Romio, H.Zogg, R.Wendt and A.N.Tiwiari "Development of Effiecient and StableBack Contact CdS/CdTe Solar Celles." Colarado School, tiwari@iqe.ph-ethz.ch.

[20] F.A.Abulfotuh, H.R.Moutinho, F.Hassoon, R.K.Ahrenkied, D. Levi and L.L. Kasmreski, 23th , IEEE PVSC Conf. (p 491) 1993.

[21] C. Barrett and T.B. Massalaki "Structure of metals", 3rd, Pergammon press, (1980)144.

[22] R.W. Brikmire and P.E. Meyers "Processing Issues for Thin Film and Modules", University of Center Excellence for PV Research & Education, NREL Lab., Newark, Delaware-19716, USA.

[23] A.Romio, D.L.Bätzner, H.Zogg and A.N.Tiwiari :Thin Solid Films, 36 (2000), 420.

[24] A.Romio, D.L.Bätzner, H.Zogg and A.N.Tiwiari: Mat.Res.Symp.Proc., 688 (c) (2002), pp. H3.3.1-H3.3.6.