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The Effect of Cadmium Chloride Treatment on Close Spaced Sublimated Cadmium Telluride Thin Film Solar Cells

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Abstract — The aim of this investigation is to apply advanced microstructural characterization techniques to study the effect of the cadmium chloride treatment on the physical properties of cadmium telluride solar cells deposited via close-spaced sublimation (CSS) and relate these to cell performance. A range of techniques have been used to observe the microstructural changes as well as the chemical changes before and after cadmium chloride treatment. Electrical measurements that link the device performance with the microstructural properties of the cells have also been undertaken. Transmission Electron Microscopy (TEM) has revealed high densities of stacking faults in the as-grown CdTe samples. Further, it has been observed that these stacking faults are removed during the cadmium chloride treatment. These observations show that the presence of chlorine plays an important role in the removal of these defects and the subsequent production of high efficiency thin film CdTe solar cells. Elemental analysis in the TEM indicates chlorine rich regions appearing at the CdTe/CdS interface as well as at grain boundaries after the treatment.

Index Terms— CdTe, thin film photovoltaics, Cadmium Chloride, Close Space Sublimation.

I. INTRODUCTION

THIN film CdTe is an important low cost photovoltaic device category which is industrially important and which has demonstrated cell efficiencies of over 18% [1]. CdTe is a p-type material with a band gap of 1.45 eV, ideal for photovoltaic conversion. Also it has a very high absorption coefficient, so that only a thin layer ($\sim 2 \mu\text{m}$) is required for almost total absorption. Thin films of CdTe and CdS, which form the p-n junction, can be deposited using a number of different methods and which lead to different structural and chemical properties of the layers. Deposition methods include close spaced sublimation (CSS) [2] which is the most

commonly used method. CSS deposited films are the subject of this study. The cadmium chloride annealing process is known to improve the structural and electronic characteristics of the cell and this process is examined here. The heat treatment can be performed in a number of ways but results in similar outcomes, which normally includes an increase in grain size; grain boundary passivation and inter-diffusion at the CdTe/CdS heterojunction, causing a lower lattice mismatch [3]. Reduction in grain boundary area is considered better for the cell performance as this will reduce areas prone to become recombination centers or electrical barriers [4], while passivation of grain boundaries also works in a similar way.

II. EXPERIMENTAL

The thin film CdTe cells were deposited using close-spaced sublimation on NSG-Pilkington TEC10 fluorine doped tin oxide (FTO) coated on 3 mm soda lime glass in a superstrate configuration as shown in Figure 1. The films were deposited in an all in one vacuum process, the substrate was passed through different chambers at 40 mTorr vacuum, held a few millimeters above graphite boats. The boats were heated to 650°C with the different materials, which then sublimed onto the inverted substrate. Two samples were examined in this study; one underwent a previously optimized post deposition annealing cadmium chloride treatment. The treatment was carried out in vacuum following the layer deposition, cadmium chloride was sublimated to a thickness of $\sim 3 \mu\text{m}$, and then the sample was heated for 8 mins at 400°C in a 2% oxygen atmosphere, causing the cadmium chloride layer to evaporate, this was followed by a copper doping process by sublimating CuCl onto the CdTe layer [5]. The efficiency of this cell was measured to be 11.8%. The second cell was deposited using the same conditions but was not subjected to the cadmium chloride treatment. The efficiency of this cell was measured to be 0.1%. These two circular small area devices of $\sim 1 \text{ cm}^2$ area were then finished by applying a graphite paste back contact. Since the main difference in the processing of the two cells was the use of the cadmium

chloride treatment, any difference in microstructure provides information on the important re-crystallization mechanisms at work.

Fig. 1. A schematic diagram showing the CdTe/CdS superstrate cell structure.

A Leo 1530VP Field Emission Gun Scanning Electron Microscope FEG-SEM was used to investigate surface morphology before and after the cadmium chloride treatment. Transmission Electron Microscopy (TEM) was the tool used to investigate the detailed microstructure of the cells. TEM samples were prepared by Focused Ion Beam (FIB) milling using a dual beam FEI Nova 600 Nanolab. A standard in situ lift out method was used to prepare cross-sectional samples through the coating into the glass substrate. A platinum overlayer was deposited to define the surface of the samples and homogenize the final thinning of the samples. TEM Images were obtained using a Jeol JEM 2000FX operating at 200 kV. STEM was carried out using a Tecnai F20 (S)TEM equipped with a silicon drift detector allowing high spatial resolution Energy Dispersive X-ray (EDX) measurements and chemical mapping. STEM images were collected using a High Angular Annular Dark Field (HAADF) detector at 200 kV. The dual beam was also equipped with a Hikari (EDAX) Electron Backscatter Diffraction (EBSD) camera. Since the surfaces of the samples were rough the ion beam was used to smooth the surface of interest prior to EBSD analysis. EBSD maps were collected using a high current (nominally 10 nA) at 20 kV. A Bruker D2 X-ray Diffractometer was used to carry out all the X-ray Diffraction (XRD) measurements. A Thermo Scientific K-Alpha X-ray Photo-electron spectroscopy (XPS) system was used for depth profiling, using standard relative sensitivity factors to calculate atomic concentrations. The J-V measurements were carried out using a Pasan simulator 3B.

III. RESULTS

Grain morphology

Surface and fracture cross sections were examined using FEG-SEM to provide details of the surface morphology of the CdTe before and after the cadmium chloride treatment. No surface cleaning process was used. The micrographs in Figure 2 compare the untreated and the cadmium chloride treated CdTe surface. These show that the cadmium chloride treatment causes little effect to grain size. This observation is consistent with previously reported studies [6-11]. TEM analysis was used to study the grain structure of these samples in detail.

Fig. 2. SEM micrograph of the surface of an untreated (a) and a cadmium chloride treated (b) CdTe cell.

Figure 3 shows a bright field TEM image of the untreated CdTe cell. The different thin film layers are clearly visible and the grain microstructure can be observed. The CdTe has some small voids between the grains.

Fig. 3. Bright field TEM image of the CdTe cell before cadmium chloride treatment.

More importantly figure 3 shows a high density of stacking faults is observed clearly within the grains and are observed as multiple parallel lines. This observation has been confirmed with diffraction measurements from the same grains. The untreated cell produced much lower device efficiency. The interface between CdTe and CdS is well defined with no voids observed in the untreated cell.

Fig. 4. Bright field TEM image of the CdTe cell after the cadmium chloride treatment.

Figure 4 shows the TEM image of the grain structure after the cadmium chloride treatment. In this sample the parallel lines

within grains are not observed in this sample indicating the removal of the stacking faults. The number of inter-granular voids is also reduced in the sample subjected to the cadmium chloride treatment. The grains are seen to be more rounded, whereas the untreated CdTe is more columnar but of a similar size in cross section. Twinning is also observed in the images obtained after the cadmium chloride treatment.

Fig. 5. High angle annular dark field (HAADF) image of the cadmium chloride treated sample.

Figure 5 reveals the clear occurrence of twins in the treated cell, whereas stacking faults are not observed. It is not clear if the twins are present as a result of the cadmium chloride treatment or that they are now easier to detect in the absence of a high density of stacking faults. This will be the subject of future work.

Elemental analysis

Figure 6 provides an overview of the sample area used to provide information on the spatial distribution of chlorine and sulfur in the cadmium chloride treated cell.

The EDX maps also shown in Figure 6 reveal regions which are chlorine enriched. The enriched regions are within the CdS layer and at the interface with the CdTe layer. The enhanced signal at the surface in Figure 6 is a background signal from the platinum layer (high atomic number) used in sample preparation. The effect can be observed in both the Cl and S maps. The cadmium chloride treatment is a post deposition treatment and is carried out by depositing a layer of cadmium chloride on the surface of the CdTe and heating to 400°C for 8 mins. This is the only source of chlorine in the process. These observations indicate that the chlorine diffuses through the CdTe layer to the interface during the annealing process. A HAADF STEM image of the CdTe/CdS interface and corresponding EDX elemental maps are shown in Figure 7. This reveals the presence of a chlorine rich region located at the CdS interface. This region is approximately 250 nm x 100 nm in size. The corresponding cadmium map shows depletion of cadmium in this area.

Fig. 6. A HAADF STEM image and corresponding chemical distribution maps of chlorine and cadmium from a cadmium chloride treated CdTe cell.

Fig. 7. A HAADF STEM image with corresponding cadmium and chlorine chemical distribution maps.

Fig. 8. X-ray dispersive spectra at two points within and outside a chlorine rich region in the cadmium chloride treated cell.

Figure 8 shows two EDX spectra each collected for 90 seconds, one was obtained from the chlorine rich region featured in Figure 7 and the other in the CdTe layer. The two points for these chemical spot analyses are identified in Figure 7. The spectra show a clear chlorine peak, and lower cadmium and tellurium peaks in the chlorine rich area.

Grain boundary segregation

TEM and EDX analysis was also carried out in the region of grain boundaries. Figures 9 shows a TEM image of a triple point grain boundary and Figure 10 provides EDX spectra from the boundary region and within the grain for comparison.

Fig. 9. A HAADF STEM image of two triple point grain boundaries in the centre of the CdTe layer with the corresponding chlorine and sulfur chemical maps; grain boundaries are highlighted on the chlorine map.

Figure 9 also provides EDX maps to show the location of chlorine and sulfur relative to the grain boundaries. These analyses provide clear evidence for chlorine and sulfur segregation at the grain boundaries after the cadmium chloride treatment. The chemical map shows an increase in counts for both chlorine and sulfur along the boundaries and the spectra show a peak intensity at the grain boundary compared to inside a CdTe grain. Since the grain boundaries are very narrow, the counts recorded are low so the region of Chlorine enrichment in Figure 9 has been highlighted for clarity.

Fig. 10. Energy dispersive X-ray spectra of two points, one within a grain boundary and one within a grain in the cadmium chloride treated cell.

As most of the chlorine is observed in regions along the CdTe/CdS interface, the chlorine must diffuse from the top surface of the CdTe to the interface during the heat treatment and this is further confirmation that the likely route is from the surface through the grain boundaries to the interface.

Electron back-scatter diffraction (EBSD)

Electron back-scatter diffraction (EBSD) requires a very smooth surface for effective microstructural mapping. Therefore to analyse the surface of the CdTe directly a section of the surface was smoothed with a Focused ion beam. The result of this sample preparation is shown in Figure 11 and this provides an adequately smooth surface for EBSD.

Fig. 11. An SEM image of the area smoothed with the ion beam for EBSD analysis.

EBSD can provide a wide range of useful measurements and information, such as grain size and preferred orientation. Figure 12 shows an EBSD derived inverse pole figure/ image quality composite map from the cadmium chloride treated cell. The range of colours contained within this map suggests that the microstructure possesses none or only weakly preferred

grain orientation, a conclusion which was confirmed with more detailed analysis of the EBSD data. This map also shows that the microstructure contains a significant number of twin boundaries.

Fig. 12. EBSD derived IQ/IPF composite map of treated CdTe surface after being polished by an ion beam.

However no twinning was observed in the untreated sample (although the high density of stacking faults may have obscured their detection). The average grain size calculated with EBSD for the cadmium chloride treated sample was $\sim 0.9 \mu\text{m}$, which is slightly smaller than most measurements for CSS grown thin films [8]. For the untreated sample, a similar section again taken at the middle of the CdTe layer had a grain size of approximately $0.8 \mu\text{m}$ and is similar to that of the treated cell.

Fig. 13. XRD plot of the treated and untreated sample.

The XRD analysis shown in Figure 13 was carried out to show the effect of the cadmium chloride treatment on the CdTe layer. The XRD analysis shows that although the same peak positions are present, their relative intensities are different which is indicative of a change in the preferred orientation of grains in the two samples.

Composition-Depth profile – XPS

Fig. 14. XPS composition depth profile (atomic percent against etch time (seconds)) of the untreated CdTe/CdS cell.

XPS composition depth profile measurements were carried out to examine the elemental distribution of the layers with depth after the cadmium chloride treatment and to examine the level the chlorine diffusion through the layers, over a larger area than can be measured in TEM. The untreated cell shows well defined layers and an increasing Cd and decreasing Te concentration nearer the interface. The XPS composition depth profile of the cadmium chloride treated sample revealed a constant level of chlorine as well as oxygen in the CdTe. Both of these elements were introduced during the cadmium chloride treatment. This is the main difference between the two composition depth profiles. The chlorine concentration in the treated cell rises at the CdS interface. This is shown clearly in Figure 15.

Fig. 15. A chlorine composition depth profile of the treated CdTe device structure. The chlorine peaks at the CdS interface.

J-V Characteristics of the treated and untreated cells.

The current-voltage curve in Figure 16 shows the substantial change in electrical performance after the cadmium chloride

treatment. Before the treatment, an efficiency of 0.1% was measured, which increased to 11.77% after the treatment as is shown in Table 1.

Fig. 16. Current-Voltage curve of the treated and untreated cell.

The changes to the microstructure following the treatment include removal of stacking faults, recrystallization of grains and alteration of the chemical properties of the CdTe/CdS layers and their interface. These changes are responsible for the increase in the conversion efficiency of the cell.

	Treated	untreated
Voc (V)	0.770	0.465
Jsc (mA/cm ²)	-21.68	-0.92
FF	0.71	0.23
Efficiency (%)	11.77	0.10

Table. 1. Electrical performance of the treated and untreated cells.

IV. CONCLUSIONS

The motivation for this work is to further understand the effect of the cadmium chloride treatment process, linking the physical microstructural properties of the cell to the electrical performance. Using the in situ lift out technique within a dual beam TEM samples of the coating cross-sections were prepared. TEM analysis revealed the microstructural changes brought about by the cadmium chloride treatment. This has been complemented by EBSD and XRD as well as elemental analysis carried out using EDX mapping in STEM and XPS in composition-depth profiling mode. The combination of these techniques on an as deposited CdTe cell and cadmium chloride treated CdTe cell has provided new insight into the effects of the cadmium chloride treatment.

The primary and unexpected observation is that the untreated CdTe contains high densities of stacking faults and that these are completely removed by the cadmium chloride treatment. This important observation has not been reported previously. Stacking faults in the untreated material have been previously observed [6,7,11] but the effect of their total removal during the cadmium chloride treatment has not been reported.

Chlorine segregation has been observed directly at the CdTe/CdS interface, as well as segregation of chlorine at the grain boundaries. This implies that the chlorine, probably in the form of cadmium chloride, penetrates the CdTe layer during the annealing process and travels along the grain boundaries to the CdS interface. XPS composition depth profiling shows a steady concentration of chlorine throughout the CdTe of around 0.15% which then increases to 0.3% in the CdS. During this process the stacking faults are removed. Further work is now planned on cells processed under different conditions to confirm this remarkable observation.

The cadmium chloride treatment has other effects. Changes in other micro-structural properties include grain size and orientation. Sulfur from the CdS is also observed to have migrated into the CdTe grain boundaries. Twins are observed in the CdTe in the cadmium chloride treated cell and not in the as-deposited cell. This observation is not yet definitive since their detection could be obscured by the high density of stacking faults. This requires further analysis. The electrical performance of the CdTe/CdS solar cell is highly dependent on these changes. Prior to the cadmium chloride treatment an efficiency of 0.1% is measured but following the annealing/cadmium chloride treatment, the cell efficiency improves to 11.77%.

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