

THE MICROSTRUCTURE OF THIN FILM CADMIUM TELLURIDE PHOTOVOLTAIC MATERIALS

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Abstract

In this work cadmium telluride thin film photovoltaic devices have successfully been produced using a novel closed-field magnetron sputtering technique. This technique offers the possibility of producing cells in an all-in-one vacuum process with the potential to provide a new lower cost production route. The sputtered cadmium telluride layers were characterised in detail using a range of advanced microscopy based techniques both in the as deposited and after the cadmium chloride treated state, a treatment that is necessary to produce a working cell. In the as deposited condition the cadmium telluride layer was seen to have a fine-grained columnar structure containing a high density of stacking faults. After the cadmium chloride treatment these grains recrystallized and the new grains were equiaxed with a much lower density of intragranular defects. Similar effects were also observed in samples prepared using close space sublimation.

To understand this recrystallization behaviour during the cadmium chloride treatment, the key treatment parameters were systematically varied. Chemical analysis in Scanning Transmission Electron Microscopy (STEM) showed that chlorine travelled down the cadmium telluride grain boundaries and accumulated adjacent to the cadmium telluride/cadmium sulphide interface. This interface is where the cadmium telluride grains were found to recrystallise first during interrupted cadmium chloride treatments.

The nature of the stacking faults was examined using High Resolution Transmission Electron Microscopy (HR-TEM). This showed that in localised regions up to one plane of atoms per sequence was missing based on the expected zinc blende structure. This changed the packing of the atoms such that a local change in crystal structure occurred. This local change in phase was successfully mapped using Electron Backscatter Diffraction in planar section produced using Focused Ion Beam milling. This was subsequently studied in more detail using Transmission Electron Backscatter Diffraction in the Scanning Electron Microscope, where the intra-granular arrangement of the phases was observed.

HR-TEM was used to quantitatively measure the linear defects in the cadmium telluride layer after thermal annealing with and without the cadmium chloride present. This showed that annealing alone resulted in only a modest reduction in the density of linear defects and grain recrystallisation only occurred in the presence of cadmium chloride.

Cadmium magnesium telluride (CMT) was successfully grown epitaxially onto the cadmium telluride as an electron reflector layer to improve cell performance. During deposition the cell experienced high temperatures and this caused the stacking faults to return in a cell that had been previously cadmium chloride treated. This resulted in a reduction in cell efficiency, providing another link between linear defects and a degradation in cell performance.

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وَقَالَ الَّذِينَ كَفَرُوا لَا تَأْتِينَا السَّاعَةُ قُلْ بَلَىٰ وَرَبِّي لَتَأْتِيَنَّكُمْ عَالِمِ الْغَيْبِ لَا يَعْزُبُ عَنْهُ مِثْقَالُ ذَرَّةٍ فِي
السَّمَاوَاتِ وَلَا فِي الْأَرْضِ وَلَا أَصْغَرُ مِنْ ذَلِكَ وَلَا أَكْبَرُ إِلَّا فِي كِتَابٍ مُّبِينٍ

...He is the Knower of the Unseen, Whom not an atom's weight eludes, either in the heavens or in the earth (Qur'an, 34:3)

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2. Abbas, A., Maniscalco, B., Bowers, J.W., Kaminski, P.M., West, G.D., Walls, J.M., 2013a. Initiation of the cadmium chloride assisted re-crystallization process of magnetron sputtered thin film CdTe, in: 2013 IEEE 39th Photovoltaic Specialists Conference (PVSC). IEEE, pp. 1930–1934. doi:10.1109/PVSC.2013.6744847
3. Abbas, A., Maniscalco, B., Bowers, J.W., Kaminski, P.M., West, G.D., Walls, J.M., 2014. Cadmium Chloride Assisted Re-Crystallization of CdTe: The Effect of Varying the Annealing Time. MRS Proceedings.
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Table of Contents

CERTIFICATE OF ORIGINALITY	II
ABSTRACT	IV
ACKNOWLEDGEMENT	V
LIST OF PUBLICATIONS	VII
TABLE OF CONTENTS	VIII
CHAPTER 1. INTRODUCTION.....	1
1.1 GLOBAL ENERGY DEMAND.....	1
1.2 FACTORS INFLUENCING ENERGY PRODUCTION ROUTES	2
1.3 RENEWABLE ENERGY TECHNOLOGIES.....	2
1.4 PHOTOVOLTAICS AS A SOURCE OF ENERGY	2
1.5 PHOTOVOLTAIC SYSTEMS	3
1.6 THIN FILM SOLAR CELLS	4
1.7 PROJECT MOTIVATION AND OBJECTIVES FOR CADMIUM TELLURIDE BASED SOLAR CELLS	4
CHAPTER 2. BACKGROUND	5
2.1 INTRODUCTION	5
2.2 THE P-N JUNCTION – CADMIUM TELLURIDE	5
2.3 ELECTRICAL CHARACTERISTICS OF SOLAR CELLS.....	9
2.4 MATERIAL CHARACTERISTICS OF A CADMIUM TELLURIDE SOLAR CELL.....	11
2.5 CADMIUM TELLURIDE MATERIAL PROPERTIES.....	12
2.6 CADMIUM TELLURIDE CELL STRUCTURE	13
2.7 CADMIUM SULPHIDE – THE WINDOW LAYER	15
2.8 BACK CONTACT PROPERTIES	15
2.9 APPROACHES TO INCREASE DEVICE EFFICIENCIES.....	17
2.10 MICROSTRUCTURAL CHARACTERIZATION OF CADMIUM TELLURIDE SOLAR CELLS.....	18
2.11 THE CADMIUM CHLORIDE TREATMENT.....	18
2.12 STRESSES AND GRAIN SIZE IN CADMIUM TELLURIDE FILMS	19
2.13 CHARACTERISATION OF CADMIUM CHLORIDE TREATED CELLS	20
2.14 THEORY OF CADMIUM CHLORIDE HEAT TREATMENT TO DATE.....	21
2.15 THEORY OF DEFECTS IN CADMIUM TELLURIDE	22
2.16 PROJECT OBJECTIVES.....	23
CHAPTER 3. EXPERIMENTAL METHODOLOGIES.....	25
3.1 INTRODUCTION	25

3.2	PROCESSING SAMPLES – DEPOSITION METHODS	25
3.2.1	<i>Magnetron Sputtered Solar Cells</i>	25
3.2.2	<i>Closed Space Sublimated Solar Cells</i>	27
3.2.3	<i>Chemical Bath Deposition (CBD) of Cadmium Sulphide</i>	29
3.2.4	<i>Transparent Conducting Oxides</i>	29
3.2.5	<i>Gold/Copper Back Contact</i>	30
3.3	CADMIUM CHLORIDE TREATMENT	30
3.3.1	<i>Solution Based Cadmium Chloride Treatment</i>	30
3.3.2	<i>Vapour Based Cadmium Chloride Treatment</i>	31
3.3.3	<i>Cadmium Chloride Deposition via Evaporation</i>	32
3.4	ANNEALING TREATMENT WITHOUT CADMIUM CHLORIDE.....	32
3.5	CHARACTERIZATION	32
3.5.1	<i>Current-Voltage Measurements (J-V)</i>	32
3.5.2	<i>Spectrophotometer Transmission Measurements</i>	33
3.6	MICROSTRUCTURAL CHARACTERIZATION	33
3.6.1	<i>Scanning Electron Microscopy</i>	33
3.6.1.1	Preparing samples for SEM	33
3.6.1.2	Field Emission Gun-Scanning Electron Microscope.....	33
3.6.1.3	Fracture Cross Section (SEM)	34
3.6.2	<i>TEM Sample Preparation using a Focussed Ion Beam</i>	34
3.6.3	<i>Transmission Electron Microscopy (TEM)</i>	35
3.6.3.1	Stacking Fault Characterization in TEM.....	36
3.6.3.2	High Resolution Transmission Electron Microscopy (HRTEM)	36
3.6.3.3	Scanning Transmission Electron Microscopy (STEM).....	37
3.6.3.4	Energy Dispersive X-ray (EDX) in Scanning Transmission Electron Microscopy (STEM).....	37
3.6.4	<i>X-Ray Diffraction (XRD)</i>	37
3.6.5	<i>Electron Backscatter Diffraction (EBSD)</i>	38
3.6.6	<i>Transmission Electron Backscatter Diffraction (T-EBSD)</i>	39
3.6.7	<i>X-Ray Photoelectron Spectroscopy (XPS)</i>	39
3.6.7.1	XPS Depth Profile.....	40
3.6.8	<i>Secondary Ion Mass Spectroscopy (SIMS)</i>	40
CHAPTER 4. THE DEVELOPMENT OF CADMIUM TELLURIDE SOLAR CELLS DEPOSITED BY CLOSED FIELD MAGNETRON SPUTTERING.....		41
4.1	CHAPTER BACKGROUND AND AIMS.....	41
4.2	THE DEPOSITION OF THE CADMIUM SULPHIDE WINDOW LAYER VIA MAGNETRON SPUTTERING	42
4.2.1	<i>Closed Field Magnetron Sputtered Film Properties</i>	42
4.2.1.1	Cadmium Sulphide Surface Morphology.....	42
4.2.1.2	Cadmium Sulphide Growth Morphology.....	43
4.2.1.3	Sputtered Cadmium Sulphide Crystallographic Properties	43
4.2.2	<i>Comparison of Closed Field Magnetron Sputtered and Chemical Bath Deposited Thin Film Cadmium Sulphide</i>	45

4.2.2.1	Surface Morphology	45
4.2.2.2	Cadmium Sulphide Benchmark Crystallographic Sample Properties	46
4.3	THE DEPOSITION OF THE CADMIUM TELLURIDE ABSORBER LAYER VIA MAGNETRON SPUTTERING ...	48
4.3.1	<i>Thin Film Cadmium Telluride Properties</i>	49
4.3.2	<i>The Effect of Argon Flow Rates on Thin film Cadmium Telluride</i>	50
4.3.2.1	Annealing a Stressed Cadmium Telluride Thin Film.....	54
4.3.3	<i>The Effect of Deposition Temperature on Thin film Cadmium Telluride</i>	55
4.3.3.1	The Effect of the Substrate on Sputtered Thin Films	56
4.3.4	<i>Comparison of Novel Sputtered Cadmium Telluride with Close-Spaced Sublimated Cells</i>	59
4.4	THE DEVELOPMENT OF A PIN-HOLE FREE CADMIUM SULPHIDE/CADMIUM TELLURIDE THIN FILM CLOSED FIELD SPUTTERED CELL	60
4.4.1	<i>Bi-Layer Structure Thin Film Cadmium Telluride</i>	61
4.4.2	<i>Surface Contamination and Pre-deposition TCO Surface Cleaning</i>	62
4.5	CADMIUM CHLORIDE TREATMENT OF MAGNETRON SPUTTERED CADMIUM TELLURIDE THIN FILMS .	63
4.5.1	<i>Solution Based Cadmium Chloride Treatment of Cadmium Telluride Thin Films</i>	63
4.5.1.1	Initial Treatment Results using a Saturated Solution of Cadmium Chloride in Methanol.....	63
4.5.1.2	Delamination of Thin Film Depositions during Cadmium Chloride Treatment.....	64
4.5.1.3	Reduced Cadmium Chloride Solution Concentration Treatments.....	66
4.5.1.4	Summary of the Solution Based Cadmium Chloride Treatment	72
4.5.2	<i>Vapour Transport Based Cadmium Chloride Treatment of Cadmium Telluride Thin Films</i>	73
4.5.3	<i>Pre-Optimised Evaporated Cadmium Chloride Treatment of Cadmium Telluride Thin Films</i>	74
4.6	COMPARISON OF THE CLOSED FIELD MAGNETRON SPUTTERED CELLS TO OTHER DEPOSITION TECHNIQUES	79
4.6.1	<i>Comparison of the Novel Closed Field Magnetron Sputtered Cells to Closed-Space Sublimated Benchmark Cells</i>	79
4.7	SUMMARY.....	80
CHAPTER 5. ANALYSIS OF TRANSPARENT CONDUCTING OXIDES FOR CADMIUM TELLURIDE BASED SOLAR CELLS.....		81
5.1	INTRODUCTION	81
5.2	BACKGROUND TO TRANSPARENT CONDUCTING OXIDES	81
5.3	FLUORINE DOPED TIN OXIDE (FTO) TEC GLASS	82
5.4	PROPERTIES OF PILKINGTON TEC15 TCO	83
5.5	MICROSTRUCTURAL ANALYSIS OF TEC10 TCO.....	85
5.6	MICROSTRUCTURAL ANALYSIS OF TEC7 TCO.....	86
5.7	SURFACE CLEANING OF TEC GLASS.....	87
5.7.1	<i>Cleaning Methods</i>	87
5.7.1.1	Surface Analysis of the Untreated TEC10 Sample	89
5.7.1.2	Surface Analysis of the Annealed TEC10 Sample.....	89
5.7.1.3	Surface Analysis of the TEC10 Sample Cleaned in a Ultrasonic Bath of Isopropanol	90
5.7.1.4	Surface Analysis of the TEC10 Sample after Soapy Water Ultrasonic Bath Cleaning	91
5.7.1.5	Surface Analysis of the TEC10 Sample which underwent a Plasma Clean	92

5.7.1.6	Surface Analysis of the TEC10 Sample Cleaned using a Standard 3 Step RCA Cleaning	93
5.7.1.7	Surface Analysis of the TEC10 Sample Cleaned using a 4 stage Process.....	93
5.8	<i>DEVELOPMENT OF INDIUM DOPED TIN OXIDE (ITO) TRANSPARENT CONDUCTOR</i>	95
5.9	SUMMARY.....	95
CHAPTER 6. THE EFFECTS OF CADMIUM CHLORIDE ON CLOSE-SPACED SUBLIMATED CADMIUM TELLURIDE SOLAR CELLS		96
6.1	CHAPTER SCOPE	96
6.2	EXPERIMENTAL PROCESSING	97
6.2.1	<i>Sample Performance</i>	97
6.3	MICROSTRUCTURAL CHARACTERIZATION OF UNTREATED AND TREATED CADMIUM TELLURIDE.....	99
6.3.1	<i>Grain Morphology</i>	99
6.3.2	<i>Cross-Section Analysis</i>	99
6.4	CADMIUM TELLURIDE GRAIN CHARACTERISTICS	100
6.4.1	<i>Analysis of the Untreated Cadmium Telluride Cells using TEM</i>	100
6.4.2	<i>Cadmium Telluride Stacking Defect Analysis in the Untreated Cell</i>	103
6.4.3	<i>Analysis of the Treated Cadmium Telluride Cells using TEM</i>	106
6.4.4	<i>Characterization of Defects within the Treated Cadmium Telluride Grains</i>	108
6.4.5	<i>Interdiffusion during the Cadmium Chloride Treatment</i>	110
6.4.6	<i>Grain Boundary Segregation during the Cadmium Chloride Treatment</i>	111
6.5	STACKING FAULT REMOVAL VIA CADMIUM CHLORIDE TREATMENT OBSERVATION IN TEM	113
6.5.1	<i>Morphological Changes during the Cadmium Chloride Treatment</i>	114
6.6	INTERDIFFUSION INVESTIGATION VIA DEPTH PROFILING.....	115
6.6.1	<i>Depth Profiling using XPS for Chemical Distribution throughout the Cell</i>	115
6.6.2	<i>Dynamic Secondary Ion Mass Spectrometry (SIMS) Depth profiles</i>	116
6.7	INVESTIGATION OF CADMIUM TELLURIDE GRAIN CRYSTALLOGRAPHY.....	118
6.7.1	<i>X-Ray Diffraction Comparison of Treated and Untreated Cadmium Telluride</i>	118
6.7.2	<i>Electron Backscatter Diffraction on Cadmium Telluride Solar Cells</i>	119
6.7.3	<i>Electron Backscatter Diffraction of the Untreated Cadmium Telluride</i>	119
6.7.4	<i>Crystallographic and Grain Morphology of Treated Cadmium Telluride Thin Films</i>	120
6.7.5	<i>Transmission Electron Backscatter Diffraction (TEBSD) for Twin Analysis</i>	121
6.8	SUMMARY.....	122
CHAPTER 7. THE INVESTIGATION OF CADMIUM CHLORIDE ASSISTED RE-CRYSTALLIZATION OF CADMIUM TELLURIDE.....		123
7.1	CHAPTER SCOPE	123
7.2	CADMIUM CHLORIDE ASSISTED RE-CRYSTALLIZATION OF CADMIUM TELLURIDE: THE EFFECT OF TREATMENT TIME.....	123
7.2.1	<i>Introduction</i>	123
7.2.2	<i>Sample Description with Varying Treatment Times</i>	125
7.2.3	<i>Cadmium Chloride Treatment: Initiation and Under Treatment</i>	126

7.2.4	<i>Cadmium Chloride Treatment: Partial Activation</i>	128
7.2.5	<i>Cadmium Chloride Treatment: Optimum Activation.....</i>	130
7.2.6	<i>Cadmium Chloride Treatment: Over-Treatment</i>	131
7.3	CADMIUM CHLORIDE ASSISTED RE-CRYSTALLIZATION OF CADMIUM TELLURIDE: THE EFFECT OF THE ANNEALING TEMPERATURE	132
7.3.1	<i>Introduction</i>	132
7.3.2	<i>Morphological Changes of the Cell with Treatment Temperature</i>	132
7.3.3	<i>Crystallographic Changes of the Cadmium Telluride Thin Film with Treatment Temperature... 133</i>	133
7.3.4	<i>Change of Chlorine Concentration Build-up at the Interface using X-ray Photo-Electron Spectroscopy</i>	135
7.3.5	<i>Characterization of Defects in the Cadmium Telluride Grains</i>	136
7.3.6	<i>Performance Properties of the Cells.....</i>	137
7.3.7	<i>Summary of Varying the Cadmium Chloride Treatment Temperature</i>	138
7.4	THE EFFECT OF ANNEALING TREATMENTS ON CLOSE SPACED SUBLIMATED CADMIUM TELLURIDE THIN FILM SOLAR CELLS	139
7.4.1	<i>Introduction and Objectives of the Annealing Treatment without Cadmium Chloride</i>	139
7.4.2	<i>Sample Description for the Annealing Treatments</i>	139
7.4.3	<i>Methodology for Stacking Fault Density Measurements</i>	140
7.4.4	<i>Reference Cadmium Chloride treated and Untreated Cadmium Telluride Cells</i>	140
7.4.5	<i>Change in Defect Density with Treatment Time and Temperature.....</i>	140
7.4.6	<i>Summary of Varying the Annealing Temperature and Time without the Presence of Cadmium Chloride</i>	141
7.5	CHAPTER SUMMARY	142
CHAPTER 8. INVESTIGATION OF LOCALIZED PHASE CHANGES IN THIN FILM CADMIUM TELLURIDE PHOTOVOLTAIC MATERIAL WITH HIGH LATTICE DEFECT DENSITIES.....		143
8.1	CHAPTER SCOPE	143
8.2	INTRODUCTION	143
8.3	TRANSMISSION ELECTRON BACK-SCATTER DIFFRACTION (TEBSD) AS A TOOL TO BETTER INDEX THIN FILM CADMIUM TELLURIDE SOLAR CELLS	147
8.4	EMBEDDED HEXAGONAL PHASES IDENTIFIED USING TRANSMISSION ELECTRON BACK-SCATTER DIFFRACTION	149
8.5	EMBEDDED HEXAGONAL ATOMIC STACKING IN UNTREATED CADMIUM TELLURIDE GRAINS	150
8.6	SUMMARY.....	151
CHAPTER 9. MICROSTRUCTURAL ANALYSIS OF CADMIUM MAGNESIUM THIN FILMS FOR ELECTRON REFLECTOR APPLICATION FOR CADMIUM TELLURIDE SOLAR CELLS..		152
9.1	CHAPTER SCOPE	152
9.2	INTRODUCTION	152
9.2.1	<i>Samples Analysed</i>	153
9.3	INITIAL CMT DEPOSITION	154

9.4	EFFECT OF MAGNESIUM CONCENTRATION ON CMT	157
9.4.1	<i>Low Magnesium Containing CMT Electron Reflector</i>	157
9.4.2	<i>Medium Magnesium Containing CMT Electron Reflector</i>	160
9.4.3	<i>High Magnesium Containing CMT Electron Reflector</i>	162
9.5	EFFECT OF THE CADMIUM CHLORIDE TREATMENT ON CMT	163
9.6	EFFECT OF DEPOSITION TEMPERATURE ON CMT ELECTRON REFLECTOR THIN FILM	167
9.7	THE EFFECT OF CMT AND CADMIUM CHLORIDE ON CADMIUM TELLURIDE CELLS.....	172
9.7.1	<i>Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT</i>	173
9.7.2	<i>Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT /Anneal</i> <i>175</i>	
9.7.3	<i>Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT</i> <i>/Anneal/Cadmium Chloride</i>	176
9.7.4	<i>Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT</i> <i>/Cadmium Chloride</i>	179
9.8	SUMMARY.....	181
CHAPTER 10.	CONCLUSIONS AND FURTHER WORK	182
10.1	CONCLUSIONS.....	182
10.2	SUGGESTED FURTHER WORK.....	184
REFERENCES		185

CHAPTER 1. INTRODUCTION

1.1 Global Energy Demand

The global energy demand stands today at approximately 16 terawatts and is expected to double over the next 30 years¹. This is due to an increasing population which is expected to add an extra 2 billion people by 2040, according to UN predictions². In addition the continued growth of developing countries will demand an increasing amount of energy for both industrial and domestic purposes.

Figure 1.1a shows the world energy consumption prediction of energy sources from 2000 until 2050 and extrapolated to 2100. Over the 50 years there is increasing proportion of energy provision from renewable energy sources and by 2050 it is predicted to account for the largest proportion of energy production. The demands for energy will almost triple in this 50 year period, if the trend seen over the last two decades continues³. Most new energy demand will come in the form of electricity, as the world's population increase and life styles change to a more energy dependent way. The ever increasing demand for energy is inevitably going to continue for the foreseeable future. Currently fossil fuels are the main source of this energy, however fossil fuel stocks are finite and are predicted to start to deplete over the next 50 years⁴. Alternate energy sources are required; this has provided a strong motivation to develop more sustainable energy sources as well as improved energy production technologies as demonstrated in Figure 1.1b.

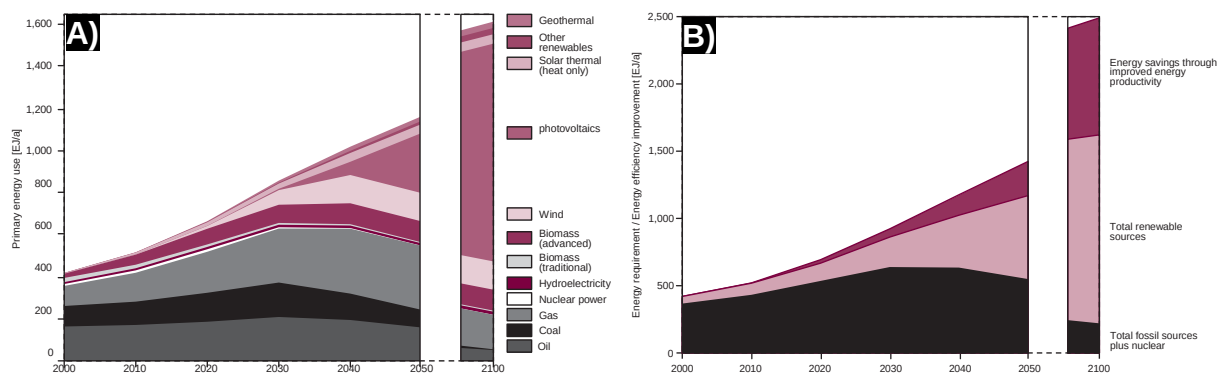


Figure 1.1- a) World energy consumption predictions from 2000-2100 showing contributing energy sources, b) prediction of energy source (renewable/fossil fuels) and gains from improved efficiency of energy production⁵

Fossil fuels currently dominate energy production. The use of coal is predicted to decrease with oil remaining constant, and gas increasing two fold⁵. However as there is an increase in demand for energy, renewable energy is predicted to fill the shortfall in energy production.

The largest predicted renewable contributors include biomass, wind and solar energies. The move to renewable resources is underpinned by a combination of political pressure to implement “greener” technologies, depletion of current energy sources⁴ and rising cost of current raw materials⁶.

1.2 Factors Influencing Energy Production Routes

The decision to move from traditional energy sources to renewable/sustainable sources is made at different levels in society. These include members of the public decisions to buy hybrid/electric cars or installing solar panels and government decisions for incentives such as feed-in tariffs for renewable energy production. Also international decisions have a major impact, such as a change in tax laws and emissions trading by providing economic incentives if a reduction of emission of pollutants is achieved.

1.3 Renewable Energy Technologies

There are several categories of renewable energy technologies harnessing energy from different sources; these include solar, wind, geothermal, hydro and biomass. A range of technologies are required to fulfil the energy requirements of the future. Historically the production of energy from renewable sources has had a higher cost than traditional sources (coal, oil and gas). However with improvement in technologies the cost of renewable energy production has decreased. This includes photovoltaic technologies, where the module price over the last 4 years has decreased three fold to less than £0.60/watt-peak⁷, rivalling the cost of fossil fuel energy production.

1.4 Photovoltaics as a Source of Energy

Of the renewable energy technologies, photovoltaics have the potential to play a key role in energy production over the next few decades as the non-renewable conventional sources start to deplete and increase in cost. Photovoltaic power plants are attractive as planning time is shorter than most other methods. In addition, after installation, little maintenance is required resulting in an extremely low running cost, and a reasonable unit lifetime of approximately 25 years can be expected⁸.

Electromagnetic radiation is converted to electricity via the photovoltaic effect, where the sun is the source of the radiation. Different wavelengths of light will ultimately affect the amount of radiation which is converted into electricity. Therefore extensive work has been done to characterize the radiation from the sun in different locations, to allow modelling of the

radiation in the lab in order to calculate the efficiency of cells under the sun's light using a light source other than the sun.

At sea level the sun provides approximately 1 kW/m^2 , giving a 24 hour annual average of 0.2 kW/m^2 , with a power of $102,000 \text{ TW}^9$. This powers the ecosystem and the environment, and helps sustains life on earth. The solar energy from the sun that reaches the earth's surface is over 10,000 times the global energy demands¹⁰, but the distribution of this is not homogeneous due to the curvature of the earth and atmosphere. AM0 is reference to the radiation outside of the atmosphere, AM1 is reference to the radiation when the sun is directly overhead and passes through the atmosphere at its exact thickness. AM1.5 is reference to the radiation with a typical solar spectrum at sea level on a clear day, and is the standard usually used to characterise solar cells. The spectral irradiance under these conditions is illustrated in Figure 1.2.

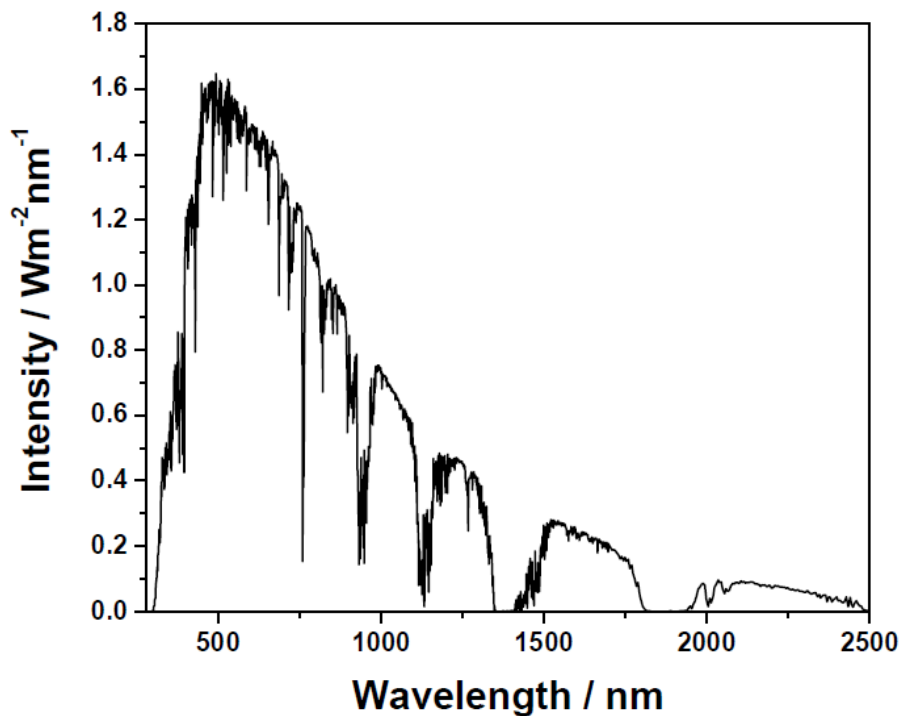


Figure 1.2 - Spectral irradiance of the AM1.5G standard spectrum¹¹

1.5 Photovoltaic Systems

The two main photovoltaic technologies used now are silicon based and thin film devices. Silicon based systems are more widely used, accounting for 87% of all solar panels¹². These systems are more developed with cell efficiencies recorded at 25% for mono-crystalline devices¹³, whereas thin film photovoltaics are more novel and less developed and account for only 11% of the market¹⁴. Thin film devices therefore have a larger potential to be improved and become a main source of electricity production. This study will be based on further

understanding and development of low cost high efficiency thin film solar cells.

1.6 Thin Film Solar Cells

Thin film solar cell development has improved dramatically over the last 20 years, where cadmium telluride cells have reached an efficiency of 20.4% (recorded by First Solar/General Electric) and amorphous silicon has reached 14%¹³. The major advantages of thin films compared with silicon is their potential for lower cost and the increased geometric flexibility of the substrate. Thin film technologies include cadmium telluride, copper indium gallium diselenide, dye sensitised cells, gallium arsenide and amorphous silicon. Of these materials cadmium telluride has by far been the most successful with a 43% market share of all thin film technologies¹⁴.

1.7 Project Motivation and Objectives for Cadmium Telluride Based Solar Cells

Cadmium telluride is well known for its good photoelectric properties and is reaching upwards of 20% in lab efficiencies¹³, however this could still be improved and has the most potential for being a key producer of electricity in the future. Therefore it is the chosen material for this study. As only a 2 μm layer is required for almost full absorption of visible light, the material costs are considerably lower than other technologies, as well as a wide range of substrates can be used.

The novel deposition technique close field pulse DC magnetron sputtering will be studied as it has many advantageous features such as low deposition temperatures with high deposition rates¹⁵, as well as uniformity and accuracy and has not been used in this way before. Magnetron sputtering also has the potential to be scaled up into an industrial in-line process, potentially mass producing solar cells in a continuous low cost process.

Close space sublimated cadmium telluride solar cells will also be studied in detail, as it is the standard way to produce cells in industry. Focus is on the cadmium chloride treatment, by a systematic study to examine how the key process parameters used to produce the cells, affects the microstructure. This is a key part of the process which activates the cell and is not currently fully understood.

CHAPTER 2. BACKGROUND

2.1 Introduction

This chapter starts with a description of how cadmium telluride solar cells generate electricity from light energy (photons). This fundamental understanding is necessary to study the interrelationship between the microstructure and the electrical properties of the thin films. The material properties and fabrication procedures used to produce cells are examined, together with the characterization techniques used to study microstructural behaviour. A current literature review of characterization techniques used to study the cadmium telluride cell properties and the effects of the cadmium chloride properties is also included. A recent review detailing the properties of cadmium telluride and role of defects within the material is available in the literature and this topic will not be reproduced here¹⁶.

2.2 The p-n Junction – Cadmium Telluride

The basic structure of a solar cell is a p-n junction which is comprised of two layers; a p-type material and an n-type material. When these layers are illuminated a potential difference is created between the layers via the photovoltaic effect. The voltage causes a current which can be used to power electrical devices. A solar cell must have three main parts:

- 1- A semiconductor which is sensitive to light
- 2- A p-n junction which separates the electron hole pairs
- 3- Electrical contacts on either side of the p-n junction to allow the generated current to be used for useful work

A wide range of materials can be used for each of these parts of the cell; the majority of solar cells are mono or poly crystalline silicon. The p-n junction of a silicon based cell is known as a homo-junction as both the p-type and n-type material is silicon, but they are doped with impurities in order to form the p-n junction. Thin film p-n junctions include cadmium sulphide/cadmium telluride and cadmium sulphide/copper indium gallium diselenide.

Understanding the main principals of photovoltaics and the physics behind the photovoltaic effect is fundamental to further develop solar cells. This includes the microstructural and electrical properties which are also interlinked.

Figure 2.1 shows the band energy diagram for a p-type and n-type material, the Fermi level (E_F) is shown in the p-type material to be closer to the valence band (V_B) whereas in the n-

type it is closer to the conduction band (C_B). The conduction band (C_B) is populated with free electrons and the valence band (V_B) is populated with free holes.



Figure 2.1– A schematic model of a p-n junction showing the energy band positions¹⁷.

This means when the p-type and n-type material are brought into contact they will form a p-n junction. The electrons will move from the n-type to the p-type material and the holes will move in the opposite direction as the donor level (E_D) is higher in the n-type material and the acceptor level (E_A) is lower in the p-type material. The carriers diffuse from the higher to the lower concentration, until there is a depleted region formed which is positive on the p-side due to a high concentration of ions and negative on the n-type side as there is an equally high concentration of holes.

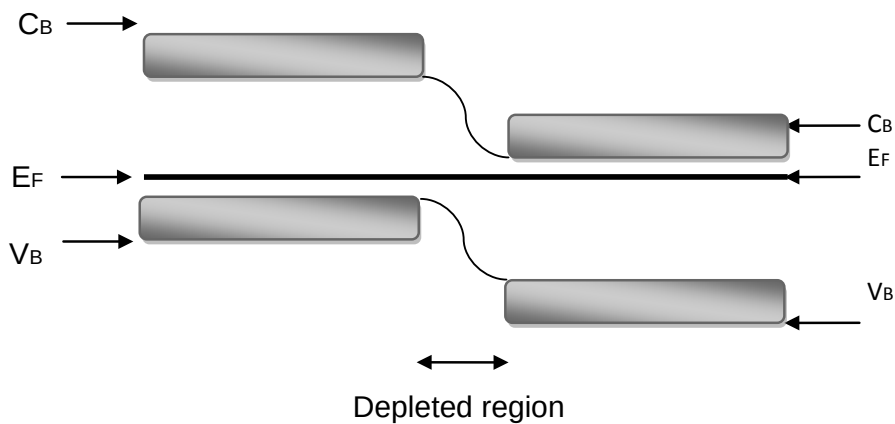


Figure 2.2– A schematic model showing a p-n junction with a depleted region and energy bands

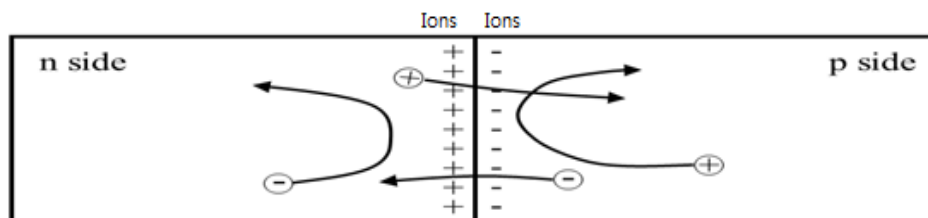


Figure 2.3 – A schematic model of a p-n junction at equilibrium showing the movement of electrons and holes¹⁷

Once the concentration of the electrons and holes has built up on either side of the junction the diffusion will stop when the gradient of carriers is balanced. This causes the Fermi levels in the p and n type material to become equal and therefore the conduction and valence band is

forced to bend as shown in Figure 2.2 and Figure 2.3. Due to the build-up of charge on either side of the junction an electric field is formed, this is critical to the photovoltaic effect. There are two main types of p-n junction; this is due to the material or materials which are used to form the junction. A homojunction is made from the same material, but each side of the junction is doped with impurities. The main advantage of this type of junction is perfect band alignment and perfect lattice match across the junction. This has a positive effect on the cell's electrical properties, and, ultimately the performance of the cell.

The cadmium sulphide/cadmium telluride is a heterojunction cell. This is shown in Figure 2.4 which shows the difference in band energy states. The materials must be selected carefully to avoid lattice mismatch or the cell's performance will be diminished although inter-diffusion of the materials during manufacture will reduce the lattice mismatch. In the cadmium sulphide/cadmium telluride cell, the cadmium sulphide is n-type as it has a wider band gap which allows for a larger current generation from the higher energy electromagnetic waves (photons).

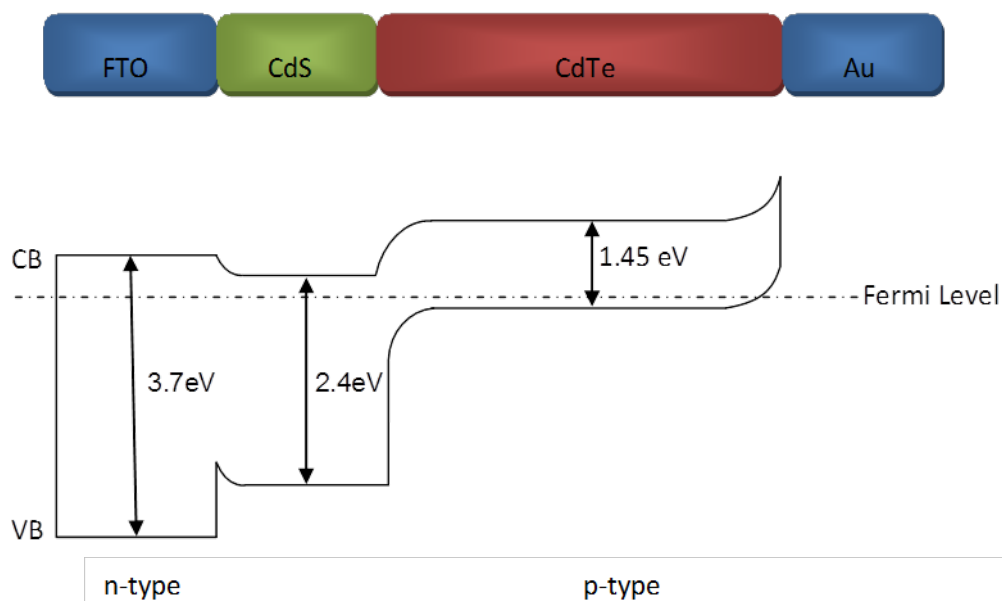


Figure 2.4– A schematic model of band diagram energies of a cadmium sulphide/cadmium telluride cell.
Adapted from ¹⁷

Essentially the two types of p-n junction work in the same way. Electricity is generated via the photovoltaic effect. First the electromagnetic radiation is absorbed by the semiconductor material and electron hole pairs are generated, which are the charge carriers. Next the electron hole pairs are separated at the junction, followed by the migration of the charge carriers to a junction where they are collected by the electrical contacts. The generation of

electron-hole pairs can only happen when the photon energy is greater than the band gap energy; this is shown in Figure 2.5.

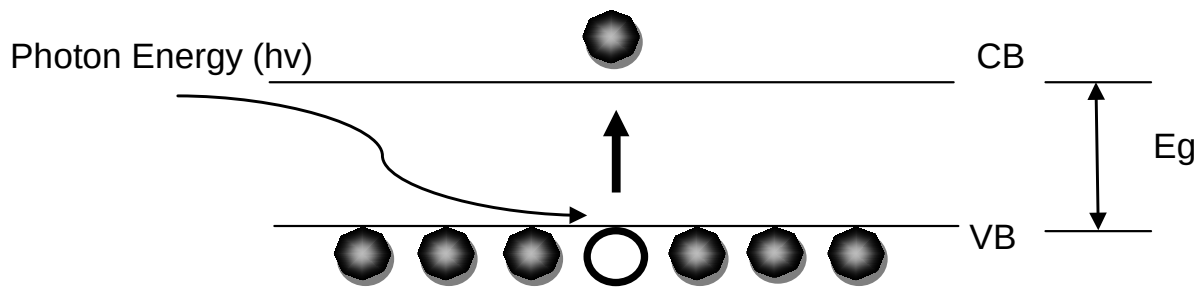


Figure 2.5– A schematic model of the photovoltaic effect showing the separation of the electron hole pair

Absorbing semiconducting materials can have direct or indirect band gaps; they are distinguished by the k-vector from the maximum energy state of the valence band gap to the minimum energy state of the conduction band gap, in the Brillouin zone, shown in Figure 2.6.

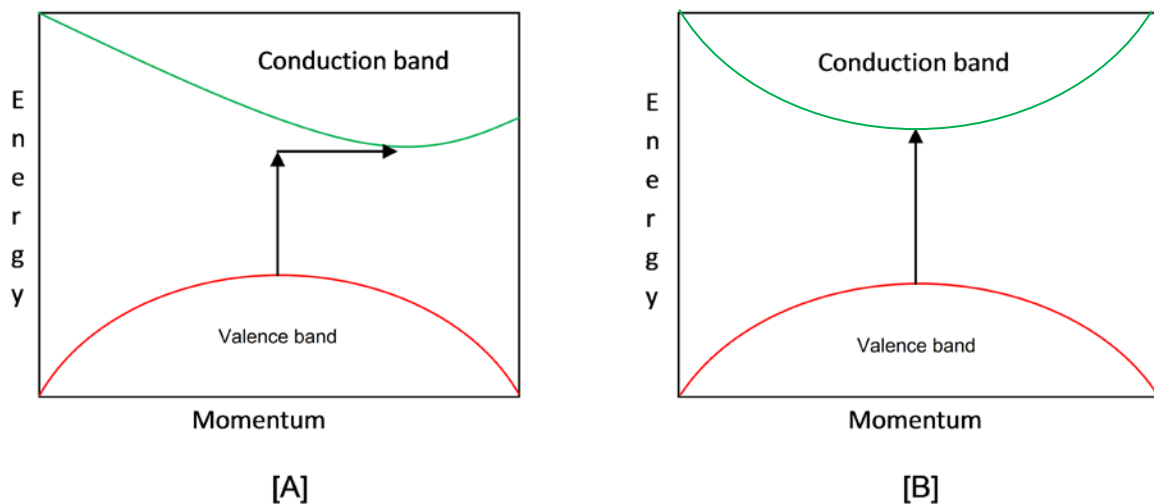


Figure 2.6 - A schematic model illustrating the difference between [A] an indirect band gap showing the electron cannot transfer from the valence band to the minimal energy conduction band without changing its momentum and [B] a direct band gap semiconductor material

Cadmium telluride has a direct band gap; therefore the photons are absorbed within 2 μm , whereas an indirect band gap material such as silicon will need a much thicker width of approximately 200 μm to absorb all the radiation. Therefore direct band gap materials if they have a band gap close to the photon energy will be good photovoltaic materials; hence cadmium telluride, which has a band gap of 1.45 eV is close to the optimum for electron hole pair generation. Every photon which is absorbed and possesses energy higher than the band gap will cause the generation of one free electron and one free hole. To be able to create a voltage and a current to do external work the electron-hole pair must separate first and then

recombine. An electric field is generated due to the build-up of charge on either side of the p-n junction; this favours the diffusion of electrons to the n-type side. The electrons generated at the n-type material which fall into the electron field will be forced “downhill” across the p-n junction interface show in Figure 2.7.

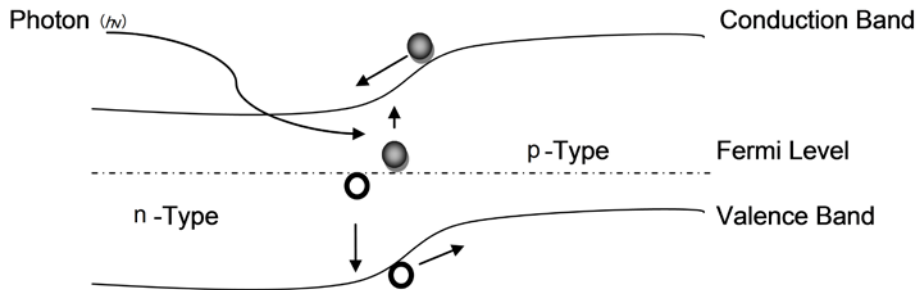


Figure 2.7– A schematic model of a p-n junction showing the influence of an electric field during charge separation²⁶

The hole generated will interact with the electric field and be forced into the p-type material. This means when the photon energy is absorbed, holes are influenced to the p-type material and electrons are encouraged to go the opposite way to the n-type material, causing them to separate. This movement caused by the electric field within the depleted zone is called drift; all these charge carriers contribute to the current generated. There are electron-hole pairs generated outside the junction, which are required to keep separated until they can travel to the junction. The time the electron hole pairs stay separated is called their lifetime. If they are close enough to travel to the junction within their lifetime, the electron-hole pair will contribute to the charge generated. The time they spend in their mobile state depends on the material. Whether the band gap is direct or indirect will influence the lifetime of the electron hole pair. Lifetime can also be effected by defects in the material, such as dislocations and impurities. Direct band gap materials inherently have a shorter carrier lifetime, however their absorption rate is much higher than the indirect materials, and therefore the absorber layer can be thinner (2 μm for cadmium telluride) and still have total absorption of the visible spectrum. The surface of the absorbing layer is the area where most of the charge carriers will be generated and it is important that the surface properties minimise the loss of free carriers.

2.3 Electrical Characteristics of Solar Cells

When a solar cell is not illuminated then it will act like a diode. A solar cell is very similar to a diode except it is composed of energy absorbing material and has a large area to collect the electromagnetic radiation (photons). Another main characteristic of a solar cell is that the junction is very close to the surface, in order to allow as many photons as possible to

penetrate through. As a solar cell has similar properties as a diode the current relationship of a solar cell can be expressed as:

$$I = I_S [e^{\frac{qV}{nV_T}} - 1]$$

where I is the cell current, I_S is the reverse saturation current, V is the voltage across the cell, q is the electronic charge, n is the ideality factor, V_T is the thermal voltage.

The main performance characteristics of a solar cell are the short circuit current density I_{sc} , open circuit voltage V_{oc} , its fill factor FF and efficiency η . The cell reaches its maximum operating point at the Maximum Power Point (MPP), which takes place at V_{MPP} and I_M , this point is shown in Figure 2.8.

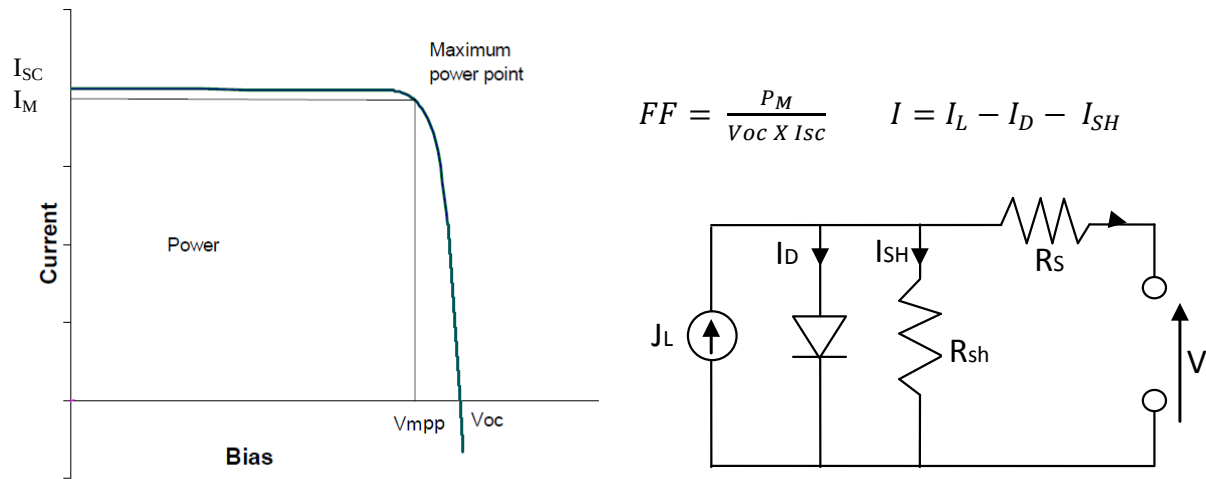


Figure 2.8- A model IV graph to illustrate the point of maximum power and a schematic model of the equivalent solar cell showing the electrical components involved

The fill factor (FF) is described as the ratio of power available at the MPP against the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}). In Figure 2.8 and the equation above, I is the output current, I_L is the photo-generated current, I_D is the diode current, I_{sh} is the shunt current.

V_{oc} is defined as the open circuit voltage. This is the voltage measured across the cell terminals with an open circuit and $I = 0$.

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{I_L}{I_0} + 1\right)$$

I_{sc} is defined as the closed circuit current or short circuit current, I_L is actual load which is:

$$I_{SC} = I_L$$

The efficiency of the cell η is the amount of electromagnetic radiation (photons) converted to electrical power, calculated as:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{FF V_{oc} I_{SC}}{P_{in}}$$

An alternative more accurate method of measuring the performance of a solar cell is by measuring the quantum efficiency (Q.E.). This means viewing the spectral response of the cell by measuring the efficiency over a range of wavelengths. Quantum efficiency is the measure of probability that a photon of a given wavelength will cause an electron to be generated for the photocurrent of the cell. This shows the effectiveness of the cell to produce an electronic charge from electromagnetic radiation with varying wavelengths.

For a given wavelength (λ):

$$Q.E.(\lambda) = \frac{1}{q} \frac{hc}{\lambda} \frac{I_{SC}(\lambda)}{P(\lambda)}$$

λ is the electromagnetic wavelength, q is the unit charge, h is Plank's constant, c is the speed of light, $I_{SC}(\lambda)$ is the short circuit current and $P(\lambda)$ is the incident light power.

2.4 Material Characteristics of a Cadmium Telluride Solar Cell

Thin film solar cells are mainly composed of polycrystalline materials which often have randomly orientated grains, but can have preferred grain orientation depending on the manufacture route. In efficient commercially produced cadmium telluride cells the average grain size is of the order of several microns¹⁸. However in quantum mechanical terms the grain size is very large and therefore the band structure and absorption coefficient can be modelled similar to that of a single crystal material. The main effects of grain boundaries are on the transport and recombination properties of the semiconductor, however the cadmium sulphide/cadmium telluride interface and inter-diffusion at this interfaces also plays a large role. Grain boundaries produce trap states in the band gap due to the defects in and around the boundaries, due to the difference in crystal orientations between the adjacent grains. These traps can be seen as a “sheet” of charge impurities which pull the carriers from the areas around the boundary. Therefore in the n-type material the traps cause the surrounding electrons to move into the trap and this area becomes negatively charged, with the

surrounding areas becoming positively charged due to the depletion of electrons. This then causes an electrostatic force to build up a potential barrier, which in turn causes reduced majority carrier migration across this region. This causes band bending and results in the charge carriers moving to the grain boundaries where they will recombine. In the p-type material the holes will be drawn towards the traps at the grain boundaries and there will be a negative region around the boundaries and the boundary itself will be positively charged.

Figure 2.9 shows the electric field formed by the build-up of holes at the grain boundary, resulting in the bending of the energy levels.



Figure 2.9– A schematic model illustrating band bending showing the electric field and band gap profile at a grain boundary

2.5 Cadmium Telluride Material Properties

Cadmium telluride is a semiconducting material with a band gap of 1.44 eV which almost perfectly matches the photo conversion efficiency shown in Figure 2.10. As cadmium telluride has a direct band gap, complete absorption of visible light occurs within 2 μm of the material¹⁹. The maximum recorded laboratory efficiency of cadmium telluride produced is now over 20% for a small area device, although modular efficiencies are inherently lower¹³.

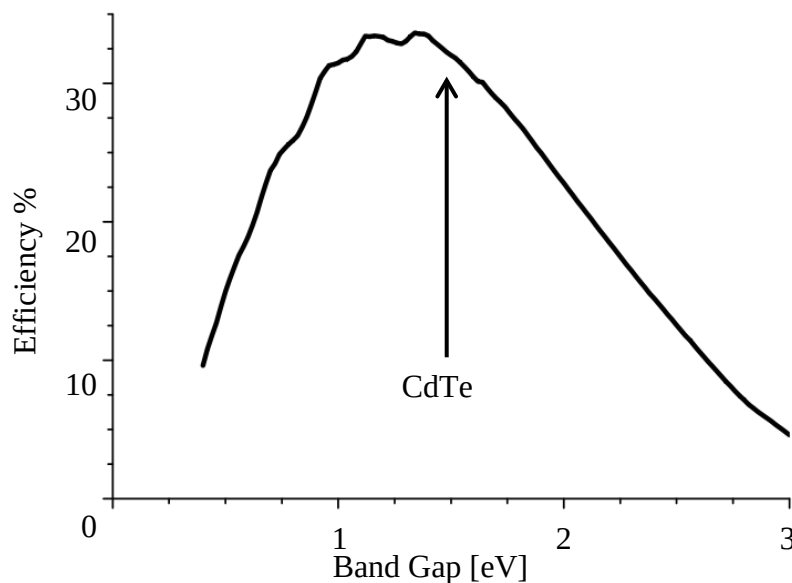


Figure 2.10 - A graph showing the Shockley-Queisser theoretical maximum efficiencies for cadmium telluride. Adapted from²⁰

Band Gap CdTe	1.44eV
Theoretical max J_{SC}	30.5 mA/cm ²
CdS/CdTe Maximum potential	1.1 V
Theoretical V_{OC}	1 V
Theoretical Maximum efficiency	~30%

Table 2.1 – A summary of the photovoltaic properties of cadmium ^{21,22}

Table 2.1 shows the properties of cadmium telluride semiconductor material; this shows that the efficiency can be almost doubled to the theoretical maximum of 30% calculated from the Shockley-Queisser limit shown in Figure 2.10. This has generated considerable research momentum to better understand the cadmium sulphide/cadmium telluride cell in terms of microstructure so to further improve the efficiency of the cell¹³.

2.6 Cadmium Telluride Cell Structure

Cadmium telluride can be deposited in a superstrate or substrate configuration. For a superstrate structure the p-n junction is illuminated through the glass. Therefore the glass must be as transparent as possible illustrated in Figure 2.11. The alternative is a substrate structure which consists of depositing the p-n junction onto a back contact, which can be the substrate. Alternatively the back contact can be deposited directly onto the glass, and the p-n junction therefore onto the back contact, and the p-n junction is illuminated directly.

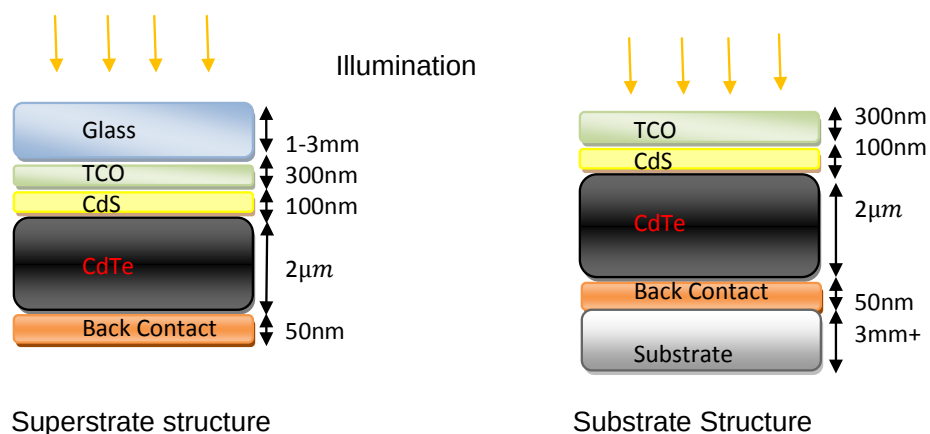


Figure 2.11 – A schematic model of a cadmium telluride cell structure in the superstrate and substrate configuration

There is a large effect on the cell between the two configurations as there are different interfaces to consider. The superstrate configuration has been shown to give the best efficiencies. The glass used in the superstrate configuration is usually a few millimetres thick and as transparent as possible to allow as much light through so there is a trade-off between the strength of the glass and how transparent the glass is, as the thinner the glass, the more

light will be allowed to pass to the absorbing semiconductor. The transparent conducting oxide (TCO) is usually fluorine doped tin oxide (FTO) and this has a thickness of approximately 300 nm. FTO is used as it is very transparent over the visible spectrum and offers a low sheet resistance. It also forms a good Ohmic contact with the cadmium sulphide layer as it has an electron affinity below 4.5 eV and therefore results in good band alignment. Another commonly used material is indium doped tin oxide, which also possesses similar desirable properties. The cadmium sulphide n-type layer is often referred to as a window layer or buffer layer. Its thickness is minimised to let as much light pass through to the next layer, which is the absorbing layer, as possible. However the cadmium sulphide must be sufficiently thick that there is no possibility that the TCO comes into contact with the cadmium telluride layer. The TCO can often penetrate through the cadmium sulphide as it usually has a slightly rough surface. The cadmium telluride layer is the p-type material and 2 μm is the optimum thickness, as it is the minimum thickness where a large majority of the photons which enter are absorbed.

Irradiation of a cadmium sulphide/cadmium telluride cell is made more complicated due it being a layered device; therefore at each interface some of the incoming photons are reflected as shown in Figure 2.12.

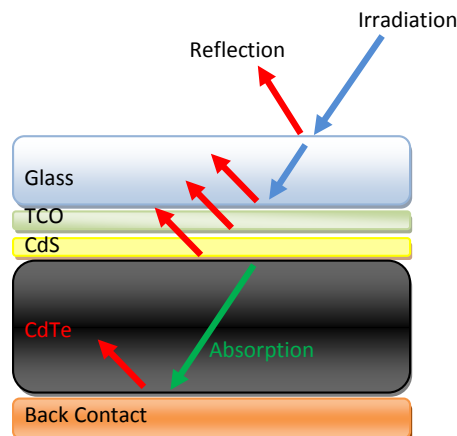


Figure 2.12– A schematic model of a cadmium telluride cell showing the interactions of light

The transparent conducting oxide (TCO) is the front contact; this layer allows light to pass through as well as being electrically conducting and can therefore collect the charge. An intrinsic layer of tin oxide can be deposited between the fluorine doped tin oxide and the cadmium sulphide layer, to prevent possible shunting (due to any pin holes in the cadmium sulphide layer). This keeps the cadmium telluride from forming an electrical contact with the conducting oxide as the buffer layer is highly resistive.

The cadmium telluride layer is the p-type absorber layer of the solar cell; it is also the

thickest and most important as its properties will greatly reflect the overall properties of the cell. The cadmium telluride layer can be deposited using a wide range of methods. These include high and low temperature methods and in vacuum and in air deposition techniques. High temperature techniques include close space sublimation (CSS) or close space vapour transport, which are both carried out above 500°C. Sputtering is a low temperature process and layers can be deposited at temperatures as low as 200°C. There are, however some disadvantages to this technique. As larger grains are preferable since they yield a higher efficiency, a post deposition process must be carried out to coarsen the grains. The higher temperature deposition techniques generally have large grains ranging from 5 to 10 μm , whereas the lower deposition techniques range from 100 nm to 500 nm. This large difference in grain size is due to the difference in mobility of the atoms at the growth surface.

2.7 Cadmium Sulphide – The Window Layer

The cadmium sulphide window layer is an n-type semiconductor which has a high energy band gap of 2.4 eV and a low absorption coefficient to allow the maximum amount of light to pass to the absorbing cadmium telluride layer²³. Cadmium sulphide and cadmium telluride form a heterojunction as cadmium telluride is not easily doped to form a homo-junction device. Its high absorption will not allow much light to reach the junction therefore the best option is to have a window layer and form a heterojunction. Cadmium sulphide has a stoichiometric form usually with a hexagonal wurtzite structure²³. There are many ways in which to deposit a thin cadmium sulphide layer. One of the most commonly used methods is chemical bath deposition (CBD)²⁴, however there are many other successful methods with other advantages such as vacuum evaporation²⁵, sputtering²⁶, close spaced sublimation (CSS)²⁷, close space vapour transport (CSVST)²⁸, spray pyrolysis²⁹ and metal organic chemical vapour deposition³⁰. When depositing cadmium sulphide it is imperative that an optimum thickness is deposited. This is so that it completely isolates the cadmium telluride from the TCO, but also allows as much light as possible through as cadmium sulphide is not as photo generating as the cadmium telluride layer. The cadmium sulphide layer tends to absorb the lower wavelength electro-magnetic radiation from 300 nm to 550 nm³¹.

2.8 Back Contact Properties

The metal back contact is an important part of the cell, as it collects the charge, and if this is done inefficiently then the overall cell properties will be diminished. The back contact must have some key properties in order to be a good charge collector. The metal contact must form

an Ohmic contact with the cadmium telluride layer shown in Figure 2.13, therefore it needs a work function over 5.7 eV or a Schottky barrier will be created and this will cause a poor charge collecting contact.

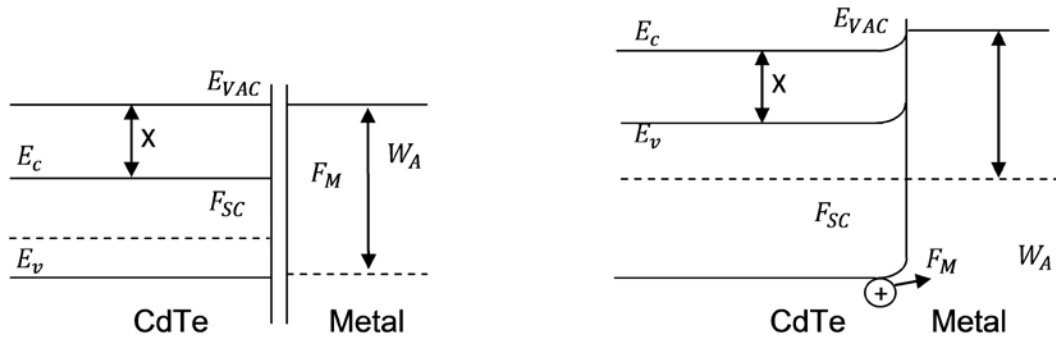


Figure 2.13 – Illustration to show the band energies at the cadmium telluride/metal interface before and after contact

To prevent the formation of a Schottky barrier formation the cadmium telluride back surface is highly p doped using a chemical etch (usually bromine³³⁻³⁴) also a buffer layer which has a high carrier concentration is deposited. This causes the contact barrier to be lowered and therefore causes a quasi-Ohmic contact illustrated in Figure 2.14.

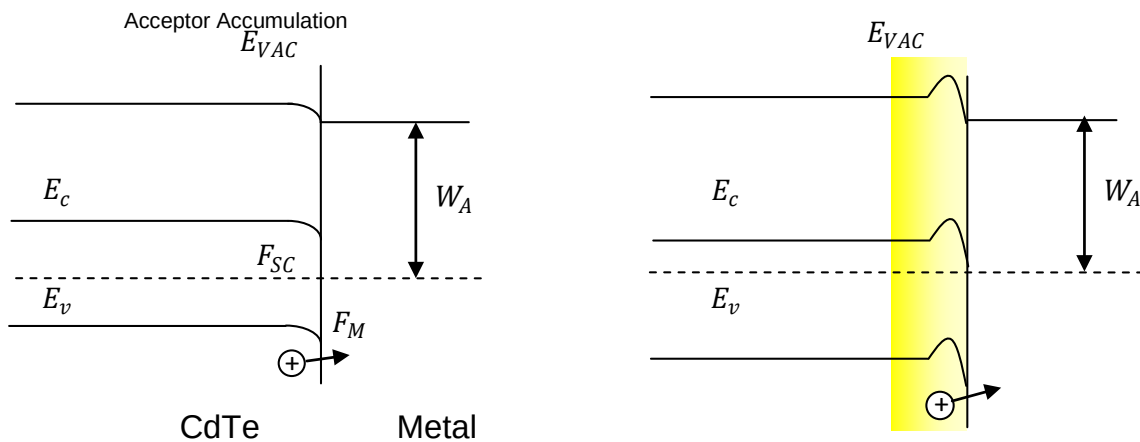


Figure 2.14 – Illustration of a Schottky barrier and a tunnelling contact band diagram

The diffusion of the metal contact is often an issue when using metals which rapidly diffuse to the cadmium sulphide/cadmium telluride interface as these often accumulate and diminish the cells electrical properties, and therefore its overall performance. Metals which are known for this include copper, silver, aluminium and nickel. Metals which are known to have a good Ohmic contact and do not diffuse to the interfaces are molybdenum and gold¹⁹.

A good cadmium telluride cell provides a voltage of approximately 850 mV¹⁹; therefore each module must be divided into smaller cells in order to increase the total voltage. This is carried

out by a series of interconnects which cut the cell up and connect each smaller cell up in series. This is a very precise operation as to connect the cells in series the back contact of one cell must be connected to the TCO of the cell parallel to it³⁴.

2.9 Approaches to Increase Device Efficiencies

The transparent conducting oxide (TCO) can be made from a range of materials. The two most common are fluorine doped tin oxide (FTO) and indium doped tin oxide (ITO), however there are many others which have been used with success.

Novel materials have been used in order to reach higher efficiencies although these are not commercially available. It has proved to be somewhat successful using cadmium stannate Cd_2SnO_4 (CTO) as the TCO layer¹⁹. Transmittance measurements were taken of CTO and commercially available FTO for the same resistivity; these results clearly show that the CTO is more transparent than the FTO across most of the wavelengths. High resolution TEM was used to view any deformations such as twins or dislocations, however the CTO showed a high degree of perfection; whereas the commercial FTO has a high density of twins and dislocations. The equivalent transmittance comparing CTO to commercial FTO is shown in Figure 2.15.

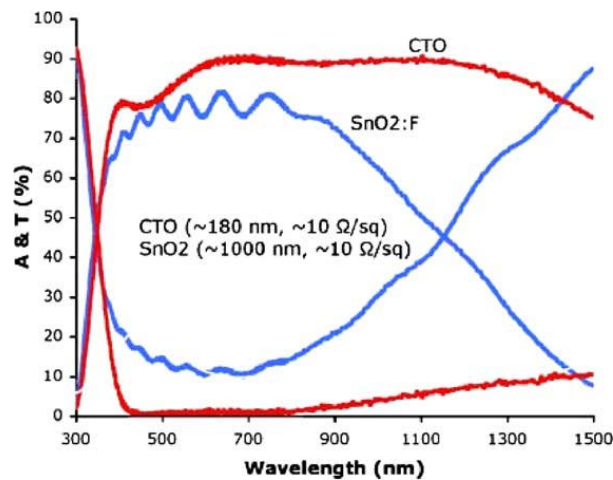


Figure 2.15 – Transmittance and absorbance spectra for CTO and FTO showing the variation in transmittance with wavelength¹⁹

A tin oxide buffer layer is often implemented to prevent shorting between the TCO and cadmium telluride layers, which is usually composed of un-doped tin oxide³⁵ as this layer is highly resistive. Novel materials have also proved successful for this application, such as $ZnSnO_x$. CTO/ZTO/CdS/CdTe polycrystalline thin-film solar cell was produced by NREL (National Renewable Energy Laboratory, USA) with a confirmed total-area efficiency of

16.5%, Voc of 845.0 mV, Jsc of 25.88 mA/cm² and fill factor of 75.51% on an area of 1.032 cm² ¹⁹.

2.10 Microstructural Characterization of Cadmium Telluride Solar Cells

The simplest way to characterize the device is to take one layer at a time and observe the optimum properties and characteristics of the layer according to the literature and try to mirror some of these properties.

With relation to the substrate the most transparent material should be used. This is usually soda-lime glass, as it is commercially available. The substrate has little effect on the morphology of the rest of the cell and therefore is not usually characterized.

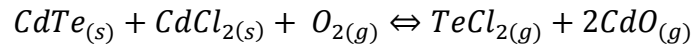
The cadmium sulphide layer is generally 100 nm thick³⁵. It has been shown that the hexagonal phase is preferred in high efficiency cells³⁶. As the layer is very thin, TEM is the main method of characterizing these layers³⁷ but SEM is used for observing the surface structure³⁸. TEM diffraction is also used to determine the crystal structure³⁹ and high resolution EDX through a cross section to observe inter-diffusion at interfaces⁴⁰. The cadmium telluride layer is much thicker than the cadmium sulphide layer and therefore a common technique to view its morphology is by fracture cross section SEM⁴¹. This is a fast method of getting a cross sectional image without extensive sample preparation. XRD is commonly used to analyse the cadmium telluride layers orientation, crystal size, stress and lattice spacing⁴².

To measure the performance of the cell, the current – voltage (J-V) curve can be drawn, or the external quantum efficiency (EQE) can be calculated, which is the most accurate and detailed method to check the overall performance of the cell⁴³.

2.11 The Cadmium Chloride Treatment

To produce efficient cadmium telluride solar cells, the deposited thin films in most cases are treated by applying cadmium chloride and annealing simultaneously^{17,40,44–51}. The exact effects the treatment has on the thin films and reasons why it is required to produce devices with good efficiencies (>10%) is still much debated. The post deposition treatment is usually carried out to both high and low temperature deposited layers⁴⁶; however the treatment has a different effect on each of the layers⁴⁵. Cadmium chloride is the ‘catalyst’ of the treatment, in the high temperature layers⁵²; the cadmium chloride reduces the structural defects and affects the grain boundaries^{19,38}. In the layers with the smaller grains the cadmium chloride causes

re-crystallization resulting in larger crystal size^{17,19,32,40,44,46–49,52–54} although crystal texture is lower after the treatment^{33,46,55}. The cadmium chloride treatment is an annealing treatment and usually takes place around 400°C⁵⁶, this treatment can also be carried out in vacuo or in air³², this treatment can increase the efficiency in most cases dramatically^{18,48,51,57,58}. This is due to the improvement of the structural quality by a reduction in stacking faults and misfit dislocations^{34,37,38,59}, which in turn improves the electronic characteristics of the cadmium telluride/cadmium sulphide layers. This is carried out in the recovery stage of recrystallization. CdS_xTe_{1-x} will form at the junction reducing the lattice mismatch between the cadmium telluride and the cadmium sulphide layers^{37,60,61}, which is important to improve the electrical properties of the junction. The treatment provides a flux which reduces the grain boundary atomic diffusion barrier⁶⁰. This results in grain coarsening; also increasing the inter-diffusion at the cadmium telluride/cadmium sulphide junction reducing lattice mismatch³⁷. The cadmium chloride treatment is a post deposition treatment which therefore adds an extra processing step, therefore to treat the cadmium telluride/cadmium sulphide cell in-situ would be beneficial in reducing time and cost. The reaction between the cadmium chloride and the cadmium telluride is as follows^{46,59,62,63}:



2.12 Stresses and Grain Size in Cadmium Telluride Films

In physical vapour deposition and sputtered devices, the grains are smaller than the higher temperature techniques usually with a grain size of $\sim 0.3 \mu m$ ⁶¹ and $0.5 \mu m$ respectively[49,65]. Recrystallization and grain growth are notable changes which occur during the process, so that grains can grow to over a micron in diameter after the cadmium chloride treatment. A comparatively large grain size over $1 \mu m$ is typical in close spaced sublimated films²² and often little or no changes can be observed regarding recrystallization or grain growth at higher temperature depositions⁴⁴.

Stress reduction in cadmium telluride thin films has been observed in low temperature deposited films using XRD⁶³. A reduction was observed after the cells was annealed at a temperature of 350°C reducing further when the temperature was raised to 400°C⁶⁵.

It has been found that although the treatment does not have an effect on the grain size, it is still used to improve device characteristics such as V_{oc} and the fill factor⁶⁶. Some evidence of small grain elimination was observed, and it is believed that the cadmium chloride treatment acts as a fluxing agent to increase the atomic mobility of cadmium and telluride atoms⁵².

2.13 Characterisation of Cadmium Chloride Treated Cells

Extensive studies of the effect of cadmium chloride on the properties of cadmium telluride have been carried out; however there are some gaps in characterisation of the microstructure. Therefore the full mechanism of the recrystallization process during the treatment taking place in the cadmium telluride and its buffer layer is not yet known.

TEM has been used in various ways to study crystallographic and elemental characteristics⁶⁷, high resolution TEM has been carried out on the cadmium sulphide/cadmium telluride interface in order to study the difference in orientation and phase along with their Fourier transformations[39,69]. Energy filtered TEM has been used to view the concentration distribution of certain elements across grain boundaries and EDX used in conjunction with analytical TEM to produce elemental maps of samples⁴⁰. Transmission spectra are often plotted to compare treated and untreated cells, as well as to see the change in optical band gap of the samples by plotting $(\alpha h\nu)^2$ vs. $h\nu$ ⁶⁹ where α is and $h\nu$ is the photon energy. Photoluminescence is traditionally used to study the actively radiative intrinsic and extrinsic electron hole defect levels within the band gap to study the defect structure and distribution^{34,70}. High resolution TEM imaging has been used in conjunction with TEM diffraction to show the crystal orientation³⁸.

XRD is a commonly used technique for studying the effect of cadmium chloride on the bulk crystallographic properties of the sample^{52,54,59,71}. It has also been used to see the change in stress levels in the layers by using the lattice spacing change as well as crystal size change⁵⁵.

AFM can be used to see the change in surface roughness of the samples, as well as showing the grain size on the top surface³⁸.

SIMS and Auger spectroscopy have been used to do depth profiling to view the change in concentration through the layers, therefore showing any inter-diffusion^{53,59} to examine the change in performance properties the standard tests are current voltage curves and EQE measurements to give the device efficiency⁵⁸.

Studies have used EDX mapping in conjunction with TEM to show the diffusion of chlorine during the annealing treatment. It was shown that the chlorine diffused along the grain boundaries as there was higher concentrations there, with EFTEM to verify this⁴⁰.

Several electrical effects have been detected as a result of the cadmium chloride process. These include interdiffusion between the cadmium telluride/cadmium sulphide interface, a

change in current transport mechanism, lower surface resistivity and an increase in the minority carrier lifetime²².

Interdiffusion of cadmium sulphide into the cadmium telluride layer forms an interfacial layer which is believed to be responsible for lowering the interfacial defect density and hence improving the device efficiency²². It is suggested that this is because it reduces the recombination within the device⁷². A decrease in the diode ideality factor is proposed, whereby there is a reduction in the interface state density³³. The interdiffusion has also been seen to cause a reduction in the cadmium sulphide layer thickness⁵².

A change in the current transport mechanism is another effect from the activation process. Prior to treatment, the transport is by tunnelling/interface recombination whereas after it is dominated by junction recombination³³.

The cadmium chloride treatment effects on the resistance of the cadmium telluride have been shown to reduce the film resistance due to the addition of chlorine during the treatment. The series resistance of the film was also seen to decrease with an increase in annealing temperature⁵⁸. This could be due to the reduction of defects which cause carrier sinks in the cadmium telluride grains⁷³. It has been shown that series resistance increases when the cells are annealed above 400°C without cadmium chloride being present and above 450°C with cadmium chloride⁷⁴. An improvement in spectral response was recorded during quantum efficiency measurements for a cadmium telluride film which had undergone a 400°C anneal⁷⁴.

Studies have shown no major changes in the structural properties of the close spaced sublimation cell after a cadmium chloride treatment⁴⁴, but a significant increase in the minority carrier lifetime. The value increased dramatically after the cadmium chloride treatment was carried out at 400°C. The increase in carrier lifetime was attributed to the elimination of deep defect levels during the treatment⁵⁴.

2.14 Theory of Cadmium Chloride Heat Treatment to Date

It is understood that cadmium chloride heat treatment causes the recrystallization of cadmium telluride and cadmium sulphide, however its mechanism is not clearly understood, although the highest efficiency cells have been produced with this treatment. Studies have given an insight into the physical affect and what happens precisely during the annealing treatment⁴⁴; however this also will depend on the treatment process as well as the deposition technique, as the starting structure has an effect on the final structure.

It has been noted that during the recrystallization, grain size increases⁷¹, and a passivation of the grain boundaries occurs to allow inter-diffusion to occur more easily⁷². It has been shown that sulphur diffuses to the cadmium telluride/cadmium sulphide interface during the recrystallization as chlorine diffuses along the grain boundaries. A tellurium chloride phase is formed at the grain boundary in a gaseous phase⁴⁰ which favours the growth of the cadmium telluride grains as it enhances the mobility of cadmium and tellurium atoms, which leads to a more random arrangement after recrystallization⁴⁴. After the treatment the cadmium sulphide layer should have a homogeneous contact with the chlorine once it diffuses down the cadmium telluride boundaries⁴⁰.

2.15 Theory of Defects in Cadmium Telluride

Cadmium telluride has been seen to exist as both zinc-blende cubic and hexagonal phases. It has been seen that due to the low energy difference between the two phases, they can both form within the same grain. This can only be the case when the atomic stacking sequence changes from AaBaCcAaBbCc (zinc blende) to AaBbAaBa (hexagonal). This change in atomic structure gives rise to a large density of stacking faults within the cadmium telluride grains^{37,77}.

Point defects are defects within a crystal lattice which affects the structure at a localised site. These can be intrinsic point defects or extrinsic. Intrinsic defects can occur in pure materials (no external atoms/ions needed). These are due to an atom missing in the lattice or an extra atom occupying an interstitial site in which an atom usually does not sit. Extrinsic point defects are due to external atoms which are impurities in the lattice, sitting in a location not usually occupied by atoms or displacing atoms from the lattice structure.

Defects can often form at interfaces between two materials due to the change in atomic spacing, cadmium telluride and cadmium sulphide have a 10% lattice mismatch, which can induce stacking defects.

Grain Boundaries are considered defects, high or low angle boundaries will affect the material properties, such as conductivity. High angle boundaries will give larger diffusion paths, promoting segregation or increase diffusion.

Stacking Faults occur in cadmium telluride due to their low formation energy. These can be Extrinsic, intrinsic or twin boundaries shown in Figure 2.16. They occur when there is a change in the stacking sequence. For a cubic material a perfect stacking structure can be

written as AaBbCcAaBbCc...If an extrinsic stacking fault appears the stacking sequence will include an extra plane of atom: AaBbCc|C|AaBbCc. Intrinsic stacking faults occur when an atomic plane is missing from the sequence: AaBbCc||AaBbCc. Twin boundaries occur when either side of the twin boundary mirrors each other: AaBb|Cc|bBaA.

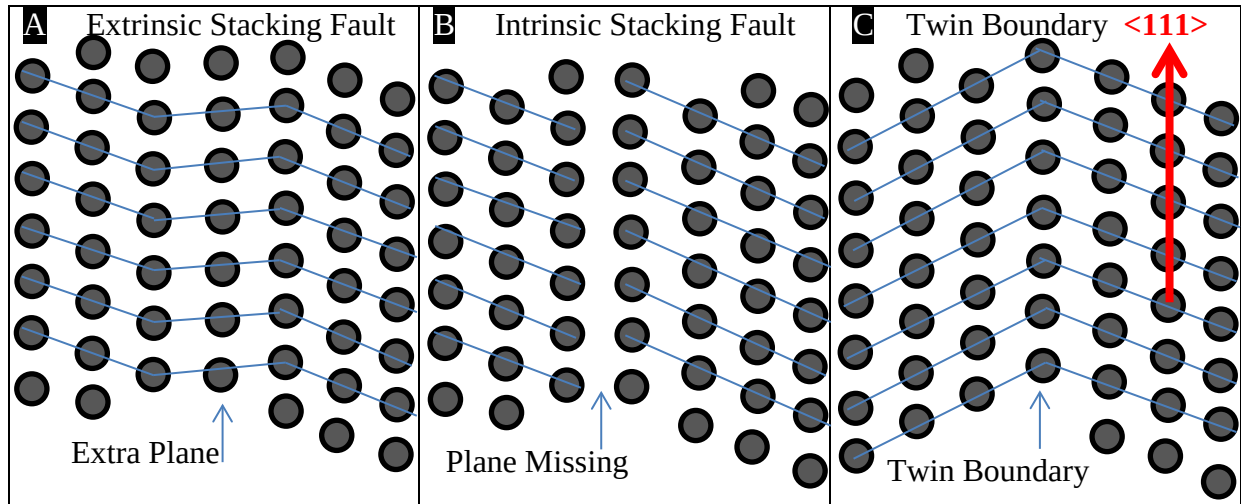


Figure 2.16 – Schematics of defect types in cadmium telluride material

A study has been carried out using cathodoluminescence (CL) to see the effect of defects within cadmium telluride. CL carried out in a SEM at 50 to 300 K, with electron beams from 5 to 30 kV. CL was collected with a semi-parabolic mirror attached to an optical guide^{38,75}. Looking at high temperature and low temperature deposition, the higher temperature cells showed larger grains (2-5 μm), due to higher surface mobility during deposition⁶⁰. This improved the electrical properties, but recombination is still dominant and a high density of planar faults was observed as stacking faults and lamellar twins, with similar density⁷⁵. After the cadmium chloride treatment the samples grain growth was observed to increase with annealing temperature³⁸.

2.16 Project Objectives

The main objectives of this project are to evaluate a new DC magnetron sputtering deposition technique which promises an all-in-one cadmium telluride cell production route, and to fully understand the effects of the post deposition treatment on microstructure and electrical properties.

To achieve these objectives Chapter 3 describes the experimental methodologies, Chapter 4 focuses on characterisation of sputter depositions of cadmium telluride and cadmium sulphide, and the effects of the cadmium chloride treatment. The TCO layer will be studied in Chapter 5 as its morphology will highly influence the morphology following layer

depositions. The cadmium chloride treatment will be examined in Chapter 6 in detail on close spaced sublimated cells by comparing devices before and after the treatment. Chapter 7 will then systematically vary the treatment parameters to further develop the understanding of the cadmium chloride treatment to gain a better understanding of the mechanisms involved. Chapter 8 examines structural defects within the cadmium telluride grains using the novel technique of high resolution transmission back-scatter electron diffraction. Chapter 9 will examine cadmium magnesium telluride depositions on cadmium telluride cells to act as an electron reflector. Throughout the chapters thin films will be characterized using EDX, TEM, SEM, XRD, XPS, SIMS and other techniques which prove useful.

CHAPTER 3. EXPERIMENTAL METHODOLOGIES

3.1 Introduction

This investigation of cadmium telluride thin film solar cells incorporates depositing and processing thin film cadmium telluride and its constituting layers as well as characterising the microstructural, physical and chemical properties together with the cell performance properties.

The layers investigated were deposited using a number of techniques including sputtering, closed space sublimation, chemical bath deposition and electro-deposition. Various experiments were carried out in this investigation so the depositions were performed under a range of conditions to better understand certain aspects of cadmium telluride thin film solar cells. A large part of this study is in optimisation of the cadmium chloride annealing treatment of the cadmium telluride/cadmium sulphide cell which was also carried out using different methods and parameters that are specified in this chapter.

3.2 Processing Samples – Deposition Methods

3.2.1 Magnetron Sputtered Solar Cells

One of the main objectives of this project is to produce cadmium telluride solar cells in one in-line vacuum process. This means the cell will only be put in vacuum once, which will improve the efficiency of the manufacture in terms of both time and cost. Using magnetron sputtering for this application is novel and in this initial study simpler and more established deposition techniques were used for the other layers of the cell such as chemical bath deposition (CBD) for the cadmium sulphide layer. Only cadmium telluride was initially deposited via magnetron sputtering.

The magnetron sputtering configuration used in this study was initially developed for wear resistant coatings by Teer⁷⁶ and more recently for precision optical coatings⁶⁴. The configuration links magnetic field lines between the magnetrons by reversing the polarity of adjacent magnetrons. The magnetrons are also unbalanced to further intensify the field and increase the ion current density in the plasma. Using this arrangement, the deposition volume in which the substrates are located is surrounded by linking magnetic field lines. This traps the plasma region, prevents losses of ionizing electrons, and results in significant plasma enhancement. The closed magnetic field system produces dense coatings due to the high ion

current density. The deposition energy is determined by the induced voltage on the substrate carrier which is typically in the range 25 V to 50 V. This combination of high ion current density and low ion energy produce ideal conditions for thin film growth.

The rotating substrate holder is in the form of a vertical drum which is normally faceted to accept flat substrates as shown in Figure 3.1. This arrangement enables the creation of high ion current densities $\sim 5 \text{ mA/cm}^2$ and the revolving drum⁶⁴, mounted on an insulator, is allowed to electrically float to the plasma potential. This plasma does not require a substrate bias voltage to sustain high plasma densities. The key advantage of the process is that no separate ion source, plasma source or microwave ion source is required. Nor is it necessary to partition the working vacuum chamber into deposition and reaction zones. This simplifies the system, reduces cost, and improves reliability. It also makes it economical to scale the technology to virtually any batch size. Although the closed field configuration is used in this study within a batch system, the format can also be used in “in-line” or “roll to roll” configurations.

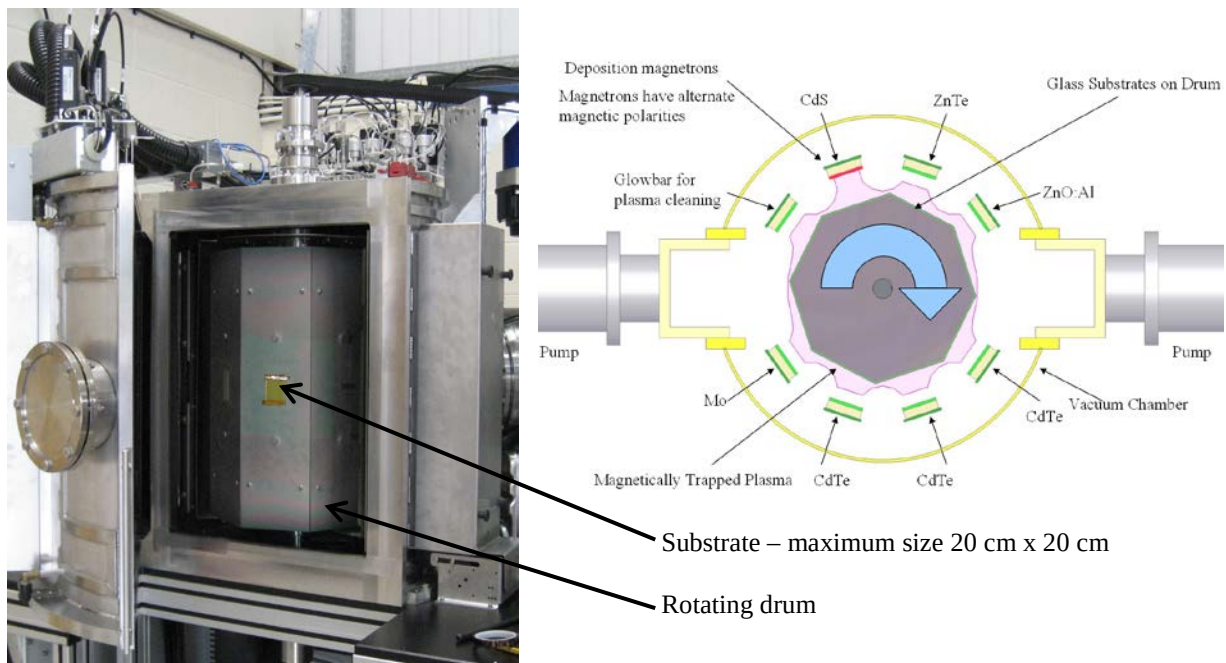


Figure 3.1 – A photograph of the closed field magnetron sputtering system with positions for 4 linear magnetrons and a faceted drum-based substrate holder and corresponding illustration of the CFM 650 designed by Applied Multilayers (CFM650, SCT Inc).

The system is also fitted with a rotating shutter to expose the substrates to the appropriate target with fine interface control. The shutter is also used to enable targets to be conditioned without exposure to the substrate. The system initially had four targets and for this study cadmium telluride, cadmium sulphide and indium doped tin oxide were used. The substrates

were either 1 mm soda lime glass or TEC glass from Pilkington (TEC7,8, 10 and 15), which had a transparent conducting oxide (TCO) previously deposited. The substrates were typically 5 cm x 5 cm in size and were cleaned with distilled water and then methanol and dried with nitrogen gas to remove any debris from the surface onto which the layers were deposited. Some substrates had cadmium sulphide previously deposited onto them using chemical bath deposition; these then had a cadmium telluride layer of varying thickness sputtered onto them.

Configurations include: Pilkington TEC glass / chemical bath deposited cadmium sulphide / sputtered cadmium telluride, Pilkington TEC glass / sputtered cadmium sulphide / sputtered cadmium telluride and 1 mm soda lime glass / sputtered indium doped tin oxide / sputtered cadmium sulphide / sputtered cadmium telluride. The cadmium telluride was deposited as a dual layer in some samples by stopping the deposition and then restarting it. Some layers were slightly plasma etched by biasing the sample inside the sputter coater before the next layer was deposited.

For the sputtered samples copper/gold back contacts were deposited using an Emitech k575XD Turbo sputter coater. Less than 5 nm of copper was deposited followed by 50 nm of gold which provided a back contact with sufficient conductivity.

3.2.2 Closed Space Sublimated Solar Cells

The thin film cadmium telluride cells that were deposited using close-spaced sublimation were fabricated at Colorado State University (CSU). They were deposited on NSG-Pilkington TEC10 fluorine doped tin oxide (FTO) coated on 3 mm soda lime glass in a superstrate configuration. The layers were deposited in an all in one vacuum process held 2 mm above graphite boats and the substrate was passed through different chambers at a vacuum of over 5 Pa. The boats were heated to temperatures ranging from approximately 620°C for cadmium sulphide to 550°C for cadmium telluride and 430°C for cadmium chloride, which then sublimed onto the inverted substrate. After all the cadmium sulphide and cadmium telluride layers were deposited respectively via close-spaced sublimation, a sample was then removed and not processed further. Another sample underwent a previously optimized cadmium chloride treatment (examined in Chapter 6). The treatment was carried out in vacuum following the layer deposition. Cadmium chloride was sublimated at a thickness of 3 µm and then the sample was heated for 8 minutes at 400°C in a 2% oxygen atmosphere, causing the cadmium chloride layer to evaporate off. This was followed by a copper doping process by

sublimating copper chloride onto the cadmium telluride layer⁷⁷. The efficiency of this cell was measured to be 11.8%; this is taken as a benchmark sample to which other treatment conditions and methods can be compared.

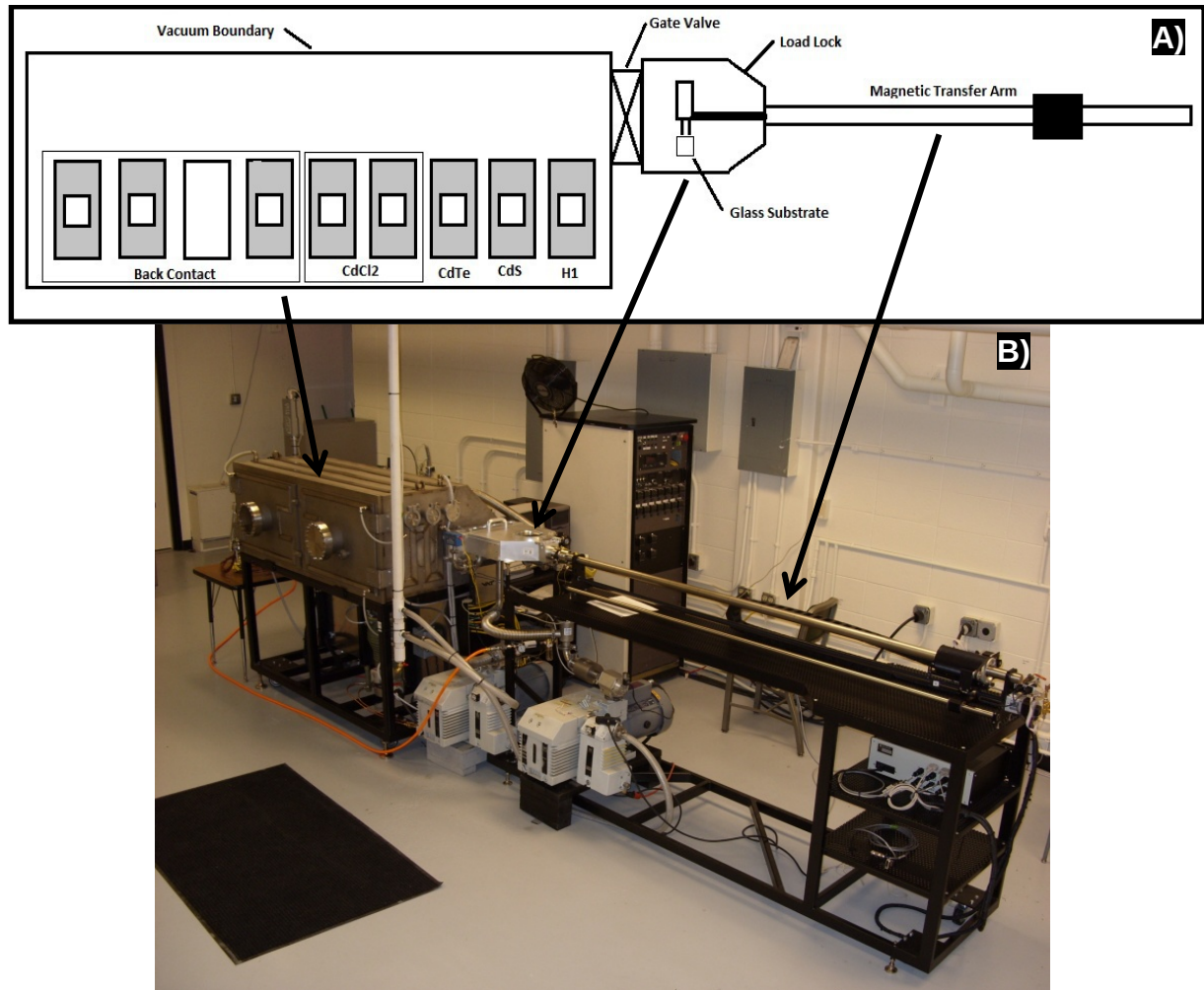


Figure 3.2- a) A schematic diagram and b) photograph of the closed space sublimation system

Figure 3.2 shows the close space sublimation system that was used, which is located at Colorado State University (CSU). Figure 3.2a shows how the glass substrate passes through different deposition stations under one vacuum system. The first is to clean the substrate before it moves to the cadmium sulphide area, then directly into the cadmium telluride station. A schematic of a station is shown in Figure 3.3. After this it moves onto the cadmium chloride area where it is also annealed. After this a back contacted is applied by spraying the electrode using a thin carbon in acrylic (Acheson EB 003) followed by about 50 μm of nickel in acrylic (Acheson electrodag 550).

This system was used to deposit a range of samples, including the optimised sample with and without the cadmium chloride treatment. Cadmium chloride was sublimated so as to achieve 2 μm thick layers. The devices were then annealed for times ranging from 2 s to 600 s at

400°C in a 2% oxygen 98% nitrogen atmosphere causing the cadmium chloride layer to evaporate. Varying the time of the cadmium chloride treatment in a series of steps from 2 s through to 120 s which is regarded as the optimum time, was undertaken to examine how the cadmium telluride microstructure and electrical performance changes with treatment time. Samples over 120 s, treatment time are expected to be “over treated” as they have undergone a longer anneal time than the optimised sample.

The system also allowed for a change in treatment temperature, so samples were treated either side of the optimum 400°C.

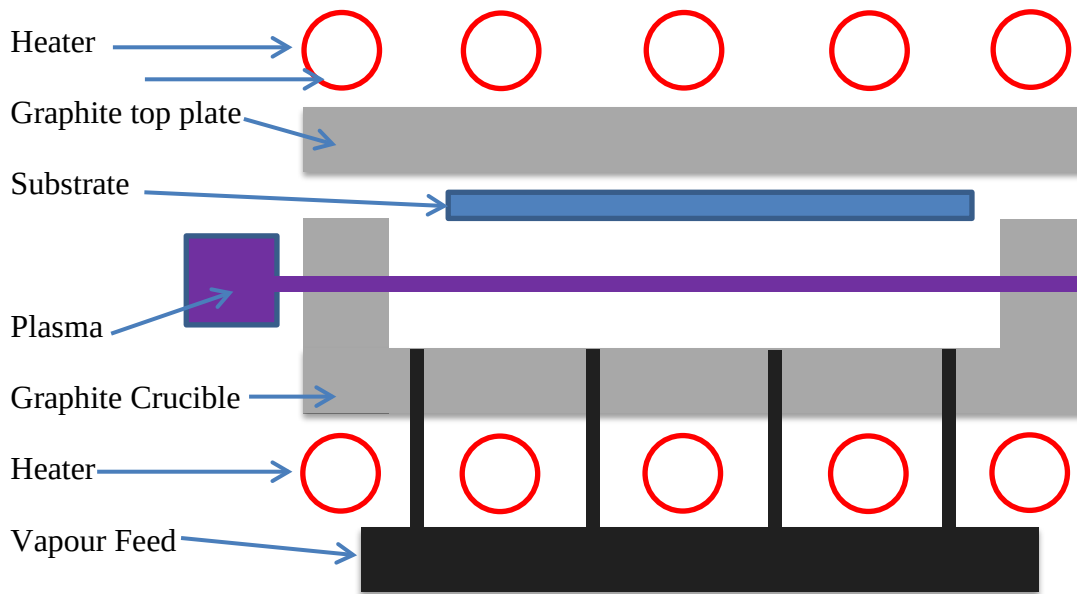


Figure 3.3 - A schematic diagram of a single graphite boat within the closed space sublimation deposition system

3.2.3 Chemical Bath Deposition (CBD) of Cadmium Sulphide

Chemical bath deposition (CBD) of cadmium sulphide is a fairly mature and a robust process and consequently high quality buffer layers with good electrical and optical properties can easily be deposited. This allows the cadmium telluride layer to be studied in isolation from the cadmium sulphide layer, which was always deposited using the standard process.

3.2.4 Transparent Conducting Oxides

The glass coated transparent conducting oxide was either bought from Pilkington or the TCO was sputtered in-house. There are a variety of transparent conducting oxides available from Pilkington; these are TEC7, TEC8 and TEC15, which are commonly used in photovoltaic applications. The main difference between the three types are the thickness, the grain size and the surface roughness. The TEC glass was obtained from Pilkington are fluorine doped tin oxide (FTO), the dimensions are 300 mm by 300 mm sheets with a glass thickness of 3 mm.

The sheets were scribed with a diamond tip blade and then fractured using rubber pliers. The TCO layers of the TEC7 and TEC8 are approximately 700 nm thick and the TEC15 is approximately 350 nm.

3.2.5 *Gold/Copper Back Contact*

The gold/copper back contact is sputtered using a vacuum sputter coater with two targets; therefore the copper and gold can be deposited in the same vacuum chamber. It is standard for only a few nanometres of copper to be deposited and after the copper, 50 – 100 nm of gold.

3.3 Cadmium Chloride Treatment

3.3.1 *Solution Based Cadmium Chloride Treatment*

The first method to carry out the cadmium chloride treatment was using wet chemistry based techniques. This involved dissolving pure cadmium chloride in methanol and diluting it to a range of concentrations, from a saturated solution to 6% of the saturated solution. Once the different concentrations of cadmium chloride were formulated the cells were placed on a hot plate and the solution dropped onto the surface using a pipette. Then the hot plate was raised to a temperature of 420°C and left for a time of 30 minutes. There are three main variables, the concentration of the cadmium chloride solution, the temperature of the hot plate and the hold time at the maximum temperature. There are also various ways that the cadmium chloride solution could be applied to the surface of the sample; the most simple was just dripping it on the surface of the sample before heating it. As the solution base was methanol the solution was seen to evaporate from the surface quickly and therefore on some treatment runs more solution was applied to the surface. Another method was immersing the sample completely in the solution and waiting five minutes for it to penetrate all the way through, then heating it.

There was also some concern with the heating method as the hot plate heats from below though the glass, therefore a temperature gradient is expected.

Safety was a significant issue as cadmium chloride is very toxic and harmful, therefore all work was carried out in a fume cupboard, and gloves and a face mask was used when handling anything that could come into contact with the cadmium chloride solution. To prevent any contamination in the laboratory, the fume cupboard and hot plate and all

equipment was only used for the treatment and all excess waste was disposed of via determined procedures.

3.3.2 Vapour Based Cadmium Chloride Treatment

Due to inadequacies with the liquid based techniques for the annealing based treatment a vapour based technique was carried out as it had many advantages over the liquid based treatment, mainly greater control over the processing conditions.

Similar cadmium chloride treatment processes have been used by other research groups, [34,35,36]. The samples were washed with DI water then with isopropanol and dried with a nitrogen gun in order to remove contamination and residue on the surface which may prevent full contact of the cadmium chloride vapour on the surface of the cadmium telluride cell. The heat furnace used was a Lenton split tube furnace with independent temperature controllers for two zones meaning that the sample and source can be put at different temperatures. The layout is shown in Figure 3.4 .

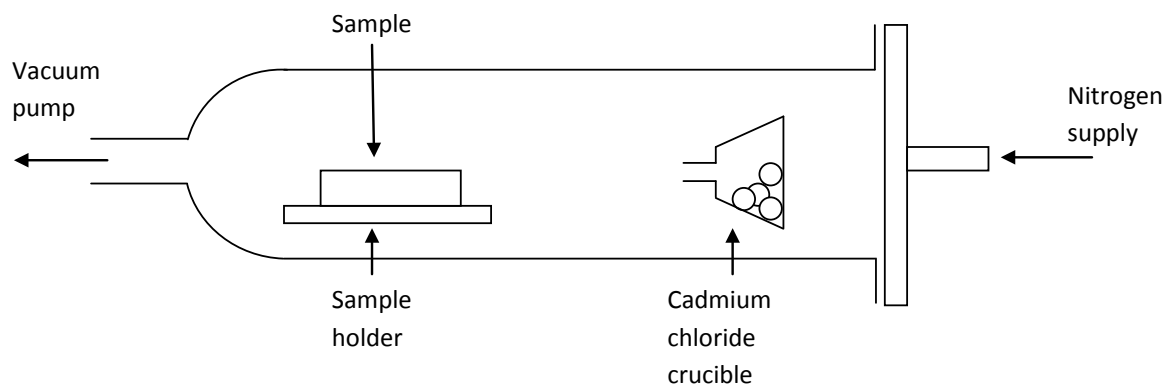


Figure 3.4- A schematic diagram of the tube for cadmium chloride vapour transport treatment

The sample was placed in one zone of the tube and cadmium chloride pellets were put in a crucible and placed in the other zone. The crucible was weighed before and after the treatment. The heating method was programmed to a Step-Dwell-Reset code meaning the furnace tried to achieve the set target temperature as quickly as possible then stayed at the target temperature for the set time. Once the treatment was over the substrate was allowed to cool to room temperature. The tube was put under vacuum and nitrogen was used as a carrier gas which carried the cadmium chloride vapour over the cadmium telluride sample. After the treatment the sample was etched by dipping it in a 0.1% bromine-methanol solution to remove any oxides formed during the annealing, and then a copper/gold back contact was deposited using an Emitech k575XD Turbo sputter coater. Less than 10 nm of copper was deposited followed by 400 nm of gold. Once this was done the sample was heated in a

furnace in air at 150°C for 30 minutes. The temperature of the substrate was varied in the 300°C to 500°C range and the temperature of the cadmium chloride pellets were varied in the 400°C to 600°C range.

3.3.3 Cadmium Chloride Deposition via Evaporation

Cadmium chloride was evaporated using a bell jar, at various thicknesses onto untreated close spaced sublimated samples which had not previously undergone any post deposition treatments. The sample was then removed and annealed in air either on a hot plate or in an oven for different times and temperatures.

3.4 Annealing Treatment without Cadmium Chloride

Close spaced sublimated samples were annealed post deposition at various temperatures and times to observe any recrystallization or any change in microstructural defects in the cadmium telluride layer. The samples were heated in a standard laboratory oven which was preheated to the desired temperature and then cooled to room temperature by removing the sample and placing it on a ceramic brick.

3.5 Characterization

3.5.1 Current-Voltage Measurements (J-V)

To measure the solar cell's performance properties, current-voltage measurements were taken as well as external quantum efficiency (EQE) readings. This was done to the complete cells which had both front and back contacts. Usually each stack had a large number of individual contacts of a few millimetres square in order to generate a large number of readings from only one sample. There are many advantages to this as on a 5 cm x 5 cm stack, 30 individual cells can be produced; this will give a better indication of the average efficiencies. For an I-V curve measurement the sample is placed in a holder which is illuminated by a xenon short-arc lamp at standard test conditions STC (AM 1.5G, 1000 W/m², 25°C). The current-voltage measurements give enough information to solve the equation:

$$I = I_0 [e^{\frac{qV}{nV_T}} - 1]$$

Where: I = output current, I_0 = dark saturation current, q = elementary charge, V=voltage, n = diode ideality factor, V_T = thermal voltage.

However this is the ideal case and in reality there are further considerations. Therefore the external quantum efficiency (EQE) will be measured to see the reaction of the cell with

respect to the wavelength of the incoming photons.

3.5.2 Spectrophotometer Transmission Measurements

A Varian Cary 5000 spectrophotometer was used to measure the optical transmission in the range 175 – 3300 nm through the cadmium sulphide and the transparent conducting oxide (TCO).

3.6 Microstructural Characterization

3.6.1 Scanning Electron Microscopy

3.6.1.1 Preparing samples for SEM

Sample preparation is very important if good results are to be recorded. This means the sample must be fairly flat and the samples must be conductive. As the surface is imaged, the samples must be clean. Isopropanol was used to clean the sample and then nitrogen was used to dry it to minimise surface residuals. The size of the samples is also limited due to the size of the chamber; the ideal size is 1 cm² as many samples can be placed into the SEM at one time. The samples were cut with a glass cutter and mounted onto SEM aluminium stubs with silver electrodag. As cadmium telluride is not conductive enough to fully dissipate the incoming primary electrons, there was a charge build up on the surface and the images collected were distorted. To overcome this charge an extremely thin layer of palladium-gold was deposited onto the surface using an Emitech SC7640 sputter coater for 60 seconds at a current of 20 mA. This allowed the charge to dissipate without affecting the surface morphology of the sample. This allowed for clear undistorted micrographs to be taken of the surface of the cadmium telluride, cadmium sulphide or the TCOs.

3.6.1.2 Field Emission Gun-Scanning Electron Microscope

A Leo 1530VP Field Emission Gun Scanning Electron Microscope (FEG-SEM) was used for microstructural analysis of the cadmium telluride solar cell stacks, as well as the individual layers which make up a cell. The FEG-SEM was generally used to look at the surface of the depositions using an in-lens detector, which requires a short working distance as it detects low energy secondary electrons coming from the surface of the sample. A high acceleration voltage of 20 kV with an aperture of 30 µm was used. Energy Dispersive X-ray (EDX) analysis was also carried out in the FEG-SEM using a 20 kV acceleration voltage and 60 µm aperture to give both qualitative and quantitative chemical analysis.

3.6.1.3 Fracture Cross Section (SEM)

Taking SEM fracture cross sections is a fast and easy technique which was regularly used to view the microstructure of the treated cells in cross-section. The samples were fractured using a glass cutter and mounted on SEM stubs at 90°. However it is hard to quantify the grain size from the SEM image as they are not clearly shown due to topography in the fracture section. Therefore TEM is a much better technique for grain size measurements.

3.6.2 TEM Sample Preparation using a Focussed Ion Beam

In TEM the quality of samples prepared is normally reflected in the quality and integrity of the results obtained. High quality TEM samples were prepared using an FEI Nova 600 Nanolab dual-beam system where, a standard insitu liftout procedure was used.

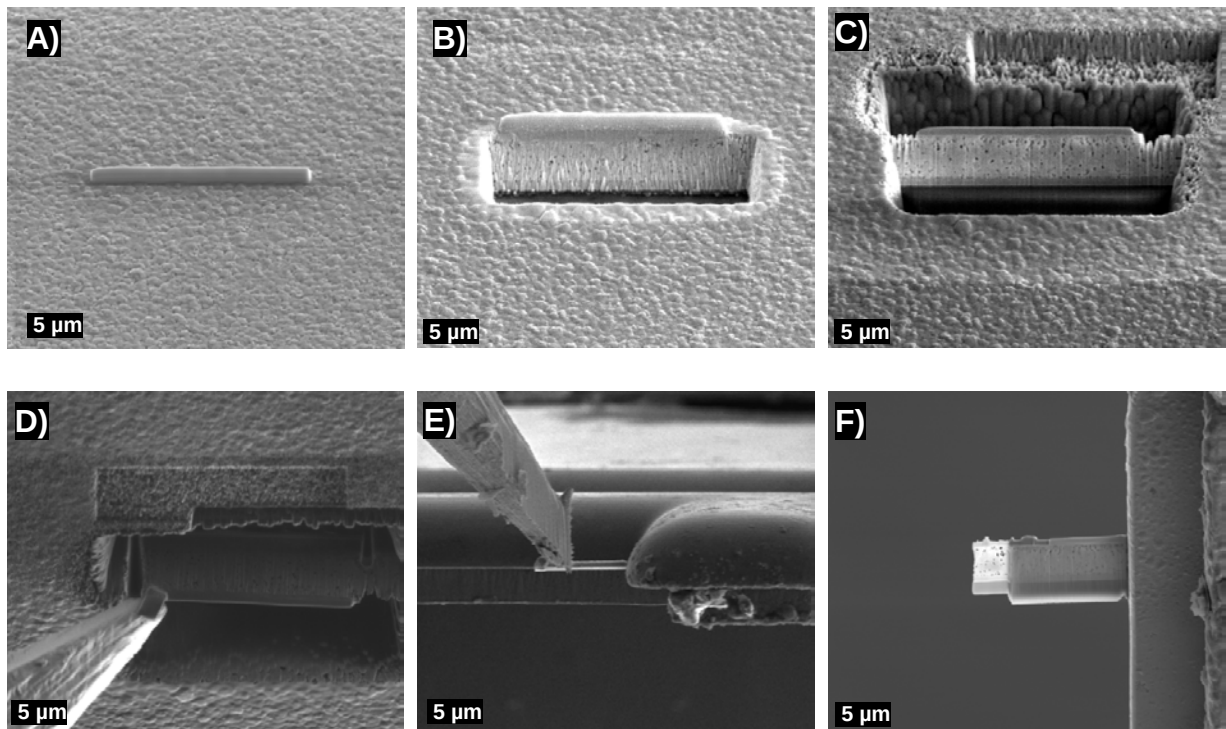


Figure 3.5– SEM and FIB induced SE micrographs taken at various stages of the in-situ TEM lift-out procedure
A) shows a SEM image of the platinum layer deposited onto the surface; B) show the trench formation; C) shows the sample after the cleaning cross section; D) shows the omniprobe attached to the TEM sample with the U-shape cut; E) shows the TEM sample attached to the probe and the copper grid; F) shows the final thinned sample.

This involved depositing a layer of platinum onto the sample surface above the area to be analysed, using the ion beam with a current of 0.5 nA. A typical area of 20 µm by 2 µm was covered, with a thickness of 2 µm. An SEM image showing the sample after it is deposited is shown in Figure 3.5a. If the top 50 nm of the sample is required for analysis then a layer of electron beam deposited platinum (using a voltage of 5 kV and current of 1.1 nA) was deposited before the ion beam platinum. Electron beam platinum has the advantage that it

does not implant ions into the sample surface, however the deposition of platinum with the electron beam is too slow to use for the whole platinum layer thickness. Two staircase trenches are then cut either side of the platinum layer which are approximately $25\text{ }\mu\text{m} \times 15\text{ }\mu\text{m}$, the depth depends on the sample etching rate, but it is usually of the order of less than $10\text{ }\mu\text{m}$ using an ion beam current of 20 nA shown in Figure 3.5b. After the formation of the trenches a few micrometers from the platinum, a cleaning cross section is used at the lower current of 7 nA to clean up to the platinum, leaving a sample of approximately $1\text{ }\mu\text{m}$ thick shown in Figure 3.5c. Once this is done the sample is tilted to 7° and a U-shaped cut is formed leaving a small uncut part to support the sample shown in Figure 3.5d. The omniprobe is then inserted and welded onto the platinum protective layer, with platinum at 50 pA shown in Figure 3.5d and the final support of the TEM sample to the bulk sample is disconnected using 1 nA beam. Once this is done the sample should be free and lifted out on the needle by lowering the stage. The next step is to attach the TEM sample to a copper grid and detach it from the omniprobe, using a platinum weld at 50 pA and ion beam at 1 nA respectively shown in Figure 3.5e.

Once the sample is attached to the copper grid it can be further thinned down to approximately 100 nm as shown in Figure 3.5f. This is achieved by milling the sample with the ion beam starting at 1 nA with the sample tilted 0.7° either side of 52° . The sample is milled until it is 500 nm thick. The ion beam current is then reduced to 0.5 nA and the end $10\text{ }\mu\text{m}$ of the sample is milled each side until the sample is 200 nm thick. The current is further reduced to 0.3 nA and the end $5\text{ }\mu\text{m}$ is thinned to 150 nm . Finally the last $5\text{ }\mu\text{m}$ of the sample is thinned using a 100 pA current until the thickness is $\sim 100\text{ nm}$.

3.6.3 Transmission Electron Microscopy (TEM)

TEM was carried out using a Jeol JEM 2000FX equipped with an Oxford Instruments 30 mm^2 EDX detector and a Gatan Erlangshen ES500W digital camera above the phosphor screen. The TEM provides a more clear view of the grain structure than most other electron based techniques as the electrons are passing through the sample and being detected the other side giving a small interaction volume. As the sample is ultra-thin EDX can also be carried at a higher resolution; therefore the detection of any inter-diffusion between layers is possible.

The TEM samples dimensions are relatively small in comparison to SEM samples. A normal size would be $5\text{ }\mu\text{m} - 10\text{ }\mu\text{m}$ in length. This means that the location where the sample must be

extracted from must be chosen with care. If a sample is not homogenous several TEM samples must be produced at different locations to be able to see any variation.

3.6.3.1 Stacking Fault Characterization in TEM

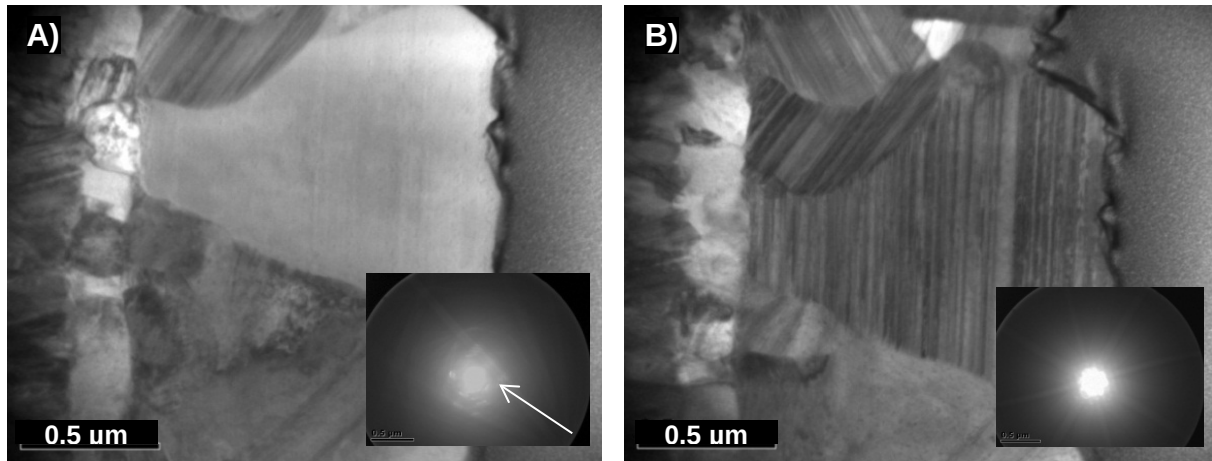


Figure 3.6 – Bright field TEM micrographs showing the effect of orientation on the visibility of stacking faults, [a] shows the grain not at a low order zone axis [b] shows the same grain tilted to the [011] zone axis (convergent beam diffraction patterns for these orientations are inset).

The stacking fault density was measured by counting how many stacking faults intersect a 1 micron line orthogonal to the stacking faults. For each sample 10 grains were measured and an average calculated. As the visibility of stacking faults changes with grain orientation, a double tilt holder was used in the TEM. The grain was tilted to the [110] zone axis prior to analysis by moving the Kikuchi pattern into the centre as shown in Figure 3.6a. In Figure 3.6a the grain shows almost no signs of stacking faults and when the Kikuchi pattern is collected from the grain, no zone axis was in the centre. The sample was then tilted until the [110] axis is centred. The electron beam is then directed along the (111) plane which makes the stacking faults visible as shown in Figure 3.6b. This exercise was performed for each grain to measure stacking fault density.

3.6.3.2 High Resolution Transmission Electron Microscopy (HRTEM)

High Resolution Transmission Electron Microscopy (HRTEM) was also carried out using a FEI Tecnai F20 (S)TEM. When the samples were prepared they underwent an extra step, a low voltage FIB clean-up of each side of the sample. The voltage of the ion beam was reduced to 5 kV and the current to 70 pA and the sample was tilted 2° each side of 52° (in-line with ion beam) and milled with the ion beam for 2 minutes. This reduces the amount of ion implantation and beam damage for better lattice imaging. HRTEM can be a useful technique for characterizing defects within the lattice of cadmium telluride and cadmium sulphide grains. Providing the sample is prepared well and the orientation of the sample is at

the correct zone axis, a resolution of 0.2 nm can be obtained. This gives atomic resolution images so that stacking sequences can be interpreted and defects characterised as twin boundaries, intrinsic stacking faults or extrinsic stacking faults. Lattice spacing can be measured from the atomic resolution images using software to characterise the image.

3.6.3.3 Scanning Transmission Electron Microscopy (STEM)

Scanning Transmission Electron Microscopy (STEM) was carried out in a FEI Tecnai F20 S/TEM equipped with Gatan Bright and Dark field STEM detectors, Fischione High Angle Annular Dark Field (HAADF) STEM detector, Gatan Enfina Electron Energy Loss Spectrometer and an Oxford Instruments X-Max 80mm² windowless energy-dispersive spectrometer (EDX). STEM imaging was performed at 200 kV with a camera length of 100 mm and condenser aperture size of 70 μm using a spot size of 7. HAADF images were collected in conjunction with STEM bright field images. HAADF imaging gives a unique perspective as the higher the atomic weight of the material the more the electrons passing through the sample will be detected. Therefore the amount of signal collected will depend on the atomic weights of the sample, giving atomic weight contrast in the image.

3.6.3.4 Energy Dispersive X-ray (EDX) in Scanning Transmission Electron Microscopy (STEM)

The (S)TEM system is equipped with a Silicon Drift Detector (SDD) allowing high spatial resolution Energy Dispersive X-ray (EDX) measurements and chemical mapping. This was largely used for mapping diffusion of elements such as chlorine and sulphur in the cadmium telluride matrix. Point analysis is also useful as quantification of elements can be acquired with a sensitivity of ~ 0.5 at% for light elements such as chlorine. EDX spectra were collected for 120 seconds. Maps were collected using the largest condenser aperture (150 μm) with the largest spot size. This allowed for a high number of counts. The dead time was controlled by changing the process time; each frame took approximately 120 seconds to collect. Maps were collected from 10 minutes up to 1 hour with no discernible sample drift.

3.6.4 X-Ray Diffraction (XRD)

Bruker D2 and D8 XRD spectrometers were used to carry out all XRD measurements. XRD is a powerful non-destructive technique for the characterisation of crystalline samples. It is used to find information on crystallographic structures, phases, crystallinity, residual stress, orientations and also the average grain size can be determined from the data produced. Both the XRD systems used copper monochromatic X-rays with a 1.542 Å wavelength at 30 kV/10

mA. Typical scans were carried out from 20° - 90° using a dwell time of 0.1 second with a step size of 0.02°. High resolution scans of some peaks were carried out using a longer dwell time of up to 1 second. The samples are required to be flat and cut to a size of 2 cm x 2 cm. There are some constraints that there is no depth information and signal can come from up to 2 µm into the sample, causing some issues for multi-layered devices. XRD also has a minimum spot size of 50 µm. A Bruker D2 was also used for longer scans of thinner films due to the faster collection rate than the Bruker D8.

3.6.5 Electron Backscatter Diffraction (EBSD)

Electron Backscatter Diffraction (EBSD) is a microstructural crystallographic technique which can be used to map grain orientation as well as phase identification, grain boundary angle information, grain defect information and grain size measurements. EBSD was carried out in the dual beam FEI Nova 600 nanolab using an ultra-high speed Hikari EBSD camera. The sample was tilted to 70° and a background signal subtracted to improve the Kikuchi patterns. An electron beam voltage of 20 kV was used with a nominal current of 24 nA. The collection rate of the Kikuchi patterns was 46 frames per second due to the slow scan speed required due to the small grain size of the material, which were indexed against a cubic/hexagonal cadmium telluride structure file. EBSD requires a very smooth surface for effective microstructural mapping. Therefore to analyse the surface of the cadmium telluride directly, a section of the surface was smoothed with a FIB using a beam current of 1 nA. The result of this sample preparation provides an adequately smooth surface for EBSD measurements to be obtained as shown in Figure 3.7.

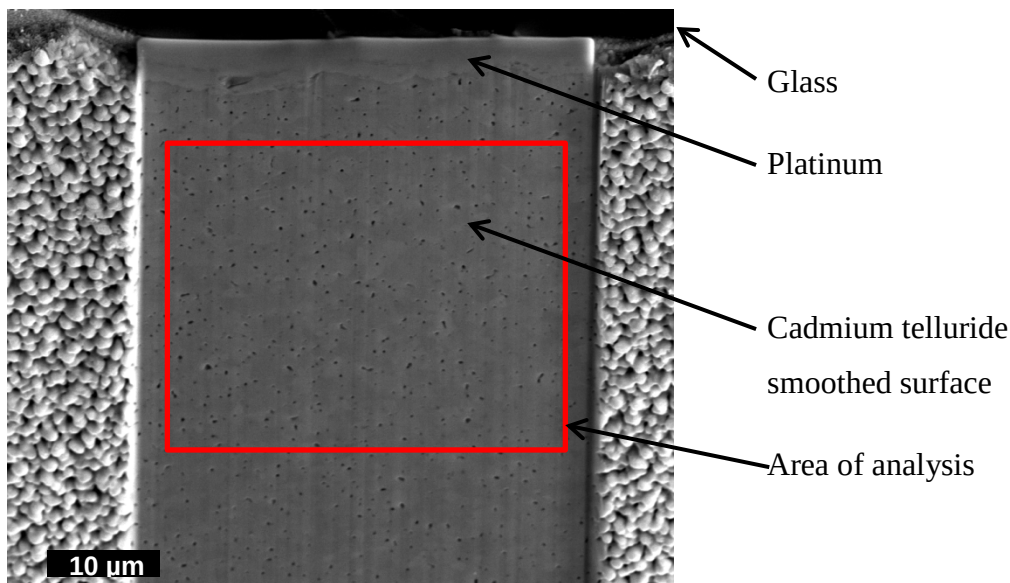


Figure 3.7- SEM image showing the area of analysis of treated cadmium telluride sample after being polished by a FIB.

3.6.6 Transmission Electron Backscatter Diffraction (T-EBSD)

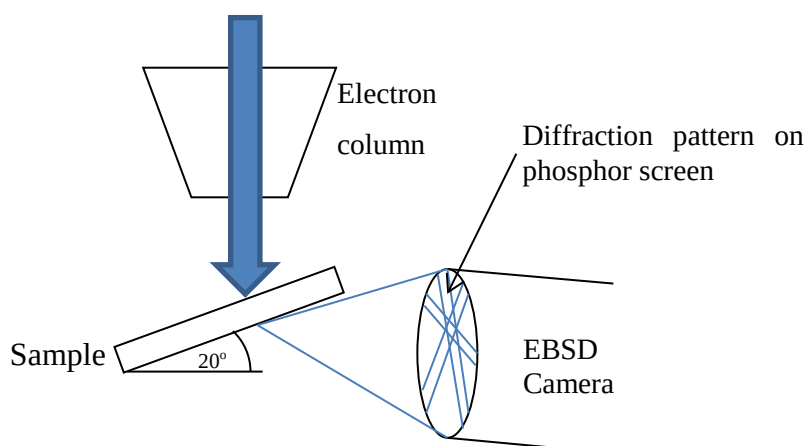


Figure 3.8- A schematic diagram of Transmission Electron Backscatter Diffraction hardware and sample position

The resolution of Electron Backscatter Diffraction can be improved from tens of nanometres[20,21] to around 5 nanometres if an electron transparent film is produced and positioned at 20° to the horizontal. Kikuchi patterns can be produced and collected from transmitted electrons from the underside of the sample. This setup is shown in Figure 3.8. An electron beam voltage of 30 kV was used and a current of 6.9 nA. This increases the spatial resolution of EBSD which is advantageous for this study due to the small grain size and defects such as twins present in some of the samples.

3.6.7 X-Ray Photoelectron Spectroscopy (XPS)

A VG ESCALAB Mk 1 was used for surface analysis and a Thermo Scientific K-Alpha X-ray Photo-electron spectroscopy (XPS) system was used for depth profiling and surface and subsurface analysis, using standard relative sensitivity factors to calculate atomic concentrations. XPS is a quantitative technique and chemical information can be obtained from binding energy shifts. XPS possesses a very high surface sensitivity as the signal is generated from the top few atomic planes. This makes it a valuable technique for detecting surface contamination. The Thermo Scientific XPS was also equipped with an ion beam, allowing for a surface etch prior to analysis to remove any surface contamination giving detailed compositional information of the deposited films. Surface survey scans were carried out using an X-Ray spot size of 150 μm with a pass energy of 50 eV and a step size of 1 eV from 0 eV to 1350 eV. 10 scans were carried out and an average plotted. Higher resolution scans were also carried out looking at certain peaks. For this the range was reduced to only

scan 10 eV either side of the peak and the step size reduced to 0.1 eV. 10 passes were carried out for each scan, on average. For sub surface scans a 100 eV ion beam etch was carried out for 50 seconds prior to the analysis.

3.6.7.1 XPS Depth Profile

The Thermo Scientific XPS was also used to carry out depth profile measurements of cadmium telluride cells. This was done by taking snapshot scans of the binding energies of the elements of interest. The sample was then etched for 120 seconds using a low current ion beam as the sample was rotated for a more homogenous etch. The sample was then scanned again. This was done 300 times and an elemental depth profile was produced from the data.

3.6.8 Secondary Ion Mass Spectroscopy (SIMS)

Secondary Ion Mass Spectroscopy (SIMS) was carried out at Loughborough Surface Analysis (LSA) for elemental distribution of cadmium, tellurium, copper, oxygen, chlorine, tin and sulphur. A Cameca IMS 3F and 4F were used for SIMS depth profiling. The analysis was performed using Cs^+ primary ion bombardment at 10 keV with a current of 1 μA with a spot size of 60 μm and negative secondary ion detection to optimise the sensitivity to chlorine. O^{2+} primary ion bombardment at 10 keV with a current of 20 μA with a spot size of 10 μm and positive secondary ion detection was used to optimise the sensitivity to copper. The chlorine data was quantified using an implanted reference sample of chlorine in cadmium telluride. No suitable reference sample was available with which to quantify the copper data.

CHAPTER 4. THE DEVELOPMENT OF CADMIUM TELLURIDE SOLAR CELLS DEPOSITED BY CLOSED FIELD MAGNETRON SPUTTERING

4.1 Chapter Background and Aims

A new magnetron sputtering strategy was introduced, for deposition of thin film cadmium telluride solar cells. It utilises a high plasma density ($\sim 5 \text{ mA.cm}^{-2}$) to avoid or reduce high temperature processing. The technique uses magnetrons of opposing magnetic polarity to create a “closed field” in which the plasma density is enhanced without the need for high applied voltages. The configuration links magnetic field lines between the magnetrons by reversing the polarity of adjacent magnetrons. The magnetrons are also unbalanced to further intensify the field and increase the ion current density in the plasma. Using this arrangement, the deposition volume in which the substrates are located is surrounded by linking magnetic field lines. This traps the plasma region, prevents losses of ionizing electrons, and results in significant plasma enhancement. The closed magnetic field system produces dense coatings due to the high ion current density. Magnetron sputtering has the advantage of producing uniform coatings over large areas with up to 1% thickness accuracy. This is essential if the absorber thickness is to be optimised. Magnetron sputtering is also controllable with deposition rates comparable to closed space sublimation, and inherently cost effective.

The chapter will follow the development of thin film depositions of cadmium sulphide and cadmium telluride by sputtering and compare them to chemical bath and close space sublimated films. Issues with continuous coverage of the thin films and the removal of inherent pinholes will be investigated. Optimisation and characterisation of the cadmium chloride processes for these devices is also undertaken. The treatment was done by solution processing, vapour transport and evaporation. Characterization includes identifying the crystal structure and grain morphology of the thin films and how it is affected by the cadmium chloride annealing heat treatment.

The thin film cadmium sulphide/cadmium telluride cell is deposited in a superstrate configuration detailed in Chapter 3.

4.2 The Deposition of the Cadmium Sulphide Window Layer via Magnetron Sputtering

Cadmium sulphide is the n-type window layer on which the p-type cadmium telluride is deposited forming a heterojunction. The cadmium sulphide typically possesses a stoichiometric chemistry and has a hexagonal wurtzite structure, but can also be cubic or a mixture of both these structures. It is an n-type semiconductor with a high energy band gap (2.4 eV) and low absorption coefficient to allow light to pass through to the absorbing cadmium telluride layer.

Cadmium sulphide was initially deposited via chemical bath deposition (CBD) as this is a well-established technique for this deposition and is known to yield good properties for cadmium telluride solar cells²⁴.

4.2.1 Closed Field Magnetron Sputtered Film Properties

4.2.1.1 Cadmium Sulphide Surface Morphology

Cadmium sulphide was sputtered using close-field magnetron sputtering on glass and fluorine doped tin oxide as well as indium doped tin oxide (sputtered in house). Initial results were promising as uniform layers with good adhesion properties were produced, and the samples were characterized to determine the films morphological and crystallographic properties.

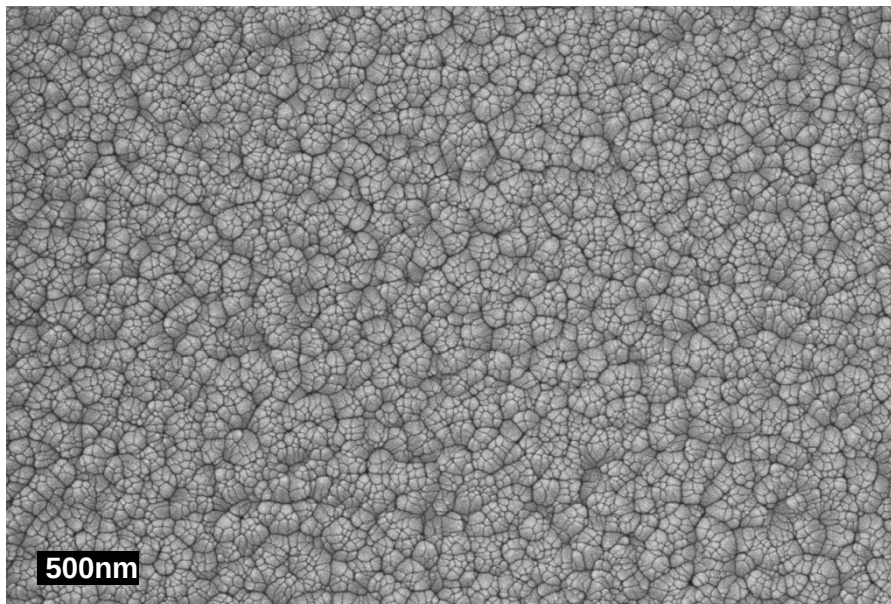


Figure 4.1 – An inlens SEM surface image of sputter deposited cadmium sulphide on FTO coated glass

Figure 4.1 shows the surface of the cadmium sulphide layer deposited onto TEC15 fluorine doped tin oxide (FTO)-coated glass. The image shows that the grains have a diameter of approximately 30 nm. It also reveals a uniform, pinhole free surface. The thickness of this

cadmium sulphide layer in this image was 250 nm.

4.2.1.2 Cadmium Sulphide Growth Morphology

Figure 4.2 shows a TEM image of the cadmium sulphide sputter coated on a glass substrate. The image shows that the film has a columnar through thickness thin grains. At the glass interface the grains are only several nanometres in diameter but as the grains grow up their diameter increases to approximately 100 nm.



Figure 4.2 – A Bright Field TEM image of a cadmium sulphide sputtered sample with columnar grain structure

4.2.1.3 Sputtered Cadmium Sulphide Crystallographic Properties

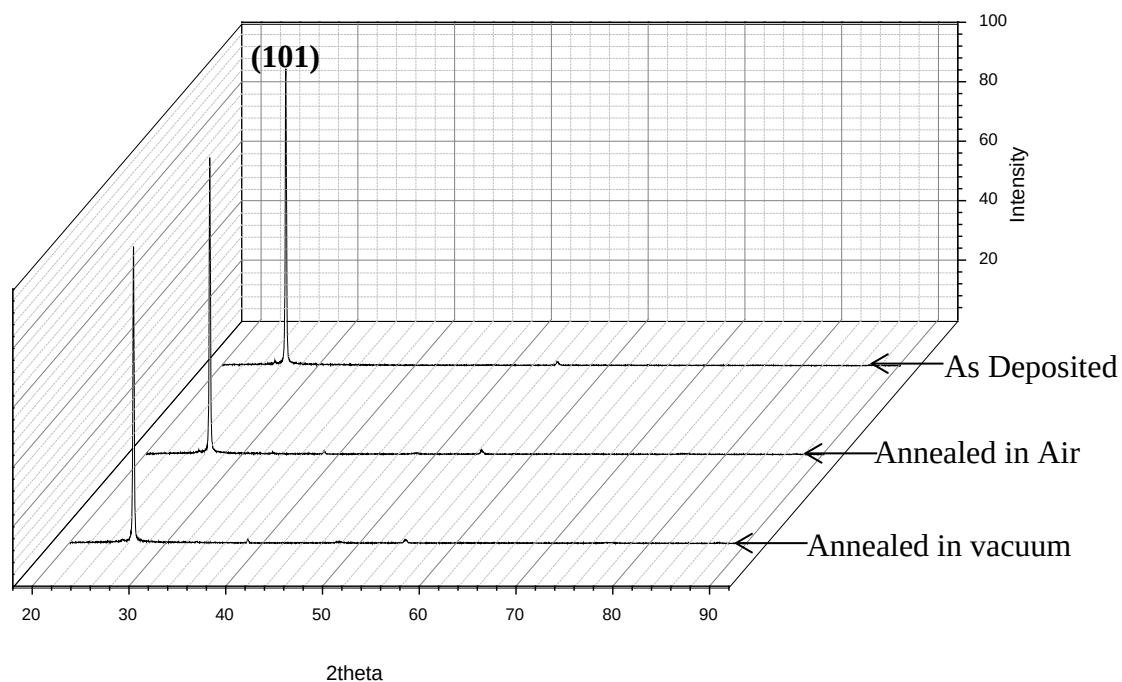


Figure 4.3 - X-ray diffraction (XRD) graph of cadmium sulphide layers, which underwent different post deposition treatments

The sputter deposited cadmium sulphide is hexagonal as shown in the XRD spectrum in Figure 4.3. All the samples have a (101) hexagonal peak and annealing has no effect on the crystallography measured by XRD. An advantage of sputter deposition is the accuracy and reproducibility with which this layer can be deposited since optimized layer thickness leads to maximum light transmission into the cadmium telluride absorber layer. The cadmium sulphide layer tends to absorb the lower wavelength electro-magnetic radiation from 300 nm to 550 nm, so a thinner layer is more advantageous as more light will reach the cadmium telluride absorber.

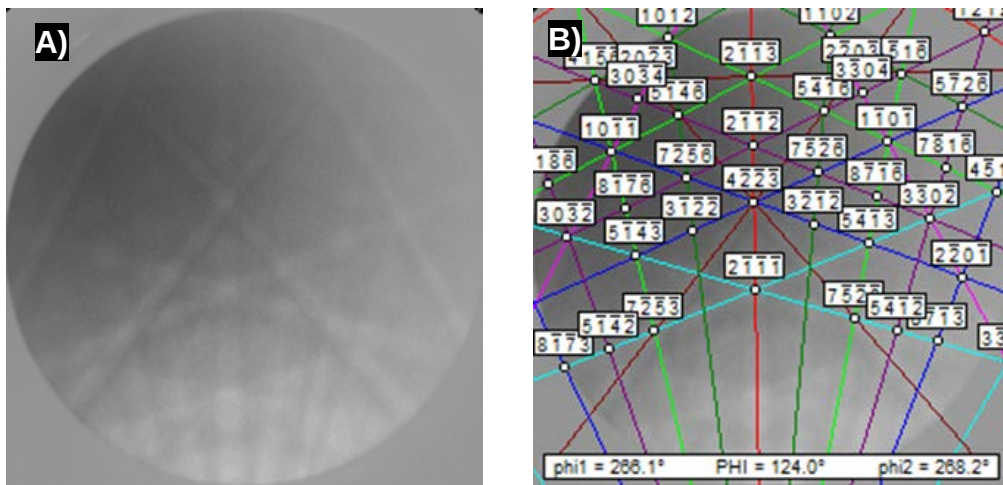


Figure 4.4 – a) A Kikuchi pattern collected from the cadmium sulphide layer and b) after indexing against the hexagonal cadmium sulphide structure file

Figure 4.4a shows a Kikuchi diffraction pattern collected in Transmission Electron Backscattered Diffraction (T-EBSD) from a cadmium sulphide grain. Figure 4.4b shows the Kikuchi pattern overlaid with the hexagonal miller indices, which indexed with a high confidence giving a clear indication that the grain is from an hexagonal phase. All Kikuchi patterns that were collected from various grains all index well to this hexagonal structure file.

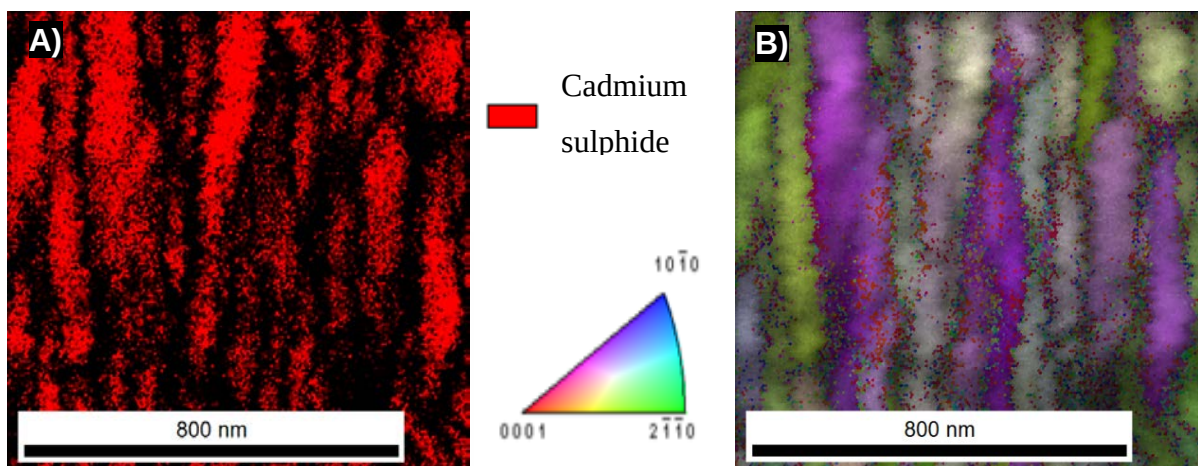


Figure 4.5 – a) Transmission Electron Backscatter Diffraction derived phase/confidence index map from a CdS sputtered sample b) IPF map of the sputtered cadmium sulphide layer

Figure 4.5a shows a high resolution T-EBSD derived phase/confidence index map from the cadmium sulphide sputtered sample shown in Figure 4.2. This map was collected over a 10 μm area to look for any phase changes from grain to grain, as from literature it is known that cadmium sulphide often forms a cubic, hexagonal or a mixture of both phases²⁴. However Figure 4.5a shows the sputtered cadmium sulphide film grains all possessed the hexagonal structure. As the sputtered cadmium sulphide possesses such small grains, conventional EBSD was not suitable but T-EBSD was able to produce a viable map due to its improved resolution capabilities. Figure 4.5 shows that reliable patterns are obtained within grains, however at grain boundaries lower CI and IQ values are obtained, as is expected.

The inverse pole figure (IPF) map shown in Figure 4.5b shows crystal orientation of individual grains in relation to the growth direction of the sputtered cadmium sulphide sample. The maps show that the sputtered grains seem to have a preferred growth direction.

4.2.2 Comparison of Closed Field Magnetron Sputtered and Chemical Bath Deposited Thin Film Cadmium Sulphide

4.2.2.1 Surface Morphology

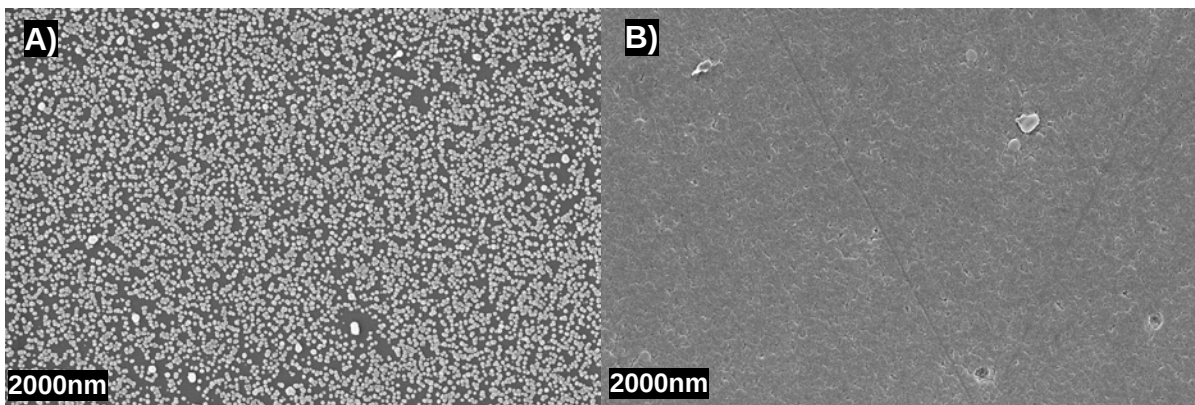


Figure 4.6 –Inlens SEM images of a cadmium sulphide surface deposited on glass via CBD for a) 30 minutes b) 90 minutes

Cadmium sulphide was also deposited via CBD in order to give a benchmark as it is a well-established technique for depositing the window layer for cadmium telluride solar cells[25,48,54,70]. The growth of CBD cadmium sulphide on glass is shown in Figure 4.6. The grains initially nucleate separately as shown by Figure 4.6a until they join together after a longer period of time (90 minutes) as shown in Figure 4.6b. The grains are seen to be fairly rounded and evenly dispersed except where there appears to be some surface contamination. This could possibly lead to pinholes in the layer as the cadmium sulphide is expected to be approximately 100 nm thick. Pinholes in the cadmium sulphide would be detrimental to the

cell, as it could lead to shunting of the cell if the cadmium telluride layer, which is deposited onto the cadmium sulphide, comes into contact with the underlying transparent conducting oxide. Therefore the substrate must undergo rigorous cleaning before the cadmium sulphide is deposited, as they have not been stored in vacuum prior to deposition. The grain size of the nucleating cadmium sulphide can be seen to be around 50 nm in diameter.

Apart from the pinholes and areas with surface contamination the cadmium sulphide appears very smooth and complete with an estimated grain size of typically 100 nm as seen in Figure 4.7, indicating that the grains kept growing in diameter until they formed a compact layer. The cadmium sulphide deposited via CBD is well known to have desirable properties for cadmium telluride solar cells, from a morphological point of view this can be seen to be true for these samples. A fairly smooth and complete layer was seen to be forming. The only exception was due to surface contamination. If the substrate undergoes a better surface cleaning procedure a pinhole free cadmium sulphide layer can be achieved. An example shown in Figure 4.7 was plasma cleaned before deposition.

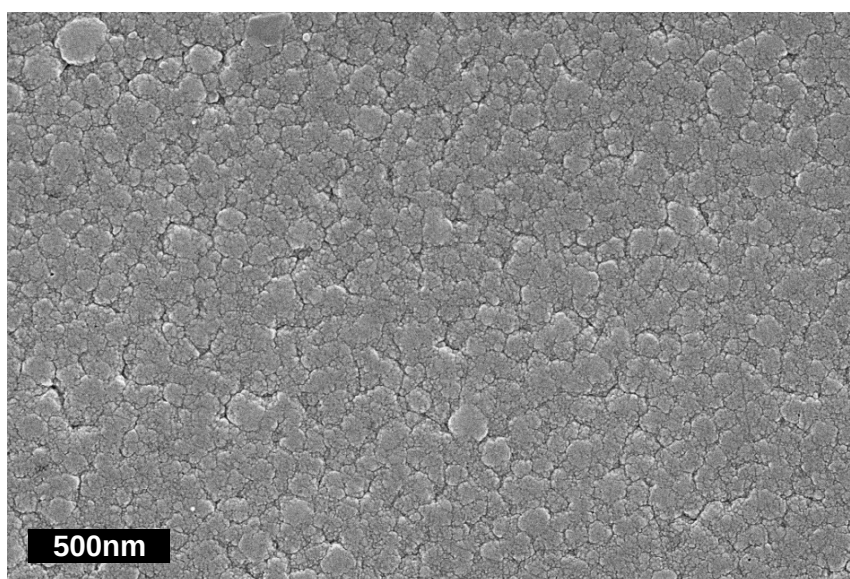


Figure 4.7 – An inlens SEM image of cadmium sulphide deposited via CBD on glass after plasma cleaning

4.2.2.2 Cadmium Sulphide Benchmark Crystallographic Sample Properties

The crystallography of the benchmark CBD samples were investigated using XRD to reveal the phase of the material so it can be compared to the sputtered samples. The cadmium sulphide layer analysed was deposited for 90 minutes to form a thicker layer. Due to the penetration depth of the X-rays being up to 1 μm , the thicker layer will reduce the signal from the underlying substrate. The underlying substrate is usually fluorine doped tin oxide, which contained diffraction peaks in similar regions to that of cadmium sulphide.

Although a thicker layer of cadmium sulphide was deposited, a signal was still generated from the FTO substrate dwarfing the cadmium sulphide peak. To overcome this, the cadmium sulphide was deposited onto a glass substrate.

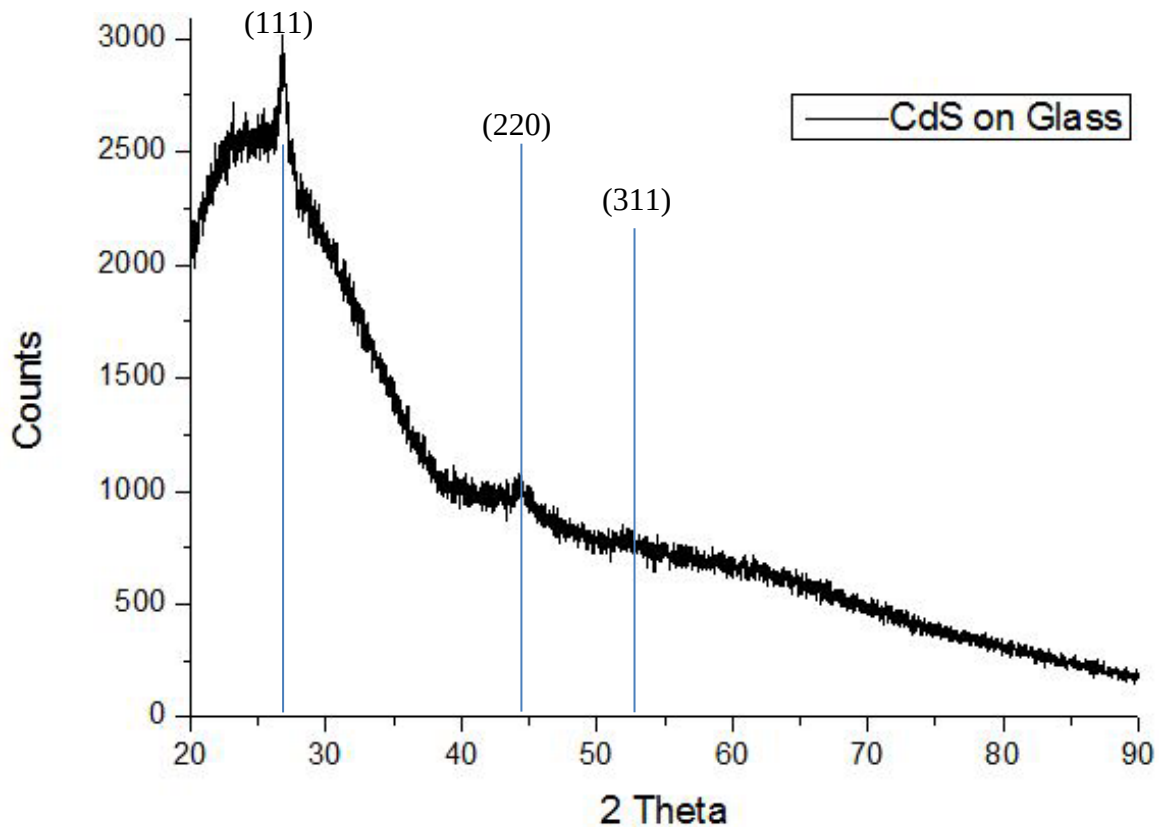


Figure 4.8 - a) – An XRD spectra of a 90 minute deposition of cadmium sulphide on glass substrate overlaid with corresponding powder diffraction card (PDF card) number 00-001-0647 peaks

The XRD spectra of the cadmium sulphide deposited on a glass substrate is shown in Figure 4.8a. The amorphous structure of the glass substrate is shown by the broad shaped peak, however two sharper peaks can be seen protruding, relating the (111) reflector plane at 26.5° and (220) plane at 43.9° which indexed to the cubic phase as shown by the powder diffraction file (PDF) number 00-001-0647 in Figure 4.8. The PDF in Figure 4.8 shows that the (111) and the (220) display the highest intensity and these peaks are the only ones clearly visible. The next highest intensity is the (311) diffraction plane at 51.2° which is just noticeable in Figure 4.8. As all the other intensities are much lower than the (111), (220) and (311) diffraction planes, they are not visible. The small grain size also causes peak broadening making the peaks harder to see.

In conclusion, the benchmark cadmium sulphide can be seen to have a grain size of around

100 nm, and display a cubic crystallographic structure.

4.3 The Deposition of the Cadmium Telluride Absorber Layer via Magnetron Sputtering

The cadmium telluride layer was deposited using close-field magnetron sputtering. The target was more resistive than the cadmium sulphide target and therefore more power was needed in order to sputter at a fast rate.

The initial samples were of only a single layer of cadmium telluride deposited onto a soda-lime glass substrate; the depositions were initially examined using a FEG-SEM which was used to image the surface. Figure 4.9 shows that the coating had a fairly smooth deposition; however it also showed a large amount of cracking. The initial cadmium telluride layers were deposited much thicker than the desired 2 μm , and since the stress in the layers is expected to increase with increasing film thickness, thinner coatings were produced. The cadmium telluride was deposited onto glass, reducing the thickness with each deposition in order to observe any change in the cracking of the layer. Any cracks in the cadmium telluride layer would cause shorting if a cell was constructed as the back contact (copper or gold) would diffuse down the cracks and make contact with the front contact so that no current or voltage would be observed. Therefore it was fundamental that no cracks were present in the cadmium telluride layer. The results showed that the cracking was reduced as the layer was thinned, until it was completely overcome, illustrated in Figure 4.10a.

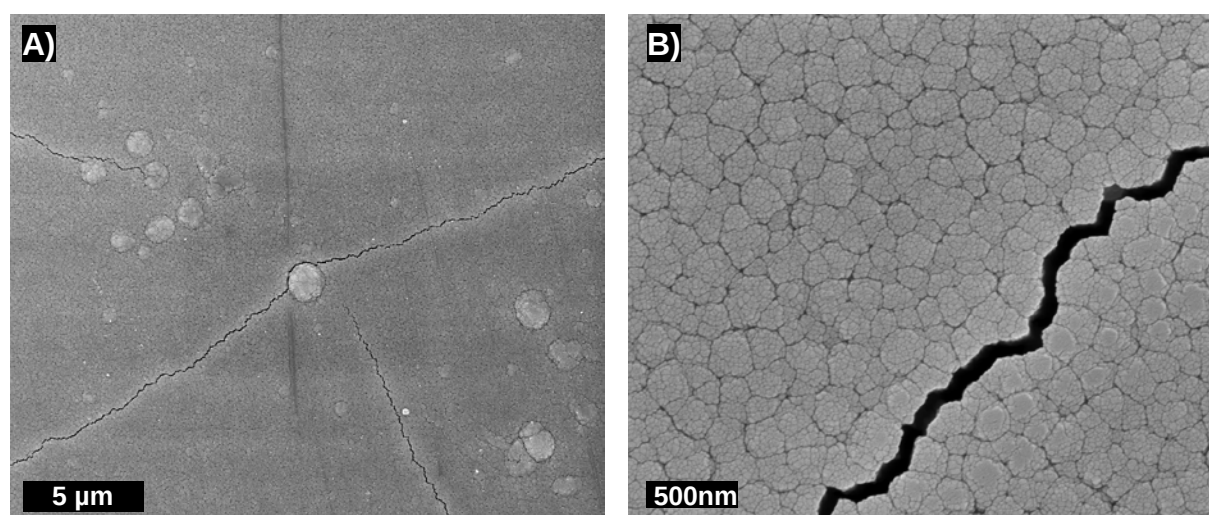


Figure 4.9 – Inlens SEM surface images of cracks in the cadmium telluride layer at a) low magnification, b) high magnification

4.3.1 Thin Film Cadmium Telluride Properties

Figure 4.10a shows a surface image of the sputtered cadmium telluride layer, which has a thickness of approximately 2 μm . The layer appears uniform and smooth with a grain size of less than 100 nm. Film thickness control to 1% is possible with magnetron sputtering using time and power only, which is advantageous as this minimises the waste of the expensive materials. The smoothness of the film is shown in Figure 4.10b, which also displays the columnar morphology of the grains. A magnetron sputtering configuration that produces high argon plasma densities has been used to deposit each of the layers in a thin film cadmium sulphide/cadmium telluride photovoltaic stack. The SEM shows that sputter deposition of cadmium telluride results in highly compact layers and the morphology is dominated by columnar grain growth.

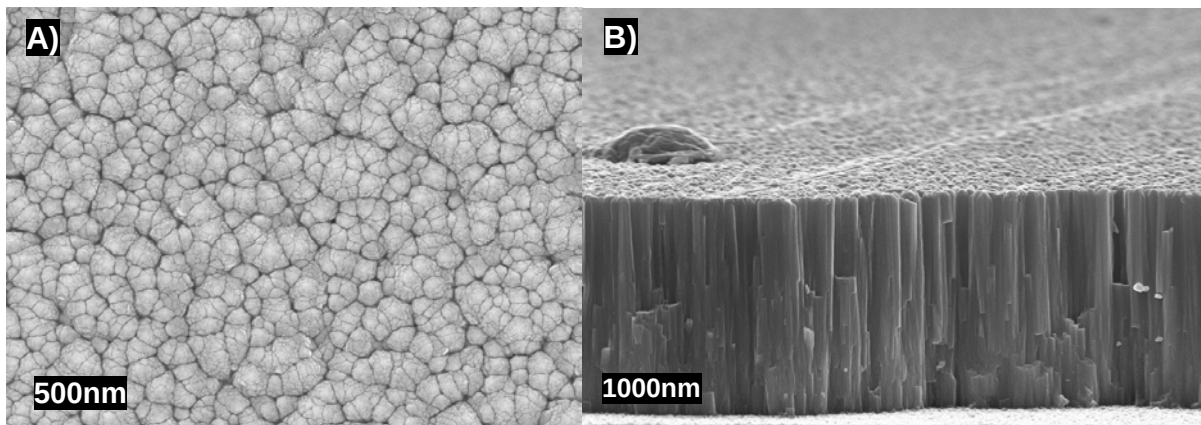


Figure 4.10 - Inlens SEM image of the surface morphology of sputter deposited cadmium telluride and b) cross section SEM image of a thick cadmium telluride on FTO coated glass cell with thin through thickness columnar grains

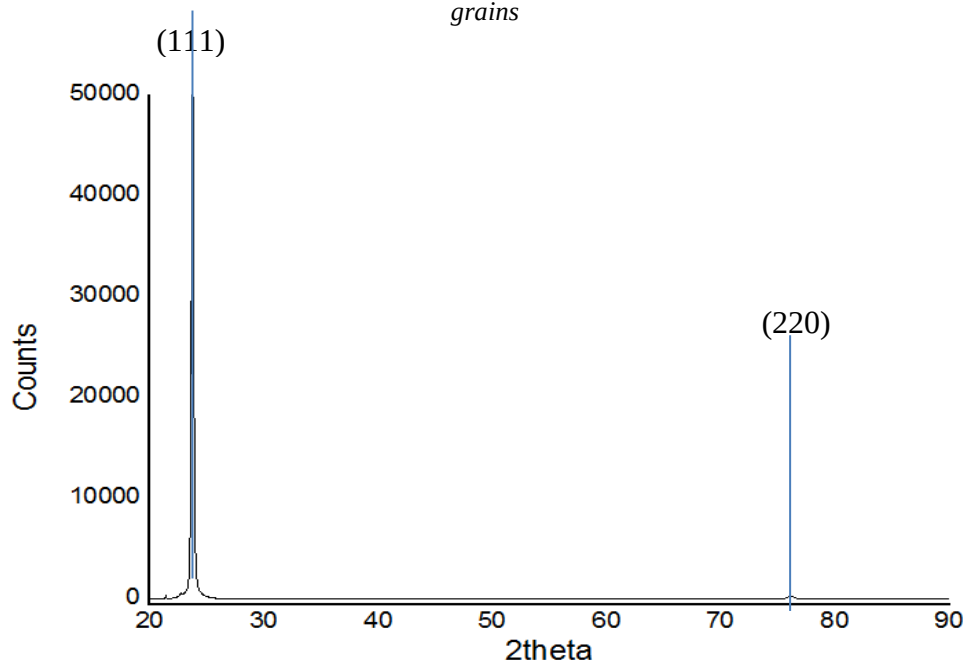


Figure 4.11 An XRD spectra of the sputtered cadmium telluride and overlaid with the corresponding powder diffraction file

Figure 4.11a shows the XRD spectra of the sputtered cadmium telluride film with a dominating (111) peak with room temperature depositions. The grain size is typically 50 nm in diameter and through thickness in a 2 μ m thick coating. The cadmium telluride grain morphology follows that of the sputtered cadmium sulphide layer, which is also columnar with a grain size of $\sim$ 30 nm in a thin film thickness of 100 nm.

Magnetron sputtering with high plasma densities may be used to deposit all the layers in a cadmium telluride/cadmium sulphide photovoltaic stack. The study has also revealed that sputtering results in highly uniform thin film thicknesses both for individual layers and for multilayer stacked structures. This uniformity is important since it means that the cadmium telluride absorber thickness can be controlled accurately leading to potential cost reduction and the production of consistent device performance.

4.3.2 The Effect of Argon Flow Rates on Thin film Cadmium Telluride

The argon pressure (controlled by the gas flow rate) is well known to have an impact on the deposition rate and film properties. The gas flow rate is measured in standard cubic centimetres per minute (SCCM). At higher argon sputtering pressures the sputtered and reflected neutral atoms arriving at the substrate inherently have low energies. This is due to the increased number of collisions before arriving at the substrate. This causes the atoms arriving at the substrate to have a lower surface mobility. This in turn has a large effect on the growth kinetics of the depositing film, and therefore on its structural, morphological and crystallographic characteristics.

At low argon flow rates the sputtered and reflected neutral atoms have much higher energies than the plasma gas between the target and substrate and arrive at the substrate with high energy due to undergoing fewer collisions before their arrival. Therefore the sputtered atoms in low argon pressure conditions have a high surface mobility when they arrive at the substrate. It is therefore essential that the sputtering pressure is carefully investigated to obtain viable thin films. The argon flow rate can be varied to alter the stress in the deposited film. At lower flow rates the film will be under compressive stress, whereas at a higher argon flow rates the films will have tensile stress¹⁵. So there is an optimum argon flow rate to achieve a maximum sputter rate, with unstressed films. The effect of argon flow rates on the films was investigated using TEM and XRD analysis. The sample conditions are shown in Table 4.1 with varying argon flow rates ranging from 20 sccm to 100 sccm, and with the sample P1 (20 sccm) also with and without a post deposition anneal at 400°C for 20 minutes.

Sample	Sputter Tool	Argon Flow
P1	CdS(RT)/CdTe(RT)	20 sccm
P1 post-annealed	CdS(RT)/CdTe(RT)	20 sccm
P2	CdS(RT)/CdTe(RT)	50 sccm
P3	CdS(RT)/CdTe(RT)	70 sccm
P4	CdS(RT)/CdTe(RT)	100 sccm

Table 4.1- A summary of the sputtered sample deposition conditions with varying argon flow

Figure 4.12 shows Bright-Field-STEM images of complete cross-sections through the cadmium telluride/cadmium sulphide layers deposited onto TEC10 TCO substrates, with varying argon flow rates during the cadmium telluride layer deposition. Figure 4.12a shows the cadmium telluride layer deposited at the lowest rate. The image shows a very dense cadmium telluride layer, with a grain size less than 10 nm. The underlying cadmium sulphide has a similar grain width to the cadmium telluride, as the grain boundaries follow on from the underlying layer. Due to the small grain size it is not clear that the thickness of the TEM samples is more than the grain thickness, therefore the TEM sample is made up of several grains in width. Linear defects are observed perpendicular to the growth direction. Figure 4.12b shows a sample with an argon deposition flow rates of 50 sccm. This appears less dense than the sample deposited with 20 sccm of argon and the grains appear to form in nodules, with pore channels between nodules. These form due to the roughness of the underlying TCO as the cadmium sulphide is very conformal. In the valleys of the TCO, the cadmium sulphide also has a valley directly above this point. The cadmium telluride therefore grows on this uneven surface, which causes pore channels forming at the minima. The samples at higher argon pressure shown in Figure 4.12c and Figure 4.12d also have pore channels at these points. The pore channels are thin voids which run between each nodule of the grain. If these samples were treated, it would allow diffusion along these channels. The samples deposited with 50, 70 and 100 sccm of argon all appear to have a similar grain size of ~20 nm. This indicates that the argon pressure has reached a critical point for maximum grain size, somewhere between 20 sccm and 50 sccm as the mobility of the arriving atoms are similar with an argon pressure above 50 sccm. The pore channels in the three samples deposited above 50 sccm of argon are between 100-150 nm apart. All the samples appear to have a very high density of stacking faults running perpendicular to the growth direction.

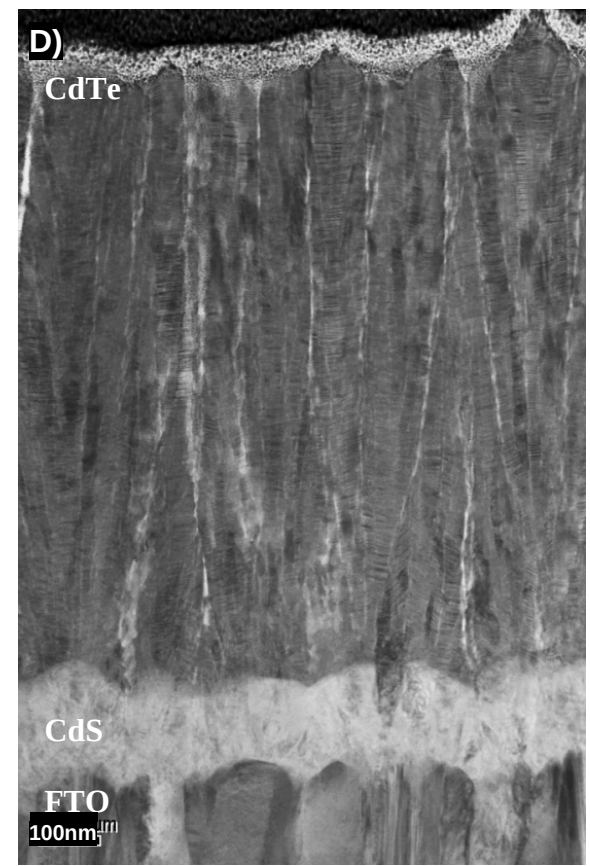
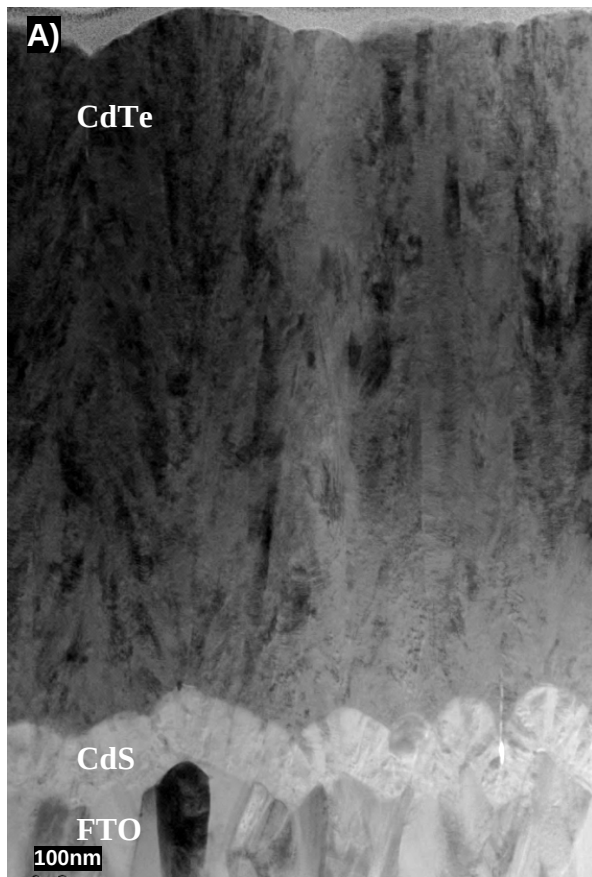


Figure 4.12 – BF-STEM images of cadmium telluride cells sputter deposited at varying argon flow rates of a) 20 sccm, b) 50 sccm, c) 70 sccm and d) 100 sccm

The XRD plot in Figure 4.13 shows the (111) reflection for the cubic cadmium telluride phase, with the (111) reflection highlighted from the PDF ICCD database at 23.7771°. The sample deposited with 20 sccm of argon shows the greatest peak shift, which corresponds to the highest film stress. This is also indicated by the dense films shown in Figure 4.12a. The other 3 samples show little signs of peak shift as they are not far from the PDF database angle. The sample deposited at 20 sccm also shows a much broader peak than the other samples. This is due to the smaller grain size. From the TEM images in Figure 4.12 it shows the sample deposited at 20 sccm has grains of less than 15 nm, whereas the other three samples all have similar grain sizes.

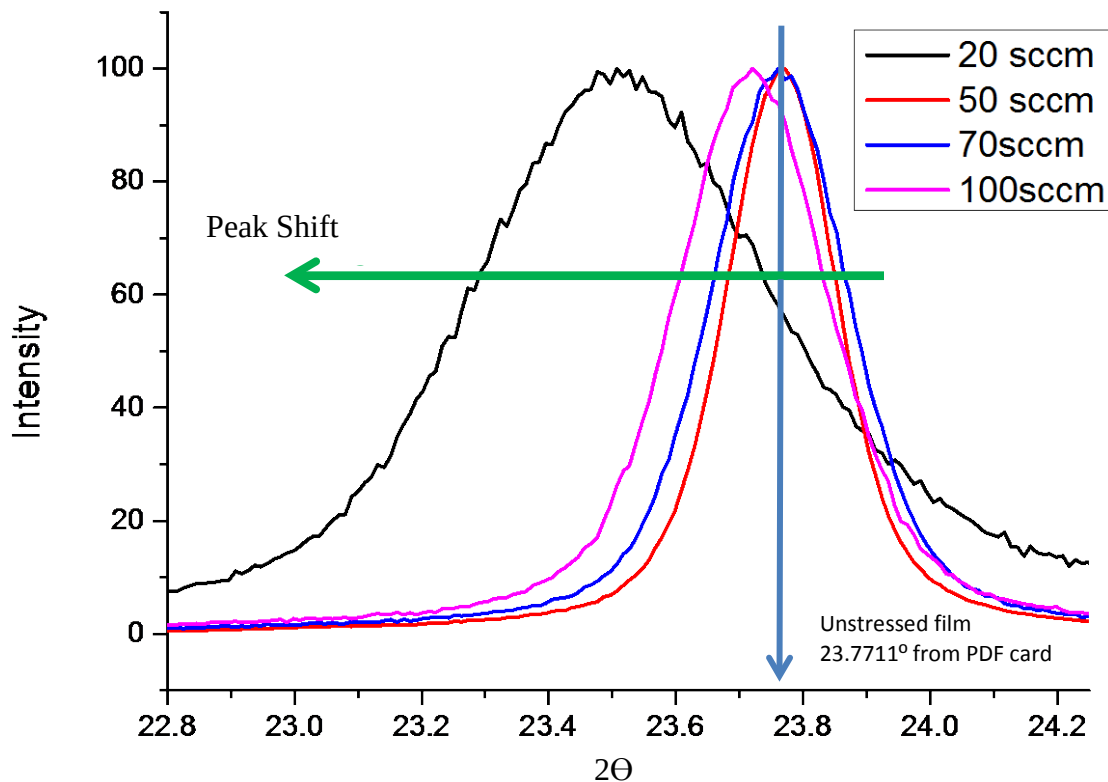


Figure 4.13 – A XRD spectra of the (111) peak for the samples deposited at different argon pressures

By use of the Scherrer equation the grain sizes of the four samples were calculated shown in Table 4.2

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where: τ = The calculated mean grain size, K = dimensionless shape factor (1 for columnar growth), β = the line broadening at half the maximum intensity (FWHM) and θ = the Bragg angle

Sample	Θ (degrees)	β	λ (nm)	τ
1P	23.5	0.59	1.54056	14 nm
2P	23.85	0.28	1.54056	29 nm
3P	23.8	0.28	1.54056	29 nm
4P	23.7	0.28	1.54056	29 nm
1p annealed	23.7	0.34	1.54056	25 nm

Table 4.2 – A table showing the scherrer equation parameters for each sample

From the TEM image in Figure 4.12a it is hard to estimate a mean grain size due to the grain width being thinner than the width of the TEM sample. The XRD has shown a grain size of the three samples over 50 sccm of argon are similar ~ 29 nm, which correlates well with the TEM results. The sample deposited with the lowest gas flow at 20 sccm has a much smaller grain size of ~ 14 nm, which is also consistent with the TEM results.

4.3.2.1 Annealing a Stressed Cadmium Telluride Thin Film

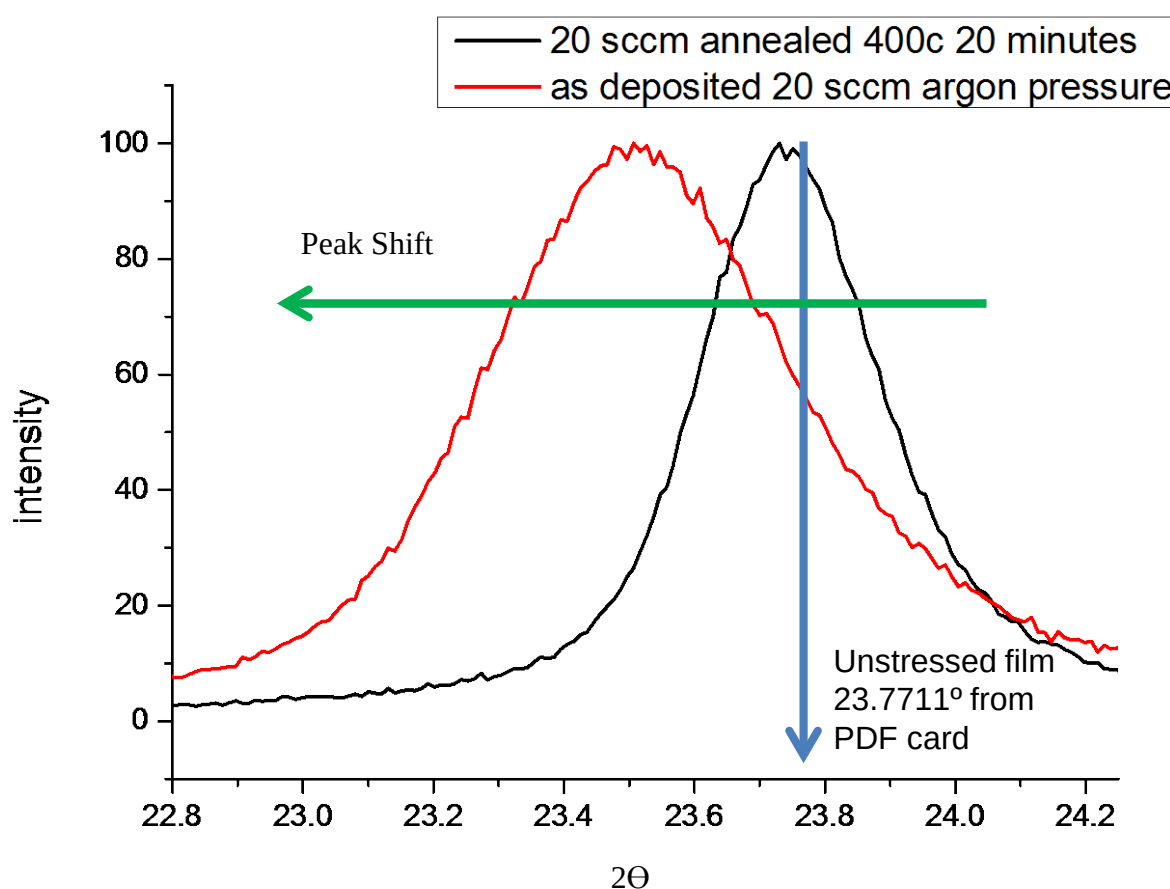


Figure 4.14- A XRD spectra of the (111) peak for the sample deposited with 20 sccm of argon and then the same sample but annealed at 400°C for 20 minutes

Magnetron sputtered samples using low gas pressures are often under tensile stress due to the high mobility of the atoms during deposition. Annealing the sample post-deposition can often relieve stress in the thin film¹⁵. In Figure 4.13 the sample deposited with a low gas pressure of 20 sccm showed the largest peak shift away from the PDF reference point. After a 20 minute anneal the film showed a large reduction in peak shift shown in the XRD plot in Figure 4.14. The peak shift correlates to a change in lattice parameter, therefore is stress relieved as the lattice parameter has increased.

4.3.3 The Effect of Deposition Temperature on Thin film Cadmium Telluride

The temperature of the substrate during magnetron sputtering can also have a large impact on the deposited film and can control the morphology and crystal properties of the deposition. Stress can be induced in the thin film if the thermal expansion coefficient of the substrate and film are dissimilar. An increase in deposition temperature will also increase the surface mobility of the arriving atoms, ultimately altering the morphology of the deposition. The samples analysed in this section are summarised in Table 4.3.

Sample	Substrate	Sputter Tool	Argon Flow Rate (Sccm)
T250	3mm SLG/TEC10	CdS(RT)/CdTe(250°C)	100
T250i	1mm Glass	ITO/CdS(RT)/CdTe(250°C)	100
T300	3mm SLG/TEC10	CdS(RT)/CdTe(300°C)	100
T400	3mm SLG/TEC10	CdS(RT)/CdTe(400°C)	100

Table 4.3 - A summary of the sputtered sample deposition conditions with varying substrate and deposition temperatures

Figure 4.15 shows the cells morphology after sputtering at 250°C. It is immediately apparent that the cadmium telluride grain size has increased from the room temperature deposition from around 30 nm to over 250 nm, increasing almost 10 fold. Figure 4.15a shows the top of the cadmium telluride film. The grains are larger at the top of the coating compared with the bottom of the coating. All grains appear to be highly faulted perpendicular to the growth direction, with the stacking defects terminating at the grain boundaries. In both Figure 4.15a and Figure 4.15b showing the top and the bottom of the cadmium telluride layer respectfully, voids can be seen between some grains. These voids relate to the roughness of the FTO substrate, as the cadmium sulphide is conformal with the FTO. Where there is a dip in the FTO the cadmium sulphide also has a dip. This subsequently causes voids in the proceeding cadmium telluride film. The cadmium sulphide grain size is observed to be less than 2 nm in diameter shown in Figure 4.15b. The cadmium telluride in some cases appears to follow the

grain boundaries of the previous layer and this causes the cadmium telluride grains initially to have a smaller diameter at the cadmium sulphide interface. All layers appear columnar in nature including the FTO conductor.

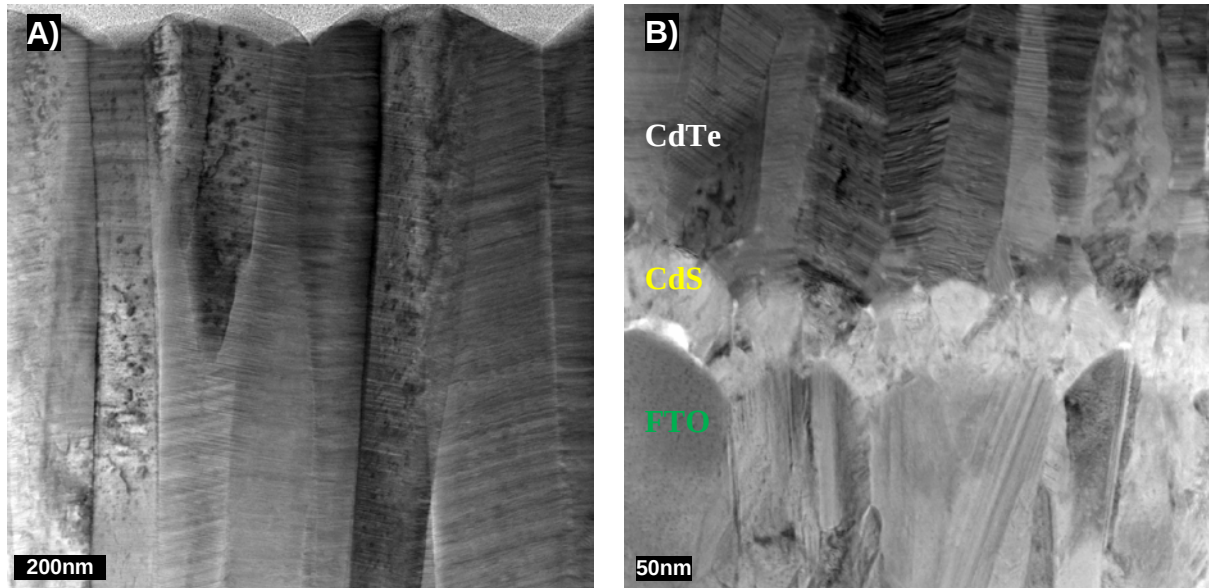


Figure 4.15 – BF-STEM images of sample T250 showing A) top of the cadmium telluride B) cadmium telluride/cadmium sulphide/FTO interface

4.3.3.1 The Effect of the Substrate on Sputtered Thin Films

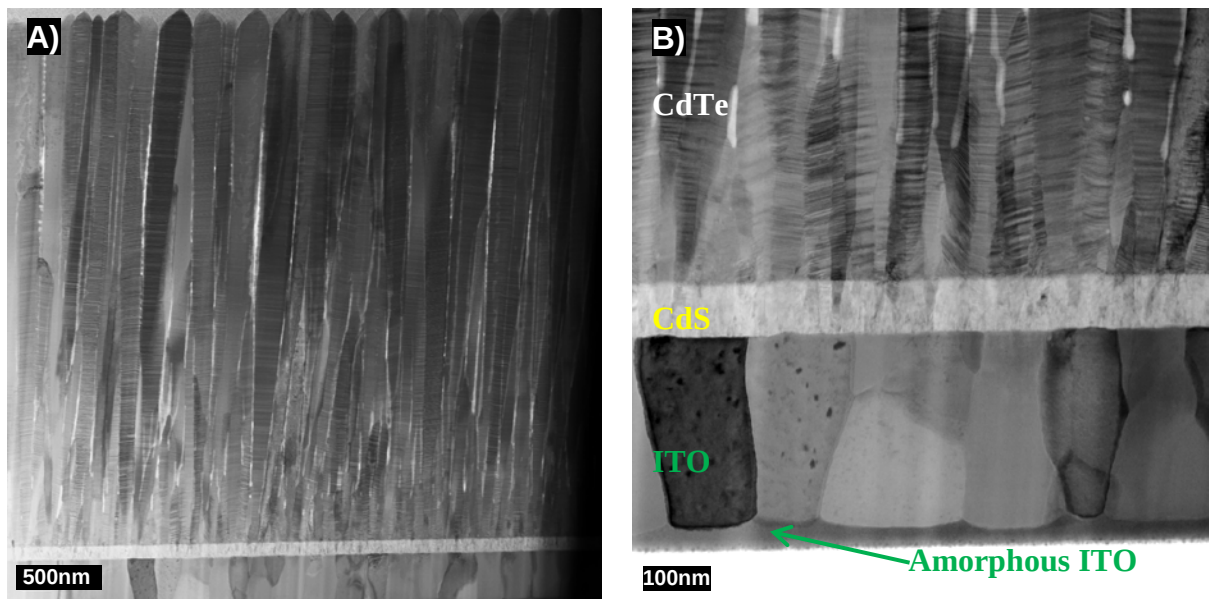


Figure 4.16 – BF-STEM images of sample T250i showing A) top of the whole cell B) cadmium telluride/cadmium sulphide/ITO interface

Figure 4.16 shows the cell deposited with the same conditions as Figure 4.15 but with a tin doped indium oxide (ITO) substrate, which is much smoother than the Pilkington FTO. Figure 4.16a shows the whole morphology of the cell with the pores still present between some grains. Figure 4.16b shows the ITO/cadmium sulphide/cadmium telluride interface, which shows the ITO is extremely smooth with mainly through-thickness columnar grains,

however there is an amorphous initial growth layer less than 50 nm in thickness. The ITO grains are ~ 200 nm in width. However the proceeding cadmium sulphide layer does not follow the grain boundaries of the ITO and possesses a similar grain size to Figure 4.15. The cadmium sulphide layer now is also very smooth. Due to the smoothness, the cadmium telluride initially appears dense but after ~ 300 nm the voids start appearing between grains. The cadmium telluride also follows some of the underlying cadmium sulphide grain boundaries, causing grains at the interface to be smaller. The grains become larger with increasing distance from the cadmium sulphide interface. All cadmium telluride grains appear to have a very high density of linear defects throughout the film.

The rest of the samples deposited at various temperatures were deposited onto Pilkington TEC10 FTO coated soda lime glass, as this is the main substrate used throughout this study, giving a better comparison.

Figure 4.17 shows the morphology of the sample with the cadmium telluride deposited at 300°C . From Figure 4.17a the top of the cadmium telluride grains can be seen. They are ~ 300 - 400 nm in width. All the grains appear highly faulted, with some thin voids running between grains. Figure 4.17b shows that in the cadmium telluride layer close to the cadmium sulphide interface wider voids between grains are observed. The grain growth between cadmium sulphide and cadmium telluride is related, as some grain boundaries are observed to continue between the layers.

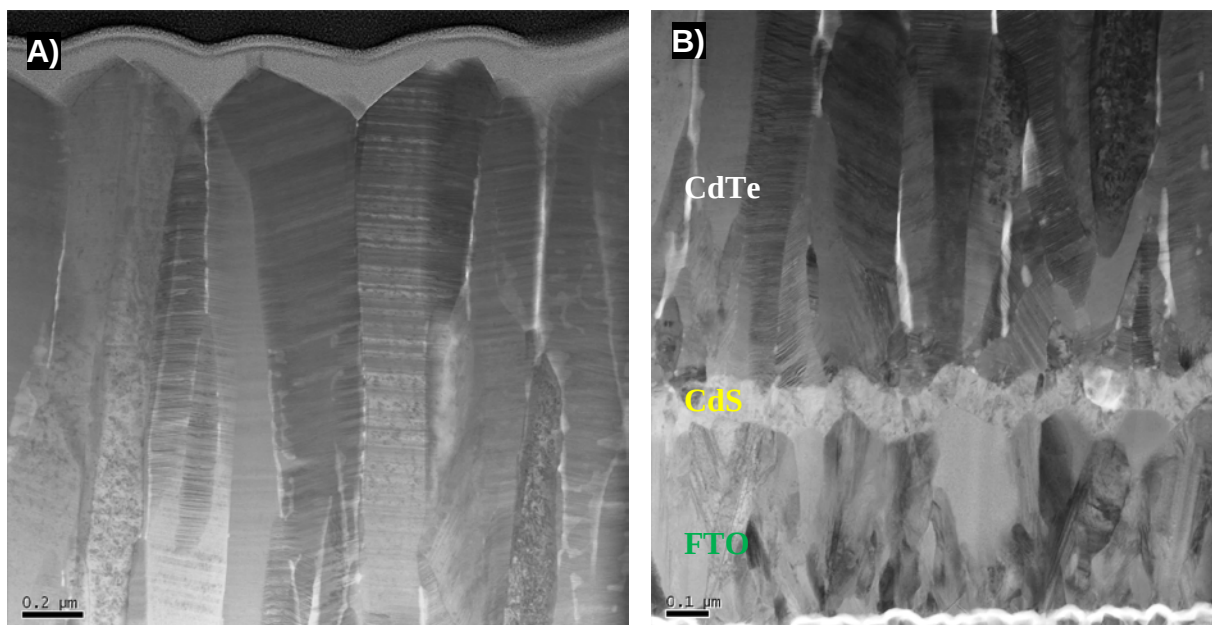


Figure 4.17 - TEM images of sample T300 showing A) top of the cadmium telluride B) cadmium telluride/cadmium sulphide/FTO interface

Figure 4.18 shows the grain morphology of the sample with the cadmium telluride deposited at 400°C. Figure 4.18a shows the whole cell. The cadmium telluride grain growth starts with smaller grains at the bottom of the film and reaches up to 500 - 600 nm in diameter at the top of the film. Figure 4.18b shows the cadmium sulphide/cadmium telluride interface. The thin cadmium sulphide has a grain size of less than 15 nm in diameter. This suggests that the cadmium telluride nucleates initially with smaller grains ~50-100 nm in diameter.

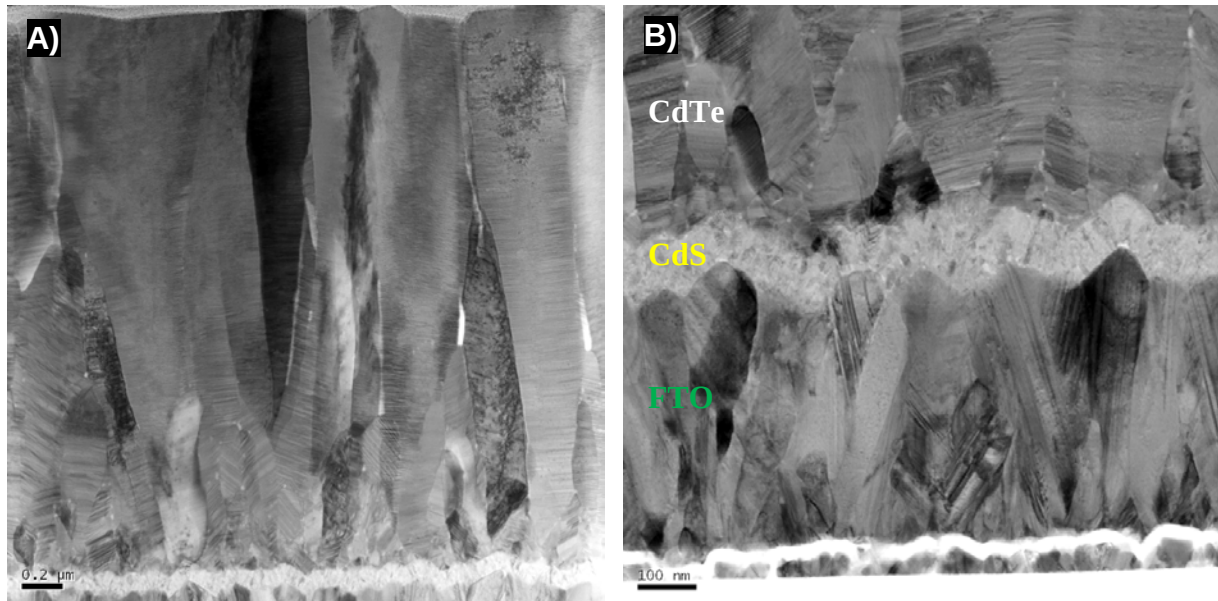


Figure 4.18- BF-STEM images of sample T400 showing A) top of the cadmium telluride B)cadmium telluride/cadmium sulphide/FTO interface

Varying the cadmium telluride deposition temperature has an effect on the microstructure of the film. With an increase in temperature grain growth is apparent up to ~600 nm. However the initial growth of the cadmium telluride film for all the samples is smaller than the top of the film due to a continuation of grain boundaries from the underlying cadmium sulphide. All samples possessed a high density of stacking defects within the cadmium telluride grains.

4.3.4 Comparison of Novel Sputtered Cadmium Telluride with Close-Spaced Sublimated Cells

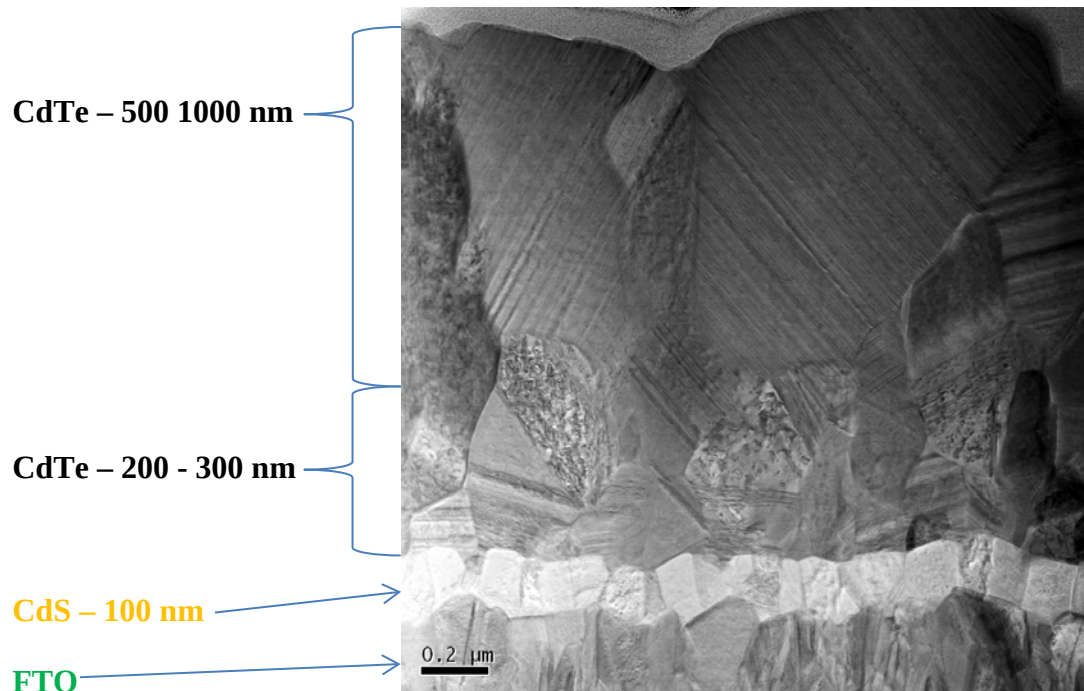


Figure 4.19 – A BF-STEM image of an untreated cadmium telluride solar cell deposited via closed space sublimation

As the sputtering of cadmium telluride solar cells is a novel technique, a comparison to a more established process route is advantageous. Closed space sublimated (CSS) cells will be examined in depth in Chapters 6-8. Figure 4.19 shows the morphology of the optimum CSS device before the cadmium chloride treatment. Comparing this to the sputter deposited samples both the grain size of cadmium sulphide and cadmium telluride is larger. The cadmium sulphide has a grain size of ~100 nm compared to less than 10 nm in the sputtered samples. Subsequently the cadmium telluride film has larger grains of up to 1000 nm, compared to 15 - 500 nm in the sputtered samples. There is however a similarity in the growth morphology of the cadmium telluride layer as the initial nucleation of the film has smaller grains with larger grains developing growing out towards the top of the film. The cadmium telluride in both materials has a high density of linear stacking defects.

4.4 The Development of a Pin-Hole Free Cadmium Sulphide/Cadmium Telluride Thin Film Closed Field Sputtered Cell

Figure 4.20a shows the formation of a pinhole in a sputtered cadmium telluride film. It appears much lighter in the image than the rest of the surface as the glass substrate below is charging during imaging. Figure 4.20b shows the pinhole to be approximately 2 μm in diameter which is more than enough to allow fast penetration of the metal back contact down to the TCO layer causing the cell to short circuit. Therefore all pinholes must be prevented from forming during deposition, so the cause must be identified and rectified.

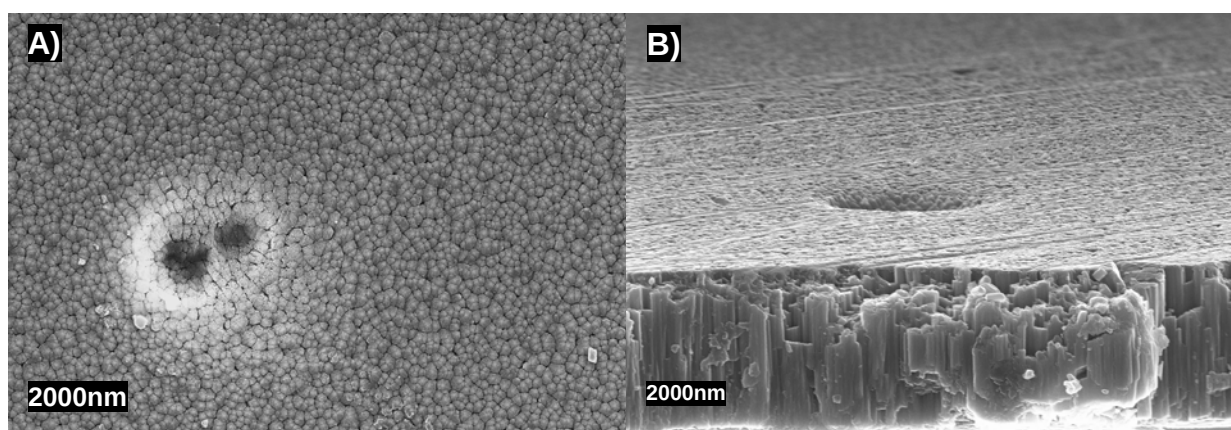


Figure 4.20 – An SEM image of a) pinhole on the surface of cadmium telluride layer with electron beam induced charging due to the glass substrate b) fracture cross section near a pinhole in the cadmium telluride layer

In the initial stages of cell fabrication, chemical bath deposition (CBD) was used to deposit the cadmium sulphide layer. From literature documenting this well established process⁵⁷, it was shown that the chance of achieving the optimum properties of a working cell increased. Therefore the cadmium telluride layer could be deposited via sputtering knowing that the cadmium sulphide layer is a good window layer with n-type properties. This illustrated that the cadmium telluride was the main variable in the performance of the cell. The formation of pin holes was observed, which is a common problem in thin films deposited via sputtering and many other deposition methods. The pin holes were seen to develop in the cadmium telluride layer when deposited onto the cadmium sulphide film deposited via CBD. The pinholes appeared less obvious when cadmium telluride was deposited directly onto a soda-lime glass substrate.

4.4.1 Bi-Layer Structure Thin Film Cadmium Telluride

To try to eliminate the pinholes, initially a bi-layer structure was deposited. The reason for this was that if the sputtering process was stopped, then restarted, the chance that two pinholes will directly line up is very low, giving a complete coverage of the substrate as demonstrated in the illustration shown in Figure 4.21.

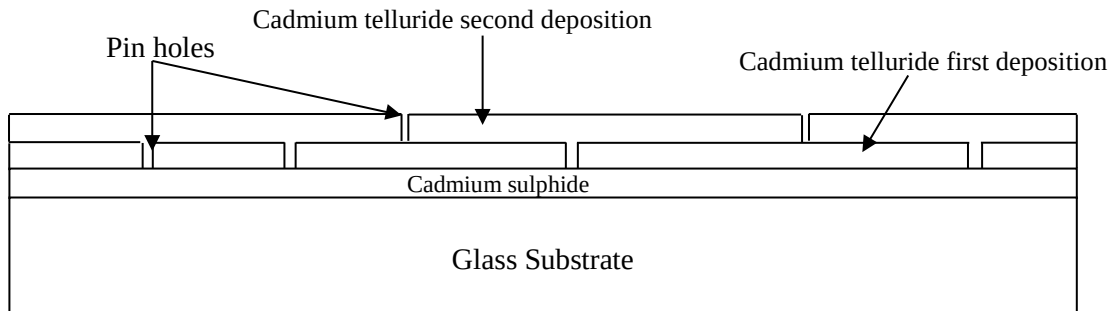


Figure 4.21 – Illustration of bi-layer cadmium telluride structure to eliminate through thickness pinholes

This method eliminated the pinholes, however this also meant that the thickness of the cadmium telluride was less controlled, as well as introducing a new interface. This caused a discontinuity and was seen to impair the electrical properties of the cell. This could cause a loss of charge carriers in this region, as shown in Figure 4.22b. As the second cadmium telluride layer did not continue growth from the original layers grains (non-epitaxial growth) and new grains nucleated. The method used to produce the bi-layer structure was to halt the initial deposition and mechanically rub the surface. After this the second layer of cadmium telluride was deposited. By taking a surface and fracture cross section micrograph using the SEM it was seen that there was a change in grain size of the second layer. Grain size was seen to increase to over double the size from the first layer to the second cadmium telluride layer shown by the surface grains in Figure 4.22a and in cross section in Figure 4.22b.

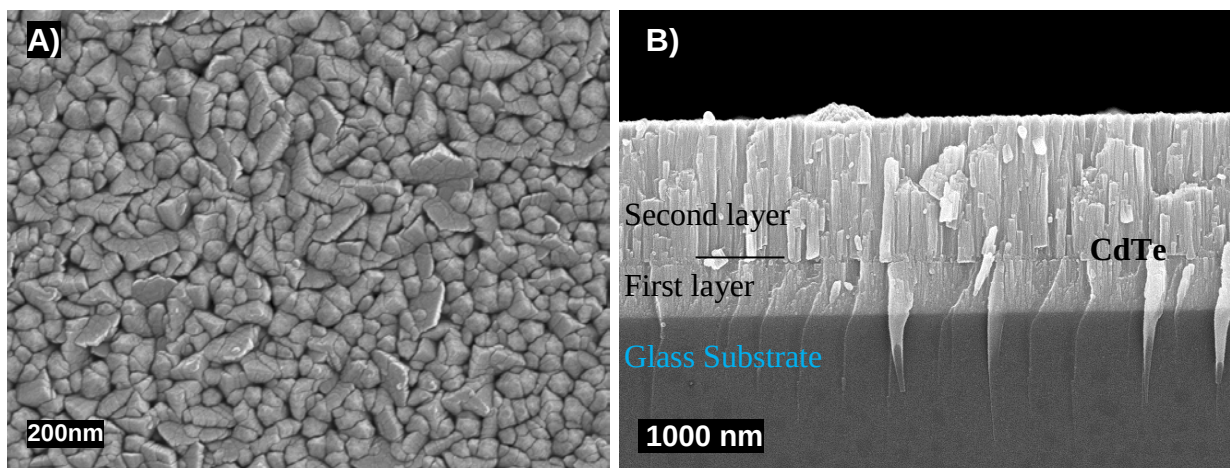


Figure 4.22 – Inlens SEM images of the cadmium telluride bi-layer structure a) surface and b) cross section

Mechanically rubbing the surface was seen to cause a large discontinuity, therefore a new process of etching the surface with a plasma in vacuum was attempted. This was seen to reduce the intensity of the discontinuity and width of the interface. However it still adversely affected the electrical properties. Therefore it was determined that the bi-layer structure was an inappropriate method of preventing pinhole formation. After a second layer of cadmium telluride was deposited, fewer pinholes were seen. The likely reason for this was the first cadmium telluride film was deposited in vacuum and never exposed to air, therefore the second cadmium telluride layer was deposited onto a highly active and ultra clean surface.

4.4.2 Surface Contamination and Pre-deposition TCO Surface Cleaning

As the second layer of cadmium telluride in the bi-layer structure had less pin holes, an investigation of surface contaminants on the substrate was carried out. X-ray photoelectron spectroscopy (XPS) was used to examine the surface of the cadmium sulphide on fluorine doped tin oxide (FTO) and indium doped tin oxide (ITO) to look for any surface contamination which may be the cause of the occurrence of the pinholes.

The results from the XPS spectra shown in Figure 4.23, summarised in Table 4.4 revealed that there were the expected elements present, however in the cadmium sulphide on ITO/glass substrate indium was present. This is unexpected as XPS generally penetrates only the top 5 nm of the sample, and the cadmium sulphide is expected to be at least 100 nm in thickness. This may be due to pinholes forming in the cadmium sulphide layer therefore allowing signal from the substrate. There is a large presence of carbon which is standard for any sample analysed via XPS as it is easily picked up from the atmosphere before the sample is tested. The presence of sodium can be due to contamination from handling the sample prior to the analysis. The conclusion of the XPS was that there was some contamination which could be responsible for pin holes and could have caused the surface of the cadmium sulphide to be less reactive in these areas.

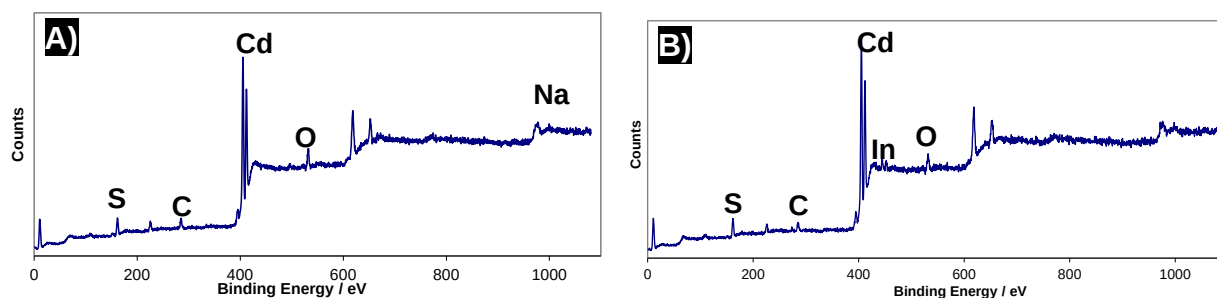


Figure 4.23 –XPS spectra of cadmium sulphide surface on a) FTO/Glass substrate b) ITO/Glass substrate

Sample	Element (Peak)											
	C 1s		O 1s		Cd 3d		S 2p		Na 1s		In 3d	
	B.E.	at%	B.E.	at%	B.E.	at%	B.E.	at%	B.E.	at%	B.E.	at%
Cadmium sulphide/FTO	285	31.7	531.8	16.2	405.2	29.2	161.7	22	1072	0.9	0	0
Cadmium sulphide/ITO	285	25.7	531.4	17.2	405	30.9	161.6	24.7	0	0	444.5	1.5

Table 4.4 - XPS quantification of cadmium sulphide surface looking for contamination

Surface cleaning to remove any surface contamination of the substrate prior to deposition is therefore needed to produce a pin hole free layer. This will be examined in chapter 5 using plasma cleaning, ultrasonic bath and other techniques to find the best surface clean.

4.5 Cadmium Chloride Treatment of Magnetron Sputtered Cadmium Telluride Thin Films

After a cell was deposited using the sputter coater, a cadmium chloride treatment is needed in order to produce an efficient cell. This can be done using a variety of methods. In this section a simple wet chemistry based technique was initially used, then a more controlled vapour transport technique, and finally a well-established evaporation based method. The deposited cells were treated and then completed with a gold back contact and their performance tested and their microstructure analysed.

4.5.1 Solution Based Cadmium Chloride Treatment of Cadmium Telluride Thin Films

4.5.1.1 Initial Treatment Results using a Saturated Solution of Cadmium Chloride in Methanol

Initially a wet chemistry based technique was established where a complete cell stack (3 mm glass/FTO/cadmium sulphide/cadmium telluride) without a back contact was dipped in a saturated solution of cadmium chloride dissolved in methanol and then air annealed at a set temperature for a given time. The initial experiment was carried out using a saturated solution of cadmium chloride, which was dipped in the solution for approximately 30 seconds, placed immediately onto a hot plate at 450°C, left there for 30 minutes and then left to cool to room temperature. Once this was done the stack was washed with isopropanol and dried, then a back contact of gold was deposited to complete the cell. The surface of the cell looked uneven after observation using an optical microscope. It was seen that there was a large

amount of protrusions on the sample surface. This was studied in more detail using SEM.

Figure 4.24 shows the cell which has been treated by the saturated cadmium chloride solution. There is a dramatic difference in the microstructure after the treatment. The grain structure is no longer seen to be columnar through thickness grains and instead they appear more equiaxed and rounded. This is similar to what has been reported in literature⁴⁶. However the cadmium telluride layer was seen to contain a significant amount of large voids. The voids are observed throughout the layer but the voids are larger nearer the cadmium sulphide interface as seen in Figure 4.24.

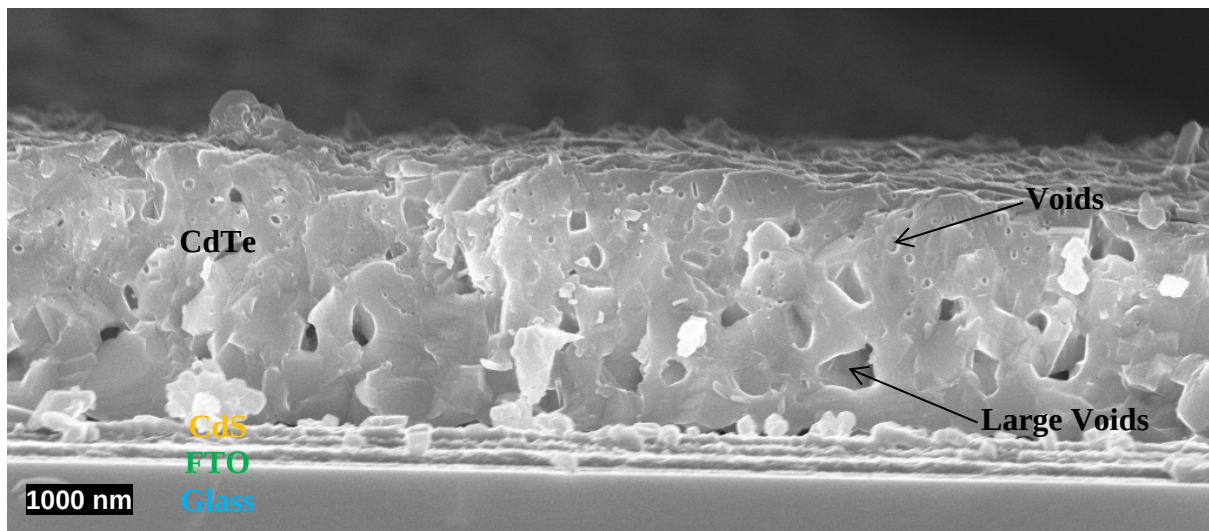


Figure 4.24 – An Inlens SEM image of a fracture cross section of cadmium telluride treated with a saturated solution of cadmium chloride in methanol

4.5.1.2 Delamination of Thin Film Depositions during Cadmium Chloride Treatment

Figure 4.25 shows a low magnification cross section of the cell treated with the saturated solution of cadmium chloride. A large amount of de-lamination of the cadmium telluride layer can be seen. This resulted in a poor p-n junction and cracking can also be seen which will lead to shorting once the back contact is deposited. The delamination and cracking of the cadmium telluride is most likely due to the stresses within the initial sputtered material, as it was deposited at a low temperature. Once the cadmium chloride was applied and the cell was heated up, rapid recrystallization occurred. The sudden grain growth during recrystallization caused an increase in stress due to the introduction of voids which ultimately forced the cadmium telluride to buckle and delaminate. Due to the extent of the delamination no reasonable cell efficiency could be recorded.

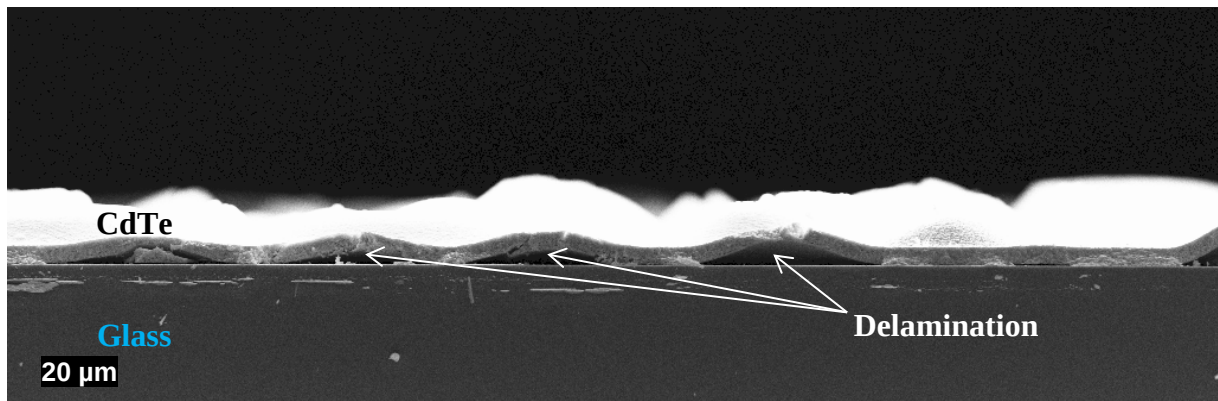


Figure 4.25- An Inlens SEM image of a fracture cross section of cadmium telluride treated at full cadmium chloride concentration

Figure 4.26a shows the surface of the cadmium telluride which has been treated with the saturated solution of cadmium chloride. It clearly shows an increase in grain size. The average grain size has visibly increased from 50-100 nm to 500 nm. Figure 4.26b shows the surface of the cadmium telluride that has delaminated. It can be seen that the cadmium telluride layer has cracked, leaving a gap which the gold back contact can easily migrate down and short the cell.

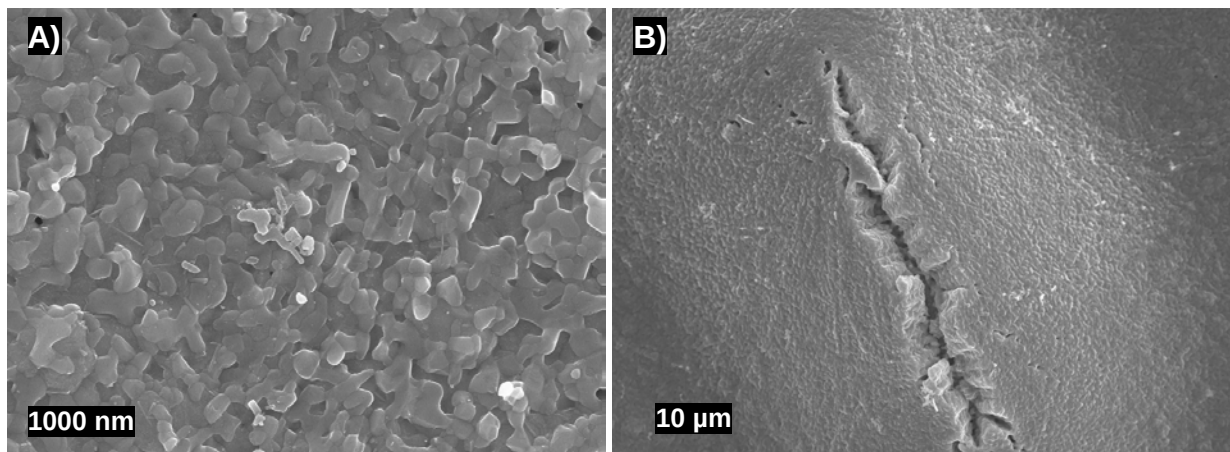


Figure 4.26 –SEM images showing the a) surface of a cadmium chloride cell after treatment b) one of the bumps on the surface of the cadmium telluride

Figure 4.27 shows EDX data and the corresponding SEM image illustrating where the spot analysis was carried out. The first area is where de-lamination had occurred and the top of the bump had broken off. This area indicated a larger amount of sulphur present and absence of tin, silicon or oxygen shown in Figure 4.27a and the EDX data in Figure 4.27c. Figure 4.27b also shows a point on the cadmium telluride that had not suffered delamination. This area only showed high concentrations of cadmium and tellurium in Figure 4.27c. Therefore it can be concluded that the de-lamination occurred between the cadmium sulphide/cadmium telluride interface.

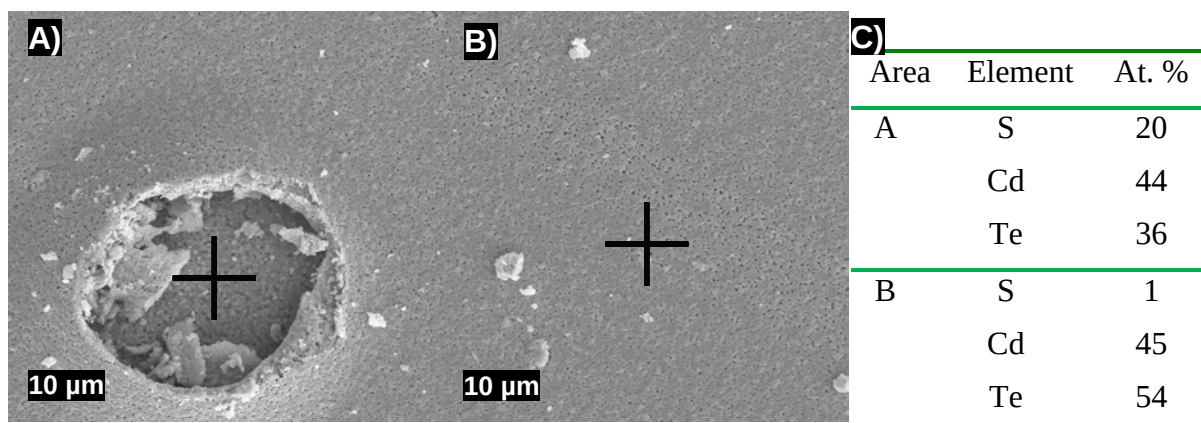


Figure 4.27 - SEM images showing where the EDX spot analysis was carried out on a) within a delaminated area and b) cadmium telluride surface and c) corresponding EDX data

4.5.1.3 Reduced Cadmium Chloride Solution Concentration Treatments

After the initial cadmium chloride treatment was carried out at the maximum concentration (saturated solution), the treatment was found to be too aggressive due to the high concentration of the cadmium chloride solution. To combat this, the saturated solution of cadmium chloride was diluted using pure methanol. It was diluted by adding the same amount of methanol as the initial amount, therefore diluting it to 50%, then again to reduce the concentration to 33.3% and so forth.

4.5.1.3.1 50% Saturated Solution of Cadmium Chloride in Methanol

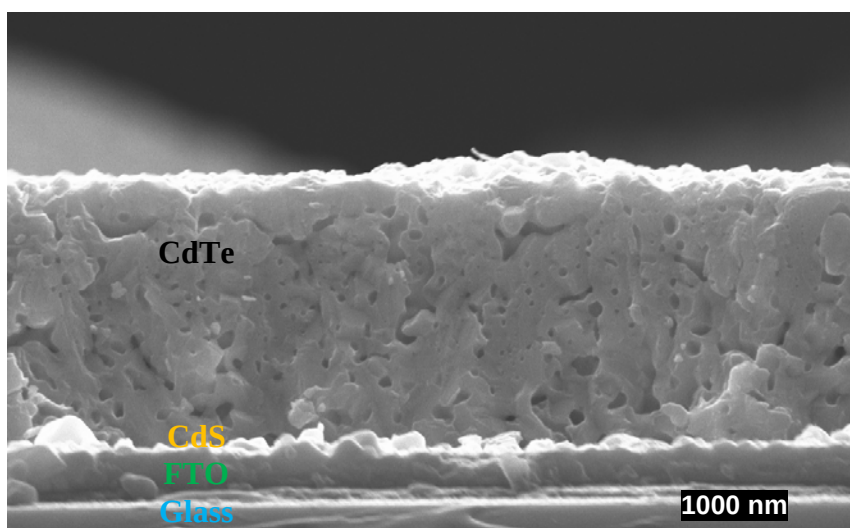


Figure 4.28 - An SEM image of a cross section of the cadmium telluride cell treated with a diluted solution of cadmium chloride

Figure 4.28 shows a fracture cross section of a cadmium telluride cell treated with cadmium chloride at 50% concentration of the saturated solution. The treatment seems slightly less aggressive although de-lamination was present as shown in Figure 4.30. A good voltage was obtained as displayed in Table 4.5 but large amount of voids were also present seen in Figure 4.28.

Figure 4.29 shows an XRD plot of the sample treated by the 50% diluted saturated solution of cadmium chloride. The as-sputtered sample only showed a (111) cubic peak. After the treatment the XRD now shows (220), (311) and (411) peaks present.

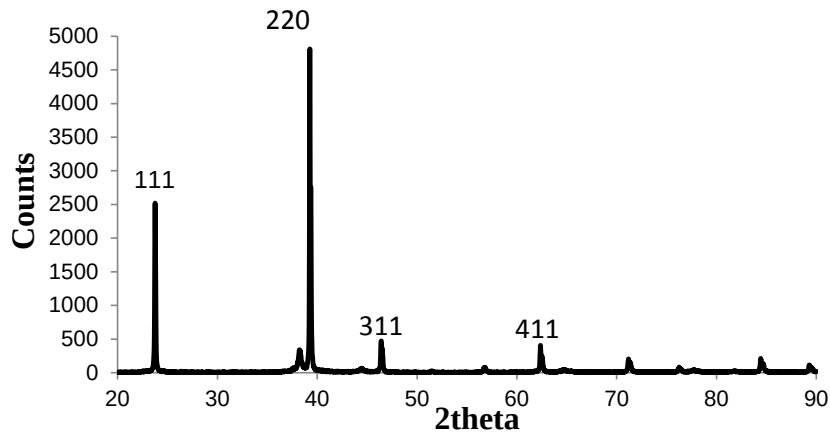


Figure 4.29 – XRD plot of the cadmium telluride cell treated with a diluted solution of cadmium chloride

Figure 4.30 shows that the grain size of the cadmium telluride is between 0.5 μm and 2 μm . Large voids are also present in the sample. The cadmium sulphide layer is reduced in thickness possibly due to intermixing with the cadmium telluride. Delamination was also observed between the cadmium telluride and cadmium sulphide

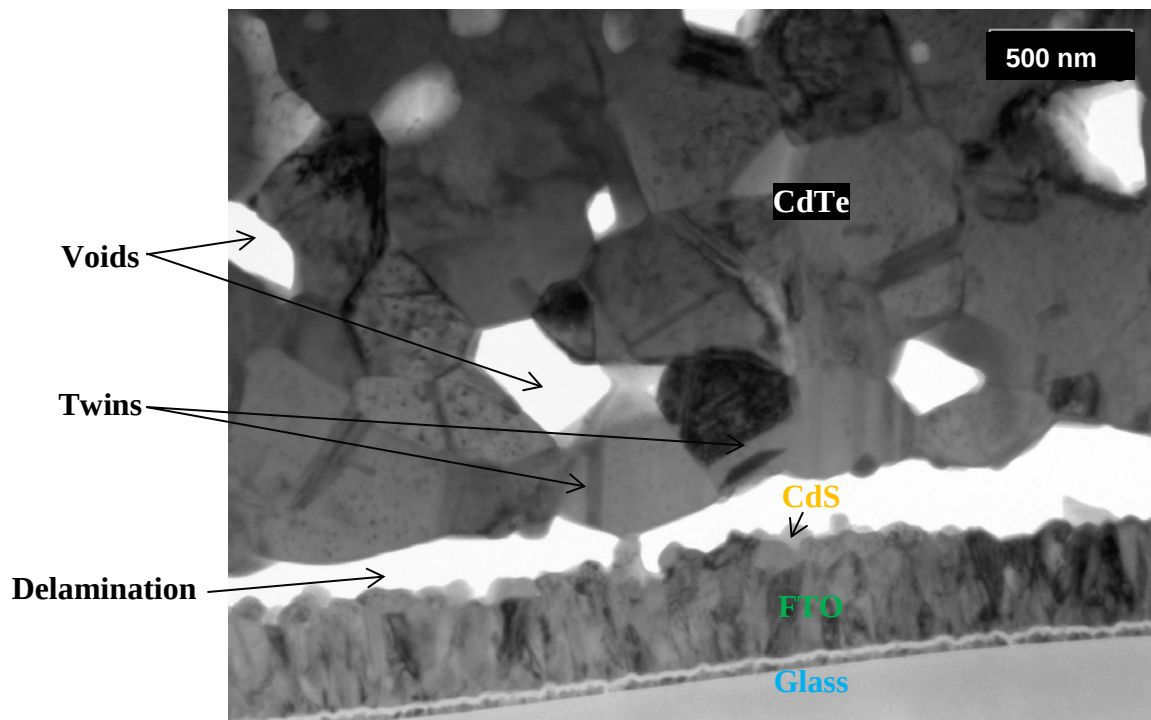


Figure 4.30 – BF-TEM image of a cross section view of the cadmium telluride layer treated at 50% diluted concentrated solution of cadmium chloride

The results yielded by this process were encouraging as the grain size was seen to greatly increase. However the performance properties were not as encouraging, despite the voltage produced showing an increase after the treatment in some of the samples displayed in Table 4.5. No current was produced by the samples due to the large amount of de-lamination and cracking of the cadmium telluride layer, as it was expected that the gold contacted the TCO through the gaps and caused the cell to short. The delamination was likely caused by stresses in the initial deposited cadmium telluride layer, due to the low sputter temperature and low argon pressure. Once the recrystallization started to occur, the film delaminated due to the formation of voids and grain growth. With the formation of voids there is a film expansion and the stress resulting from this caused the film buckle and de-laminate.

4.5.1.3.2 33% Saturated Solution of Cadmium Chloride in Methanol

Figure 4.31 shows a fracture cross section of a cadmium telluride cell treated with cadmium chloride at 33% concentration of the saturated solution. In the film treated with the 33% concentrated solution less delamination of the cadmium telluride has occurred compared with the saturated solution and 50% concentration solution of cadmium chloride. Figure 4.31 shows that the bottom half of the cadmium telluride film has recrystallized whereas the top part has not. The cadmium chloride solution was applied on the surface, indicating that the cadmium chloride treatment initiates crystallization at the cadmium sulphide interface. This has not been previously reported and is likely the reason for the delamination of cadmium telluride thin films. The reduction in concentration of cadmium chloride has had a marked affect and the evidence shows that a certain amount of cadmium chloride is needed to recrystallize the whole cadmium telluride film. In this case a 33% concentration was not enough as only the bottom 1.2 μm of the 2 μm has recrystallized.

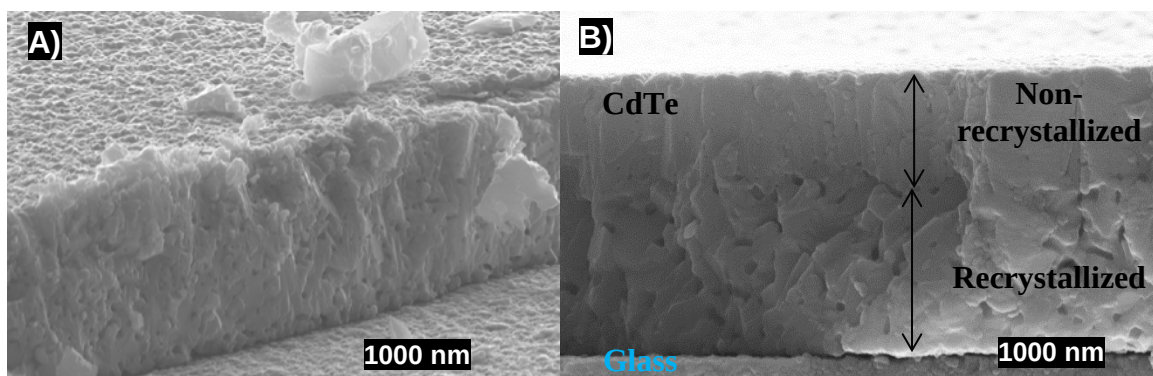


Figure 4.31 – Inlens SEM cross sections of a cadmium telluride cell treated at 33% concentration, a) and b) are of the same sample

4.5.1.3.3 20% Saturated Solution of Cadmium Chloride in Methanol

Figure 4.32 shows a fracture cross section of a cadmium telluride cell treated with cadmium chloride at 20% concentration of the saturated solution. The treatment can be seen to be much less aggressive than the previous solutions as only the bottom half of the cell shows signs of re-crystallization. The 20% solution is seen to undertreat the cell however the concentration of the solution will be reduced further in order to investigate how the recrystallization of the cadmium telluride is occurring.

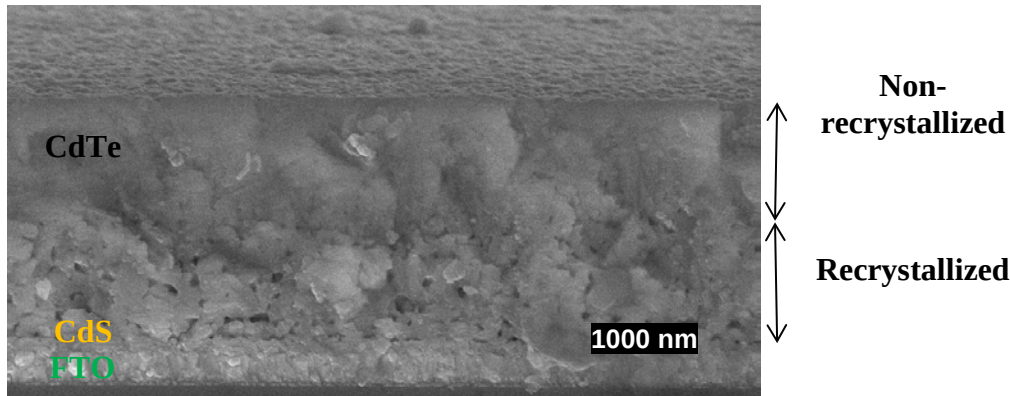


Figure 4.32 - SEM Cross section of the cadmium telluride cell treated at 20% of the saturated solution of cadmium chloride showing half the cell recrystallized

4.5.1.3.4 14% Saturated Solution of Cadmium Chloride in Methanol

Figure 4.33 shows a fracture cross section of a cadmium telluride cell treated with cadmium chloride at 14% concentration of the saturated solution. This cell shows only the bottom third of the cadmium telluride has been recrystallized as voids are seen in this region. The morphology of the top of the cadmium telluride layer appears columnar, again indicating that the recrystallization has initiated near or at the cadmium sulphide interface. To investigate this in more detail a TEM sample of the 14% concentration treated cadmium telluride cell was prepared. Figure 4.34 shows a BF-STEM image of the cadmium telluride cell. The glass substrate, FTO, cadmium sulphide, cadmium telluride, gold contact and platinum layer are all visible. The main interest is within the cadmium telluride layer, as a distinct difference can be seen from the top of the layer to the bottom. The top surface of the cadmium telluride near the gold back contact has thin columnar grains similar to that seen in the untreated sample. The cadmium telluride grain morphology nearer the cadmium sulphide interface can be seen to be distinctively different, as more rounded equiaxed grains are present. Another significant difference is that the grains which are still columnar and not recrystallized can be seen to have a very high density of linear defects, whereas these are not present in the recrystallized grains.

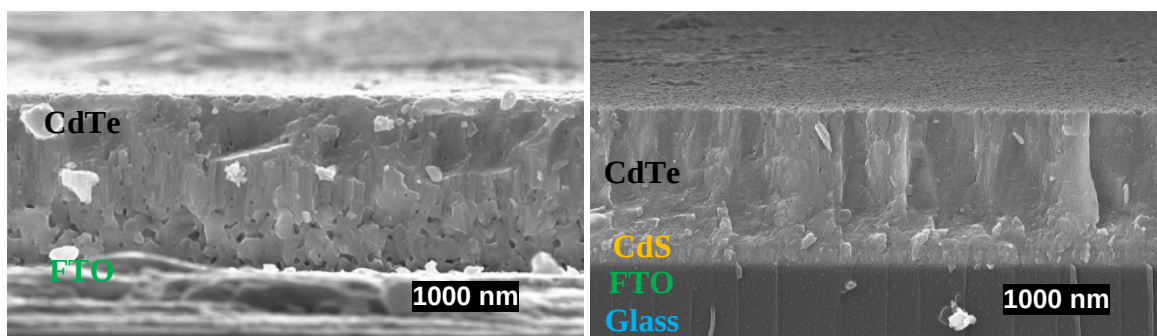


Figure 4.33 - SEM Cross sections of the cadmium telluride layer treated at 14% concentrated solution of cadmium chloride

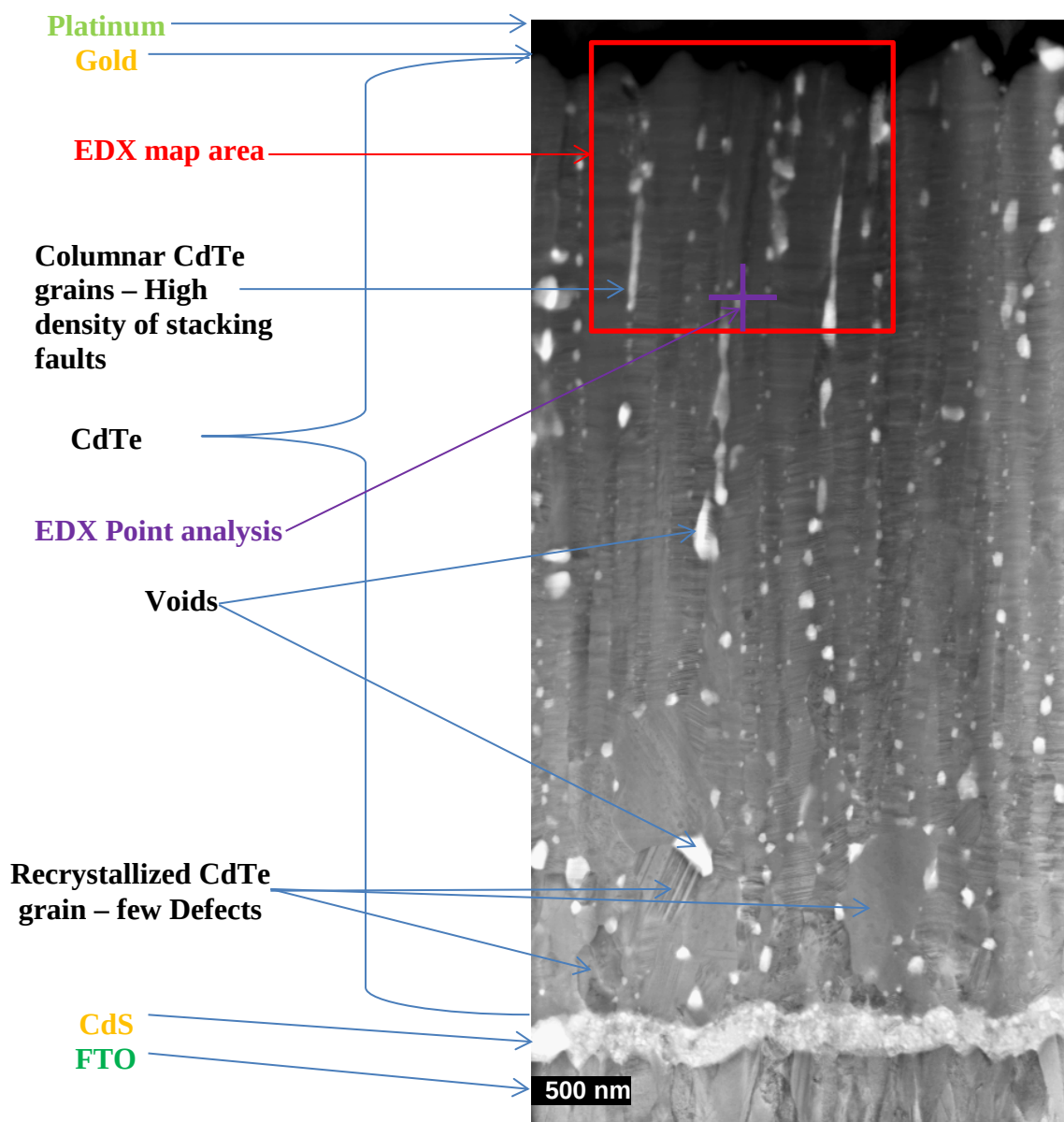


Figure 4.34 - TEM Cross section of the cadmium telluride layer treated at 14% concentrated solution of cadmium chloride

Figure 4.35 shows HAADF-STEM EDX chemical distribution maps for cadmium, tellurium and chlorine. The chloride map indicates some chlorine present at grain boundaries and around voids.

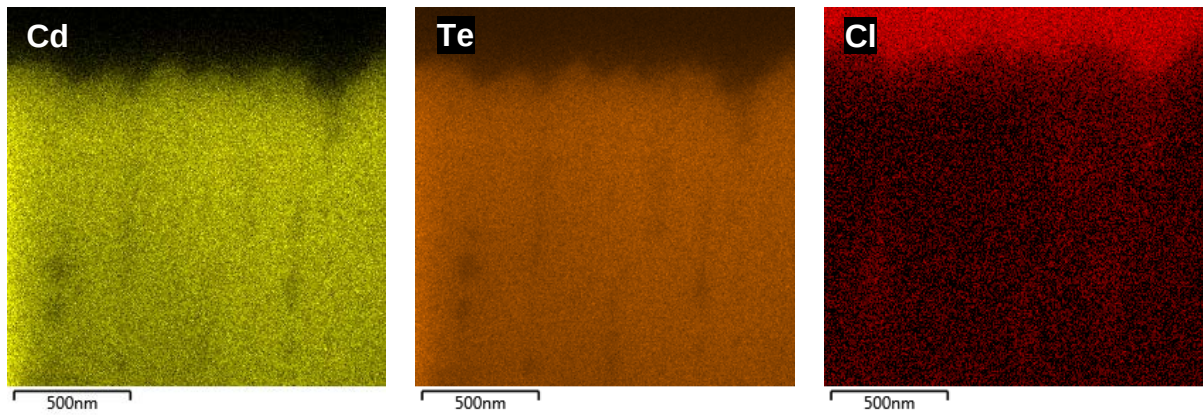


Figure 4.35 –STEM EDX chemical distribution maps for cadmium, tellurium and chlorine of the area highlighted in Figure 4.34

Figure 4.36 shows an EDX spectra of the point highlighted in Figure 4.34 of the cadmium telluride cell treated using a low concentration of cadmium chloride. The point is located at a cadmium telluride grain boundary. 0.8 at% of chloride was detected, with cadmium at ~ 50at% whereas tellurium dipped slightly to 49.2 at%. This suggests that chlorine diffuses down the cadmium telluride grain boundaries until reaching the cadmium sulphide interface.

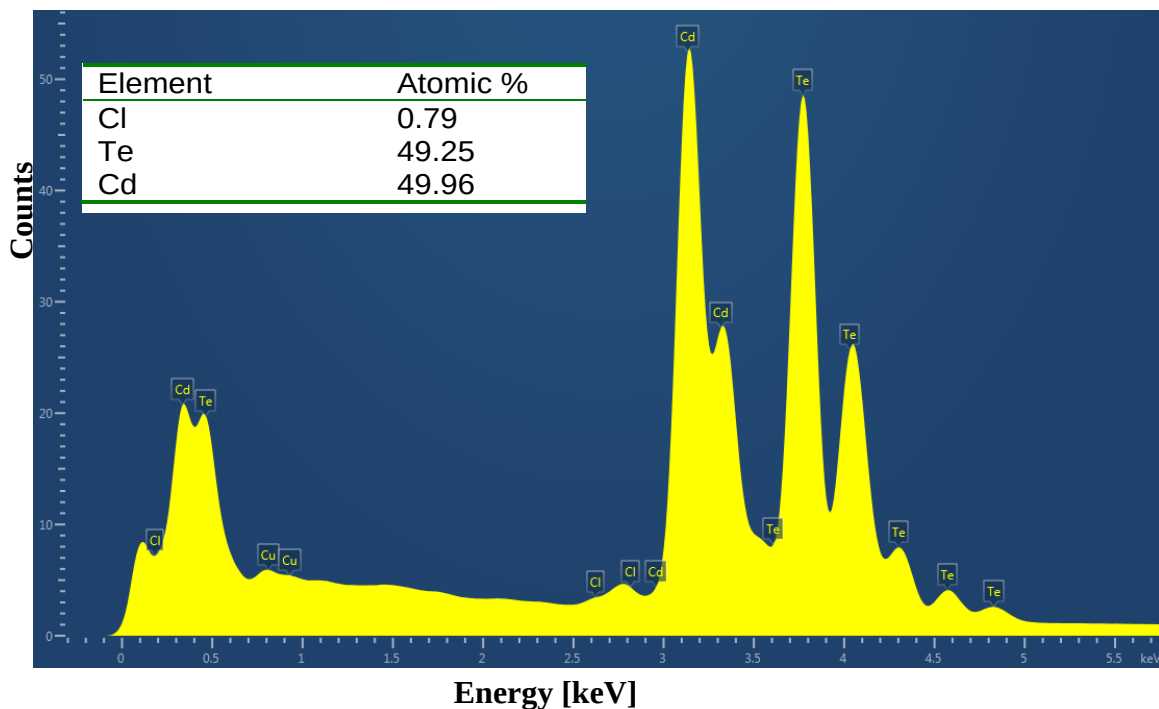


Figure 4.36 – An EDX spectra of the point highlighted in Figure 4.34 of the cadmium telluride cell treated using a low concentration of cadmium chloride

4.5.1.3.5 Performance of Solution Treated Cadmium Telluride Cells

On each sample three gold contacts were deposited making three cells for each sample, some shorted and this is indicated in Table 4.5 by a dash.

Ratio	Concentration from Saturated	Voltage Produced (mV) cell 1	Voltage Produced (mV) cell 2	Voltage Produced (mV) cell 3
1:1	50%	579	282	249
1:2	33%	40	-	-
1:4	20%	578	595	577
1:6	14%	139	56	351
1:8	11%	397	452	499
1:10	9%	512	-	-
1:15	6%	427	-	-
1:20	4.5%	410	-	-
untreated	0%	442	430	66

Table 4.5 – Summary of the voltage produced by the cells and the concentration of cadmium chloride solution

Table 4.5 shows the obtained voltages from the cells treated at the various concentrations. The 50% concentrated solution treated cell and the 20% concentrated solution treated cell are the only two which showed an increase from the untreated cell. The 33% cell was shorted when the back contact was deposited, due to delamination and cracking of the cadmium telluride layer.

4.5.1.4 Summary of the Solution Based Cadmium Chloride Treatment

The solution treatment process had a lack of control of substrate temperature when annealing in air. As a hot plate is used the temperature of the hot plate can vary greatly from the sample as well as in the sample itself. The heat source is coming from the bottom of the sample and therefore there will be a heat gradient through the sample as the only way the top of the sample will heat up is via heat conduction through the thickness of the sample.

The distribution of the cadmium chloride solution over the surface of the samples was heterogeneous. A good treatment will give a homogeneous distribution of the cadmium chloride, however with a solution based treatment this was not possible. Once the samples were treated, even observing the sample surface by eye a variation in colour could be seen due to an uneven distribution of the cadmium chloride, this was having an effect on the microstructural changes between areas within the same sample.

Due to these reasons using this method is not advisable to produce an efficient cell. Another

disadvantage is that it is a hard process to scale up as wet chemistry is used. To overcome these disadvantages a vapour transport method can be used, as it provides a homogeneous concentration and temperature since it is under vacuum and heated from all directions.

4.5.2 Vapour Transport Based Cadmium Chloride Treatment of Cadmium Telluride Thin Films

The vapour transport method is used to treat the cadmium telluride solar cell with cadmium chloride by heating the cell up in a tube furnace, along with cadmium chloride tablets in a crucible and using argon as the carrier gas.

The main parameters that were varied were; the substrate temperature, cadmium chloride crucible temperature, ramp up time, anneal time and gas flow.

A large amount of samples were produced with various treatment conditions and their cell efficiencies were measured. The highest recorded efficiency was measured at 1.11%; this sample was then characterized to examine its microstructure.

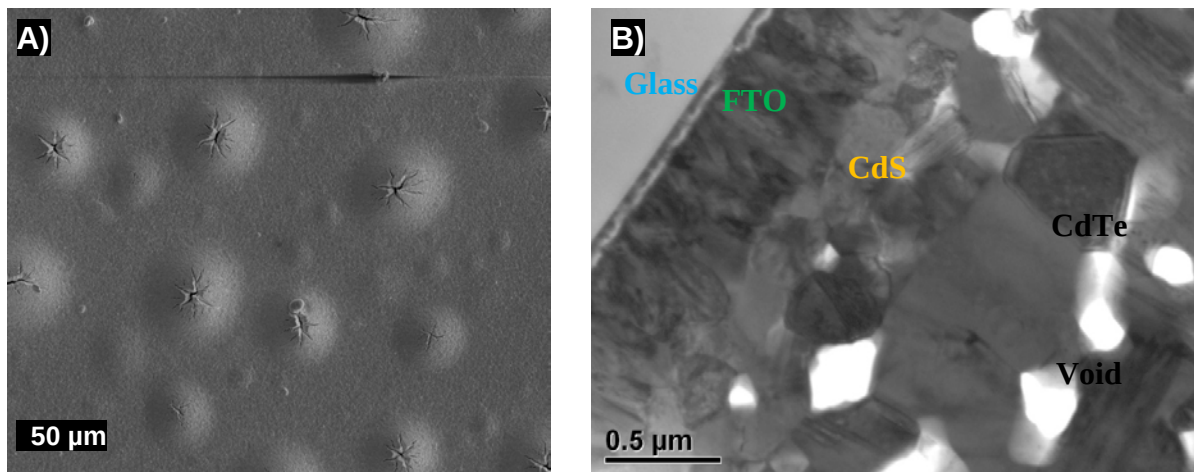
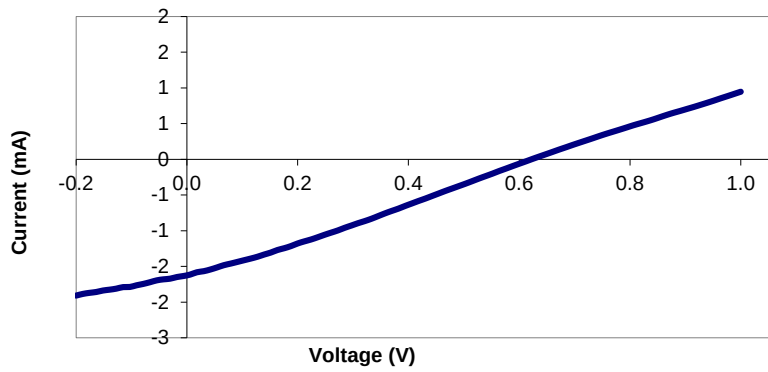


Figure 4.37 – a) A SEM surface image of the sample with the highest cell efficiency treated by vapour transport
b) A BF-TEM image of the cell treated via vapour transport

Figure 4.37a shows the surface of the sample treated by vapour transport. The cadmium chloride source temperature was held at 590°C and the cell was held at 420°C, the ramped up time was 20 minutes and left at this anneal temperature for 120 minutes, with an argon gas flow rate of 25sccm. It was then left to cool down naturally. Figure 4.37 shows that there was still the formation of bubbles which crack on the surface. As this has occurred in both treatment methods it may be the properties of the initial deposited layers and not the treatment itself. The initial stress of the film can be controlled by varying the temperature and pressure when the layers are sputtered. The cell produced an efficiency of 1.11%. The current voltage graph is shown in Figure 4.38 and performance data in Table 4.6.



V_{oc}	0.622mV
J_{sc}	6.48mA/cm ²
fill factor	28%

Table 4.6 - Electrical performance data summary of the cell treated via vapour transport

Figure 4.38 – J-V curve for the cell with 1.11% efficiency treated via vapour transport

To understand the performance data of the cells the microstructural and crystallographic properties were examined. Figure 4.37b illustrates that the sample had a radically changed microstructure from the as deposited sample. The grains increased from 50 to 100 nm to over 1 μm near the surface and 0.5 μm near the cadmium sulphide/cadmium telluride interface. However large amounts of voids can be seen in the bulk of the cadmium telluride layer; however a p-n junction was formed, which may indicate why the cell worked even with voids in the cadmium telluride layer.

Using the vapour transport method has not been very successful in terms of sample performance properties. This could be due to the initial film properties or the treatment itself. So far a wide range of temperatures and annealing times have been used but the same initial sample deposition parameters were always used. The cadmium chloride pellets used were not pure, therefore it would be highly recommended that pure pellets be used to see if any change in results could be achieved.

4.5.3 Pre-Optimised Evaporated Cadmium Chloride Treatment of Cadmium Telluride Thin Films

A sputtered cadmium telluride sample was sent to the Swiss Federal Laboratories for Materials Science and Technology where it was treated using an optimised cadmium chloride treatment. The results were encouraging as a highest efficiency of 5.8% was measured.

Once the sample was returned it was analysed so it could be used as a benchmark sample.

Figure 4.39 shows a cross section of the sample treated with a pre-optimized cadmium chloride treatment which was carried out by EMPA. The treatment involved evaporating the cadmium chloride as a layer onto the cadmium telluride, followed by annealing in air. The cross section in Figure 4.39 shows a large amount of voids through the layer, and the whole

cadmium telluride layer has been affected as the columnar morphology of the as deposited layer has been replaced by equiaxed grains throughout the layer.

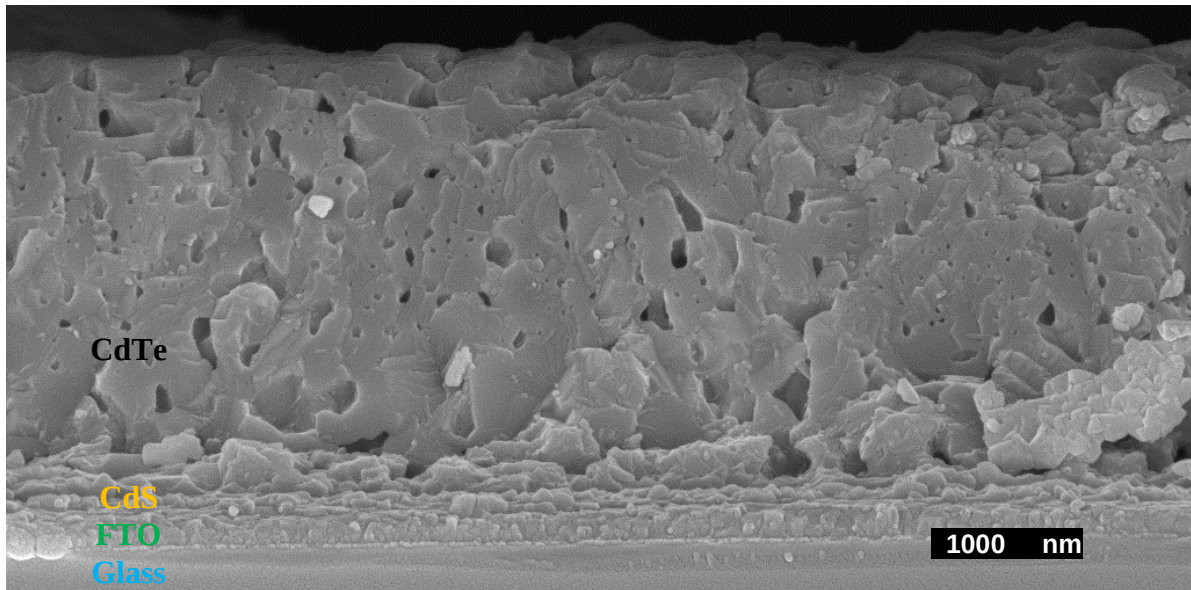


Figure 4.39 – Cross-section SEM image of a pre-optimized cadmium chloride treated cell

Figure 4.40 shows that there are voids present and the bubble formation in the cadmium telluride layer, therefore it can be concluded that the properties of the initial deposited cadmium telluride layers is partly the cause of this. The voids seem less abundant in the cross section than some of the previous samples, however it is hard to tell the grain size from these images, therefore TEM samples were produced.

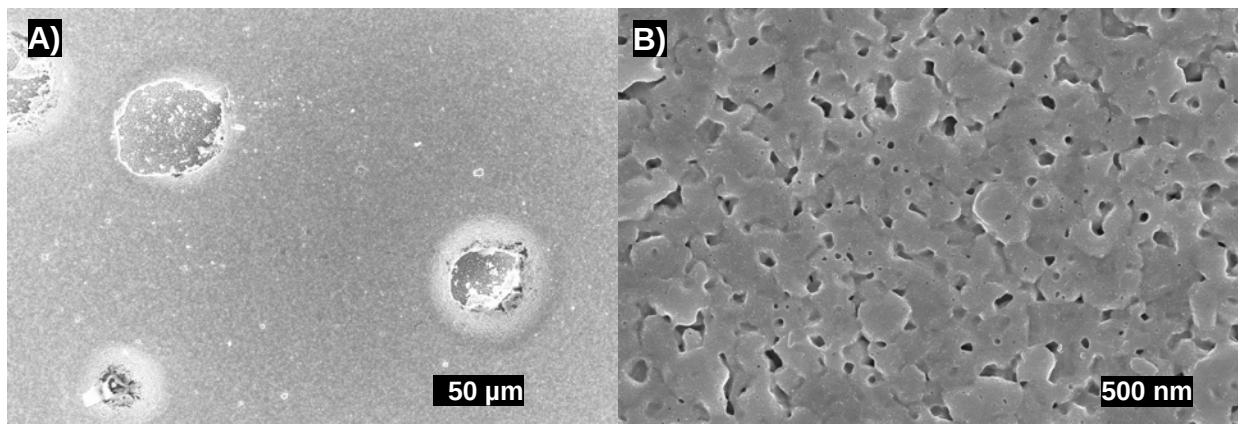


Figure 4.40 – a) Low magnification surface SEM images of pre-optimized cadmium chloride treated cell b) higher magnification SEM surface image of pre-optimized cadmium chloride treated cell

Figure 4.41 shows that voids are present however the grains are very large near the surface and slightly smaller near the junction. The cadmium telluride grains display a large density of voids however they have radically increased in size from the pre-treated sample. They have become more equiaxed and rounded compared to the columnar structure, indicating total recrystallization. The cadmium sulphide has changed dramatically and all the grains are seen

to be of similar size of around 250-500 nm. The larger voids are located near the cadmium sulphide/cadmium telluride interface and are over 1 μm in diameter; however near the surface they have a diameter of less than 0.5 μm .

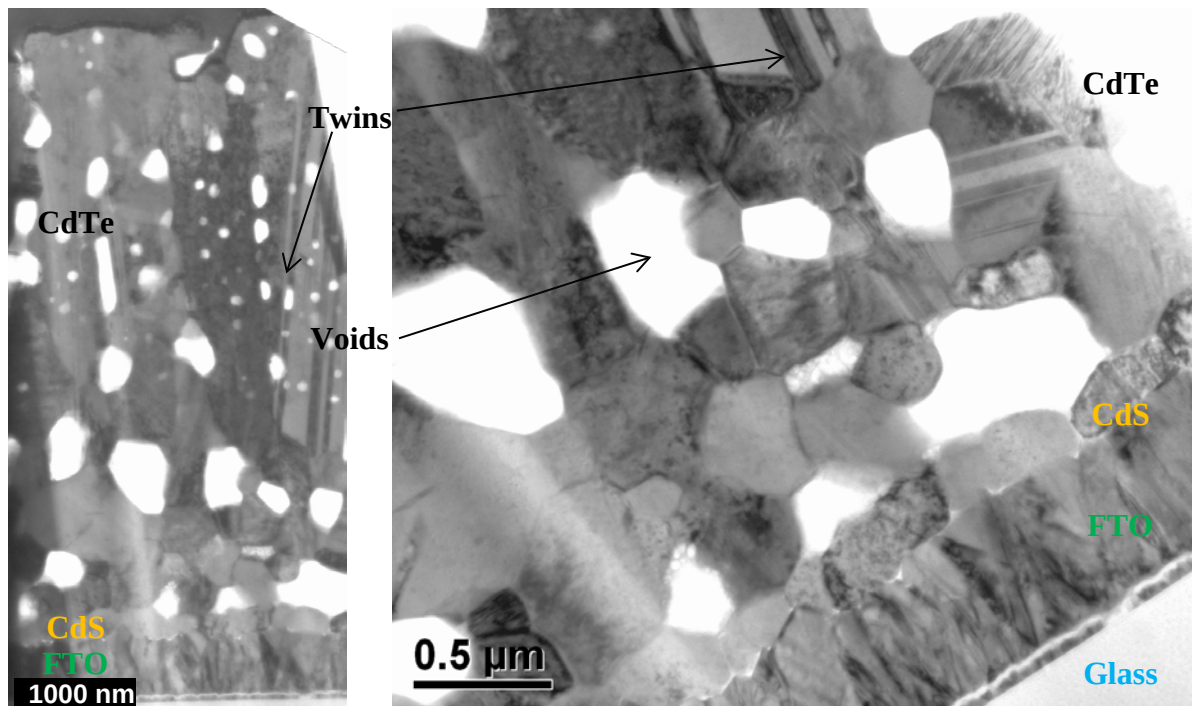


Figure 4.41–BF-TEM images of pre-optimized cadmium chloride treated cell

Figure 4.42 shows a planar EBSD map of pre-optimized cadmium chloride treated cell. The scan was carried out on an ion beam smoothed surface described in Chapter 3. It was used to illustrate the micro orientation. It shows that there is a large degree of texture present.

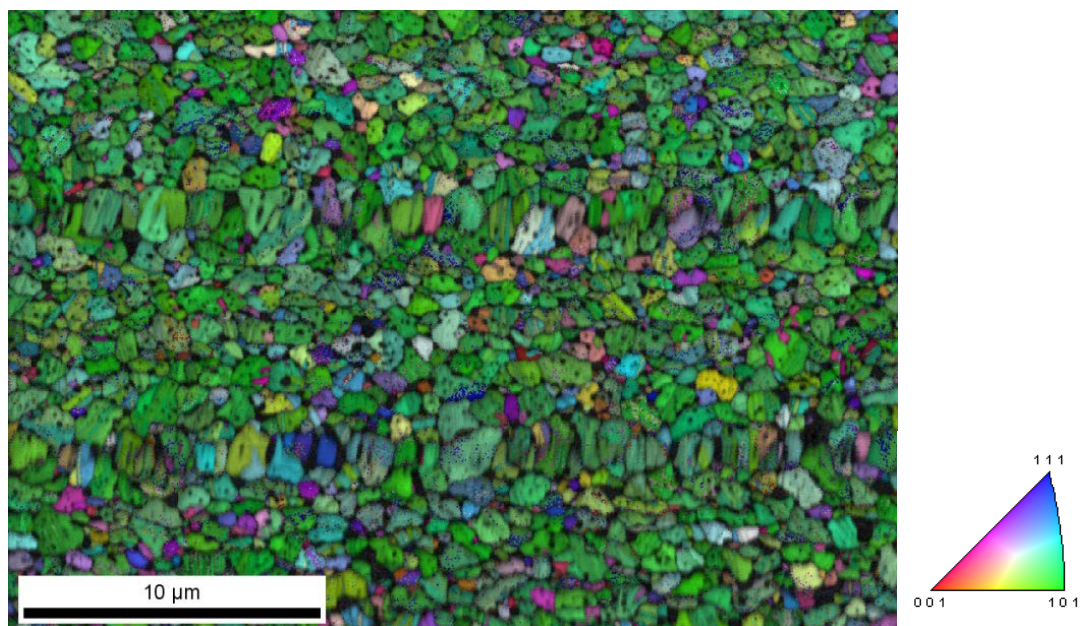


Figure 4.42 - EBSD Image of pre-optimized cadmium chloride treated cell

A Tecnai Osiris™ TEM was used (by FEI) for HADDF imaging and to provide chemical mapping for cadmium, sulphur, tellurium, chlorine and oxygen presence of pre-optimized cadmium chloride treated cell. This system has a high sensitivity for light elements. EDS chemical maps were obtained using ~1 nA beam current for a total acquisition time of 300 seconds. The analyzed area was 800 x 800 pix, obtained with 500 µs dwell time and multiple frames.

Figure 4.43 shows a HADDF image of the of pre-optimized cadmium chloride treated cell. A large amount of voids can be seen clearly as the black regions. Larger voids are seen closer to the cadmium sulphide interface with smaller voids visible nearer the surface. The gold back contact is seen as a bright layer above the cadmium telluride, with electron deposited platinum and ion beam deposited platinum above this. The cadmium sulphide layer is free of voids; however some small voids can be seen at the interface with the transparent conducting oxide.

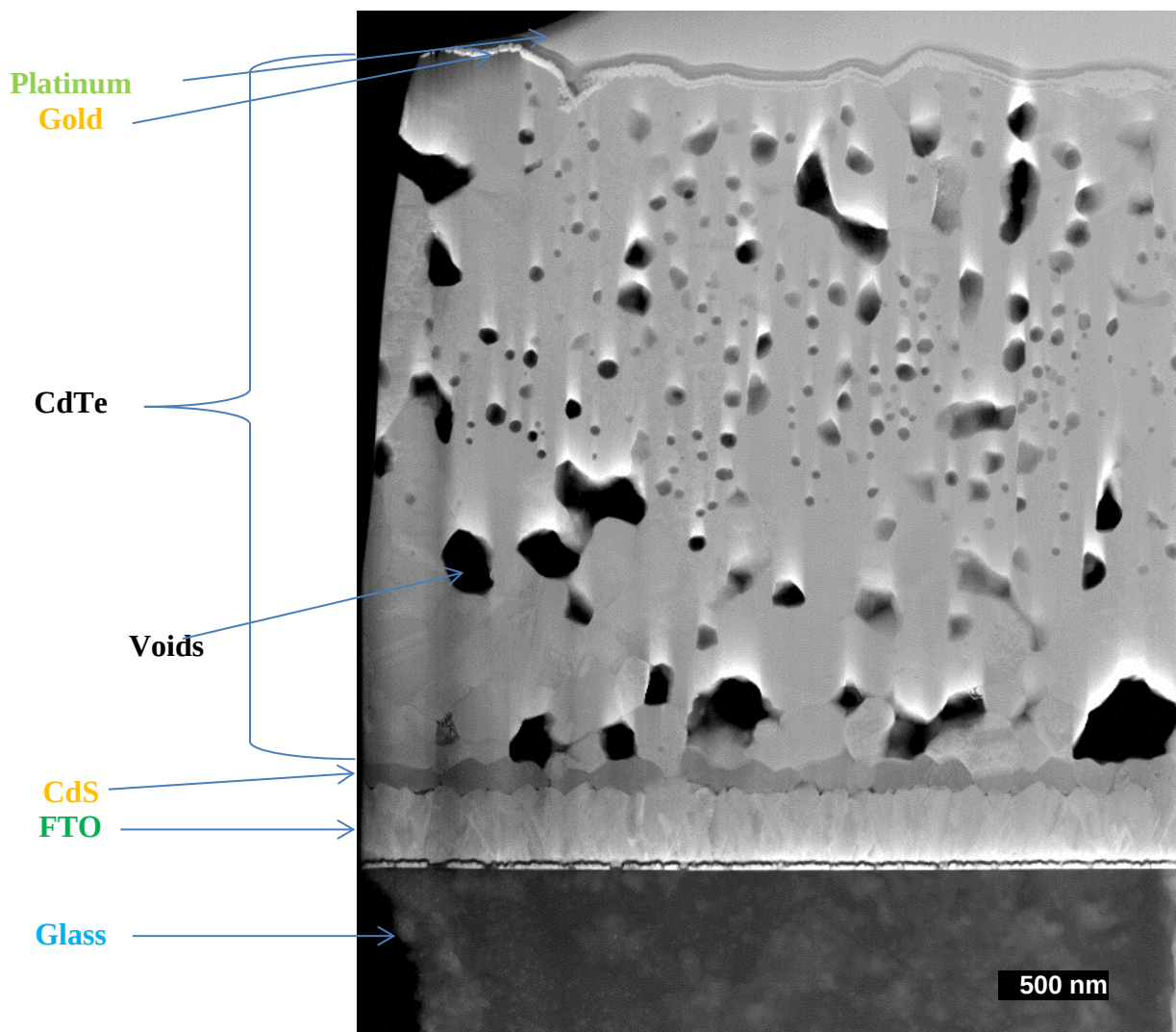


Figure 4.43 - STEM-HAADF Image of a pre-optimized cadmium chloride treated cell

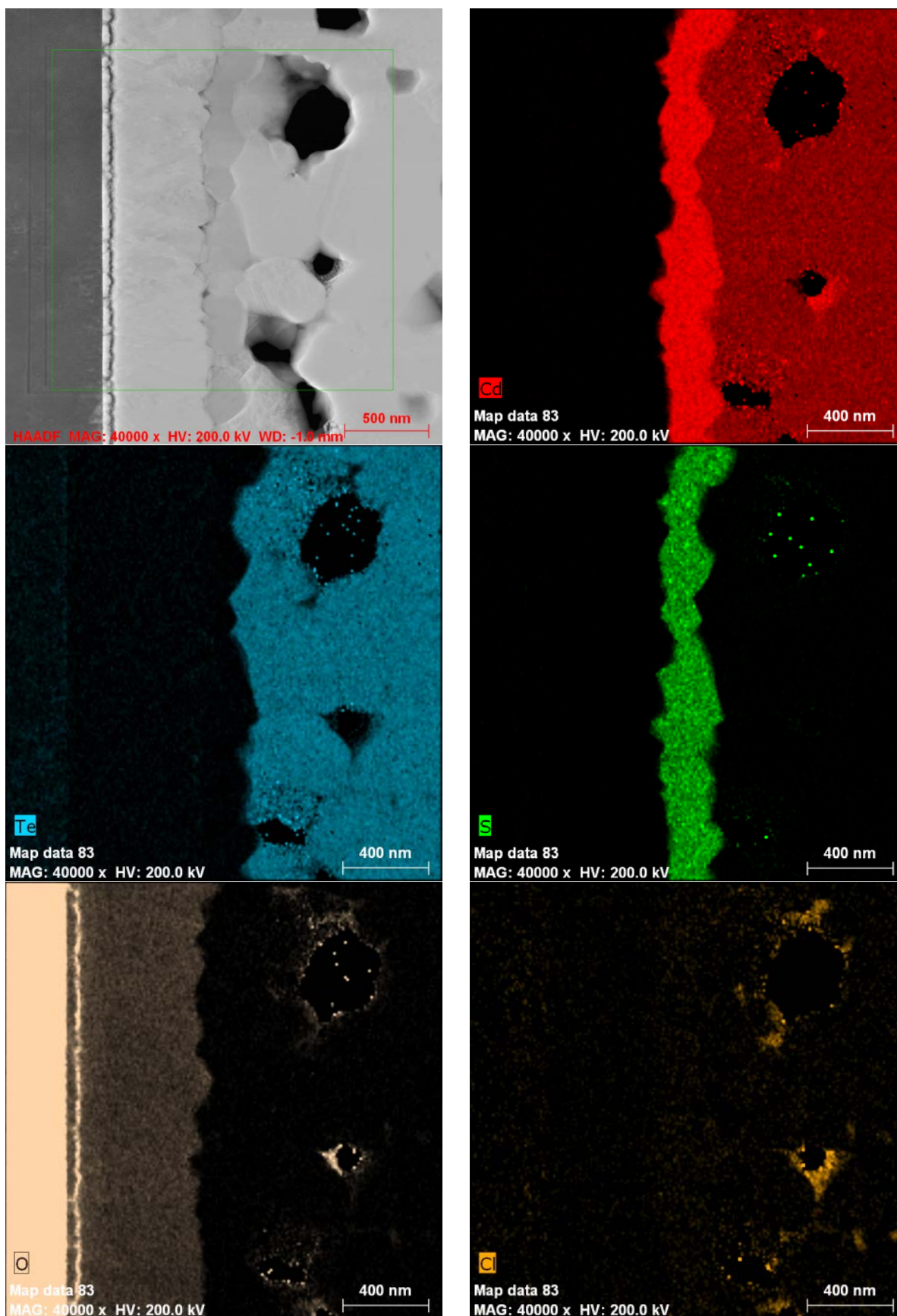


Figure 4.44 – HAADF STEM image and corresponding EDX chemical distribution maps for cadmium, tellurium, sulphur, chlorine and oxygen of the treated sample (data courteous of FEI)

Figure 4.44 shows the chemical distribution maps for cadmium, tellurium, sulphur, chlorine and oxygen around the cadmium telluride/cadmium sulphide interface. The maps show that cadmium is present at highest concentration in the cadmium telluride film around the pores, which also contain increased levels of oxygen and chlorine. Limited sulphur diffusion can be seen into the cadmium telluride layer from the cadmium sulphide layer. No chlorine, tellurium or oxygen can be seen in the cadmium sulphide which indicates little intermixing. The results indicate that the cadmium chloride does diffuse down to near the cadmium sulphide interface, with some remaining around pores and grain boundaries.

4.6 Comparison of the Closed Field Magnetron Sputtered Cells to Other Deposition Techniques

As sputtering of cadmium telluride in this manner is a novel process the initial deposition is likely to vary from other established techniques. However after the cadmium chloride treatment a more standard cell should be produced with a similar microstructure to that of other techniques.

4.6.1 Comparison of the Novel Closed Field Magnetron Sputtered Cells to Closed-Space Sublimated Benchmark Cells

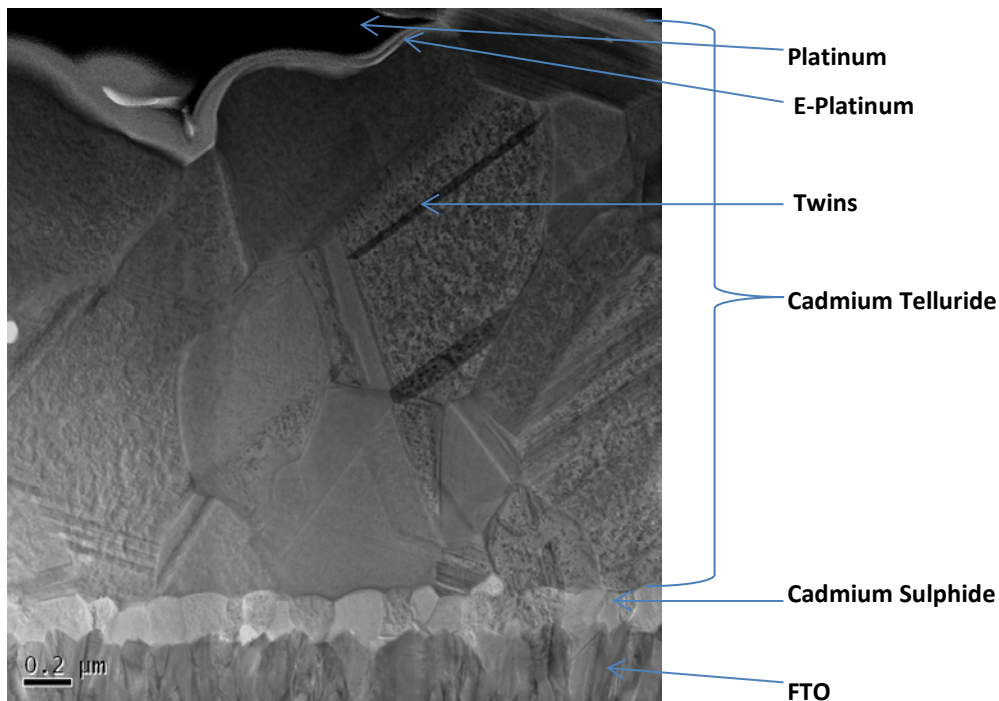


Figure 4.45 – A BF-STEM image of a treated CSS deposited cadmium telluride solar cell

Figure 4.45 shows a BF-STEM image of a cadmium telluride cell with 13% efficiency deposited via closed space sublimation which has undergone an optimal cadmium chloride treatment. The microstructure has similar aspects to the novel sputtered treated cell shown in

Figure 4.41, as it has several twin boundaries in some grains. The grain size is of a similar magnitude; however no voids are present in the CSS cell. This could be the biggest contributor to the lower cell efficiency of the sputter deposited cell.

4.7 Summary

Cadmium telluride based solar cells were sputtered with close-field magnetron sputtering for the first time. Cadmium telluride cells were deposited at a high deposition rate, which formed small through thickness columnar grains. Working cells were produced after a cadmium chloride treatment. An evaporation based technique yielded the highest efficiency. The morphology of the grains changed to larger more equiaxed grains. By altering the amount of cadmium chloride present during the treatment, it has been discovered that recrystallization of sputtered cadmium telluride occurs during the treatment starting at the cadmium sulphide interface, as well as removal of stacking defects in post-recrystallized grains.

CHAPTER 5. ANALYSIS OF TRANSPARENT CONDUCTING OXIDES FOR CADMIUM TELLURIDE BASED SOLAR CELLS

5.1 Introduction

This chapter focuses on the transparent conducting oxides used in cadmium telluride based solar cells, as the properties of every layer is crucial for the devices to function well. The ideal transparent conducting oxide will have the highest possible transparency in the wavelength range that the absorbing cadmium telluride functions at. A high conductivity level is needed so that it can collect charge without losses. Another requirement, especially for cadmium telluride based solar cells, is to ensure a smooth surface to prevent any protrusion of the oxides grains through the thin cadmium sulphide that would result in shunting of the cell.

The chapter will also focus on the morphology of the different TCO's available and the surface chemistry, as this affects the subsequent layers (cadmium sulphide and cadmium telluride) morphology, especially grain size. This chapter also investigates the ability of various cleaning methods to remove surface contamination from the surface of the TCO. This is important as Chapter 4 has shown pinholes in cadmium sulphide and cadmium telluride are due to TCO surface contaminants. The materials investigated in this chapter are the various fluorine doped tin oxides from Pilkington as these are available and widely used. Indium doped tin oxide (ITO) was also used as it was sputtered using the same system as cadmium telluride. In addition ITO possesses the desired properties such as a high transparency and high conductivity.

5.2 Background to Transparent Conducting Oxides

Transparent conducting oxides are used in many common electrical devices, such as flat panel televisions and touch screen devices. The transparent conducting oxide is needed in cadmium telluride based solar cells for the electrical contact on the cadmium sulphide (n-type) side of the cell, as light must pass through in order to reach the cadmium telluride absorbing layer. Transparent conducting oxides are metal oxides doped with an element or compound. A wide range of possible materials can be used including tin oxide, indium oxide, zinc oxide and cadmium oxide all with various dopants, as long as they have a carrier concentration of more than 10^{20} cm^{-3} with a band gap of approximately 3 eV⁸⁰. Apart from

the main properties required by a transparent conducting oxide, some secondary properties are also desirable, such as being chemically and thermally stable up to temperatures above the deposition temperatures of the proceeding layers. The deposition methods by which the material will be put down is also important, as this will impact the properties of the film, such as the maximum coating area, or film thickness control.

5.3 Fluorine Doped Tin Oxide (FTO) TEC Glass

Fluorine doped tin oxide (FTO) deposited by Pilkington branded as TEC glass, is available in different grades. Four FTO-TEC glass grades will be examined in this chapter; they are TEC7, TEC 8, TEC 10 and TEC 15. Each transparent conducting oxide has slightly different properties, but all are tin oxide, doped slightly with fluorine deposited using an atmospheric CVD process.

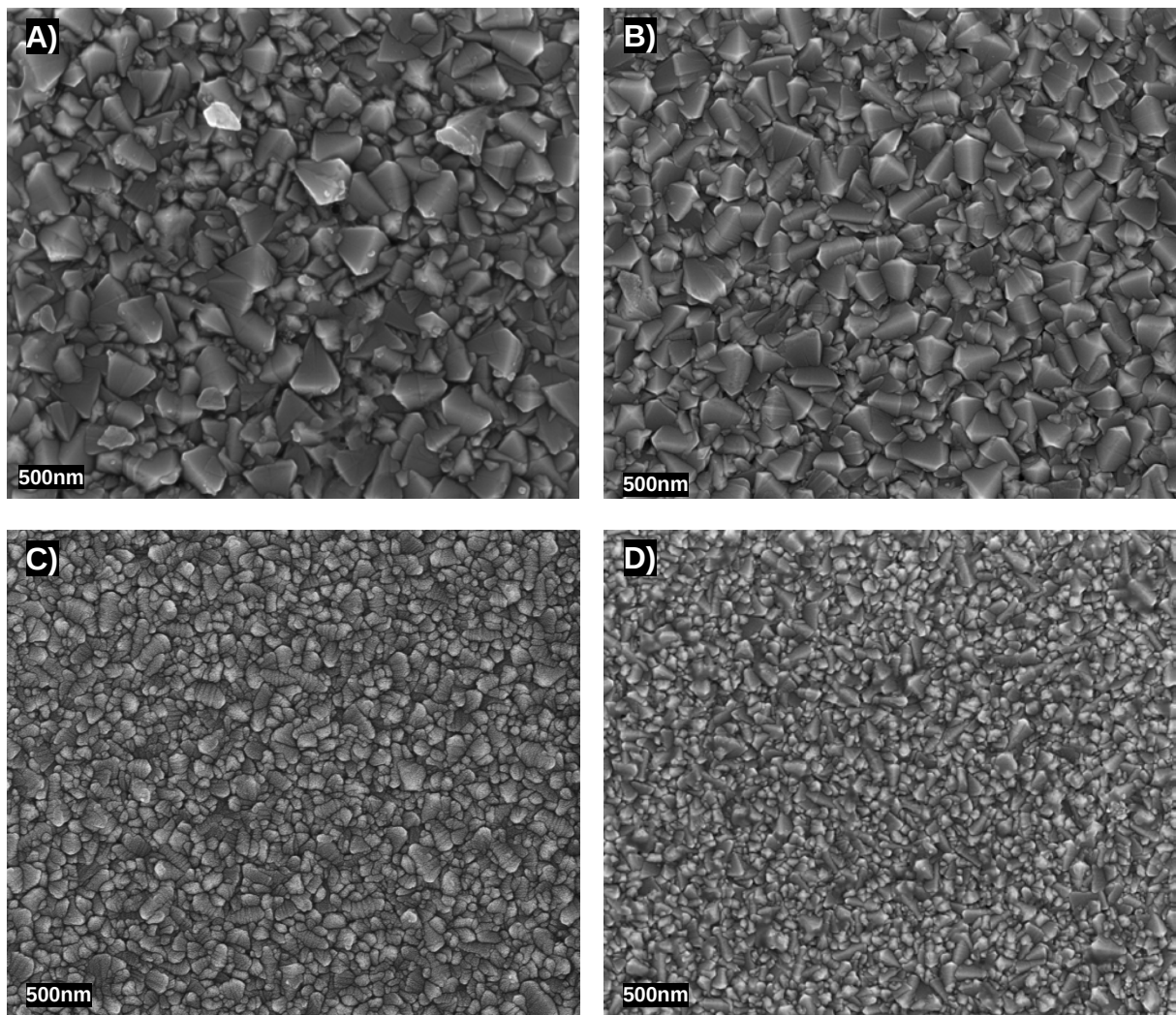


Figure 5.1 – Inlens SEM images showing the surface morphology of a) TEC7, b) TEC8, c) TEC10 and d) TEC15 fluorine doped tin oxide TCO

Figure 5.1a shows an SEM surface image of TEC7 and Figure 5.1b shows TEC8. The sheet

resistances for these are $7 \Omega \text{ cm}^{-2}$ and $8 \Omega \text{ cm}^{-2}$ respectively. The surface morphologies are only slightly different as TEC7 shows slightly larger grains which range from around 50 nm to 3000 nm in diameter. Some grains can be seen to protrude out, giving a higher surface roughness than the TEC8, those grains have a slightly smaller, more homogenous grain size with most of them around 200 nm, giving a lower surface roughness. As a thin layer of cadmium sulphide will be deposited onto the FTO any protruding grains will penetrate through the cadmium sulphide shorting the cell.

Figure 5.1c shows SEM surface images of TEC10 and Figure 5.1d TEC15, the sheet resistance for these are $10 \Omega \text{ cm}^{-2}$ and $15 \Omega \text{ cm}^{-2}$ respectively. The surface morphologies are only slightly different as TEC10 shows slightly larger grains. Comparing these to TEC7 and TEC8 the grain sizes are much smaller, at approximately 50-100 nm. This inherently gives a much smoother surface.

5.4 Properties of Pilkington TEC15 TCO

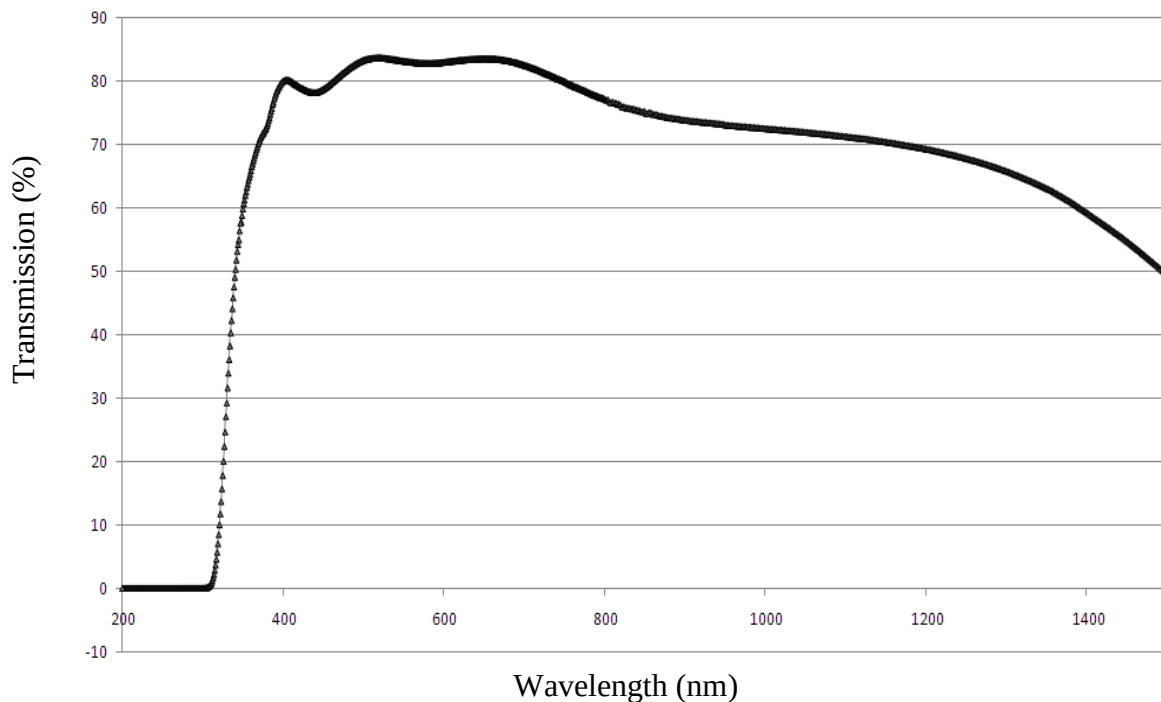


Figure 5.2 - The transmittance of TEC 15 fluorine doped tin oxide TCO

The transmission of TEC15 is shown in Figure 5.2, which is transparent in the visible range (400 nm-700 nm) although at higher wavelengths the transmittance reduces due to high carrier absorption losses. In the visible range the transparency is on average above 80%.

A)

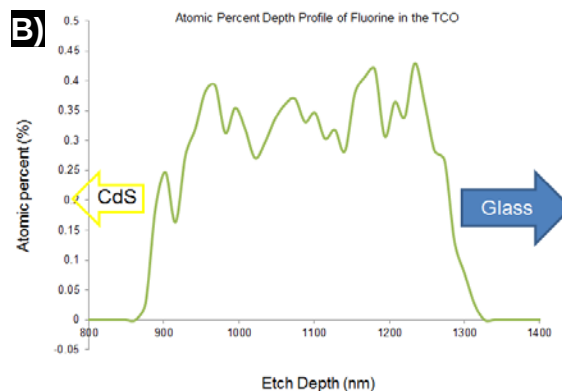


Figure 5.3 – XPS depth profiles of a) cadmium telluride solar cell on TEC15 coated glass, b) fluorine concentration throughout the FTO

The XPS depth profile in Figure 5.3a shows the TEC15 chemical profile. TEC15 is comprised of three layers which are shown by the change in elemental concentrations in the XPS depth profile analysis. The top layer shows tin and oxygen in a 2:1 ratio, indicating a chemical formula of SnO_2 which is as expected. The XPS depth profile in Figure 5.3b shows the varying amount of fluorine dopant in the tin oxide layer. The average throughout the layer can be seen to be approximately 0.35at%. On the surface the concentration of fluorine appears slightly less than the bulk; however this is more likely due to etching unevenly.

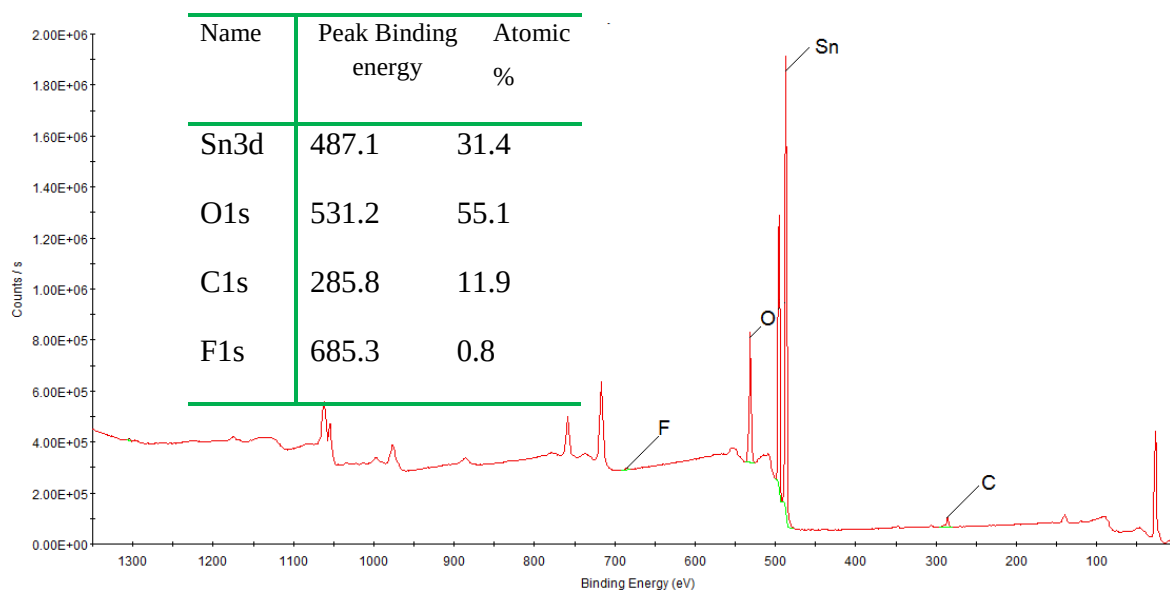


Figure 5.4 – An XPS broad survey scan surface scan of TEC15 showing atomic composition and corresponding atomic percentages

The XPS surface survey scan shown in Figure 5.4 gives the atomic composition of the FTO after a 30 second etch was carried out to remove the majority of the carbon surface contamination. The tin oxygen ratio is 1:2 as expected with the amount of fluorine at ~0.8%wt. which is more than that detected by the depth profile in Figure 5.3b. This could be due to the surface of the FTO containing a higher amount of fluorine than the bulk.

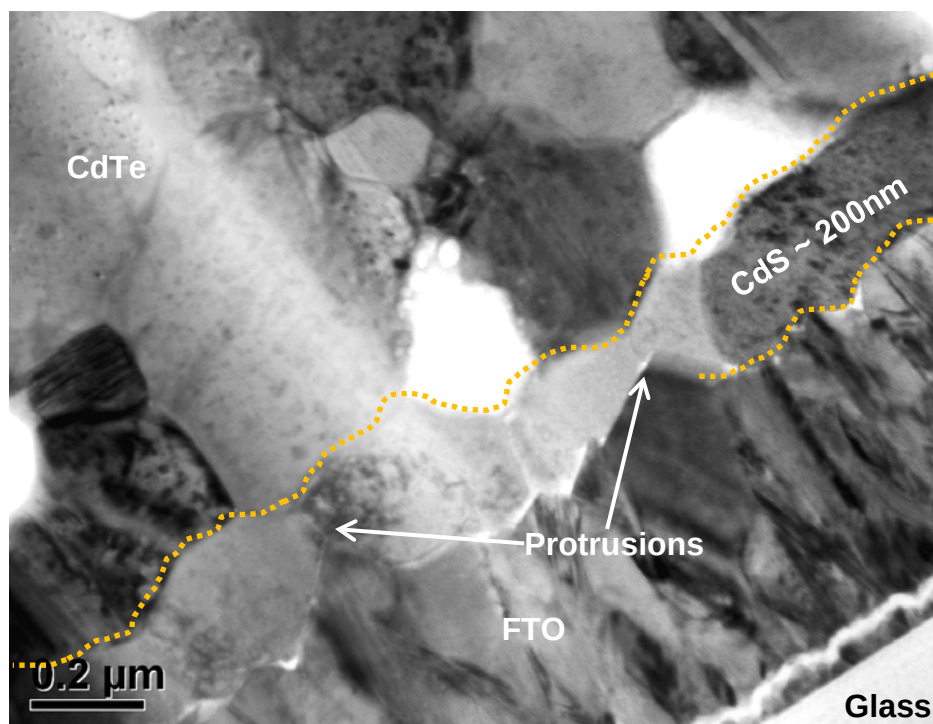


Figure 5.5 – TEM image of TEC15 with cadmium sulphide and cadmium telluride deposited in a superstrate configuration

Figure 5.5 shows a TEM image showing the FTO deposited onto a glass substrate with cadmium sulphide and cadmium telluride deposited onto the surface. The FTO layer has a 3 layer structure deposited onto the soda lime glass substrate. The first layer is only tens of nanometres thick consisting of undoped tin oxide, then another thin layer of silica, followed by 400-500 nm of fluorine doped tin oxide. The slight doping of fluorine makes the tin oxide conductive with a sheet resistance of $15 \Omega\text{cm}^{-2}$ (as measured by Pilkinton). The microstructure of the doped layer can be seen to be fairly columnar with the larger grains nearer the top surface reaching ~ 300 nm in width. The roughness of the FTO can be seen, particularly in the two highlighted areas in Figure 5.5 where the tin oxide grain almost protrudes through the cadmium sulphide. This shows that at least a 200 nm layer of cadmium sulphide is needed for total coverage of TEC15. The cadmium sulphide layer is contacting the FTO consistently without any voids larger than several nanometres.

5.5 Microstructural Analysis of TEC10 TCO

TEC10 is midway in the sheet resistance scale of the commercially available Pilkington TEC glass range. It has adequate sheet resistance for cadmium telluride based solar cells. The TEM image in Figure 5.6 shows the TEC10 FTO structure in cross section deposited onto a glass substrate with cadmium sulphide and cadmium telluride deposited onto the surface. The FTO layer has a 3 layer structure similar to the other TEC glasses, deposited onto the soda

lime glass substrate. The first layer is only tens of nanometres thick consisting of undoped tin oxide which in this case has an inconsistent coverage of the underlying glass. The thin layer of silica is ~15 nm thick and conformal of the undoped tin oxide. The fluorine doped tin oxide is 450 nm thick. The microstructure of the FTO layer can be seen as columnar with through thickness grains. The grains coarsen as they reach the top surface reaching ~150 nm in width. The roughness of the FTO surface is much less apparent than the other TEC glasses which will allow for a much thinner cadmium sulphide window layer to be used without risk of protrusion of the tin oxide grains. The surface is much smoother and less jagged with some waviness.

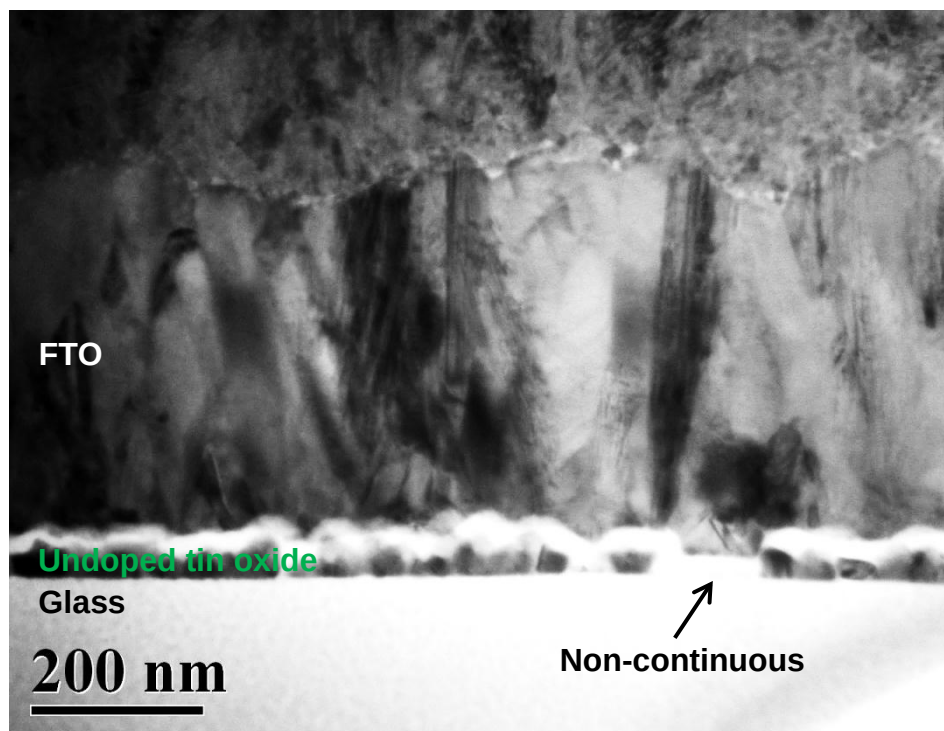


Figure 5.6 – BF-TEM image of TEC10 glass showing the three layer structure

5.6 Microstructural Analysis of TEC7 TCO

TEC7 is the best preforming TCO available commercially at Pilkington, therefore from an electrical performance point of view will be most ideal for cadmium telluride based solar cells.

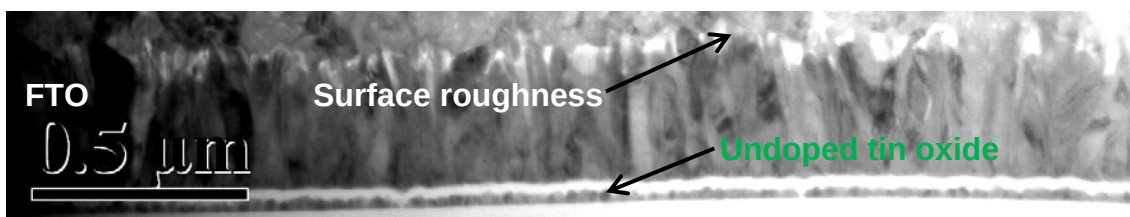


Figure 5.7 – BF-TEM image of TEC7 glass showing a high degree of surface roughness

Figure 5.1 and Figure 5.7 shows that TEC7 has a very high surface roughness. The surface of fluorine doped tin oxide layer can be seen as extremely jagged causing a non-conformal coating on its surface, with many large voids between the peaks. As a good contact is needed with the cadmium sulphide layer for electrical conductivity, the large amount of voids will reduce this, leading to a poor performance from the device.

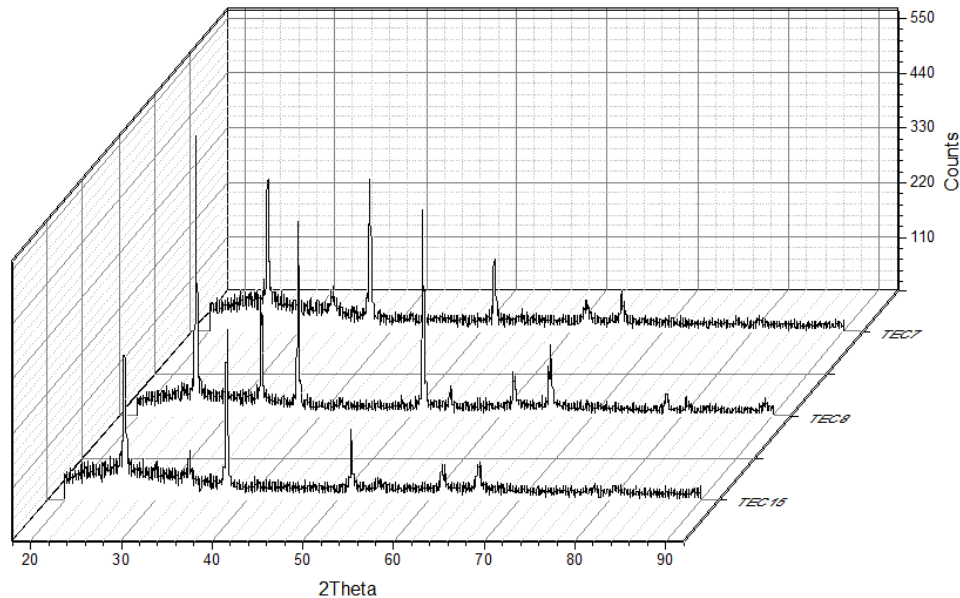


Figure 5.8 – XRD scans of TEC7, 8 and 15

Figure 5.8 shows XRD plots of three of the TEC glasses, consistent with the hexagonal phase of tin oxide, suggesting that the fluorine is distributed within the tin oxide layer as an interstitial.

5.7 Surface Cleaning of TEC Glass

From Chapter 4 it has been found that surface contamination of the TCO can cause pinholes in the cadmium sulphide window layer and subsequently in the cadmium telluride absorber. Therefore XPS has been utilized to test various cleaning methods in order to determine the optimum procedure. XPS is the best analysis technique for examining surface contamination layers due to its high sensitivity as well as having an extremely shallow surface penetration depth (~5 nm). XPS also has a broad X-ray beam, therefore collecting data from a fairly large area (diameter of beam 150 μm).

5.7.1 Cleaning Methods

Several techniques were used to clean the surface and some in conjunction with others. An untreated sample was analysed as a reference.

- A sample underwent a 20 minute anneal on a belt furnace set to 600°C.

- A sample was immersed in a 200 ml ultrasonic bath of soapy water for 50 minutes before being cleaned with deionised water and dried with nitrogen.
- A sample was immersed in a 200 ml ultrasonic bath of isopropanol with 20 ml of deionized water for 50 minutes before being cleaned with deionised water and dried with nitrogen.
- A sample underwent a plasma cleaning process using a Glen100-P AE Advanced Energy plasma cleaner at a pressure of 335 Torr with a gas flow of 20 sccm of oxygen and 30 sccm of argon at a power of 100 Watts. The total cleaning time was 5 minutes.
- A sample underwent a standardised RCA c3 stage clean, firstly immersing the sample in a solution of 5 parts deionized water, 1 part ammonium hydroxide, 1 part hydrogen peroxide for 10 minutes at 70°C to remove any organics/particles. Secondly the sample underwent ionic cleaning using a solution of 5 parts deionised water, 1 part hydrochloric acid, 1 part hydrogen peroxide at 70°C for 10 minutes. Finally the sample is removed and cleaned with deionised water and dried with nitrogen.
- A sample underwent a 4 step process consisting of isopropanol ultrasonic bath followed by the soapy water bath, followed by an anneal and finally plasma cleaning.

All the samples were properly handled and transferred into the XPS vacuum chamber within 30 minutes of being treated to avoid recontamination of the surface.

Sample	Description
Untreated	No surface clean
Furnace	Heated on a belt furnace at 600°C
IPA	Ultrasonic bath using IPA
Plasma	Plasma cleaning cycle
Soapy water	Ultrasonic bath using soapy water
RCA clean	3 step standard RCA clean procedure
4 step process	Ultrasonic bath using IPA then soapy water, annealed at 600°C finally plasma cleaned

Table 5.1 – Summary of TEC glass cleaning procedures

5.7.1.1 Surface Analysis of the Untreated TEC10 Sample

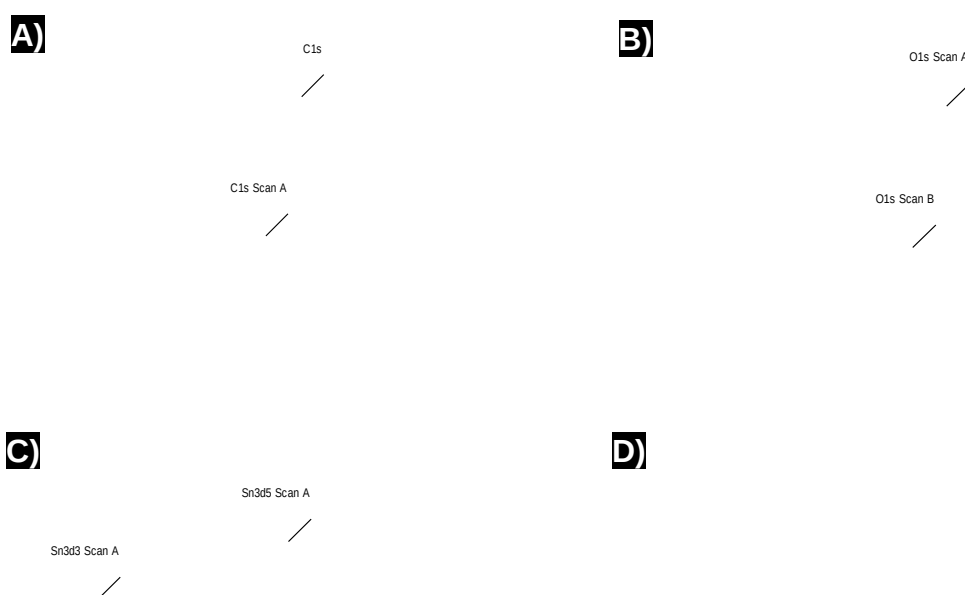


Figure 5.9 –High resolution XPS scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks, for the untreated sample

Figure 5.9 shows the high resolution XPS scans of the individual elements found on the FTO surface. Figure 5.9a shows the carbon peak due to contamination from the atmosphere. However this is usual in most XPS scans unless a long etch is carried out. Figure 5.9b shows the oxygen peak where the larger peak corresponds to the peak from the tin oxide, however a smaller peak was fitted with a higher binding energy, likely due to a surface oxide contaminant. Figure 5.9c shows the tin 3d3 and 3d5 double peaks from the tin oxide. Figure 5.9d shows no fluorine is detectable unlike in Figure 5.4 as it underwent an ion etch in the XPS chamber to remove most contaminants from the surface. This shows the untreated sample had a significant amount of surface contamination and that no fluorine was detectable on the surface of the sample.

5.7.1.2 Surface Analysis of the Annealed TEC10 Sample

Figure 5.10 shows the high resolution XPS scans of the individual elements found on the FTO surface after the sample underwent a 20 minutes anneal on a belt furnace at 600°C. The sample was annealed in order to evaporate off any volatile contaminants. Figure 5.10a shows two carbon peaks one due to contamination from the atmosphere another possibly from the annealing process. Figure 5.10b shows the oxygen peaks where the larger peak corresponds

to the peak from the tin oxide. A smaller peak was fitted with a higher binding energy similar to the untreated sample but with a higher intensity which may be a result of annealing. Figure 5.10c shows the annealed sample had a significant amount of surface contamination and that no fluorine was detectable on the surface of the sample.



Figure 5.10 – High resolution XPS scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks, for the annealed sample

5.7.1.3 Surface Analysis of the TEC10 Sample Cleaned in a Ultrasonic Bath of Isopropanol

Figure 5.11 shows high resolution XPS scans of the individual elements found on the FTO surface after undergoing an isopropanol ultrasonic bath clean. Figure 5.11a shows two carbon peaks due to contamination from the atmosphere and residues from the IPA solution. Figure 5.11b shows the oxygen peak where the larger peak corresponds to the peak from the tin oxide and a smaller oxygen peak was fitted with a higher binding energy, likely due to a surface oxide contaminant. However it was less prominent than other samples indicating some oxide contaminant removal. Figure 5.11c shows the tin 3d3 and 3d5 double peaks from the tin oxide. Figure 5.11d shows no fluorine detectable on the surface of the sample, whereas a 0.8 atomic % could be detected if the sample undergoes a 30 seconds ion beam etch as demonstrated in Figure 5.4

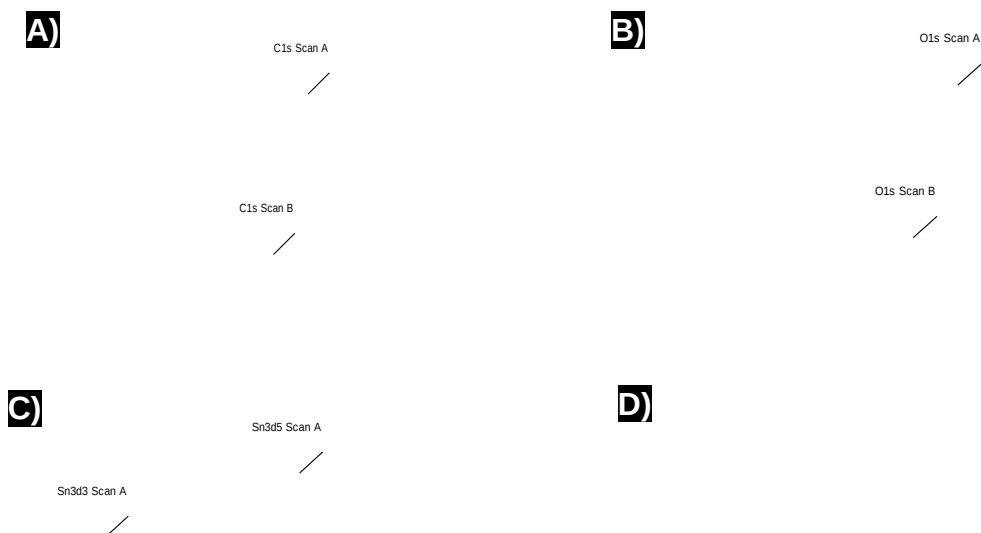


Figure 5.11 – High resolution XPS scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks, for the IPA cleaned sample

5.7.1.4 Surface Analysis of the TEC10 Sample after Soapy Water Ultrasonic Bath Cleaning

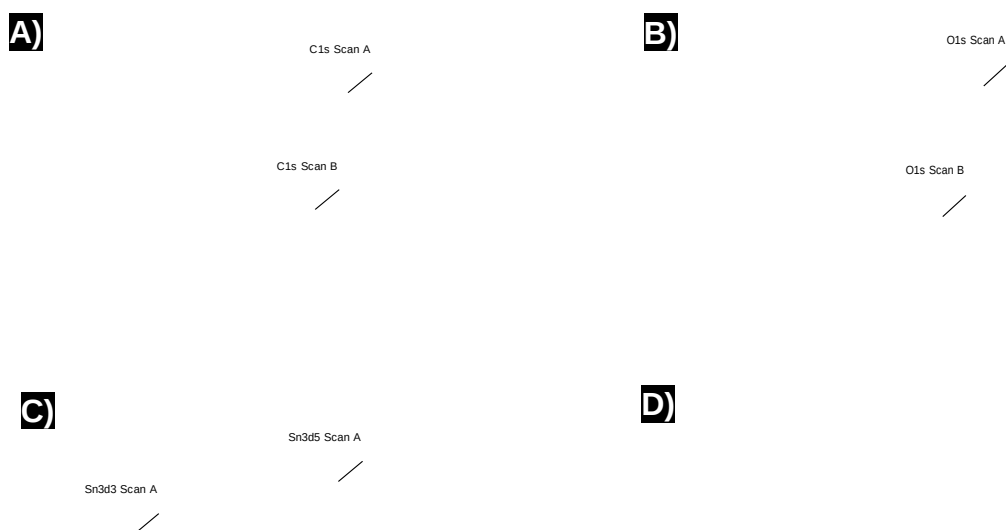


Figure 5.12 – High resolution XPS scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks, for the soapy water cleaned sample

Figure 5.12 shows similar results to the IPA sample, however there is less carbon

contamination as the soapy water did not contain any carbon containing elements, therefore less residue was detected on the surface. Figure 5.12d shows that no fluorine was detectable again, indicating this is not an ideal cleaning method. However it did remove some carbon contaminants as shown by the smaller peak in Figure 5.12a compared to the untreated sample.

5.7.1.5 Surface Analysis of the TEC10 Sample which underwent a Plasma Clean

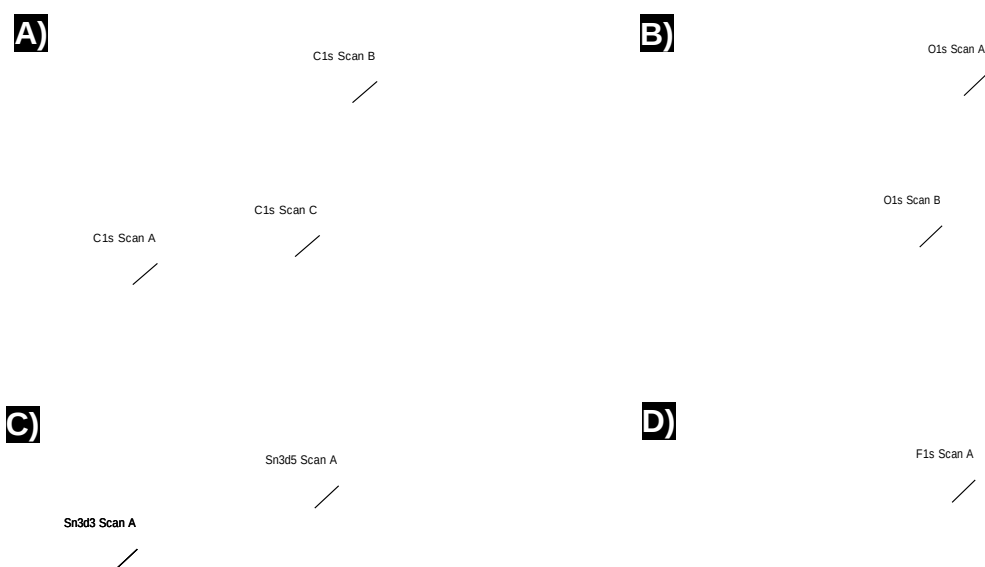


Figure 5.13 – High resolution XPS scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks, for the plasma cleaned sample

Figure 5.13 shows XPS scans of carbon, oxygen tin and fluorine for the sample which underwent a plasma cleaning treatment for 5 minutes. The carbon and oxygen peaks remain as shown in Figure 5.13a and Figure 5.13b, however Figure 5.13d clearly shows a fluorine peak giving a concentration of just over 1 at.%. So far only this treatment has been aggressive enough to give any fluorine readings. However some oxygen and carbon contamination remains on the surface.

5.7.1.6 Surface Analysis of the TEC10 Sample Cleaned using a Standard 3 Step RCA Cleaning

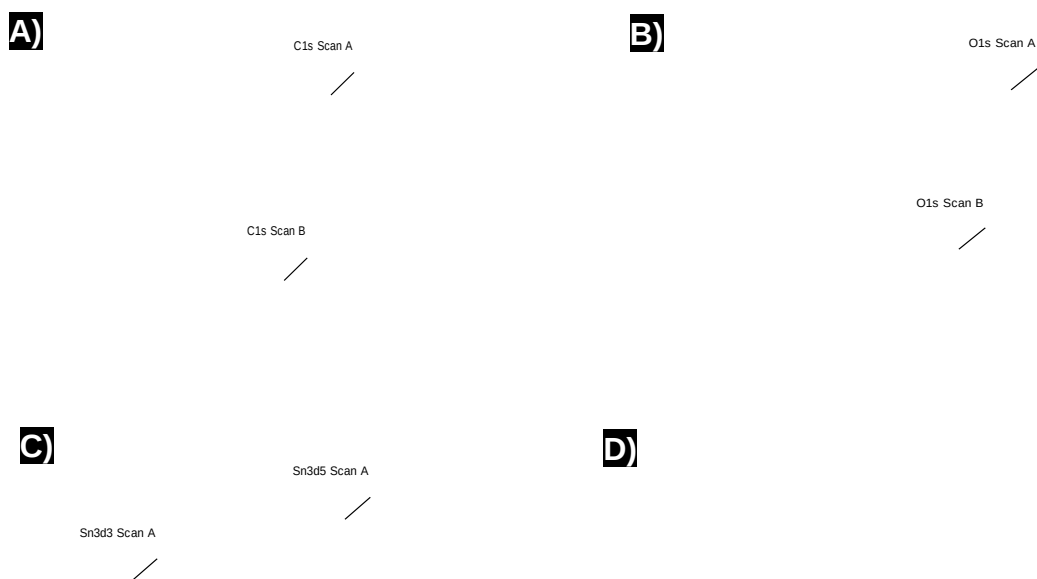


Figure 5.14 – High resolution XPS scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks, for the RCA cleaned sample

Figure 5.14 shows the XPS high resolution scans for the sample which underwent a RCA cleaning procedure. Carbon and oxygen contamination of the surface remains as shown in Figure 5.14a and Figure 5.14b. Figure 5.14d shows that no fluorine is detectable, suggesting that the surface contamination is still too thick to pick up any signal from the TCO materials.

5.7.1.7 Surface Analysis of the TEC10 Sample Cleaned using a 4 stage Process

As some of the cleaning methods had some success, combining these together to remove the difference constituents which make up the surface contamination may provide a cleaner surface. Therefore undergoing the two ultrasonic bath cleans could remove some carbon and oxides from the surface, followed by an anneal in a furnace to evaporate the remaining residue from the ultrasonic baths. Finally a plasma clean should help to remove any formed layers from the surface.

Figure 5.15 shows the results of the XPS scan for the sample which underwent all four treatments in succession.

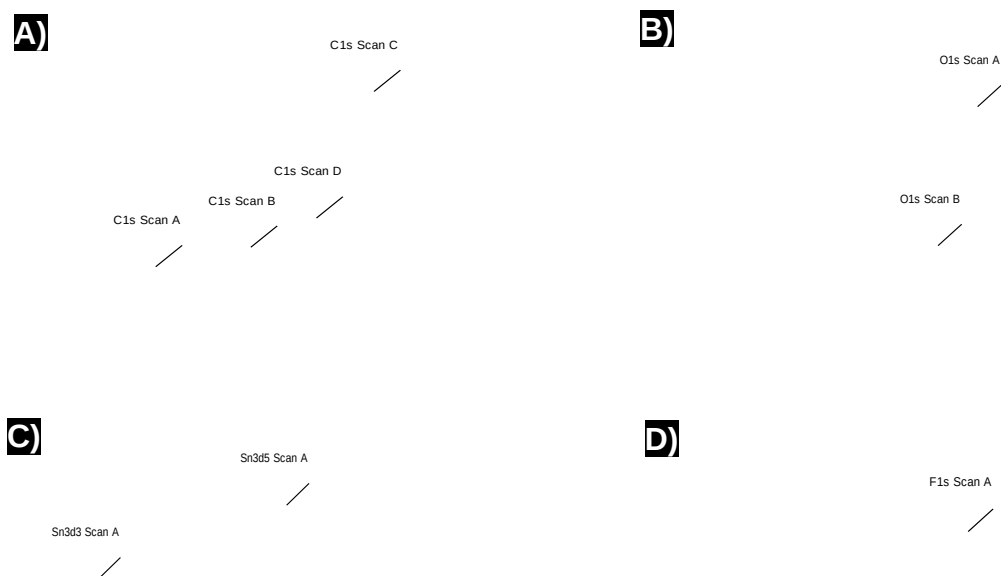


Figure 5.15 – The samples which underwent 4 stage cleaning process XPS high resolution scans of; a) carbon 1s; b) oxygen 1s; c) tin 3d and d) fluorine 1s peaks

Figure 5.15d clearly shows a fluorine peak with an atomic concentration of just over 1%. However Figure 5.15a still shows carbon contamination and Figure 5.15b shows some oxidation of the surface. Combining the treatments has not had the desired effect of removing all constituent surface contaminants.

Overall the plasma cleaning appears to have the best results, therefore it is recommended that all substrates undergo at least a 5 minutes plasma clean before any thin film is deposited.

5.8 Development of Indium Doped Tin Oxide (ITO) Transparent Conductor

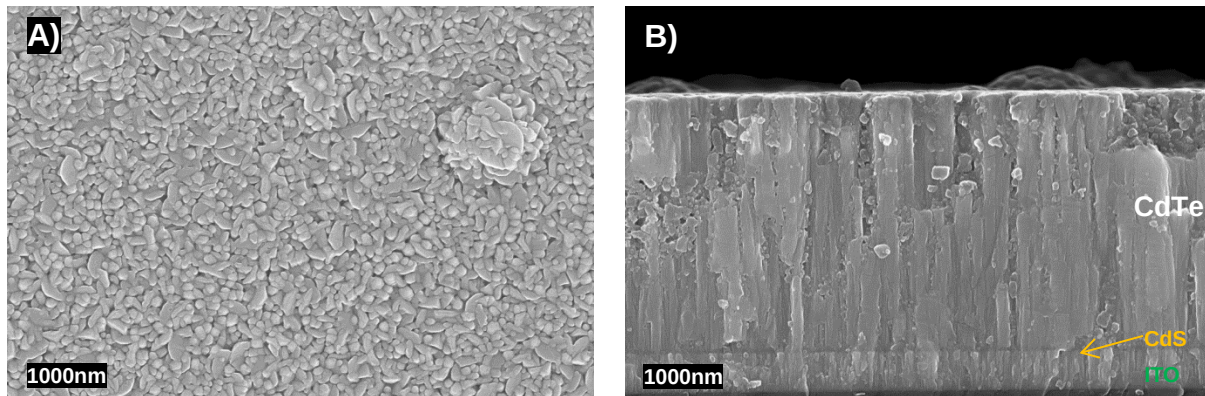


Figure 5.16 –Inlens SEM; a) surface image of ITO on a glass substrate and b) cross section image of Glass/ITO/CdS/CdTe solar cell stack

Figure 5.16a shows an SEM image of indium doped tin oxide deposited via close-field magnetron sputtering. The surface is very flat as most grains are of similar magnitude, around 50 nm in diameter. Figure 5.16b shows a cross section of a complete cadmium telluride cell. The ITO layer can be seen to have a columnar structure, which is 600 nm thick. Above this a thin layer of cadmium sulphide can be seen with a thickness of 70 nm. This smooth interface demonstrates how flat the sputtered indium doped tin oxide layer is. This is advantageous as the films are very conformal, therefore any roughness in underlying films often leads to rougher depositions of the overlying films.

5.9 Summary

From the commercially available TEC glasses from Pilkington the most suitable substrate for the cadmium telluride based solar cells is TEC10. As the roughness of the FTO surface is much less apparent than the other TEC glasses, this will allow a much thinner cadmium sulphide window layer to be used without risk of protrusion of the tin oxide grains, and still providing an adequate sheet resistance of $10\Omega\text{cm}^{-2}$.

Indium doped tin oxide would make an ideal TCO for cadmium telluride based solar cell due to its excellent conductivity as well as a very low surface roughness allowing a cadmium sulphide layer of less than 100 nm to be used.

CHAPTER 6. THE EFFECTS OF CADMIUM CHLORIDE ON CLOSE-SPACED SUBLIMATED CADMIUM TELLURIDE SOLAR CELLS

6.1 Chapter Scope

This chapter will focus on the effects of the cadmium chloride treatment on close spaced sublimated cadmium telluride solar cells. The relationship between performance and microstructural properties will be investigated by means of extensive characterization of pre-treated and post-treated closed space sublimated samples.

The investigation of the cadmium chloride treatment is highlighted in this chapter as it is the most crucial and challenging step during the manufacture of high efficiency cadmium telluride solar cells.

Much debate about the actual role of the cadmium chloride treatment in the processing of the solar cells is evident from the literature survey in Chapter 2. In industry it is taken as a “must do” processing step, although it is not known exactly what the process step is doing to the solar cell. The untreated solar cell is unusable commercially as cell efficiencies are often negligible. However after undergoing a cadmium chloride treatment the efficiencies can rival that of single crystal silicon solar cells. No extra layers are left on the sample after the treatment, therefore it is affecting the existing layers in the solar cell and altering them to form a working viable cell. Understanding what the treatment is doing to the cadmium telluride/cadmium sulphide p-n junction is therefore paramount to increasing the efficiency. The Shockley-Queisser limit for cadmium telluride solar cells is approximately 30% and so far the highest efficiencies of cadmium telluride based solar cells has reached ~20% so further significant increases are still possible. Understanding in detail the exact effects the cadmium chloride treatment is having on the as deposited cell stack is then important, to understand the desired microstructure for high efficiency cadmium telluride cells.

6.2 Experimental Processing

The thin film cadmium telluride 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.

The films were deposited in an all in one vacuum process. The substrate was passed through different chambers at 40 mTorr vacuum, held above graphite boats with no space between. The boats were heated to 650°C with the different materials, which then sublimed onto the inverted substrate.

Two samples were examined in this chapter, a treated and an untreated cadmium telluride cell.

The treated sample 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 minutes 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 copper chloride onto the cadmium telluride layer⁷⁷.

6.2.1 Sample Performance

The cell efficiencies were measured using standard J-V measurements shown in Figure 6.1. The treated sample recorded an efficiency of 11.8%. The second untreated cell was deposited using the same conditions but without the cadmium chloride treatment was measured to have a cell efficiency of just 0.1%. The electrical performance data is summarised in Table 6.1. 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 changes which causes the better performance.

Figure 6.1 shows how differently the two samples behave. The treated sample acts as it should giving a standard JV curve, however the untreated sample produces a JV plot of a straight line acting more as a resistor than a solar cell.

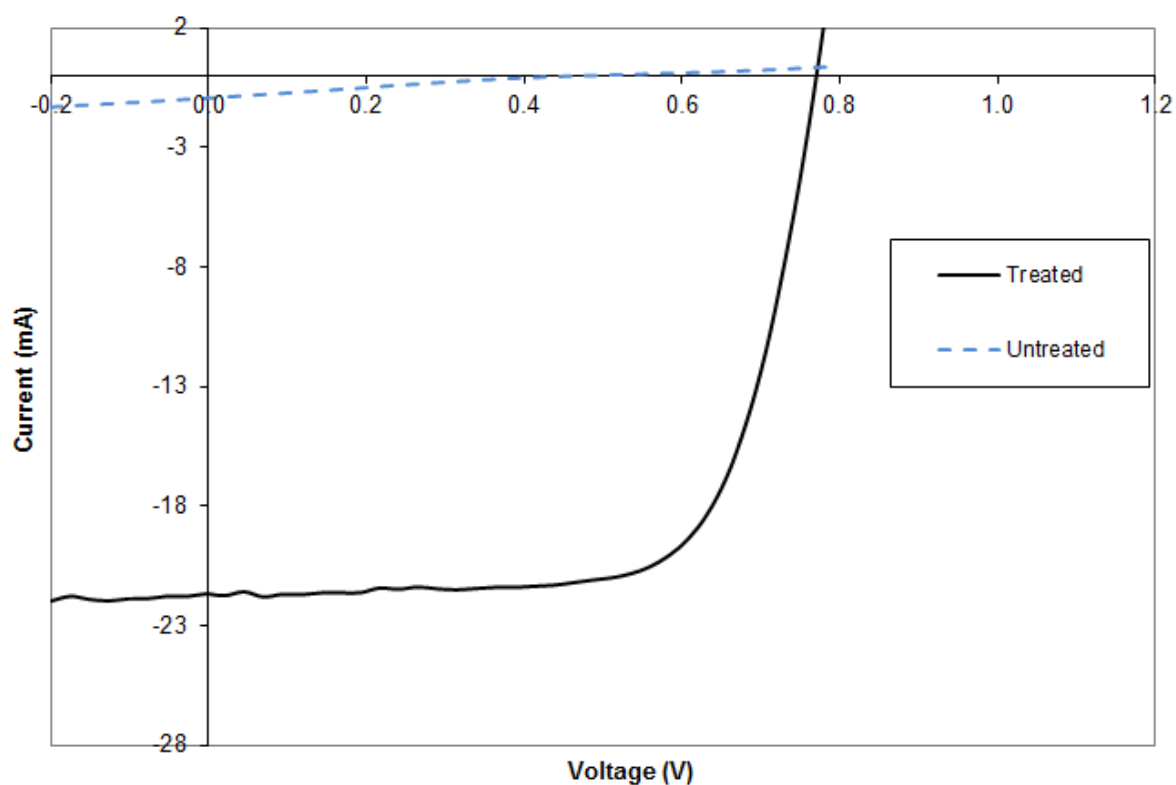


Figure 6.1 - Current-Voltage curve showing the cell performance of the treated and untreated cells

Table 6.1 shows the breakdown of the factors affecting solar cell efficiencies. The treated sample performs better in all aspects, as is expected. However the voltage increase after the treatment is only approximately 300 mV whereas the main improvement comes from the current. Before the treatment the current is negligible but after the treatment almost 22 mA/cm² is measured.

Electrical Property	Treated	Untreated
Voc (V)	0.770	0.465
Jsc (mA/cm ²)	-21.68	-0.92
Fill Factor	0.71	0.23
Efficiency (%)	11.77	0.10

Table 6.1 - Electrical performance values of the treated and untreated cells.

6.3 Microstructural Characterization of Untreated and Treated Cadmium Telluride

6.3.1 Grain Morphology

Surface and fracture cross sections were examined using a FEG-SEM to provide details of the grain morphology of the cadmium telluride before and after the cadmium chloride treatment. No surface cleaning or preparation was used for the surface images shown in Figure 6.2. The micrographs compare the untreated and the cadmium chloride treated cadmium telluride surface. These show that the cadmium chloride treatment causes little effect to the grain size or shape, however the grains are seen to be more coalesced after the treatment. The surface seems smoother after the treatment with less valleys. These changes on the surface most likely occur due to some recrystallization and grains reforming throughout the cadmium telluride layer as seen in Chapter 4. Cross sectional SEM images were taken to see if these changes happen throughout the stack.

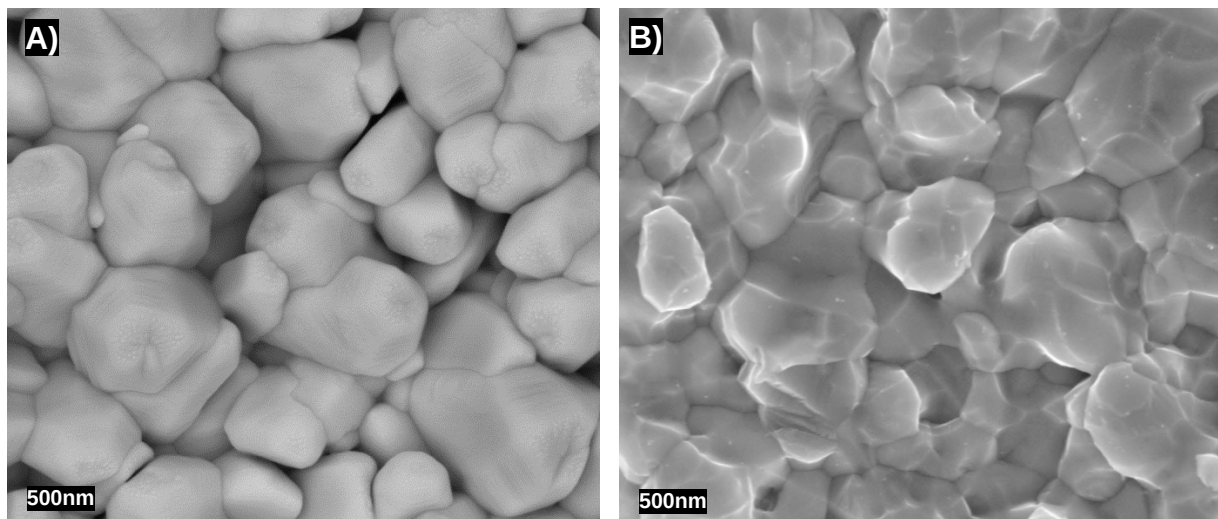


Figure 6.2 – Inlens SEM micrographs of the surface of an a) untreated and b) cadmium chloride treated cadmium telluride cell

6.3.2 Cross-Section Analysis

Figure 6.3 shows a fracture cross sectional image of the two samples. The fracture is mainly intergranular however there is a transgranular component which makes grain size harder to visualise. The fracture cross-section gives a good measure of the thickness of each layer and it can be seen that the thickness of the cadmium telluride in both samples is $2.2\text{ }\mu\text{m}$. The main difference in the cadmium telluride layer between these two samples is the surface roughness. The untreated sample possesses large protruding boulder shaped grains, whereas the treated sample has a less rough surface which is evident in Figure 6.3. It also shows that the grains in the cadmium sulphide layer seem more defined and rounded, whereas in the untreated stack

they are more square. Both samples show compact layers free of large voids. Figure 6.2 and Figure 6.3 indicates that the cadmium chloride treatment has an effect on both the cadmium telluride and the cadmium sulphide layers and more detailed characterization in the succeeding section will examine their changes in more detail.

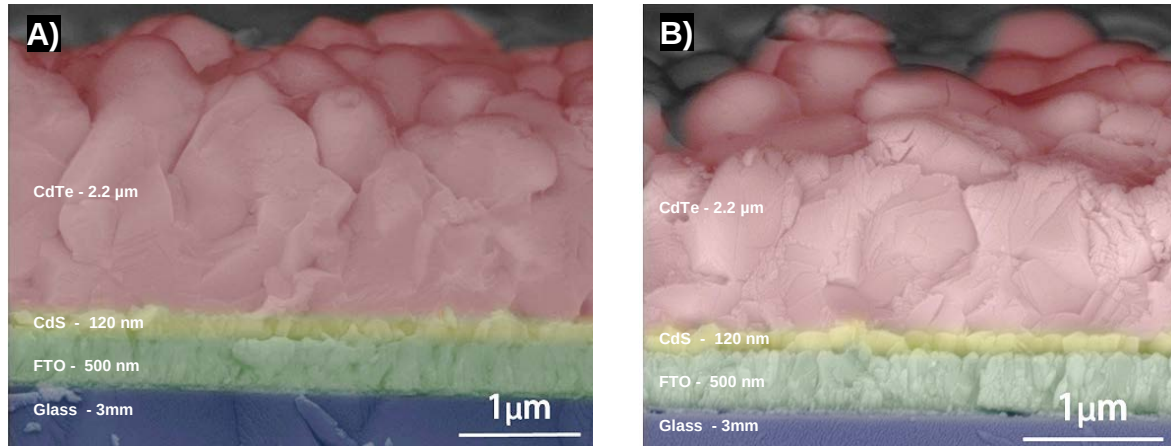


Figure 6.3 – Inlens SEM fracture cross section images of; a) Untreated CdTe cell; b) treated CdTe cell

6.4 Cadmium Telluride Grain Characteristics

6.4.1 Analysis of the Untreated Cadmium Telluride Cells using TEM

Figure 6.4a shows a BF-STEM image through the cross section of the untreated cell. In Figure 6.4a the layers can be clearly distinguished due to their different morphologies. The transparent conducting oxide (TCO) is fluorine doped tin oxide (F:SnO₂), which is deposited by Pilkington glass. It has a 3 layer structure but only the top of the 500 nm fluorine doped tin oxide is shown in Figure 6.4a, as is discussed in detail in Chapter 5. The grains of the tin oxide possesses a columnar morphology and the surface of the fluorine doped tin oxide can be seen as a jagged surface due to the shape of the grains which are fairly wide at the top. The jagged surface of the TCO can often cause shorting of the cell if the tip of the grain protrudes through the cadmium sulphide layer and contacts the cadmium telluride grains so the device will not function. In this cell the cadmium sulphide can be seen as fairly thick (around 200 nm), and also appears very constant in thickness without pinholes or voids so shorting will not occur. The cadmium sulphide grains have a good contact with the TCO as no voids can be seen and are conformal absorbing the roughness of the tin oxide grains. The top surface of the cadmium sulphide grains is very flat, giving the grains a very square shape 200 nm by 200 nm. From the TEM images in Figure 6.4a it can be seen that within the cadmium telluride grains there is an obvious structure of linear defects shown as parallel lines within

the cadmium telluride grains. Figure 6.4b shows a HRTEM image of one of the cadmium telluride grains from Figure 6.4a. A high density of defects are visible.

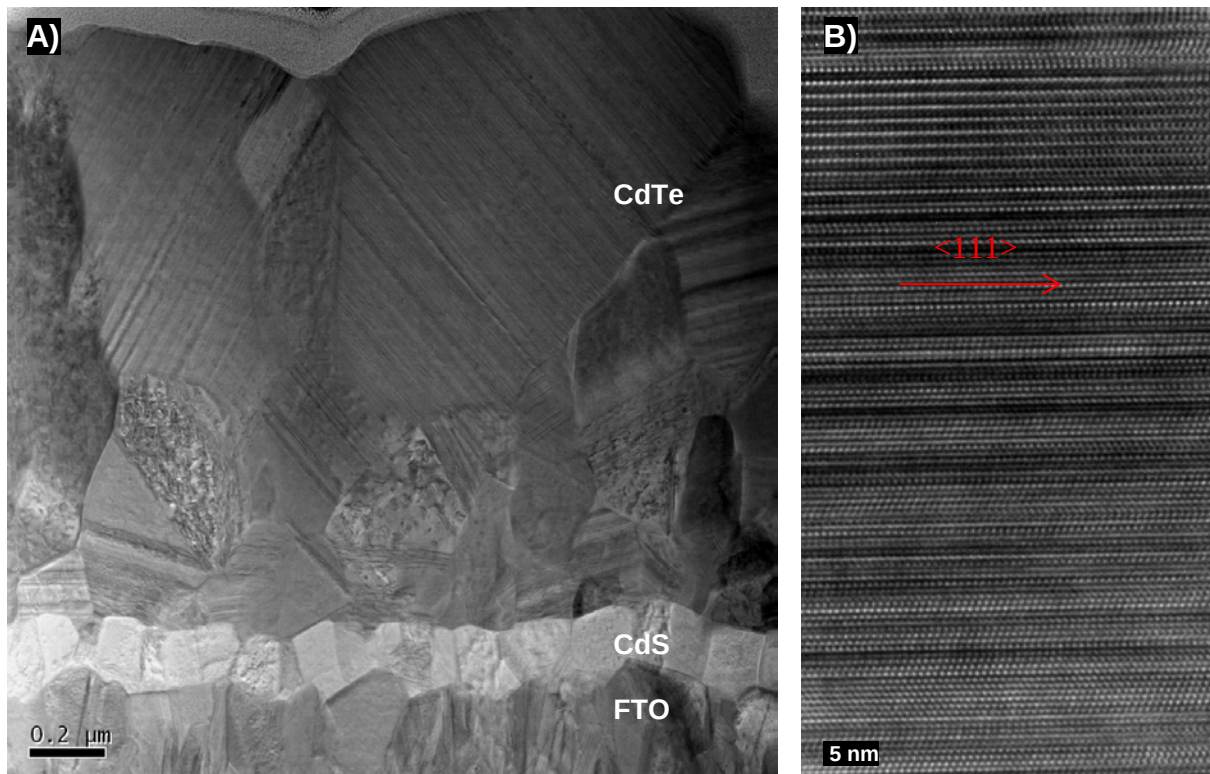


Figure 6.4 – a) A BF-STEM micrograph of the untreated cadmium telluride cell in cross section; b) HRTEM micrograph of a untreated cadmium telluride grain tilted to the [110] zone axis

The cadmium sulphide grains affect the geometry of the cadmium telluride grains deposited onto them. The morphology of the underlying cadmium sulphide grains impact the nucleation of the cadmium telluride as evidenced in Figure 6.4a and Figure 6.5a which shows that some grain boundaries continue from the cadmium sulphide to the cadmium telluride, which effects the grain size of the cadmium telluride. Some cadmium telluride grains grow over two cadmium sulphide grains giving a wider cadmium telluride grain. Due to this growth and the small cadmium sulphide grains, the cadmium telluride grains are smaller nearer the interface, as can be seen in the bottom half of the layer. Towards the top end of the cadmium telluride layer away from the interface with cadmium sulphide the grains become larger shown in Figure 6.4a. The cadmium sulphide grains are uneven at the top due to the roughness of the FTO giving the cadmium telluride layer a high degree of roughness shown in Figure 6.5a. The nature of the shape of the grains causes voids between the larger grains, usually halfway through the layer. Figure 6.5b shows a HRTEM image of the cadmium sulphide cadmium telluride interface. A schematic diagram of the layers is shown in Figure 6.6 highlighting the key aspects of the cells grain morphology.

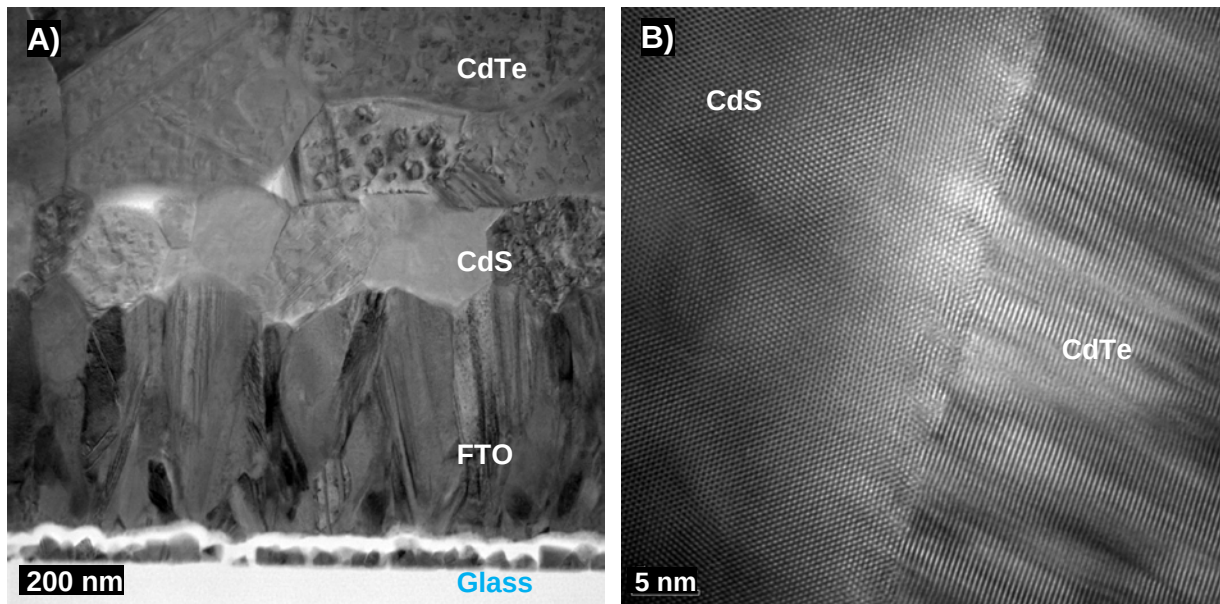


Figure 6.5 – A) BF-STEM micrograph of the untreated in cross section showing the Glass/TCO/cadmium sulphide/cadmium telluride interface and b) HRTEM image of the cadmium sulphide/cadmium telluride interface

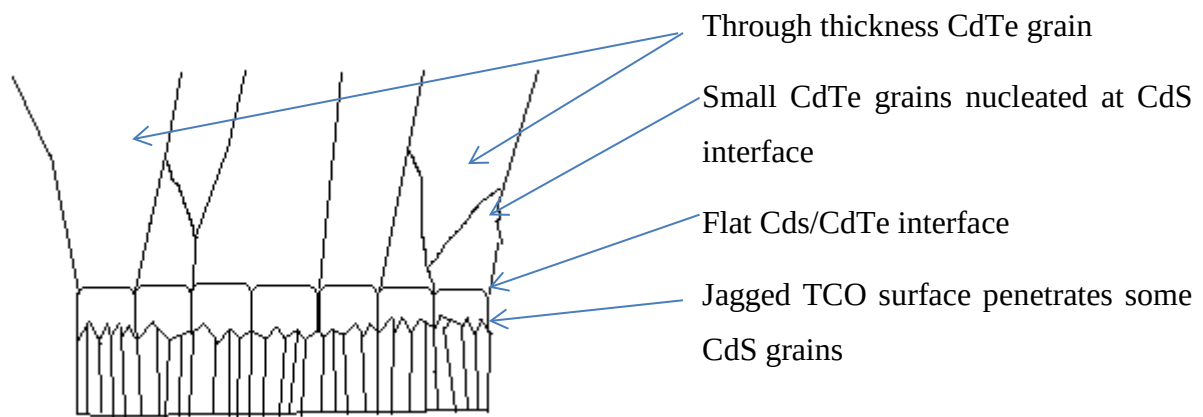


Figure 6.6 – A schematic diagram showing the key aspects of the grain morphology of the layers within the untreated CSS deposited cell

Stacking defects can be seen in almost all of the cadmium telluride grains of this sample where the defects extend from one side of the grain to the other. Within the same grain the lines are all parallel to one another, but between grains the angle varies. The defects observed have the properties of linear defects within the cadmium telluride lattice structure, as they are parallel in nature. Using TEM diffraction Figure 6.7b shows lines at the diffracting spots from a cadmium telluride grain containing a high density of defects shown in Figure 6.7a.

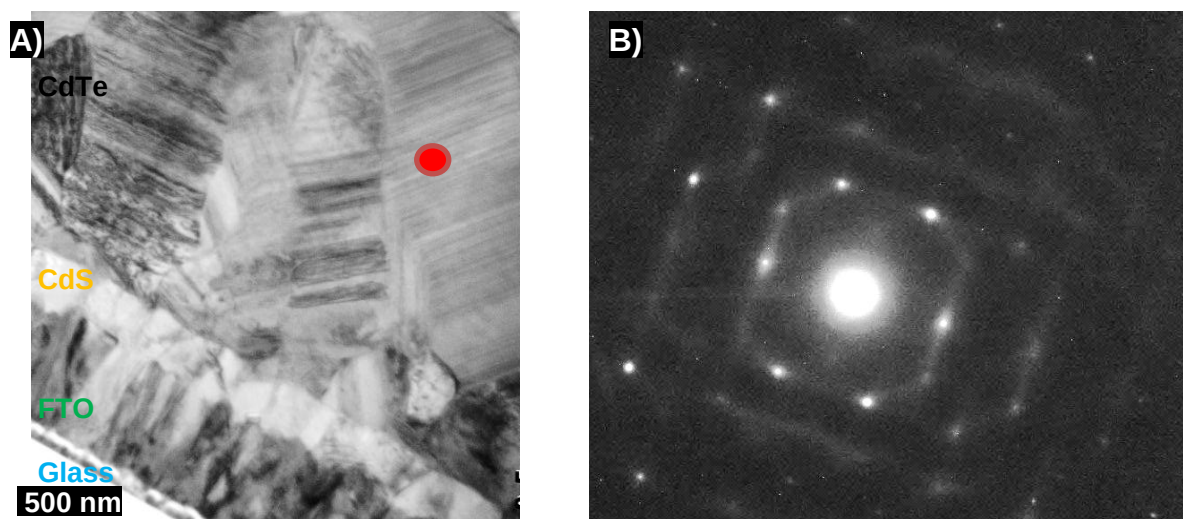


Figure 6.7 – a) BF-TEM image of highlighting a cadmium telluride grain b) corresponding diffraction pattern

6.4.2 Cadmium Telluride Stacking Defect Analysis in the Untreated Cell

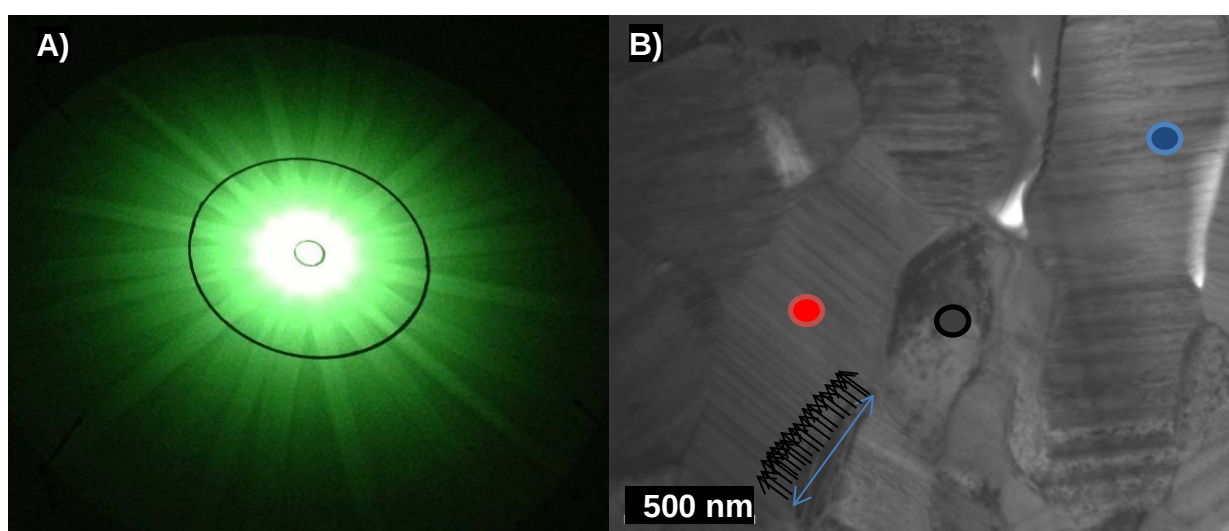


Figure 6.8 – a) Image of a centred [1-10] Kikuchi pattern b) shows one grain of untreated samples tilted to the (111) plane

The linear defects could be one of three types of faults within the cadmium telluride lattice. These are either stacking faults which could be intrinsic or extrinsic, as well as twin boundaries. The defects are shown in most grains; however some grains appear to show the stacking faults more clearly than others. This is due to the different orientation of each grain to the incident electron beam. If a grain was tilted to a certain orientation the defects would appear much more clearly. Indexing the zone axis which looks directly down the lattice plane containing the defects can be done by viewing the Kikuchi patterns. Using the double tilt holder, which enables the sample to be tilted around the α and β axes, grains were oriented with the correct Kikuchi pattern being centred. It was found that tilting so that the incident beam is parallel to the [110] zone axis shown in Figure 6.8a, the beam would be looking directly down the (111) plane on which the defects are seen to lie.

As the grains are all of different orientations, only one grain can be correctly oriented at one specific tilt to observing the stacking faults clearly. Therefore some grains which contain a large number of stacking faults appear hazy or clear of defects until that grain is properly oriented to view the defects along the (111) plane. Figure 6.8b shows that the tilt of the sample greatly affects the clarity of the defects within the cadmium telluride grains. The grain with the red marker clearly shows stacking faults and over 20 defects can be counted intersecting a half micron line perpendicular to the stacking faults. The grain with the blue marker shows a grain which has a hazy pattern, and no clear stacking faults can be seen within this grain in Figure 6.8b. However if the beam is then focused on this grain and the [110] zone axis is brought to the centre by tilting the sample around the α and β axes, the grain will reveal just as many defects as the grain highlighted by the red marker. The grain highlighted by the black marker in Figure 6.8b, appears free of stacking faults and only has some darker and lighter regions due to scattering. This grain again possesses a large density of stacking faults only revealed once the grain is correctly oriented.

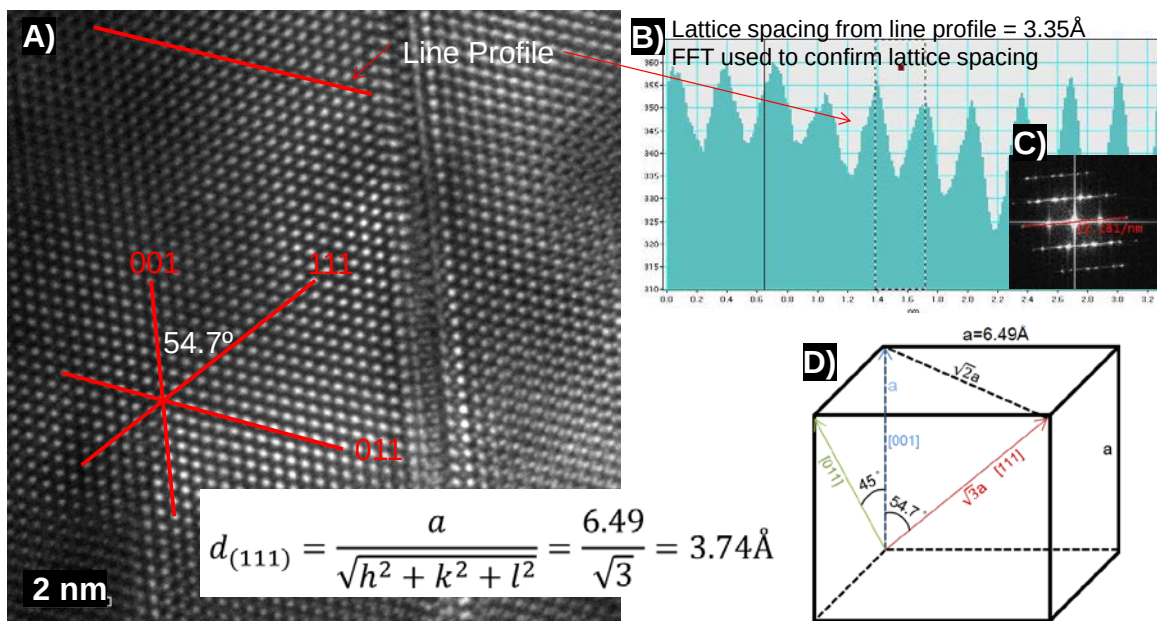


Figure 6.9 – a) HRTEM image of an untreated cadmium telluride grain with b) corresponding lattice spacing profile, c) FFT and d) HKL planes indicated

Figure 6.9 shows a high resolution TEM image of an untreated cadmium telluride grain, this area has been imaged as it contained few defects, so that lattice spacing measurements and atomic planes could be calculated. The lattice spacing along the (011) plane was measured over 10 atoms and the average calculated, as 3.35 Å. It was checked by measuring the spacing from the FFT image, which gave a similar result. The theoretical atomic spacing for cadmium telluride was calculated using Equation 6.1.

$$d_{(111)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{6.49}{\sqrt{3}} = 3.74\text{\AA}$$

Equation 6.1 - Theoretical atomic spacing for cadmium telluride

The theoretical and measured atomic spacing have ~10% difference between them some of which could be due to residual strain within the layer. This strain may have been induced from rapid cooling after deposition as the films were sublimated at high temperatures and then allowed to cool.

Figure 6.10a shows a HRTEM image of an untreated cadmium telluride grain in an area with several stacking fault defects. The defects can be seen to be a stacking fault as the atomic layers either side of the defect are seen to be in the same direction. The stacking fault can be characterized as an extrinsic stacking fault as there is an extra layer of atoms present, demonstrated by the schematic in Figure 6.10b. This extra layer of atoms disrupts the perfect lattice, which causes the movement of electrons to be impaired, and can cause recombination within the cadmium telluride layer, ultimately reducing the cell efficiency.

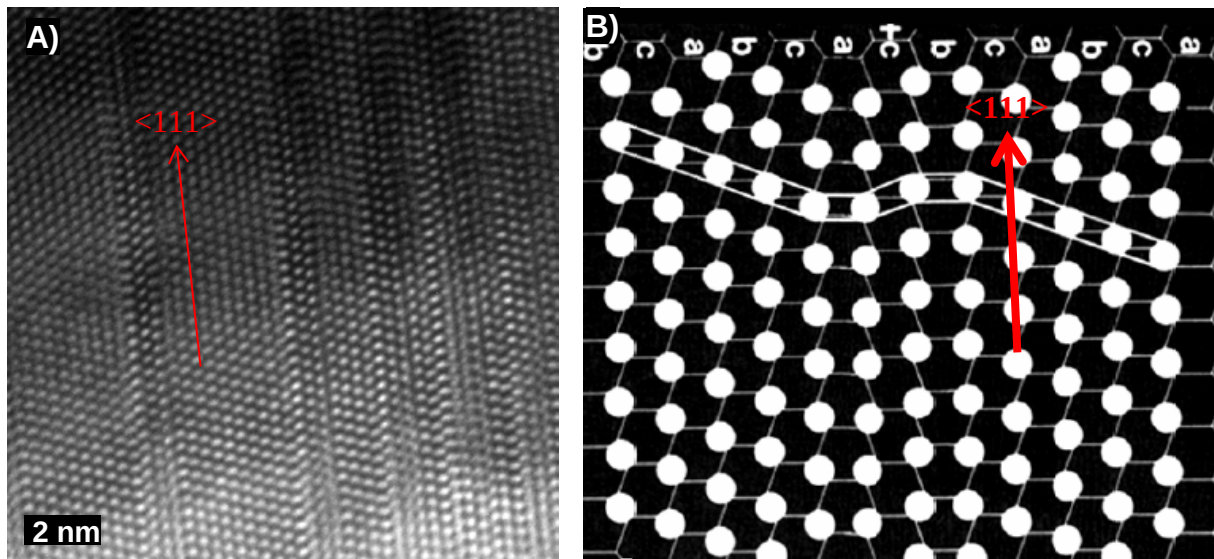


Figure 6.10- a) HRTEM micrograph of an untreated cadmium telluride grain showing several stacking faults b) schematic of an extrinsic stacking fault in cadmium telluride

Figure 6.11a shows an untreated cadmium telluride cell with a high resolution image taken within one of the cadmium telluride grains which shows a large number of linear defects. The lower resolution bright field image in Figure 6.11b shows some of the cadmium telluride grains have no defects within them, some grains show a number of defects and some appear hazy. This is due to the different orientation of the grains, which gives a misleading appearance, the grains have large densities of stacking faults but do not appear in some grains and a haze can be seen in others. Once a grain is oriented correctly to the [011] zone axis, it

will diffract strongly and the defects will be visible at a high enough magnification. The image in Figure 6.11a is at a high resolution correctly aligned to the appropriate zone axis and a large density of linear defects can be seen faulting along the (111) plane. This area is representative of most grains in an untreated cadmium telluride grain. Both twin boundaries and stacking faults are evident before the cadmium chloride treatment. Over 20 defects are observed within just a 30 nm area. The defect density is non-uniform since some areas contain a high density of faults whereas some areas contain less faults. However, the average cadmium telluride grain in the untreated material contains very high densities of defects per grain. The defects are also all parallel to each other as they favour forming along the (111) plane due to the lower formation energy needed⁴⁰.

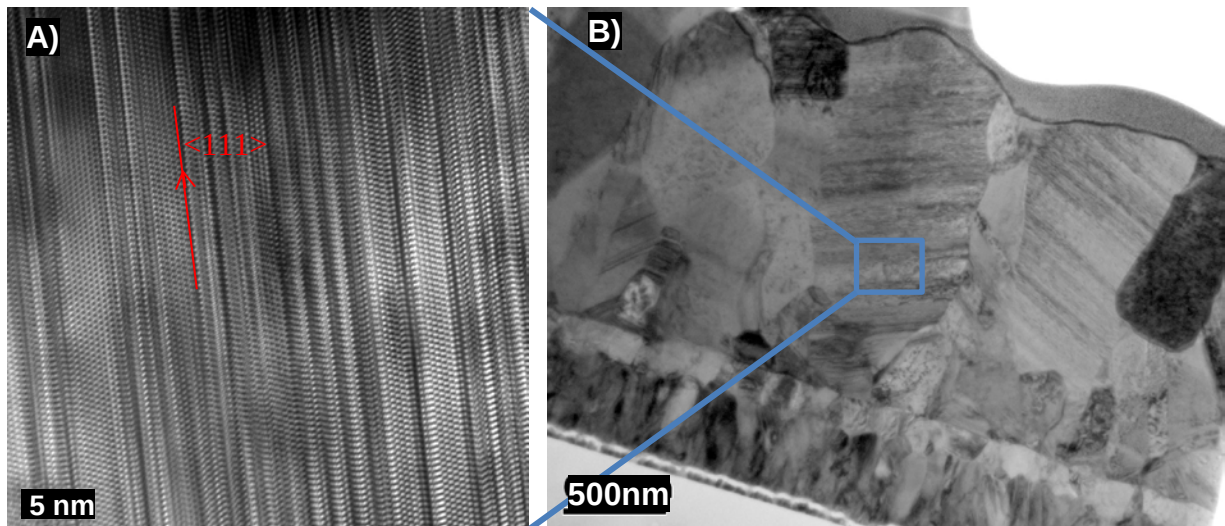


Figure 6.11 – a) HRTEM image of the untreated cell with b) corresponding BF-TEM image highlighting the area the HRTEM image was taken

6.4.3 Analysis of the Treated Cadmium Telluride Cells using TEM

Figure 6.12 shows a BF-STEM image of the cadmium chloride treated cell. The image shows the same layers as the treated sample however the morphology of some of the individual layers has changed. The TCO of TEC10 tin oxide appears identical to that of the untreated sample with columnar grains with a jagged surface, with an estimated roughness from peak to trough of approximately 30 nm. The cadmium sulphide, which is deposited directly onto this layer, shows some change although the grains are still single through thickness grains with an average size of 150 nm. There is less order and more variety in grain size as much smaller grains down to 50 nm can be seen, which were not present in the untreated cadmium sulphide layer. The shape of the grains is seen to be more rounded than the untreated cell on the top surface, as well as the sides between the grains. The TCO/cadmium sulphide interface is similar to that of the untreated cell with the triangle tips of the tin oxide grains protruding

partially into the cadmium sulphide but not penetrating all the way. The cadmium sulphide/cadmium telluride interface is not as flat as before the chlorine treatment as more rounded grains are seen and as before the interface was very flat. Figure 6.12 shows cadmium sulphide grains at the interface with the rounded tops and the boundaries lower than the tops of the grains. This indicates a change in the cadmium sulphide which could be recrystallization or inter-diffusion with the surrounding layers. Another new feature at the cadmium sulphide/cadmium telluride interface is a new region of lighter material which is seen just above the cadmium sulphide layer and has appeared after the treatment. These can be seen spaced out every few microns all along the interface.

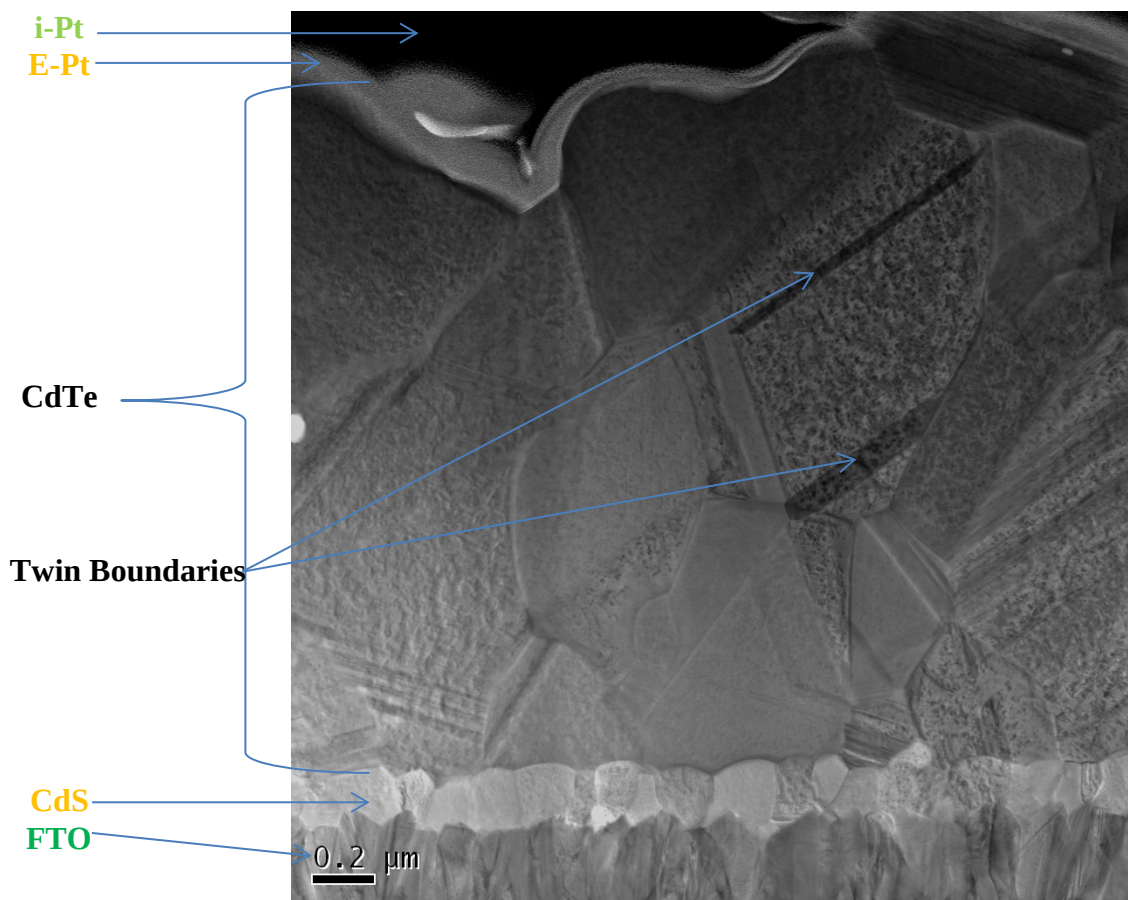


Figure 6.12 – BF-STEM image of the treated in cross section showing the TCO/cadmium sulphide/cadmium telluride interface

The cadmium telluride layer in Figure 6.12 can be seen to have changed clearly from the untreated cell as recrystallization has occurred during the cadmium chloride treatment process. The cadmium telluride grain morphology has changed in that the grains shape has become more equiaxed whereas the untreated sample had long thinner columnar grains. The grains are now covering more cadmium sulphide grains at the interface whereas before the chlorine treatment the cadmium telluride grains were seen to nucleate from one or two

cadmium sulphide grains. In Figure 6.12a single cadmium telluride grain can be seen contacting several cadmium sulphide grains. The other main observation is that all grains are free of defects apart from a few apparent twin boundaries seen by the parallel lines within grains along the cadmium telluride lattice plane. The surface of the cadmium telluride grains has become less rough after the treatment mainly due to the change in grain morphology as the tall thinner grains before the treatment had high peaks and caused deeper troughs between the grains which also led to some voids, whereas after the treatment the larger more square grains have less peaks and troughs between the grains giving a more smooth surface.

6.4.4 Characterization of Defects within the Treated Cadmium Telluride Grains

Figure 6.13 shows a high resolution image of two twin boundaries terminating at a grain boundary in a treated cadmium telluride layer. The grain with the twin boundaries is oriented to show the (111) plane on which the defects lie, by positioning the grain along the [011] zone axis whereas the adjacent grain has a slightly different orientation. The two defects can be characterized as twin boundaries as the atomic layers alter direction by 60° either side of each boundary. Twin boundaries are known to be less detrimental to the electronic characteristics of the material than stacking faults, as the grains within the treated cadmium telluride layer have fewer defects remaining since most are seen as twins. The cell efficiency can be expected to be higher from a microstructural point of view. Figure 6.13 shows both twin boundaries terminating at a grain boundary and not continuing into the next grain, which is true for the majority of the defects in both the treated and untreated grains. As the grains extend across the entire grain width, cadmium chloride diffusion down the grain boundaries will have direct contact with all the edges of the defects within the grains, allowing for the shift of the entire lattice forming a more perfect structure. The grain boundary shown in this image also shows that the mis-orientation between the two grains is a low angle. As the image still shows the perfect lattice structure, different angle boundaries will allow different rates of cadmium chloride diffusion, which may promote the passivation of stacking faults in some grains before others. The twins in high resolution images can also be seen more clearly in the treated sample as all the stacking faults in the grains have all been passivated by the cadmium chloride treatment. Some twins remain in the cadmium telluride films as they would require much more energy to be removed. Once only few remain the distance between them becomes larger, as a stacking fault only requires the lattice to shift over by one atom to form a perfect lattice. So if an odd number of twins are present in an area before the treatment it is expected that one twin remains in this area due to all the atoms on one side of the twin

require to switch orientation by 60° to the $\langle 111 \rangle$ direction. Whereas if in an area an even number of twins are present before the treatment, only the layers of atoms between the two twins need to shift orientation in order for a perfect lattice to be formed. Effectively the twins can cancel each other out provided they are close enough.

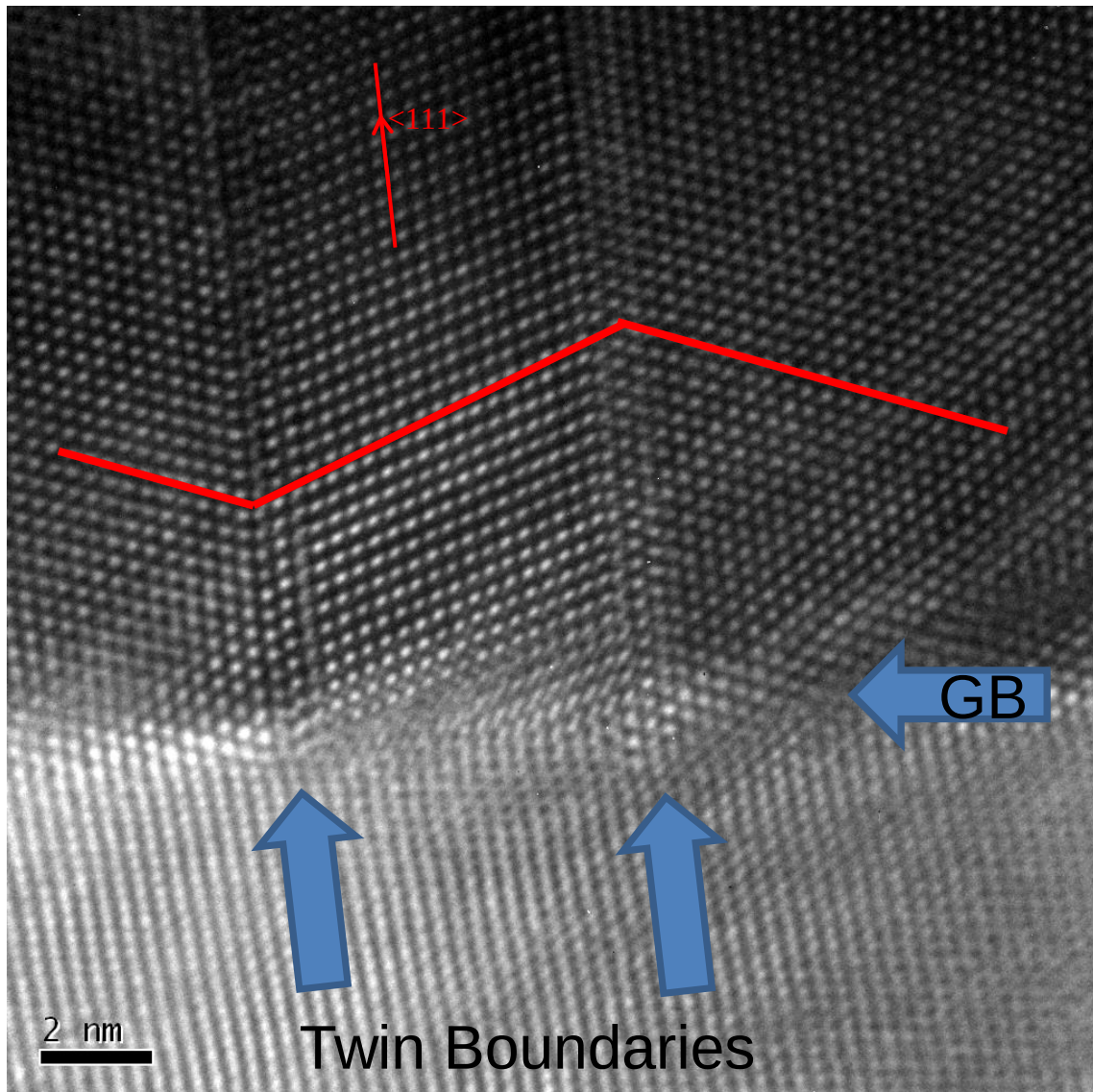


Figure 6.13 – HRTEM image of two twin boundaries terminating at a grain boundary in a treated cadmium telluride layer

6.4.5 Interdiffusion during the Cadmium Chloride Treatment

Chemical distribution maps of the treated cadmium telluride cells show interdiffusion during the cadmium chloride annealing treatment. Figure 6.14 shows a STEM-HAADF image with corresponding chlorine and sulphur chemical maps. It reveals regions which are chlorine enriched. The enriched regions are within the cadmium sulphide layer and at the interface with the cadmium telluride layer. The enhanced signal at the surface is due to the background signal from the platinum layer (high atomic number) used in sample preparation. The effect can be observed in both the chlorine and sulphur 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 cadmium telluride and heating to 400°C for 8 minutes. This is the only source of chlorine in the process. These observations indicate that the chlorine is transported through the cadmium telluride layer to the interface during the annealing process.

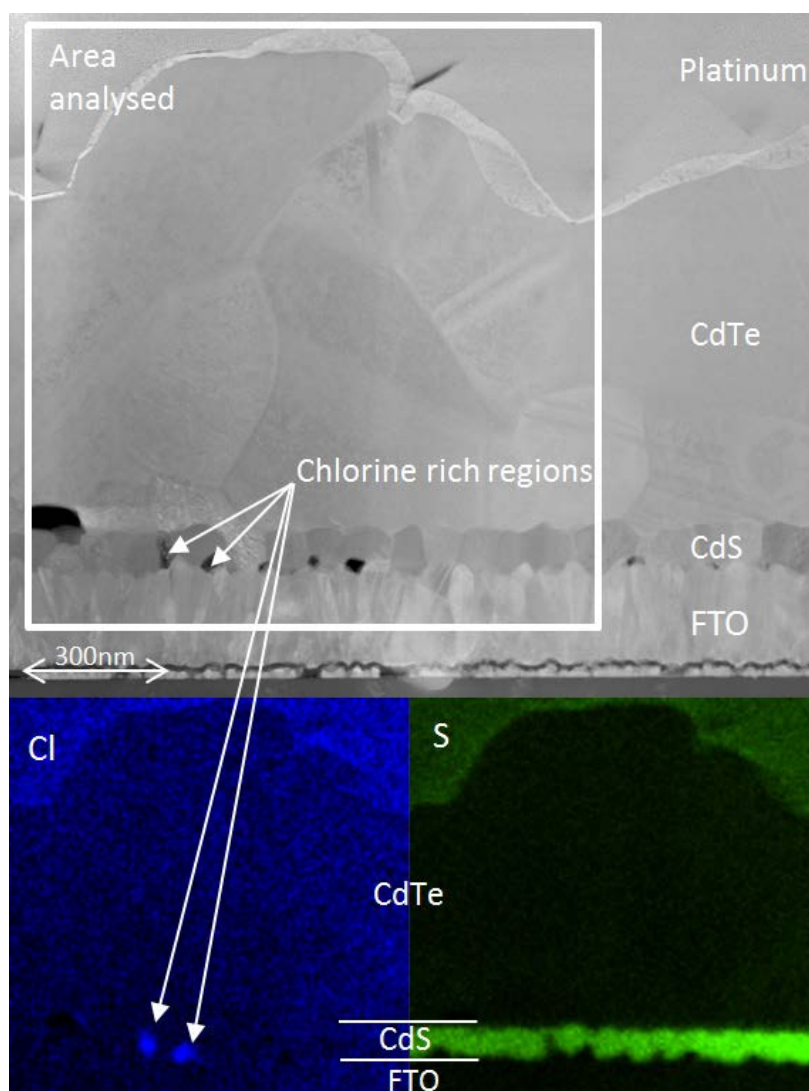


Figure 6.14 - A HAADF STEM image and corresponding EDX chemical distribution maps of chlorine and cadmium from a cadmium chloride treated cadmium telluride cell

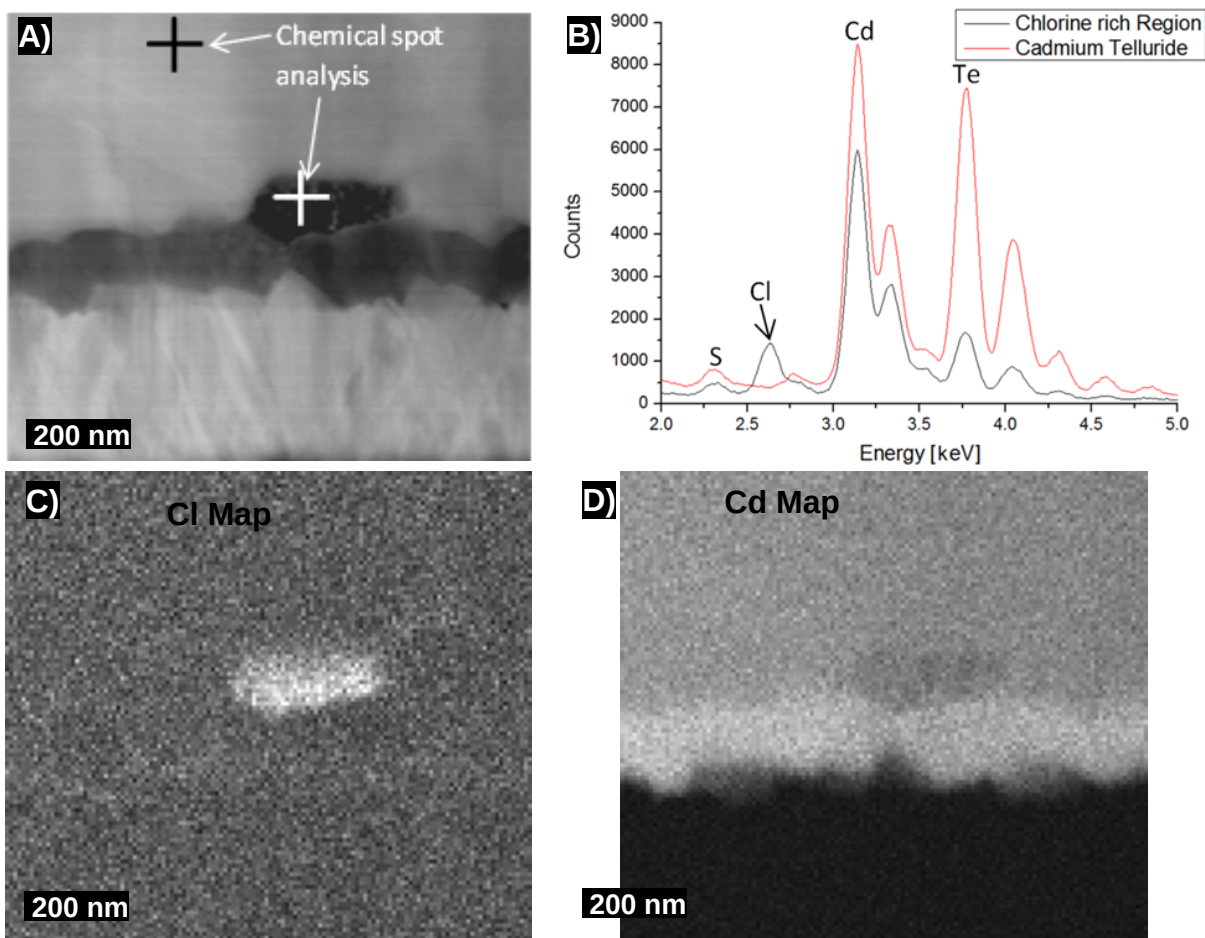


Figure 6.15 – a) STEM-HAADF image of the cadmium telluride/cadmium sulphide interface, b) corresponding EDX spectra at two points within and outside a chlorine rich region c) corresponding chlorine chemical distribution map, d) corresponding cadmium chemical distribution map of the treated cell.

Figure 6.15a shows STEM- HAADF image of the cadmium telluride/cadmium sulphide interface. Figure 6.15b shows two EDX spectra each collected for 90 seconds. One was obtained from the chlorine rich region featured in Figure 6.15a and the other in the cadmium telluride layer. The spectra show a clear chlorine peak and lower cadmium and tellurium peaks in the chlorine rich area. Figure 6.15c and Figure 6.15d shows corresponding EDX elemental maps of the area in Figure 6.15a. This region is approximately 250 nm x 100 nm in size. The corresponding cadmium map shows depletion of cadmium in this area.

6.4.6 Grain Boundary Segregation during the Cadmium Chloride Treatment

TEM and EDX analysis was carried out in the region of grain boundaries. Figure 6.16a shows a TEM image of a triple point grain boundary and Figure 6.16b provides EDX spectra from the boundary region and within the grain for comparison. The spectra show a slight chlorine peak at the grain boundary whereas no chlorine is detected from the point taken from within a grain.

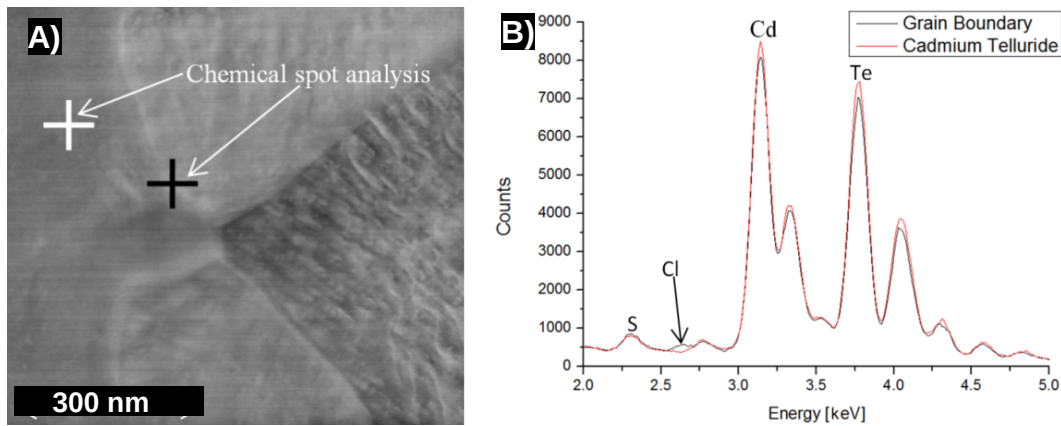


Figure 6.16 – a) A HAADF STEM image of two triple point grain boundaries in the center of the cadmium telluride layer b) EDX spectra of two points highlighted

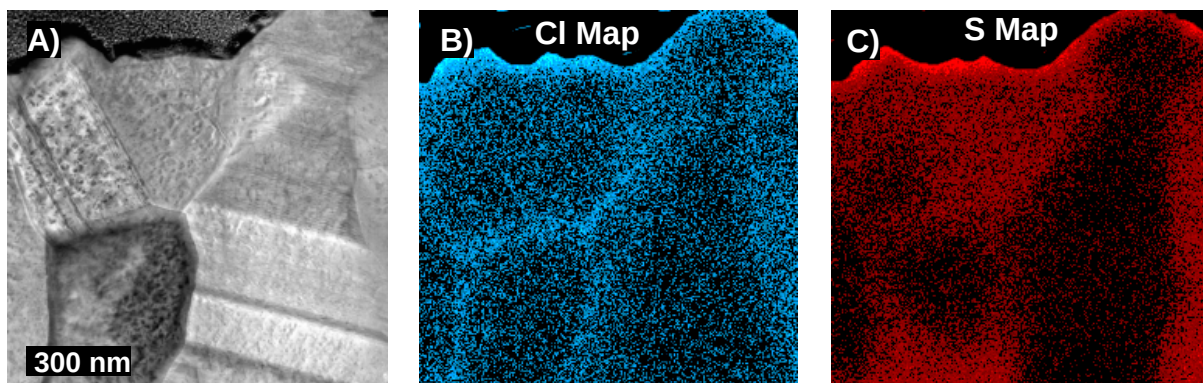


Figure 6.17- a) BF-STEM image with corresponding EDX chemical distribution maps of b) chlorine c) sulphur

Figure 6.17 provides EDX maps to show the location of chlorine and sulphur relative to the grain boundaries. These analyses provide clear evidence for chlorine and sulphur segregation at the grain boundaries after the cadmium chloride treatment. The chemical map shows an increase in counts for both chlorine and sulphur along the boundaries. Sulphur is seen to diffuse into the grains further than the chlorine, also indicated by the EDX spectra in Figure 6.16b.

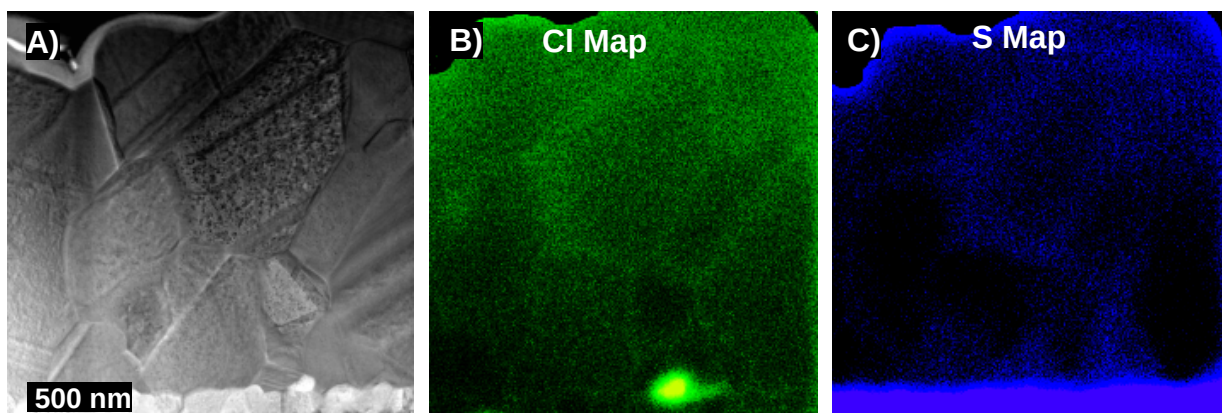


Figure 6.18- a) shows BF-STEM image with corresponding chemical distribution maps of b) chlorine c) sulphur

As most of the chlorine is observed in regions along the cadmium telluride/cadmium sulphide interface, the chlorine must diffuse from the top surface of the cadmium telluride 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. This is shown more clearly in Figure 6.18. Figure 6.18a shows a BF-STEM image of the cadmium telluride and cadmium sulphide layers and Figure 6.18b shows a chlorine chemical distribution map of the same area. The map shows a chlorine region at the interface with slight increase in intensity at grain boundaries, which is an indication of the diffusion path of the chlorine. Figure 6.18c shows a sulphur distribution map, indicating that sulphur is diffusing up during the cadmium chlorine treatment and initially along grain boundaries but more diffusion into the cadmium telluride grain is visible.

6.5 Stacking Fault Removal via Cadmium Chloride Treatment Observation in TEM

Through the use of TEM it has been discovered that the as-grown cadmium telluride grains have a very high density of linear defects. During the annealing cadmium chloride treatment, it appears that the cadmium telluride grains undergo recrystallization and rearrangement at the atomic scale to remove the large majority of defects present in the crystals. This is one of the key factors that produces a working cell, as before the cadmium chloride treatment when the cadmium telluride grains had a large density of defects, no photovoltaic device efficiency is recorded. After the treatment very few defects remain and they can be seen more clearly due to the reduction. The remaining defects appear to be twin boundaries as the contrast alters either side of the twin indicating a change in lattice direction, whereas a stacking fault will not. The removal of defects in particular stacking faults can therefore be seen as one of the most important roles of the cadmium chloride annealing treatment to the cell. From the literature stacking faults and other defects are known to act as electron sinks/recombination centres and prevent charge collection and inhibit the free movement of elections within the lattice. From the TEM images in Figure 6.4 the untreated sample, it can be seen if an electron hole pair is separated within a cadmium telluride grain, by an incoming photon, near the centre of the cadmium telluride layer, the electron/hole must travel through 1 μm of the cadmium telluride material passing over tens of stacking faults in the imperfect lattice. Every stacking fault within the cadmium telluride lattice will be a potential sink for the electron which will then recombine and not produce any charge. The treated cell in Figure 6.12 shows that many of the cadmium telluride grains have an almost perfect lattice structure, with only some twins present, which from literature are said to be less detrimental to the electronic properties of the material than stacking faults.

6.5.1 Morphological Changes during the Cadmium Chloride Treatment

The high angle annular dark field (HAADF) detector detects the electrons which have been deflected the most, and have undergone elastic scattering. Therefore the heaviest elements will show up brightest in the images.

Figure 6.19a displays a HAADF STEM image of the untreated stack. The thin columnar shape of the cadmium telluride grains can be seen clearly with a large amount of linear defects within the grains. The grains can be seen to be only several hundred nanometres in diameter but some are through thickness with the linear defects going across the width of the grains terminating at the boundaries. This indicates that as the grains grew from the cadmium sulphide the stacking sequence could be faulted as each monolayer was added. This is likely due to the low stacking fault energy of cadmium telluride⁴⁰.

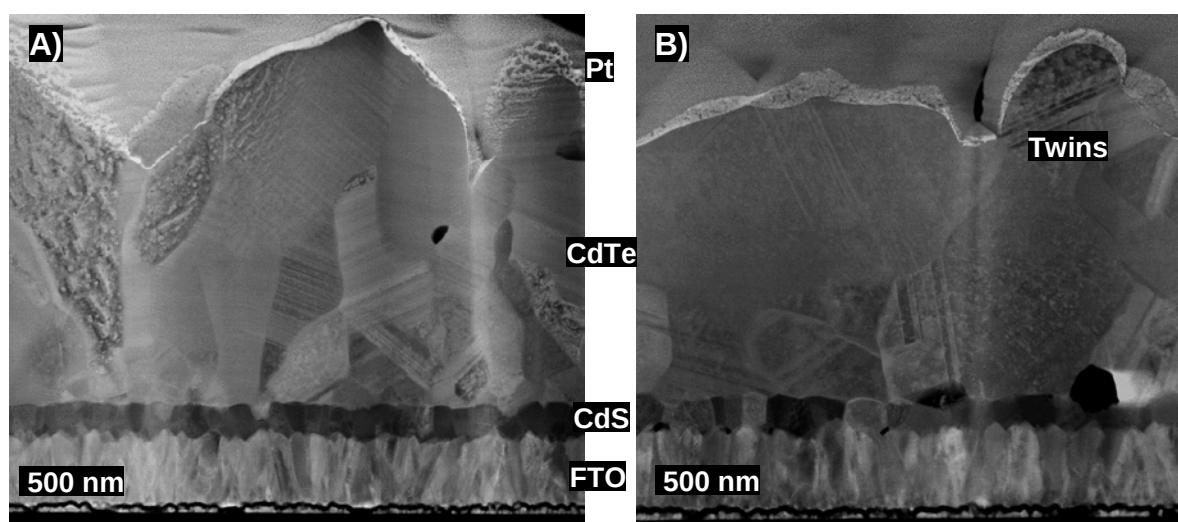


Figure 6.19 – HAADF STEM image of a) untreated cell showing stacking faults b) Treated cell showing twin boundaries

Figure 6.19b shows that the treated sample has a large density of twin boundaries. The layers can be seen clearly due to the difference in atomic weight between them. The gold back contact can be seen clearly as a thin layer between the platinum and the cadmium telluride as it has the highest atomic number. The cadmium telluride grains can be seen to range from a few hundred nanometres up to 2 μm in diameter. Most of the cadmium telluride grains have a large amount of twin boundaries within them which are seen as the parallel lines going from one side of the grain to the other always terminating at the grain boundaries. Between the twins there is a change in contrast due to the change in lattice direction by 60° . The cadmium sulphide layer has a large void above it and smaller voids under it after the treatment process. There is also a region of lighter elemental composition above the cadmium sulphide layer which is likely to be a chlorine rich area. The fluorine doped tin oxide is seen to have long

columnar grains which penetrate partly into the cadmium sulphide layer. Figure 6.19b shows a high magnification HAADF image of the cadmium telluride/cadmium sulphide interface, voids can be seen to have appeared above and below the cadmium sulphide layer. HAADF imaging gives a different perspective so that the elements with the higher atomic number appear bright whereas voids appear dark. The image also shows an area of low atomic weight, which is indicated by the darker regions in the cadmium sulphide layer. These are most likely chlorine rich regions. The cell may have been slightly over treated, leaving some residual chlorine at the interface, which is seen to agglomerate, forming only in certain regions. These regions may be detrimental to the properties of the cell, as they obstruct the p-n junction. In one area of the cadmium sulphide, a grain is seen to be replaced by a chlorine rich particle, seen by the change in contrast of the grain. The void formation around the p-n junction will also have a negative effect on the cell properties as the contact area is reduced, limiting the electrical activity at the junction. The tin oxide grains can also be seen to clearly penetrate part way into the cadmium sulphide grains.

6.6 Interdiffusion Investigation via Depth Profiling

6.6.1 Depth Profiling using XPS for Chemical Distribution throughout the Cell

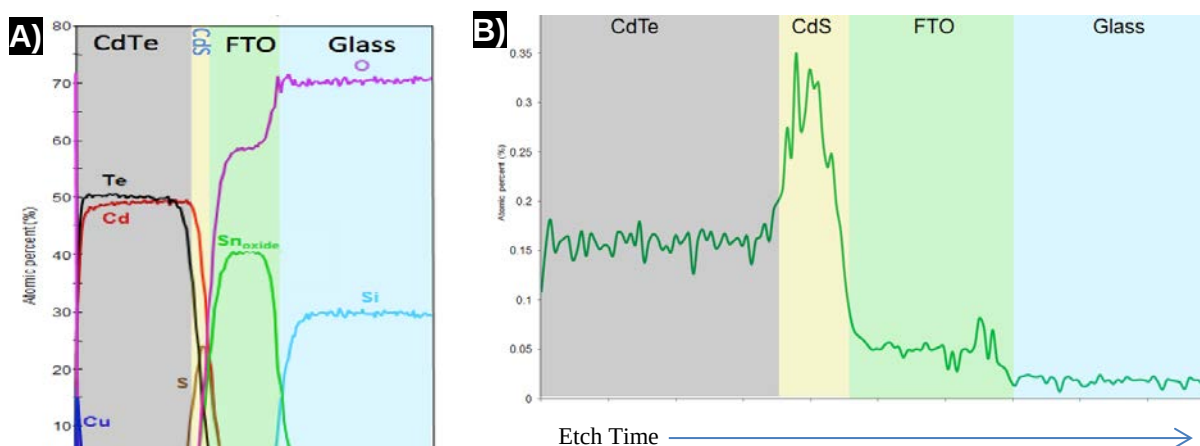


Figure 6.20 – a) XPS composition depth profile (atomic percent against etch time (seconds)) of the treated cadmium telluride/cadmium sulphide cell, b) a chlorine composition depth profile of the cell

XPS composition depth profile measurements shown in Figure 6.20 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 XPS composition depth profile of the cadmium chloride treated sample revealed a constant level of chlorine as well as oxygen in the cadmium telluride. Both of these elements were introduced during the cadmium chloride treatment.

The chlorine concentration in the treated cell rises at the cadmium sulphide interface from 0.15 at% to 0.3 at%. This is shown clearly in Figure 6.20b.

6.6.2 *Dynamic Secondary Ion Mass Spectrometry (SIMS) Depth profiles*

Dynamic secondary ion mass spectrometry (SIMS) was carried out on the treated sample. SIMS was non-quantitative apart from the chlorine in the cadmium telluride layer as a standard reference sample of chlorine in cadmium telluride matrix was obtained. Therefore the chlorine concentration can be calculated within the cadmium telluride layer only. Figure 6.21a shows the SIMS depth profile for caesium ions. The main elements of interest which ionise well with the positive caesium ions are chlorine, oxygen, sulphur and tellurium. Two chlorine isotopes were scanned for, 35 chlorine and 37 chlorine. It can be seen that at the surface, the concentration is around 0.4 at% which then drops down rapidly in the first several seconds of etch time to around 0.07 at%. After this in the bulk cadmium telluride the chlorine concentration increase very steadily from 0.07 at% to 0.08 at% until reaching the cadmium sulphide interface at which it peaks to its maximum concentration 0.7 at% ten times that within the bulk cadmium telluride. This reinforces the results seen in EDX and XPS, which indicate that the chlorine is diffusing down to the cadmium sulphide interface, where it builds-up. However some residue is remaining on the surface from the treatment. The sulphur concentration with depth can be seen to increase from the surface to the cadmium sulphide layer, increasing down the cadmium telluride layer toward the cadmium sulphide. This indicates that as the chlorine is diffusing down the sulphur is diffusing up. Indication of this has also been seen in EDX as sulphur has been observed at grain boundaries in Figure 6.18c. The oxygen profile shows that the largest amount is at the surface, which is most likely due to a thin oxide layer, then decreases through the cadmium telluride, which is due to oxygen diffusion effects, as it is further away from the surface where the source of oxygen is located. The oxygen then increases rapidly as only the tin oxide layer is penetrated.

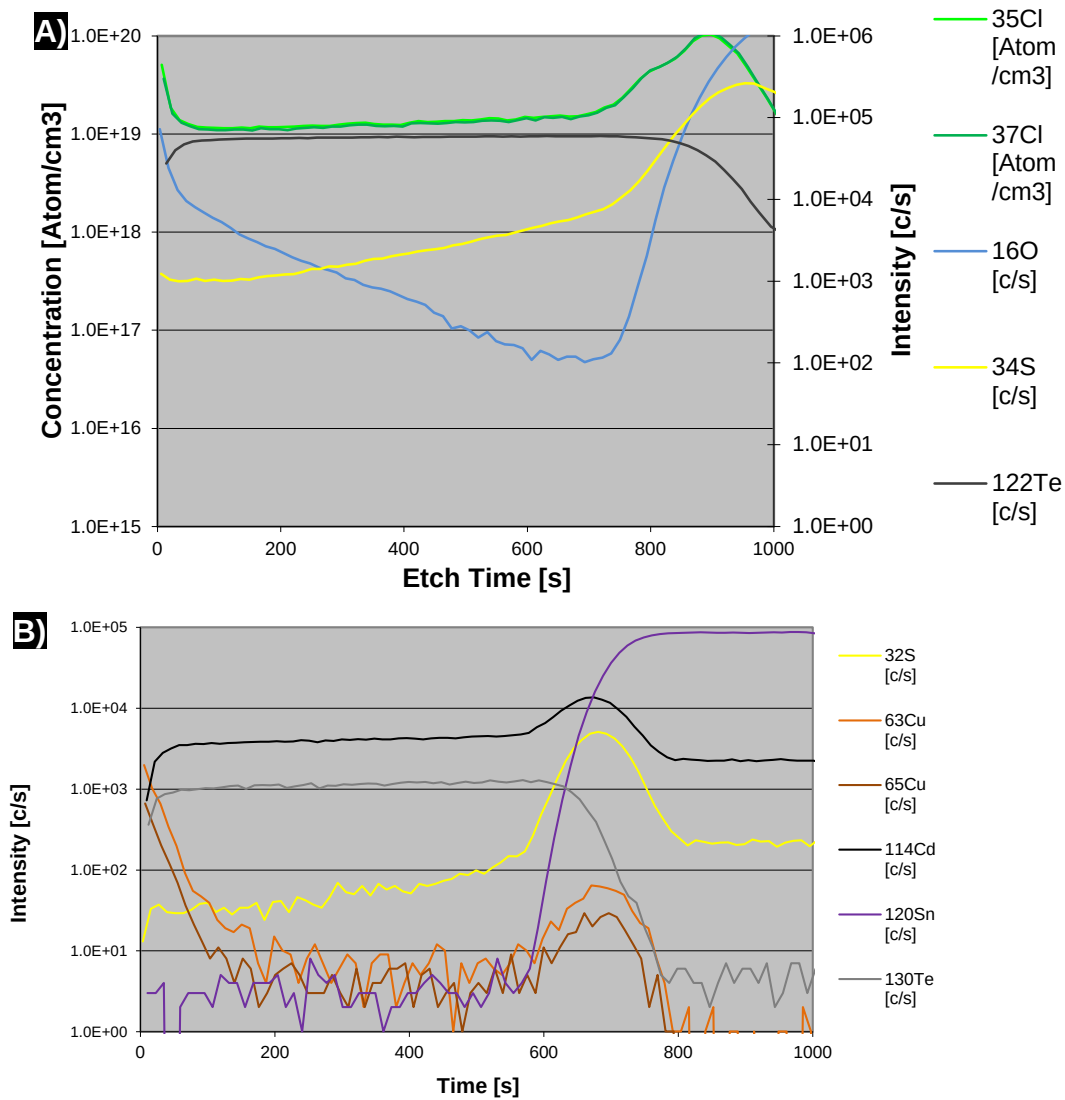


Figure 6.21 – SIMS depth profile of the treated cadmium telluride cell using a) caesium ions b) oxygen ions

Figure 6.21b shows the SIMS depth profile generated using positive oxygen ions. The elements of interest which are readily ionized by oxygen are sulphur, copper, tin, cadmium and tellurium. The sulphur which is also ionised by caesium ions follows the same pattern, only there is a slight drop of sulphur at the surface which then increases towards the cadmium sulphide due to sulphur diffusion upwards towards the top of the cell. The tellurium distribution is as expected apart from a decrease at the surface like the sulphur. The cadmium follows the same trend as the tellurium except within the cadmium sulphide, in which it increases whereas the tellurium decreases as is expected. The tin follows the expected distribution which is minimal through all the layers until the tin oxide layer is penetrated. Copper is of much interest and two isotopes were scanned for, 63 copper and 65 copper. They both follow each other with a ratio of 1:6 which is the correct ionisation rate between the two isotopes, therefore the possibility of any overlapping masses can be observed. The two

copper profiles follow each other well, indicating no particles with similar masses were being detected as copper. The copper at the surface is of highest concentration, which may have impacted the ionisation rate of the other elements at the sample's surface. The copper concentration decreases during the first quarter of the cadmium telluride layer. After this it drops to a negligible amount, and then peaks up again toward the cadmium sulphide interface.

6.7 Investigation of Cadmium Telluride Grain Crystallography

6.7.1 X-Ray Diffraction Comparison of Treated and Untreated Cadmium Telluride

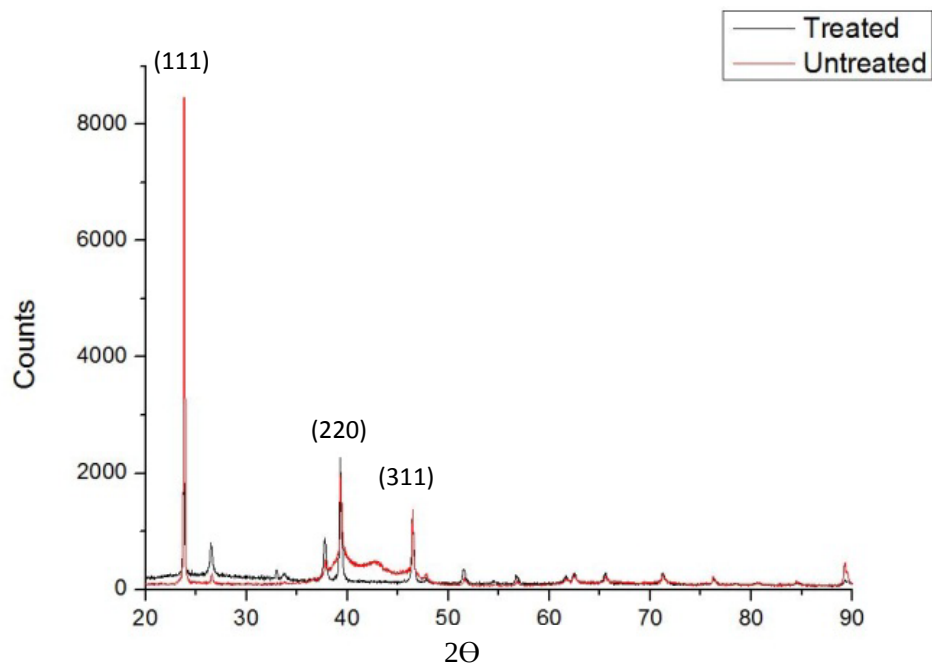


Figure 6.22 - XRD plot of the treated and untreated sample.

The XRD analysis shown in Figure 6.22 was carried out to show the effect of the cadmium chloride treatment on the cadmium telluride 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. The untreated XRD scan shows a broadening of the (220) peak. This is further investigated in chapter 8 by use of transmission electron backscatter diffraction (TEBSD).

6.7.2 *Electron Backscatter Diffraction on Cadmium Telluride Solar Cells*

Electron back-scatter diffraction (EBSD) requires a very smooth surface for effective microstructural mapping. Therefore to analyse the surface of the cadmium telluride directly a section of the surface was smoothed with a Focused Ion Beam. The result of this sample preparation is shown in Figure 6.23 and this provides an adequately smooth surface for EBSD. EBSD can provide a wide range of useful measurements and information, such as grain size and preferred orientation.

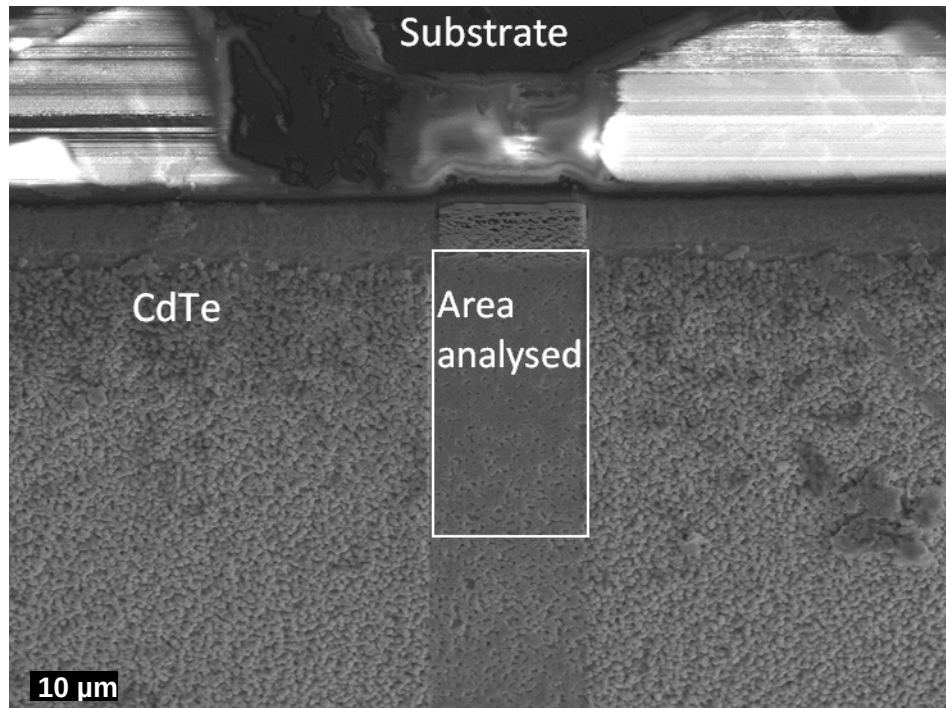


Figure 6.23 - An SEM image of the area smoothed with the ion beam for EBSD analysis.

6.7.3 *Electron Backscatter Diffraction of the Untreated Cadmium Telluride*

Electron backscatter diffraction (EBSD) was carried out on the untreated cadmium telluride surface however the maps collected were of poor quality due to a large degree of misindexing of the Kikuchi patterns by the cubic phase file. This is further investigated in Chapter 8.

6.7.4 Crystallographic and Grain Morphology of Treated Cadmium Telluride Thin Films

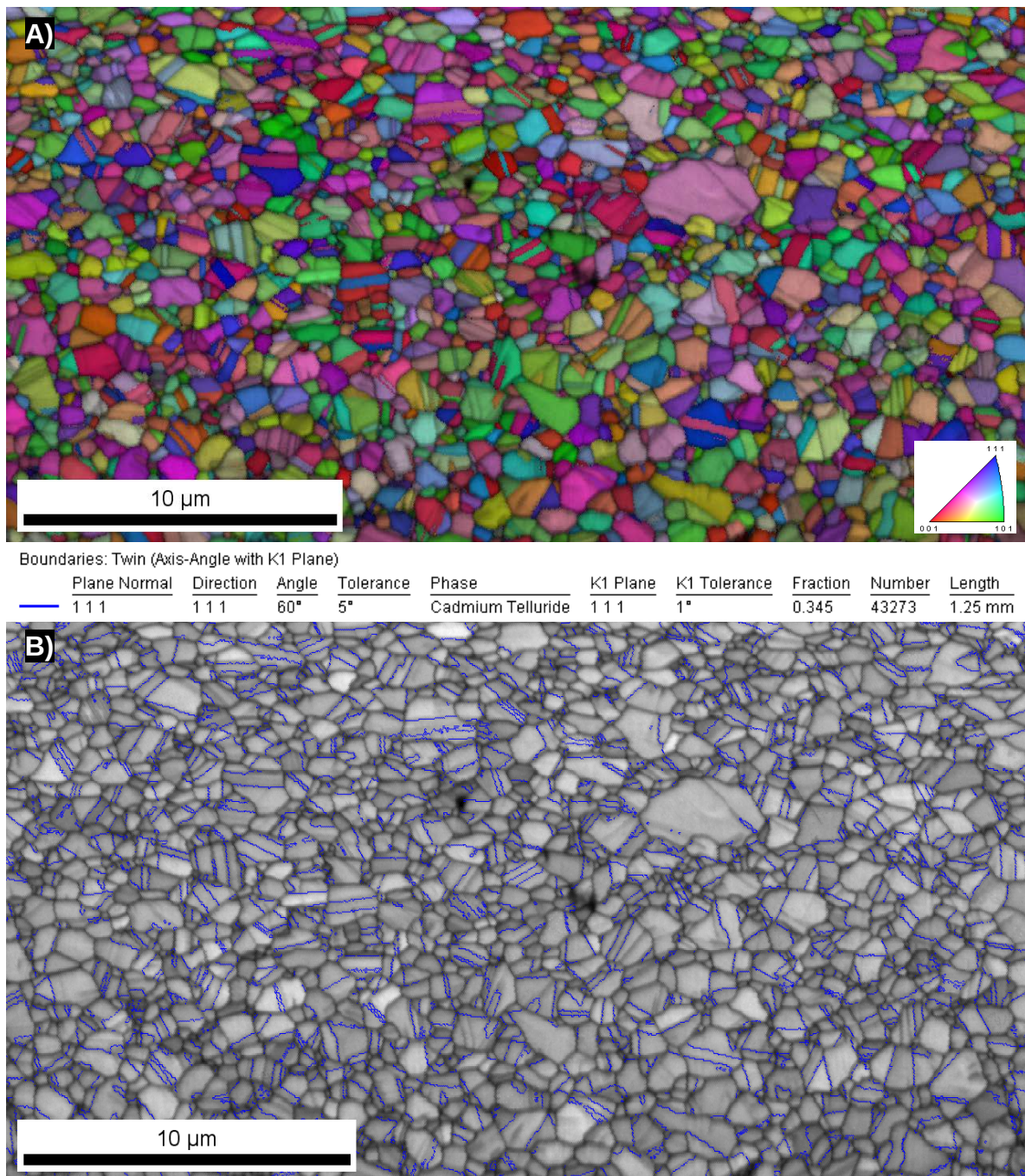


Figure 6.24 –a) An EBSD derived image quality map with IPF and b) twin boundaries overlaid in blue of the cadmium chloride treated cadmium telluride layer, after FIB polishing

Figure 6.24a 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. Figure 6.24b shows the EBSD map of the twin boundary distribution, highlighting the 60°

angle boundaries. This shows there is a high amount of twins present within the treated sample. The vast majority of the twins can be seen running along the width of grains always terminating at grain boundaries. The untreated sample did not index well enough to be able to produce a twin boundary distribution map, possible due to the high density of stacking faults. 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.

6.7.5 Transmission Electron Backscatter Diffraction (TEBSD) for Twin Analysis

Transmission electron backscatter diffraction was carried out in cross section of the cadmium telluride cells in order to characterize the grain boundaries and twin boundaries as it provided a higher spatial resolution than standard EBSD.

Figure 6.25 shows a transmission electron backscatter diffraction derived image quality map of the treated cadmium telluride cell. All the subsequent layers can be seen.

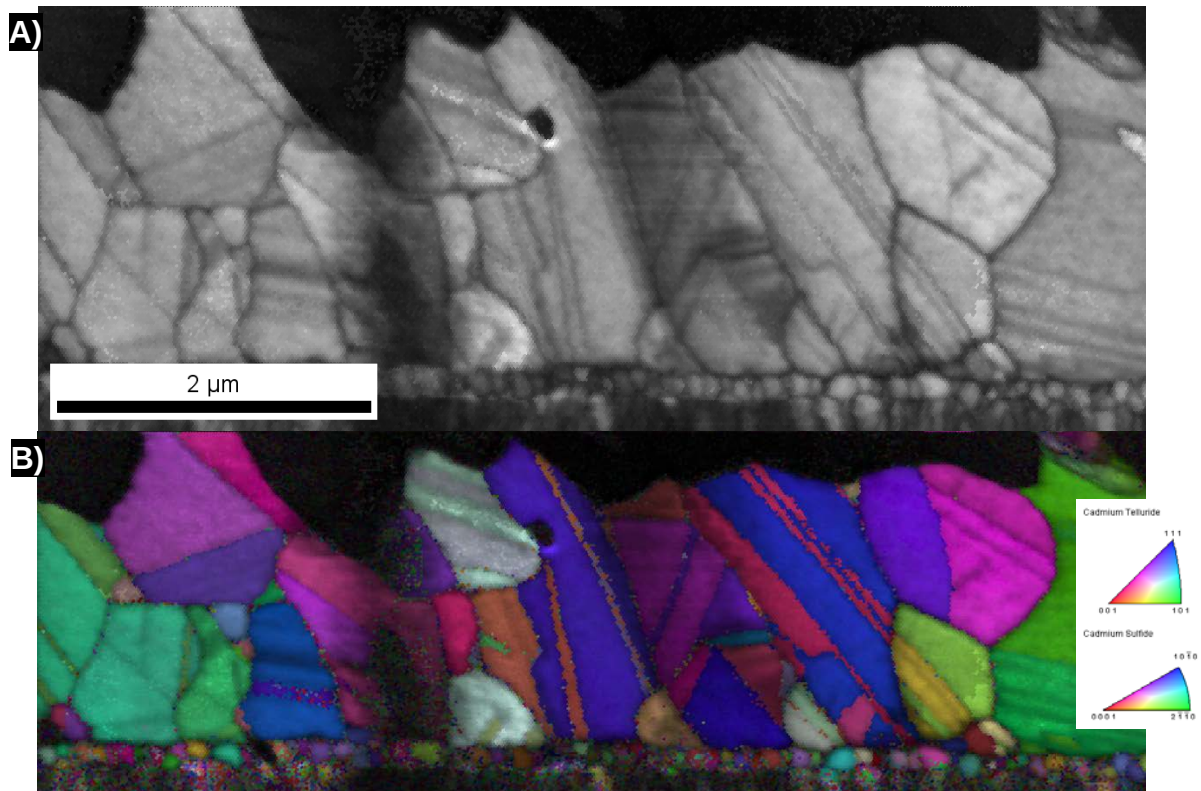


Figure 6.25 – Transmission electron backscatter diffraction maps of the treated cadmium telluride cell showing
a) image quality b) image quality overlaid with inverse pole figure

Figure 6.25b shows a transmission electron backscatter diffraction derived image quality overlaid with inverse pole figure map of the treated cadmium telluride cell, the colours

indicate a grain orientation. The cadmium telluride grains can be seen to have twins within them as orientation change can be seen by a change in colour, occurring within many of the grains. Most of the grains include the twins, as seen by the planar EBSD in Figure 6.24b. The grain structure can also be clearly seen by these maps as each grain is at a different orientation. The cadmium telluride layer does have through thickness grains as well as smaller grains nearer the cadmium sulphide interface. The cadmium sulphide grains index well to the hexagonal phase, which shows a fairly random orientation distribution.

6.8 Summary

The primary and unexpected observation is that the untreated cadmium telluride 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^{38,40,75} but the effect of their total removal during the cadmium chloride treatment has not been reported.

Chlorine segregation has been observed directly at the cadmium telluride/cadmium sulphide 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 cadmium telluride layer during the annealing process and travels along the grain boundaries to the cadmium sulphide interface. XPS composition depth profiling shows a steady concentration of chlorine throughout the cadmium telluride of around 0.15 at% which then increases to 0.3% in the cadmium sulphide. During the cadmium chloride treatment recrystallization occurs, a process which removes the stacking faults. Chapter 7 investigates further by processing cells systematically under different conditions to confirm this interesting observation. Twins are however observed in the cadmium telluride layer after cadmium chloride treatment.

The cadmium chloride treatment has other effects. Changes in other microstructural properties include grain size and orientation. Sulphur from the cadmium sulphide is also observed to have migrated into the cadmium telluride grain boundaries. The electrical performance of the cadmium telluride/cadmium sulphide solar cell is highly dependent on these changes. Prior to the cadmium chloride treatment, an efficiency of 0.1 at% is measured but following the annealing/cadmium chloride treatment and the cell efficiency improves to 11.77%.

CHAPTER 7. THE INVESTIGATION OF CADMIUM CHLORIDE ASSISTED RE-CRYSTALLIZATION OF CADMIUM TELLURIDE

7.1 Chapter Scope

Cadmium telluride solar cells deposited via close space sublimation, before and after a pre-optimised cadmium chloride treatment were studied in Chapter 6. This chapter will expand on this by studying the effects of cadmium chloride treatment on microstructure by varying the treatment parameters systematically.

These include varying the deposition and anneal time from a very short time of 2 seconds and then increasing the time incrementally to the optimum treatment time, to produce a time-line of how the treatment initiates and recrystallizes the cell into a working device. This will be expanded further by “over treating” the cell to see what microstructurally is causing the drop in performance in these conditions.

The next set of experiments varied the annealing temperature of the cadmium chloride treatment from slightly below to slightly above the optimum temperature to reveal what affect it has on the cell and why the optimum parameters are needed to be so precise. This revealed how the increase in temperature accelerated the diffusion of chlorine to the cadmium telluride interface and caused an increase in average grain size, whereas a lower treatment temperature had the opposite effect.

The cadmium chlorine treatment consists of two constituents, the addition of cadmium chloride and the anneal. To investigate the role of each, the cells were subjected to only an anneal at a variety of temperatures and times to see the effect on the defects within the cadmium telluride grains, giving an insight into the role each constituent plays.

7.2 Cadmium Chloride Assisted Re-Crystallization of Cadmium Telluride: The Effect of Treatment Time

7.2.1 Introduction

In the previous chapter the untreated and fully treated close-space sublimated cells were studied. This section will investigate the cadmium chloride process in more detail by taking snapshots through the process by analysing samples treated for varying times up to and over the optimised treatment time. This will reveal how the treatment process affects the cell on a

microstructural level throughout the process. The initiation of the process will be examined and compared with results from sputtered samples. As shown in Chapter 4 the initial effects of the cadmium chloride treatment started at the cadmium sulphide interface, after enough concentration of chlorine was reached, recrystallization began moving upwards through the cadmium telluride layer. However the sputtered samples had a very different microstructure to the close space sublimated samples.

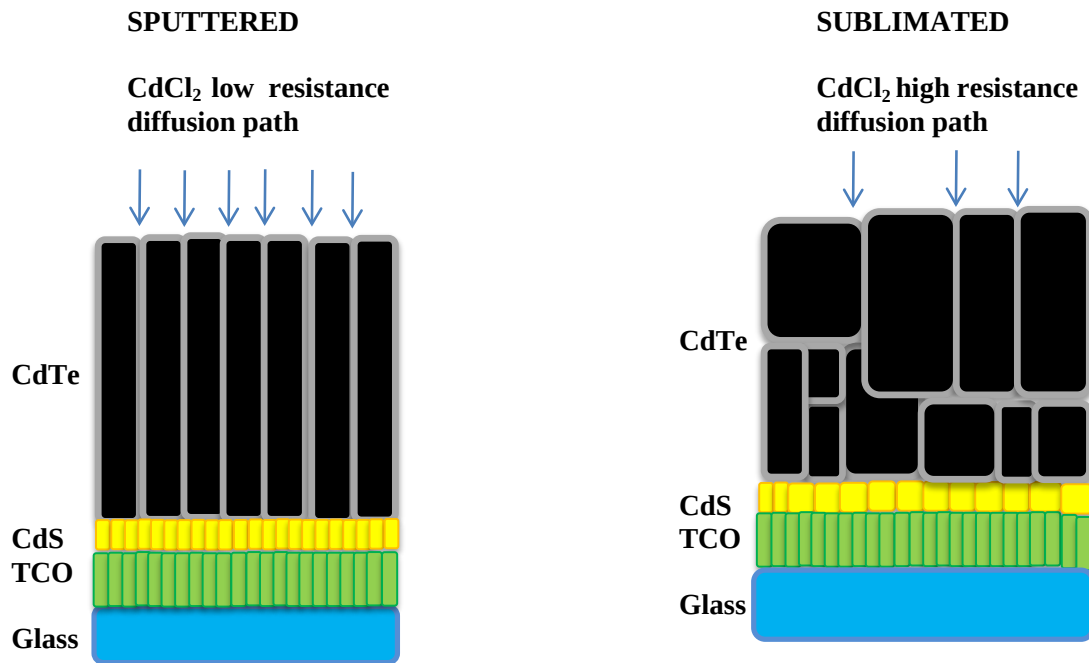


Figure 7.1 – Schematic diagram showing grain boundary diffusion path comparison between sputtered and sublimated cadmium telluride grains

Figure 7.1 shows a schematic diagram of the microstructure of sputtered and sublimated cells, the main difference being the morphology of the cadmium telluride grains. As sputtered grains are columnar and through thickness, they allow rapid diffusion of chlorine down the grain boundaries to the cadmium sulphide layer. Sputtered cadmium telluride has small grains giving more diffusion paths for the chlorine to migrate down. Close spaced sublimated cells have larger equiaxed grains, of which the majority are not through thickness, so the chlorine diffusion path is longer to reach the cadmium sulphide layer. Therefore it is likely that the recrystallization induced by the cadmium chloride treatment will be different in the sputtered and close space sublimated cells.

A key process step in the production of high efficiency cells is the activation annealing treatment using cadmium chloride. This annealing treatment causes a dramatic improvement in cell performance and is known to radically change the structural and electrical characteristics of the device as shown in Chapter 6. Cadmium chloride is observed to recrystallize the grains, which completely removes the stacking faults. This study will concentrate on varying the time of the cadmium chloride treatment in a series of steps from 2 seconds through to 120 seconds, which is regarded as the optimum time. Then increasing the time further to over-treat the sample, from 120 seconds to 600 seconds. As the annealing time is increased its effect on cell microstructure and the distribution of chlorine will be investigated, these observations will then be linked to the change in cell performance. This provides a further insight into the mechanisms by which the cadmium chloride treatment causes changes to the cadmium telluride microstructure and improves cell efficiency. This study on close spaced sublimated films provides further evidence that the recrystallization process initiates preferentially at the cadmium telluride/cadmium sulphide interface as seen in Chapter 4 for sputtered films.

7.2.2 Sample Description with Varying Treatment Times

The samples were deposited via close space sublimation similarly to the samples in Chapter 6. The treatment and anneal time are, however varied. Table 7.1 shows the sample list for the varying time treatments. 5 samples are under treated to give a time-line of the microstructural evolution during the cadmium chloride treatment and 2 over treated samples, which may exaggerate the treatment effects on the cell. The untreated and optimised treated samples were analysed in Chapter 6 and the results will not be reproduced in this chapter.

Sample Description	Treatment time
Untreated	untreated
Untreated	2 second CdCl ₂ deposition and 2 second anneal
Untreated	5 second CdCl ₂ deposition and 5 second anneal
Untreated	10 second CdCl ₂ deposition and 10 second anneal
Untreated	30 second CdCl ₂ deposition and 30 second anneal
Untreated	60 second CdCl ₂ deposition and 60 second anneal
Optimum	180 second CdCl ₂ deposition and 180 second anneal
Over Treated	2 X180 second CdCl ₂ deposition and 360 second anneal
Over Treated	4 X 150 second CdCl ₂ deposition and 600 second anneal

Table 7.1 – Sample list showing treatment conditions for the samples studied in this section

7.2.3 Cadmium Chloride Treatment: Initiation and Under Treatment

In this experiment the thin film cadmium telluride cell was treated and then annealed for 2 seconds to allow determination of how and where the cadmium chloride activation process begins to recrystallize the material. As reported in Chapter 6 the grains in the untreated cadmium telluride layer contained high densities of linear defects, which were predominantly stacking faults. Figure 7.2a shows a BF-TEM image of the cell treated which was then annealed for 2 seconds. The cadmium sulphide is unaffected by the treatment. The cadmium telluride layer shows similar grain morphology to that of the untreated sample, with smaller grains at the cadmium sulphide interface and some through-thickness grains. The majority of the cadmium telluride grains have a high density of defects. However one grain ~ 500 nm in diameter at the cadmium sulphide interface is free of stacking faults, but exhibits several twin defects. This implies that the cadmium chloride has diffused to the cadmium sulphide interface and initiated the recrystallization of this cadmium telluride grain. The removal of stacking faults in a grain during activation appears to occur throughout the whole grain, leaving a grain with an almost perfect lattice with only twin defects remaining.

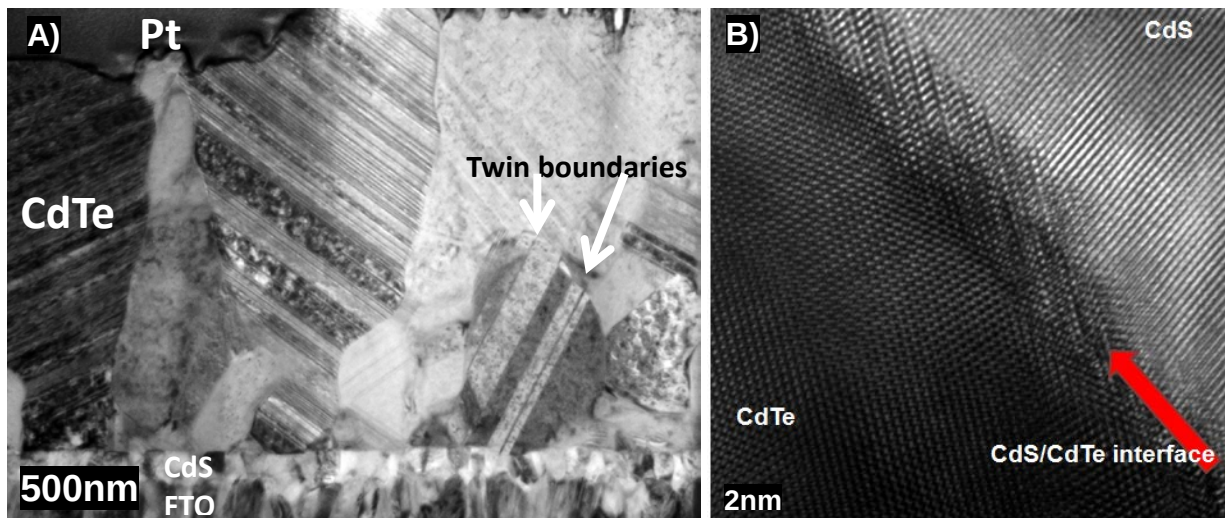


Figure 7.2 – a) Shows BF-TEM image of the cadmium telluride cell treated for 2 seconds and annealed for 2 seconds, b) HRTEM image of the cadmium sulphide/cadmium telluride interface after 2 seconds cadmium chloride treatment

Diffusion of sulphur between the cadmium sulphide and cadmium telluride occurs as observed in Chapter 6. Figure 7.2b shows a high resolution image of the cadmium sulphide/cadmium telluride interface of the 2 seconds treated sample. The cadmium telluride grain has been orientated to the $[011]$ zone axis.

Figure 7.3a shows images of a cadmium telluride grain at the cadmium sulphide/cadmium telluride interface of the sample treated and annealed for 2 seconds. The grain located

adjacent to the cadmium sulphide interface has been recrystallized. The grain was tilted to the [011] zone axis for observation along the (111) plane to enable imaging of the lattice. The grain has a perfect lattice except for two areas shown in the high resolution images in Figure 7.3b and Figure 7.3c. One area has a number of twins and the second area only has one twin defect. This supports the observation that the stacking fault defects are removed from the whole grain instantaneously, as the surrounding grains still have high quantities of stacking faults. The process progresses grain by grain and adjacent grains still have high densities of stacking faults. These grains are directly in contact with the cadmium sulphide interface and recrystallize preferentially. The grains are ~500 nm in diameter. This suggests that the cadmium chloride has diffused to the interface and reached the concentration required for recrystallization and stacking fault removal.

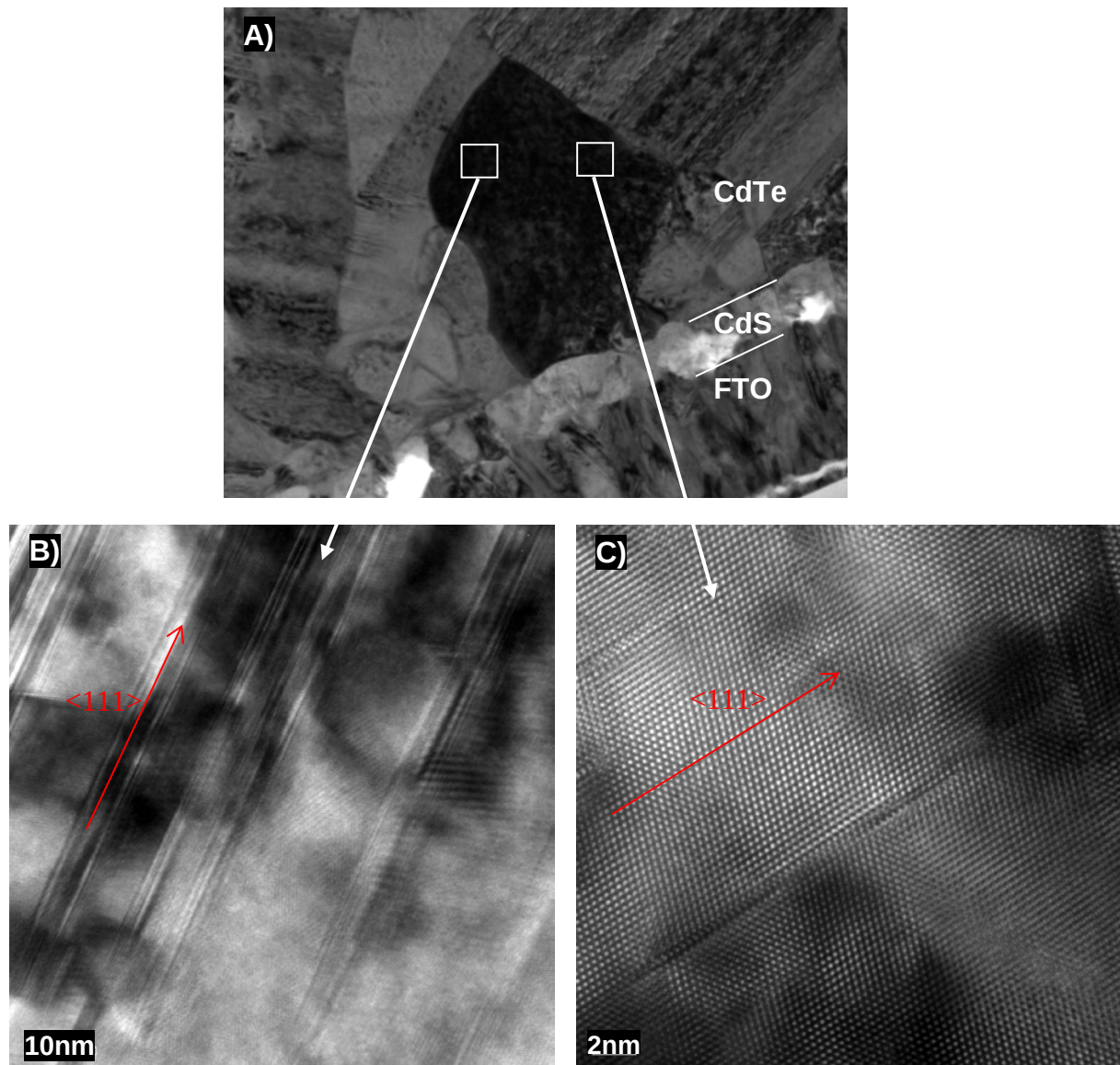


Figure 7.3 – a) A BF-TEM image with b) and c) corresponding HRTEM images of defects within the grain of the sample treated for 2 seconds

7.2.4 Cadmium Chloride Treatment: Partial Activation

Figure 7.4a shows a bright field TEM image of the sample treated for 5 seconds. This shows some cadmium telluride grains have been recrystallized and the majority of defects removed. Most of these grains are located adjacent to the cadmium sulphide interface, which are the smaller grains. Most of the larger cadmium telluride grains have a high density of linear defects (stacking faults and twins) still present. This implies that the larger grains require more energy or cadmium chloride diffusion to recrystallize. The cadmium sulphide interface appears unaffected. Figure 7.4b shows the sample treated for 10 seconds. Several cadmium telluride grains along the cadmium sulphide interface are recrystallized and twin defects are visible.

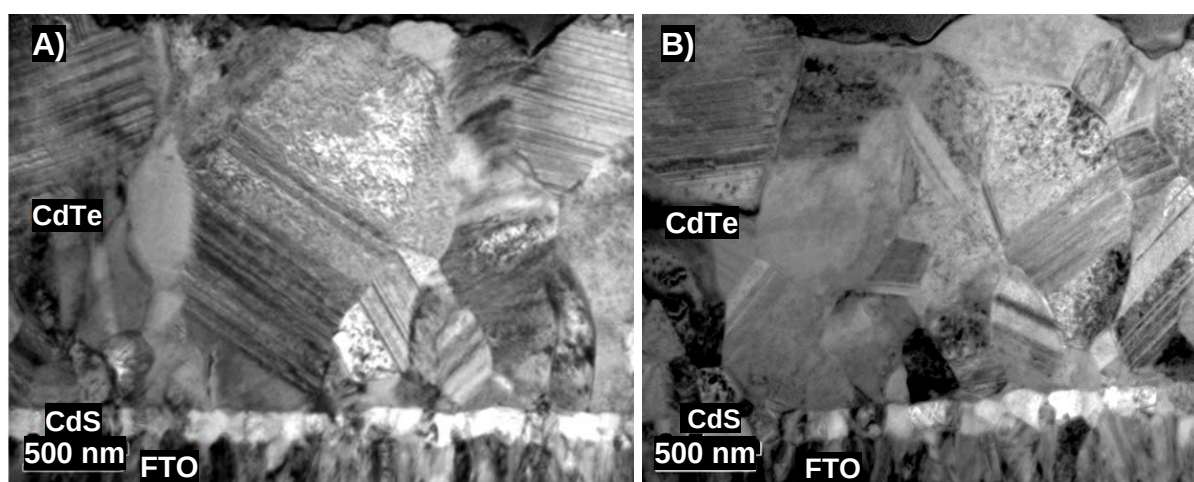


Figure 7.4 - BF-TEM images of samples treated for a) 5 seconds and b) 10 seconds

Dynamic secondary ion mass spectrometry (SIMS) was carried out on the sample treated for 30 seconds. The SIMS analysis was non-quantitative apart from for chlorine, as a reference sample of chlorine in cadmium telluride matrix was obtained; therefore the chlorine concentration can be accurately calculated within the cadmium telluride layer only.

Figure 7.5a shows the SIMS depth profile for caesium ions, the main elements of interest which ionise well with the positive caesium ions are chlorine, oxygen, sulphur and tellurium. Two chlorine isotopes were scanned for, ^{35}Cl and ^{37}Cl . It can be seen that at the surface, the concentration is around 0.1 at% whereas the fully treated (120 seconds) sample in Chapter 6 had a concentration of 0.4 at%. The chlorine then drops down slightly in the first several seconds of etch time. After this in the bulk cadmium telluride the chlorine concentration increase very steadily from 0.05 at% until reaching the cadmium sulphide interface at which it peaks to its maximum concentration 0.25 at% five times that within the bulk cadmium telluride. The sulphur concentration with depth can be seen to increase from

the surface to the cadmium sulphide layer, and increased further toward the cadmium sulphide. The oxygen profile shows the largest amount at the surface and steadily decreases through the bulk of the cadmium telluride and then increases rapidly due to the tin oxide layer. Figure 7.5b shows the SIMS depth profile generated using positive oxygen ions. The elements of interest which are readily ionized by oxygen are sulphur, copper, tin, cadmium and tellurium. The sulphur which also ionises by oxygen ions follows the same pattern seen by the caesium which showed sulphur diffusing into the cadmium telluride from the cadmium sulphide layer. The cadmium and tellurium has constant amounts throughout the cadmium telluride film.

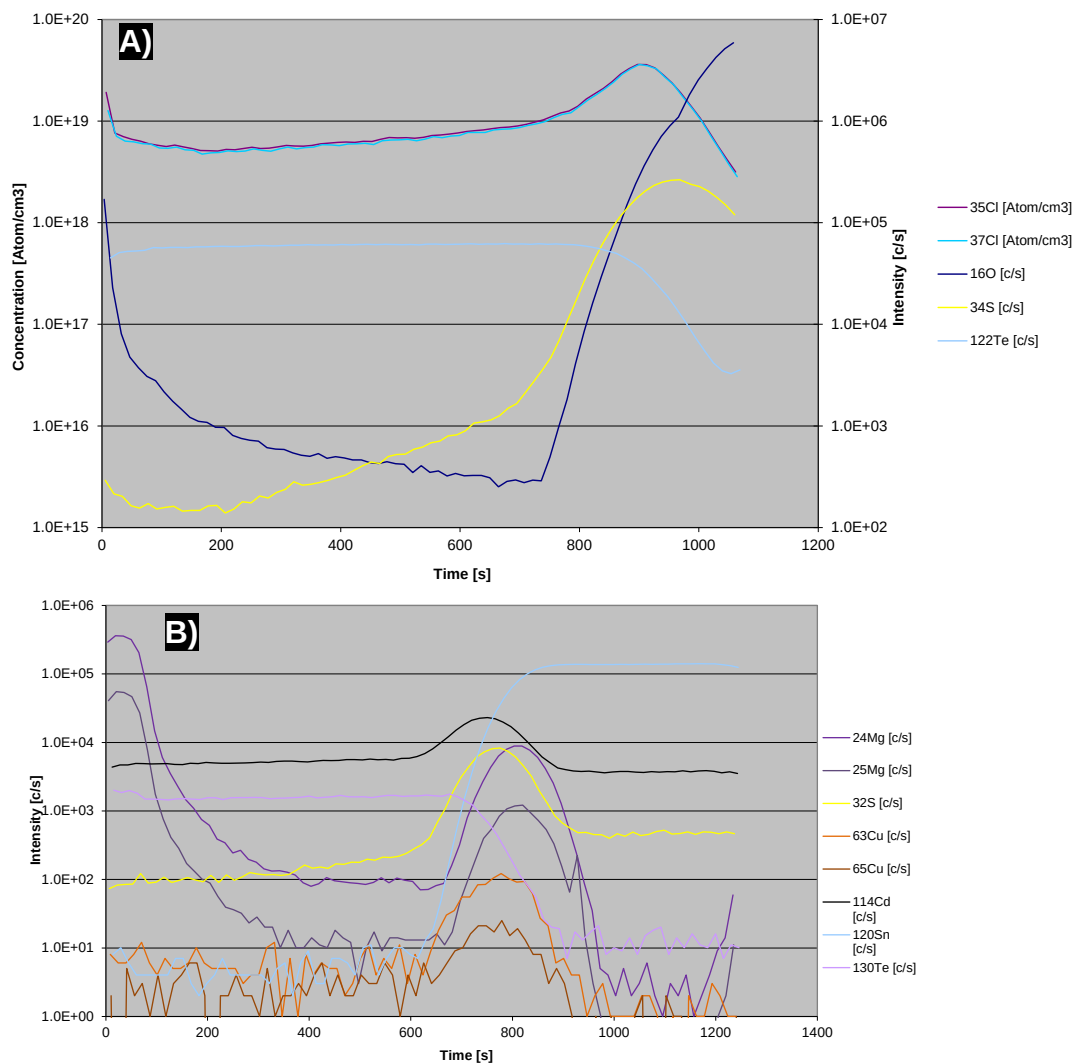


Figure 7.5 - SIMS depth profile of the 30 second treated cadmium telluride cell using a) caesium ions b) oxygen ions

Figure 7.6a shows a TEM image of the sample which has been treated for 30 seconds. It shows that many more of the grains have now been recrystallized. Stacking faults have been removed leaving only twin defects. Many of the larger cadmium telluride grains now show

no stacking faults. The cadmium sulphide/cadmium telluride interface has become rounded suggesting some diffusion has taken place. Figure 7.6b is a TEM image of the device treated for 60 seconds showing further progression of these effects.

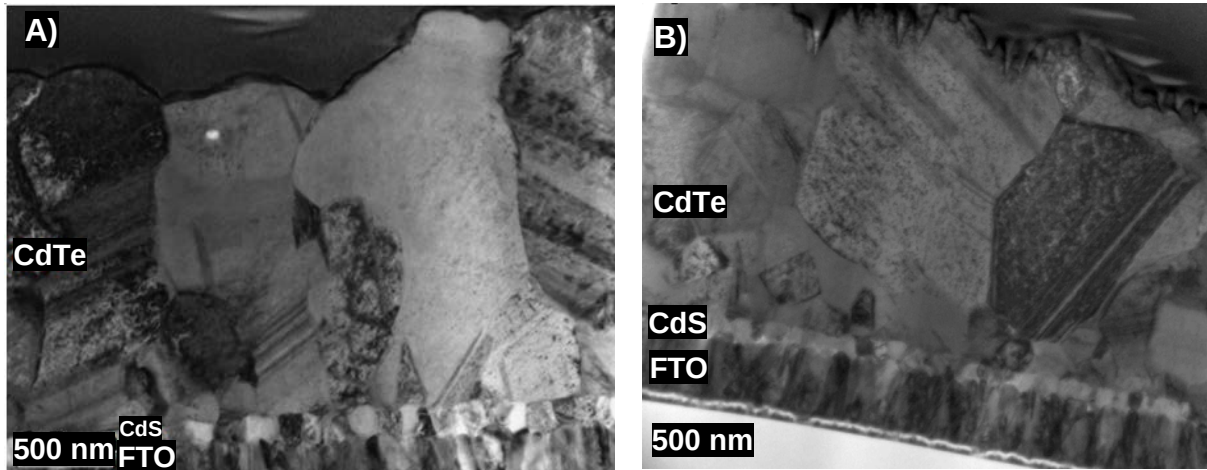


Figure 7.6 - BF-TEM images of samples treated for (a) 30 seconds and (b) 60 seconds

7.2.5 Cadmium Chloride Treatment: Optimum Activation

Figure 7.7 shows a HAADF STEM image showing the device treated for 120 seconds and which has been found empirically to yield the most efficient cells (~13%) has a number of twin defects but no stacking faults. The size of the cadmium telluride grains ranges from ~0.5 μm to 2 μm in diameter. The twin defects in the grains are observed as parallel lines going from one side of the grain to the other always terminating at the grain boundaries. There is a change in intensity in image between the twins due to the change in grain orientation of 60° . There is also a darker region above the cadmium sulphide layer which is a chlorine rich area as determined by EDX.

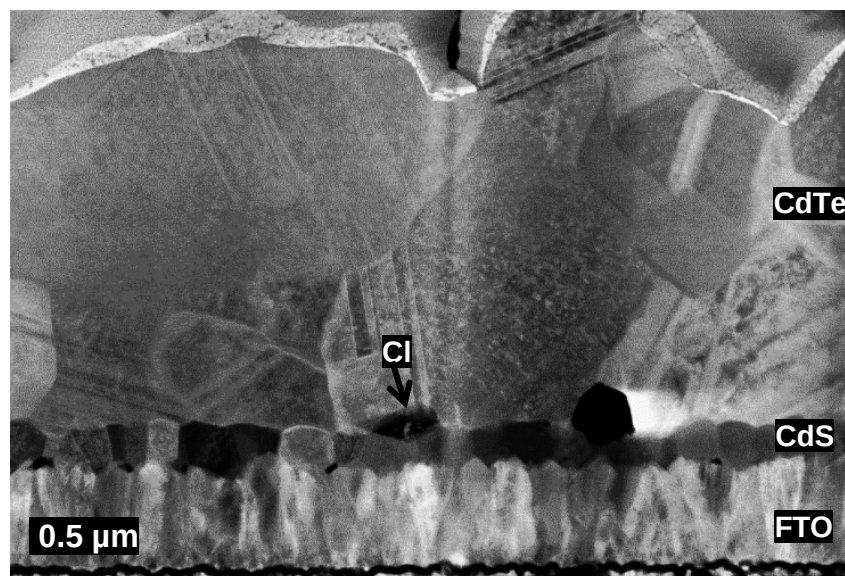


Figure 7.7 – HAADF STEM image of optimum treated sample (120 seconds)

7.2.6 Cadmium Chloride Treatment: Over-Treatment

Figure 7.8a shows a BF-STEM image of the cadmium telluride cell treated for 300 seconds. This process creates larger cadmium telluride grains with fewer defects. The interface has more regions containing chlorine observed as lighter areas and confirmed by EDX analysis in Figure 7.8b. Most of the chlorine which has travelled through the cadmium telluride is at the cadmium telluride/cadmium sulphide interface, however some is observed at the cadmium sulphide/FTO interface without diffusing further, showing the FTO acts as a block. Figure 7.8b also shows the chlorine travelling along grain boundaries and as well as building up at triple point grain boundary nodes. Figure 7.8c shows the sulphur chemical distribution map with no clear sign of further diffusion into the cadmium telluride. This is likely due to the EDX map taken over a large area, and sulphur only diffusing in small quantities.

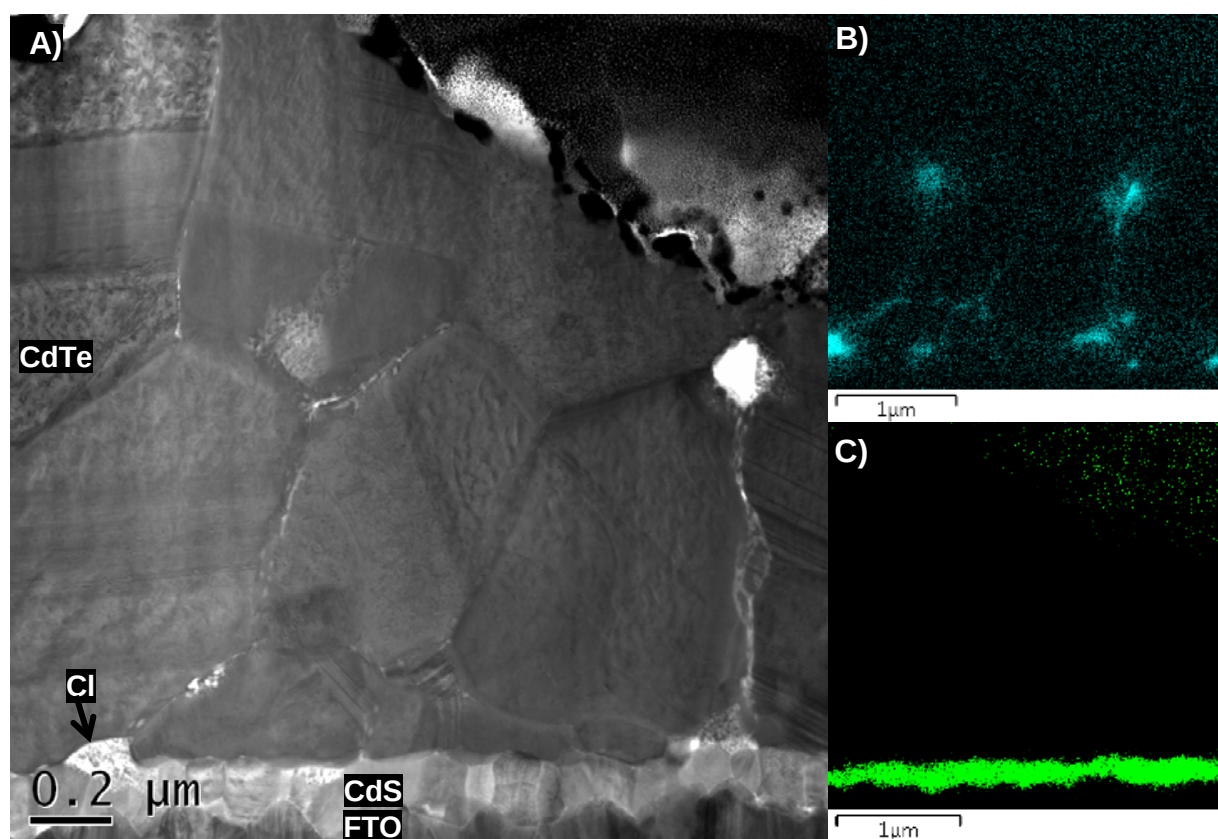


Figure 7.8 – a) BF-STEM images of 300 seconds treated sample with corresponding EDX chemical distribution maps for b) chlorine and c) sulphur

Figure 7.9 shows an image from a cell over-treated for 600 seconds. The cadmium telluride grains are large with a grain size of up to $\sim 3 \mu\text{m}$. Fewer defects are visible. The cadmium sulphide interface has many regions with chlorine present. This was confirmed with XPS depth profiling in Figure 7.14. The optimized treated sample showed a peak concentration of 0.3 at% of chlorine at the cadmium sulphide/cadmium telluride interface whereas the 600

second treated sample had a peak concentration of 3.4 at%. This build-up of chlorine rich regions is detrimental to the p-n junction and correlated to a decrease in efficiency to 8.3%.

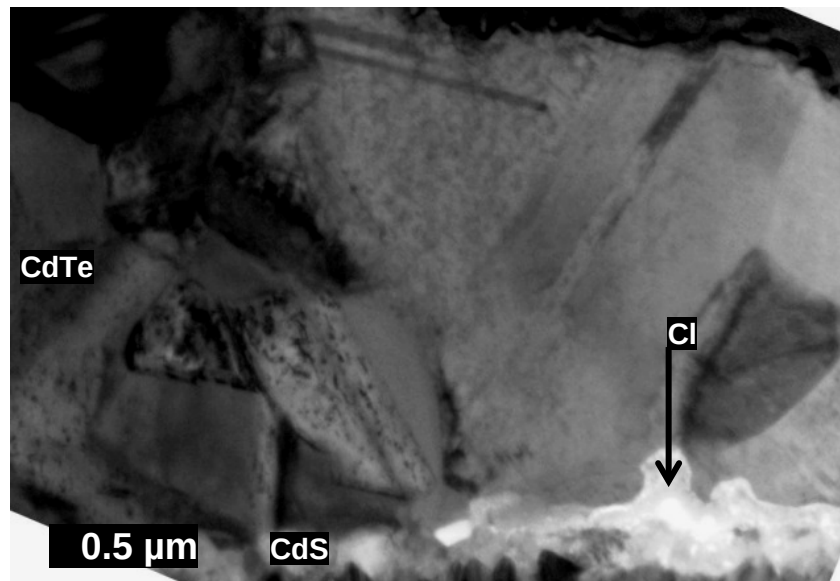


Figure 7.9 – BF-TEM image of the sample treated for 600 seconds

7.3 Cadmium Chloride Assisted Re-Crystallization of Cadmium telluride: The Effect of the Annealing Temperature

7.3.1 Introduction

The aim of this section is to apply advanced microstructural characterization techniques to study the effects of varying the cadmium chloride annealing temperature on the microstructure of cadmium telluride solar cells deposited by close spaced sublimation (CSS) and relate this to cell performance. A range of techniques has been used to observe the morphological changes to the microstructure as well as the chemical and crystallographic changes as a function of treatment parameters. Electrical tests that link the device performance with the microstructural properties of the cells have also been undertaken.

7.3.2 Morphological Changes of the Cell with Treatment Temperature

Three samples were studied. One underwent a previously optimized post deposition annealing cadmium chloride treatment. The treatment was carried out in vacuum following the cadmium telluride layer deposition. Cadmium chloride was sublimated at a thickness of 3 μm , and then the sample was heated for 8 minutes at 400°C in a 2% oxygen atmosphere, causing the cadmium chloride layer to evaporate off. This was followed by a copper doping process by sublimating copper chloride onto the cadmium telluride layer. The efficiency of this cell was measured to be 13%. The second cell was deposited using the same conditions but annealing was carried out at a lower temperature of 381°C. The third sample was

annealed above the optimum temperature to 429°C. The efficiency of this cell was measured to be 7.7%. The circular, small area devices of $\sim 1 \text{ cm}^2$ area were then finished for each sample by applying a graphite paste contact. The only difference between the samples is the annealing temperature, as they underwent the cadmium chloride treatment. Figure 7.7 shows a TEM image of the optimized treated cell, showing that the cadmium telluride grains are equiaxed and sized in the range $0.5 - 1 \text{ }\mu\text{m}$. Some twinning is evident by the change in signal intensity within the same grain. No voids can be seen between any of the grains or at the cadmium telluride/cadmium sulphide interface, although there are areas between the cadmium telluride and cadmium sulphide that are brighter and possibly caused by a build-up of cadmium chloride. No stacking faults are observed in this treated cell. Figure 7.10a shows a TEM cross section of the sample treated at 381°C, a lower temperature than optimum. The grains are smaller near to the interface, indicating that the grains have not recrystallized fully. Figure 7.10b shows a TEM image of the cell treated above the optimized cadmium chloride treatment, the main difference observed is the increase in grain size as they are now sized in the range $1 - 2 \text{ }\mu\text{m}$. Some twinning is still observed within the cadmium telluride grains.

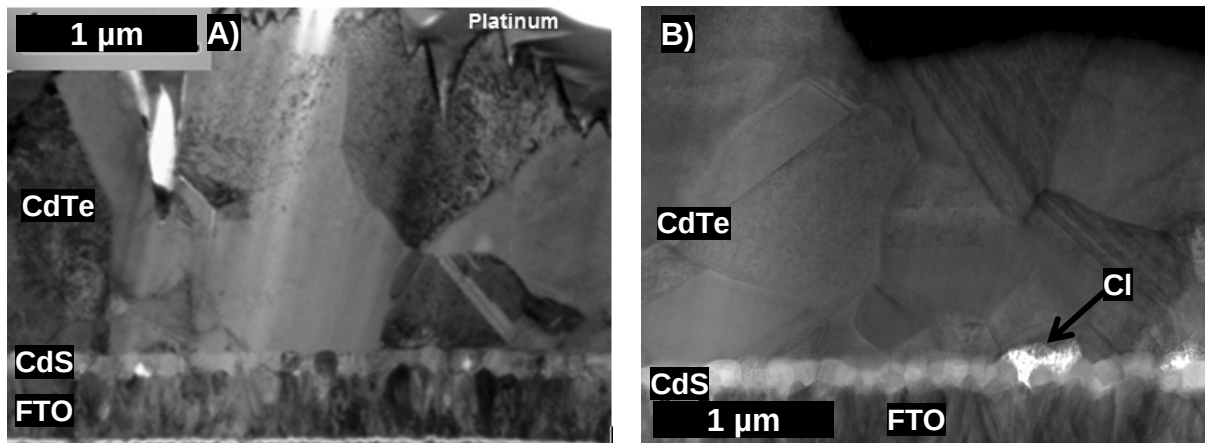


Figure 7.10 – BF-TEM images of the cell after the cadmium chloride treatment at a) 381°C b) 429°C

7.3.3 Crystallographic Changes of the Cadmium Telluride Thin Film with Treatment Temperature

Figure 7.11 shows an EBSD derived inverse pole figure overlaid with the image quality (IQ) composite map from the cadmium chloride cell treated at 429°C (higher than the optimum temperature) and at 381°C (lower than optimum).

Figure 7.11a shows texture maps and pole figures show a random orientation for the samples treated at higher temperatures. The sample treated at the lowest temperature had a different crystal texture shown in Figure 7.11b.

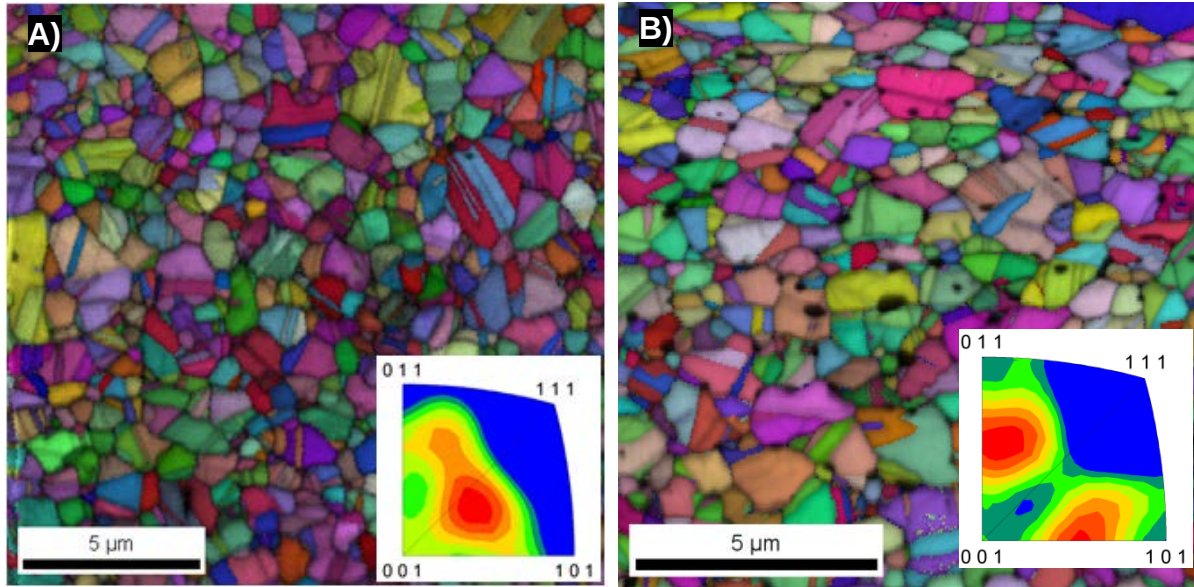


Figure 7.11 - EBSD derived IQ/IPF composite map of the cadmium telluride surface treated at a) 429°C and b) 381°C after being polished by an ion beam.

All the treated samples showed that the microstructures contain a significant number of twin boundaries. The EBSD data was used to calculate the amount of twinning in each of the samples. An EBSD map of the cadmium telluride layer treated at 391°C with the 60° twin boundaries highlighted is shown in Figure 7.12a.

The length of twin boundaries were calculated from the EBSD data and are shown in Figure 7.12b. The data shows as the temperature of the cadmium chloride treatment increases the length of twin boundaries per unit area decreases. The largest decrease in twin boundaries is between 391°C and 400°C (which is the optimum temperature).

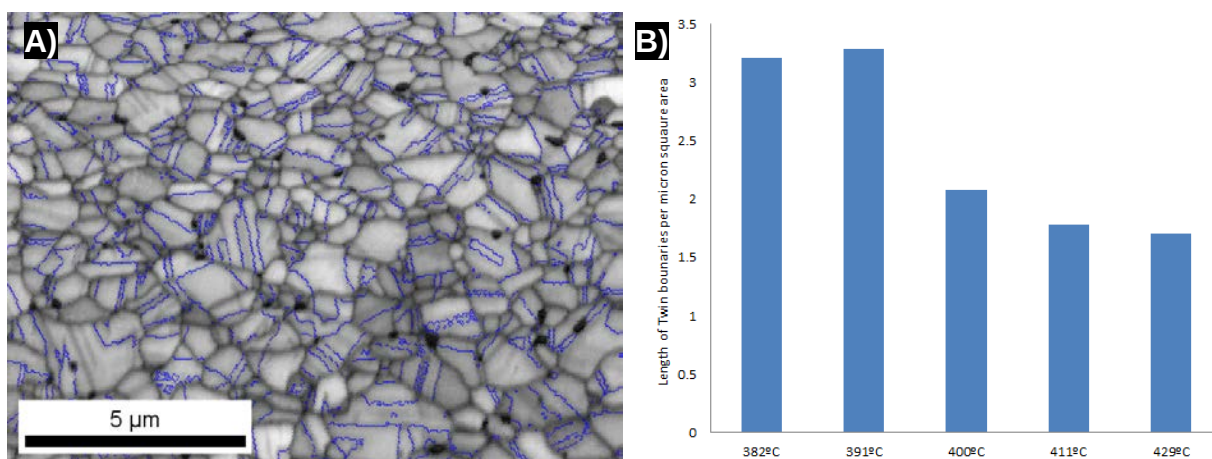


Figure 7.12 – a) An EBSD derived IQ map with twin boundaries highlighted in blue b) graph showing the length of twin boundaries per micron square

From the EBSD data the average grain size can be calculated and is displayed in Figure 7.13. The sample treated at 381°C had the smallest grain size with an average of 1210 nm as well

as the lowest standard deviation. The optimised treatment cell at 400°C has an average cadmium telluride grain size of 1330 nm whereas the highest temperature treatment at 429°C has a grain size of over 1500 nm. This indicates that an increasing treatment temperature results in an increase in grain size.

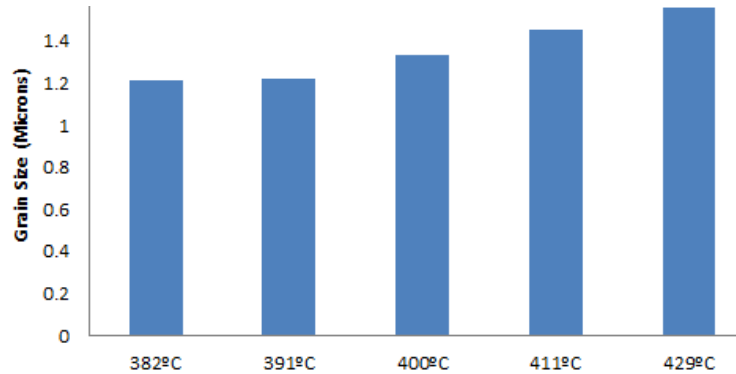


Figure 7.13 - Grain size variation calculated from EBSD in microns as the treatment temperature increases.

7.3.4 Change of Chlorine Concentration Build-up at the Interface using X-ray Photo-Electron Spectroscopy

X-ray Photo-electron spectroscopy was used to measure the chlorine concentration through the layers of the stack. The optimized sample contained a low concentration of chlorine throughout the cadmium telluride layer of 0.15 at% with a build up at the cadmium sulphide interface to a maximum of 0.75 at%. This indicates that the chlorine has diffused through the cadmium telluride and builds up at the cadmium sulphide interface. The sample treated at a lower temperature contained very low concentration close to the cadmium sulphide interface close to the XPS detection limit of ~0.1 at%. This sample also showed the least amount of recrystallization of the cadmium telluride grains, which is an indication that the amount of diffused chlorine is important. The sample treated at 429°C had the highest concentration of chlorine (2.6 at%) at the cadmium sulphide interface, illustrated in Figure 7.14.

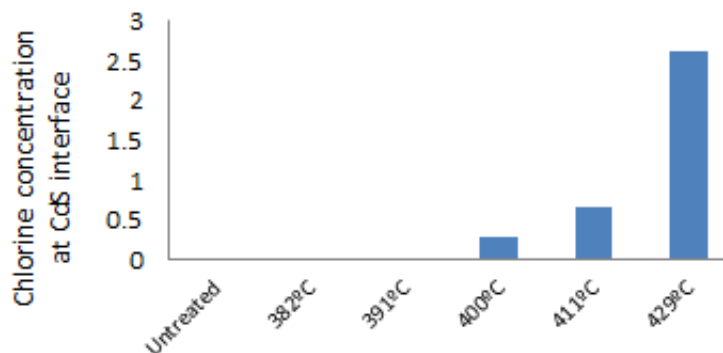


Figure 7.14 - Chlorine concentration at cadmium sulphide/cadmium telluride interface at increasing annealing temperatures

7.3.5 Characterization of Defects in the Cadmium Telluride Grains

High resolution TEM was used to examine defects in the cadmium telluride grains by tilting the grain to the [011] zone axis, along the (111) plane. As shown in Chapter 6 the untreated cadmium telluride grains had a high density of twins and stacking faults.

The treated samples all possessed a much lower density of defects. The density of defects per grain was measured by drawing a line perpendicular to the defects and counting how many defects intersected the line. Since some defects occurred in close proximity to one another higher magnification images were required. Figure 7.15a shows a cadmium telluride grain from the sample treated at 391°C. It is strongly diffracting, more than the surrounding grains as it has been tilted to the (111) plane on which the defects lie. The two white arrows indicate the areas with defects the rest of the grain has a perfect lattice. The two areas at which defects occur were then imaged in high resolution in order to resolve the density of linear defects present and if they were twins or stacking faults.

Figure 7.15b shows area 1 from the grain identified in Figure 7.15b, the image clearly shows 1 twin boundary present in the area. This can be characterized as a twin as the atom planes change direction across the defect. Either side of the twin boundary the grain is observed to have a perfect lattice with ordered spacing and direction of the atomic planes. Figure 7.15c shows Area 2 of the grain identified Figure 7.15a. The high resolution image shows a cluster of twin boundaries. Seven twins can be seen in this area.

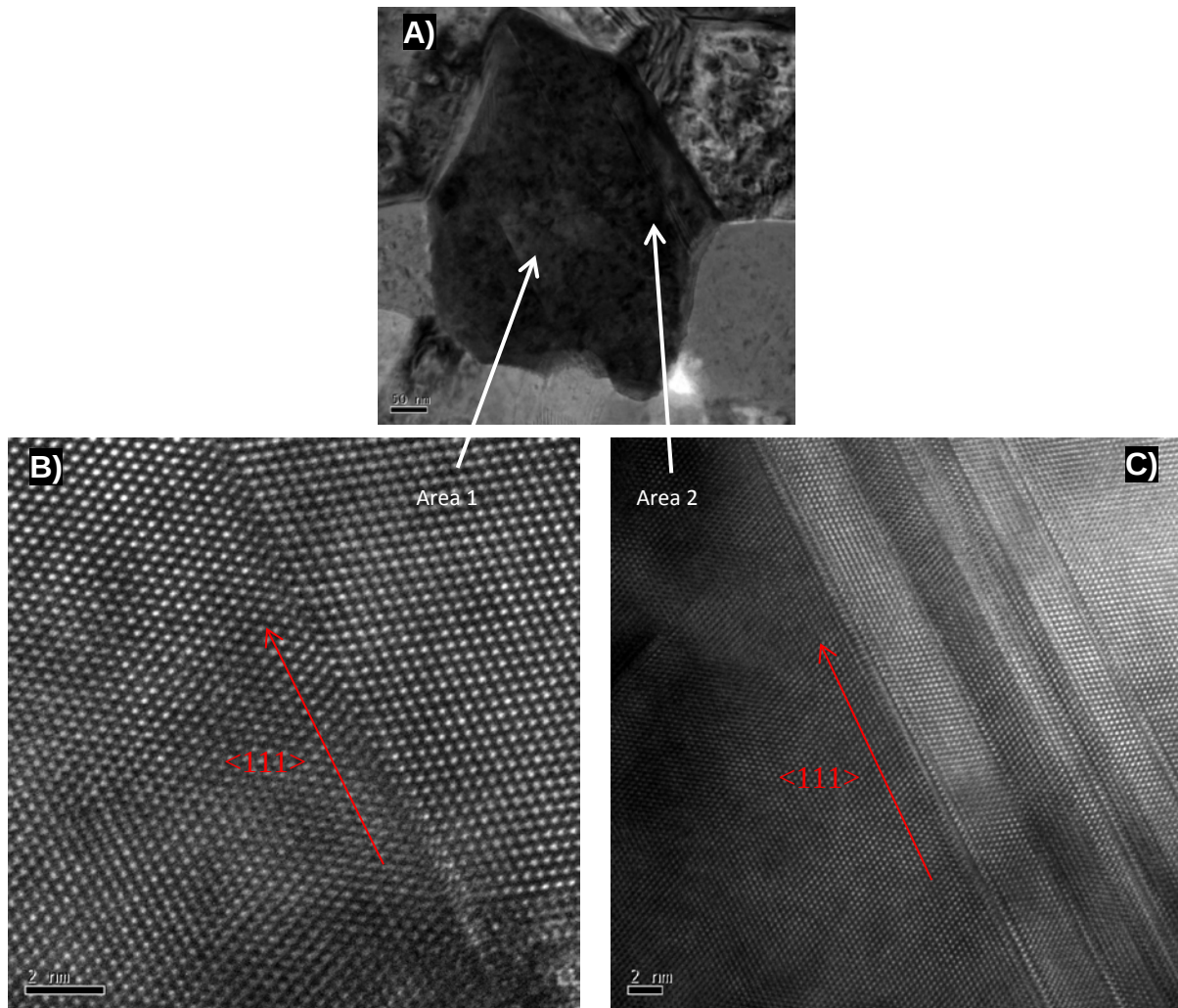


Figure 7.15 – a) A BF-TEM image of a cadmium telluride grain oriented to look at the (111) plane and HRTEM images of b) area 1, c) area 2

The average density of defects was calculated for each sample by analysing 5 grains per sample. The sample treated at the lowest temperature had an average of 9 defects per grain whereas the sample treated at the highest temperature had 12 defects on average; this however could be due to the larger grain size of the higher temperature samples. The number of defects varied slightly but the average for all the treatments was ~ 10 defects per grain. All grains analysed had at least 2 defects with a maximum of 20 defects in one grain. All treated samples showed a dramatic reduction in the defect density compared with the untreated sample. The defects in the untreated samples included both stacking faults and twins. The majority of the defects in the treated samples were twin boundaries.

7.3.6 Performance Properties of the Cells

Figure 7.16 shows the change in performance of the cells with change in the treatment temperature. A range of cells for each temperature were measured and the average efficiency calculated. The data indicates that the cells efficiency increases until 400°C which is the optimum treatment temperature (consistent with industrial experience) and then decreases

from then as the temperature increases indicating that the cells are becoming over treated as the temperature increases the rate of recrystallization of the cadmium telluride layer. All treated cells recorded much higher cell efficiencies than the untreated sample.

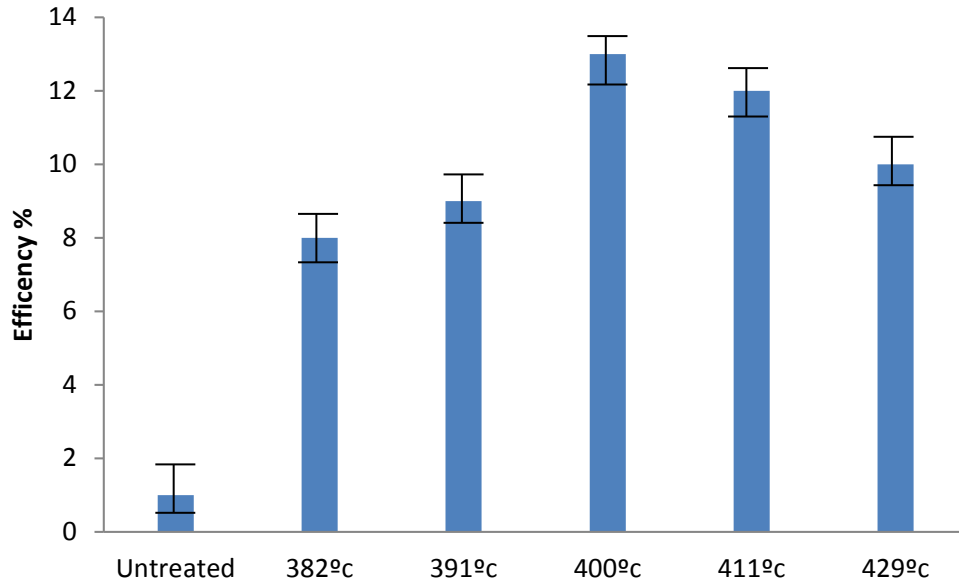


Figure 7.16 - Cell efficiencies corresponding to different cadmium chloride treatment temperatures

7.3.7 Summary of Varying the Cadmium Chloride Treatment Temperature

This study has shown that the temperature of the cadmium chloride treatment is critical to cell performance. When carried out at a lower temperature (381°C) than optimum, the cadmium telluride grains were smaller than the optimum sample and had the largest amount of twins per unit area; this corresponds to a lower cell efficiency of ~7.7%. This sample also had the smallest grain size and highest density of defects. The optimised treated sample at 400°C had an efficiency of 13%. However the cell treated at a higher temperature, although exhibiting larger cadmium telluride grains, exhibited a lower cell efficiency indicating that a large grain size does not necessarily lead directly to high efficiency cells. The annealing temperature has a marked effect on the diffusion of chlorine to the cadmium sulphide interface; the sample treated at 429°C was over-treated causing too much chlorine diffusion, which concentrated at the cadmium sulphide interface. All defects in the treated samples were characterised as twins. The untreated samples contained high densities of both twins and stacking faults.

7.4 The Effect of Annealing Treatments on Close Spaced Sublimated Cadmium Telluride Thin Film Solar Cells

7.4.1 Introduction and Objectives of the Annealing Treatment without Cadmium Chloride

It is well known that the cadmium chloride annealing treatment is an essential step in the manufacture of efficient thin film cadmium telluride solar cells. It has been observed that the combination of annealing at $\sim 400^{\circ}\text{C}$ together with the addition of cadmium chloride at the surface induces re-crystallisation of the cadmium telluride layer and also affects the n-type cadmium sulphide.

It has been found that the as-deposited films contain a high density of stacking faults which correspond to low cell efficiency. The cadmium chloride annealing treatment causes a significant increase in cell performance and is known to radically change the structural and electrical characteristics of the cell. It consists of two parts, first the introduction of cadmium chloride onto the cadmium telluride surface and second, the heating of the device stack. The aim of this investigation is to determine the change in the microstructure of the cadmium telluride caused by annealing alone. This allowed us to distinguish the role of annealing during the cadmium chloride treatment.

7.4.2 Sample Description for the Annealing Treatments

The thin film cadmium telluride 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. The films were deposited by CSS in an all in one vacuum process.

One sample underwent a previously optimized post deposition cadmium chloride annealing treatment. The treatment was carried out in vacuum following the layer deposition. Cadmium chloride was sublimated as a fairly thick layer and then the sample was heated for 8 minutes at 400°C in a 2% oxygen atmosphere, causing the cadmium chloride layer to evaporate completely. This was followed by a copper doping process. The efficiency of this cell was measured to be 11.8%. The rest of the samples were deposited using the same conditions but were not subjected to the cadmium chloride treatment. Some of the samples were instead annealed in air, at the same temperature as the cadmium chloride sample (400°C) for 8, 10, 20 and 30 minutes. Samples were also annealed for 8 minutes at 350°C , 400°C and 450°C . The samples were then analysed using TEM to observe the effects of the treatments.

7.4.3 Methodology for Stacking Fault Density Measurements

Stacking fault density was measured by counting how many stacking faults intersect a 1 micron line orthogonal to the stacking faults. For each sample 10 grains were measured and an average calculated. As the visibility of stacking faults can change with grain orientation, a double tilt holder was used in the TEM. The grain was tilted to the [011] zone axis prior to analysis by moving the Kikuchi pattern into the centre. This exercise was performed for each grain to measure stacking fault density.

7.4.4 Reference Cadmium Chloride treated and Untreated Cadmium Telluride Cells

Chapter 6 has a detailed analysis of the untreated and cadmium chloride treated cells, the untreated cell possessed a high density of stacking faults whereas the treated sample had on average several defects per grain.

7.4.5 Change in Defect Density with Treatment Time and Temperature

The results shown in Figure 7.17a indicate that there is a slight decrease in stacking fault density as the annealing time increases. Figure 7.17b shows the relationship between treatment temperature and stacking fault density. A drop in stacking fault density is observed with an increase in annealing temperature; each sample was annealed for 8 minutes except the untreated sample. The cadmium chloride treated sample shows a much more dramatic effect on the stacking fault density. In fact, stacking faults were completely removed and the line defects recorded were all twins.

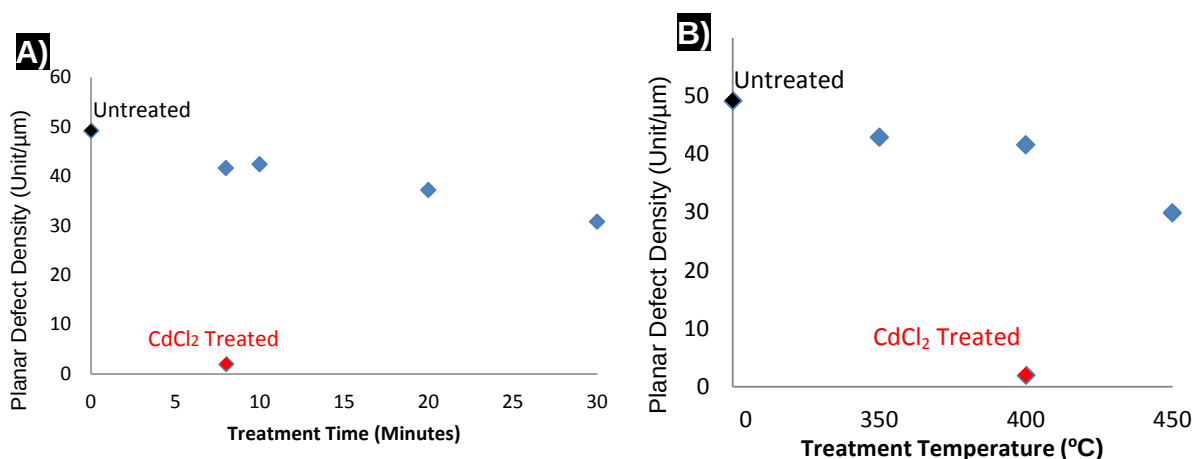


Figure 7.17 – A graph showing line defect density change with treatment a) time c) temperature

Figure 7.18 shows the difference observed in TEM after different anneal times, Figure 7.18a shows the sample after 8 minutes of annealing treatment at 400°C, which is the same time used in the cadmium chloride treatment. It has an average line defect density of 41.6 whereas the treated sample has a density of only 2 (only twins).

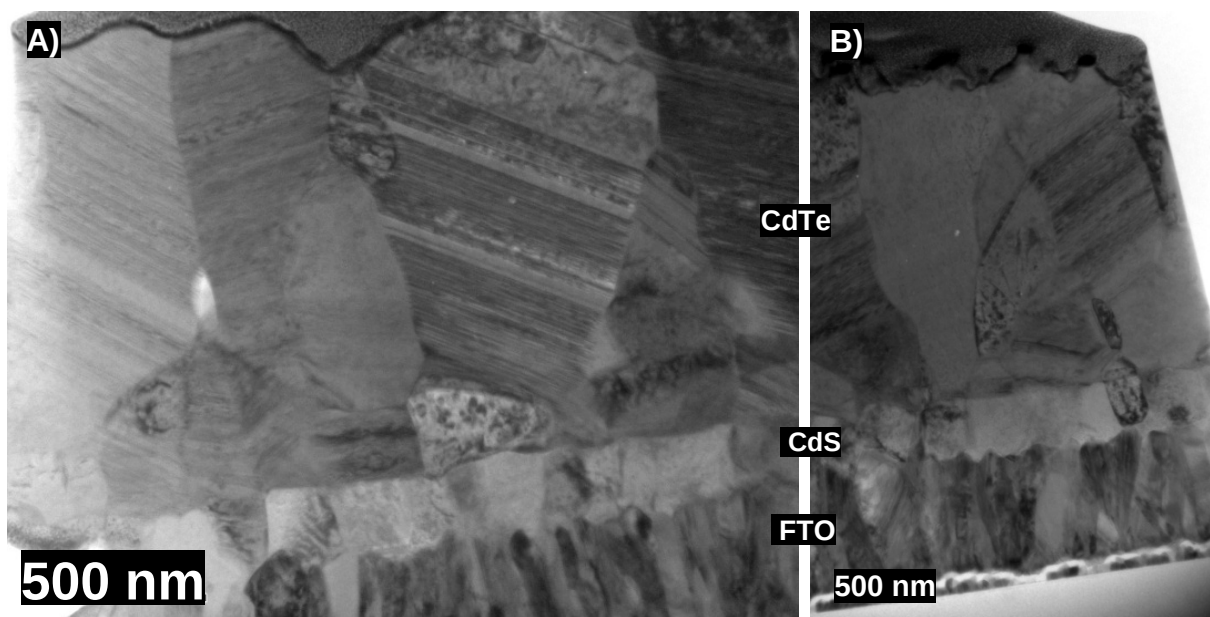


Figure 7.18 – shows BF-TEM images indicating the change in stacking fault density for the samples annealed at a) 400°C for 8 minutes b) 400°C for 30 minutes

7.4.6 Summary of Varying the Annealing Temperature and Time without the Presence of Cadmium Chloride

In Chapter 6 it was observed that as-deposited cadmium telluride contains high densities of stacking faults in all the grains. It was also observed that the stacking faults are completely removed by the recrystallization process established by the cadmium chloride treatment. Even though this process had only a small effect on to grain size, the efficiency of the cell was dramatically improved. Elemental analysis showed that chlorine, probably in the form of cadmium chloride, was present at the grain boundaries. It was also present at the cadmium telluride/cadmium sulphide interface implying the movement of the cadmium chloride from the surface and through the cadmium telluride layer.

This study has focused on the effect of the heat treatment part of the cadmium chloride treatment and in particular on its effect on stacking fault density. TEM has shown a variation in stacking fault density with annealing temperature and annealing time. Stacking faults observed within the cadmium telluride grains in TEM were partially removed during an anneal. This shows that the energy input during the anneal caused some stacking faults to be removed. However, in Chapter 6 it has been observed that almost a complete removal of stacking faults with annealing in combination with cadmium chloride.

Microstructural changes are observed in the cadmium telluride caused by increasing the temperature in the range 350°C to 450°C. It was also observed that the changes were caused by increasing the annealing time from 8 to 30 minutes at an annealing temperature of 400°C.

In both experiments, the measurement of the stacking fault density has observed a reduction with increasing annealing temperature and annealing time. However, in neither case did the process eliminate the stacking faults or reduce the defect density anywhere close to that observed with the addition of cadmium chloride. Although the annealing temperature is important, it is clear that the cadmium chloride facilitates the cadmium telluride grains to completely recrystallize, removing most of the defects in the process.

7.5 Chapter Summary

This chapter has investigated the cadmium chloride assisted recrystallization of CSS cadmium telluride solar cells.

By varying the cadmium chloride treatment time from 2 seconds up to the optimum time (120 seconds), the time-line of the effects of the process has been observed. This showed the initial effects of the treatment take place within smaller cadmium telluride grain nearer the cadmium telluride/cadmium sulphide, recrystallizing them first and removing the majority of stacking defects. It was also observed that if a grain recrystallizes, the entire grain is usually affected. Increasing the treatment time up to 600 seconds, caused further grain recrystallization, as an increase in grain size has been observed, further removing stacking defects. Increasing the treatment temperature had a similar effect, as treating the cadmium telluride cell for a longer time, as a higher temperature accelerated the treatment effects. Some effects such as grain coarsening and further defect removal are seen as advantageous, which occurs when the cadmium telluride is subjected to either a higher treatment temperature or a longer treatment time. However deviating from the optimum time and temperature of the treatment, to a longer treatment time or a higher temperature, increases diffusion of chlorine down to the p-n junction, damaging the cell, leading to a drop in cell performance.

By only annealing the cadmium telluride cell, a slight drop in stacking defects is observed; however without the presence of cadmium chloride the cadmium telluride grains do not recrystallize, leaving the majority of the initial stacking defects to remain.

CHAPTER 8. INVESTIGATION OF LOCALIZED PHASE CHANGES IN THIN FILM CADMIUM TELLURIDE PHOTOVOLTAIC MATERIAL WITH HIGH LATTICE DEFECT DENSITIES

8.1 Chapter Scope

This chapter studies the microstructural and crystallographic characteristics of cadmium telluride thin film photovoltaic materials in detail. In Chapter 6 TEM revealed high densities of defects in cells deposited via close space sublimation in cadmium telluride before the cadmium chloride treatment. It has also been observed that on a focused ion beam smoothed planar section, EBSD maps showed signs of mis-indexing of the untreated cadmium telluride grains. The cadmium telluride grains recrystallized after the cadmium chloride treatment and possessed very different intra-granular defects than before the treatment. The crystallographic characteristics of the material before the treatment could not be studied with conventional EBSD as it had inadequate spatial resolution. To overcome this, the materials have been studied using Transmission Electron Backscatter Diffraction in the SEM (T-EBSD), which promises improved spatial resolution.

8.2 Introduction

In Chapter 6 the planar EBSD maps collected in untreated cadmium telluride samples were found to possess a significant amount of mis-indexed points in the middle of grains. Figure 8.1 compares EBSD derived maps collected from treated and untreated cadmium telluride planar surfaces. The image quality maps shows that high quality Kikuchi patterns are collected from both samples. A comparison of the inverse pole figure/image quality composite maps shows speckling within the grains in the untreated sample that is not present in the treated sample. A comparison of the confidence index/inverse pole figure composite maps shows that these intra granular speckles have a low confidence index and are consequently likely to be mis-indexed points. This behaviour is not observed in the treated samples.

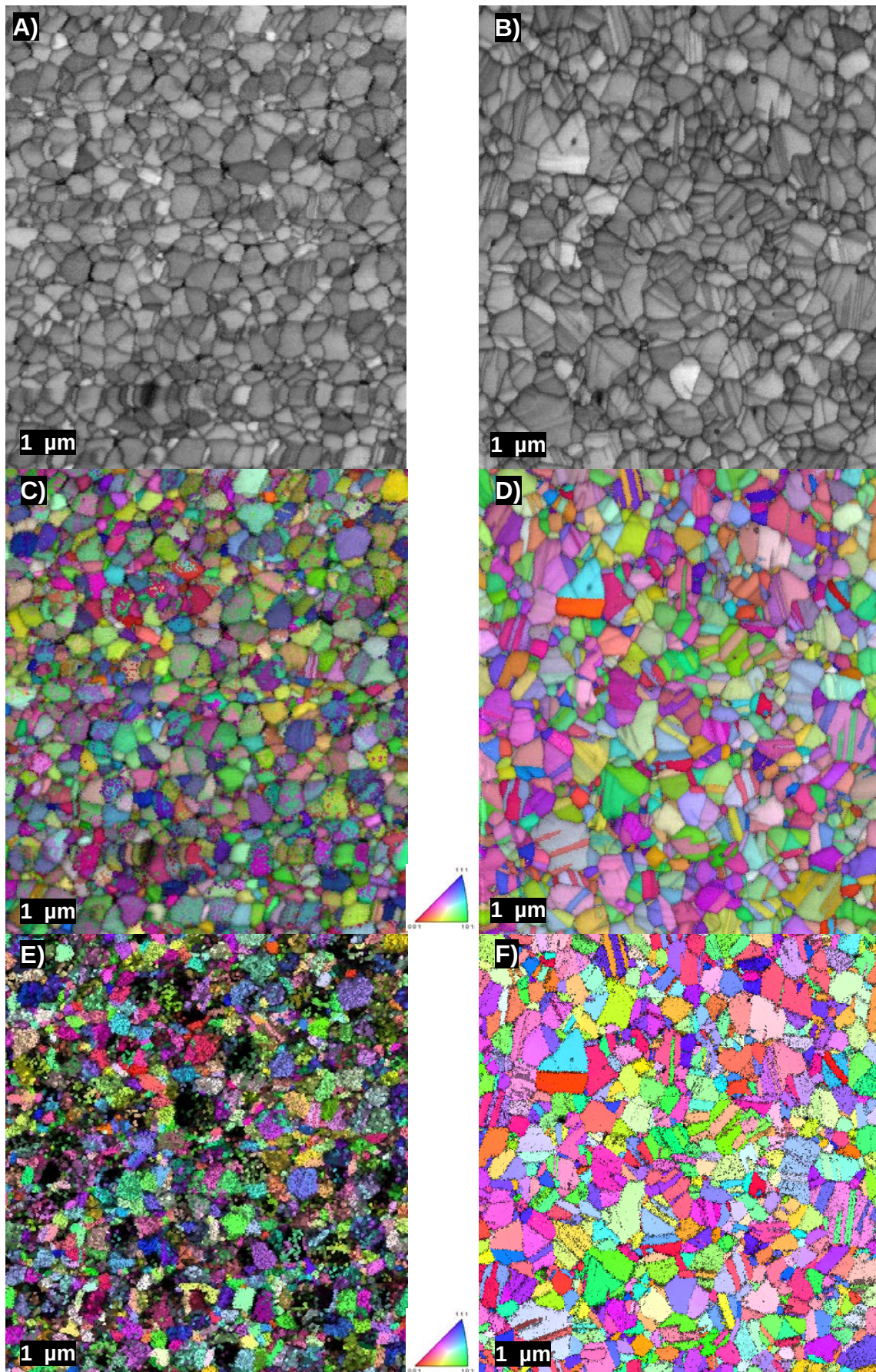


Figure 8.1 - EBSD derived IQ map of a) untreated and b) treated, IQ/IPF composite map of c) untreated and d) treated, and CI/IPF maps of e) untreated and f) treated cadmium telluride surface

To investigate the observed mis-indexing, high quality Kikuchi patterns were collected from various regions in the treated and untreated samples, a selection of which are compared in Figure 8.2. It was found that some of the patterns in the untreated material did not index satisfactorily to the cubic cadmium telluride structure file.

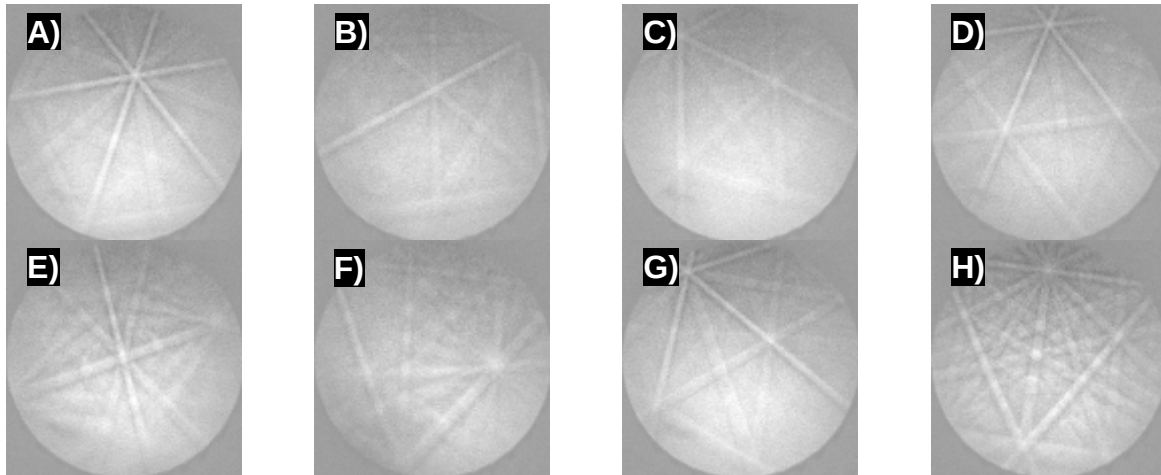


Figure 8.2 – Kikuchi patterns collected from a-d) untreated, e-h) treated cadmium telluride layer

Figure 8.3 compares XRD scans for the treated and untreated samples. The main differences observed are the broad peaks located at 39.2° corresponding to the (110) hexagonal peak and 42.7° corresponding to the (103) hexagonal peak in the untreated sample. The position of these peaks is consistent with the main peaks expected in the hexagonal cadmium telluride phase. These peaks could be from a phase with a fine grain size with Scherrer line broadening causing the peaks to appear broad.

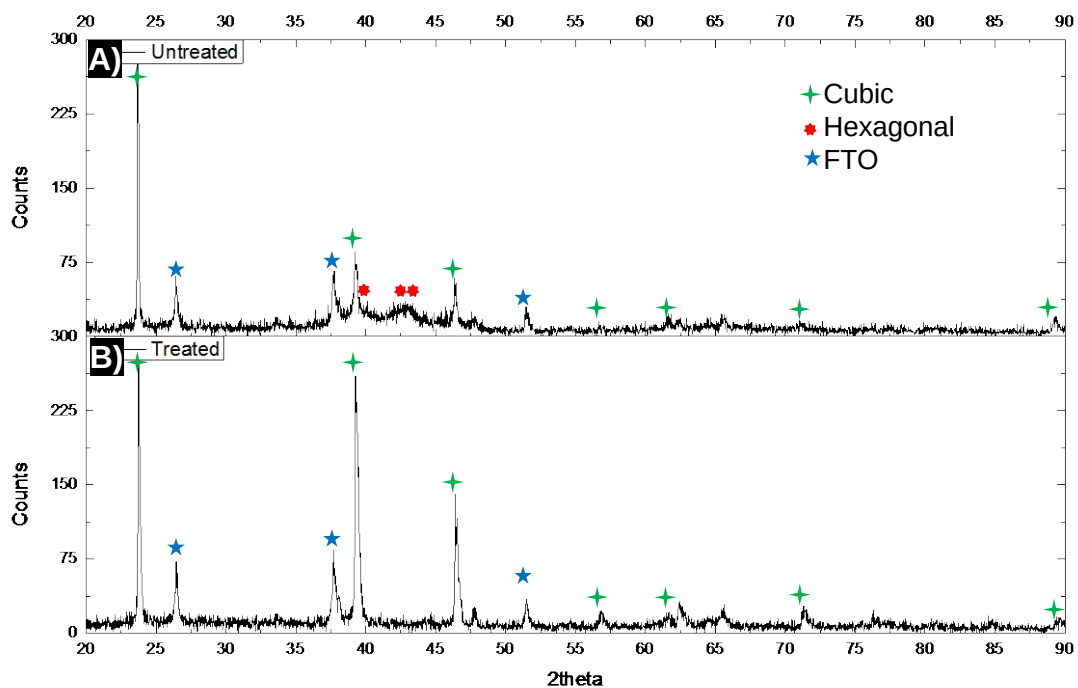


Figure 8.3 – An XRD scan of a) untreated b) treated cadmium telluride layer

The XRD data in Figure 8.3 suggested that a hexagonal cadmium telluride phase is present in the untreated condition. To investigate this and map the phase distributions a planar EBSD map of this sample was collected using both cubic and hexagonal phase files and the maps are shown in Figure 8.4. These maps clearly show that in the untreated condition the material contains both cubic and hexagonal phases and high confidence index is achieved in all intragranular locations. Although this technique shows the distribution of phases, more spatial resolution is needed to study this interesting result in more detail to see how the phases are distributed within a grain.

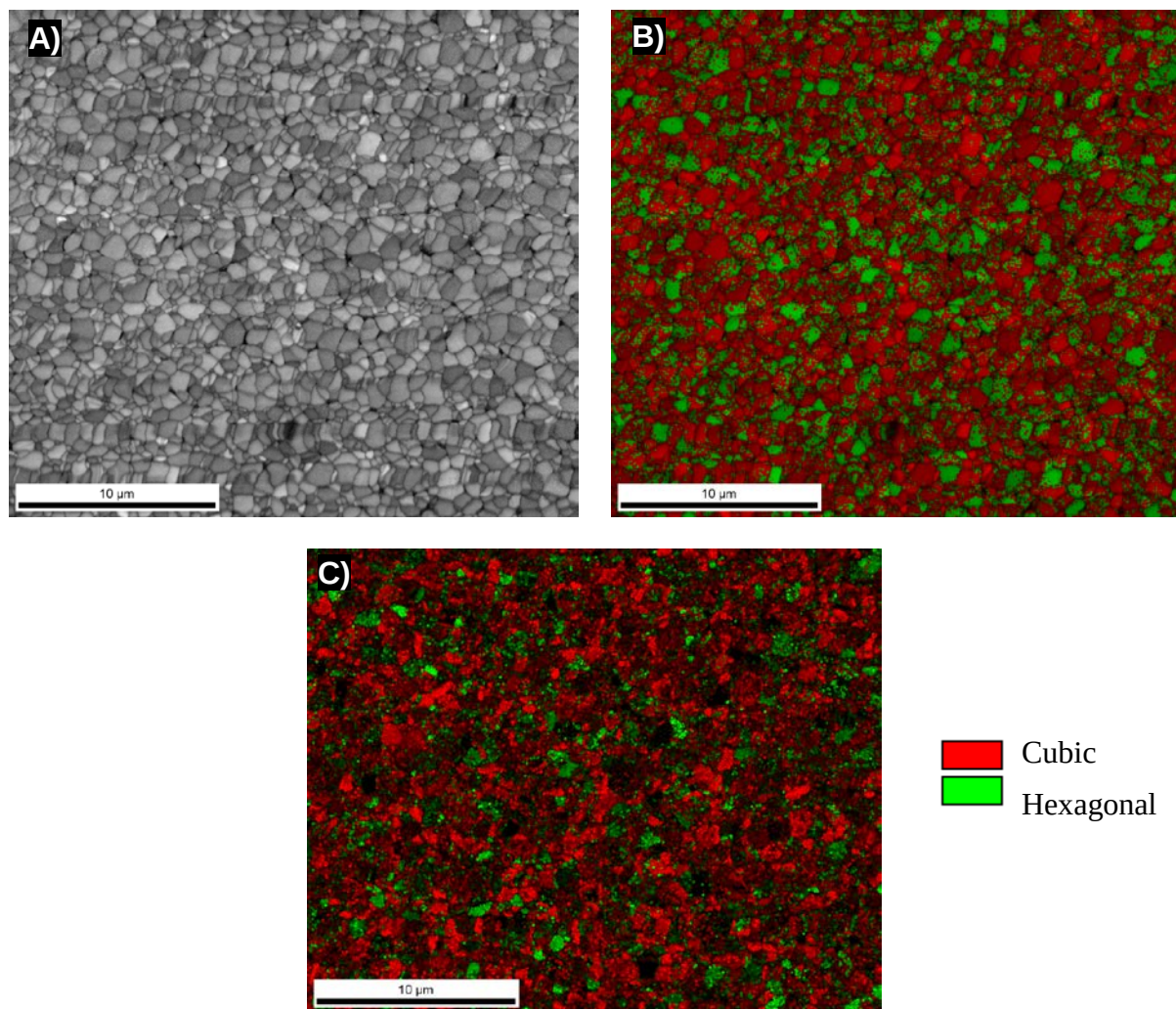


Figure 8.4 - EBSD derived a) IQ, b) IQ/phase composite and c) CI/Phase composite maps of the untreated cadmium telluride surface

8.3 Transmission Electron Back-Scatter Diffraction (TEBSD) as a Tool to better index Thin Film Cadmium Telluride Solar Cells

Figure 8.5 shows a TEBSD image quality/inverse pole figure composite map of the untreated cadmium telluride cell. The grains show no clear preferred orientation and some evidence of twinning are observed.

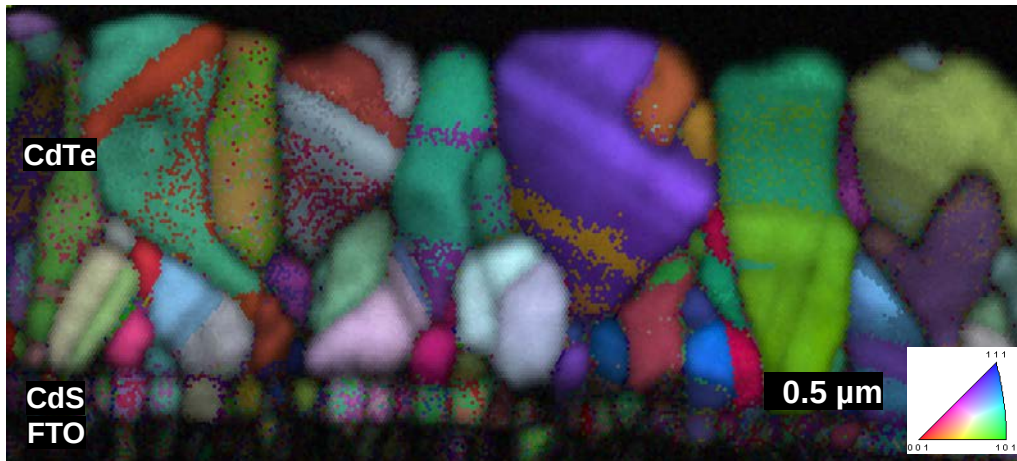


Figure 8.5 – A TEBSD IQ/IPF composite map of untreated cadmium telluride cell

Figure 8.6 shows transmission electron back-scatter diffraction image quality/inverse pole figure maps of treated cadmium telluride cell. No hexagonal phase was observed in the treated condition.

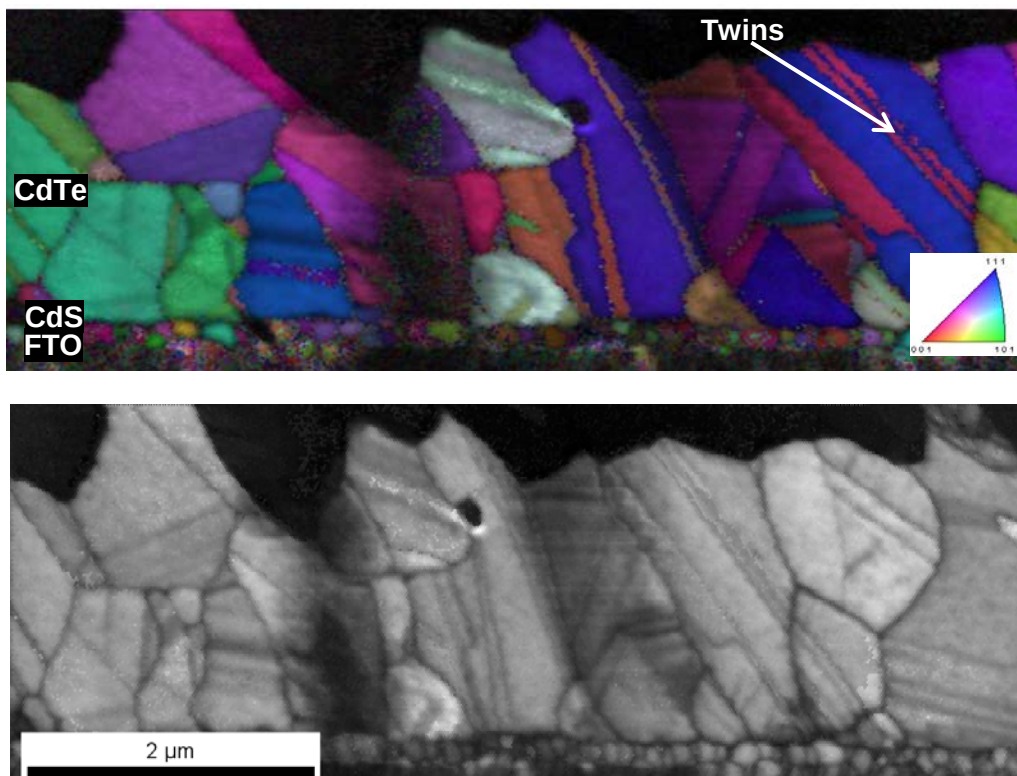


Figure 8.6 – A TEBSD IQ/IPF composite map of treated cadmium telluride cell

Figure 8.7 shows two Kikuchi patterns collected from different areas of nominally the same grain. Figure 8.7a indexed to the cubic phase and Figure 8.7b indexed to the hexagonal phase. This shows that both the cubic and hexagonal phases coexist in the same grain.

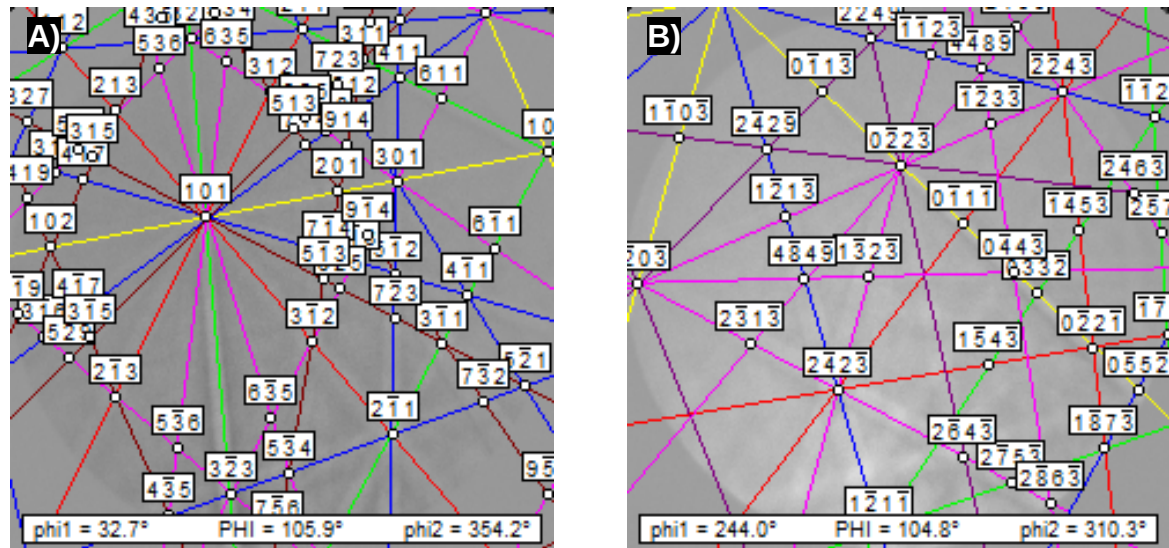


Figure 8.7 – Kikuchi patterns taken from different regions in the same cadmium telluride grain indexing to a) cubic, and b) hexagonal phase files

8.4 Embedded Hexagonal Phases Identified using Transmission Electron Back-Scatter Diffraction

Figure 8.8 is derived from a TEBSD scan of a cross section of untreated cadmium telluride indexed against both cubic and hexagonal phase structure files. Figure 8.8a shows the image quality map overlaid with phase. Within the untreated cadmium telluride some grains have formed bands of hexagonal material. These bands are usually in 20 - 100 nm thick and run across the width of the cadmium telluride grain approximately perpendicular to the growth direction.

Figure 8.8b shows a TEBSD phase map overlaid with a confidence index map. The bands of hexagonal phase are seen to index with high confidence index to the hexagonal phase structure file indicating that the hexagonal phase is embedded within the cubic grains.

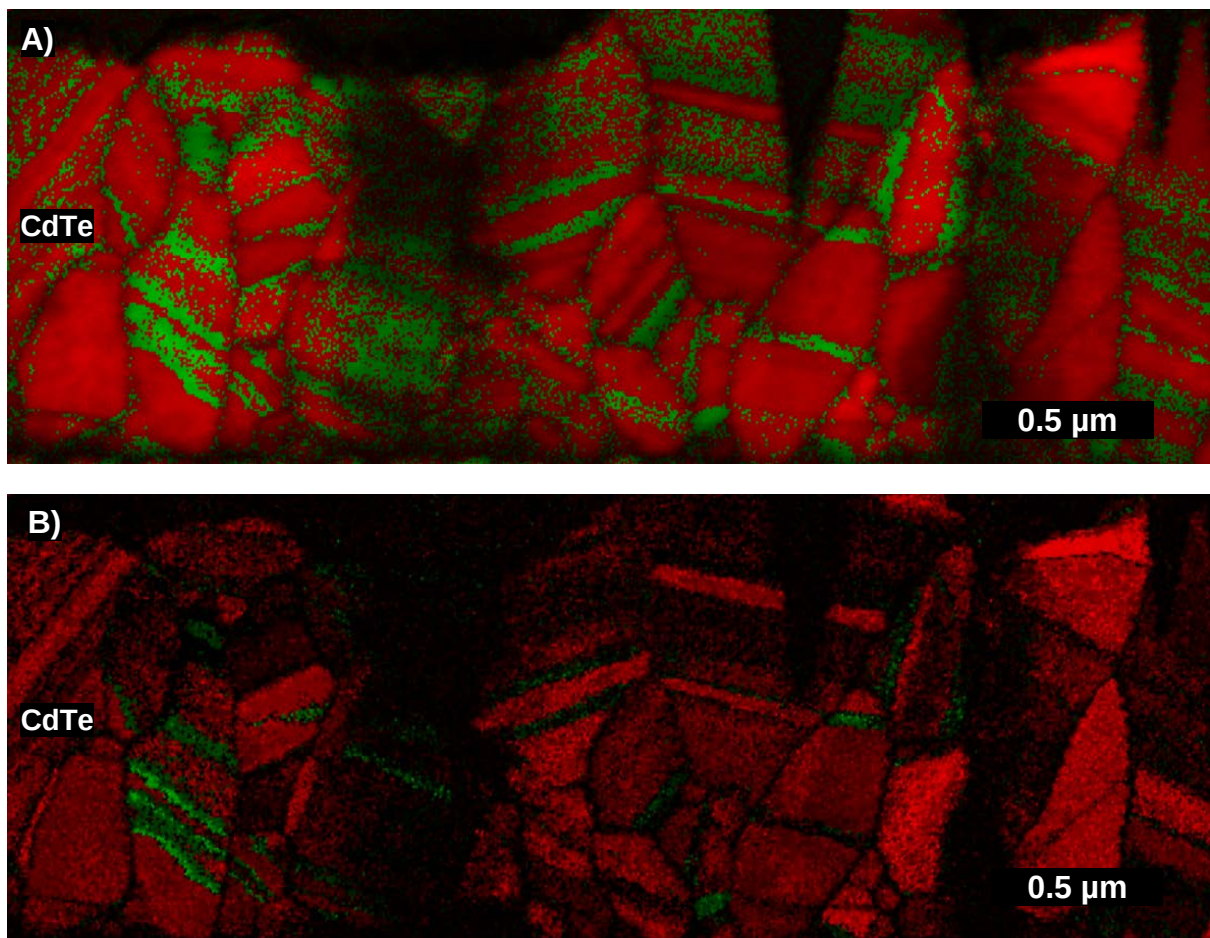


Figure 8.8 – High resolution TEBSD derived maps showing the distribution of the two phases, showing the cubic phase in red and hexagonal phase in green overlaid with a) image quality and b) confidence index

8.5 Embedded Hexagonal Atomic Stacking in Untreated Cadmium Telluride Grains

As seen from TEM results in Chapter 6, the main difference between the untreated and treated cadmium telluride cells is the high density of stacking faults within the untreated material. From TEBSD it has been shown that bands of hexagonal phase have formed within cubic cadmium telluride grains. Figure 8.9a shows a HRTEM image of the untreated cadmium telluride layer. This shows a high density of defects within the grain. The defects consist of stacking faults and twins, however the distribution is non-homogeneous. Two distinct regions of stacking faults every 2 atomic planes for several atomic layers can be seen. The stacking in a perfect cubic lattice is AaBbCcAaBbCc... however as a plane is missing from every sequence the stacking sequence becomes AaBbAaBa... this is hexagonal wurtzite packing. The hexagonal regions have been marked in Figure 8.9a, which appear in bands and a schematic diagram of the buried hexagonal phase with cubic phases either side is shown in Figure 8.9b. This high density of stacking faults causes a shift from cubic material to hexagonal material. Therefore both phases are present within the same grain, as seen by TEBSD. This localized change of phase has been reported previously^{38,75,81}, however this is the first time this behaviour has been used to explain the micro-scale behaviour of these materials.

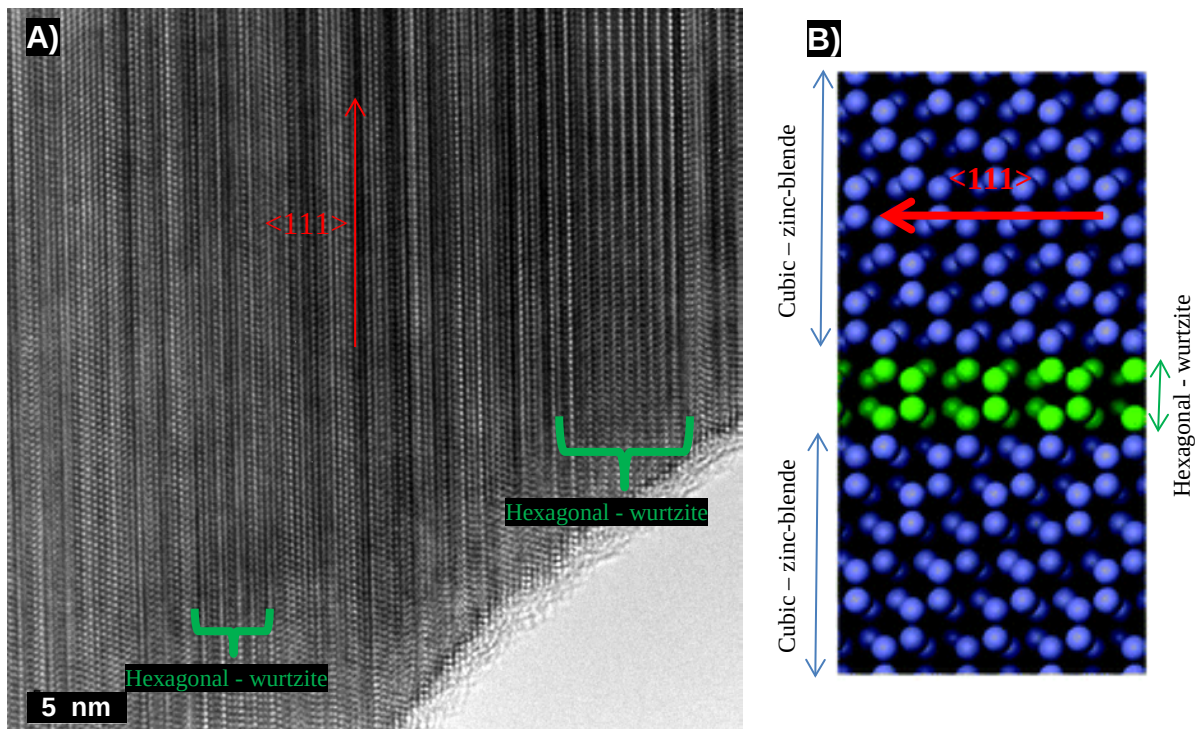


Figure 8.9 – a) A HR-TEM micrograph of a untreated cadmium telluride grain with highlighted hexagonal stacking highlighted, b) schematic diagram of cubic and hexagonal stacked atomic layers

8.6 Summary

TEBSD has been used to produce high resolution phase maps within the cadmium telluride layer in solar cell materials for the first time, showing hexagonal areas within cubic cadmium telluride grains. This phenomenon has been observed in cadmium telluride grains prior to the cadmium chloride treatment. Cadmium telluride grains after the cadmium chloride treatment have recrystallized, forming pure cubic grains.

The hexagonal areas within the untreated cadmium telluride grains are shown using HRTEM to form due a high density of stacking faults; in areas which a plane of atoms is missing in every sequence.

CHAPTER 9. MICROSTRUCTURAL ANALYSIS OF CADMIUM MAGNESIUM THIN FILMS FOR ELECTRON REFLECTOR APPLICATION FOR CADMIUM TELLURIDE SOLAR CELLS

9.1 Chapter Scope

This chapter will focus on the development of an electron reflector layer for cadmium telluride based solar cells deposited via co-sublimation at Colorado State University. The electron reflector used is cadmium magnesium telluride, $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ (CMT). The CMT layer was deposited using different conditions as well as onto cadmium chloride treated and untreated cells, some samples undergoing post deposition treatments. The cells were studied using SEM, STEM/EDX, TEM, EBSD, SIMS and XPS to investigate whether the deposition/treatments could be modified to improve cell efficiency.

9.2 Introduction

As seen in Chapter 6 cadmium telluride material readily forms inter-granular defects which act as electron sinks. These defects can be reduced with use of a cadmium chloride treatment, but it is not possible to eliminate all defects and impurities entirely, as the cadmium chloride treatment itself induces impurities into the junction. Therefore to improve the efficiency of the cadmium telluride based solar cell, alternative ways of increasing the voltage or current of the device should can be considered. One way to increase the voltage of the cell is by use of an electron reflector layer, which can be introduced onto the cadmium telluride layer before the back contacted is deposited. The reason for the introduction of an electron reflector layer is to increase the voltage of the cell by reducing the recombination near the back contract as it acts as a conduction band barrier. This should increase the cell voltage by approximately 200 mV which in-turn will increase the solar cell efficiency by a few percent. Cadmium magnesium telluride has a band gap of ~ 1.9 eV which is high enough to produce an increased voltage⁸². Cadmium telluride and cadmium magnesium telluride are both cubic and have similar lattice parameters, therefore the CMT layer could be deposited onto the cadmium telluride epitaxially. This will be desirable as the introduction of a new discontinuity between the two layers will likely reduce the cell's performance.

9.2.1 *Samples Analysed*

A range of CMT samples were deposited via co-sublimation by Colorado State University, varying the deposition conditions systematically to investigate the microstructural and chemical changes induced by the addition of the CMT layer, and its effects on the cadmium chloride treatment.

- Initially a thick CMT was deposited onto an untreated cadmium telluride cell. A thick layer was produced to allow for easier analysis to determine if it grew epitaxially on the cadmium telluride layer.
- CMT was deposited with three varying amounts of magnesium, to study its effects, as varying the magnesium content will alter the band gap of the material⁸².
- A set of samples were produced with the CMT deposited before and after the cadmium chloride treatment to investigate how the CMT layer reacts.
- A range of samples were produced to further understand how the CMT reacts to the cadmium chloride treatment and post deposition anneals, including undergoing a second cadmium chloride treatment.
- A fourth set of two samples were deposited at two temperatures (400°C and 470°C) as the higher temperature depositions of CMT caused detrimental effects to the cadmium telluride.

The samples examined in this chapter are summarised in Table 9.1.

Sample description	Temperature of CMT deposition	CMT thickness	Magnesium concentration
CdS/CdTe/CMT/CdCl ₂	470°C	900 nm	Medium
CdS/CdTe/CMT	470°C	750 nm	Low
CdS/CdTe/CMT	470°C	750 nm	Medium
CdS/CdTe/CMT	470°C	750 nm	High
CdS/CdTe/CMT/CdCl ₂	470°C	200 nm	Medium
CdS/CdTe/CdCl ₂ /CMT	470°C	200 nm	Medium
CdS/CdTe	n/a	0 nm	n/a
CdS/CdTe/CdCl ₂	n/a	0 nm	n/a
CdS/CdTe/CdCl ₂ /CMT	470°C	200 nm	Medium
CdS/CdTe/CdCl ₂ /CMT/post anneal	470°C	200 nm	Medium
CdS/CdTe/CdCl ₂ /CMT/post anneal/CdCl ₂	470°C	200 nm	Medium
CdS/CdTe/CdCl ₂ /CMT/CdCl ₂	470°C	200 nm	Medium
CdS/CdTe/CdCl ₂ /CMT	470°C	200 nm	Medium
CdS/CdTe/CdCl ₂ /CMT	400°C	200 nm	Medium

Table 9.1 – List of samples and descriptions and deposition conditions studied in this chapter

Low magnesium content is up to 2 at%, medium is up to 20%, high is above 20 at%.

9.3 Initial CMT Deposition

Figure 9.1 shows a BF-TEM image of the 900 nm thick CMT layer deposited onto a cadmium telluride cell. The CMT layer appears slightly lighter than the cadmium telluride layer due to the different absorption between the two materials. In the larger grain highlighted in Figure 9.1 several twin boundaries pass from the cadmium telluride to the CMT layer. The twin boundaries appear uninterrupted suggesting epitaxial growth of the CMT. In Figure 9.1 continuation of the cadmium telluride grain boundaries into the CMT is also observed. The CMT deposition also appears very conformal and follows the structure of the underlying cadmium telluride.

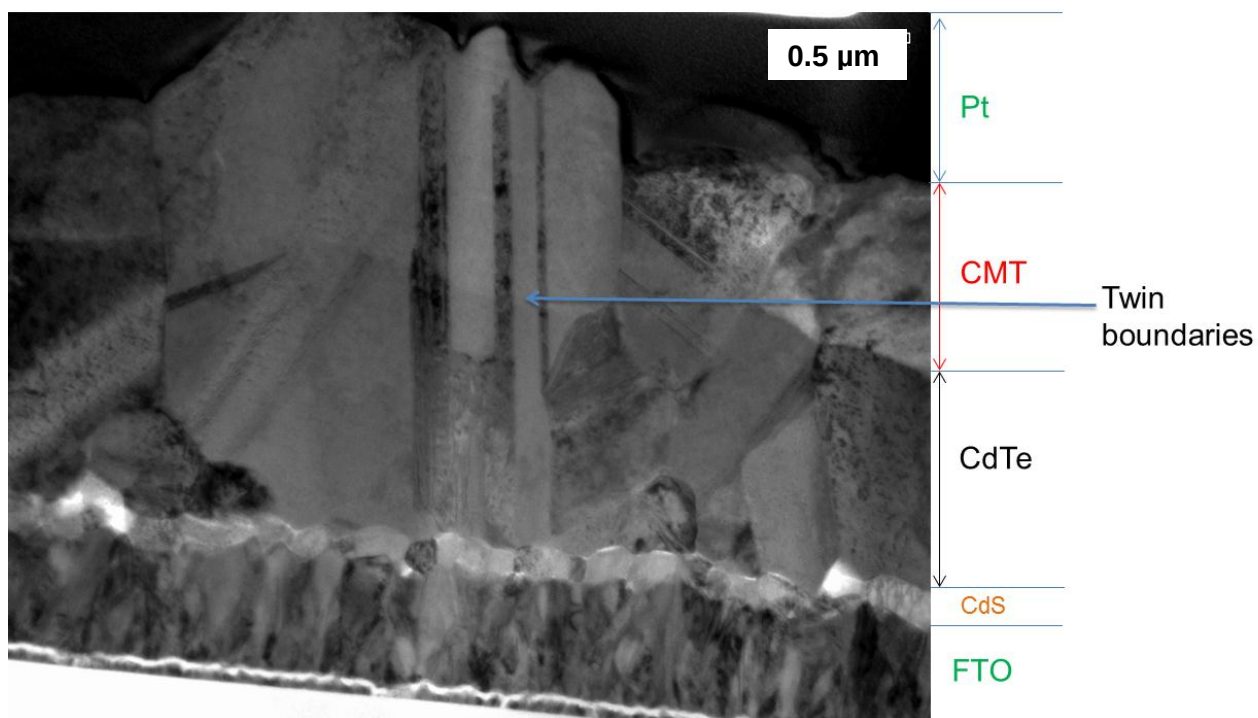


Figure 9.1 - A BF-TEM micrograph of an initial CMT deposition of 900 nm onto a cadmium telluride cell

Figure 9.2 shows two diffraction points taken from the same grain but just above and below the cadmium telluride/CMT interface. They indicate epitaxial growth and cubic phase for both layers.

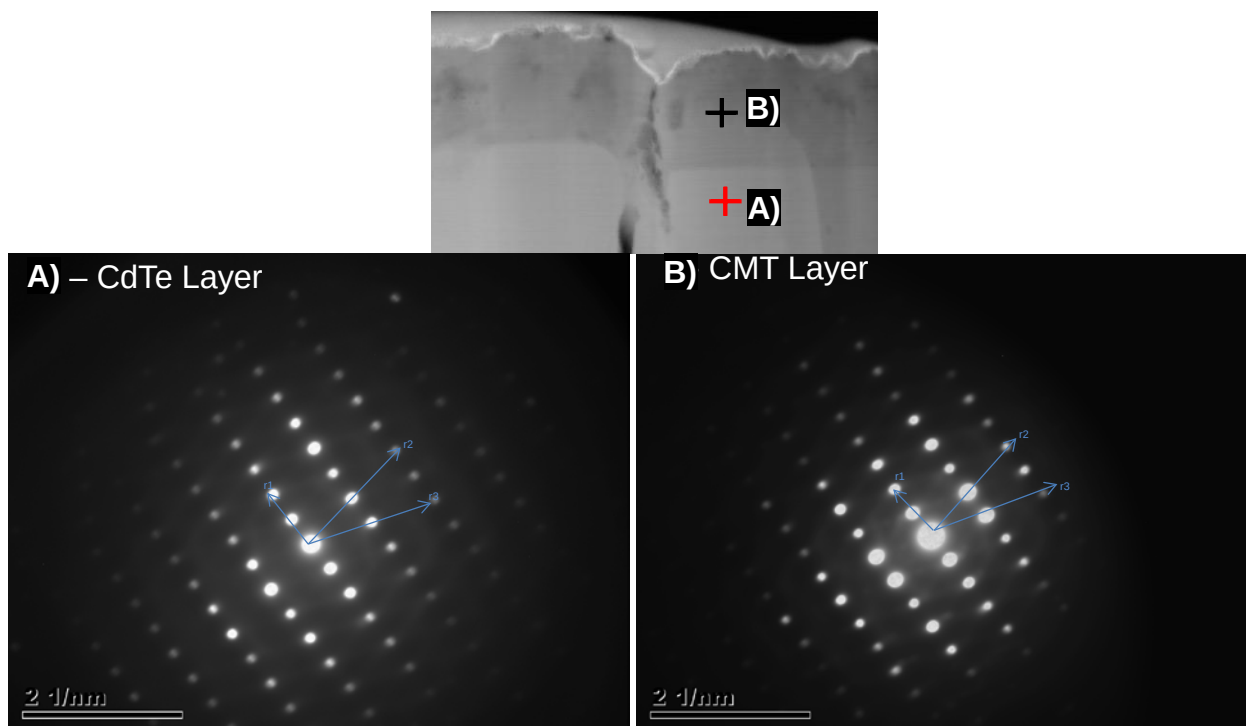


Figure 9.2 – A HAADF-STEM image showing the two areas diffraction points were taken from, a) within the cadmium telluride layer and b) within the CMT layer

Electron Backscatter Diffraction can be used to map grain by grain orientation, which will be useful in showing epitaxial growth. This will need to be done in cross section to see the relationship between the cadmium telluride substrate and the CMT thin film. This will be carried out in transmission as an increase in spatial resolution will be achieved as shown in Chapter 8.

Figure 9.3 is a T-EBSD derived inverse pole figure map of the same sample as was studied with TEM in Figure 9.2. It shows the cadmium telluride and adjacent CMT grain do have the same orientation as shown by grain 1 as this through thickness grain originates at the cadmium sulphide interface and extends through to the surface of the CMT layer passing through the cadmium telluride/CMT interface unaffected. The highlighted grain 2 in Figure 9.3 shows a twin boundary extending from the cadmium telluride layer to the top of the CMT similar to results seen in TEM image in Figure 9.1. The map in Figure 9.3 shows the CMT layer has grown epitaxially across the whole area.

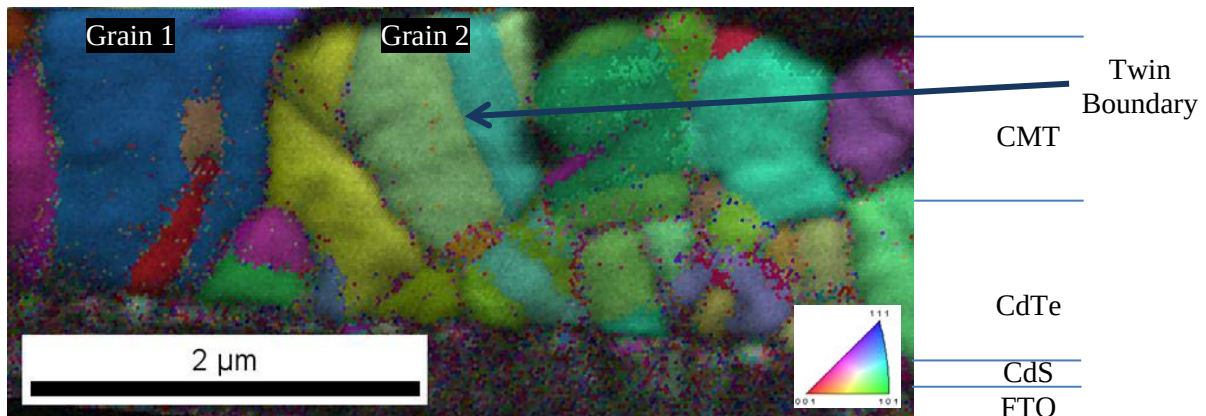


Figure 9.3 – A T-EBSD inverse pole figure map of initial CMT deposition of 900 nm onto a cadmium telluride cell

From these results there is clear evidence that the CMT layer is growing epitaxially onto the underlying cadmium telluride. This is an encouraging result for a working electron reflector layer as an introduction of a discontinuity will cause recombination, an effect which the electron reflector has been reported to reduce. Cadmium magnesium telluride has a cubic crystal structure the same as cadmium telluride with little difference in lattice spacing, which is the reason why it can grow epitaxially onto the cadmium telluride.

9.4 Effect of Magnesium Concentration on CMT

9.4.1 Low Magnesium Containing CMT Electron Reflector

Varying the concentration of magnesium in the CMT layer will ultimately change the band-gap of the layer. This provides the opportunity to tune the band gap to a desired value. In this work a band gap of 1.8 eV is required for the film to function as an electron reflector. Three samples of varying magnesium concentration were studied to see the effect on the microstructure and behaviour of the layers using TEM and STEM/EDX.

Figure 9.4 shows a BF-TEM image. There is some indication of epitaxial growth of the CMT on the cadmium telluride as grain boundaries continue from the cadmium telluride into the CMT. As these samples are not cadmium chloride treated, the cadmium telluride grains possess a high density of defects (stacking faults and twins) as shown in Chapter 6. These defects can be seen to continue from into the CMT from the underlying layer. As the concentration of magnesium is low, little difference is seen between the cadmium telluride and CMT. High angle annular dark field (HAADF) imaging can be used to more clearly distinguish between the layers.

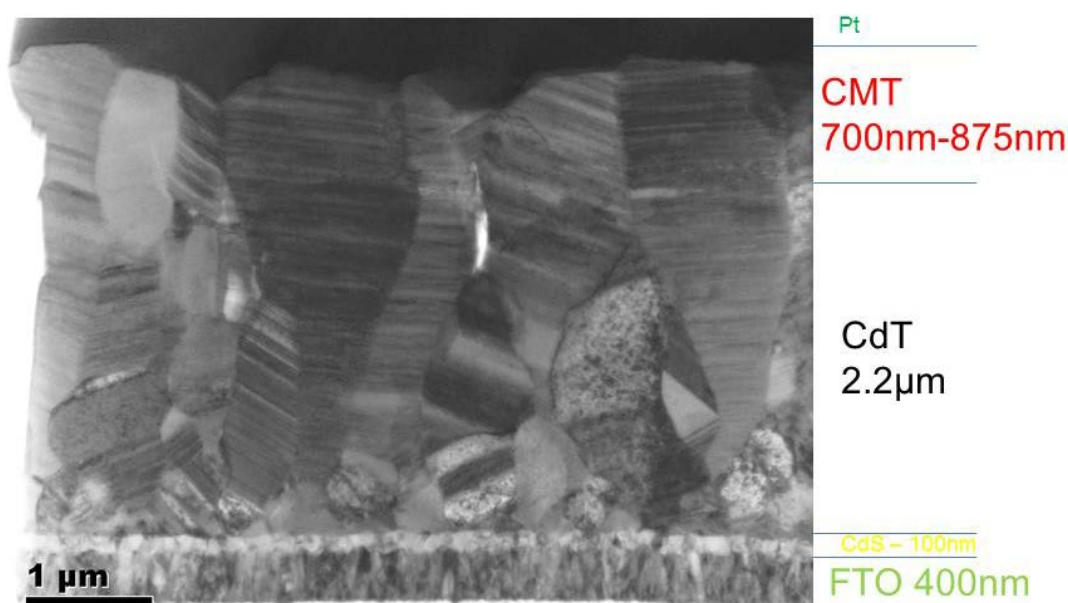


Figure 9.4 - A BF-TEM micrograph of low concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell

Figure 9.5 shows a HAADF image which gives compositional contrast, and corresponding chemical maps. From the HAADF image it can be seen that the CMT is approximately 750 nm thick and is conformal on the cadmium telluride layer. Therefore the CMT layer appears slightly darker than the cadmium telluride. A darker region extends from the cadmium telluride to the CMT; the chemical maps indicate that it is cadmium deficient and magnesium

rich. The grains in the CMT layer do appear to have varying concentrations of magnesium and cadmium.

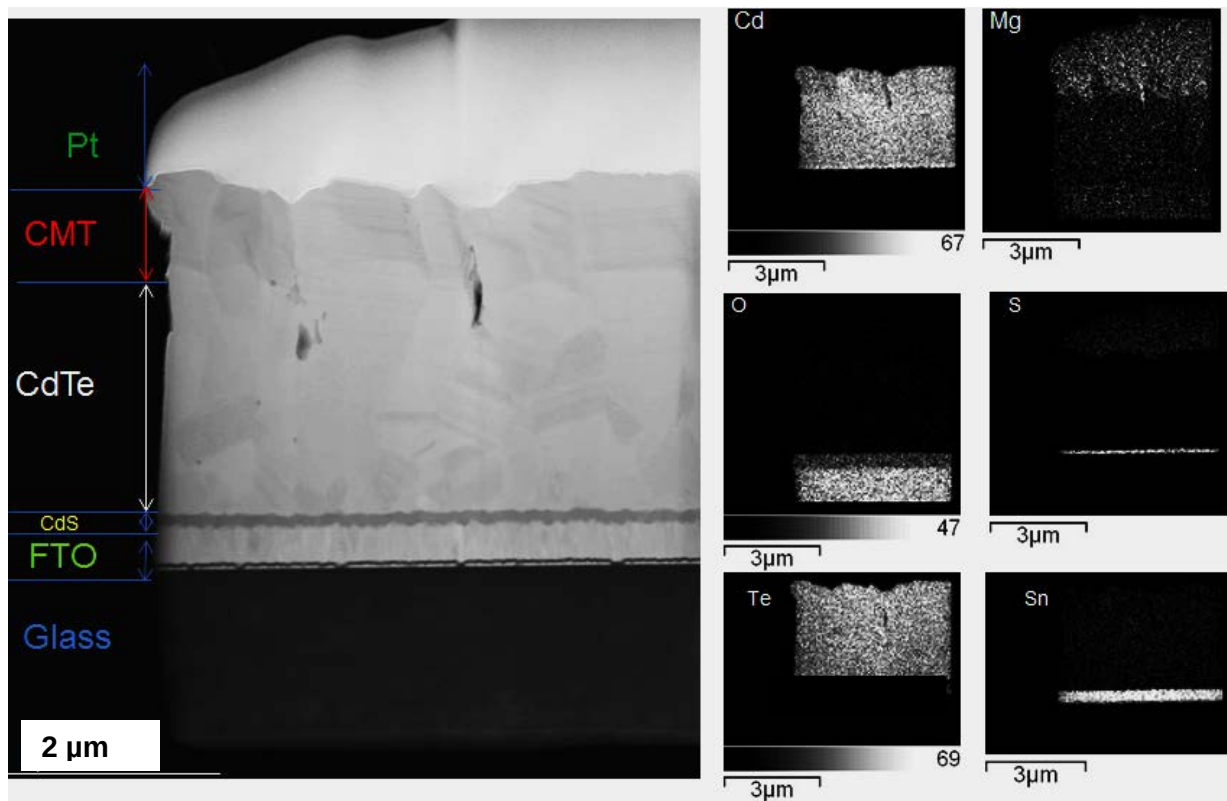


Figure 9.5- A HAADF STEM micrograph of low concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell and corresponding STEM/EDX chemical maps

Figure 9.6 shows a higher magnification HAADF STEM image of the same low concentration magnesium containing CMT deposition as in Figure 9.5 and corresponding STEM/EDX chemical maps. The tellurium and oxygen maps in Figure 9.6 show no variation throughout the CMT and cadmium telluride. The cadmium chemical map however does show variation in the concentration from grain to grain, which corresponds inversely with changes in the magnesium concentration.

Figure 9.6 also displays a line profile horizontally through the CMT layer. The tellurium shown in green is constant and then decreases towards the left end of the sample, due to the inversed thinning of the TEM sample edge. The cadmium and magnesium concentrations fluctuate. As the cadmium concentration increases the magnesium is observed to decrease and vice-versa. This suggests the magnesium is displacing the cadmium.

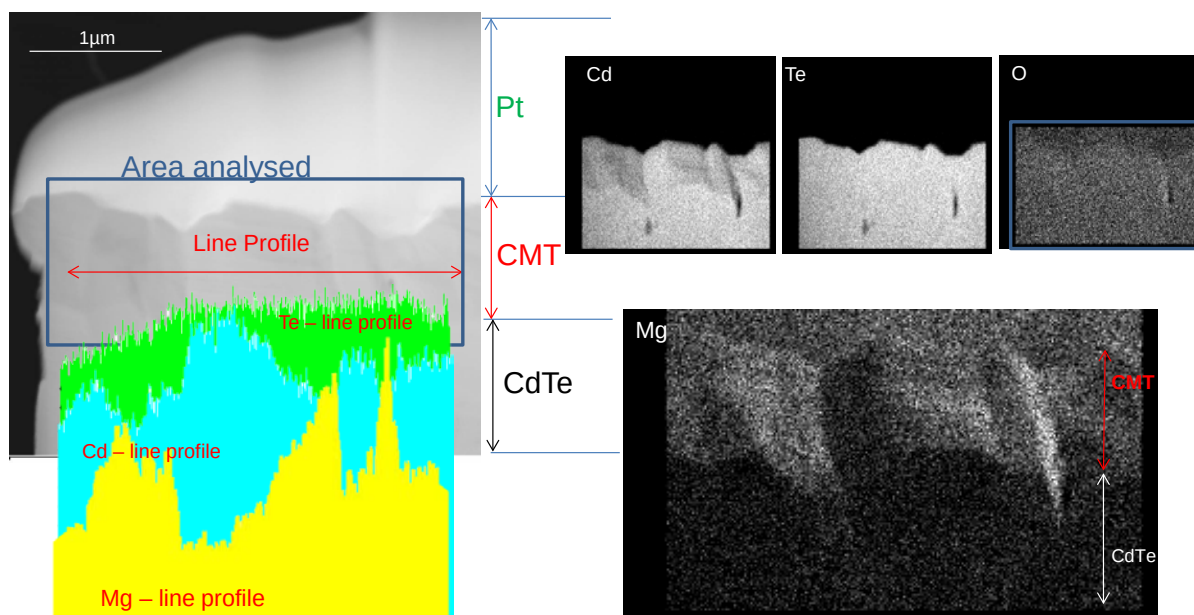


Figure 9.6 - A HAADF STEM image of low concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell and corresponding STEM/EDX chemical maps and a horizontal line scan.

The chemical mapping has shown that the CMT has a non-homogenous chemical composition. To calculate the amount of magnesium in the CMT, point chemical analysis was carried out.

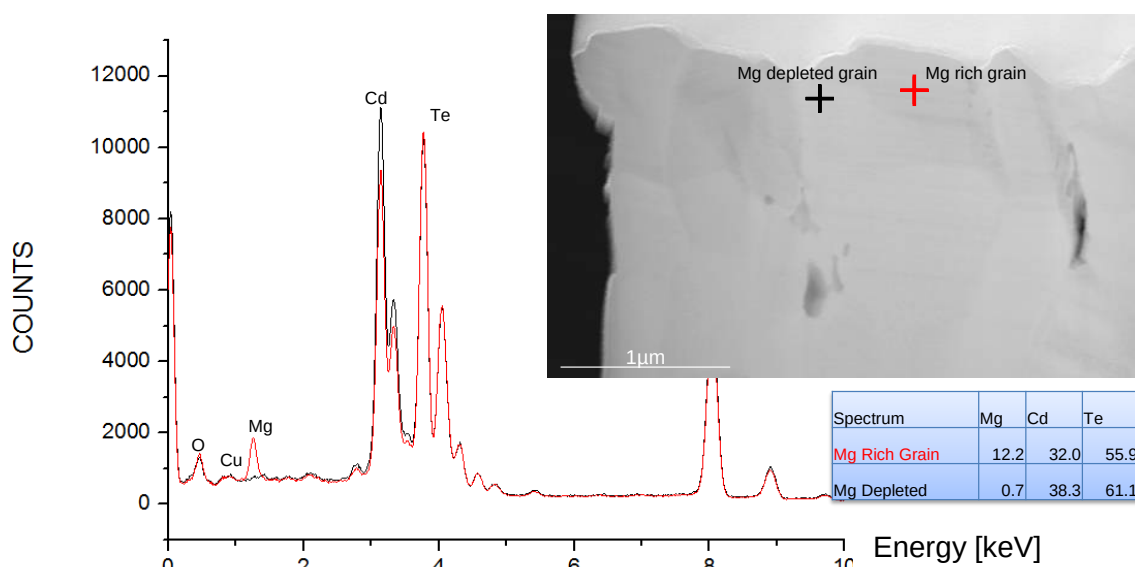


Figure 9.7 – EDX point chemical analysis of two adjacent grains in the CMT layer of the low concentration magnesium sample

Figure 9.7 shows EDX point chemical analysis of two adjacent grains in the CMT layer of the low concentration magnesium sample. The grain which is seen in the chemical maps indicates a higher concentration of magnesium and shows ~12 at%. However the grain which is directly beside this has less than 1 at% magnesium concentration. This will ultimately be

detrimental to the performance of the electron reflector as a variation in the concentration of magnesium will lead to a variation in the band-gap of the layer.

Figure 9.8 shows EDX point chemical analysis of a magnesium rich region in the CMT layer and a point analysis just below the cadmium telluride/CMT interface of the low concentration magnesium sample. The magnesium rich area shows ~17 at% magnesium whereas the area just below the CMT layer shows no magnesium. This suggests that the magnesium is not diffusing into the cadmium telluride grains.

To conclude, the CMT layer is non homogeneous in chemical composition, with a variation in magnesium and cadmium from grain to grain. In addition regions form at grain boundaries which are magnesium rich of up to 17 at%. However the CMT layer has grown epitaxially on an untreated cadmium telluride layer.

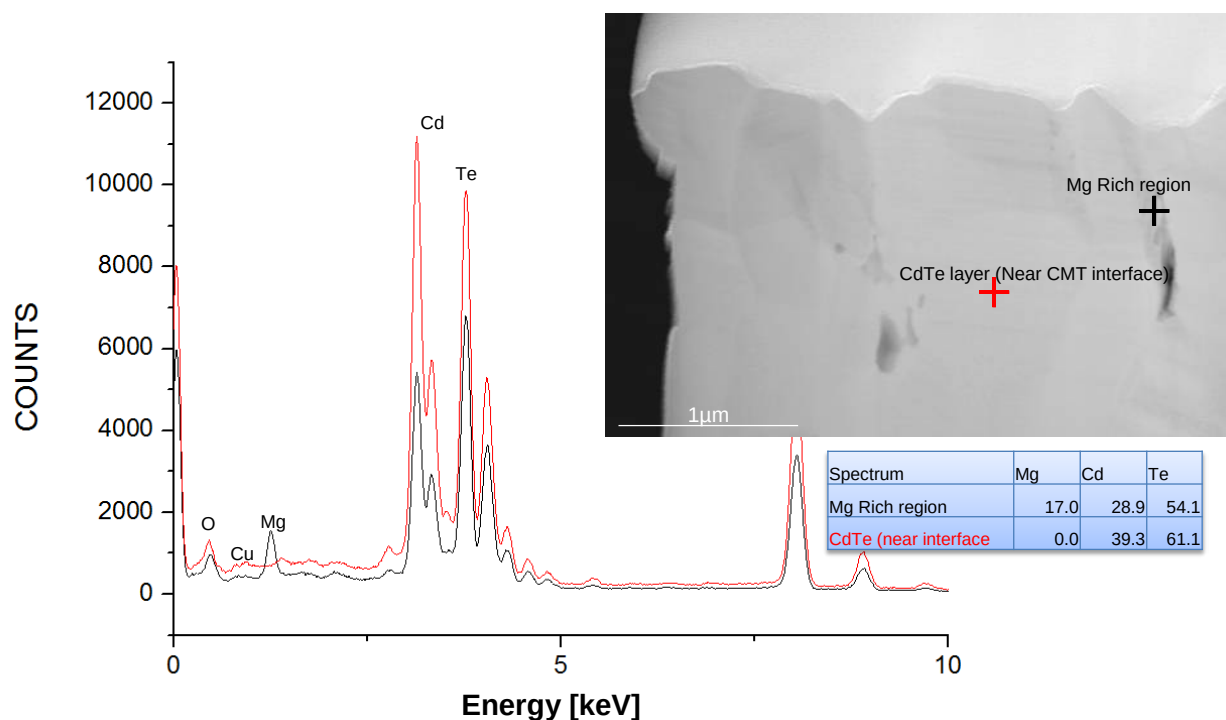


Figure 9.8 - EDX point chemical analysis of a Mg rich region in the CMT layer and a point analysis just below the cadmium telluride/CMT interface of the low magnesium concentration sample

9.4.2 Medium Magnesium Containing CMT Electron Reflector

As the concentration of magnesium is directly linked to the band gap of the electron reflector, tuning the band gap to the optimum (~1.9 eV) should be achievable by this method. The low magnesium concentration sample showed discontinuity in the distribution of magnesium, so the effect of increasing its concentration was investigated. A chemical distribution map of the cell is shown in Figure 9.9. From the maps the CMT layer appears more homogeneous

chemically. However the maps clearly indicate a magnesium rich region, which again is formed at a grain boundary. This increase in magnesium also corresponds to a depletion of cadmium.

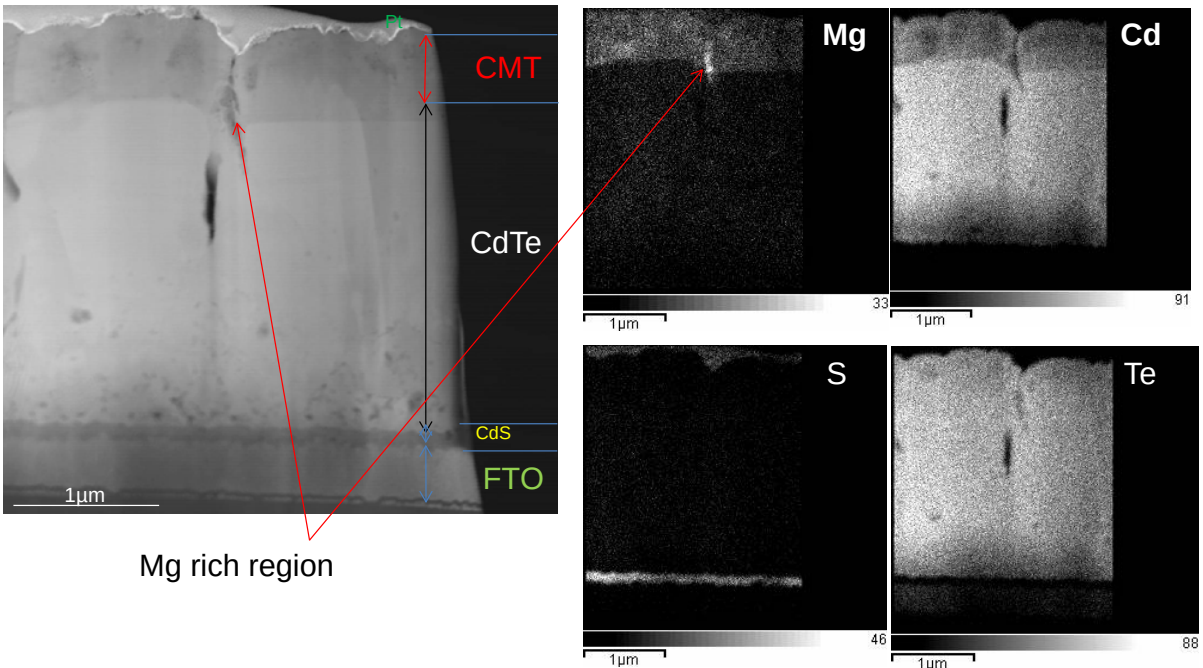


Figure 9.9 - A HAADF STEM micrograph of medium concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell and corresponding STEM/EDX chemical maps

Figure 9.10 shows EDX point chemical analysis of a region in the CMT layer and a point just below the cadmium telluride/CMT interface of the medium concentration magnesium sample. The CMT region has a magnesium concentration of ~1.9 at%, just below the CMT interface the cadmium telluride has ~0.1 at% of magnesium suggesting some intermixing between the CMT and the cadmium telluride.

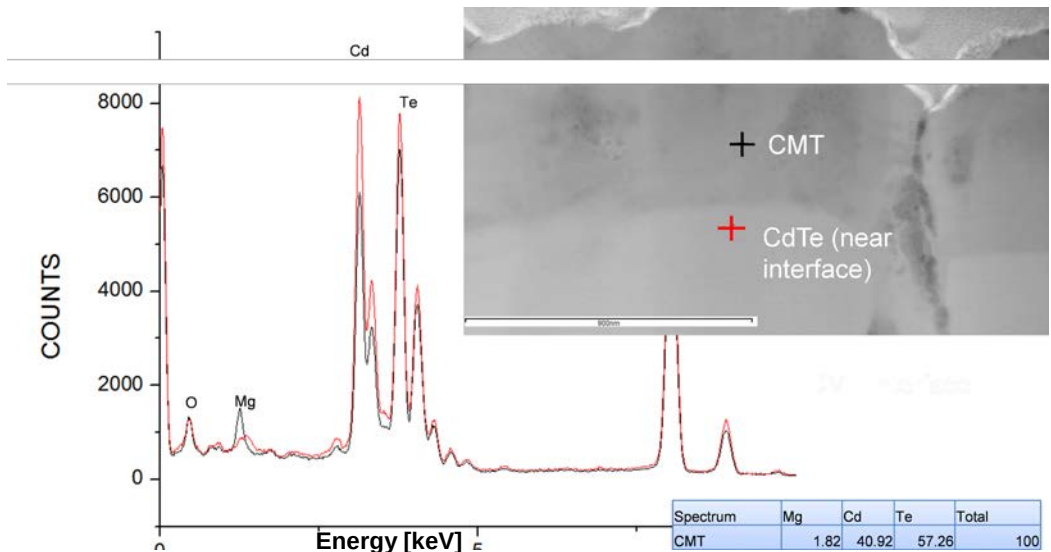


Figure 9.10 - EDX point chemical analysis of a region in the CMT layer and a point just below the cadmium telluride/CMT interface of the medium concentration magnesium sample

9.4.3 High Magnesium Containing CMT Electron Reflector

Figure 9.11 shows a bright field TEM image of high concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell. This indicates regions of varying composition at every CMT grain boundary, as the corresponding dark-field STEM image shows some voids and lighter elemental regions. Figure 9.12 displays a HAADF STEM micrograph of high concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell and corresponding STEM/EDX chemical maps. The maps show build-up of magnesium at every CMT grain boundary; this does not extend into the cadmium telluride. However the grain boundary areas are depleted of cadmium and contain an oxide. This is most likely magnesium oxide (MgO).

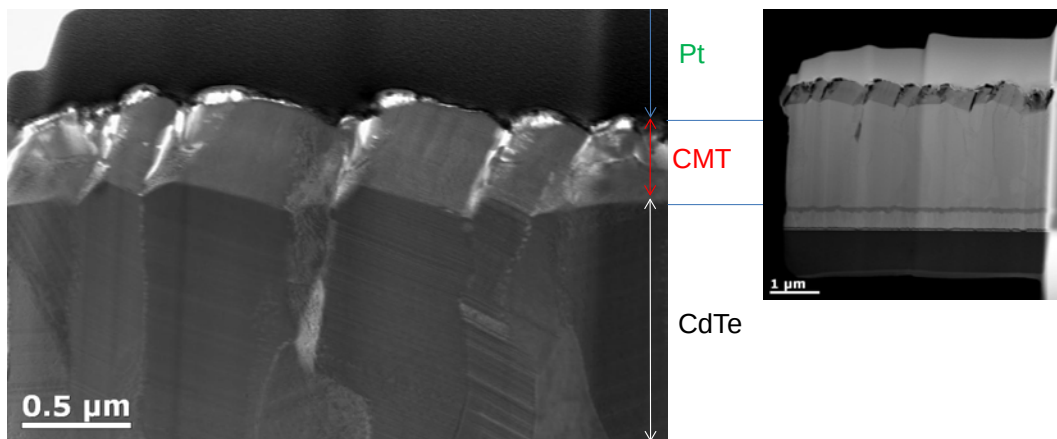


Figure 9.11- BF and DF STEM micrographs of high concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell

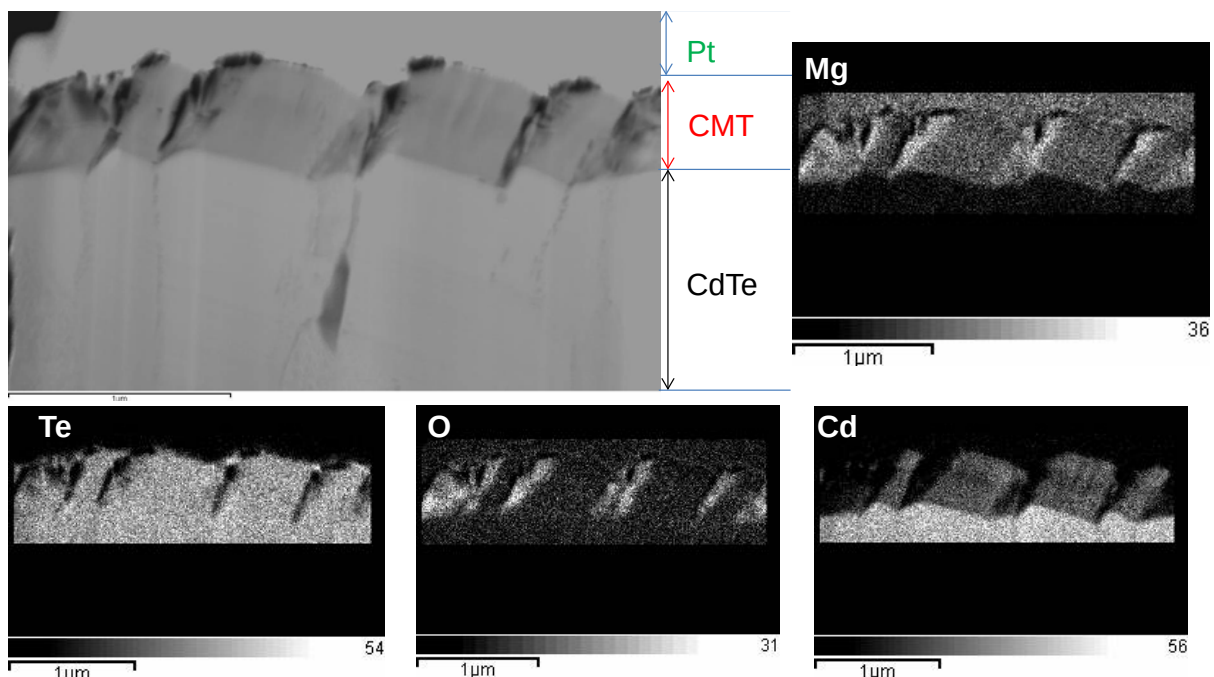


Figure 9.12 - A HAADF STEM micrograph of high concentration magnesium containing CMT deposition of 750 nm onto an untreated cadmium telluride cell and corresponding STEM/EDX chemical maps

Figure 9.13 shows EDX point chemical analysis of a region in the CMT layer and a point just below the cadmium telluride/CMT interface of the medium concentration magnesium sample. No magnesium is seen just below the cadmium telluride/CMT interface, indicating no intermixing. The CMT contains a high amount of magnesium at ~30 at%.

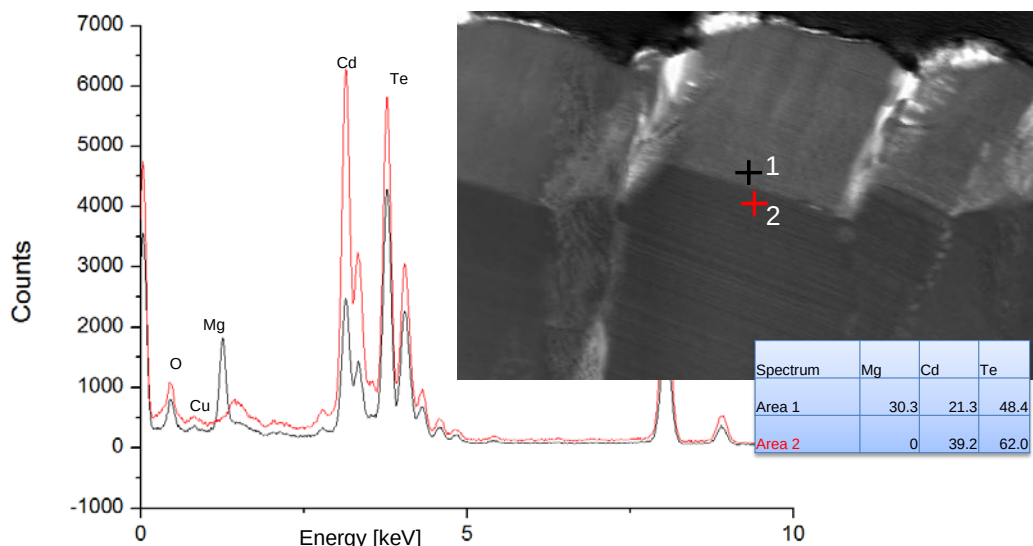


Figure 9.13 - EDX point chemical analysis of a region in the CMT layer and a point just below the cadmium telluride/CMT interface of the medium concentration magnesium sample

In conclusion the content of magnesium can be varied; however segregation of magnesium to CMT grain boundaries is likely with an increase in concentration. Oxidation of this area is likely if the amount of magnesium is further increased.

9.5 Effect of the Cadmium Chloride Treatment on CMT

As the cadmium telluride and possibly the CMT will need to be cadmium chloride treated to remove linear defects (mainly stacking faults) from the grains, the behaviour of the CMT during the treatment is paramount. Therefore this section investigates a post CMT deposition cadmium chloride treatment. Two samples before and after the pre-optimized were analysed.

The untreated cell with 200 nm CMT deposited onto the cadmium telluride grain is shown in a HAADF image in Figure 9.14. The CMT looks fairly conformal and evenly distributed over the surface. Some stacking faults can be seen within the cadmium telluride layer with some extending into the CMT layer. Therefore the CMT will need to be cadmium chloride treated as well to remove any stacking faults within it. In Chapter 6 it has been observed that the treatment causes chlorine diffusion down grain boundaries and diffusion of the cadmium sulphide into the cadmium telluride grains. The effect of the cadmium chloride treatment is not known, therefore STEM/EDX chemical distribution maps may provide an insight into any changes to the CMT layer during the treatment.

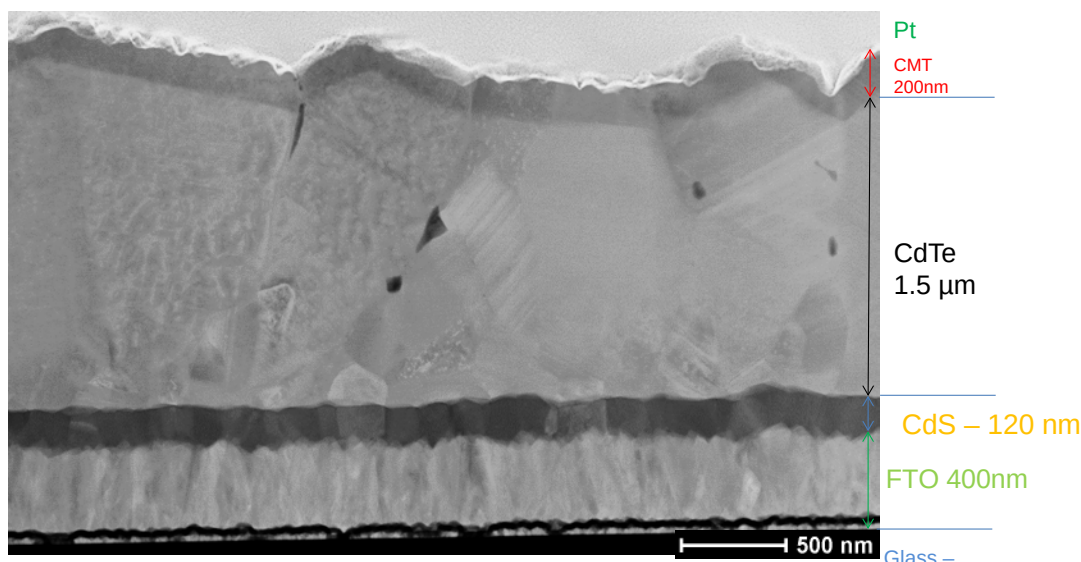


Figure 9.14 - A HAADF STEM image of CMT deposition of 200 nm onto an untreated cadmium telluride cell

Figure 9.15 displays a HAADF STEM image of CMT deposition onto an untreated cadmium telluride cell and corresponding EDX chemical maps. The maps show the concentration of magnesium varying across the layer, but no areas of increase concentration can be seen which protrude into the grains below as seen previously.

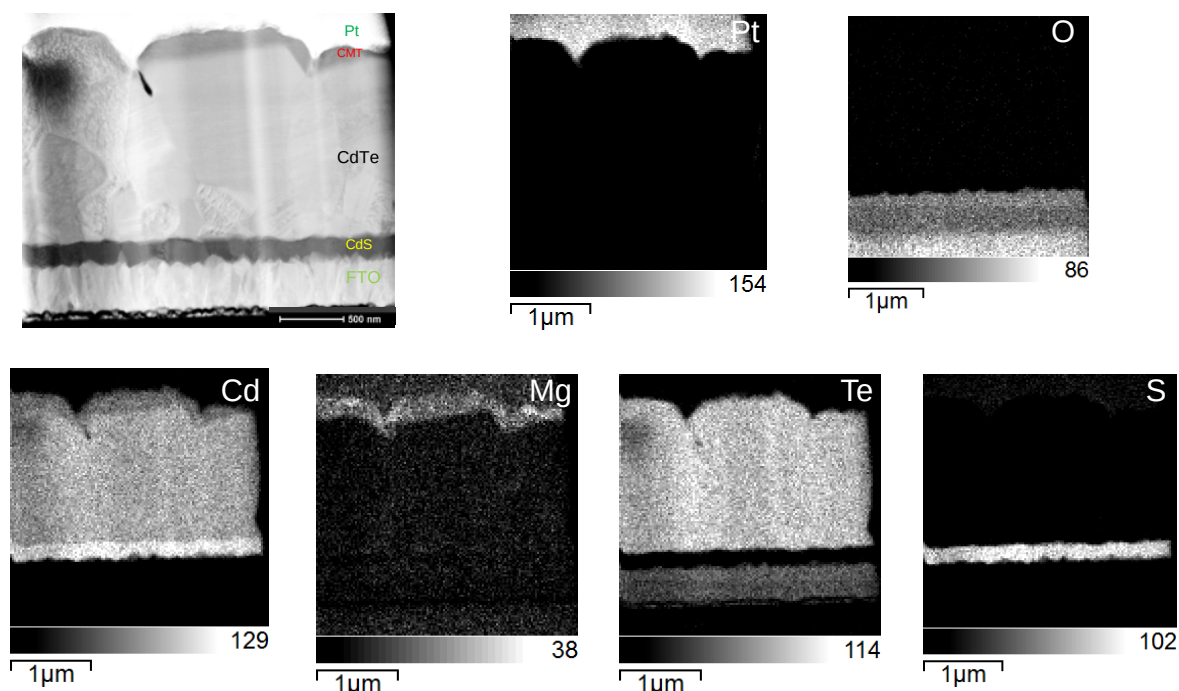


Figure 9.15 - A HAADF STEM micrograph of medium concentration magnesium containing CMT deposition of 200 nm onto an untreated cadmium telluride cell and corresponding EDX chemical maps

Figure 9.16 shows a HAADF STEM image of CMT deposition of 200 nm onto a cadmium telluride cell post-treated with cadmium chloride. It reveals that the CMT layer has almost totally migrated from the top of the cadmium telluride. A new layer has formed between the cadmium sulphide and the transparent conducting oxide. As well as the formation of a large

agglomeration of low atomic mass compound at the cadmium sulphide region. The cadmium telluride grains have recrystallized into much larger than usual through-thickness grains with a few twin boundaries passing through them from grain boundary to grain boundary. The cadmium telluride grains are approximately $1\ \mu\text{m} - 2\ \mu\text{m}$ in diameter which is considerably larger than a normally post-treated cell. This is possibly one of the effects of the magnesium on the recrystallization of the cadmium telluride.

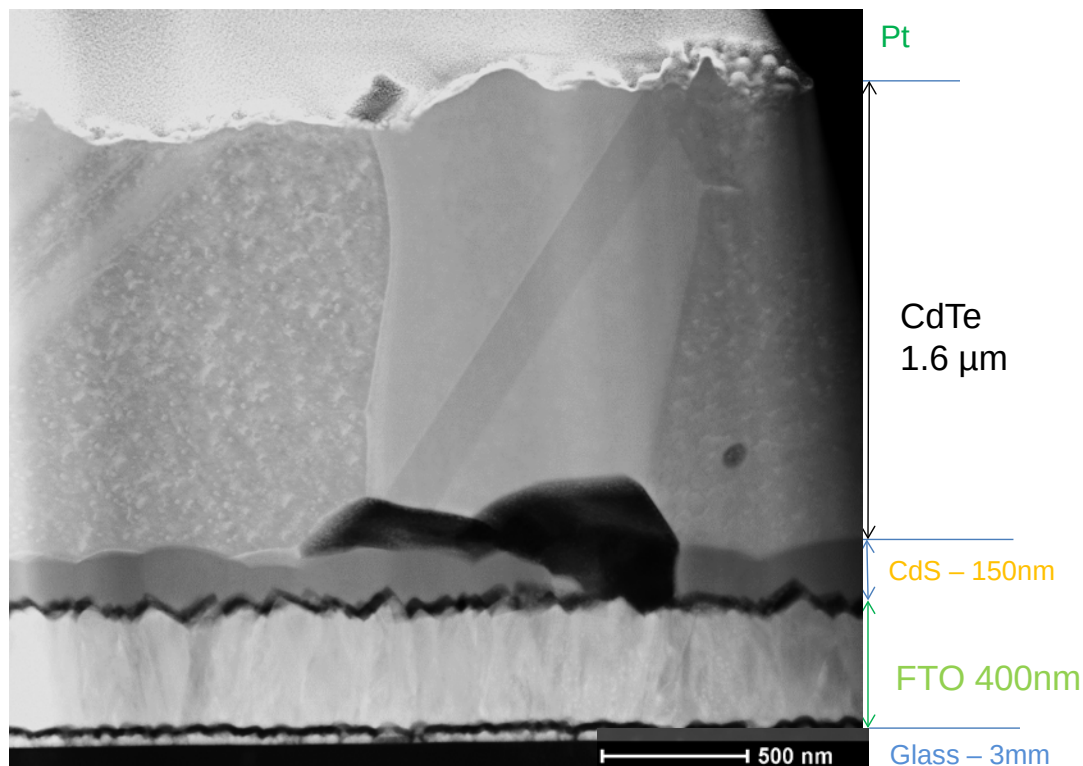


Figure 9.16- A HAADF STEM micrograph of CMT deposition of 200 nm onto a cadmium telluride cell post-treated with cadmium chloride

Figure 9.17 displays a HAADF STEM image of CMT deposited onto a cadmium telluride cell which was then post-treated with cadmium chloride. The corresponding EDX chemical distribution maps show the CMT layer is no longer present and only a small high magnesium containing particle is left on the top of the cadmium telluride layer. The large region with the low atomic number contains a large amount of chlorine and some cadmium, which has formed just above the cadmium sulphide layer at a cadmium telluride grain boundary. The layer formed below the cadmium sulphide also contains a large amount chlorine. The CMT layer appears to have increased the permeability of the cadmium telluride and cadmium sulphide and allowed more chlorine to diffuse through.

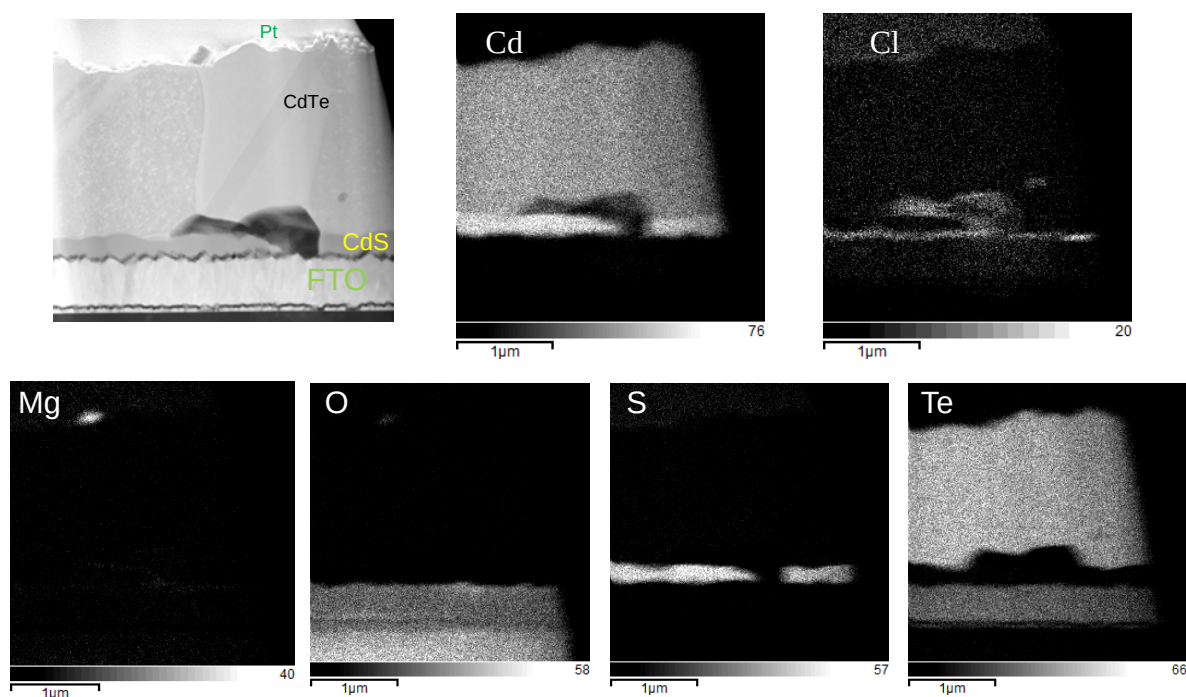


Figure 9.17- A HAADF STEM image of CMT deposition of 200 nm onto a cadmium telluride cell post-treated with cadmium chloride and corresponding STEM/EDX chemical maps

Figure 9.18 shows a HAADF TEM micrograph of the cadmium telluride/cadmium sulphide interface of the post-CMT deposited cadmium chloride treated cell. From the EDX chemical distribution maps the layer containing chlorine under the cadmium sulphide also contains magnesium as does the large agglomeration above the cadmium sulphide. This shows that the CMT layer is diffusing along with the chlorine. Although the initial CMT deposition before the treatment looked more homogenous than previous samples due to a faster deposition rate, the layer has proved to be unstable during the annealing cadmium chloride treatment.

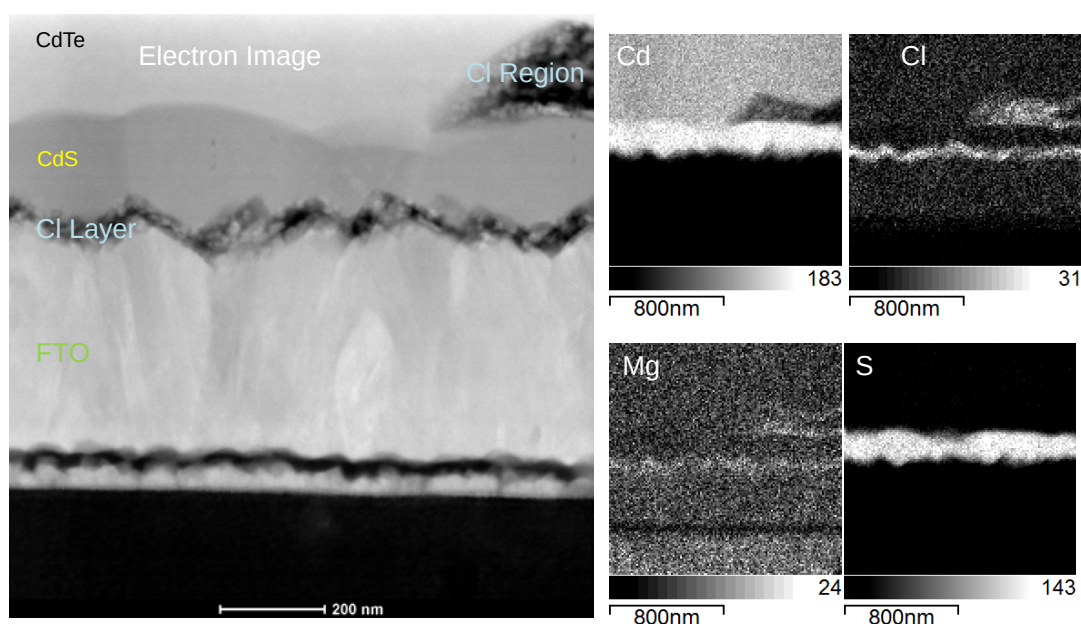


Figure 9.18- A HAADF STEM image of CMT deposition of 200 nm onto a cadmium telluride cell post-treated with cadmium chloride corresponding STEM/EDX chemical maps of the cadmium sulphide interface

9.6 Effect of Deposition Temperature on CMT Electron Reflector Thin Film

The CMT has been deposited at two temperatures, 400°C and 470 °C. Figure 9.19 shows SEM surface images of the CMT deposited onto the cadmium telluride cells. The CMT deposited at 400°C shows some areas which have a less homogenous growth. This is shown by the build-up of material at certain points and less in others.

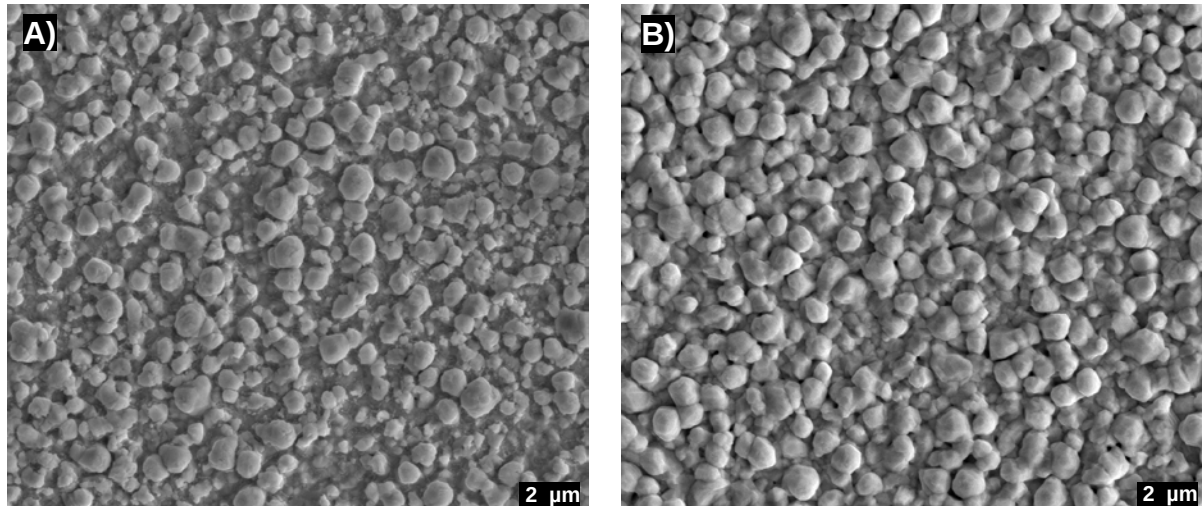


Figure 9.19 – Inlens SEM surface images of CMT deposited at a) 400°C and b) 470°C

Figure 9.20 shows a BF-STEM image of the sample deposited at 400°C. From the image the surface shows similar findings to the SEM images in Figure 9.19, which is that the CMT has formed only in certain regions leaving large gaps in the layer. No signs of magnesium/chlorine diffusion to the cadmium sulphide/cadmium telluride interface is observed as shown in previous samples.

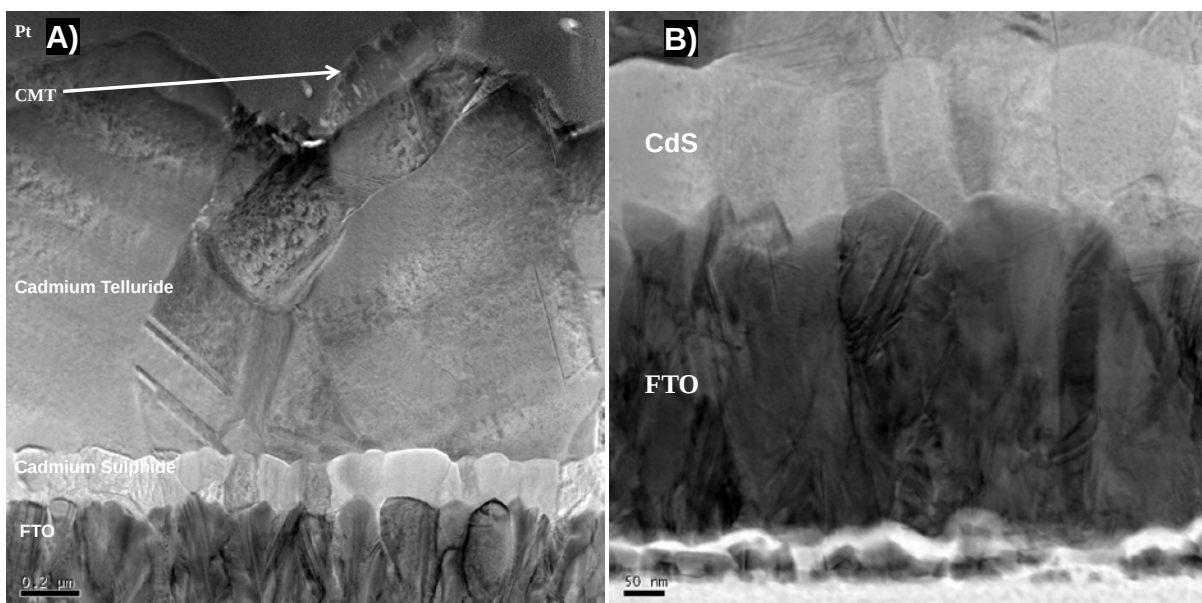


Figure 9.20 - BF-STEM images of a) CMT deposition at 400°C onto a cadmium telluride cell and b) higher magnification image of the cadmium telluride/cadmium sulphide interface

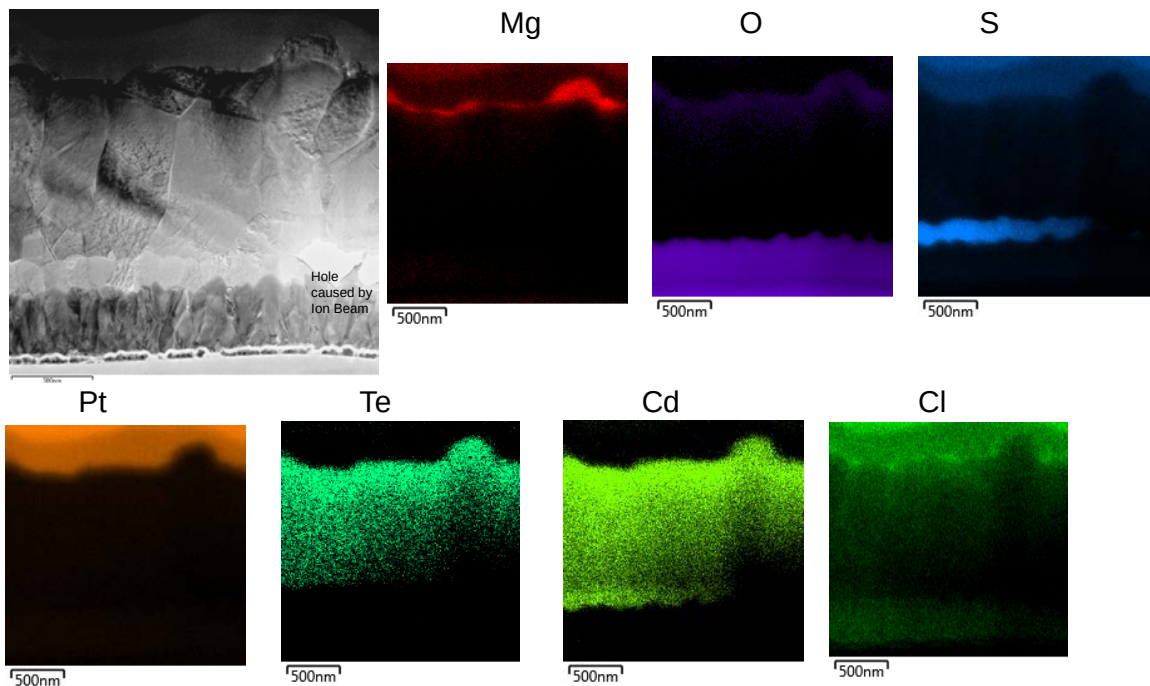


Figure 9.21 - A BF-STEM image of CMT deposition at 400°C onto a cadmium telluride cell and corresponding STEM/EDX chemical maps

Figure 9.21 shows a BF-STEM image with corresponding EDX chemical distribution maps. The maps show that the magnesium has a non-homogenous thickness in some areas with a large build-up and in some areas with only a thin layer. The oxygen map also shows oxidation of the CMT area. Chlorine appears at the CMT/cadmium telluride interface in regions with less CMT coverage. Figure 9.22 shows EDX spectra of areas within the CMT region and within the bulk cadmium telluride. The spectra from the CMT area shows ~4 at% magnesium and no magnesium is detected within the cadmium telluride layer. The CMT region contains less than 1 at% oxygen, although measuring small amounts of light elements in multicomponent systems quantitatively using EDX in TEM is not possible.

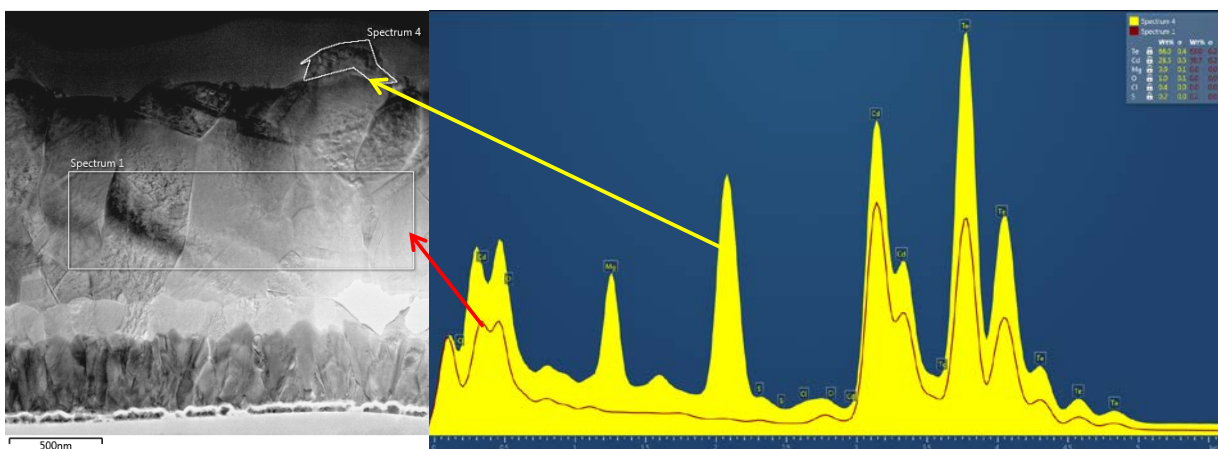


Figure 9.22- A BF-STEM image of CMT deposition at 400°C onto a cadmium telluride cell and corresponding EDX spectra

Figure 9.23 shows a bright-Field TEM micrograph of CMT deposition at 400°C with corresponding STEM/EDX chemical maps another area of the sample. The CMT area appears to have more oxygen than the cadmium telluride surface. The chlorine at the surface is again in areas with less CMT thickness. From the chemical maps, chlorine is seen to be left over from the cadmium chloride treatment causing a non-homogenous coverage. Due to the chlorine residue on the surface, an oxide layer has formed between the cadmium telluride layer and CMT. The oxide is likely to be cadmium oxide forming due to the high temperature during the CMT deposition.

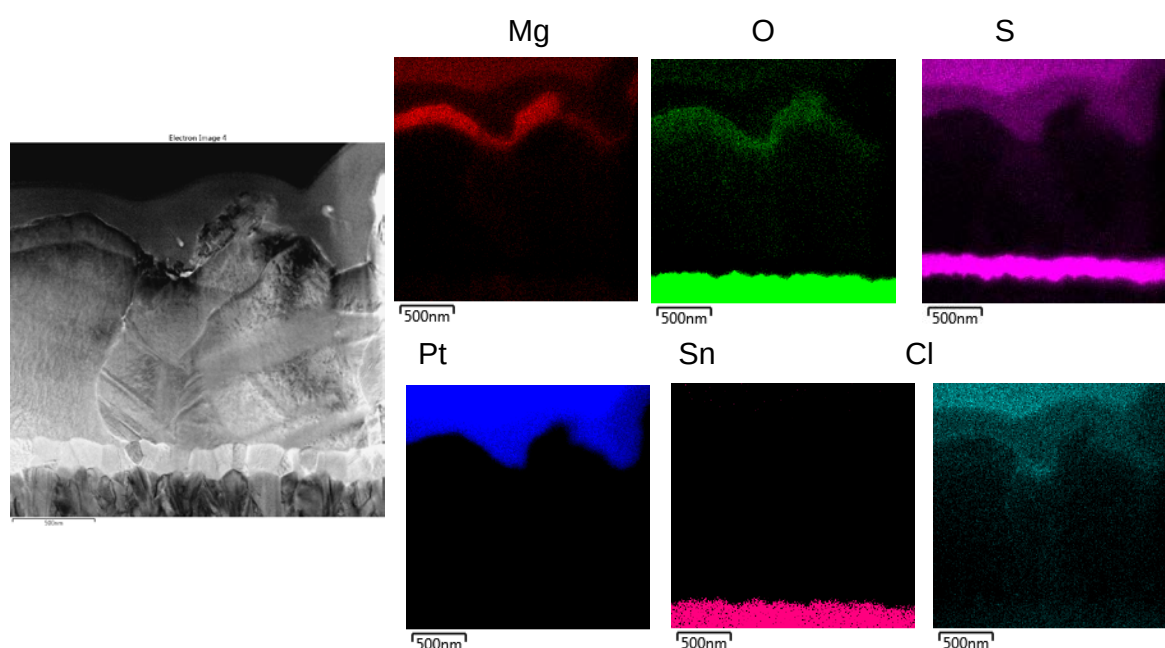


Figure 9.23 - A BF-STEM image of CMT deposition at 400°C onto a cadmium telluride cell and corresponding STEM/EDX chemical maps

Figure 9.24 and Figure 9.25 show bright field TEM images of the CMT sample deposition at 470°C. In Figure 9.24 twin defects are seen to pass from the cadmium telluride into the CMT unaffected by the interface between the two layers. As the cadmium telluride has been cadmium chloride treated prior to the CMT film depositing, no stacking faults are expected within the cadmium telluride grains. However the TEM image shown in Figure 9.25 indicates that a high density of stacking faults are present, in the top three grains. The reason for the stacking faults could either be due to the CMT deposition layer or the high temperature of the deposition. As no stacking faults are observed in the sample deposited at 400°C this would indicate that it is likely that the higher temperature causes stacking faults to re-appear in treated cadmium telluride grains. This reappearance of stacking faults also corresponds to a lower cell efficiency of 2.5% as shown in the JV data in Table 9.2.

Temperature of CMT deposition	Voc (mV)	Jsc (mA/cm ²)	Fill Factor %	Efficiency %
No CMT	791.2	21.2	65.1	10.9
400°C	779.4	20	65.9	10.3
470°C	615.6	13	31.6	2.5

Table 9.2 – JV data for cadmium telluride cells with samples with CMT deposited at different temperatures and a benchmark sample with no CMT

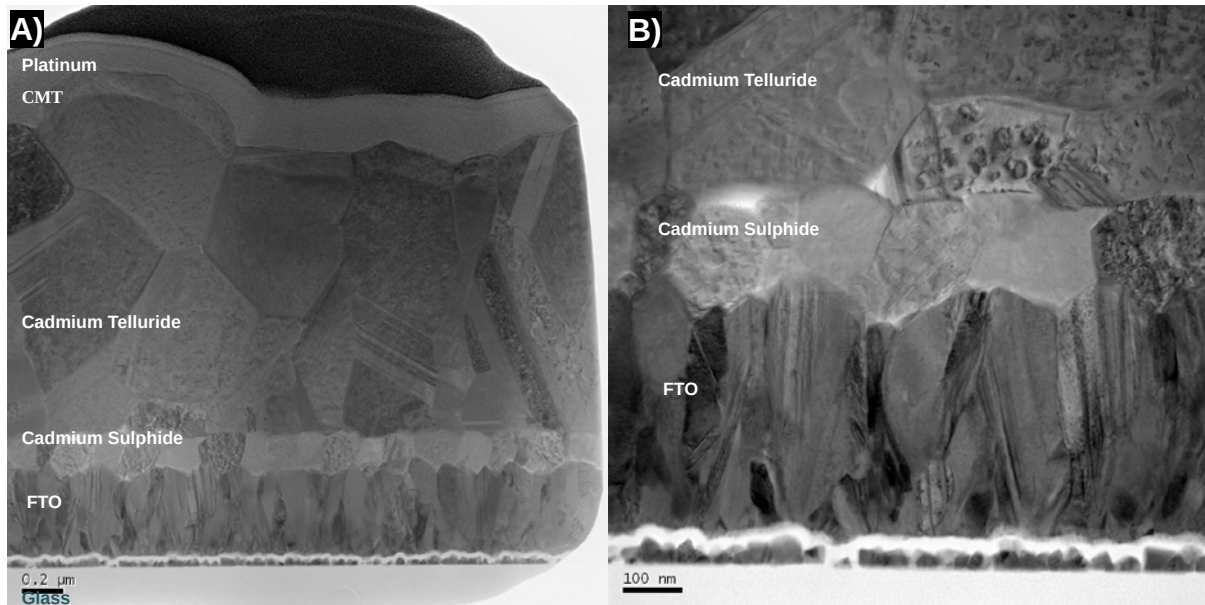


Figure 9.24 - BF-STEM images of a) CMT deposition at 470°C onto a cadmium telluride cell and b) corresponding cadmium telluride/cadmium sulphide interface

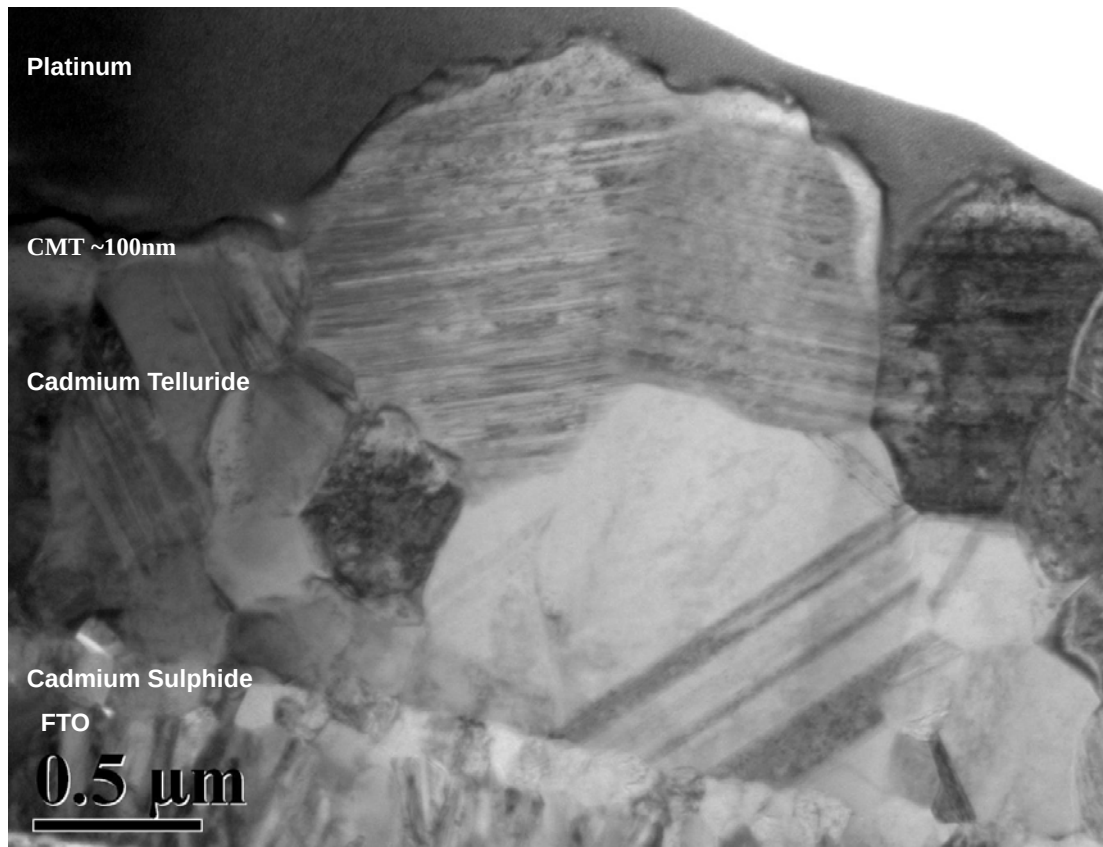


Figure 9.25 - A BF-TEM image of CMT deposition at 470°C onto a cadmium telluride cell

Figure 9.26 shows a HAADF TEM image of the cadmium telluride cell with the CMT deposited onto it. The CMT is observed to be uniformly thick and conformal. It indicates epitaxial growth as the grain boundaries of the cadmium telluride follow into the CMT layer. From the EDX chemical distribution maps in Figure 9.27 the concentration of magnesium is homogenous throughout the layer as well as the thickness. The oxygen map shows no oxidation of the CMT region and no chlorine. This is due to any chlorine residue on the surface of the cell evaporating off the cadmium telluride due to the higher temperature of the CMT deposition than the previous sample. As the chlorine evaporates off prior to deposition it does not cause oxidation or non-uniformity in the CMT film. Sulphur is observed to diffuse into the cadmium telluride grains from the cadmium sulphide which has been noted previously in Chapter 6. This occurrence is prior to the CMT deposition.



Figure 9.26 - A HAADF-STEM image of CMT deposition at 470°C onto a cadmium telluride cell

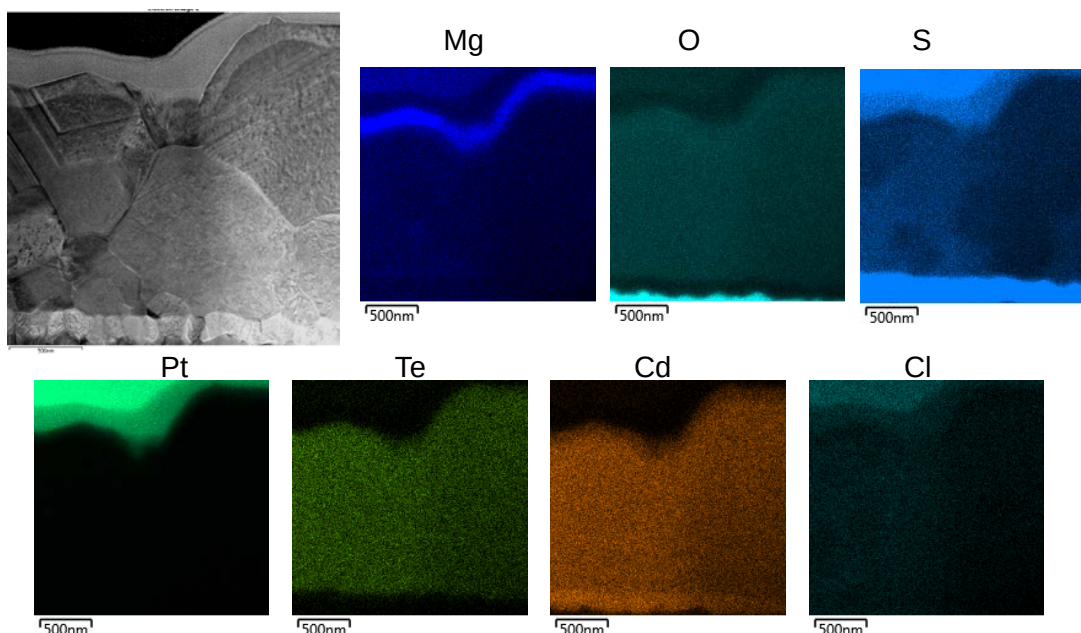


Figure 9.27 - A BF-STEM image of CMT deposition at 470°C and corresponding STEM/EDX chemical maps

In conclusion CMT films were deposited onto cadmium chloride treated cadmium telluride cells at different substrate temperatures 400°C and 470°C. At the lower temperature the CMT coverage is non-uniform in thickness. At the higher temperature the deposited CMT is observed to be uniformly thick. Although the CMT has good properties at higher temperatures the underlying cell is damaged due to the reappearance of stacking faults and therefore cell efficiency is much lower. To overcome this, the next section will look into a secondary cadmium chloride treatment after the CMT deposition.

9.7 The Effect of CMT and Cadmium Chloride on Cadmium Telluride Cells

This section will focus on the range of samples going from the untreated cadmium telluride layer to a cell with CMT and a second cadmium chloride treatment. The CMT in all cases were deposited at 470°C and as seen in the previous section stacking faults detrimental to the cells performance had been induced by the CMT and therefore a second treatment is needed to remove them again. Figure 9.28 shows SEM surface images for all the samples analyzed in this section with their corresponding treatments. The first two samples are the untreated cell cadmium telluride cell and the cadmium chloride treated cell, as both of these samples were examined extensively in Chapter 6 those results will not be repeated here. All the SEM images look to have a similar grain size of approximately 1 μm .

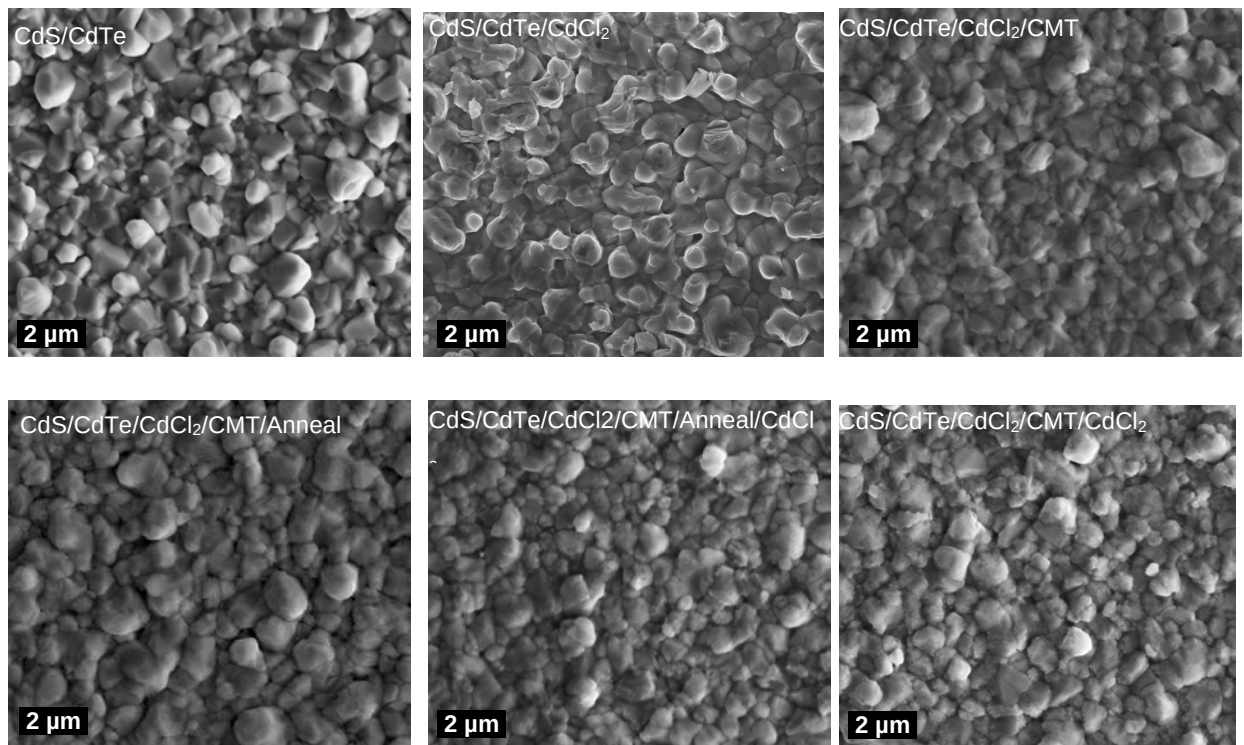


Figure 9.28 – Inlens SEM surface images of the different cells examined in this section

9.7.1 Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT

Figure 9.29 shows a TEM image of the cadmium chloride treated cadmium telluride cell with CMT deposited onto it. The CMT appears epitaxial as stacking faults can be seen to run from the cadmium telluride to the CMT. The CMT is conformal and homogenous in nature. The cadmium telluride/cadmium sulphide interface is unaffected by the deposition of CMT. Figure 9.30 shows a high resolution TEM image of the CMT/cadmium telluride interface. As the CMT and cadmium telluride both have a zinc-blende cubic crystal structure with a similar lattice parameter the interface is hard to see in TEM mode and therefore was located using the HAADF detector in the TEM. The image shows how clean and epitaxial the interface is with no discontinuity or defects at the interface. The stacking faults pass through the interface without being disrupted or deflected. The majority of stacking defects in cadmium telluride grains terminate at grain boundaries, as shown in Figure 9.30 where none of the stacking faults terminate at the interface, so it does not act as a grain boundary indicating there is epitaxial growth of the CMT.

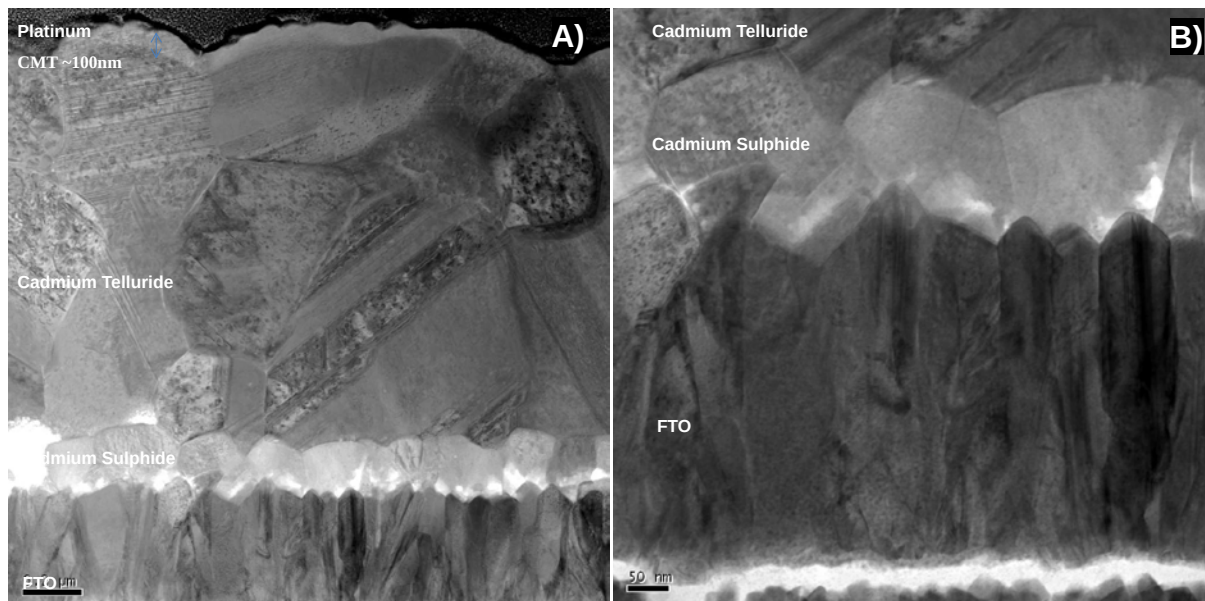


Figure 9.29 – BF-STEM images showing a) the whole cell with cadmium sulphide/cadmium telluride/cadmium chloride/CMT and b) the cadmium telluride/cadmium sulphide interface

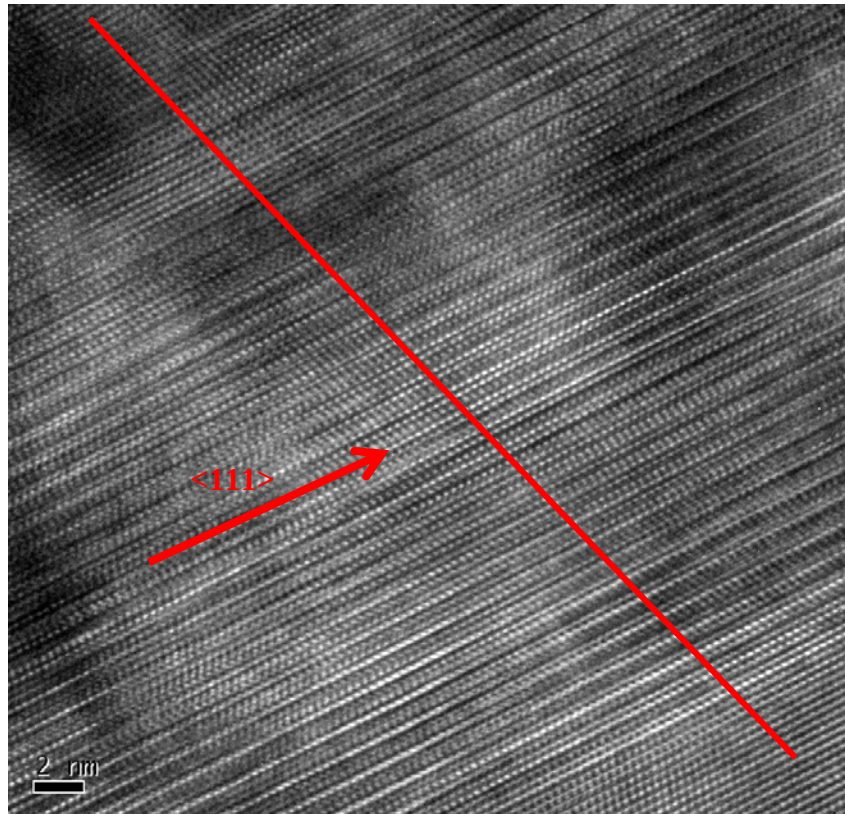


Figure 9.30- HRTEM lattice image of CMT/ cadmium telluride interface indicated by the red line, with a large amount of uninterrupted stacking faults passing through

Figure 9.31 shows a bright-field TEM image of the sample with CMT deposited onto the surface and corresponding EDX chemical distribution maps. The CMT thin film is conformal of the underlying cadmium telluride layer and the magnesium is homogenous throughout. No oxygen can be identified in the CMT. Some oxygen is located around a void at the cadmium sulphide interface.

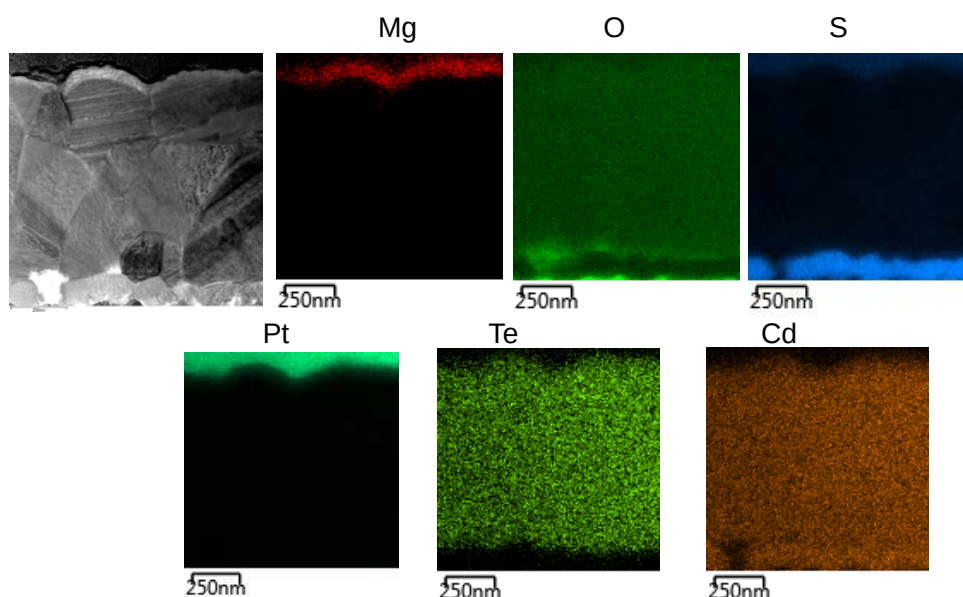


Figure 9.31 – BF-STEM image showing the sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT and corresponding EDX chemical distribution maps

9.7.2 Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT /Anneal

Figure 9.32 shows a bright field TEM image and a HAADF image of a sample configuration similar to Figure 9.29, except it has undergone a further post-CMT deposition anneal at 470°C. The CMT layer does not seem to have altered its morphology. From the HAADF image the CMT thin film appears similarly very conformal to the underlying cadmium telluride layer. This shows the CMT is not prone to diffusing or intermixing during high temperature anneals. Several voids are located within the cadmium sulphide layer. A large number of inter-granular defects remain within the cadmium telluride and CMT grains.

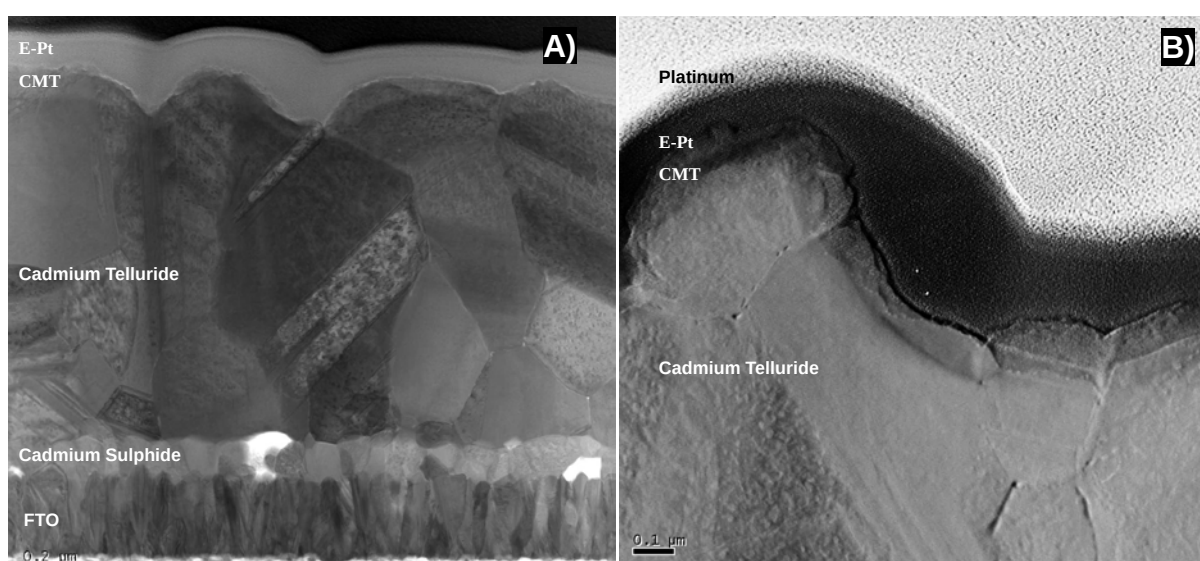


Figure 9.32 - BF-STEM image showing a) the whole sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT/Anneal and a) high magnification HAADF image of the CMT layer

The chemical distribution maps for the sample with the post CMT deposition anneal is shown in Figure 9.33. The post deposition anneal has not affected the magnesium in the CMT layer as the maps show a homogeneous continual coverage. No oxidation has been observed in the CMT layer.

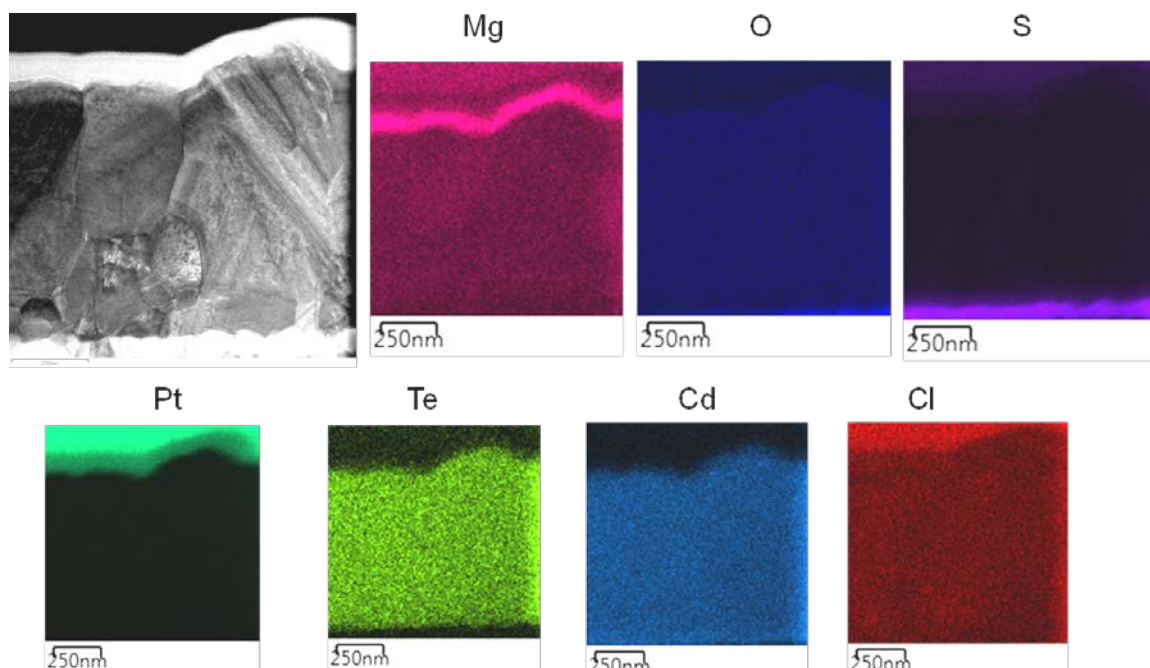


Figure 9.33 - BF-STEM image showing the sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT/anneal and corresponding EDX chemical distribution maps

9.7.3 Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT /Anneal/Cadmium Chloride

As seen in previous cadmium telluride cells which have CMT thin films deposited at 470°C to act as an electron reflector layer. The temperature has induced the reappearance of stacking faults in the underlying pre-cadmium chloride treated grains. As the initial cadmium chloride treatment removed the stacking faults from the cadmium telluride grains, a secondary treatment has been carried out after a 470°C anneal to re-remove the stacking faults.

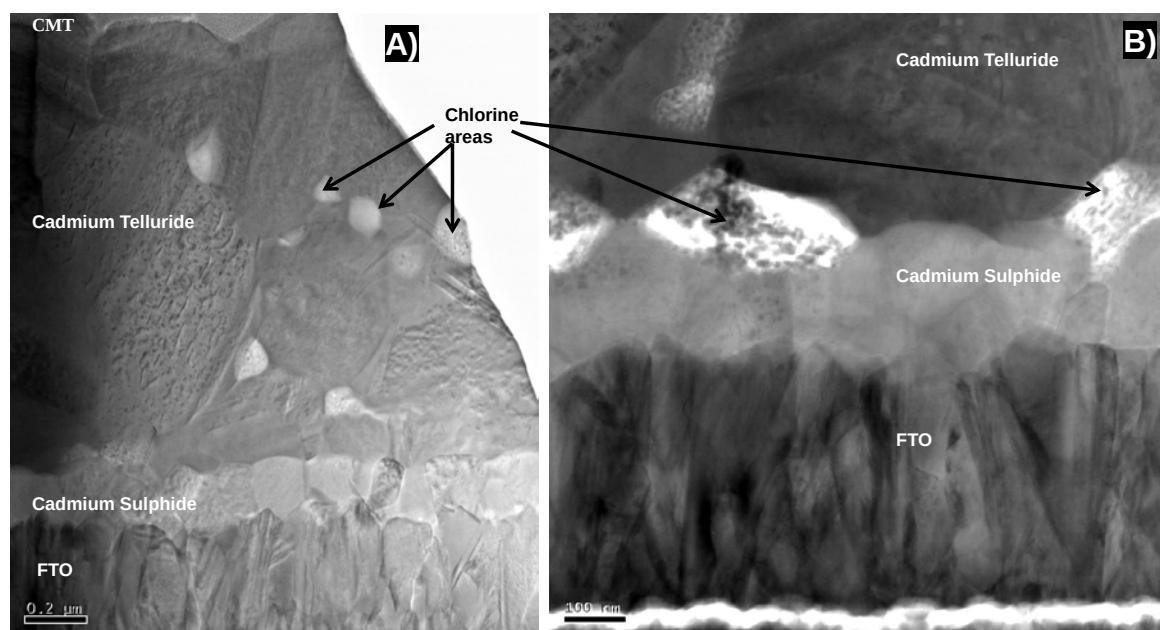


Figure 9.34 - BF-STEM image showing a) the whole sample with cadmium sulphide/cadmium telluride /cadmium chloride//CMT/Anneal/cadmium chloride and b) cadmium telluride/cadmium sulphide interface

Figure 9.34 and Figure 9.35 show bright field and HAADF STEM images of the secondary cadmium chloride treatment after the CMT deposition and a 470°C anneal. From the STEM images a large amount of chlorine regions are present not only at the cadmium sulphide interface but also at the cadmium telluride grain boundaries shown in Figure 9.36.

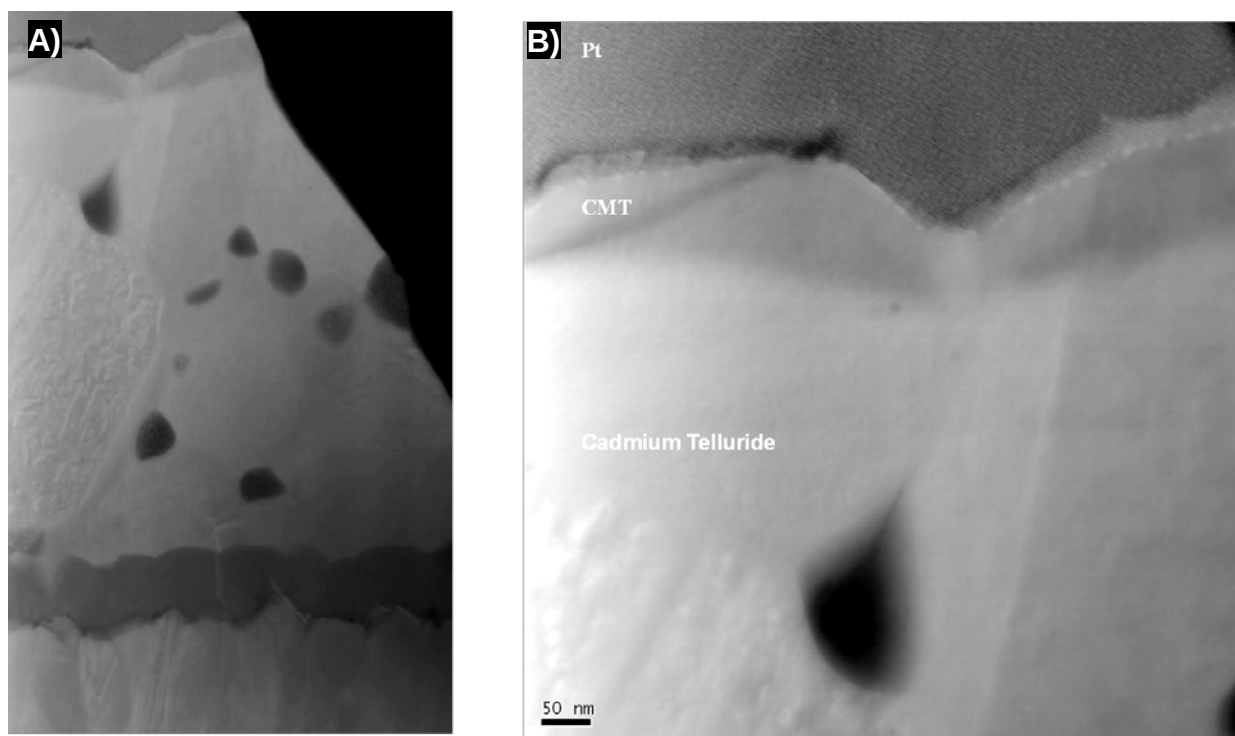


Figure 9.35 - HAADF STEM images showing a) the whole sample with cadmium sulphide/cadmium telluride/cadmium chloride/CMT/Anneal/cadmium chloride and b) cadmium telluride/cadmium sulphide interface

Figure 9.36 shows EDX chemical distribution maps of a cross section of the whole cell. The magnesium map shows a discontinuity mainly with a reduction of concentration around grain boundaries indicating magnesium is diffusing into the underlying cell during the secondary cadmium chloride treatment. The oxygen map shows a distinct layer at the top surface of the cadmium chloride treatment. It is a continuous oxide layer only at the surface of the CMT. The sulphur map suggests some sulphur from the cadmium sulphide layer has diffused into the cadmium telluride layer. The chlorine distribution map clearly shows distinct areas high in chlorine and low in tellurium. All the chlorine rich regions are seen to be adjacent to cadmium telluride grain boundaries. Chlorine areas are also seen to build up at the cadmium sulphide/cadmium telluride interface, suggesting that the cadmium sulphide acts as a boundary not allowing chlorine to diffuse through.

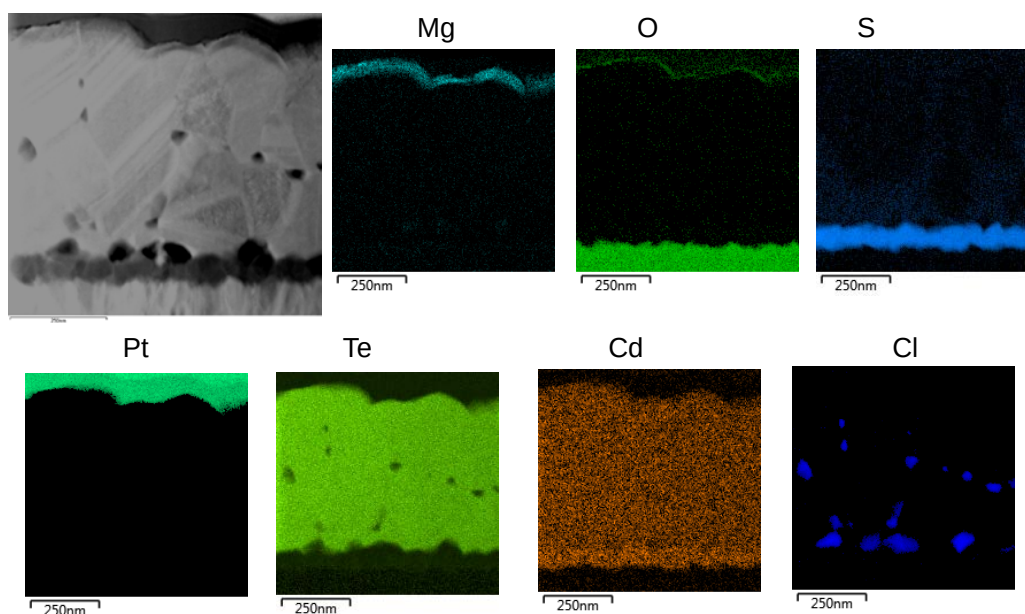


Figure 9.36 - HAADF STEM image showing the sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT/anneal/cadmium chloride and corresponding EDX chemical distribution maps

Figure 9.37 shows a higher magnification chemical distribution maps around the CMT layer. From the magnesium map it is clear that there is less magnesium concentrated at grain boundaries in the CMT. The most likely cause of the depletion in the magnesium in the grain boundary regions is, as the chlorine is diffusing down into the bulk of the cadmium telluride some of the magnesium is also diffusing. The oxide layer forming at the surface of the CMT is also seen to be not completely continuous in this map, with a reduction in similar areas to the magnesium indicating that the magnesium is oxidized to MgO. The sulphur map shows that sulphur is diffusing into the cadmium telluride during the cadmium chloride treatments and although at grain boundary regions the sulphur is not segregating to the boundaries but diffusing from the boundaries of the cadmium telluride grain into the bulk of the grains. The chlorine map clearly shows diffusion down the cadmium telluride grain boundaries from the surface during the treatment. It also forms regions ~25 nm in diameter rich in chlorine. This shows that the chlorine does not diffuse into cadmium telluride grains as the sulphur does but segregates only along the boundaries.

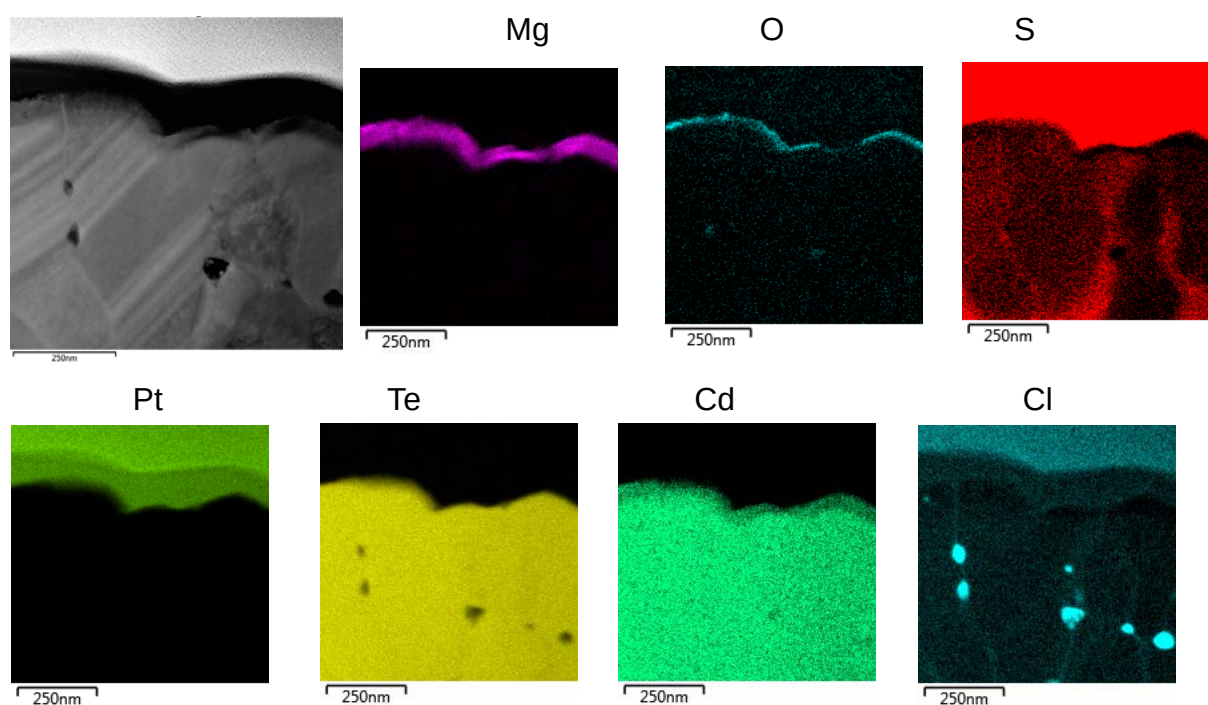


Figure 9.37- HAADF STEM image showing the sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT/Anneal/cadmium chloride and corresponding EDX chemical distribution maps

In conclusion the secondary cadmium chloride treatment appears to have removed the stacking faults but has introduced a large amount of impurities into the cell, including chlorine and formation of an oxide layer.

9.7.4 Analysis of Sample with Cadmium Sulphide/Cadmium Telluride/Cadmium Chloride/CMT /Cadmium Chloride

This sample has undergone the same secondary cadmium chloride treatment but without the anneal prior to this.

From Figure 9.38 which shows a BF-STEM image and high magnification HAADF image of the CMT layer, it is apparent that few defects are present. Twin boundaries still occur in some cadmium telluride grains. The HAADF image shows that the magnesium is again depleted at grain boundaries. Another observation is that without the anneal prior to the secondary treatment no chlorine regions are formed. This shows that the anneal inhibits faster diffusion of chlorine into the cadmium telluride.

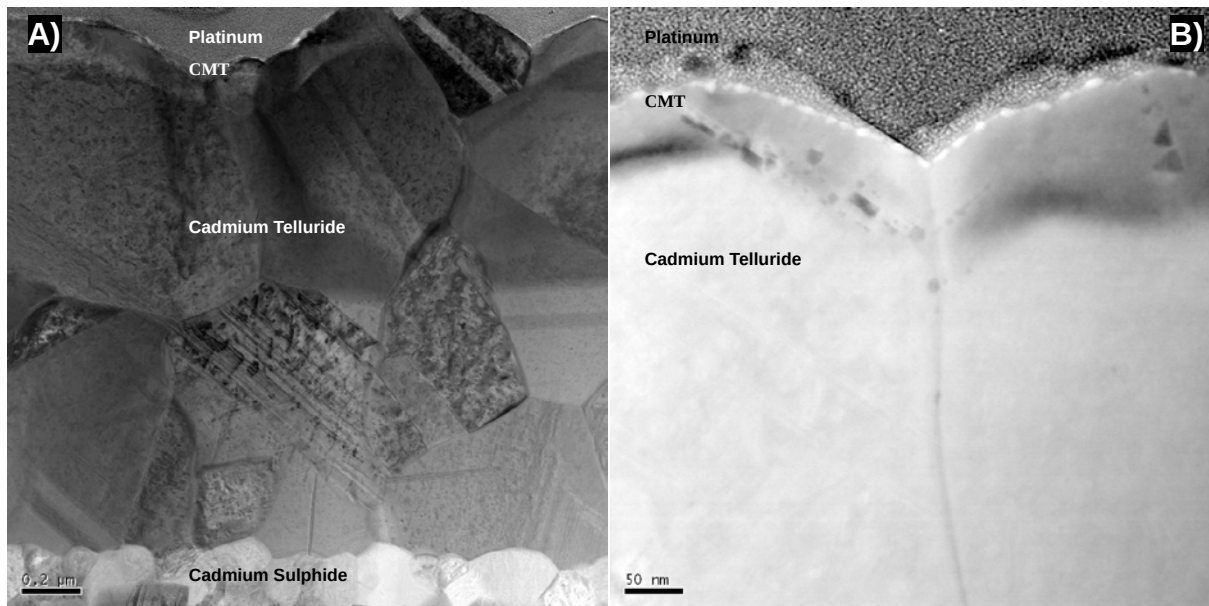


Figure 9.38- a) BF-STEM image showing the sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT/cadmium chloride and b) corresponding high magnification HAADF image of the CMT layer

Figure 9.39 show chemical distribution maps through the whole cell. The magnesium map shows clear discontinuity, with less magnesium at grain boundary regions in the CMT. The map also shows some magnesium at grain boundaries within the cadmium telluride layer. This shows that the magnesium loss in the CMT is due to the magnesium diffusing down the grain boundaries into the cell. No oxide layer is seen in the map in the CMT layer, indicating that the anneal is causing the oxide seen in the previous sample.

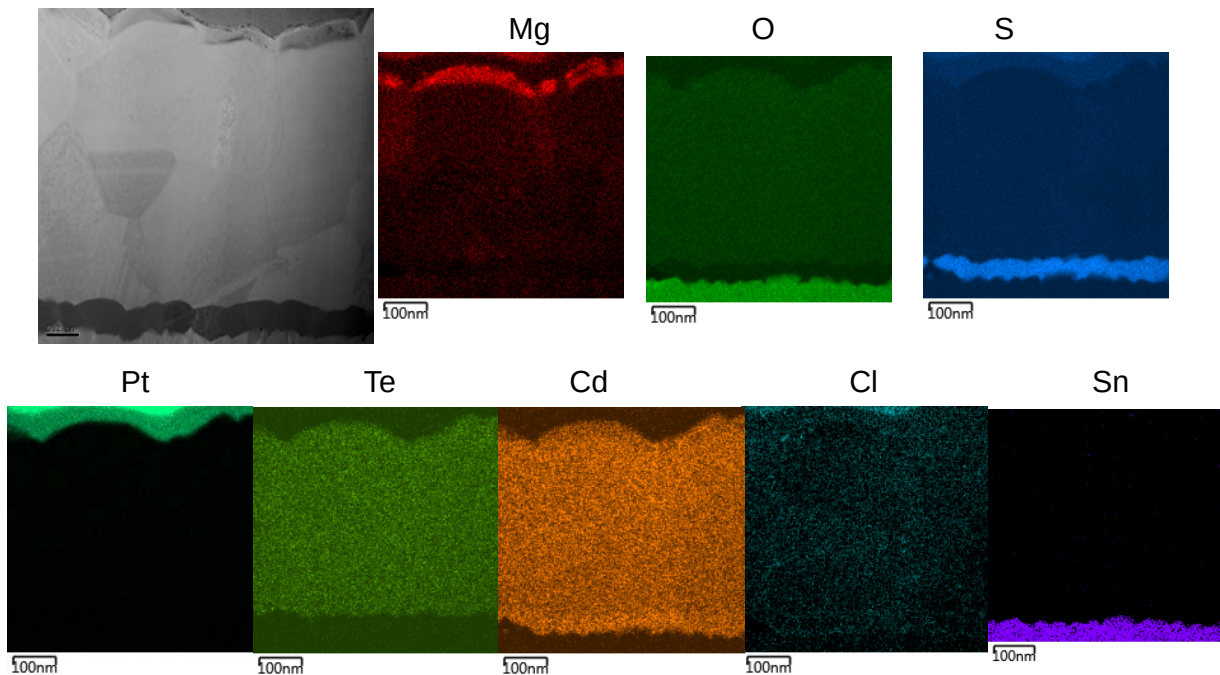


Figure 9.39 - HAADF STEM image showing the sample with cadmium sulphide/cadmium telluride /cadmium chloride/CMT/cadmium chloride and corresponding EDX chemical distribution maps

9.8 Summary

A CMT thin film was successfully deposited onto a cadmium telluride solar cell. The film layer is shown to grow epitaxially with the underlying cadmium telluride. To optimise the CMT layer the magnesium concentration was varied. A low concentration of magnesium produced layers with heterogeneous composition whereby higher concentrations of magnesium lead to oxidation of the CMT film. The intermediate concentration was found to provide layers with uniform thickness and reasonable chemical homogeneity. It was found that the CMT layer did not survive the cadmium chloride treatment. Subsequently the CMT layer was deposited after the cadmium chloride treatment.

To optimise the CMT deposition after the cadmium chloride treatment the deposition temperature was varied. It was found that at a lower temperature a layer of varying thickness was produced. When a higher temperature was used the CMT layer was found to be homogeneous in thickness and composition, however the higher temperature deposition damaged the underlying cadmium telluride by inducing stacking faults. At the lower temperature cadmium chloride residue was detected in the areas with a thinner CMT deposition. At higher CMT deposition temperatures it was found the cadmium chloride residue evaporated before the CMT was deposited, therefore a uniform thickness layer formed.

CHAPTER 10. CONCLUSIONS AND FURTHER WORK

10.1 Conclusions

In this work cadmium telluride thin film photovoltaic devices have successfully been produced using a novel closed-field magnetron sputtering technique. This technique offers the possibility of producing cells in an all-in-one vacuum process with the potential to provide a new lower cost production route. The sputtered cadmium telluride possesses through thickness columnar grains. Cells with efficiencies up to 5.4% have been produced using this method after an optimised cadmium chloride treatment.

Examining the microstructure of the sputtered cadmium telluride cells, which have undergone a cadmium chloride treatment has shown recrystallization of the cadmium telluride grains changing from a columnar to a equiaxed morphology. Varying the concentration of cadmium chloride during the treatment has shown that it is critical for enough chlorine to diffuse into the cadmium telluride layer in order for full recrystallization of the cadmium telluride. If an insufficient amount of cadmium chloride is present the cadmium telluride film will only partially recrystallize. By reducing the concentration of cadmium chloride during the treatment the initiation of the recrystallization has been captured. The recrystallization of the cadmium telluride is seen by grain shape change from columnar grains near the surface of the cadmium telluride to larger equiaxed grains near the cadmium sulphide interface where the chlorine has built up. This shows a critical amount of chlorine is required within the cadmium telluride layer before recrystallization can occur, it also shows that the recrystallization of the cadmium telluride film initiates from the cadmium sulphide interface and up. The proportion of the cadmium telluride which recrystallized, is proportional to the amount of cadmium chloride present during treatment; by treating cells with a range of concentrations this has been shown. All recrystallized cadmium telluride grains revealed a dramatic decrease in stacking defects.

Depositing cadmium telluride via close spaced sublimation with a carefully tuned cadmium chloride treatment is a more commonly used solar cells fabrication method. Analysing a cell before and after the cadmium chloride treatment has shown the role of the treatment. The main difference seen is the removal of detrimental stacking faults and the reduction of twin boundaries from within the cadmium telluride grains, similar observations to sputter

deposited cells. All untreated cadmium telluride grains possess a large number of linear defects observed with HRTEM, of which the large majority extend across the width of the grain, terminating at grain boundary. Once the grain has recrystallized during the treatment up to several twin boundaries remained, but no detrimental stacking faults. As CSS deposited cadmium telluride grains are initially equiaxed and larger than sputtered cadmium telluride grains the recrystallization did not increase grain size or change the grain shape much. Therefore the point of initiation of the treatment was less pronounced, however by reducing the treatment time evidence that cadmium telluride grains nearer the cadmium sulphide interface recrystallized preferentially has been obtained. EDX, XPS and SIMS measurements of treated CSS cells have shown that a build-up of chlorine is seen at and above the cadmium sulphide layer, similar to sputtered films. The speed of diffusion of chlorine is increased with an increase in treatment temperature. Some desired effects are seen such as larger cadmium telluride grain and fewer defects. However a reduction in cell efficiency occurs due to much larger quantities of chlorine build-up at the cadmium telluride/cadmium sulphide interface than the optimised cell. Therefore this shows why the cadmium chloride treatment requires fine tuning and deviating from the optimum parameters causes significant reductions in cell efficiency.

EBSD analysis of planar sections of the cadmium telluride layer prepared using the FIB has showed that the layer is composed of both the cubic zincblende and hexagonal wurizite structures before the cadmium chloride treatment, whereas only the cubic structure is present after the treatment. This result is consistent with XRD analysis performed on the materials. Transmission EBSD was used to examine the phase distribution within the grain in thin cross-section samples. This showed that both phases coexist within a grain. This hexagonal phase typically exists as bands of up to 50 nm in width running approximately parallel with the cadmium sulphide interface within the cubic cadmium telluride grains. HRTEM of these areas has shown that they are highly faulted to an extent where there is a missing atomic plane after every 2 planes of atoms. This results in the stacking sequence changing from AaBbCcAaBbCc to AaBbAaB, which are the stacking sequences for the cubic zincblende and hexagonal wurizite structures respectively.

Cadmium magnesium telluride (CMT) electron reflector thin films have been successfully deposited epitaxially onto cadmium telluride cells. When deposited onto a treated cadmium telluride cell at a temperature of 470°C a film with uniform thickness and composition is formed, however cell efficiency drops. TEM analysis showed that stacking faults with a

similar density to before the cadmium chloride treatment were forming in grains towards the top of the cadmium telluride layer where the CMT was grown. The presence of the stacking faults coincided with a significant reduction in measure cell efficiency.

10.2 Suggested Further Work

Stacking faults have been shown to have a detrimental effect on cell efficiencies. More work is needed to fully characterize the types of defect present and their effect on cell performance. Modelling the effect of the stacking faults on the performance of the devices and correlating this with the TEM results will further prove the detrimental effect of stacking faults in cadmium telluride solar cells.

Modelling the energies of the line defects and the formation mechanism during depositions may help improve the untreated cadmium telluride films. Varying deposition parameters such as temperature/gas pressure/oxygen content and calculating the variation in defect densities may provide details of which parameters fabricate higher quality untreated cadmium telluride films.

Further studies of the defects in the cadmium sulphide layers may provide an insight into other factors limiting device performance.

To do this techniques such as Electron Beam Induced Current (EBIC) and Cathodoluminescence in the TEM provide the opportunity to study electrical effects at high spatial resolution. In addition studying the atom positions directly near the linear defects using ultra-high resolution STEM is a highly desirable experiment to perform.

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