

Article

Electro-Plating and Characterisation of CdTe Thin Films Using CdCl₂ as the Cadmium Source

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Academic Editor: Alessio Bosio

Received: 12 July 2015 / Accepted: 24 September 2015 / Published: 29 September 2015

Abstract: Cadmium telluride (CdTe) thin films have been successfully prepared from an aqueous electrolyte bath containing cadmium chloride (CdCl₂)·H₂O and tellurium dioxide (TeO₂) using an electrodeposition technique. The structural, electrical, morphological and optical properties of these thin films have been characterised using X-ray diffraction (XRD), Raman spectroscopy, optical profilometry, DC current-voltage (I-V) measurements, photoelectrochemical (PEC) cell measurement, scanning electron microscopy (SEM), atomic force microscopy (AFM) and UV-Vis spectrophotometry. It is observed that the best cathodic potential is 698 mV with respect to standard calomel electrode (SCE) in a three electrode system. Structural analysis using XRD shows polycrystalline crystal structure in the as-deposited CdTe thin films and the peaks intensity increase after CdCl₂ treatment. PEC cell measurements show the possibility of growing p-, i- and n-type CdTe layers by varying the growth potential during electrodeposition. The electrical resistivity of the as-deposited layers are in the order of 10⁴ Ω·cm. SEM and AFM show that the CdCl₂ treated samples are more roughness and have larger grain size when compared to CdTe grown by CdSO₄ precursor. Results obtained from the optical absorption reveal that the bandgap of as-deposited CdTe

(1.48–1.52) eV reduce to (1.45–1.49) eV after CdCl₂ treatment. Full characterisation of this material is providing new information on crucial CdCl₂ treatment of CdTe thin films due to its built-in CdCl₂ treatment during the material growth. The work is progressing to fabricate solar cells with this material and compare with CdTe thin films grown by conventional sulphate precursors.

Keywords: electroplating; cadmium telluride (CdTe); CdCl₂ treatment; material characterisation

1. Introduction

CdTe is one of the most promising photovoltaic (PV) thin film materials for solar cell applications with the conversion efficiency of 21.5%, reported by First Solar in February 2015 [1]. CdTe has high optical absorption coefficient with a direct bandgap of 1.45 eV at room temperature (300 K), which is close to the ideal band gap for absorbing the maximum amount of the solar spectrum using one bandgap p-n junction.

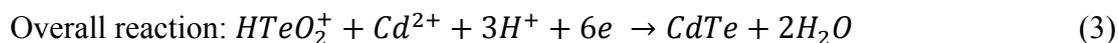
Various techniques have been reported for preparation of CdTe thin films such as physical vapour deposition (PVD) [2], RF sputtering [3], spray pyrolysis [4], close-space sublimation (CSS) [5,6] and electrodeposition (ED) [7–12]. Electrodeposition is an attractive technique for the preparation of CdTe because of its low-cost, simplicity, scalability, manufacturability and ability to obtain p-, i- or n-type materials by controlling the cathodic voltage during electrodeposition [12–14]. Cathodic electrodeposition of CdTe using an aqueous solution of CdSO₄ and TeO₂ was first reported by Mathers and Turner in 1928 [7]. There was no further work on this electrodeposition technique for 50 years until Panicker *et al.* [8] reported their study on CdTe electrodeposition in 1978. Since then, the electrodeposition technique has been widely used and later modified to anodic [15] and non-aqueous deposition [16,17].

In electrodeposition, the Cd source of CdTe was used to be from CdSO₄ precursor [8–11]. Then, the deposited CdTe layer should undergo CdCl₂ treatment to activate the properties of CdTe for a better performance in CdS/CdTe solar cell. CdCl₂ treatment is well known since 1979 [18] as activation step of CdTe solar cells and the efficiency of solar cells always improved by an order of magnitude with this so called “magic step” [19,20]. The CdCl₂ treatment is believed to promote the grain growth, improve recrystallization and lifetime of charge carriers, change the doping concentration, remove defects and Te precipitations in the CdTe thin films [21,22]. With regard to these advantages, a systematic study on CdTe electrodeposition from an aqueous solution containing chloride precursor was carried out in this work by using CdCl₂ as the Cd source instead of CdSO₄. Although Bonilla and Dalchiale [23] have reported their initial efforts on this, no systematic study has been made so far. This paper presents the summary of a comprehensive study on cathodic electrodeposition of CdTe thin films grown by 3-electrode system using CdCl₂ as the Cd source. The structural, electrical, morphological and optical properties on these films are reported in this paper.

2. Experimental Method

All the chemicals and substrates used in this study were purchased from Sigma Aldrich (Dorset, UK). Initially, 1.0 M of hydrated cadmium chloride ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$) with purity of 98% was dissolved in 800 mL of deionised water. The solution was electro-purified by applying a cathodic potential below the required potential for reduction of Cd^{2+} for ~100 h before any cyclic voltammetry study. A cyclic voltammetry was then recorded on the aqueous solution containing only CdCl_2 at the pH of 2.00 ± 0.02 and temperature of 65 ± 2 °C. The initial Te-solution was prepared by adding 1 mM equivalent of 99.999% (5N) TeO_2 powder into concentrated hydrochloric acid (HCl) and continuously stirring for 24 h. The TeO_2 solution was then diluted with de-ionised water and pH value was adjusted to 2.00 ± 0.02 using either HCl or NH_4OH and a cyclic voltammetry for aqueous solution containing only TeO_2 was recorded at temperature of 65 ± 2 °C.

About 1 mL of prepared 1 mM TeO_2 solution was then added into 800 mL aqueous solution containing purified 1.0 M $\text{CdCl}_2 \cdot \text{H}_2\text{O}$. The pH of the resulting deposition electrolyte was adjusted to 2.00 ± 0.02 . The electrodeposition of CdTe in an acidic bath involved the reduction of HTeO_2^+ to Te, which in turn reacts with Cd^{2+} to produce CdTe. The reactions for the formation of CdTe thin film on the cathode can be described by Equations (1)–(3) [24]:



A three-electrode system with high-purity graphite rod as anode, saturated calomel electrode(SCE) as a reference electrode and FTO coated glass substrate as working electrode were used for this study. The deposition temperature of 65 ± 2 °C was used to avoid detrimental effects on the SCE reference electrode due to its 70 °C upper temperature limit. The working electrode, FTO-coated glass substrate with sheet resistance of $7 \Omega/\square$ was prepared into $2 \times 2 \text{ cm}^2$ size. The cleaning process started by washing the substrates in an ultrasonic bath containing soap solution for 10 min followed by rinsing in deionised water and immersing them in acetone solution. These were then rinsed thoroughly in de-ionized water and dipped in methanol solution. The substrates were finally rinsed in deionised water before electrodeposition.

Before electroplating of CdTe, a cyclic voltammogram was obtained to estimate the approximate voltage range for film deposition. Using the approximate growth voltage range estimated, CdTe thin films were grown at different growth voltages (V_g) and the growth conditions were optimised after characterisation. The structural properties of CdTe thin films deposited on glass/FTO substrates were characterised using X-ray diffraction (XRD) and Raman spectroscopy. The XRD measurements were carried out using an X'pert pro-diffractometer (Philips, Nottingham, UK) with a $\text{Cu-K}\alpha$ excitation wavelength of 1.541 Å, while Raman spectroscopy was carried out with a Renishaw Raman microscope with a CCD detector and 514 nm argon ion laser source. Electrical properties were studied using DC electrical conductivity measurements and photo-electrochemical (PEC) cell measurements. The DC electrical conductivity measurements were carried out using a fully automated I-V system including a Keithley 619 electrometer and multimeter (Keithley, Cleveland, OH, USA), while the photo-electrochemical (PEC) cell method was carried out using an electrolyte of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$. The morphology, grain size and

surface roughness of CdTe thin films were observed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM images were taken using the FEG NOVA NANO system (Scanservice Corporation, Tustin, CA, USA), while AFM measurements were carried out using a ISPM-5200 System (JEOL, Tokyo, Japan). Optical properties were measured using a (Jasco, Uttlesford, UK) to determine the absorption and transmittance properties of the electrodeposited layers.

3. Results and Discussion

3.1. Cyclic Voltammetry

Cyclic voltammetry provides information on electric current flow in the electrolyte and results are obtained by measuring the current passing through the working electrode during the potential scans. Figure 1 shows a typical cyclic voltammogram of aqueous solutions of (a) 1.0 M CdCl₂; (b) 1 mM TeO₂; and (c) mixture of 1.0 M CdCl₂ and 1 mL of prepared 1 mM TeO₂ during the forward and reverse cycles between 0 and 2000 mV. The scanning rate was fixed at 3 mV·s⁻¹ and the solution temperature was kept at 65 ± 2 °C.

As observed on the cyclic voltammogram for aqueous solution of 1.0 M CdCl₂ in Figure 1a, Cd²⁺ from CdCl₂ solution starts to deposit at cathodic voltage of ~673 mV with respect to SCE in the forward cycle. Cd has a reduction potential of $E = -403$ mV with respect to H₂ reference electrode [25]. As the voltage increases, the current density increases and thus more Cd is deposited. The noise in the cyclic voltammogram at high cathodic voltages could be due to H₂ gas evolution. The current becomes negative after 670 mV due to the dissolution of Cd from the cathode surface during reverse cycle.

From the cyclic voltammogram for aqueous solution of 1 mM TeO₂ in Figure 1b, it is observed that Te deposition starts at ~343 mV with respect to SCE in the forward cycle and dissolved at ~764 mV in the reverse cycle. Also, the deposition rate of Te is equal to dissolution rate at points a, b, and c, therefore the resultant current density is zero. Te has a reduction potential of $E = +593$ mV with respect to H₂ electrode [25]. Therefore, Te is depositing at lower cathodic potentials compared to Cd.

From the cyclic voltammogram of a mixed solution of 1.0 M CdCl₂ and 1 mL of prepared 1 mM TeO₂ shown in Figure 1c, Te and CdTe mixed phase deposition start from ~277 mV. As the cathodic voltage is gradually increased, it is observed that the film colour starts changing to dark in appearance at $V_g \geq 300$ mV due to the Te rich CdTe region. This film starts turning to honey-black colour at cathodic voltage around 650–700 mV, thus suggesting the deposition of stoichiometric CdTe. As the cathodic potential increased to ≥ 730 mV, the layer becomes silvery bluish metallic which suggests that the cathodic voltages above 730 mV produce Cd-rich CdTe. Changing the applied potential can vary the composition of the deposited layer. The deposition rate is equal with dissolution rate of materials at $V_g = 648$ mV and therefore the current density is zero at this voltage during reverse cycle. Therefore, from the voltammogram observed in this work, the suitable V_g range for the stoichiometric CdTe layer is observed from 660 to 710 mV. The detailed study on the V_g was carried out within this range in order to obtain the optimum V_g to grow stoichiometric CdTe thin films, via relevant material characterisations.

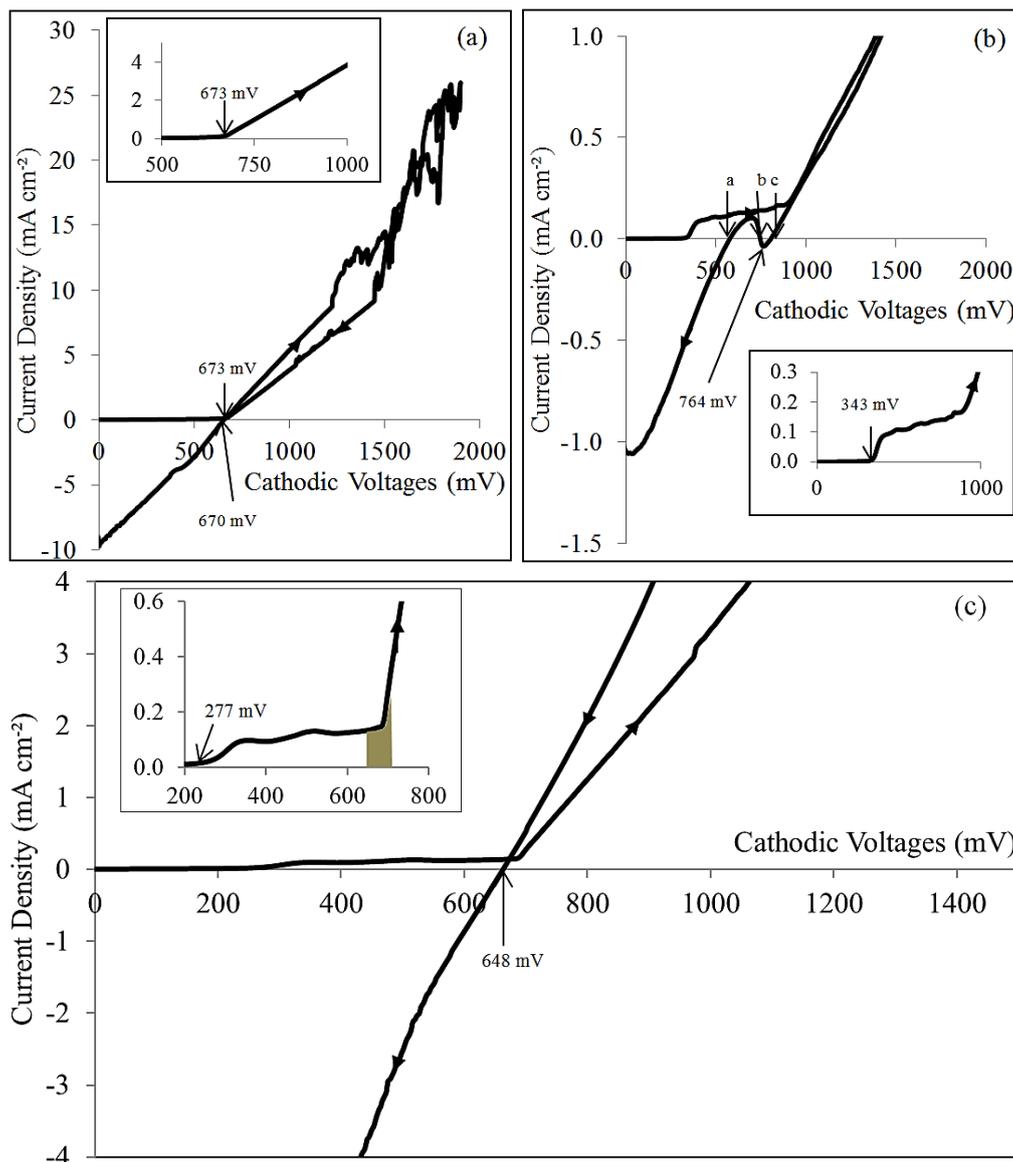


Figure 1. Cyclic voltammogram for aqueous solutions of (a) 1.0 M CdCl₂; (b) 1 mM TeO₂; and (c) mixture of 1.0 M CdCl₂ and 1 mL of 0.1 mM TeO₂ using glass/FTO as the cathode, a graphite rod as the anode and SCE as the reference electrode. The arrows indicate the directions of the voltage scan.

3.2. Structural Analysis

3.2.1. X-ray Diffraction

The X-ray diffraction studies were carried out on as-deposited and CdCl₂ heat-treated CdTe layers and typical results are shown in Figure 2a,b respectively. In this study, CdTe thin films were electrodeposited at different cathodic voltages from 680 to 709 mV. The CdCl₂ heat treatment was performed at 400 °C for 20 min in air. According to Figure 2, both graphs show the presence of the noticeable peak of CdTe at $2\theta = 24.15^\circ$ corresponding to the (111) cubic phase. The highest crystallinity was observed at cathodic potential of 698 mV for both as-deposited and CdCl₂ treated CdTe layers. In Figure 2b, most of the CdCl₂ treated samples show a reduction of (111) CdTe peak as a general trend. Also the other peaks of

cubic CdTe at $2\theta = 39.46^\circ$ and 46.58° were observed, corresponding to diffraction of (220) and (311) planes, respectively after CdCl₂ treatment. This suggests that the reduction in (111) XRD peak is due to the loss of preferred orientation and grains becoming randomly orientated after CdCl₂ heat treatment.

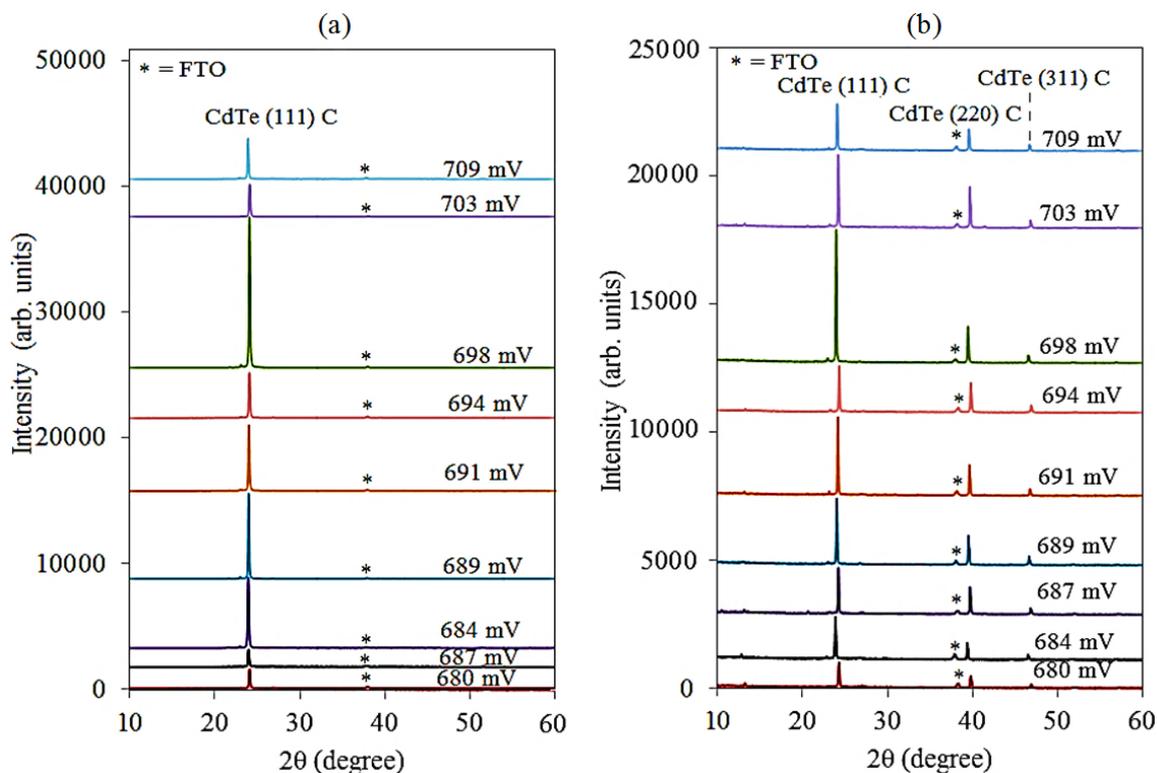


Figure 2. XRD patterns of CdTe thin films grown at cathodic voltage range of 680 to 709 mV for (a) as-deposited; and (b) CdCl₂ treated samples at 400 °C for 20 min, in air.

From Figure 3, it is observed that the most intense XRD peak is at $V_g = 698$ mV for both as-deposited and CdCl₂ treated material. The high intensity of (111) peak indicates high crystallinity related to a stoichiometric material. The deviation from stoichiometric point reduced the crystallinity due to the Cd-rich or Te-rich CdTe. In a recent publication [19], a sudden phase transition was identified when CdTe layer is heat treated at 385 ± 5 °C in air, in the presence of CdCl₂. At this temperature, the grain boundaries melt, and CdTe solid grains begin to float in a thin layer of melted liquid. Therefore, the grains suddenly lose their preferred orientation of (111) and show random orientations. Due to this sudden change, (111) peak collapses and the other two peaks (220) and (311) appear in the XRD spectra. In our heat treatment at 400 °C, this transition has just occurred and therefore intensity decreased in (111) peak and appearance of the other two peaks have been observed.

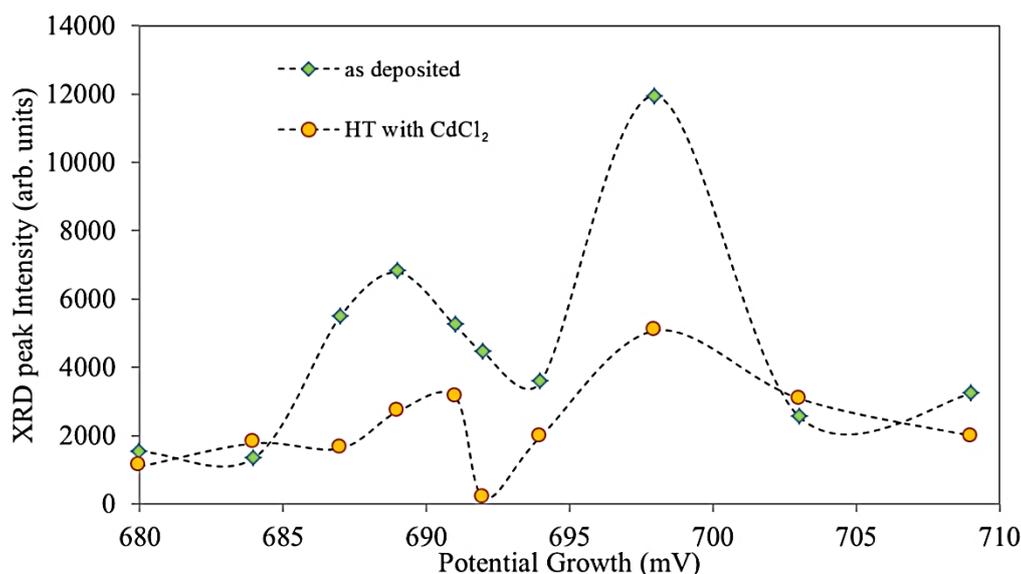


Figure 3. The intensity of (111) peak for as-deposited and CdCl₂ treated CdTe layers.

Figure 4 shows the XRD spectra plotted in log-scale in order to identify all peaks. These spectra are for as-deposited and CdCl₂ treated CdTe layers grown at $V_g = 698$ mV. The as-deposited sample shows the appearance of small crystalline peaks of TeO₂ and Cd_xTeO_y at $2\theta = 21.94^\circ$ and 23.11° corresponding to the (011) orthorhombic and (111) monoclinic planes, respectively. These compounds incorporating oxygen are expected on the surface or in the material, since the layers are grown in atmospheric condition in aqueous solution. Also the prominent peak of (111) cubic CdTe is observed in as-deposited sample. The TeO₂ peak disappeared while both (111) Cd_xTeO_y and (111) CdTe peaks slightly reduced after CdCl₂ treatment at 400 °C for 20 min. Also, after CdCl₂ heat treatment, extra peaks were observed at $2\theta = 39.46^\circ$ and 46.58° which represent the cubic CdTe with (220) and (311) reflections respectively. It is well known that CdCl₂ treatment usually improves the crystallinity of CdTe up to certain temperature [19,26,27]. However, after this temperature, a rapid reduction of (111) CdTe peak and the appearance of (220) and (311) peaks have been observed [12,28,29]. In a recent publication, this transition temperature has been identified as 385 ± 5 °C [19]. The XRD peak intensities, angles and occurrence of new peaks can be attributed to the random orientation of the grains in CdTe layers after melting of grain boundaries at ~ 385 °C. The summary of XRD data and obtained structural parameters of CdTe thin films grown at $V_g = 698$ mV are shown in Table 1. The crystallite size, D was calculated using the Scherrer's formula:

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$

where λ is the wavelength of the X-rays used (1.541 Å), β is the full width at half maximum (FWHM) of the diffraction peak in radian and θ is the Bragg angle.

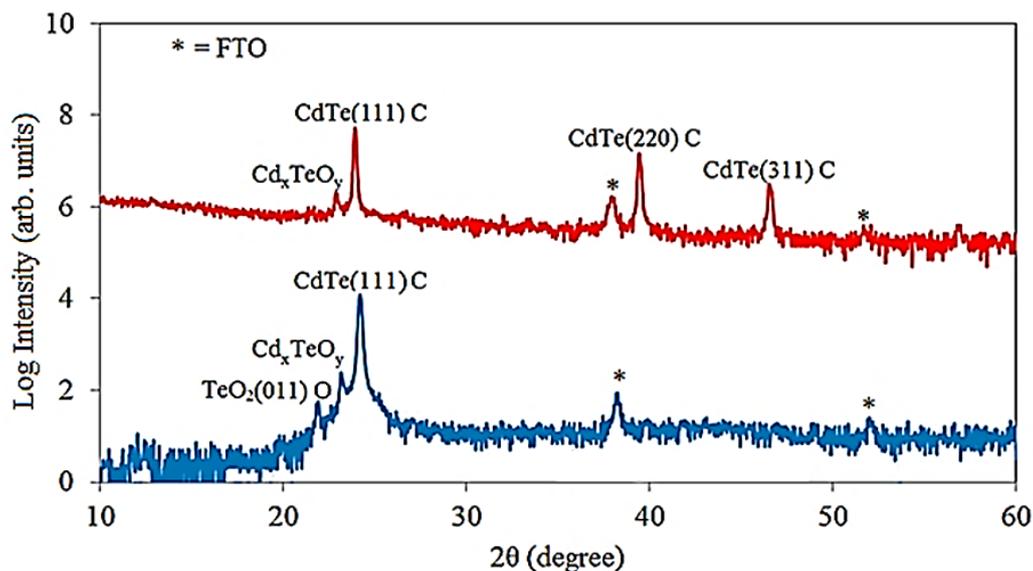


Figure 4. XRD patterns of as-deposited and CdCl₂ treated CdTe layers grown at cathodic potential of 698 mV plotted in log-scale.

Table 1. Summary of XRD data for as-deposited and CdCl₂ treated CdTe layers grown at cathodic potential of 698 mV.

Sample	Angle 2θ°	Lattice spacing D (Å)	Intensity (a.u.)	FWHM (Degrees)	Crystallite size D (nm)	Plane of orientation (hkl)	Assignments
As-deposited CdTe	21.94	4.00	56	0.173	48.9	(0 1 1)	TeO ₂ /Orthorhombic
	23.11	3.88	239	0.134	63.2	-	Cd _x TeO _y
	24.05	3.71	12,325	0.134	63.3	(1 1 1)	CdTe/Cubic
CdCl ₂ HT CdTe	23.04	3.91	129	0.134	63.2	-	Cd _x TeO _y
	24.15	3.70	4102	0.134	63.3	(1 1 1)	CdTe/Cubic
	39.46	2.28	1367	0.167	52.8	(2 2 0)	CdTe/Cubic
	46.58	1.93	238	0.233	38.8	(3 1 1)	CdTe/Cubic

XRD spectra of CdTe layers after CdCl₂ treatment at different temperatures up to 500 °C are shown in Figure 5. It seems that natural growth trend of CdTe on FTO is along (111) preferred orientation. The results in Figure 5 and Table 2 show that the intensity of (111) peak increases up to ~385 °C at the beginning. 385 ± 5 °C has been identified as the sudden transition temperature in the previous publication [19]. At this transition, the grain boundaries melt and the CdTe grains become randomly orientated. After melting of grain boundaries, the grains start to coalesce and form larger grains. The limitation of the Scherrer equation and XRD instrumentation prevent the determination of the size of these large grains, but SEM in Figure 11, later clearly shows the formation of larger grains in the μm size. CdTe film treated at 420 °C demonstrated appearance of the other two peaks (220) and (311). However, heat treatment at 500 °C leads to reduction of all three peaks due to the loss of material via evaporation and sublimation. Therefore, the optimum temperature for heat treating lies in between 420 °C and 450 °C for electrodeposited CdTe layers from CdCl₂ precursor.

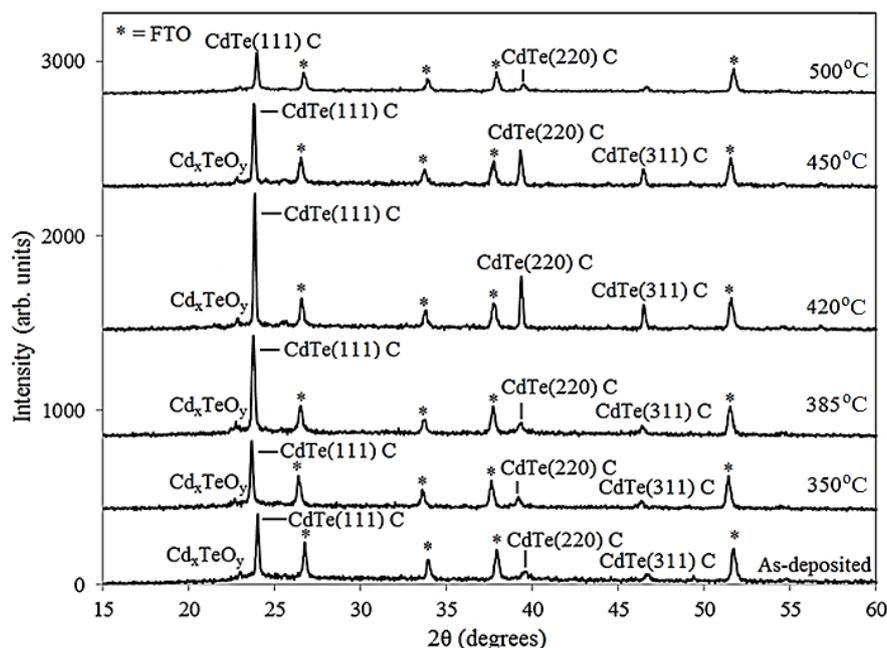


Figure 5. Typical spectra for as-deposited CdTe and after CdCl₂ treatment at 350, 385, 420, 450 and 500 °C for 20 min in air.

Table 2. Analysis of XRD peaks of CdTe for as-deposited and heat-treated with CdCl₂ at different temperatures from 350 to 500 °C for 20 min in air.

Annealing temperature, T (°C)	Peak intensity			% Peak relative to 111 Peak			Crystallite size calculated from (111) Peak, D (nm)
	(111)	(220)	(311)	(111)	(220)	(311)	
As-deposited	373	15	9	100	4	2	63.3
350	383	26	12	100	7	3	63.3
385	501	38	10	100	8	2	63.3
420	730	241	109	100	33	15	65.8
450	433	176	66	100	41	15	63.3
500	235	32	11	100	14	5	63.3

3.2.2. Raman Spectroscopy

Raman spectroscopy is an alternative and convenient method to identify material phases and determine the degree of crystallinity of the thin films. In this technique, vibration, rotation and other low-frequency modes in molecules are observed based on inelastic scattering of monochromatic radiation. The excitation source used in this work was 514 nm argon ion laser. The Raman spectra for as-deposited and CdCl₂ treated CdTe layers are shown in Figure 6. The prominent peak of the as-deposited CdTe spectrum is observed at the wave number 140 cm⁻¹ which represented the CdTe fingerprint. The Raman shift increased from 140 cm⁻¹ to 142 cm⁻¹ after CdCl₂ treatment. This blue shift is due to the energy gained by the photon by increasing in the vibration mode and the lattice strain. The FWHM of this peak also increase slightly after CdCl₂ treatment. There are two possible effects influencing the FWHM of the Raman peak which are size effect and the lattice dislocation effect [30]. In this case, the size effect is more pronounce since we observed the enlargement in crystallite size after CdCl₂ heat-treatment. This trend is similar to the previous XRD results. It is also observed from this

figure a Te peak at wave number of 122 cm^{-1} and the peak increased intensely after the CdCl_2 heat-treatment. The spectrum for CdCl_2 treated CdTe also shows one appearance of a small hump representing a CdTe peak at 168 cm^{-1} . This particular sample shows improved crystallisation of excess Te in the CdTe layer after CdCl_2 treatment. The summary of the Raman analysis is presented in Table 3.

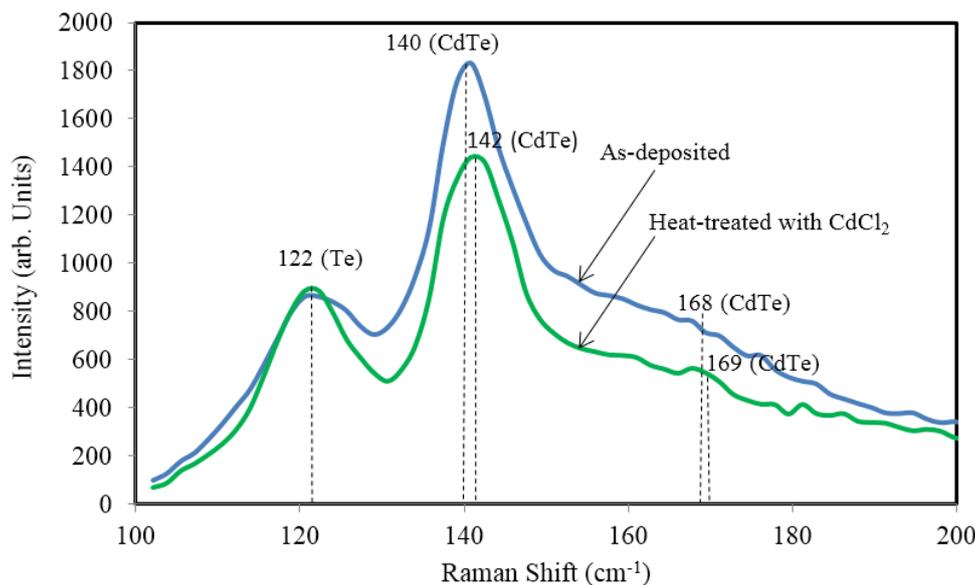


Figure 6. Typical Raman spectra of CdTe thin films for as-deposited and CdCl_2 treated at $400\text{ }^\circ\text{C}$ for 20 min.

Table 3. Summary of Raman peak details for as-deposited and CdCl_2 treated CdTe layers grown at 698 mV.

Samples	As-deposited		HT with CdCl_2		
Raman peak positions (cm^{-1})	122 (Te)	140 (CdTe)	122 (Te)	142 (CdTe)	168 (CdTe)
Intensity (a.u.)	860	1831	866	1421	545
FWHM (cm^{-1})	6.73	8.65	8.41	10.20	1.78

3.3. Thickness Measurement

The thicknesses of electrodeposited CdTe layers at $V_g = 698\text{ mV}$, for different deposition periods were calculated theoretically by using Faraday's laws of electroplating and experimentally using an optical profilometer. As shown in Figure 7a, the thickness obtained from the theoretical and experimental methods are similar. This shows that the loss of electronic charges for electrolysis of water is minimal under these growth conditions. It is observed that the deposition rate of CdTe thin film calculated from both theoretical and experimental values are 6 nm per minute. The thickness of CdTe thin films as a function of heat treatment temperatures from 350 to $500\text{ }^\circ\text{C}$ were measured using optical profilometry and shown in Figure 7b. From these measurements, it is observed that the thickness of the films decreased from 800 nm (as-deposited) to $\sim 500\text{ nm}$ when the samples were heat treated at temperature up to $450\text{ }^\circ\text{C}$. The thickness shows rapid decline to 200 nm at temperature $500\text{ }^\circ\text{C}$ which is due to the rapid loss of material through sublimation. Therefore the heat treatment of CdTe thin films in the presence of CdCl_2

should be limited to temperature range of 420–450 °C to avoid the loss of material, and get all benefits of heat treatment.

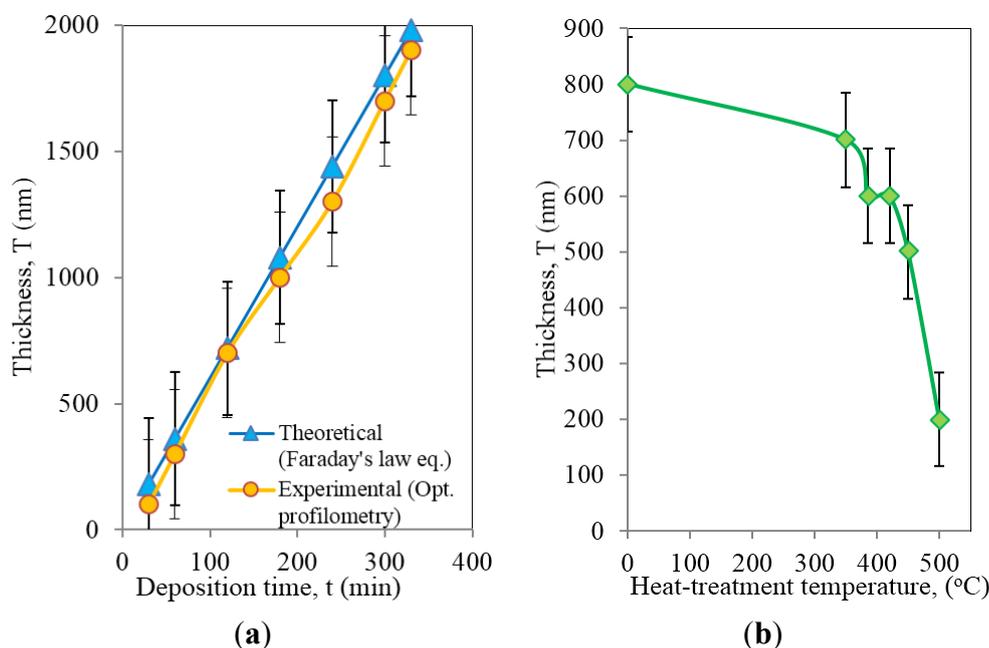


Figure 7. Thickness of CdTe thin films as a function of (a) different deposition time at $V_g = 698$ mV; and (b) different heat treatment temperatures in the presence of CdCl_2 .

3.4. Electrical Characteristics Measurement

3.4.1. Photoelectrochemical (PEC) Cell

The PEC cell measurements were carried out in order to test the electrical conductivity type of CdTe layers. Glass/FTO/CdTe were immersed in 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution to form a solid/liquid junction at CdTe/electrolyte interface. The voltage produced at the junction was measured with respect to a carbon counter electrode under dark and illuminated conditions. The difference in voltages provides the open circuit voltage of the solid/liquid junction, or the PEC signal. The system was first calibrated with a known material like n-CdS, and the sign of the PEC signal shows the electrical conductivity type of the CdTe layers. Figure 8a shows the trend of PEC signal for as-deposited and CdCl_2 treated CdTe thin films as a function of growth voltage, V_g . It is observed that the as-deposited CdTe samples grown at lower voltages ($V_g < 700$ mV) are n-type and those which are grown at higher voltages ($V_g \geq 700$ mV) are p-type.

These results show complete contrast to the CdTe grown by CdSO_4 [19] and $\text{Cd}(\text{NO}_3)_2$ [12] precursors in Figure 8b,c, respectively. Figure 8b,c show typical PEC results obtained from CdTe layers grown using sulphate and nitrate pre-cursors without the presence of Cl^- in the bath. These results behave according to electrodeposition principles. According to E° values of Te (+0.593 V) and Cd (−0.403 V) with respect to hydrogen electrode, CdTe electrodeposited below the stoichiometric point (V_i) show p-type electrical conductivity due to Te-richness, while CdTe layers grown above V_i show n-type electrical conductivity due to Cd-richness. This variation is mainly due to the change of composition in the absence of external doping agent. This has been reported earlier from our previous work using

sulphate and nitrate precursors [11,12,19]. Completely opposite results observed for CdTe layers grown from chloride precursor are therefore due to the “built-in CdCl₂ treatment” during the growth. This needs careful further experimentation and critical analysis, and future work is focused on this subject.

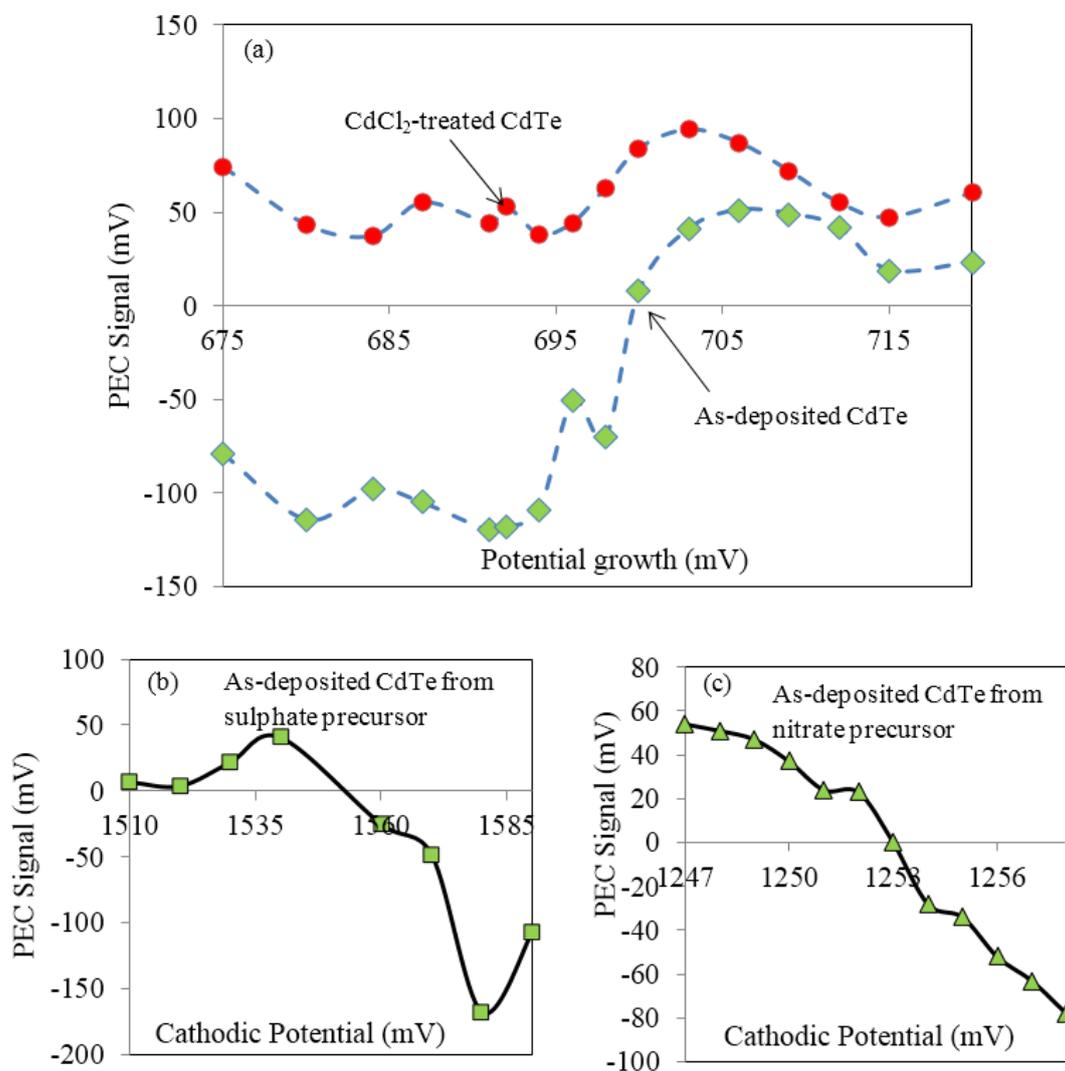


Figure 8. PEC signals as a function of growth voltage, for (a) as-deposited and CdCl₂ treated CdTe layer grown from chloride precursor and as-deposited CdTe layers grown using; (b) sulphate [19]; and (c) nitrate precursor [12].

After heat-treatment at 400 °C for 20 min, in the presence of CdCl₂, all samples become p-type in electrical conductivity. This provides a clue for CdTe becoming p-type in electrical conductivity when high concentration of Cl is present in the material. Therefore doping effects seem to be drastic depending on the initial composition of CdTe layer and the concentration of Cl present for doping the material. In this case, the electrical conductivity depends on these doping effects, namely the composition variation and the inclusion of Cl during growth in CdCl₂ solution. The detailed investigation is currently progressing to improve our understanding on CdCl₂ treatment.

PEC cell measurements for samples heat-treated with CdCl₂ at different temperatures are shown in Table 4. The as-deposited CdTe thin film electrodeposited closed to 698 mV is n-type. However, the electrical conductivity type of these samples have changed to p-type after CdCl₂ treatment at 350, 385

and 420 °C. This can happen due to the changing of doping profile or material deterioration. Doping profile could change due to incorporation of elements such as Cl, in CdTe crystal. During deposition, Cl can be within grain boundaries, but heat treatment electrically activated these by adding to the CdTe crystal lattice. Doping profile can also change due to loss of one element during heat treatment. As shown in Figure 9, Cd has higher vapour pressure than Te [31]. Therefore Cd tends to evaporate easily during annealing since material with higher vapour pressure tends to evaporate earlier than those with lower vapour pressure. Krishnamurthy *et al.* have also reported that the Cd sublimation energy to terminate the surface of CdTe layer is much smaller than Te [32]. Therefore, Cd atom should be much easier to remove than Te leaving Te-rich p-type CdTe layer. Therefore, the as-deposited CdTe with n-type electrical conductivity changed to p-type after annealing at 350 to 420 °C. However, those samples annealed at 450 °C and above have demonstrated n-type electrical conductivities. We believe that the high annealing temperature ($T \geq 450$ °C) has initiated deterioration of the layer through sublimation. Also CdTe annealed at 550 °C did not show any PEC signal since the layer has completely deteriorated (see Figure 10). These results agree with XRD data presented in Table 2.

Table 4. The PEC signal of CdTe grown near cathodic potential of 698 mV with variation of annealing temperature from 350 °C to 550 °C.

Sample	PEC signal	Electrical conductivity type	Comments
As-deposited	-70	n	grown at $V_g = 698$ mV
350	62	p	conductivity change due to doping effects
385	78	p	
420	55	p	
450	-64	n	material degradation is taking place
500	-9	n	
550	no signal	the layer did not survive	

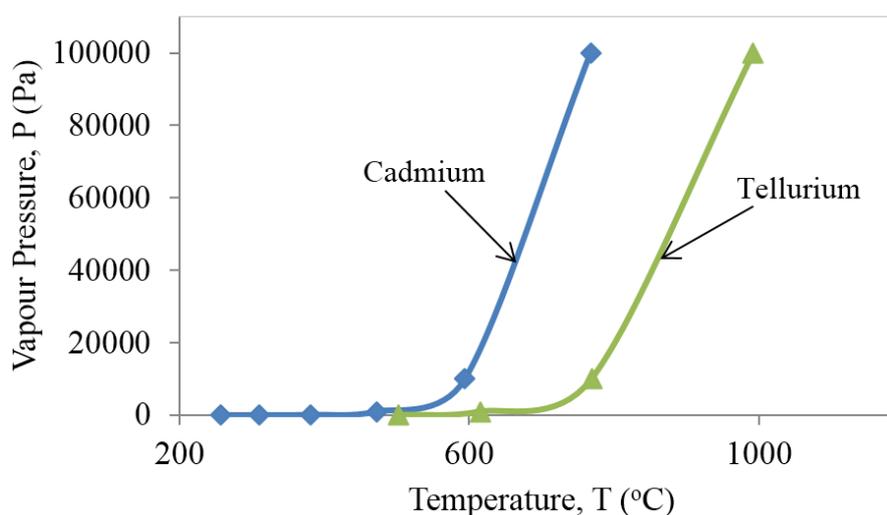


Figure 9. The vapour pressure of cadmium and tellurium as a function of temperature.

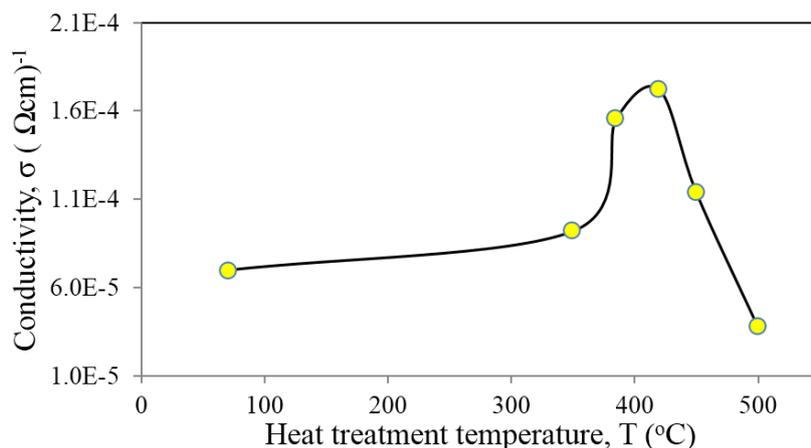


Figure 10. The electrical conductivity of CdTe after CdCl₂ treatment at different annealing temperatures.

3.4.2. DC Conductivity Measurements

DC conductivity measurements were carried out in order to determine the electrical conductivity of as-deposited and CdCl₂ heat-treated CdTe layers. For these experiments, thicker layers were used in order to avoid leakage through pinholes. 2 mm diameter and circular ohmic contacts were made by evaporating Al layer for n-type samples and Au layer for p-type samples through a metallic mask. The resistance of CdTe layers were measured using I-V characteristics and the average resistance of each sample was measured and the conductivity was calculated with known thicknesses and area of FTO/CdTe/Al or Au structures.

Table 5 summarizes the measurements of average resistances, resistivity and electrical conductivity of CdTe layers deposited near $V_g = 698$ mV (n-type) and heat treated with CdCl₂ at different temperatures. Figure 10 shows that the value of electrical conductivity has increased from 6.97×10^5 to 17.19×10^5 ($\Omega\cdot\text{cm}$)⁻¹ after heat treatment with CdCl₂ at temperature of 420 °C. The conductivity enhancement is due to the improvement of crystallinity, enlargement of the grain size and re-distribution of dopants [33] which promote higher mobility of electrons. However, a decrease in conductivity was observed for the CdCl₂ treated samples at annealing temperatures ≥ 450 °C. This must be due to the deterioration of the material at higher annealing temperatures and this trend also is consistence with the material deterioration observed in both XRD and PEC analyses in previous sections.

Table 5. The summary of electrical properties of CdTe thin films grown near $V_g = 698$ mV, and heat treated at different temperatures in the presence of CdCl₂.

Samples	Average resistance(Ω)	Resistivity, $\rho \times 10^4$ ($\Omega\cdot\text{cm}$)	Conductivity, $\sigma \times 10^{-5}$ ($\Omega\cdot\text{cm}$) ⁻¹
As deposited	31.1	1.43	6.97
CC-350	26.0	1.09	9.19
CC-385	12.3	0.64	15.53
CC-420	11.1	0.58	17.19
CC-450	14.0	0.88	11.42
CC-500	17.6	2.67	3.75

3.5. Microstructure and Morphological Studies

3.5.1. Scanning Electron Microscopy

Figure 11 shows the SEM images of CdTe thin films for as-deposited and annealed at 350, 385, 420, 450, 500 and 550 °C in the presence of CdCl₂. The as-deposited CdTe shows the grains size in a range of 150 to 200 nm. As the annealing temperatures were increased, the grains start to coalesce together forming larger grains. The CdCl₂ treated CdTe at 420 and 450 °C show grain sizes in (700–900) nm and (1000–4000) nm ranges, respectively. The presence of CdCl₂ during the heat treatment has enhanced the coalescence of smaller nano-crystallites into larger crystals to improve material layers. Many researchers observed the grain growth appearance together with gaps in between grains after CdCl₂ treatment. The existence of gaps in the CdTe layers will cause a catastrophic impact on the performance of solar cells due to short circuiting devices. However, CdTe layers grown in this work show a compact grain growth without any gaps appearing after CdCl₂ heat-treatment around 420 °C. This suggests that CdCl₂ treated CdTe produced from chloride precursor has a better quality for solar cell devices since it has no obvious gaps and the larger grain sizes for less scattering at grain boundaries and with high electron mobility. Heat treatment at 500 °C and above seems to open up gaps between grains and therefore deteriorates the layers. Also, Figure 11g shows the SEM image for CdTe annealed at 550 °C. It exposes the appearance of FTO surface image since CdTe layer did not survive at high temperature due to the loss of material. These observations confirm the results observed from XRD, PEC and DC measurements in this work. The optimum heat treatment seems to be between 420 and 450 °C and this could be finalised during device fabrication. It is also an important point to note that the ED-CdTe layers grown at low temperature (~65°) attain comparable grain sizes (~few micron size) to CSS-CdTe after CdCl₂ treatment.

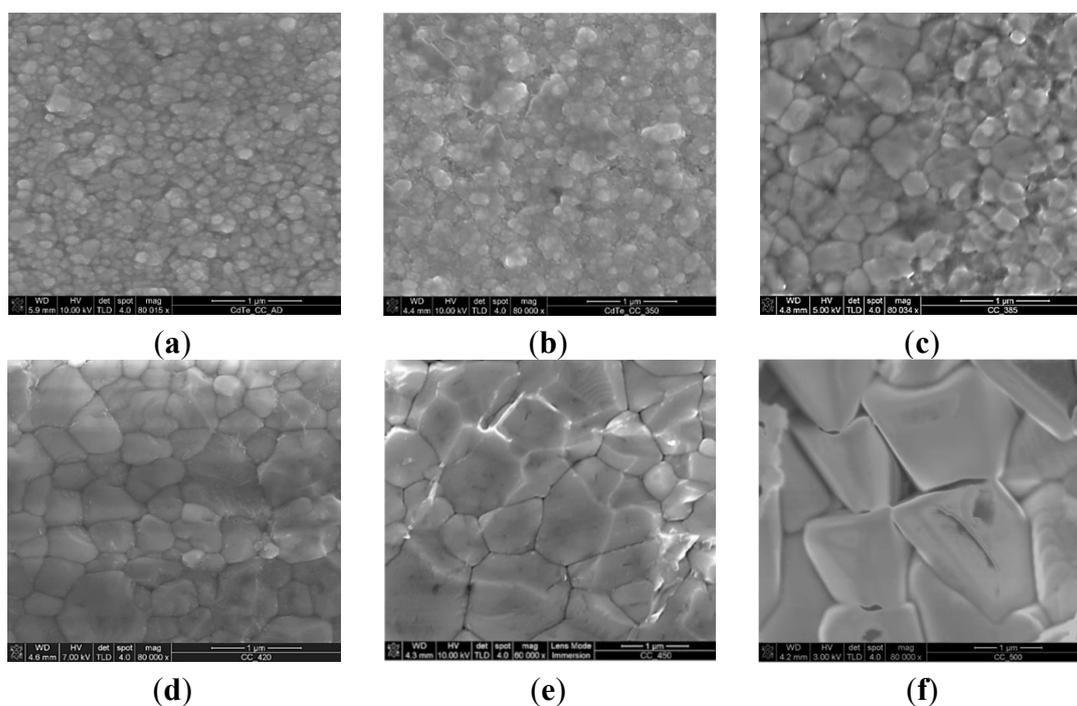
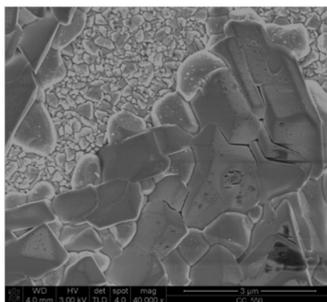


Figure 11. *Cont.*



(g)

Figure 11. SEM images of CdTe grown at 698 mV for (a) as-deposited; and annealed at (b) 350; (c) 385; (d) 420; (e) 450; (f) 500; and (g) 550 °C for 20 min.

3.5.2. Atomic Force Microscopy

AFM is a convenient technique to study the morphology and surface roughness of thin films. Figure 12 shows the typical $1.5 \mu\text{m} \times 1.5 \mu\text{m}$ AFM micrographs of (a) as-deposited; and after CdCl₂ treatment at temperatures (b) 385; (c) 420; and (d) 450 °C. The brightness of these micrographs indicate the variation of depth of the surface morphology. It is observed that the as-deposited CdTe shows a surface with homogeneous brightness which suggest that the layer is uniform due to the formation of smaller grains. The CdCl₂ treated samples show variation of brightness which represents the formation of valleys and peaks on the surface. The roughness of the films increased as the annealing temperature increased due to the enlargement of the grain size especially forming columnar type grains, growing upwards. The average surface roughness for the as-deposited CdTe and CdCl₂ treated CdTe are shown in Table 6.

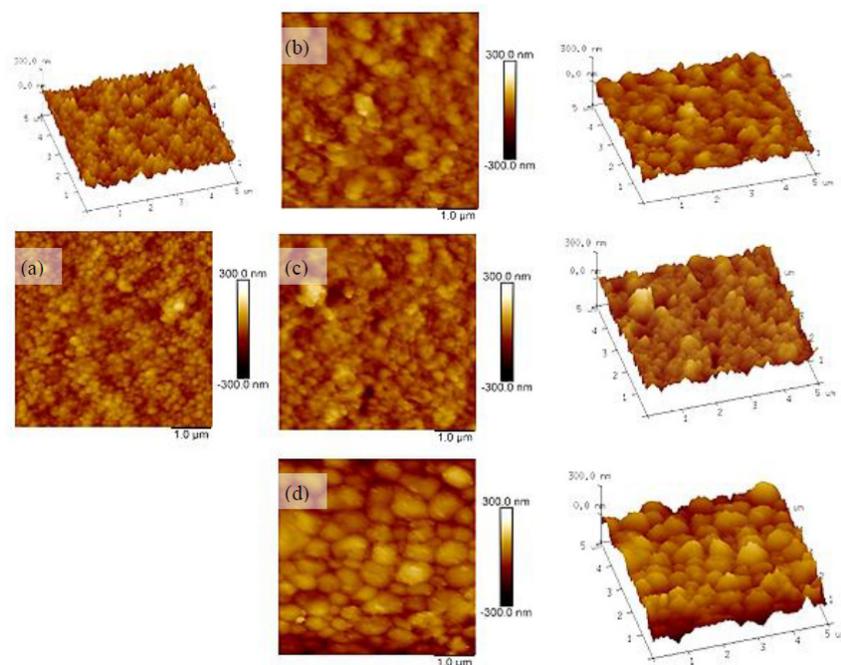


Figure 12. Typical AFM images of (a) as-deposited; and heat treated with CdCl₂ at (b) 385 °C; (c) 420 °C; and (d) 450 °C. These layers have been annealed for 20 min in atmospheric condition.

Table 6. The AFM data on surface roughness of CdTe thin films, as a function of annealing temperatures.

Sample	R_{ms} (nm)
As-deposited	25.7
CdCl ₂ heat-treated at 385 °C	38.0
CdCl ₂ heat-treated at 420 °C	54.3
CdCl ₂ heat-treated at 450 °C	68.7

3.6. Optical Properties

The optical absorption measurements of the CdTe layers were carried out using a UV-Vis spectrophotometer in the wavelength range 600–1000 nm. The square of absorbance (A^2) has been plotted as a function of photon energy, and the bandgap energy was estimated by extrapolating the straight-line segment of the graph to the photon energy axis. Figure 13a shows optical absorption of the as-deposited CdTe thin films grown at different cathodic voltages from 680 to 709 mV. It is observed that the bandgap energy of as-deposited CdTe films was in the range of 1.48 to 1.51 eV. The average error of these measurements is ± 0.02 eV. The graphs in Figures 13a and 14 show that the trend of applied absorption edge is increased with V_g up to 698 mV and then gradually reduces with further increment of V_g . The reduction of bandgap with higher V_g is due to deposition of metallic Cd with zero bandgap. Figure 13b shows the optical absorption spectra of CdTe thin films heat treated at temperatures from 350 to 500 °C in the presence of CdCl₂.

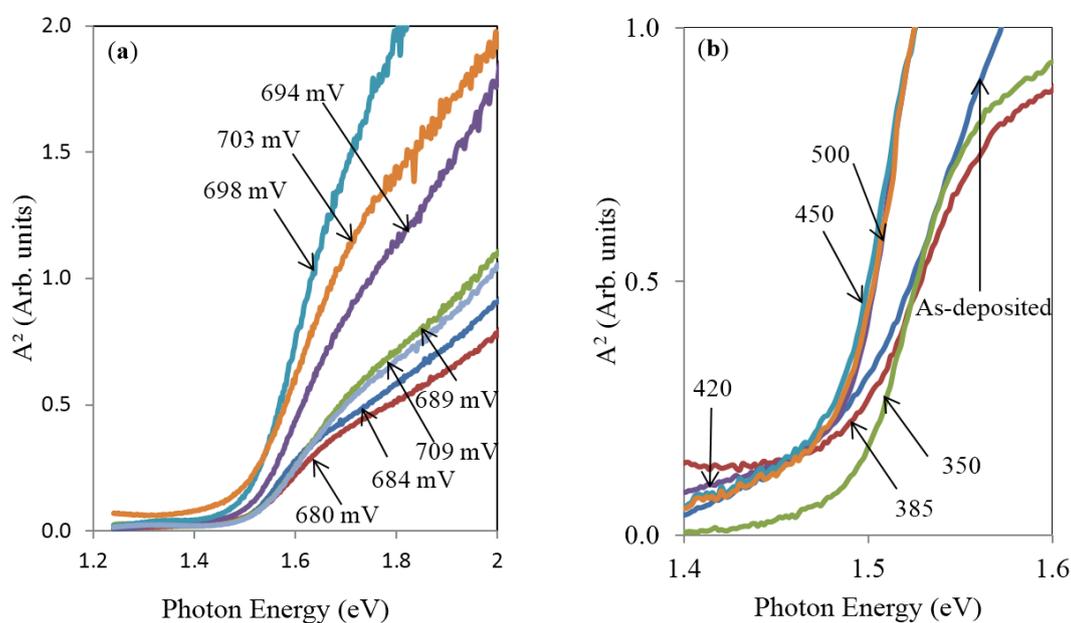


Figure 13. Optical absorption of CdTe thin films for (a) as-deposited with different V_g ; and (b) as-deposited and CdCl₂ treated at different temperatures.

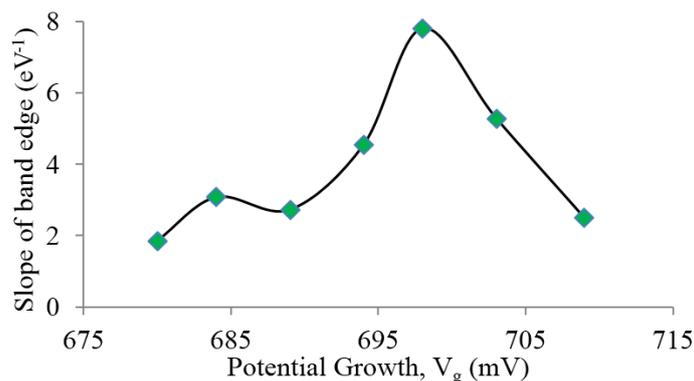


Figure 14. Slope of band edge *versus* V_g for as deposited CdTe thin films. Highest absorption edge indicates the optimum growth voltage.

The bandgap of CdTe layers have decreased with higher annealing temperature. The decrease in the bandgap after annealing temperature >385 °C can be due to the recrystallization, increase in grain size and stress [34]. This can also be due to the removal of pin-holes in the layer thereby preventing the photons through the pin-holes. The summary of the optical band energy with different V_g and annealing temperature of CdCl₂ treatment is shown in Table 7.

Table 7. The optical bandgap of CdTe layers grown at different V_g and bandgap as a function of CdCl₂ heat treatment temperature for CdTe grown at $V_g = 698$ mV.

Cathodic voltage, V_g (mV)	Band energy, E_g (eV)	CdCl ₂ treated temperatures, T (°C)	Band energy, E_g (eV)
680	1.48	65	1.49
684	1.49	350	1.49
689	1.51	385	1.49
694	1.51	420	1.46
698	1.49	450	1.45
703	1.48	500	1.46
709	1.49		

4. Conclusions

CdTe thin films have successfully been grown by electrodeposition using cadmium chloride precursor. XRD results show presence of the prominent peak of (111) cubic CdTe in as-deposited and appearance of another two peaks of (220) and (311) cubic CdTe after CdCl₂ treatment above 385 °C. This confirms the phase change taking place above ~ 385 °C as previously identified and reported. PEC cell measurement shows a possibility to grow p-, i- and n-type CdTe layers by tuning the V_g during electrodeposition. Noticeable changes in CdTe grain size were observed after CdCl₂ treatment and these grains up to 4 μm are comparable to high temperature grown CdTe layers with large grains. The optical bandgap of stoichiometric CdTe grown at 698 mV is 1.47 eV. The work is progressing to understand the unique properties observed in electrical conduction type, morphology and to use these layers in solar cell device structures.

Acknowledgments

The authors would like to thank A. Ojo, B.Y. Kadem, P.A. Bingham, F. Fauzi and O.K. Echendu for their valuable contributions. The main author would also like to acknowledge the Ministry of Higher Education, Malaysia and National Defence University of Malaysia for financial support. The authors declare there is no conflict of interest.

Author Contributions

The preparation and electrodeposition of CdTe thin films were done by Nor Azlian Abdul-Manaf. She was also responsible for the thin film characterisations. In addition, this work was also performed under the advisement of and regular feedback from Prof I. M. Dharmadasa, who also revised the manuscript critically. Moreover, Hussein I. Salim, Mohammad L. Madugu and Olajide I. Olusola also gave some useful suggestions for this work and helped revise the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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