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DISO, D. G., FAUZI, F., ECHENDU, O. K., OLUSOLA, O.I. and DHARMADASA, I <<http://orcid.org/0000-0001-7988-669X>>

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Optimisation of CdTe Electrodeposition Voltage for Development of CdS/CdTe Solar Cells

D. G. Diso^{1,2}, F. Fauzi^{1*}, O. K. Echendu¹ O.I. Olusola¹ and I. M. Dharmadasa¹

¹ Electronic Materials & Sensors Group, Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, United Kingdom

² Department of Physics, Kano University of Science & Technology, Wudil, PMB 3244, Kano-Nigeria

* Corresponding author: fijayfauzi@yahoo.com; Tel: +44(0)1142256910 Fax: +44(0)114 225 3501

Abstract: Cadmium telluride (CdTe) thin films have been deposited on glass/conducting glass (FTO) substrates using low-cost two electrode system and aqueous electrodeposition (ED) method. The glass/FTO substrates were used to grow the CdTe layers at different deposition voltages. The structural, electrical, optical and morphological properties of the resulting films have been characterized using X-ray diffraction (XRD), Photoelectrochemical (PEC) cell measurements, optical absorption spectroscopy and Scanning Electron Microscopy (SEM). The XRD results indicate that at voltages less than or higher than 1.576 V, crystallinity is poor due to presence of two phases. When the CdTe is grown at 1.576 V, the composition is stoichiometric, and the (111) peak is dominant in the XRD diffractogram indicating a high degree of crystallinity. SEM studies showed that as-deposited layers had pin holes between the grains. These pin holes seem to be more common in the samples grown at voltages away from the stoichiometric voltage (1.576 V). The linear I-V curves of glass/FTO/CdS/CdTe/Au structures fabricated using stoichiometric CdTe showed efficiency of 10.1% under AM 1.5 illumination.

Keywords: CdTe; electrodeposition; deposition voltage; solar cells; CdF₂

1. Introduction

Cadmium telluride (CdTe) is one of the most suitable materials for use in devices such as X-ray imaging detectors and thin film photovoltaic (PV) solar cells [1, 2]. It is a direct bandgap semiconductor with bulk bandgap energy of 1.45 eV which is close to the optimum for solar energy conversion using one bandgap p-n junction. Theoretical calculation shows that semiconductors with bandgap energy of 1.00 – 2.00 eV are suitable for solar energy conversion [3]. Only two microns of CdTe will absorb most of incident solar radiation, whereas crystalline silicon needs to be at least 100 μm thick to absorb the same amount of radiation [4]. To date, CdTe-based solar cells have achieved efficiency of 21% for small scale laboratory devices [5].

The methods used to deposit CdTe thin films include sputtering [6], thermal evaporation [7], metal-organic chemical vapour deposition (MOCVD) [8], molecular beam epitaxy (MBE) [9], close space sublimation (CSS) [10], electrodeposition [11] etc. Among the techniques mentioned above, electrodeposition offers the best solution for simplicity and low-cost in order to deposit various types of semiconductors [12]. For manufacturing macro-electronic devices such as solar panels and large display panels, electrodeposition is also suitable because it is scalable [13]. Scalability and manufacturability of solar panels using electrodeposition technique was practically proven by BP Solar in the late 1990s [14].

The initial work on electrodeposited CdTe solar cell was published by Basol in 1984 with conversion efficiency up to 9.4% [15]. The solar cell devices had glass/TCO/n-CdS/CdTe/metal structure. Over the years, this solar cell structure was followed by others and in 1993, Das & Morris reported the efficiency of 10.8% [16]. In 1995, Baker et al separated the anode and cathode by immersing them in different compartments respectively [17]. These compartments are known as ion-exchange membrane. Ion-exchange membrane for cathode contains catholyte while for the anode, it contains anolyte. Through this route they have reported the conversion efficiency of 13.5%. It is noteworthy that the reported efficiencies mentioned above were achieved from electrodeposited CdTe using 3-electrode system.

The aim of the present work is to deposit cadmium sulfide (CdS) and CdTe layers using simplified electrodeposition technique. In this work, electrodeposition was carried out in aqueous solutions using 2-electrode system. The reference electrode was omitted because the presence of foreign ions such as Ag^+ and K^+ inside the reference electrode could leak and contaminate the electrolytes and drastically affect the performance of the solar cell devices [18].

Initial experiments were concentrated on obtaining the best deposition voltage for CdTe. Subsequently, these optimized deposition voltages were employed to deposit CdTe layers. After processing stages, CdS/CdTe solar cells were fabricated by depositing 2 mm diameter circular gold contacts on top of CdTe layers.

2. Experimental details

2.1. Electrodeposition of CdS films

CdCl₂ (99% purity) and Na₂S₂O₃ (99% purity) were used as the sources of Cd and S ions respectively. All the chemicals used were supplied by Fisher Scientific, UK and used as received. The CdCl₂ powder was measured using digital weighing system to prepare an aqueous solution containing 0.3M CdCl₂ solution. Na₂S₂O₃ was dissolved separately in deionized water and the molarity of the solution was adjusted at 0.03M. By mixing these two solutions and after electro-purification, CdS layers were deposited on glass/FTO substrates. The full details of the CdS electrodeposition using 2-electrode system were given elsewhere [19].

2.2. Electrodeposition of CdTe films

CdTe thin films were cathodically electrodeposited onto glass/FTO substrates at ~85°C using an aqueous solution (pH = 2.00 ± 0.02) containing 1.0M CdSO₄ which has 99% purity. Initially, the electrolyte containing only the Cd source was electro-purified for ~100 hours to remove any impurities present. Four milliliter of diluted TeO₂ solution was added to provide low level of Te, and 1000 ppm of CdCl₂ were then added into the bath for doping purpose. Soap solution, methanol and acetone were used to clean the glass/FTO layer and rinsed thoroughly in de-ionized water prior to CdTe deposition. CdTe films of thickness ~2.0 ± 0.1 μm thick were deposited in about 4 to 5 hours while the solution is moderately stirred continuously. The working electrode was held vertically using Teflon tapes to connect glass/FTO/CdS substrate to the graphite rod. High purity carbon rod was used as the anode. Potentiostatic deposition in a conventional single compartment cell was carried out using a two-electrode set-up. The electrodeposition voltage range was estimated by recording a cyclic voltammogram.

2.3. Characterisation and Measurement Techniques

Cyclic voltammetry was performed using a Gillac computerised potentiostat (ACM Instruments). The deposited layers were rinsed with de-ionized water, dried under nitrogen air flow at room temperature. Photoelectrochemical (PEC) cell measurements using an electrolyte of 0.10M Na₂S₂O₃, were carried out to determine the electrical conductivity type of the CdTe layers. X-ray diffraction measurements (XRD) were carried out using a Philips PW 3710 X-ray diffractometer with CuK_α radiation ($\lambda = 1.5416 \text{ \AA}$) for the structural analysis of the deposited film. A Philips XL 30 ESEM-Field Emission Gun with accelerating voltage of 20 kV was used to study the surface morphology of the thin film layers. Optical absorption measurements were carried out using Cary 50 UV/Vis spectrophotometer for estimating the bandgaps of the electrodeposited layers. For the complete solar cell devices, the current-

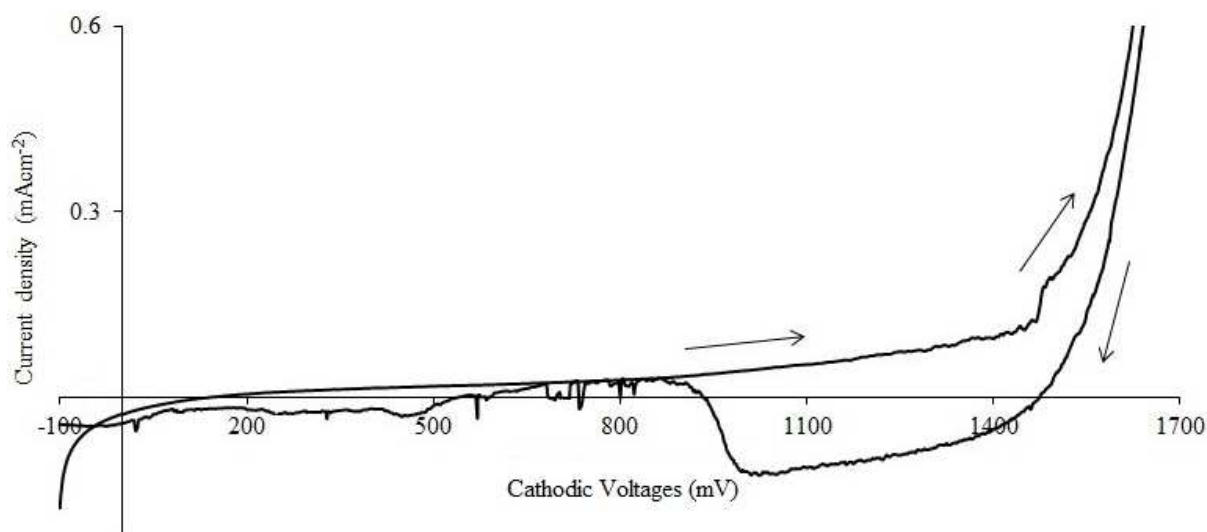
voltage (I-V) measurements were performed using computerized Keithley 619 Electrometer/Multimeter under AM 1.5 illumination condition.

3. Results and Discussion

3.1. Voltammogram

Figure 1 shows a typical voltammogram related to the electrodeposition of CdTe layers. The voltage scan was run from +100 to -1700 mV with a sweep rate of 5 mVs^{-1} . As shown in the Figure 1, Te ions begin to reduce when the current density starts to increase from cathodic voltages $\sim 200 \text{ mV}$ to $\sim 1400 \text{ mV}$. In this region, elemental Te is deposited and the layer formed is a mixture of CdTe and Te. A rapid increase of current is observed around 1500 mV, and deposition of CdTe layer is expected beyond 1500 mV cathodic voltage as can be seen from the Figure 1. Drastic increase in current at $\sim 1600 \text{ mV}$ is due to the combination of deposition of elemental Cd and hydrogen evolution at the cathode. In the reverse direction, negative currents were observed which are attributed to the removal of elemental Cd, Cd from CdTe and then Te from the cathode surface.

Figure 1. A typical voltammogram for electrolytic bath used for deposition of CdTe on glass/FTO substrate.



3.2. Photoelectrochemical (PEC) cell

Previous research within the group demonstrated that at lower cathodic voltages, p-type CdTe is grown and at higher cathodic voltages, n-type CdTe is produced [20,21]. The transition voltage occurred in between $\sim 1.570 \text{ V}$ and 1.580 V , and the present work is aimed at fine-tuning the growth voltage, and examining the behaviour of the material layers closer to the exact transition point. Therefore the CdTe layers were grown at cathodic voltages,

changing in steps of 1 mV, in the vicinity of the transition voltage. The photoelectrochemical cell values of glass/FTO/CdTe layers grown at different cathodic voltages are shown in Table 1 and the PEC signals are graphically shown in Figure 2.

Figure 2. PEC signal as a function of growth voltage for glass/FTO/CdTe layers showing the transition from p-type to n-type CdTe, when grown at voltages close to 1.576 V at pH = 2.00.

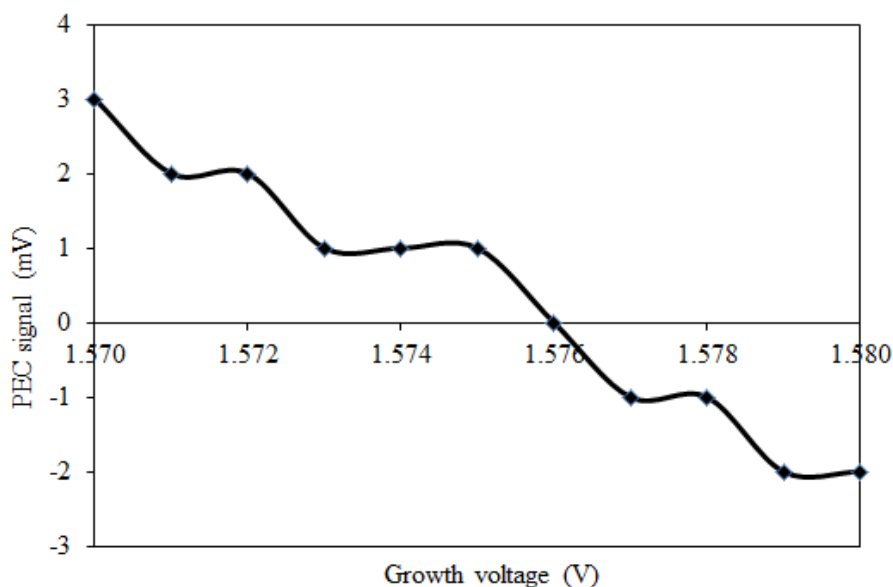


Table 1. The variations of PEC signal as a function of growth voltage for CdTe layers on glass/FTO substrates.

Sample number	Growth voltage (V)	PEC signal (mV)
1	1.570	+3
2	1.571	+2
3	1.572	+2
4	1.573	+1
5	1.574	+1
6	1.575	+1
7	1.576	0
8	1.577	-1
9	1.578	-1
10	1.579	-2
11	1.580	-2

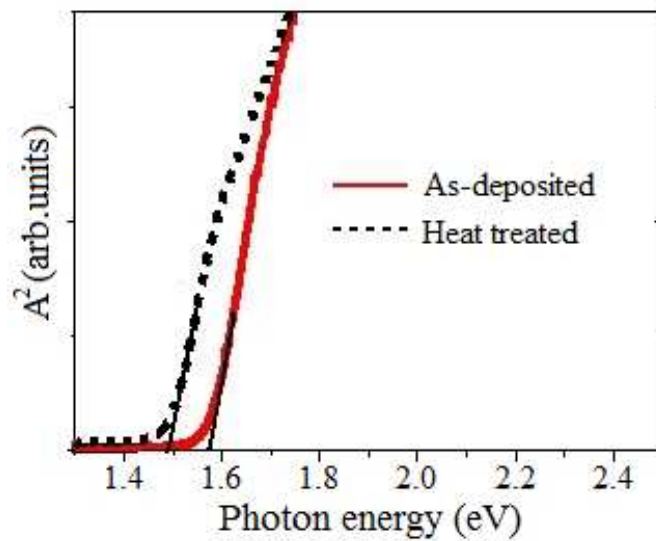
From Table 1 above, at lower cathodic voltages the polarity of the PEC signal was positive indicating p-type CdTe and at higher cathodic voltages it was negative showing n-type CdTe thus indicating Te-rich and Cd-rich regions respectively. At a deposition voltage of 1.576 V the PEC signal is zero indicating stoichiometric and intrinsic CdTe. The PEC signal arises because of the formation of PV active depletion region at the CdTe/electrolyte junction as a

result of moderate doping $\sim(10^{14} - 10^{17}) \text{ cm}^{-3}$ in CdTe. These results confirmed the work of other researchers who reported the possibility of growing either p- or n- type CdTe [22].

3.3. Optical absorption

Optical absorption measurements were carried out to estimate the bandgap of electrodeposited CdTe layers and the results are shown in Figure 3. Before annealing, the absorption edge was estimated close to 1.58 eV. After annealing in air at 450°C for 15 minutes, the absorption edge decreased to 1.49 eV. This result shows that electrodeposited layers need annealing to obtain bandgap close to the bulk values. The decrease of bandgap values after heat treatment is a well-known observation for electrodeposited semiconducting layers [23].

Figure 3. Optical absorption edges showing the estimated bandgap of CdTe. CdTe layers show bandgap close to 1.58 eV before heat treatment and moves close to 1.49 eV after heat treatment.

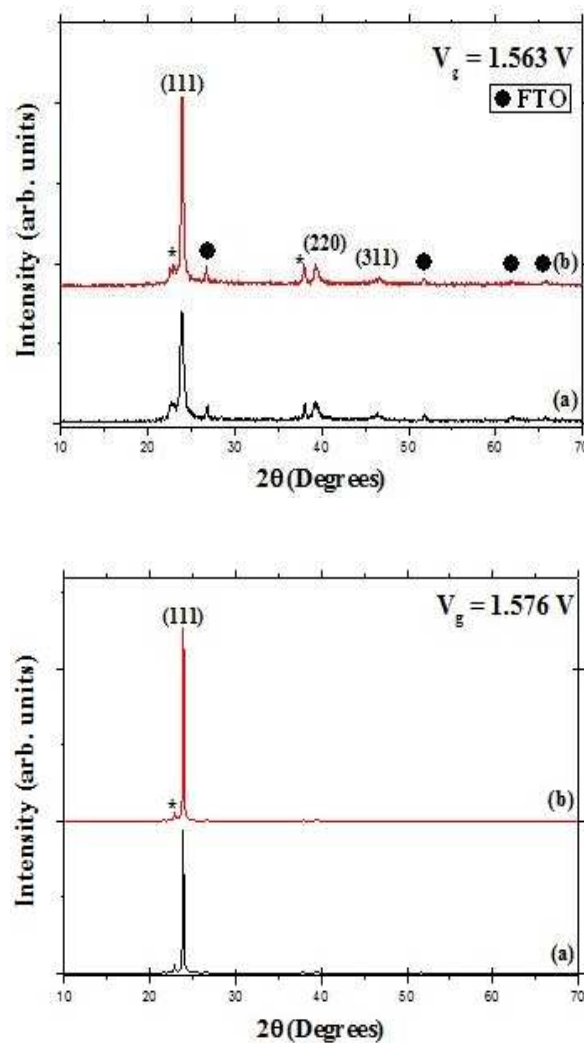


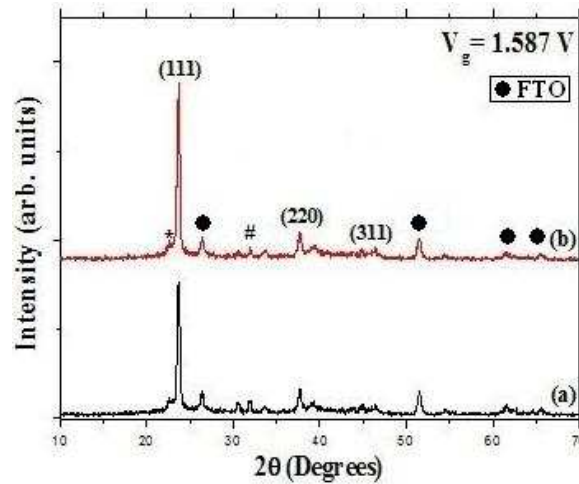
3.4. X-ray diffraction

Figure 4 shows the X-ray diffraction patterns for as-deposited and heat treated CdTe layers (at 450°C for 15 minutes in air) grown at three different growth voltages. The main diffraction peak at $2\theta = 23.64^\circ$ which corresponds to a preferred orientation along the (111) plane of cubic phase. This peak agrees with the Joint Committee on Powder Diffraction Standard, JCPDS (01-075-2086) data of cubic CdTe. From these Figures, it is observed that at lower growth voltage ($V_g = 1.563 \text{ V}$), Te is deposited more than Cd on the substrate surface, giving rise to Te-rich CdTe material. As the deposition potential increases, the Te peaks in the diffractograms diminish, at 1.576 V and above, only one peak at 22.9° ascribed

to Cd_3TeO_6 is observed. At higher growth voltages ($V_g = 1.587 \text{ V}$), more Cd than Te are deposited on the substrate surface and the resulting films produced are Cd-rich CdTe material. Weak Cd peaks were also observed as expected in this diffractogram. At the intrinsic composition grown at 1.576 V , the CdTe (111) peak is dominant and all other peaks diminished as shown in Figure 4. This material is i-type in electrical conductivity as shown from the PEC results in section 3.2.

Figure 4. X-ray diffraction patterns for CdTe layers grown at different voltages showing growth of stoichiometric CdTe at $V_g = 1.576 \text{ V}$. Spectra (a) is for as-deposited and (b) is for heat treated CdTe layers (* and # indicate Te and Cd related layers respectively).





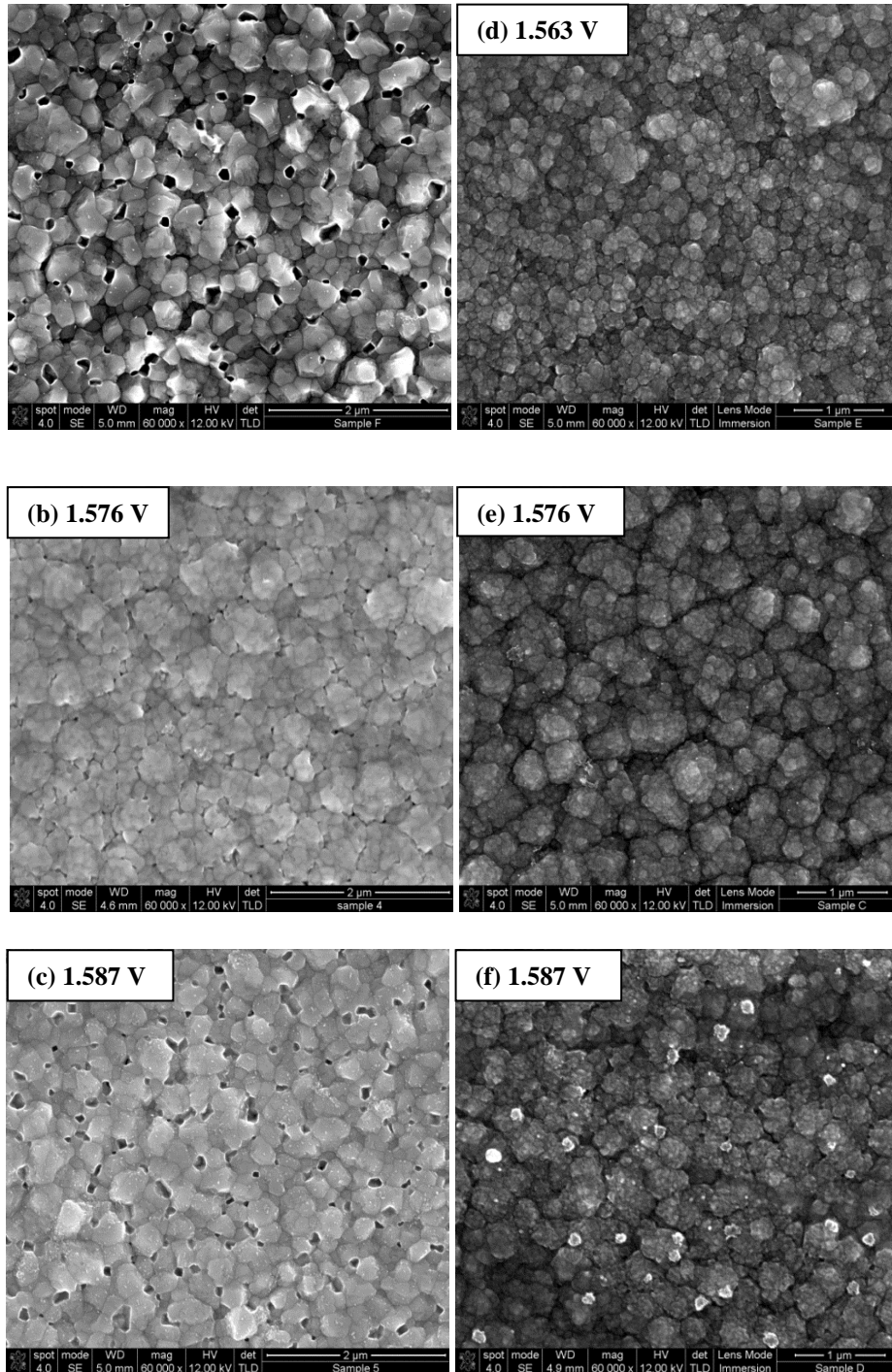
After heat treatment in air, the intensities of the peaks were different. At lower and higher growth voltages, the intensity increases as a result of the films becoming more crystalline and stoichiometric. At the intrinsic potential and the potential which are very close to stoichiometry, the intensity could go down due to loss of material through sublimation. The heat treatment enhances the recrystallisation of non-stoichiometric CdTe films reducing any stress within the films.

3.5. Scanning Electron Microscopy (SEM) studies

SEM studies were carried out to investigate the surface morphology, grain size and uniform coverage of CdTe layers. Three samples, grown at 1.563 V (Te-rich CdTe), 1.576 V (stoichiometric CdTe) and 1.587 V (Cd-rich CdTe), were selected for detailed analysis. Figure. 5 (a, b and c) and (d, e and f) show the SEM images for the as-deposited and heat treated CdTe thin films respectively. As-deposited layers show high density of pin holes (gaps) between the grains. The density, proportion and size of pin-holes depend on how far away from stoichiometry of the film composition. However, even at stoichiometry, pin holes are apparent. After heat treatment the grain size increased and density of pin holes reduced. The presence of these pin holes made the efficiency of solar cells low by shorting the back contact to the front TCO layer. These results confirmed that heat treatment enhances the recrystallisation and coalescence of grains to fill the gaps and form a uniform thin layer of CdTe.

Figure 5. SEM images (a, b and c) for as-deposited and (d, e and f) for heat treated (at 450°C for 15 minutes) CdTe layers grown at different cathodic voltages

(a) 1.563 V



3.6. Solar cell assessment using current-voltage (I-V) characteristics

The CdTe layers grown on glass/FTO/CdS substrates were treated with CdCl₂ and heat treated at 450°C for 15 minutes in air. In this work heat treated CdTe with CdCl₂ were washed with deionised water, etched in oxidising etch (chromic acid) for 5 seconds followed by reducing etch (NaOH and Na₂S₂O₃) for 2 minutes. The samples were immediately transferred to a vacuum chamber and 2 mm diameter Au contacts were evaporated at a

pressure of $\sim 10^{-6}$ Torr to make complete devices. The full details of sample preparation prior to gold metallisation have been published by Dharmadasa et al [11]. Figure 6 shows the linear I-V curves and the efficiency variations of glass/FTO/CdS/CdTe/Au contacts under AM 1.5 illuminations, for CdTe layers grown at different growth voltages. Table 2 shows the device parameters; summary of open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and efficiency (η) of these fully fabricated CdTe solar cells.

Figure 6. Linear I-V curves and efficiency of glass/FTO/CdS/CdTe/Au contacts under AM 1.5 illumination condition for CdTe layers grown at; (a) 1.563 V, (b) 1.587 V, (c) 1.572 V, (d) 1.570 V, (e) 1.576 V, (f) 1.580 V, (g) 1.574 V and (h) 1.578 V.

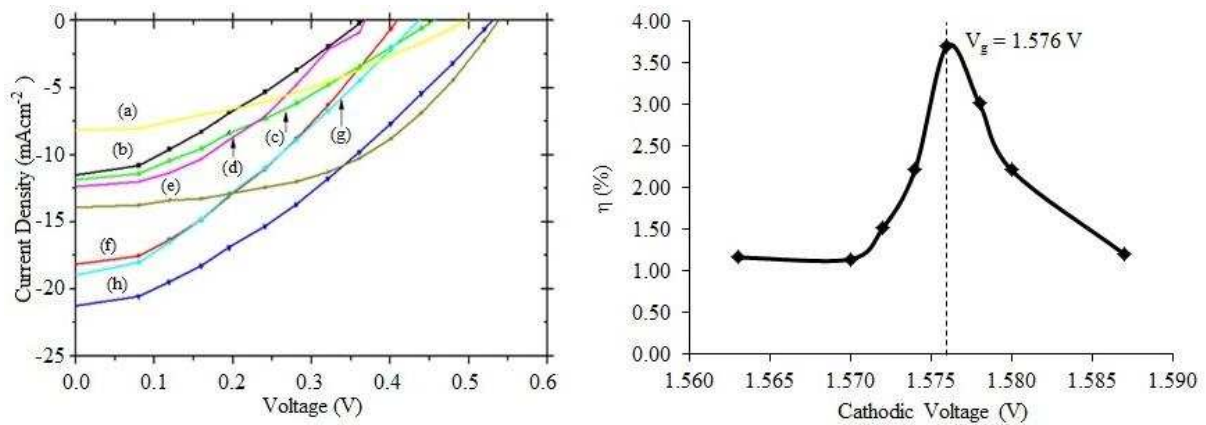


Table 2. Summary of cell parameters under AM1.5 illumination for CdTe thin film solar cells fabricated with CdTe layers grown at different growth voltages.

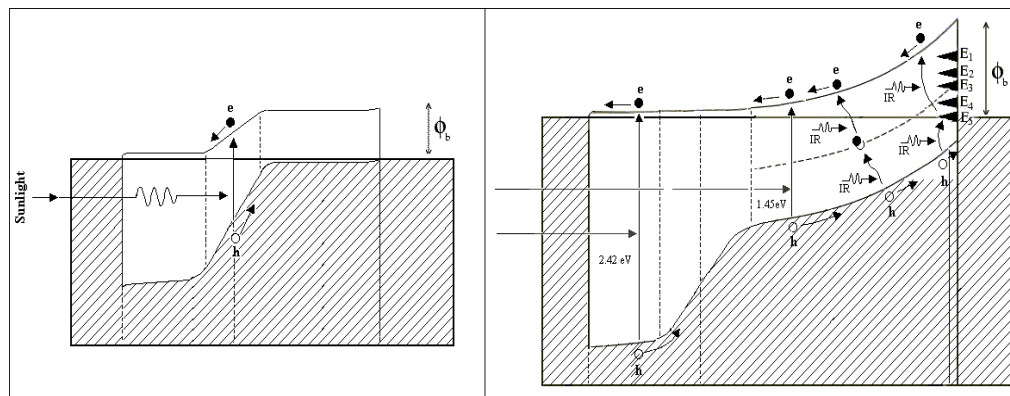
Growth voltage (V)	Conductivity type	Sample identifier	Cell parameters			
			V_{oc} (mV)	J_{sc} (mAcm ⁻²)	FF (%)	η (%)
1.563	p	a	500	8	0.29	1.16
1.570	p	d	370	13	0.30	1.44
1.572	p	c	450	12	0.28	1.51
1.574	p	g	430	19	0.27	2.21
1.576	i	e	540	14	0.49	3.70
1.578	n	h	530	21	0.27	3.01
1.580	n	f	410	18	0.30	2.21
1.587	n	b	360	12	0.28	1.20

As shown in Figure 6, the maximum efficiency of 3.70% with $V_{oc} \sim 540$ mV and FF ~ 0.49 were achieved for devices with stoichiometric CdTe ($V_g \sim 1.576$ V). The efficiency decreases as the material deviates from stoichiometry. This agrees with the PEC and XRD results discussed in section 3.2 and 3.4 respectively. At lower and higher growth voltages the CdTe compound formed is rich in Te and Cd respectively. The low FF of most of the devices at

lower and higher growth voltages could arise due to large recombination process present in non-stoichiometric CdTe and detrimental leakage paths through pinholes present within the devices.

This work identifies the existence of two different types of solar cells with CdTe. The window material used in the cells, CdS is always an n-type semiconductor. Therefore, when CdTe is rich in Te and p-type in electrical conduction, the device becomes a genuine p-n junction with the back electrical contact (Au) forming an ohmic contact to p-CdTe. However, when CdTe is grown in Cd-rich environment, CdTe becomes n-type in electrical conduction, and forms a solar cell having n-n heterojunction together with a large Schottky barrier at the n-CdTe/Au back contact [11]. Au or any other contact material forms a large Schottky barrier, due to Fermi level pinning at one of the few experimentally observed defect levels [24]. The most desirable position is the level closest to the valence band maximum, forming a Schottky barrier of 1.20 eV. This solar cell is a combination of two junctions in tandem and this performance is superior due to the presence of high electric field and the high mobility of electrons in n-CdTe. The energy band diagrams of the two possible devices are given in Figure 7 and the second structure is more desirable for achieving high efficiencies.

Figure 7. Two possible solar cell configurations could arise from glass/FTO/CdS/CdTe/Au thin film structures depending on the electrical conduction type of CdTe [24].



3.7. Modification of CdCl₂ treatment to improve the conversion efficiencies

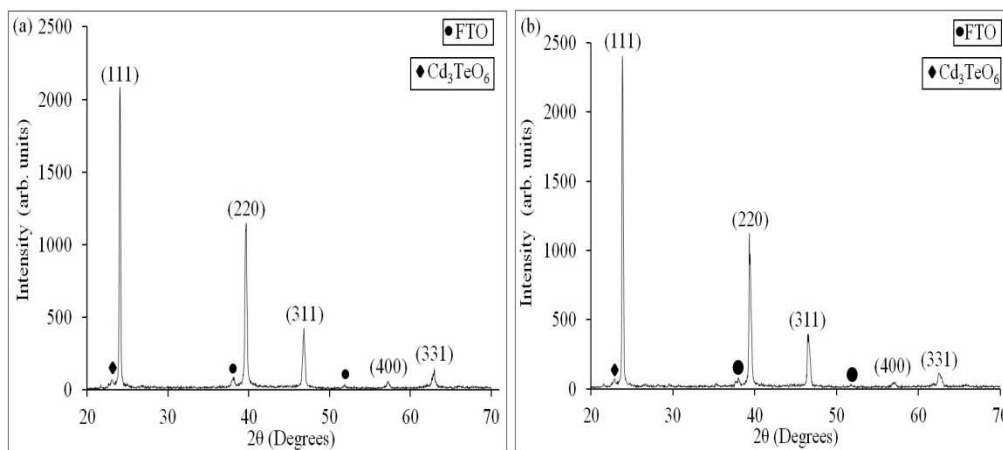
A group of researchers from Parma University, Italy has been studying the effects of CdCl₂ treatment on closed space sublimated (CSS) CdTe for several years. In order to improve the process of manufacturing CdTe solar panels, they have substituted Freon (HCFC₁₂) gas for CdCl₂ in the post-growth annealing step [25]. In this paper, they have reported the CdTe grains growth up to 10 μm after annealing with Freon gas compared to 5 μm before annealing. Recently, our group used CdCl₂ and CdF₂ solution to treat the CdTe surface, before post-growth heat treatment [26].

Two saturated CdCl_2 solutions were prepared by mixing CdCl_2 powder (99.99% purity) with deionized water. Then about ~ 0.2 grams of CdF_2 powder (99.99% purity) was added into one of the saturated CdCl_2 solutions. Electrodeposited CdS/CdTe layers were then cut into two pieces. One half of the layers was dipped into saturated CdCl_2 solution while the other half was dipped into saturated CdCl_2 solution mixed with CdF_2 . Both samples were dipped for 10 seconds and then were taken out and allowed to dry.

When dried, these samples were annealed at 450°C for 15 minutes in air. After annealing, the samples were rinsed with deionized water and then dried in a stream of nitrogen gas. The samples were then prepared for gold metallisation by etching in oxidising etchant followed by reducing etchant [11]. Results of this comparative study were analysed using XRD, SEM and I-V measurements.

Figure 8 shows the X-ray diffractograms of glass/TCO/ CdS/CdTe layers annealed with CdCl_2 only and with $\text{CdCl}_2 + \text{CdF}_2$ mixture. Both samples were electrodeposited at 1.576 V and annealed at 450°C in air for 15 minutes. Figure 8(b) shows that the addition of F helps the CdTe layers grow more preferentially along (111) planes. The (111) peak grew slightly higher with $\text{CdCl}_2 + \text{CdF}_2$ treatment. Other peaks showed no significant changes in term of the intensity. A peak emerged at 22.9° has been identified as cadmium tellurate (Cd_3TeO_6) in both cases. The presence of cadmium tellurate indicates the precipitation of tellurium on the surface of CdTe layers. Precipitation of Te is a natural phenomenon in CdTe and this behaviour has been discussed in detail by Amirtharaj and Pollak [27] and Shin et al [28].

Figure 8. X-ray diffractograms of glass/TCO/ CdS/CdTe layers (a) annealed with CdCl_2 only and (b) annealed with $\text{CdCl}_2 + \text{CdF}_2$ mixture at 450°C for 15 minutes.



SEM studies were carried out to investigate the changes in morphology of CdTe layers before and after heat treatment with halogens. Figure 9(a) shows electrodeposited CdTe layers without any heat treatment. These CdTe layers have cauliflower-like grains. Inside these cauliflower-like agglomerations, there exist smaller crystallites. The size of these crystallites was calculated using Scherrer equation and was found to be around 50 to 60 nm. Figure 9(b) shows that after heat treatment with CdCl_2 , those crystallites coalesced and

created larger grains. The grain sizes, averagely were estimated to be around 150-200 nm. Addition of F during the CdCl_2 treatment promotes the coalescence of the grains thus creating larger grains in micro-meter size. The largest grain seen from Figure 9(c) was estimated to be close to 2 μm . These larger grains are close to each other and seal any possible pin-holes. Observation on surface roughness reveals that CdCl_2 treated sample in Figure 9(b) shows higher surface roughness compared to $\text{CdCl}_2 + \text{CdF}_2$ treated sample. The 'wavy' and small particles seen from Figure 9(b) and 9(c) respectively are the CdCl_2 residues.

Figure 9. SEM images of glass/TCO/CdS/CdTe layers for (a) as-deposited, (b) annealed with CdCl_2 only and (c) annealed with $\text{CdCl}_2 + \text{CdF}_2$ mixture.

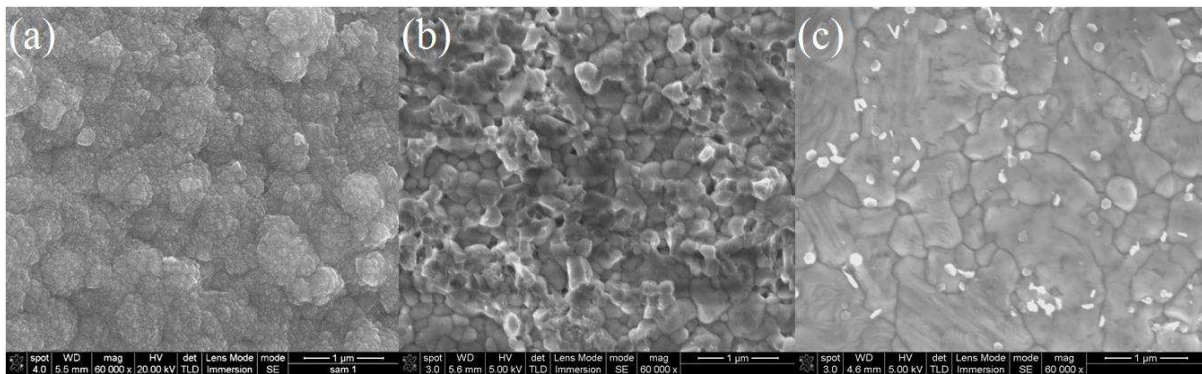


Figure 10 and Table 3 show the J-V curves under AM1.5 illumination, and the summary of device parameters obtained for solar cells fabricated with two different CdTe layers. All of $\text{CdCl}_2 + \text{CdF}_2$ treated samples showed enhanced cell parameters when compared to the CdCl_2 treated samples. The highest efficiency obtained from CdCl_2 treated samples was 6.7% while for the $\text{CdCl}_2 + \text{CdF}_2$ treated sample, the highest efficiency was 10.1%.

Figure 10. J-V curves of highest efficiency observed from CdCl_2 and $\text{CdCl}_2 + \text{CdF}_2$ treated cells.

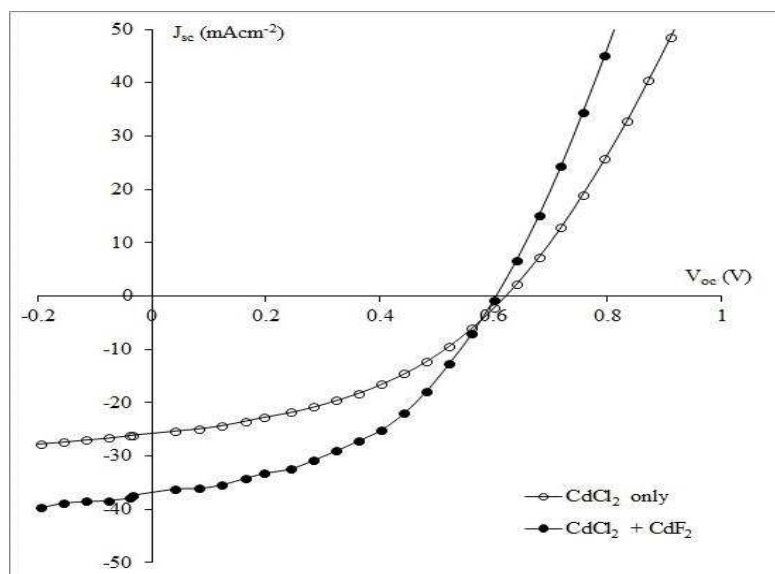


Table 3. Comparison of solar cell parameters made with CdCl₂ treated and CdCl₂ + CdF₂ treated CdTe layers.

V _g (V)	CdCl ₂ only				CdCl ₂ + CdF ₂ mixture			
	V _{oc} (mV)	J _{sc} (mAcm ⁻²)	FF	η (%)	V _{oc} (mV)	J _{sc} (mAcm ⁻²)	FF	η (%)
1.576	550	12.7	0.40	2.8	640	16.0	0.47	4.8
1.576	570	19.1	0.28	3.1	600	20.0	0.43	5.2
1.576	615	26.0	0.42	6.7	600	36.7	0.46	10.1

The improvement made with the inclusion of F towards the crystallinity and surface morphology of CdTe layers, in return, positively affect the device efficiency. Larger grain sizes as shown in Figure 9(c) contributed to the higher cell parameters, especially for J_{sc}. This is because with larger grains, less grain boundaries are present thus helping more electrons move to the external circuit with fewer scattering and recombination. Improvement in the fill factors was attributed to the creation of reduced pin-holes in the CdCl₂ + CdF₂ treated layers. This helped the solar cells to behave as more rectifying devices rather than ohmic conductors.

4. Conclusion

CdTe has been deposited on glass/FTO substrates using a low-cost aqueous electrodeposition method using two-electrode system. PEC measurements confirmed that at lower and higher cathodic voltages from the transition voltage, the signs of the PEC signal were p- and n- type, while at a growth voltage of 1.576 V the PEC signal shows growth of stoichiometric, more crystalline and intrinsic CdTe. The XRD results show that at voltages less than or higher than 1.576 V, the CdTe material layers will be either Te-rich or Cd-rich. When the CdTe is stoichiometrically grown and heat treated in air, only the (111) peak is dominant in the XRD diffractogram indicating a high degree of crystallinity with preferential orientation. When heat-treated with halogen-treatment, material layer losses its preferential orientation and show random nature. SEM studies showed that as-deposited layers had pin-holes between the crystallites and the density of pinholes increases as the layers deviate from stoichiometry. After heat treatment the grain size increase and the pinhole density are reduced. The linear I-V curve of glass/FTO/CdS/CdTe/Au solar cells under AM 1.5 illumination at different growth voltages showed the maximum efficiency of 3.70% from the stoichiometric CdTe grown at 1.576 V. More importantly, this work identifies the existence of two types of solar cell structures; genuine p-n junction type and n-n heterojunction + large Schottky barrier at the back metal contact. The efficiency decreases as CdTe layers deviate from the stoichiometry. CdCl₂ + CdF₂ treatment provides a way forward to increase the efficiency of electrodeposited CdS/CdTe solar cells. Inclusion of F during the heat treatment

induces larger grains and improves crystallinity of electrodeposited CdTe layers and enhanced device efficiency.

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Author Contributions

SHU-Solar Energy Group members (D. G. Diso, F. Fauzi, O. K. Echendu, I. M. Dharmadasa): Electrodeposition of CdS and CdTe, materials characterisation, device fabrication assessment and development, interpretation of results, understanding the science behind materials and devices, drafting of manuscript, drawing diagrams and completing the paper.

Conflicts of Interest

The authors declare no conflicts of interest.

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