

RESEARCH ARTICLE

Electrodeposition and characterization of as-deposited and annealed CdTe thin films

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Abstract: Thin films of CdTe semiconductor materials were grown on fluorine doped tin oxide (FTO) conducting glass substrates using the technique of electrodeposition. CdSO₄ at high concentrations and CdCl₂, TeO₂ at low concentrations were used as precursor salts for electrodeposition. The range of deposition potentials was estimated using cyclic voltammetric measurements. The electrical, optical, structural and morphological characteristics of as-deposited and annealed CdTe thin films were characterized using photo-electrochemical (PEC) cell studies, UV-Vis spectrophotometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM). These particular samples were converted from n-type into p-type after heat treatment. UV-Vis spectrometric measurements for CdTe layers indicated that, the energy band gaps of 1.45±0.02 eV for both as-deposited and annealed samples which exhibited the required optical property for fabricating CdS/CdTe solar cells. Little increase in (220) and (311) peaks of XRD spectra were observed for annealed layers compared to the as-deposited material. However, annealing exhibited a small reduction of cubic phase preferential orientation (111). The optical transmission for both as-deposited and annealed CdTe samples were about 60% for wavelengths longer than about 850 nm.

Keywords: Electrodeposition, cadmium telluride, solar cells, as-deposited.

INTRODUCTION

Cadmium telluride (CdTe); a (II-VI) semiconductor material with a direct energy band gap of 1.45 eV possessing a high light absorption coefficient is suitable for efficient solar energy conversion (Chu, *et al.*, 1993). According to the theoretical calculations, the semiconductors having band gap energy in the range of 1.00–

2.00 eV are suitable for solar energy conversion using single p-n junction devices (Goetzberger, *et al.*, 2003). For current commercial products, thin layers of CdTe semiconductors are required in order to reduce the manufacturing cost. CdTe layer of about 2 μm thick can absorb nearly 100% of incident solar radiation.

The CdTe thin films can be grown using various methods such as screen printing (Arita, *et al.*, 1991), vacuum evaporation (Rohatgi, *et al.*, 1989), metal organic chemical vapor deposition (Uda, *et al.*, 1982; Myers, *et al.*, 1981) and anodic and cathodic deposition (Panicker, *et al.*, 1978; Gore, *et al.*, 1989). Among various techniques, electrodeposition is a low cost, non-vacuum, scalable, reliable and a manufacturable technique which is used in growth of thin films. The most interesting feature in electrodeposition is that, the composition and the crystalline structure of the thermoelectric material can be controlled by adjusting the electrodeposition parameters (Li, *et al.*, 2009). In electrodeposition process; deposition voltage, pH of the solutions, concentrations and proportions of electrolytes in solution, deposition time, temperature of solutions, stirring rate of the solution, electrode system, annealing time and annealing temperature are the experimental variables used to optimize in order to obtain thin film semiconductors with good photovoltaic properties. Cyclic voltammetry was used to determine the deposition potential range for growing of thin film CdTe materials. Photo-electrochemical measurements, UV-visible absorption spectroscopy, X-ray diffraction studies and scanning electron microscopy were

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used to obtain (I-V) characteristics, band gaps, crystal types and surface morphologies respectively of the electrodeposited CdTe thin films.

EXPERIMENTAL

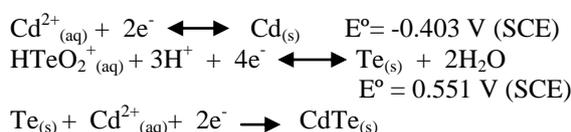
CdTe thin films were cathodically electrodeposited on glass/ FTO substrates using aqueous solutions containing 1.50 M CdSO₄, 1000 ppm CdCl₂ and 150 ppm TeO₂. In this study, a three electrode consisting of a high purity graphite electrode and a saturated calomel electrode (SCE) as the counter electrode (CE) and the reference electrode (RE) respectively were used. Potentials at the conducting glass working electrode (WE) was controlled using a "Gamry Series G 300" potentiostat/galvanostat system. Conducting glass substrates prior to depositions of CdTe layers were cleaned by a sequence of steps which included wiping out with a liquid detergent, ultrasonic washing in detergent solvents and then rinsing with de-ionized water followed by degreasing using acetone, methanol and isopropyl alcohol respectively.

A 100 ml polypropylene beaker containing aqueous electrolytic bath was kept in a 1000 ml water circulated glass beaker which was connected to the water circulating system (Lab Companion CW-05G). The water circulating system was used to keep the temperature constant for the electrolyte throughout the experiment. The high purity graphite electrode and glass/FTO were set parallel to each other and conducting side of the FTO glass was faced to the graphite electrode. Distance between two electrodes was kept constant at 1 cm. The glass beaker connected to the water circulating system was placed on the hot plate/magnetic stirrer. The electrolyte was continuously stirred to produce an orderly flow of solution throughout the deposition period. Electrodeposition conditions that can yield good quality CdTe thin films were estimated for the electrolytic baths containing 1.50 M CdSO₄, 1000 ppm CdCl₂ and 150 ppm TeO₂. It was assumed that the effect of each electrodeposition parameter on the quality of the thin film deposited was independent from each other. Accordingly, one parameter at a time; deposition potential, pH of solution, temperature

and deposition time only was varied keeping the rest of the parameters unchanged at selected values. Electrodeposited semiconductor layers were rinsed with de-ionized water, dried under pure nitrogen gas flow at room temperature in the fume hood. Conductivity type, band gap, material identification and surface morphology and thickness of the deposited films were studied using photo-electrochemical (PEC) cell measurements, UV-Vis spectrophotometry, X-ray diffraction (XRD) scanning electron microscopy (SEM) and profilometer respectively.

RESULTS AND DISCUSSION

A mechanism proposed for electrodeposition of CdTe thin films from acidic electrolyte is described below (Engelken, *et al.*, 1985):



As can be seen from the reversible electrode potentials of cadmium and tellurium elements for deposition of Cd and Te in almost equal quantities, the electrolyte must have a much higher Cd concentration than that of Te concentration.



$$\Delta G^\circ \approx -9.97 \times 10^{-4} \text{ J mol}^{-1}$$

The deposition of CdTe occurs at more positive potential than required for the deposition of Cd as a separate phase because of the free energy gain in forming CdTe (Panicker, *et al.*, 1978). However, a detailed mechanism for CdTe deposition has not been reported yet.

Cyclic Voltammogram

Figure 1 shows a cyclic voltammogram obtained for an aqueous solution containing Cd and Te in the molar proportions as used in the electrodeposition.

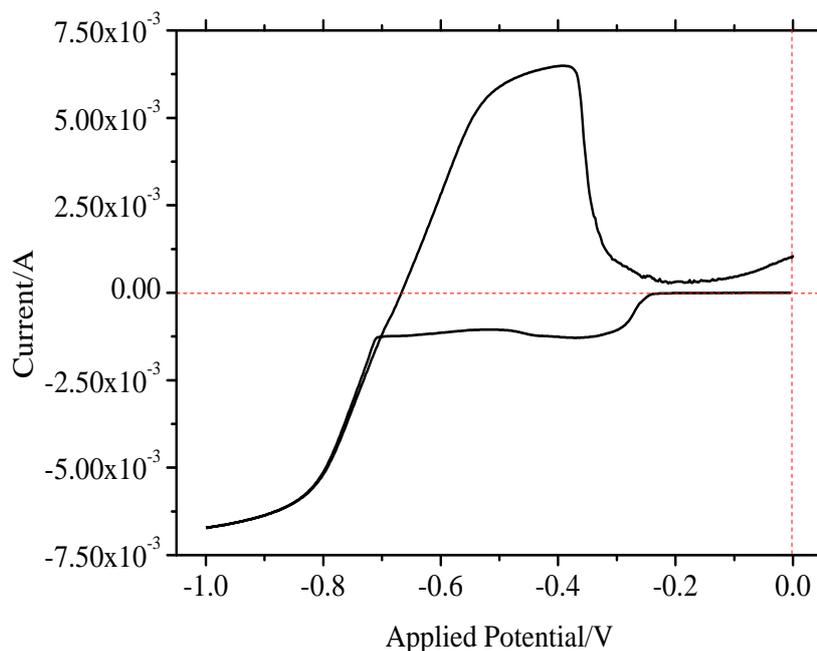


Figure 1: Cyclic voltammogram for electrodeposition of CdTe thin films produced in a solution containing 1.50 M CdSO₄, 1000 ppm CdCl₂ and 150 ppm TeO₂.

The above cyclic voltammogram indicates that CdTe can be formed over cathodic potential of about 400 mV to about 725 mV, with respect to the saturated calomel electrode. The favorable pH, deposition time, temperature and growth voltage for the formation of good quality CdTe thin films were found to be 2.00 ± 0.02 , 5 hours, $\sim 70^\circ\text{C}$ and -650 mV respectively.

Photo-electrochemical (PEC) Cell Studies

The PEC cell was used to determine the conductivity type of the grown CdTe by immersing deposited CdTe layers in 0.10 M Na₂S₂O₃ to form a solid/liquid junction. The potential difference between the CdTe and the electrolyte was measured using carbon rod immersed in the same electrolyte for both dark and illuminated conditions. The open circuit voltage (V_{oc}) was taken using the difference of the two voltage values. The sign or polarization of V_{oc} showed negative value for as-deposited CdTe layers and positive value for annealed CdTe layers investigated in this project.

X-Ray Diffraction Studies

XRD analysis data were obtained using a Philips X'pert pro diffract meter with Cu-K_α excitation wavelength of 1.54 Å. Figure 2(a) and 2(b) show the X-ray diffraction patterns of as-deposited and

annealed (at 400°C for 10 minutes in air) CdTe layers deposited at the growth voltage of -650 mV. The electrodeposited CdTe films were cubic and the main diffraction peak at $2\theta = 23.95^\circ$ which corresponds to preferred orientation along (111) plane. There are some weak reflections from the (220) and (311) planes. After annealing at 400°C for 10 minutes in air, the intensity of (111) peak decreased accompanying with an increase in (220) and (311) peaks. These peaks correspond to the JCPDS (01-075-2086) data of cubic CdTe. The peak at $2\theta = 22.96^\circ$ belongs to the (111) plane of CdTeO₃ as confirmed by the JCPDS powder file data (01-077-1906). This CdTeO₃ may form when the electrolyte solution exposed to the atmospheric oxygen, interact with the surface of the Cd and Te to make bonds. Kim (Kim, *et al.*, 2011) and Romeo (Romeo, *et al.*, 2000) have also reported that four XRD reflections which belong to (111), (220), (311) and (400) planes in high temperature grown CdTe layers. The information of peaks location, d-spacing, FWHM, growth material, orientation and phase of CdTe of the present study are shown in the Table 1.

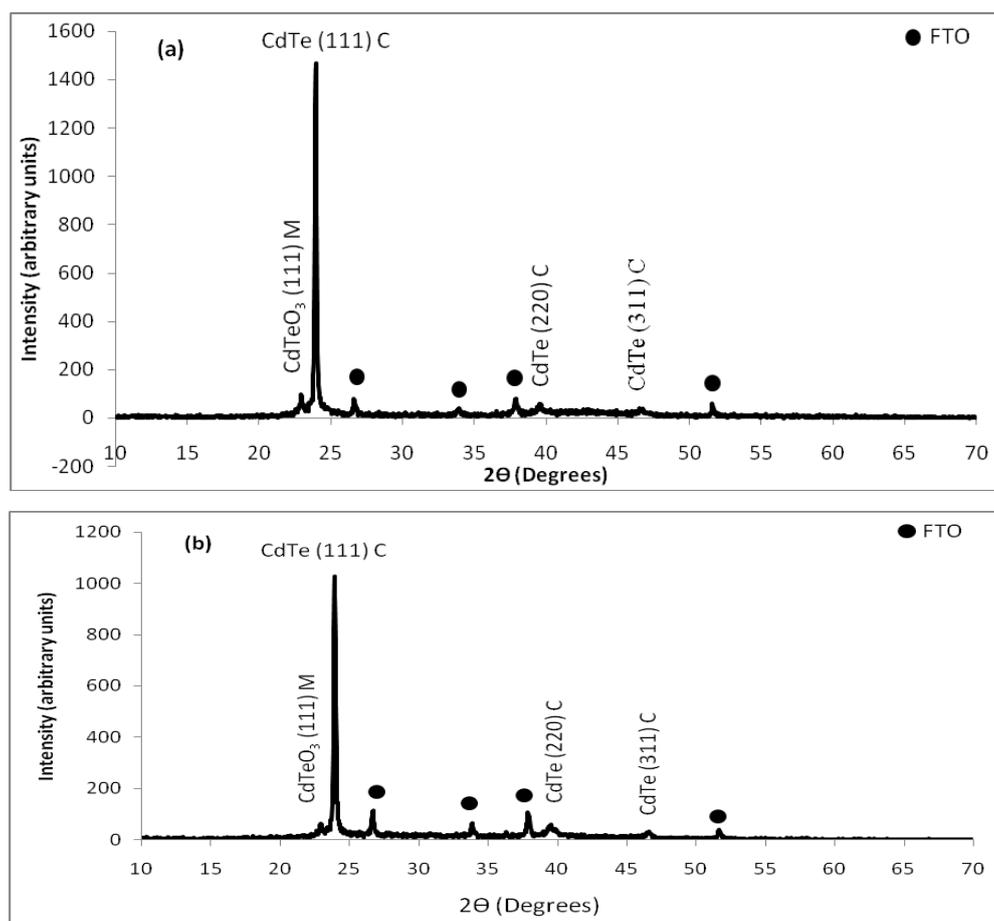


Figure 2: XRD spectra of CdTe layers under (a) as-deposited and (b) annealed (at 400 °C for 10 minutes in air) conditions.

Table 1: Structural parameters of electrodeposited CdTe thin films annealed at 400°C for 10 minutes in air.

Peak location		d-Spacing (Å)		Material	Orientation	Phase
Standard	Observed	Standard	Observed			
22.74	22.86	3.90	3.87	CdTeO ₃	111	Monoclinic
24.03	23.93	3.70	3.71	CdTe	111	Cubic
26.74	26.69	3.33	3.34	FTO	110	Tetragonal
34.00	33.83	2.64	2.64	FTO	101	Tetragonal
37.91	37.87	2.36	2.37	FTO	200	Tetragonal
39.31	39.48	2.29	2.27	CdTe	200	Cubic
46.46	46.65	1.95	1.94	CdTe	311	Cubic
51.73	51.62	1.76	1.76	FTO	211	Tetragonal

Stoichiometric CdTe films give higher efficiency due to the presence of atomic composition of Cd:Te in the ratio of 1:1. With higher Cd or Te presence in the crystal could lead to poor performances of the cell.

It has been recently identified (Dharmadasa, *et al.*, 2014) that in polycrystalline CdTe layers, the grain boundaries melt at 385±5°C in the

presence of Cl and O. At this point the preferential orientation along (111) reduces and (220) and (311) reflections increase. In this experiment, this effect is observed since the annealing temperature (400°C) is above 385±5°C. CdTe crystallites show random orientation formation of layer grains after annealing due to effect of CdCl₂ in

recrystallization of CdTe (Dharmadasa, *et al.*, 2014).

Optical Absorption

Optical absorption was carried out on as-deposited and annealed CdTe films using UV-Vis spectrophotometer to determine the band gap energy of the material. Cary 50 scan UV-Vis Spectrophotometer was used for the band gap measurements. Absorbance of each sample was measured in the wavelength range of 600-900 nm for CdTe thin films. Figure 3 indicates the variation of square of absorbance (A^2) with photon energy spectra for CdTe films deposited at -650 mV. The values for the band gaps were obtained by extrapolating the linear region of (A^2) vs. photon energy plots to (A^2) = 0. The band gap of the as deposited and annealed CdTe was $\sim 1.45 \pm 0.02$ eV which is very close to the band gap of bulk CdTe.

A transmission spectrum of electrodeposited CdTe layers at -650 mV w.r.t. SCE was taken to determine the absorption edge and transmission. Figure 4 represents the typical transmission spectra for as-deposited and annealed (at 400°C for 10 minutes in air) samples. Measurements were taken in the wavelength range 300–1000 nm on the deposited films. The optical transmission for both as-deposited and annealed CdTe samples were about 60% for wavelengths longer than about 850 nm. After annealing, the transmission increased and the absorption edge of the transmission spectrum was sharpened. Metin (Metin, *et al.*, 2003) presented that, the sharper absorption edge indicates fewer defect and impurity energy levels in the films.

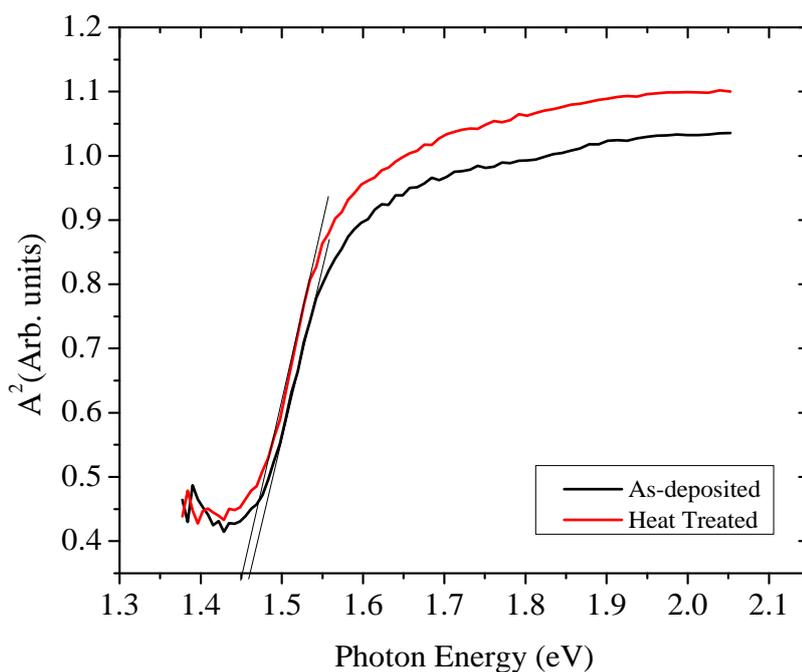


Figure 3: Optical absorption spectra of (a) as-deposited and (b) annealed CdTe films.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) technique was used to study the surface morphology, grain size and uniformity of the CdTe films. A FEI Nova 200 Nano SEM equipment with accelerating voltage of 10 kV was used to study the surface morphology of the thin film layers using secondary electron to form the image. SEM images for as-deposited and annealed CdTe films are shown in Figure 4(a) and (b) respectively. In both cases it appears that crystallites have agglomerated forming large

clusters consisting of many smaller crystallites. After annealing the CdTe films in air for 10 minutes at 400°C, the change in morphology was apparent.

The CdTe layers before annealing consists of the clusters with the small grain sizes as shown in the Figure 5. After heating at 400°C for 10 minutes in air, the uniformity of CdTe was increased. Because of the large surface/volume ratio of nano particles, the small crystallites merge into large crystals upon annealing.

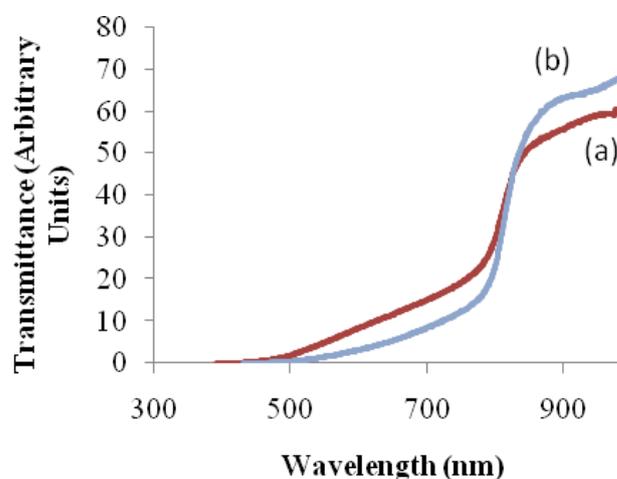


Figure 4: Transmission spectra for (a) as-deposited and (b) annealed CdTe films.

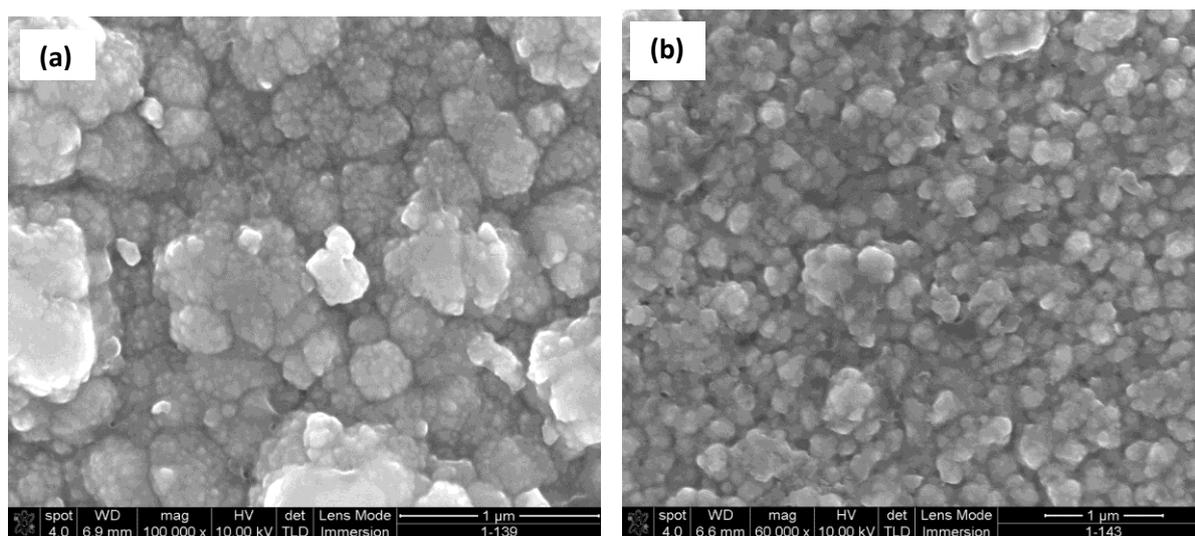


Figure 5: SEM images of (a) as-deposited and (b) annealed CdTe films.

Thickness measurement

The thickness measurements carried out using a profilometer and the average thickness observed for the samples grown under given conditions is ~1.6 μm .

CONCLUSION

CdTe films were grown by electrodeposition on glass/FTO substrates using an aqueous solutions containing 1.50 M CdSO_4 , 1000 ppm CdCl_2 and 150 ppm TeO_2 at pH 2.00 ± 0.02 and at $\sim 70^\circ\text{C}$ temperature for 5 hour deposition time at a voltage of -650 mV. These samples were subjected to a heat treatment process at 400°C for 10 minutes. The films grown under these conditions were $\sim 1.6 \mu\text{m}$ in thickness and have cubic structure with preferred growth orientation along (111) plane. The reflections from (220) and (311) planes showed little increase in their intensity upon annealing. Optical absorption spectra obtained for as deposited and annealed CdTe layers indicated the band gap of 1.45 ± 0.02 eV. After annealing the as deposited n-type CdTe thin films converted into p-type conductivity from its previous n-type conductivity. This could be assisted by the CdCl_2 treatment which boost the transformation of n-type CdTe grown by electrodeposition to p-type conduction on annealing as previously reported (Dharmadasa, et al., 2014; Dharmadasa et al., 2002)

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