Iraqi Journal of Physics, 2013 *Vol.11, No.22, PP. 8-13*

The influence of $CdCl_2$ layer and annealing process on the structural and electrical properties of CdTe films

Mohammed A. Razooqi

Department of Physics, College of Science, University of Tikreet, Tikreet, Iraq

E-mail: muhammadrazooqi@yahoo.com

Abstract

A polycrystalline CdTefilms have been prepared by thermal evaporation technique on glass substrate at room temperature. The films thickness was about700±50 nm. Some of these films were annealed at 573 K for different duration times (60, 120 and 180 minutes), and other CdTe films followed by a layer of $CdCl_2$ which has been deposited on them, and then the prepared CdTe films with $CdCl_2$ layer have been annealed for the same conditions. The structures of CdTe films without and with $CdCl_2$ layer have been investigated by X-ray diffraction. The as prepared and annealed films without and with $CdCl_2$ layer were polycrystalline structure with preferred orientation at (111) plane. The better structural properties have been observed in presence of $CdCl_2$ layer. The D.C conductivity for CdTe films with $CdCl_2$ layershowed higher values. The electrical activation energy influenced with increasing duration times of annealing. Hall Effect measurement was indicated that all CdTe films are p-type. The carrier concentration, Hall mobility and the carrier life time wereaffected by increasing duration times of annealing.

Key words

CdTe films,
Thermal Evaporation,
X- Ray Diffraction,
D.C conductivity, Hall Effect.

Article info.
Received: Oct. 2012
Accepted: Jan. 2013
Published: Dec. 2013

تأثير طبقة ثنائي كلوريد الكادميوم وعملية التلدين على الخواص التركيبية و الكهربائية لاغشية الكادميوم تيلورايد

محمد عبد الوهاب رزوقي

قسم الفيزياء، كلية العلوم، جامعة تكريت، تكريت ، العراق

الخلاصة

تم تحضير اغشية الكادميوم تيلورايد الرقيقة المتعددة التبلور بواسطة تقنية التبخير الحراري على ارضيات زجاجية بدرجة حرارة الغرفة. وكان سمك الاغشية بحدود 700±50 نانومتر. وقد تم تلدين بعض هذه الاغشية بازمنة تلدين مختلفة (60 و120و 180 دقيقة)، اما باقي اغشية الكادميوم تيلورايد فقد تم ترسيب طبقة من ثنائي كلوريد الكادميوم عليها، و بعد ذلك تم تلدينها بنفس الفترات الزمنية السابقة. وقد تم فحص التركيب البلوري لاغشية الكادميوم تيلورايد الملدنة و غير الملدنة مع و بدون ثنائي كلوريد الكادميوم بواسطة حيود الاشعة السينية. وكانت جميع الاغشية ذات تركيب متعدد التبلور و اتجاهية مفضلة للمستوي 111. كما ان افضل خواص تركيبية كانت مع وجود طبقة ثنلئي كلوريد الكادميوم. وقد اظهرت اغشية الكادميوم تيلورايد المحضرة بوجود طبقة من ثنائي كلوريد الكادميوم أعلى قيم للتوصيلة المستمرة. وكانت قيم طاقة التنشيط متقلبة مع زيادة الفترة الزمنية للتلدين. أما قياسات تاثير هول فقد أظهرت ان جميع الاغشية هي من النوع القابل. كما وان تركيز الحاملات و تحركية هول و زمن عمر الحامل تتاثر جميعها بزيادة الفترة الزمنية للتلدين.

Introduction

Photovoltaic has the potential to become a major source of energy and to have a significant effect on the global environment, due to its basic optical, electronic and chemical properties [1]. Cadmium Telluride (CdTe) solar cells are one of the important candidates for large scale photovoltaic applications[2]. The critical stage in CdTe devices fabrication is the treatment of the CdTe film with $CdCl_2$, a process that is essential in the production of high-efficiency cells [3]. Another advantage of the CdTe technology is the flexibility with regards to the method of manufacture [4]. Many methods (close spaced sublimation, electrodeposition, sputtering, spray pyrolysis and Electrophoretic etc.) were used for preparingCdTefilms [4-8]. It has been pointed out that high efficiency solar cells possess Te-rich CdTe surfaces with smooth interfaces of p-CdTe/n-CdS (Another issue is fabrication of low resistivity p- CdTe film), which can be investigated by incorporating intrinsic point defects by controlling the film stoichiometry. Intrinsic point defects strongly depend on the composition of CdTe films. Therefore, fabrication of CdTe films with controllable composition in growth process is very important [4]. In this article we presentedthe influence of the $CdCl_2$ layer and duration times of annealing on the structural and electrical properties of the p-CdTe grown by thermal evaporation, and try to investigate the development which may be happened in the structural and electrical properties of CdTe solar cell.

Experimental Work

Thermal evaporation technique was used for depositing CdTe films from high purity CdTe material of 99.999% manufactured by Balzers, Switzerland. The deposition process was done by Edward E306A coating system, under vacuum of about 10^{-6} mbar, the films deposited on ultrasonically cleaned 7059 corning glass slides (of 1mm thickness) using deionized water and pure alcohol for 15 minutes [9]. Inter gold (Au) electrodes have been deposited by thermal evaporation technique with 100 nm thickness to study the electrical properties of the prepared films. Thickness of the prepared films was measured using Fiezue fringes. The distance between the substrate and the Molybdenum boat (source) was maintained at 15 cm. The thickness of the CdTe films was about 700±50 nm with deposition rate was 75nm/second at room temperature. Next, a layer of$CdCl_2$ of 200 nm thickness was deposited on some of the as prepared CdTe films by thermal evaporation technique. Then, CdTe films without and with $CdCl_2$ layer have been annealed in vacuum oven type Memert at 573K for different duration times (60, 120 and 180 minutes). The structural analyses have doneby Phillips PW3710 X ray diffractometer with CuK_α target of 1.5405Å wavelength. The basic structures of the prepared films are illustrated in Fig.1.

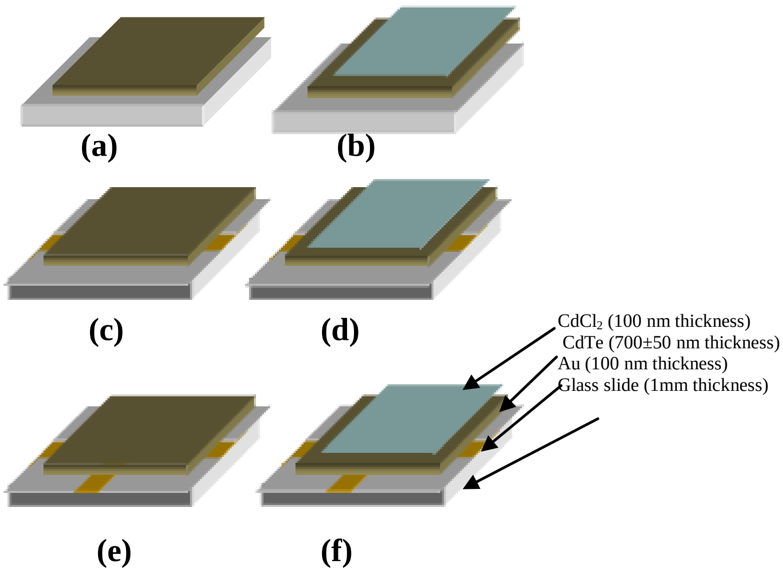

Fig. 1: Schematic of basic structure of the prepared CdTe films to study, a& b XRD, c & d d.c conductivity and e & f Hall Effect without and with $CdCl_2$ layer respectively.

Results and Discussion

1. X Ray Diffraction Results

The X-Ray diffraction spectra for CdTe powder, as prepared and annealed films at 573K for different duration times of annealing without and with $CdCl_2$ layer are illustrated in Fig. 2. The spectrum of the CdTe powder and films have been compared with ASTM cards of CdTe structure which give a polycrystalline structure containing a mixture of hexagonal and cubic phases, similar data had been also obtained by many researchers [10-14]. The spectrum of the CdTe powder had shown sharp peaks at (111), (110), (311) and (400) planes. Where (110) is a hexagonal phase and the others are cubic. The as prepared CdTe thin film without $CdCl_2$ layer was exhibited strong preferred orientation along (111) plane, as well as the weak reflections at (102), (110), (311) and (400) planes. It can be observed that the reflection from the cubic plane (400) has been disappeared. The increasing of duration times of annealing enhanced crystallinity improvement, the intensity of (111) cubic plane has been increased, indicating that the degree of preferential orientation toward this direction increased, and the intensities of (102), (110) and (311) planes had been decreased, the full width at half maximum intensity (FWHM) of the peaks decreased. Such crystallinity improvements with increasing the time of annealing had observed by Al-Dhafiri [14] and Enriques and Mathew [15]. The crystal structure improvement may be due to that the annealing produce an excess of Te atoms which are usually not bounded in the CdTe site.This lead to enhance the density of Te vacancies, then the Cd and Te atoms will rearrangement in the CdTe crystallites [14, 16]. Also it can be observed that the formation of Te oxides as TeO_x and CdTe oxides as $CdTe_yO_x$ which may due to evaporate of the highly volatile Te, thenthe vacancies have created in the lattice and provide possible way for oxygen to diffuse into the lattice [10]. The thermally grown oxides began to disappear with increasing the duration times of annealing. One can be observed that there is no diffraction peaks observed corresponding to any oxides after annealed for 180 minutes. Oxygen diffusion into II-VI semiconductors up on annealing was assumed by many authors Heiba [10], Enriques and Mathew [15], Sundri 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 169×10^{-12} m and Te atom of 207×10^{-12} m [10, 19], the oxygen atoms substitution may shrink the lattice which it finally distorted [11].

The XRD spectra of as prepared thin films with $CdCl_2$ layer showed sharper intensity at (111) plane and weak reflection at (110) and (311) planes. The recrysallization improvement with increasing the duration time of annealing were represented by decreasing the FHWM of (111), (110) and (311) planes, such decreased which is observed by Enriques and Mathew [15], while at annealing for 120 and 180 minutes the (400) plane had appeared, this indicates that the formation of another order of cubic structure.

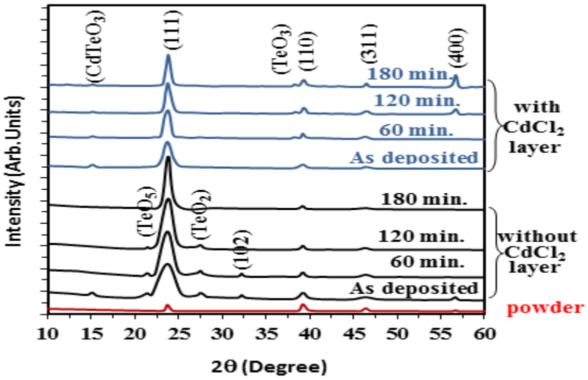

Fig. 2: The XRD spectra for CdTe powder, as deposited and annealedCdTe films for different duration times of annealing without and with $CdCl_2$ Layer.

The formation of oxides is also evident as shown in Fig. 2. These results showed that the presence of $CdCl_2$ layer enhanced the recrystallization of films. The $CdCl_2$ layer causes chloride ion (Cl^-) moves via grain boundaries diffusion through the CdTe site which was due to the fact that Cl^- atomic radius 97×10^{-12} m was expected to substitute over telluride atoms 207×10^{-12} m or cadmium atom 169×10^{-12} m [20], so that the of $CdCl_2$ eliminates the effect of the defect density [21].

2. Electrical properties

Fig. 3 illustrated the relationship between $\ln\sigma/\sigma_\circ$ and $10^3/T$, there were two stages of conductivity through the heating temperature range. In this case, the first activation energy (E_{a1}) occurred at higher temperature, this activation is due to the carrier excited into the extended states beyond the mobility edge [22].

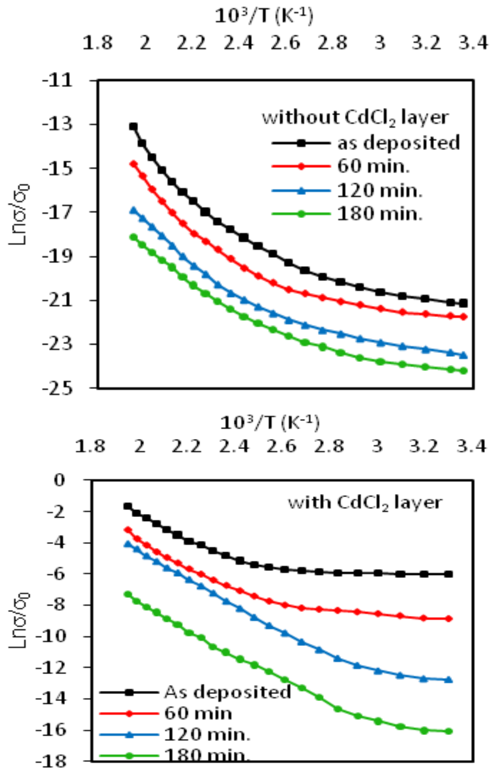

Fig. 3: $\ln\sigma/\sigma_\circ$ as a function of $10^3/T$ for the as deposited and annealed CdTe films at 573 K for different duration times without and with $CdCl_2$ Layer.

While the second activation energy (E_{a2}) occurred at lower temperature range and the conduction mechanism of this stage was due to the carrier transport to the localized states near the valance and conduction bands [22]. In absence of $CdCl_2$ layer, the values of E_{a1} had decreased with the increasing of duration times of annealing, as shown in Table 1. The values of E_{a2} have a fluctuated behavior with the increasing of duration times of annealing; this behavior may be due to creation of localized states inside the energy gap [22]. While in presence of $CdCl_2$ layer, both values of $E_{a1}$and E_{a2}had increased with the increasing of duration times of annealing. But generally, the $CdCl_2$ layer causes a slightly decrease in the average E_{a1} from 0.744 eV to 0.650 eV, and average E_{a2} from 0.179 eV to 0.172 eV. Table 2 and 3 showed the variation of conductivity measured at room temperature versus duration times of annealing. Generally conductivity of CdTe films with $CdCl_2$ layer three orders of magnitude higher than it without $CdCl_2$ layer. $CdCl_2$ permit to increase the conductivity of p-CdTe. But the conductivity at room temperature is found to decrease with increasing the duration times of annealing without and with $CdCl_2$ layer.

Table 1: Activation energies of CdTe films for different duration times without and with $CdCl_2$ layer.

Duration of annealing	$E_{a1without}$ (eV)	E_{a1with} (eV)	$E_{a2without}$ (eV)	E_{a2with} (eV)
As deposited	0.853	0.606	0.228	0.052
60 min.	0.778	0.615	0.143	0.111
120 min.	0.772	0.687	0.204	0.253
180 min.	0.575	0.695	0.144	0.274

Hall measurement showed that the CdTe films at different duration times of annealing without and with $CdCl_2$ layer were p-type, Razykov et.al. [4] Sundari et. al. [17] and

Bayhan and Erçelebi [23] have found the same results.

It can be seen from Table 2 and 3 that the carrier concentration increased with increasing duration times of annealing for CdTe films without and with $CdCl_2$ layer. The carrier concentration with $CdCl_2$ layer was less than the carrier concentration without $CdCl_2$ layer. The Hall mobility of CdTe films with $CdCl_2$ layer four orders of magnitude higher than it without $CdCl_2$ layer. The carrier's life times decreased with increasing duration times of annealing without and with $CdCl_2$ layer this may due to the scattering of the carrier from the surface and the ionized impurities [24].

Table 2: Some electrical parameters of CdTe films For different duration times without $CdCl_2$ Layer.

Duration of annealing	$\sigma_{d.c}\times10^{-5}$ $(\Omega.cm)^{-1}$	R_H cm^3/C	n_H cm^{-3}	$\mu_H\times10^{-4}$ $cm^2/V.s$	τ_p μS
As deposited	2.58	58.17	1.1E+17	14.9	0.894
60 min.	1.88	15.12	4.1E+17	2.8	0.232
120 min.	0.79	5.08	1.2E+18	0.41	0.078
180 min.	0.56	0.42	1.5E+19	0.003	0.006

Table 3: Some electrical parameters of the CdTe films for different duration times with $CdCl_2$ Layer.

Duration of annealing	$\sigma_{d.c}\times10^{-5}$ $(\Omega.cm)^{-1}$	R_H cm^3/C	n_H cm^{-3}	μ_H $cm^2/V.s$	τ_p μS
As deposited	4.91	1693	3.7E+15	83.131	26.03
60 min.	1.19	587	1.1E+16	6.977	9.03
120 min.	0.17	198	3.1E+16	0.341	3.05
180 min.	0.03	43	1.4E+17	0.014	0.67

Conclusions

Structural improvement enhanced by increasing duration times of annealing and this improvement been more effective in presence of $CdCl_2$ layer. The different duration times of annealing enhances the structure toward the (111) plane, but the $CdCl_2$ enhances the structure toward the (400) plane. $CdCl_2$ layer caused a slightly decrease in the average E_{a1}. The conductivity of films with $CdCl_2$ layer three orders of magnitude higher than it without $CdCl_2$ layer while it is decreased with increasing the duration times of annealing without and with $CdCl_2$ layer. Hall measurement showed that CdTe films at different duration times of annealing without and with $CdCl_2$ layer were p-type.

References

[1]D. K. Dwivedi, Dayashakar, M. Dubey, Rom. Journal of Phys., 55 (2010) 352.

[2]S. Krishnan, G Sanjeev, M Pattabi, X. Mathew, The Open Fuels and Energy Science Journal, 2 (2009) 110.

[3] M. Radu, V. Ghenescu, I. Stan, L. Ion, C. Besleaga, A. Nicolaev, T.L. Mitran, C. Tazlaoanu, A. Radu, O. Porumb, M. Ghenescu, M.M. Gugiu, S. Antohe, Chalcogenide Letters, 8,8 (2011) 477.

[4] T.M. Razykov, Razykov T. M., Contreras-Puente G., Chornokur G. C., Dybjec M., Emirov Yu., Ergashev B., Ferekides C. S., Hubbimov A., Ikramov B., Kouchkarov K. M., Mathew X., Morel D., Ostapenko S., Sanchez-Meza E., Stefanakos

E., Upadhyaya H. M., Vigil-Galan O., Vorobiev Yu. V., Solar Energy, 83 (2009) 90.

[5] M. Norizam Md Daud, A. Zakaria, A. Jafari, M. S. Mohd Ghazali, W. Rafizah Wan Abdullah, Z. Zainal, Int. J. Mol. Sci., 13 (2012) 5706.

[6]F. De Moure-Flores, K. Zhang, M. Brötzmann and H. Hofsäss, AIP Advances, 2 (2012) 02213.

[7]M. Becerril, O. Vigil-Gal´an, G. Contreras-Puente, O. Zelaya-Angel, Revista Mexicana De fi´sica, 57 (2011) 304.

[8]A.A. Al-Douri, Ant. J. nanoelectronics and materials, 5 (2012) 67.

[9]D. M. Mattox, Hand Book of Physical Vapor Deposition (PVD) Processing 2nd edition, New York, Elseiver, 2010.

[10]Z. K. Heiba, Crys. Res. Technol., 38 (2003) 488.

[11]H. Arízpe- Chävez, R. Ramírez-Bon, F.J.Epinoza-Beltrán and O.Zelaya-Angel, Confinement Effects on CdTe:O Sputtered Films Prepared at High Substrate Temperature. Superficies Vacio, 8 (1999)120.

[12]S. K. Pandey, U. Tiwari, R. Raman, K. V. Krishna, V. Dutta , K. Zimik, Thin Solid films, 473 (2005) 54.

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

[14]A. M. Al Dhafiri, Crys. Res. Techno., 37 (2001) 950.

[15]J. P. Enriquez, X. Mathew, Solar Energy materials and Solar Cells, 81 (2004) 363.

[16]G.G. Rusu, Solid State Communication, 116 (2000) 363.

[17] S. T. Sundari, V. Swaminthan, A. K.. Tyagi and T. Mahalingam , Phys. Stat. Sol., 177 (2000) 495.

[18]B. Bartólo- Pérez, , M.H. Farías, R. Castro-Rodríguez, J.L. Peña1, F. Caballero-Briones, W. Cauich., Superficies Y Vacio., 12 (2001) 8.

[19]H. R. Moutinho, F. S.Hasoon, , F.Abulfotuh, & L. Kazmerski,. L. J. Vac.Sci. Techno A., 13 (1995) 2877.

[20]K. Nakamura, M. Gotoh, T.Fujihara, solar cells Solar Energy materials and Solar Cells,75 (2003) 185.

[21]F. A. Abulfotuh, H. R. Moutinho, F. Hassoon, R. K. Ahrenkied, D. Levi , L. L. Kasmreski, Effects of processing on the properties of polycrystalline CDTE grown by various deposition techniques. 23th PVSC, May 10-14th 1993, Louisville, USA. IEEE, 1993, 491.

[22]N. Mott and E. Davis. Electronic Process in Non-Crystalline Materials. Oxford, Oxford University Press, 1980.

[23]H. Bayhan, Ç. Erçelebi, Turk. J. of Phys., 22, 5 (1998) 441.

[24]M. Bayhan., Turk J. Phys., 28 (2004) 379.