

**ELECTROCHEMICALLY DEPOSITED OF CdTe-USING TWO ELECTRODE SYSTEM FOR SOLAR CELL APPLICATION****G. E. A. Muftah<sup>1\*</sup>, Mabrouk Hassan<sup>1</sup> and I. M. Dharmadasa<sup>2</sup>**

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**1. ABSTRACT**

The aim of this work was to make low cost thin film solar cells by electro deposition, using cadmium telluride (CdTe) in presence of the chlorine treatment of CdTe. CdTe films were electrochemically deposited from aqueous solutions using both two. Different preparative parameters such as growth voltage and heat treatment conditions were optimised by measuring the I-V characteristic of glass/FTO/CdS/CdTe/Au devices. The device efficiency was high at a growth voltage of 1570 mV. The optimum annealing conditions were 350°C for 20 minutes in air. It is established that treating CdTe with chlorine has a beneficial effect on the solar cell device. For comparison, untreated and treated CdTe were characterised by various techniques. XRD analysis showed a cubic structure, with a significant increase in intensity from the (111) reflection in present of chlorine treatment. Optical absorption shows a band gap energy of 1.50 eV with a good absorbance slope. A considerable change in the morphology between untreated and treated CdTe was observed by SEM. I-V measurements of completed chlorine treated glass/FTO/CdS/CdTe/Au devices showed a significant improvement in efficiency. The best efficiency obtained was 8.7%.

**KEYWORDS:** The device efficiency was high at a growth voltage of 1570 mV.

## 2. INTRODUCTION

The majority of the reports and information written regarding the electrodeposition of CdTe layers for solar cells from an aqueous solution generally conclude that a three-electrode system using cathode, anode and a reference electrode is the most preferable.<sup>[1,2,3,4,5]</sup> The use of a reference electrodes such as Ag/AgCl, calomel has several disadvantages, particularly concerning impurities leaking out from the reference electrode which have the capability to contaminate the solution. This potential contamination has the effect of greatly reducing the effectiveness of the solar cell device. For example, the addition of Ag ions in parts per billion level reduces dramatically the efficiency of the electrodeposited CdTe solar cells from about 11% to 0.7%.<sup>[6]</sup> It seems that three-electrode system can be substituted with much simpler and cleaner two-electrode system. Dharmadasa *et al*<sup>[7,8]</sup> have first reported the electrodeposition of CuInSe<sub>2</sub> and CuGaInSe<sub>2</sub> using a two electrode system. This chapter presents a detailed investigation into the deposition of CdTe material using a two-electrode system, highlighting the material properties and the initial device behavior of two layer heterostructures.

## 3. Experimental Aspect

The electrodeposition of CdTe layers was performed from an aqueous solution containing 0.8 M cadmium sulphate (3CdSO<sub>4</sub>.8H<sub>2</sub>O) and 50 ppm tellurium dioxide (TeO<sub>2</sub>) with a purity of 5N (99.999%). The pH value was adjusted to 2.0 using high-purity sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The solution was purified at a cathodic voltage of 600 mV vs SCE for 100 hours in order to remove impurities. The temperature was maintained at 70°C throughout the experiment. To enhance Te deposition, the solution was stirred by a magnetic stirrer. The CdTe was deposited of 600 ppm of CdCl<sub>2</sub>.

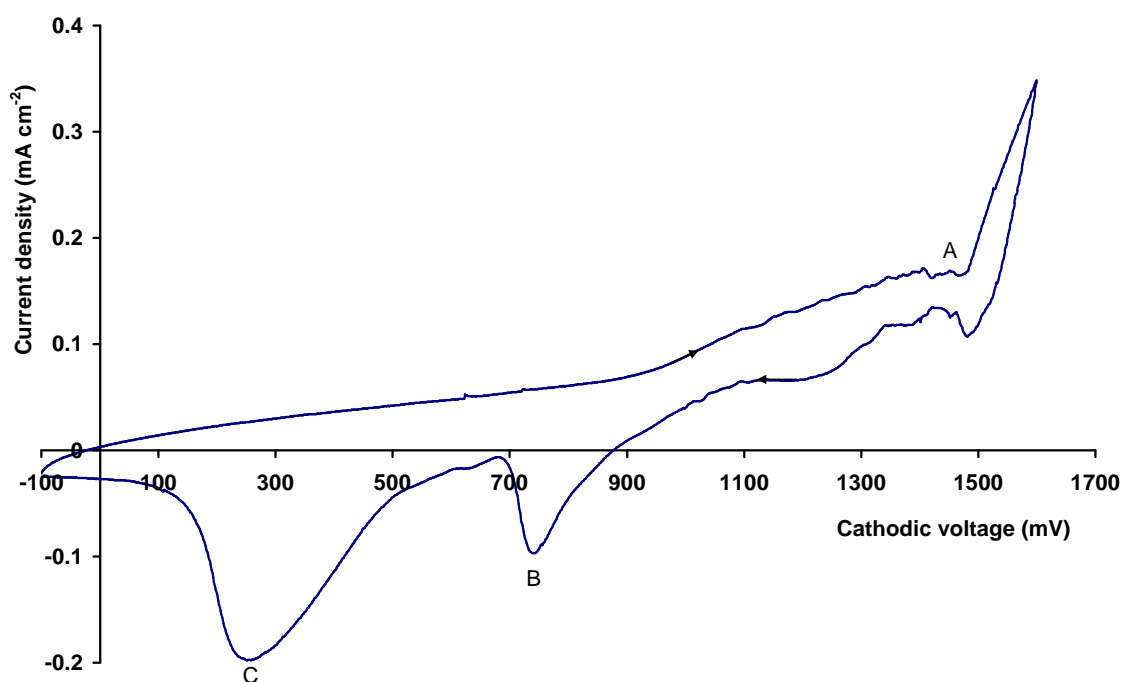
CdTe films were prepared using a three electrode system. The counter electrode was a high purity graphite rod. The reference electrode was saturated calomel (SCE) which has been filled with cadmium chloride (CdCl<sub>2</sub>) solution instead of potassium chloride (KCl) solution and the substrate was glass/FTO/n-CdS. The electrodeposition experiments and cyclic voltammetry were carried out using a potentiostat. The CdTe films were annealed in air atmosphere at various temperatures for different periods of time in order to optimise the best heat treatment condition before etching.

In order to develop CdTe based solar cells, electrodeposited films and completed devices have been characterised by the following techniques: XRD, Optical absorption and SEM for

material characterisation

#### 4. Linear sweep voltametry

In order to determine the most suitable deposition voltage range, LSV using the two electrode system were obtained from aqueous solutions containing similar concentrations and conditions (temperature, stirring speed and pH) to the solution presented in chapter 6 (6.2) for comparison. The working electrode used for LSV was FTO coated glass. Figure 1 shows a typical voltamogram for the electrodeposition of CdTe. The LSV scan was taken between +100 and -1700 mV, with the reversal to +100 mV at a sweep rate of  $5 \text{ mV s}^{-1}$ . During the forward scan, a gradual increase in current density occurred in the cathodic voltage range from  $\sim 0$  to  $\sim 1000$  mV, indicating the electrodeposition of material on the cathode. Since Te is more noble than Cd, Te element is expected to deposit before Cd element. A plateau was observed between cathodic voltages 1410 and 1485 mV. The region labeled (A) represents the formation of CdTe compound. Several authors reported that this may not be pure CdTe but the mixture of CdTe+Te.<sup>[9,10]</sup> A sharp increase in current after 1485 mV is related to more cadmium deposition or/and hydrogen evolution. Therefore, the composition of the CdTe layers varies with the deposition potential. The reverse sweep resulted in Cd stripping in the region labeled (B) and Te stripping in the region labeled (C).



**Figure 1: Voltamogram of CdTe solution containing 0.8 M  $3\text{CdSO}_3 \cdot 8\text{H}_2\text{O}$  and 50 ppm  $\text{TeO}_2$  at  $70^\circ\text{C}$ . The arrows indicate the direction of the potential sweep.**

## 5. Characterisation of treated CdTe material with chlorine

### 5.1 X-ray diffraction

Figure 2 shows the XRD pattern for as-deposited chlorine treated CdTe samples deposited at 1450, 1500, 1570, 1580 and 1585 mV. All used deposition voltages are shown to produce CdTe layers with a preferential orientation of (111) plane and identified to have a cubic structure, which is in agreement with the literature.<sup>[11,12]</sup> The (111) peak height varies with changes in the growth voltage and attains a maximum value for layers deposited at 1570 mV. The layer deposited at 1450 mV shows the lowest intensity. This variation in the peak height may also be attributed to changes in the layer composition. This indicates that chlorine treatment improves crystallinity of CdTe layers deposited using a two electrode system. In 1997 and 1998, Moutinho et al utilized XRD in order to highlight how structural changes in the CdTe layers were enhanced in the presence of CdCl<sub>2</sub>.<sup>[13,14]</sup> In this way, Moutinho et al were able to establish that recrystallization was behind the changes that occurred. This recrystallization is a process involving lattice strain energy and the time and temperature of heat treatment. For the purpose of this experiment, the time and temperature were kept the same for the non treated and CdCl<sub>2</sub> treated samples. The conclusion reached from this experiment was that the CdCl<sub>2</sub> effectively caused an increase in the initial strain energy of the material which enabled the recrystallization to take place.

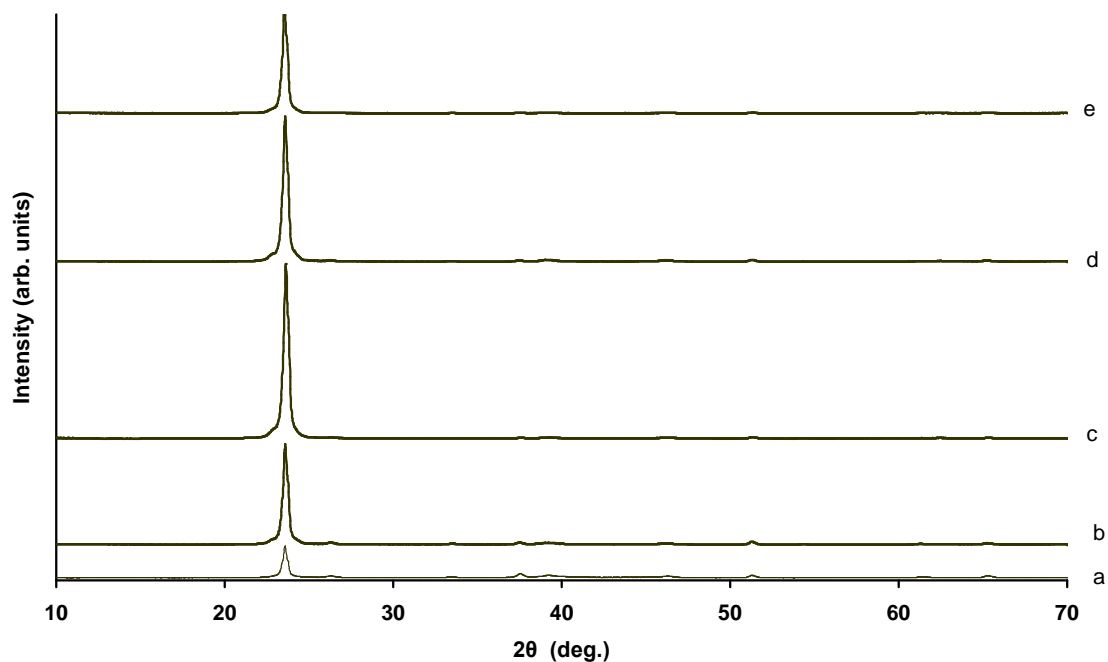
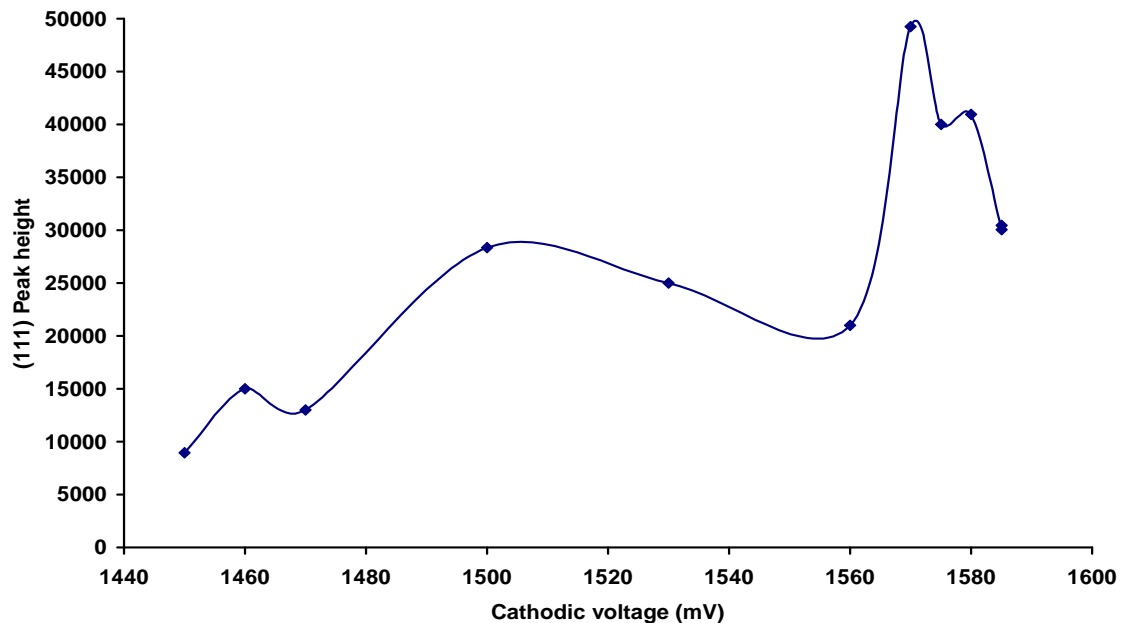


Figure 2: Typical XRD patterns for chlorine treated CdTe for layers deposited at (a) 1450, (b) 1500, (c) 1570, (d) 1580 and (e) 1585 mV.

Figure 3 presents the (111) peak height as a function of cathodic voltage for chlorine treated as-deposited CdTe layers. Table 1 gives peak position, FWHM and grain size for CdTe layers deposited at various deposition voltages. The Scherrer equation was used to calculate the grain size. Although the major preferential reflection peak height belonging to the (111) plane varied, the FWHM and the grain size values were the same for all growth voltages.

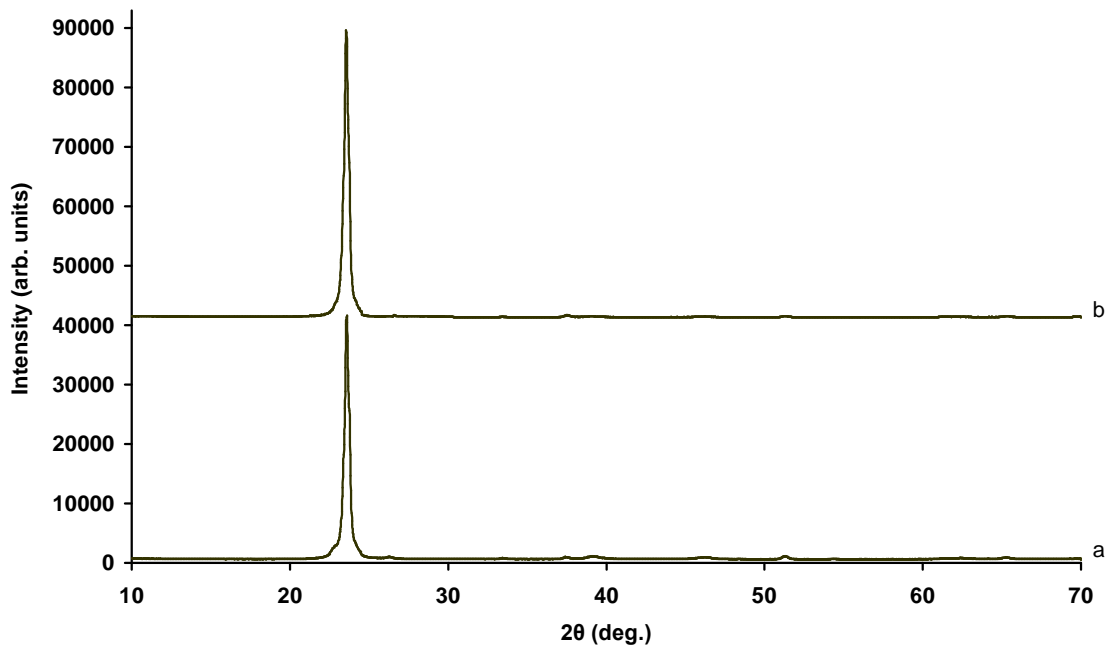


**Figure 3: Variation of the (111) peak height against cathodic voltage for as-deposited and annealed CdTe layers.**

**Table 1: Peak position, FWHM and grain size for as deposited CdTe layers.**

Growth Voltage (mV)	2 $\theta$ (deg)	FWHM (deg.)	Grain size (nm)
1450	23.59	0.35	23
1500	23.60	0.35	23
1570	23.63	0.35	23
1580	23.59	0.35	23
1585	23.59	0.35	23

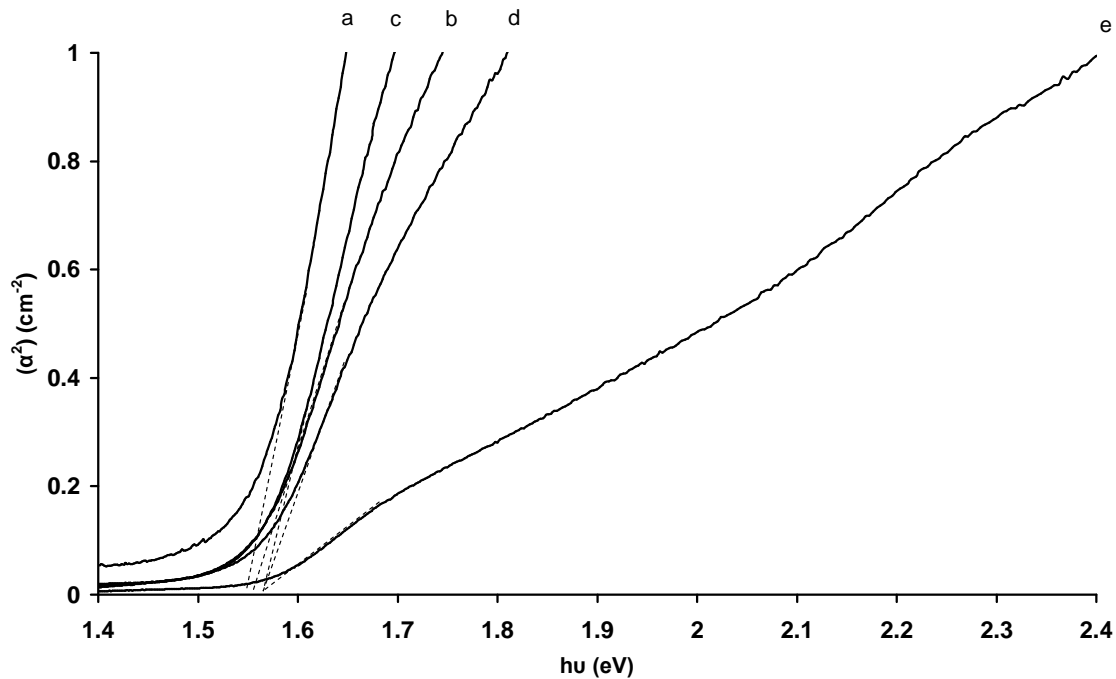
Figure 4 shows the XRD patterns of as-deposited and annealed CdTe deposited at 1570 mV. Annealing was carried out at 350°C for 20 minutes in air. It is clear that there is an improvement in the major preferential reflection peak height after annealing. The estimated grain size remained at 23 nm. The XRD data for as-deposited and annealed CdTe layers were analysed using standard data obtained from the online Deresbury Chemical Database Service.<sup>[15]</sup> The lattice parameters were calculated using the major reflection peak related to the (111) plane and the cubic d-spacing equation presented in chapter 3 (3.3), giving  $a = 6.53 \text{ \AA}$ .



**Figure 4: XRD pattern for chlorine treated CdTe for (a) as-deposited and (b) annealed (350°C for 20 minutes) CdTe deposited at 1570 mV.**

## 5.2 Optical properties

Optimisation of preparative parameters for CdTe material was carried out by observing the influence of growth voltage on band gap energy for layers deposited using a two electrode system. Figure 5 shows the optical absorption curves of glass/FTO/CdS/CdTe for CdTe deposited at 1450, 1500, 1570, 1580 and 1585 mV. All the layers were deposited onto a glass/FTO/CdS substrate for a period of 7 hours. It is evident that the rapid increase in the absorbance occurs at different photon energy presenting a different band gap energy of CdTe. The smallest band gap energy of 1.55 eV was obtained for the layer deposited at 1450 mV. The largest band gap energy of 1.56 eV obtained for layers deposited at 1570, 1580 and 1585 mV. The steepest absorbance slope was observed for layers deposited at 1450 and 1570 mV and the poorest absorbance slope was shown by the layer deposited at 1585 mV. Table 2 shows the band gap energy as a function of growth voltage for as deposited CdTe layers. Layers deposited at high cathodic voltages show a decrease in the band gap energy indicating that chlorine is more effective where  $\text{Cd}^+$  is expected to be deposited more than Te. This result in line with the result observed from XRD spectra, regarding the improvement of crystallinity at high cathodic voltage in the range 1570-1580 mV.

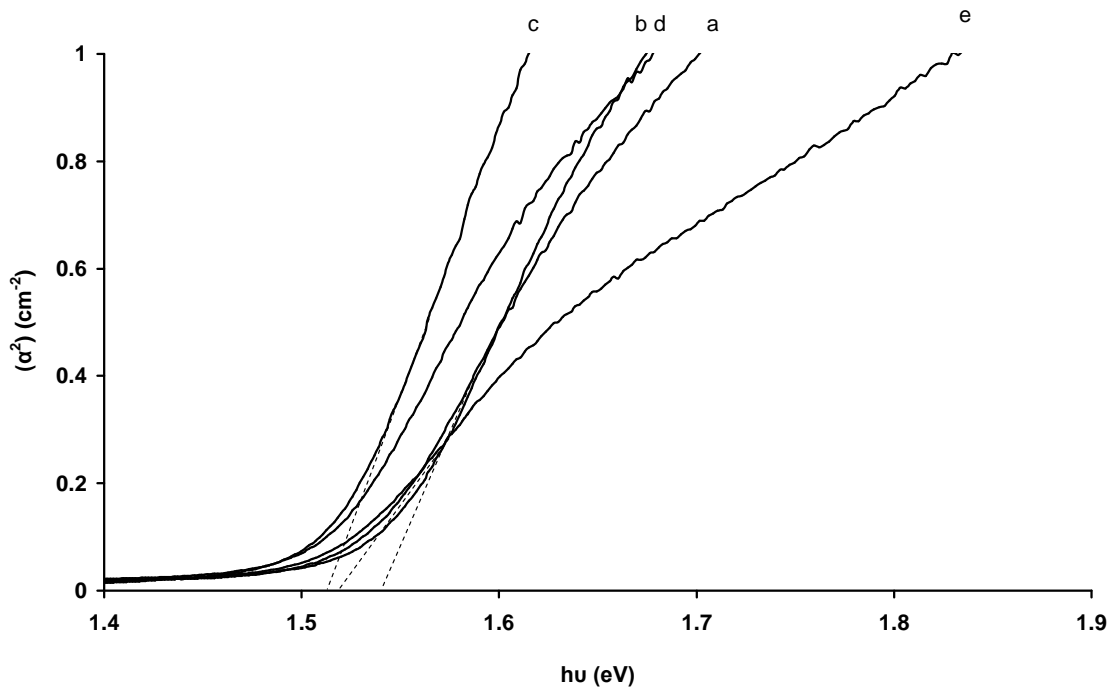


**Figure 5:** The optical absorption curves for chlorine treated CdTe for layers deposited at: (a) 1450, (b) 1500, (c) 1570, (d) 1580 and (e) 1585 mV.

**Table 2:** Band gap energy as a function of the growth voltage for as-deposited CdTe layers.

Growth voltage (mV)	1450	1500	1570	1580	1585
Band gap energy ( $\pm 0.02$ eV)	1.55	1.55	1.56	1.56	1.56

In order to investigate the effect of annealing on chlorine treated CdTe, optical absorption was carried out on glass/FTO/CdS/CdTe. The layers were annealed at 350°C for 20 minutes in air. Figure 6 shows the optical spectra for glass/FTO/CdS/CdTe for annealed CdTe deposited at 1450, 1500, 1570, 1580 and 1585 mV. Table 3 shows the band gap energy as a function of the growth voltage for annealed CdTe layers. Figure.5 shows that the band gap energy fluctuated between 1.52 and 1.54 eV, within experimental error of  $\pm 0.02$  eV. The band gaps were lower than for as-deposited layers indicating the influence of the annealing process. The largest band gap energy was recorded for layers deposited at 1580 mV and the smallest band gap energy was recorded for layers deposited at 1500 mV. The band gap energy of layers deposited at voltages of 1450, 1500 and 1480 mV increased, while the band gap energy of the layers deposited at 1585 mV remained the same. The maximum theoretical efficiency is observed for material having a band gap energy in the range 1.4 to 1.5 eV.<sup>[16]</sup> This range encompasses the values measured for layers deposited at 1500 and 1570 mV.



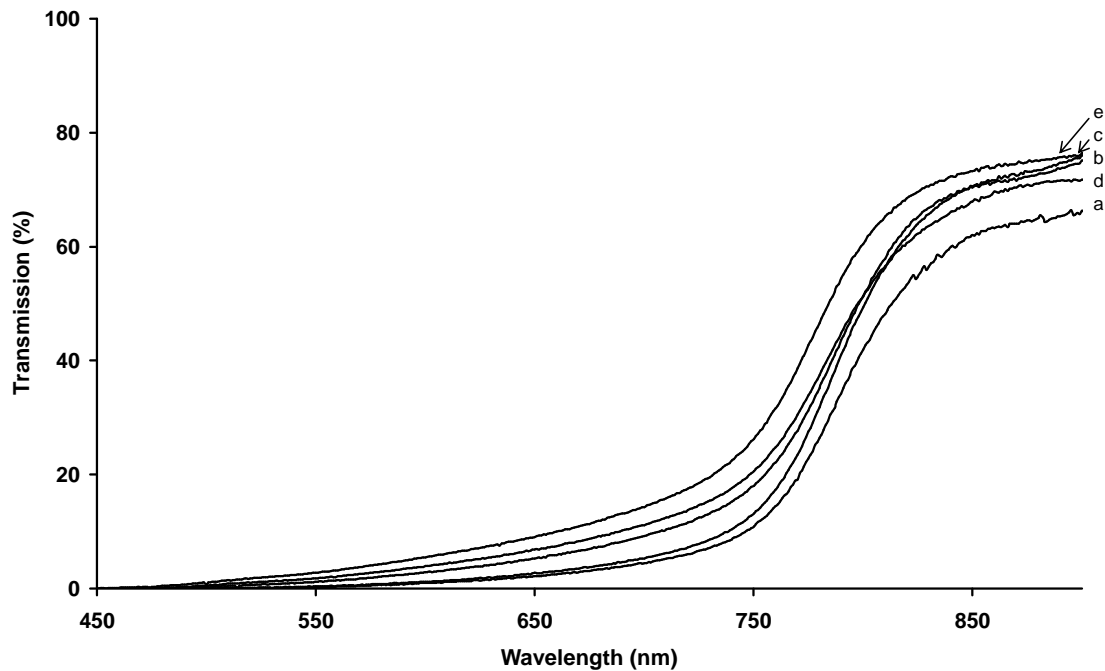
**Figure 6: Optical absorption measurement for annealed chlorine treated CdTe for layers deposited at (a) 1450, (b) 1500, (c) 1570, (d) 1580 and (e) 1585 mV.**

**Table 3: Band gap energy as a function of the growth voltage for annealed CdTe layers.**

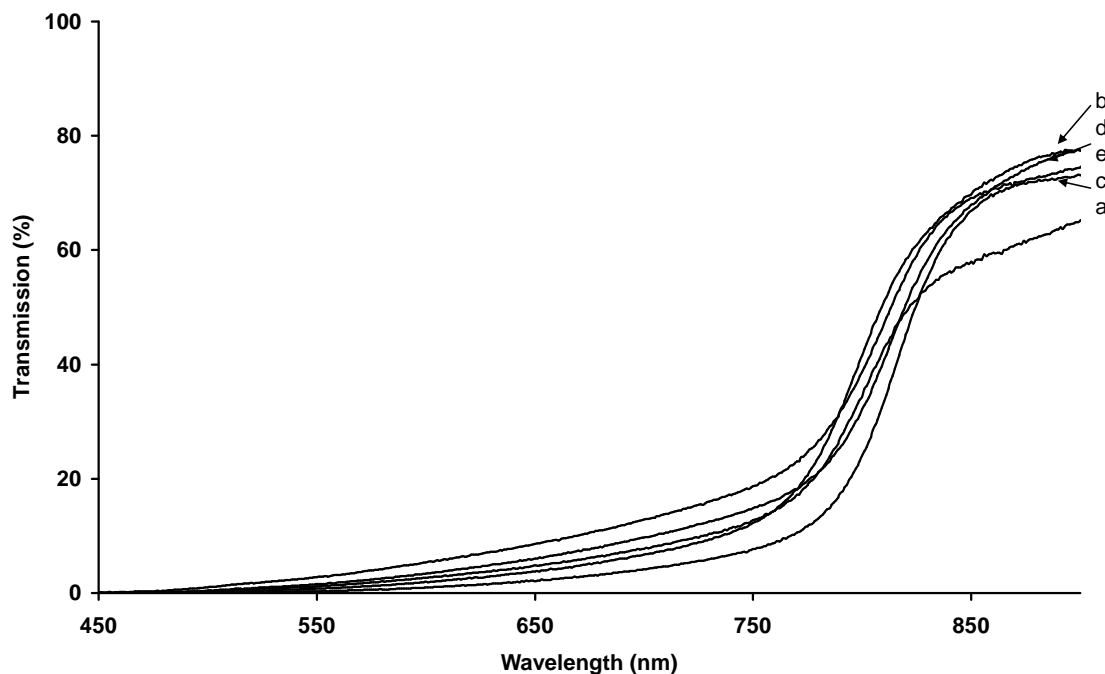
Growth voltage (mV)	1450	1500	1570	1580	1585
Band gap energy (eV)	1.52	1.48	1.50	1.54	1.52

Figure 7 shows the transmission spectra for glass/FTO/CdS/CdTe for CdTe deposited at 1450, 1500, 1570, 1580 and 1585 mV. It can be seen from the figure that the transmissions of incident photons fluctuate between ~76 and ~65%. Kampmann showed that the transmission of incident photons changes with growth voltage.<sup>[17]</sup> These changes occur due to changes in composition. The maximum transmission was observed for layers deposited at 1585 V and decreased to ~65% for the layer deposited at 1450 mV. The influence of annealing (350°C for 20 minutes) on the transmission spectra of CdTe has been studied to assess the change in the transmission of the incident photon edge. Figure 8 presents the transmission spectra for glass/FTO/CdS/CdTe for annealed CdTe deposited at 1450, 1500, 1570, 1580 and 1585 mV. The transmission for the layer deposited at 1585 mV has shifted to 74%, while a maximum transmission of 77% was observed from layers deposited at 1500 mV and a minimum transmission of ~65% was recorded from layers deposited at 1450 mV. The change in transmission percentage and absorption edge is most likely due to a change in the CdTe thickness or a change in the composition after annealing.





**Figure 7:** Transmission vs light wavelength for chlorine treated as-deposited CdTe for layers deposited at: (a) 1450, (b) 1500, (c) 1570, (d) 1580 and (e) 1585 mV.

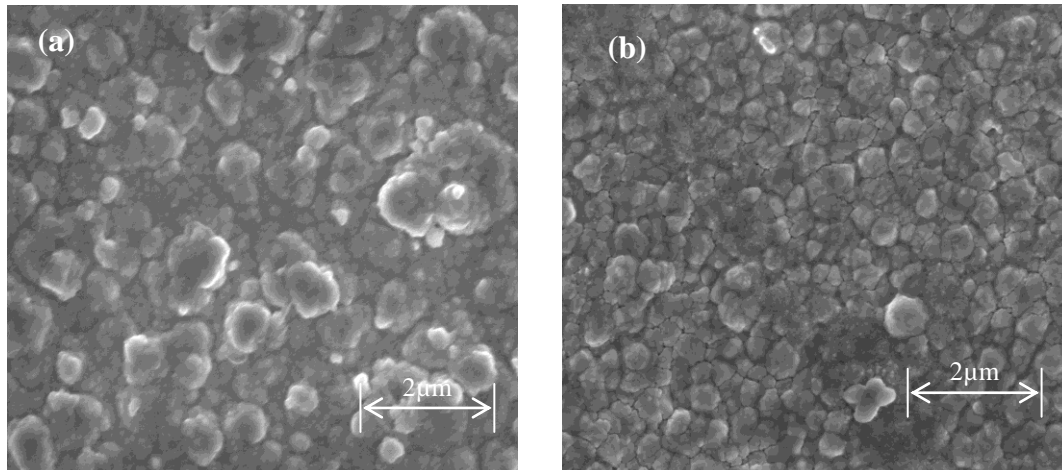


**Figure 8:** Transmission vs light wavelength of annealed chlorine treated CdTe (350°C for 20 minutes in air) deposited at: (a) 1450, (b) 1500, (c) 1570, (d) 1580 and (e) 1585 mV.

### 5.3 Scanning electron microscopy

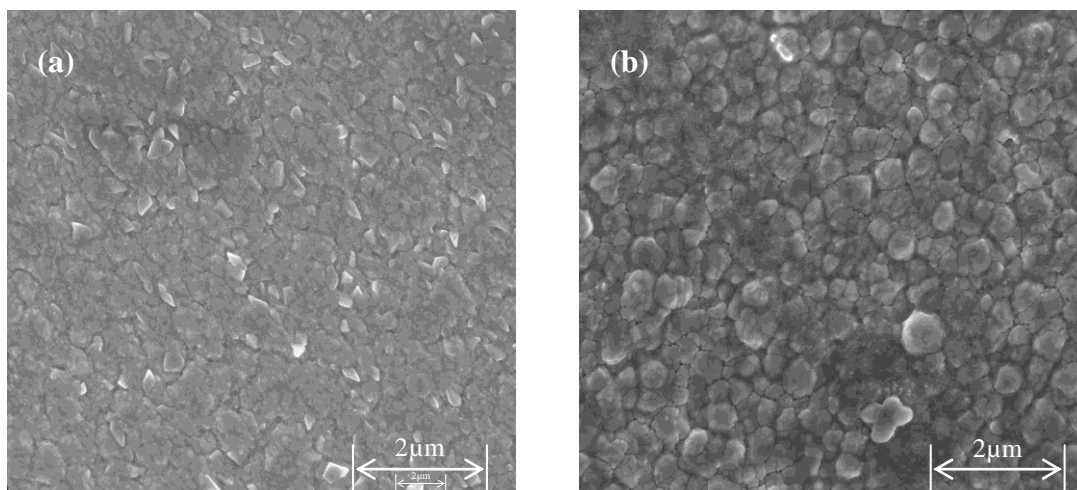
Figure 9 shows SEM pictures of the CdTe surface before and after annealing for layers deposited at 1570 mV on a glass/FTO/CdS substrate. The XRD and optical spectra obtained

for this layer showed the highest and narrowest reflection peak from the (111) plane and a good slope in optical absorption, respectively. The as-deposited layer (figure 9a) shows clusters with small 'nodules like'. After annealing the CdTe in air for 20 minutes at 350°C most of clusters and nodules disappear and the grains become more crystalline indicating the presence of polycrystalline CdTe.



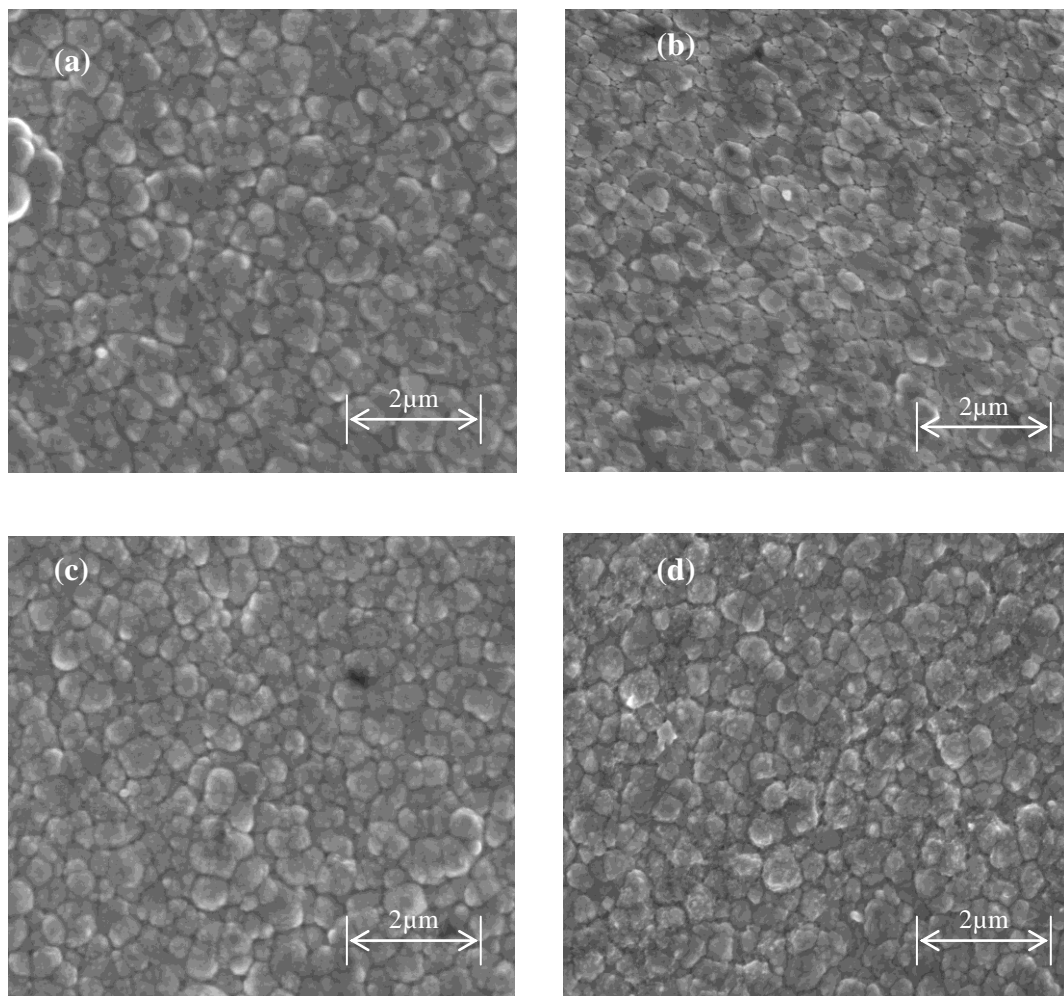
**Figure 9: SEM images of chlorine treated CdTe (a) as-deposited and (b) annealed, deposited at 1570 mV.**

Figure 10 shows SEM pictures of the CdTe surface after annealing for untreated and chlorine treated layers deposited at 1570 mV. The chlorine treated CdTe layer appear to have larger surface grains than the untreated layer.



**Figure 10: SEM pictures of annealed CdTe layers, deposited at 1570 mV for (a) untreated and (b) chlorine treated.**

Figure 11 shows the morphology of annealed CdTe layers (320°C for 20 minutes in air) deposited at 1450, 1500, 1570, 1580 and 1585 mV. Although the growth voltages varied, the overall layers are uniform with similar grain sizes. This result is consistent with the results obtained from XRD, which showed similar grain sizes. All layers do not appear to have large surface clusters as in the as-deposited layers.



**Figure 11: SEM images of annealed chlorine treated CdTe deposited at (a) 1450, (b) 1500, (c) 1580 and (d) 1585 mV.**

## **5. Devices with CdCl<sub>2</sub> treated CdTe; device characterisation**

### **5.1 Current-voltage measurements**

In order to assess the glass/FTO/CdS/CdTe/Au structure for chlorine treated CdTe layers, I-V curves under dark and illuminated conditions were used to optimize the electronic quality of the device by measuring  $J_{sc}$ ,  $V_{oc}$ , FF,  $\eta$  and rectification factor. Figure 12 (a) to 12 (e) shows typical I-V curves in both semi-log under (dark condition) and linear (under illumination) at different growth voltages. The CdTe layers were deposited at 1450, 1500, 1570, 1580 and

1585 mV and annealed at 350°C for 20 minutes in air. From the figures it is observed that  $\eta$  increases with increased growth voltage, reaching a maximum value at 1570 mV, with further increase in the cathodic growth voltage the  $\eta$  and  $J_{sc}$  decrease. This suggests that the formation of a sufficient quality and an almost stoichiometric layer composition occurs at 1570 mV. The devices made of layers deposited at 1450 and 1585 mV show lower values of efficiency.

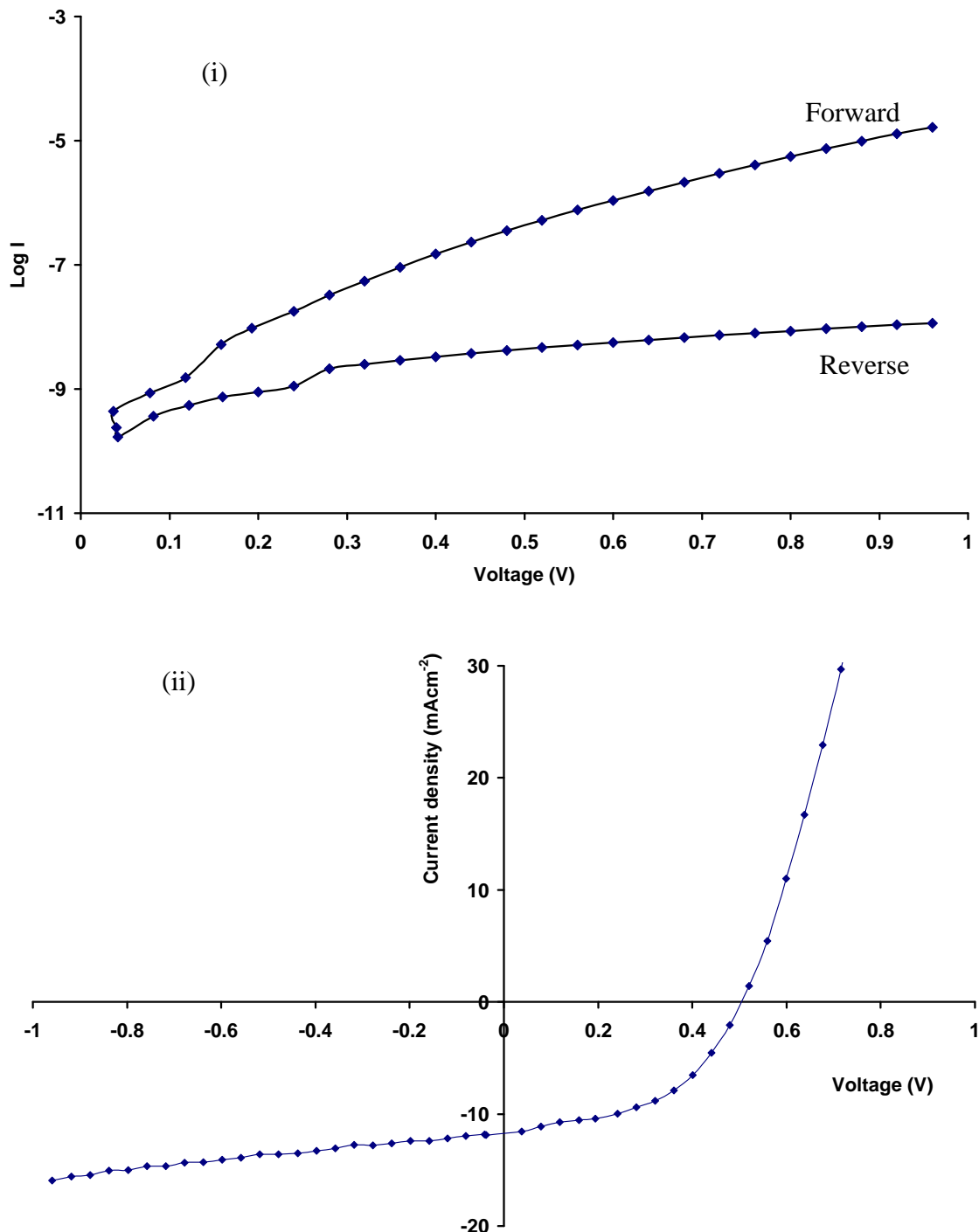


Figure 12 (a): Typical I-V curve of glass/FTO/CdS/CdTe/Au structure, for CdTe

deposited at 1450 mV. (i) log I vs V under dark conditions (ii) linear I-V curve under AM1.5 illumination. The rectification factor = 3.12 orders of magnitude at ~1 V,  $\eta = 2.9\%$ ,  $J_{sc} = 11.7 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.50 \text{ V}$  and  $FF = 0.50$ .

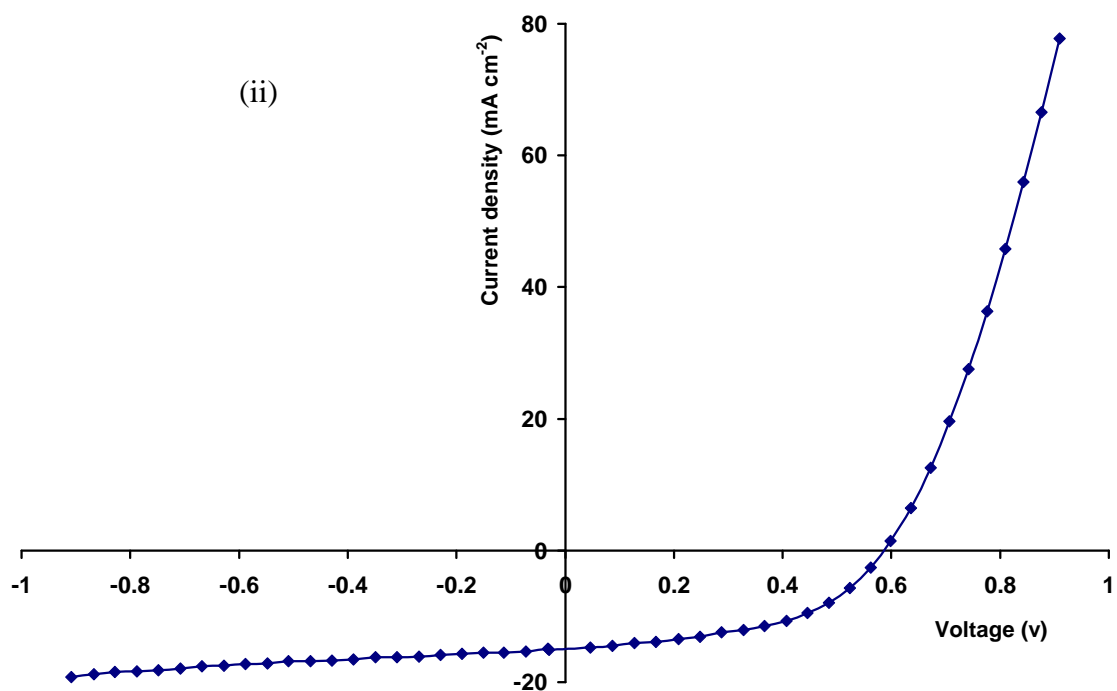
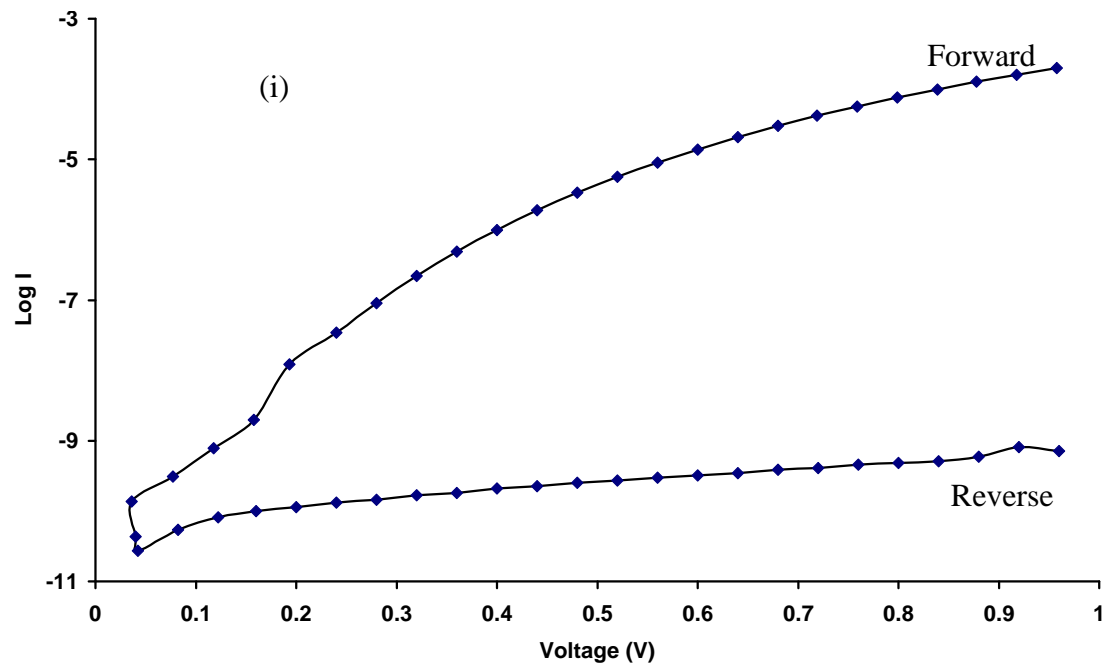


Figure 12 (b): Typical I-V curve of glass/FTO/CdS/CdTe/Au structure, for CdTe deposited at 1500 mV. (i) log I vs V under dark conditions (ii) linear I-V curve under AM1.5 illumination; The rectification factor = 5.39 orders of magnitude at 1 V,  $\eta = 4.0\%$ ,  $J_{sc} = 15.0 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.58 \text{ V}$  and  $FF = 0.47$ .

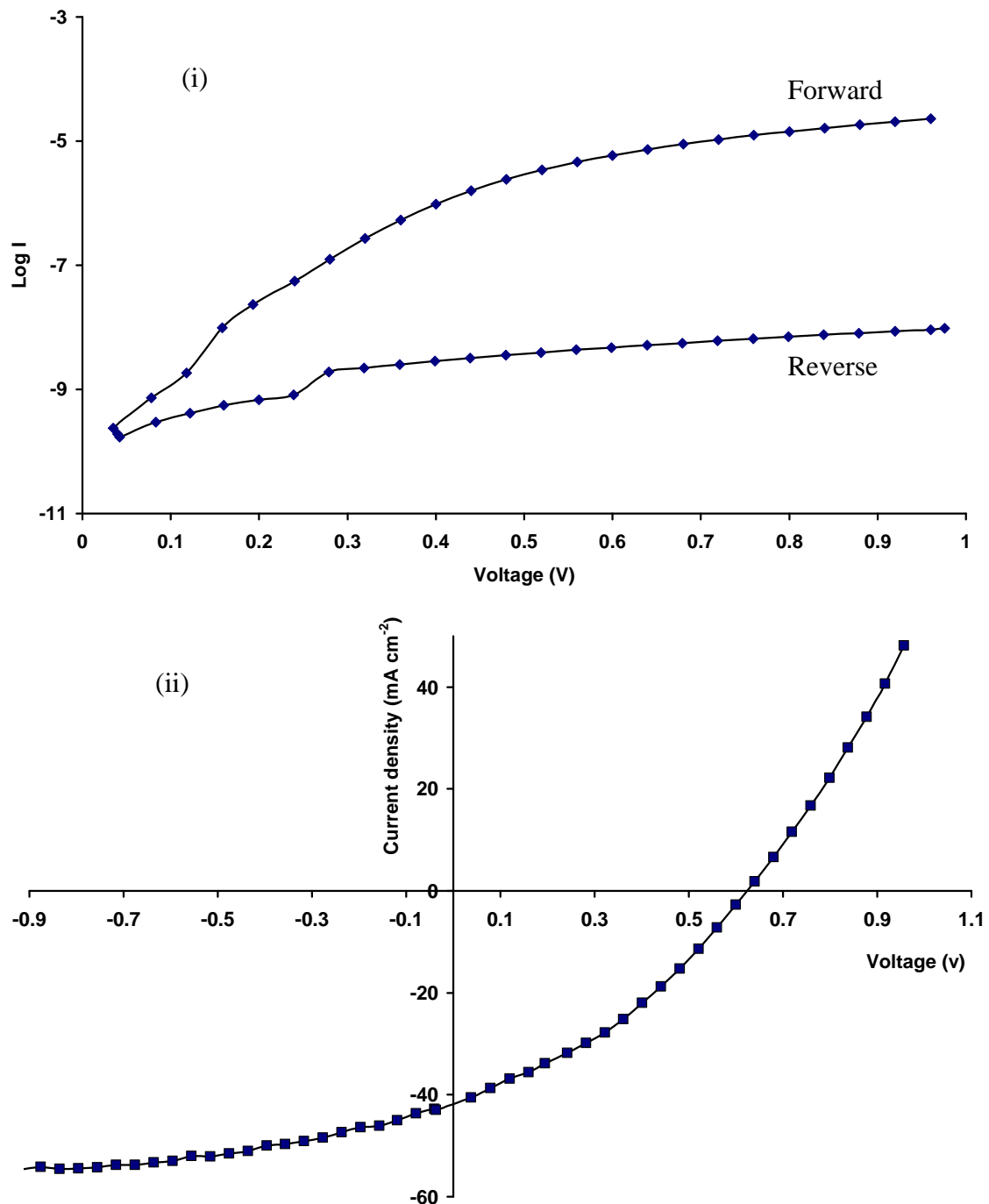


Figure 12 (c): Typical I-V curve of glass/FTO/CdS/CdTe/Au structure, for CdTe deposited at 1570 mV. (i) log I vs V under dark condition (ii) linear I-V curve under AM1.5 illumination; The rectification factor = 3.4 orders of magnitude at ~1.0 V,  $\eta = 8.7\%$ ,  $J_{sc} = 41.0 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.64 \text{ V}$ ,  $FF = 0.33$ .

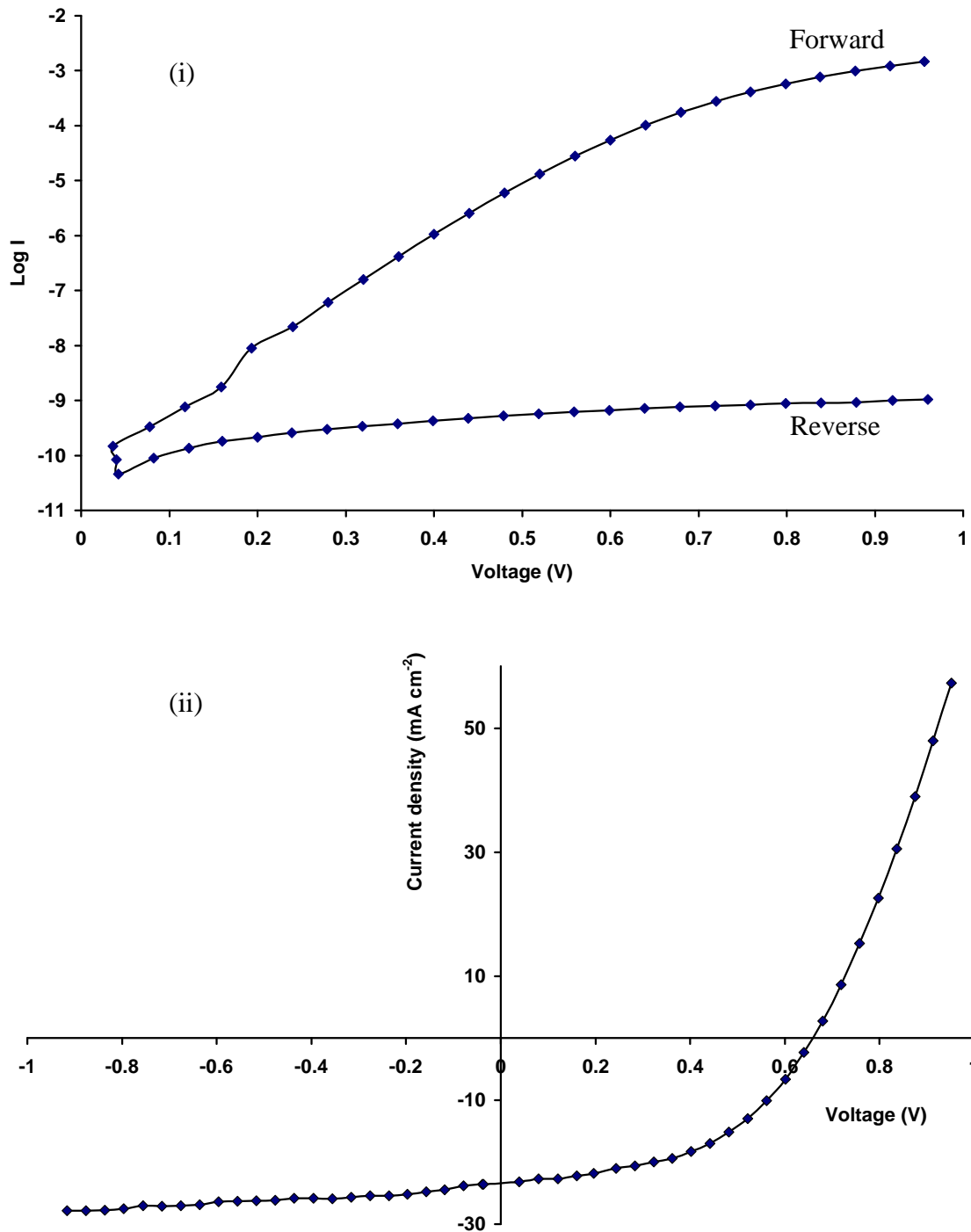


Figure 12 (d): Typical I-V curve of glass/FTO/CdS/CdTe/Au structure, CdTe deposited at 1580 mV. (i) log I vs V under dark conditions (ii) linear I-V curve under AM1.5 illumination; The rectification factor = 6.1 orders of magnitude at  $\sim 1$  V,  $\eta = 7.4\%$ ,  $J_{sc} = 23.3 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.66 \text{ mV}$  and  $FF = 0.48$ .

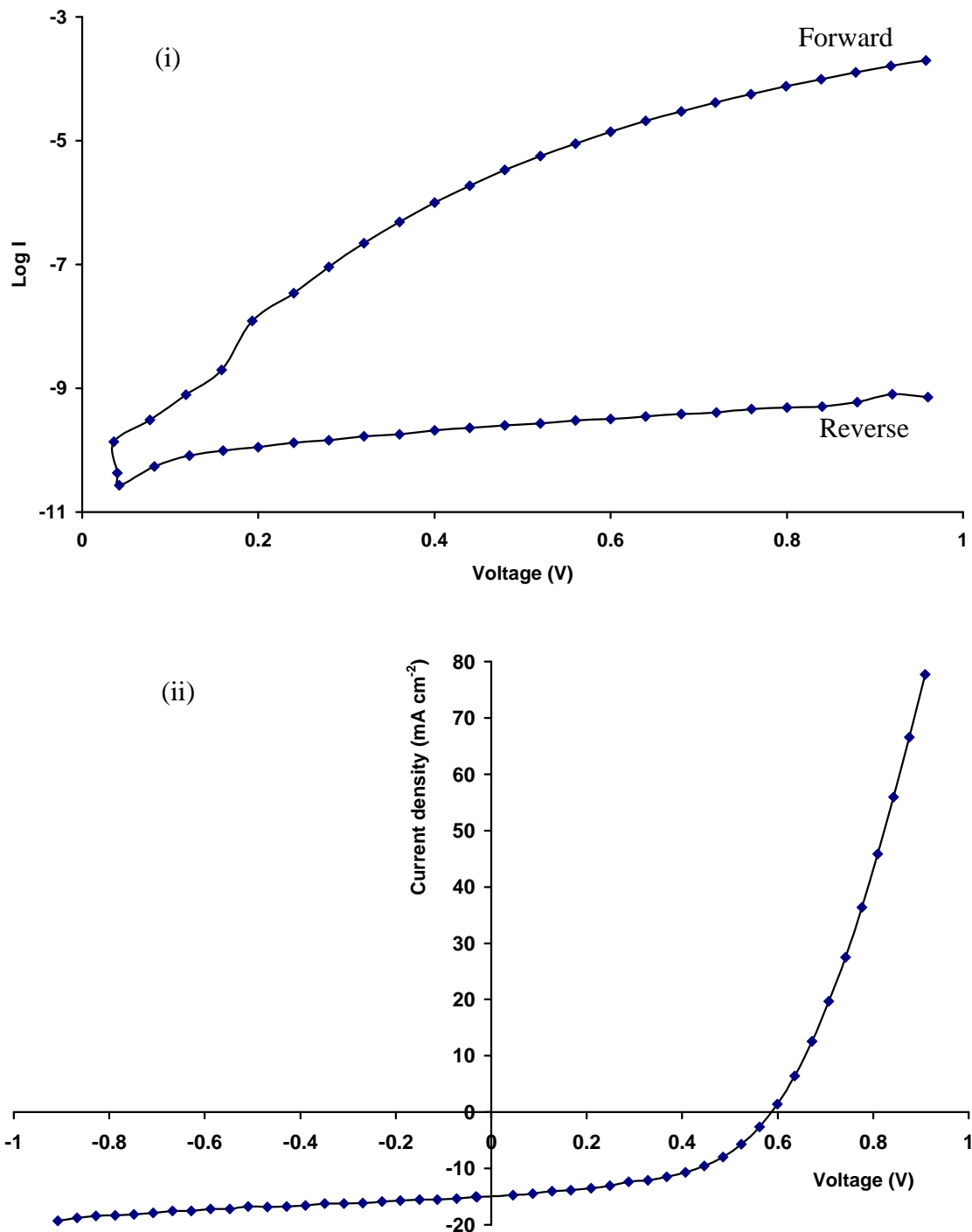
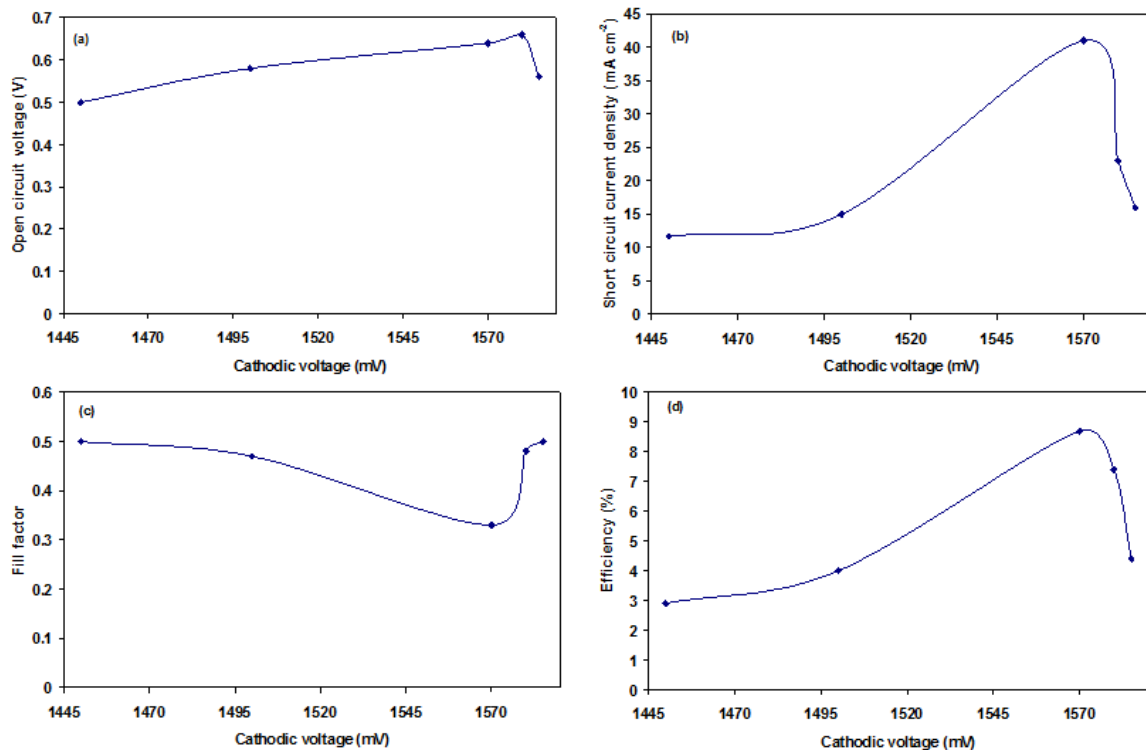


Figure 12 (e): Typical I-V curve of glass/FTO/CdS/CdTe/Au structure, for CdTe deposited at 1585 mV. (i) log I vs V under dark conditions (ii) linear I-V curve under AM1.5 illumination. The rectification factor = 6.4 orders of magnitude at 1 V,  $\eta = 4.4\%$ ,  $J_{sc} = 16.0 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.56 \text{ V}$  and  $FF=0.50$ .



**Table 4: Device parameters of glass/FTO/CdS/CdTe/Au as a function of the deposition voltage of CdTe.**

$V_g$ (mV)	$R_F$	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	$\eta$ (%)
1450	3.2	0.50	11.7	0.5	2.9
1500	5.3	0.58	15.0	0.47	4.0
1570	3.4	0.64	41.0	0.33	8.7
1580	6.1	0.66	23.0	0.48	7.4
1585	6.4	0.56	16.0	0.50	4.4



**Figure 13: (a) open circuit voltage, (b) short circuit current, (c) fill factor, and (d) efficiency as a function of CdTe growth voltage.**

## 6. CONCLUSION

The two electrode system for the preparation of chlorine treated CdTe layers in presences of chlorine and the influence of heat-treatment was investigated. The CdTe layers were deposited at 1450, 1500, 1570, 1580 and 1585 mV and annealed at 350°C for 20 minutes in air. The as-deposited and annealed layers were studied using various techniques: XRD, optical absorption, SEM and I-V measurements. It was found that a deposition voltage of 1570 mV gives an almost stoichiometric material, resulting in a high quality device. These layers showed the highest preferential reflection from the (111) plane, and a band gap energy of 1.50 eV with a good absorbance slope. Crystalline and uniform grains were also observed after annealing. All devices fabricated exhibit photovoltaic activity and the highest efficiency

was obtained from a layer deposited at 1570 mV, with device parameters of  $V_{oc} = 0.64$  V,  $J_{sc} = 41$  mA cm<sup>-2</sup>, FF= 0.33 and  $\eta = 8.7\%$ .

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