High rate deposition processes for thin film CdTe solar cells

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High rate deposition processes for thin film CdTe solar cells

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A DOCTORAL THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE AWARD OF
DOCTOR OF PHILOSOPHY OF LOUGHBOROUGH UNIVERSITY,

Loughborough University
CREST
School of Electronic, Electrical & System Engineering
To whom is so far but incredibly close..

[...] We (chemists) assemble and dismantle very small structures. We split into two main branches, those that mount and those who dismantle, the one and the other are like blind people with sensitive fingers [...] because we manipulate things that are too small to be seen, even with the most powerful microscopes; and then we invented several clever tricks to recognize them without seeing them. [The wrench-Primo Levi]
Abstract

This thesis describes the development of a fast rate method for the deposition of high quality CdS and CdTe thin films. The technique uses Pulsed DC Magnetron Sputtering (PDCMS). Surprisingly, the technique produces highly stable process conditions. CREST is the first laboratory worldwide to show that pulsed DC power may be used to deposit CdS and CdTe thin films. This is a very promising process technology with potential for eventual industrial deployment. The major advantage is that the process produces high deposition rates suitable for use in solar module manufacturing. These rates are over an order of magnitude faster than those obtained by RF sputtering. In common with other applications it has also been found that the energetics of the pulsed DC process produce excellent thin film properties and the power supply configuration avoids the need for complex matching circuits.

Conventional deposition methodologies for CdS, Chemical Bath Deposition (CBD) and CdTe thin films, Electrodeposition (ED), have been chosen as baselines to compare film properties with Pulsed DC Magnetron Sputtering (PDCMS).

One of the issues encountered with the deposition of CdS thin films (window layers) was the presence of pinholes. A Plasma cleaning process of FTO-coated glass prior to the deposition of the CdS/CdTe solar cell has been developed. It strongly modifies and activates the TCO surface, and improves the density and compactness of the deposited CdS thin film. This, in turn, improves the optical and morphological properties of the deposited CdS thin films, resulting in a higher refractive index. The pinhole removal and the increased density allows the use of a much thinner CdS layer, and this reduces absorption of blue spectrum photons and thereby increases the photocurrent and the efficiency of the thin film CdTe cell.

Replacing the conventional magnetic stirrer with an ultrasonic probe in the chemical bath (sonoCBD) was found to result in CdS films with higher optical density, higher refractive index, pinhole and void-free, more compact and uniform along the surface and through the thickness of the deposited material.

PDCMS at 150 kHz, 500 W, 2.5 μs, 2 s, results in a highly stable process with no plasma arcing. It allows close control of film thickness using time only. The CdS films exhibited a high level of texture in the <001> direction. The grain size was typically ~50 nm. Pinholes and voids could be avoided by reducing the working gas pressure using gas flows
below 20 sccm. The deposition rate was measured to be 1.33 nm/s on a rotating substrate holder. The equivalent deposition rate for a static substrate is 8.66 nm/s, which is high and much faster than can be achieved using a chemical bath deposition or RF magnetron sputtering.

The transmission of CdS can be improved by engineering the band gap of the CdS layer. It has been shown that by adding oxygen to the working gas pressure in an RF sputtering deposition process it is possible to deposit an oxygenated CdS (CdS:O) layer with an improved band gap. In this thesis, oxygenated CdS films for CdTe TF-PV applications have been successfully deposited by using pulsed DC magnetron sputtering. The process is highly stable using a pulse frequency of 150 kHz and a 2.5 μs pulse reverse time. No plasma arcing was detected. A range of CdS:O films were deposited by using O₂ flows from 1 sccm to 10 sccm during the deposition process. The deposition rates achieved using pulsed DC magnetron sputtering with only 500 W of power to the magnetron target were in the range ~1.49 nm/s ~2.44 nm/s, depending on the oxygen flow rate used.

The properties of CdS thin films deposited by pulsed DC magnetron sputtering and chemical bath deposition have been studied and compared. The pulsed DC magnetron sputtering process produced CdS thin films with the preferred hexagonal <001> oriented crystalline structure with a columnar grain growth, while sonoCBD deposited films were polycrystalline with a cubic structure and small grainy crystallites throughout the thickness of the films. Examination of the PDCMS deposited CdS films confirmed the increased grain size, increased density, and higher crystallinity compared to the sonoCBD CdS films. The deposition rate for CdS obtained using pulsed DC magnetron sputtering was 2.86 nm/s using only 500 W power on a six inch circular target compared to the much slower (0.027 nm/s) for the sonoChemical bath deposited layers.

CdTe thin films were grown on CdS films prepared by sonoCBD and Pulsed DC magnetron sputtering. The results showed that the deposition technique used for the CdS layer affected the growth and properties of the CdTe film and also determined the deposition rate of CdTe, being 3 times faster on the sputtered CdS.

PDCMS CdTe layers were deposited at ambient temperature, 500 W, 2.9 μs, 10 s, 150 kHz, with a thickness of approximately 2 μm on CdS/TEC10 coated glass. The layers appear
uniform and smooth with a grain size less than 100 nm, highly compact with the morphology dominated by columnar grain growth. Stress analysis was performed on the CdTe layers deposited at room temperature using different gas flows. Magnetron sputtered thin films deposited under low gas pressure are often subject to compressive stress due to the high mobility of the atoms during the deposition process. A possible way to reduce the stress in the film is the post-deposition annealing treatment. As the lattice parameter increased; the stress in the film is relieved. Also, a changing the deposition substrate temperature had an effect on the microstructure of CdTe thin films. Increasing the deposition temperature increased the grain size, up to ~600 nm.

CdTe thin films with low stress have been deposited on CdS/TEC10 coated glass by setting the deposition substrate temperature at ~200°C and using high argon flows ~ 70 sccm Ar.

Finally, broadband multilayer ARCs using alternate high and low refractive index dielectric thin films have been developed to improve the light transmission into solar cell devices by reducing the reflection of the glass in the extended wavelength range utilised by thin-film CdTe devices. A four-layer multilayer stack has been designed and tested, which operates across the wavelength range used by thin-film CdTe PV devices (400–850 nm). Optical modelling predicts that the MAR coating reduces the WAR (400-850 nm) from the glass surface from 4.22% down to 1.22%. The application of the MAR coating on a thin-film CdTe solar cell increased the efficiency from 10.55% to 10.93% or by 0.38% in absolute terms. This is a useful 3.6% relative increase in efficiency. The increased light transmission leads to improvement of the short-circuit current density produced by the cell by 0.65 mA/cm². The MAR sputtering process developed in this work is capable of scaling to an industrial level.
Acknowledgements

'Iron rusts from disuse, stagnant water loses its purity, and in cold weather becomes frozen, even so does inaction sap the vigour of the mind. Where the spirit does not work with the hand there is no art.'

[Leonardo da Vinci]

I’ll be using these two words - “Thank you!” - quite often, I suppose!

Let’s start, then:

For a while I was thinking how to structure this section, and in the end I thought I’d just improvise and let my feelings flow. So, first of all I would say thank you to Gianfranco! This ‘Loughborough experience’ started only because of him, so thank you, Gianfranco!

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List of Publications

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Oxygenated CdS window layers for thin film CdTe photovoltaics by pulsed DC magnetron sputtering, Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40th; 06/2014

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Lisco, F, Abbas, A, Bowers, J, Claudio, G, Kaminski, PM, Walls, JM

Patrick Isherwood, Biancamaria Maniscalco, Fabiana Lisco, Piotr M Kaminski, Jake W Bowers, John M Walls

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Lisco F., Bass K., Kaminski PM, Bowers JW, Losurdo, M, Claudio, G, Walls, JM


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Table of contents

Abstract i
Acknowledgements iv
List of Publications vi

Chapter 1  Introduction 1
1. Background and motivation: Photovoltaics (PV) 1
2. PV – Market overview 2
3. Why thin film solar cells technology? 4
4. Solar cells overview and CdTe thin film technologies 6
5. Thesis structure 10
6. References 13

Chapter 2  Basics of Photovoltaics and CdTe thin films solar cells 15
1. Introduction to photovoltaics 15
2. General structure of a thin film solar cell and Cadmium Telluride (CdTe) solar cells 21
   2.1. Solar cell structure of CdTe 23
   2.2. Critical issues with CdS and CdTe: thickness, pinholes formation and annealing treatment 29
3. References 32

Chapter 3  Thin Film processing methods for CdTe solar cells 36
1. Plasma Cleaning 36
   1.1. What is a plasma? 36
2. CdS thin films 39
   2.1. Chemical Bath Deposition 40
      2.1.1. Chemical mechanisms proposed in literature 41
   2.2. Growth mechanism 47
3. Pulsed DC Magnetron Sputtering of CdS 49
   3.1. Pulsed DC magnetron sputtering 53
4. Thin film deposition technologies for CdTe 56
   4.1. Electrodeposition (ED) of thin film CdTe 60
      4.1.1. The mechanisms of Electrodeposition 61
   4.2. Pourbaix Diagram 62
   4.3. ED CdTe from literature 63
2. Results and Discussion
   2.1. CdS composition, structure and morphology
   2.2. Optical properties of the deposited CdS films
   2.3. The effect of deposition parameters on the deposition rate

3. Conclusions

4. References

Chapter 8  Pulsed DC Magnetron Sputtering of CdS:O thin films

1. Introduction
2. Experimental
3. Results and discussion
4. Conclusions
5. References

Chapter 9  The structural properties of CdS deposited by Chemical Bath Deposition and Pulsed DC Magnetron Sputtering

1. Experimental
2. Results and Discussion
3. Conclusions
4. References

Chapter 10  Electrodeposition (ED) of CdTe thin films

1. Experimental
2. Results and Discussion
3. Conclusions
4. References

Chapter 11  Pulsed DC Magnetron Sputtering of CdTe

1. Experimental
2. Results and Discussion
   2.1. The Effect of Argon Gas Flow on CdTe Thin films
   2.2. Effect of Deposition Temperature on CdTe Thin films
   2.3. Residual stress in CdTe thin films
   2.4. Stress Analysis before Annealing Treatment
3. Conclusions
4. References

References
Chapter 12  Multilayer Broadband Antireflective Coatings for more efficient thin film CdTe solar cells

1. Introduction 211
   1.1. Multilayer antireflection coating design 212

2. Experimental 216
3. Results 217
4. Conclusion 221
5. References 223

Chapter 13  Conclusions and Suggestions for Future Work

1. References 229

Journal papers 232
Chapter 1

Introduction

1. Background and motivation: Photovoltaics (PV)

The energy of solar radiation is often utilised in two forms: direct conversion into electricity that takes place in semiconductor devices called solar cells, and accumulation of heat in solar collectors.

The direct conversion of solar radiation into electricity is often described as photovoltaic (PV) energy conversion because it is based on the photovoltaic effect. In general, the photovoltaic effect means the generation of a potential difference at the junction of two different materials in response to visible or other radiation. Photovoltaics describes the conversion of the solar radiation (photons) directly into electric power (electrons) when light strikes the surface of a solid state semiconductor [1]. Their main characteristic is the decreasing electrical resistivity with increasing temperature in a range from $10^{-2}$ to $10^9 \ \Omega\text{cm}$. [2]

The whole field of solar energy conversion into electricity is therefore denoted as the “photovoltaics”. The term Photovoltaic comes from a combination of a greek word phos, that means light and volt, from Alessandro Volta, the physicist, and inventor of the electric battery. This process dates back to 1839 when E.Becquerel observed the production of an electric current caused by the effect of light on a silver coated platinum electrode immersed in electrolyte, but it was C.Fritts who built the first solar cell in 1883, using a selenium semiconductor with a film of gold [2].

The problem of global climate change is causing increasing worldwide concern, so that renewable energies, including solar cell technology based on the photovoltaic effect, has become an important field of research. The field of photovoltaics has developed greatly leading to a growing commercial market for solar modules expanding at a rate that has been unimaginable before. This huge thrust in the industrialisation and commercialisation of solar modules has driven research for new technologies with higher efficiency and lower cost.
Chapter 1

2. PV – Market overview

Over the last two decades, the Photovoltaic (PV) market has seen an incredible expansion, with over 40 GW installed in 2013 (Figure 1) [3]. For the third year in a row, solar power attracted the largest amount of new investment in renewable energies, attracting 57.7% of all new renewable energy investments or USD 137.7 billion (EUR 105.9 billion) [4].

![Figure 1: Annual PV installations from 2000 to 2013 [4].](image1)

Over the last 40 years, prices of solar modules have decreased and have followed a price-experience or ‘learning’ curve with an average learning rate of about 80%. The average selling price of solar modules has decreased by 20% for each doubling of production volume (Figure 2).

![Figure 2: Price-experience curve for solar modules [4].](image2)
This trend was set by technological developments and by market conditions. PV modules prices remained approximately constant between 2004 and 2008, at about 4–4.5USD2012/Wp (Watt-peak), although during those years there was a significant scaling up of production by several companies and continuous improvement in manufacturing technology. Between 2005 and 2009 investments in thin film solar cells massively expanded because of a temporary price increase caused by a silicon feedstock shortage. The market share for thin-film modules increased until 2009, reaching almost 20%. Between 2008 and 2012 there was a massive 80% drop in the price of modules causing serious problems for all companies involved in PV manufacture, leading to some closures. PV systems prices followed the same reduction profile as module prices but at a slower pace. These prices are still decreasing not only in Europe but globally. Decreasing cost is an important stage necessary for photovoltaics to become a major energy provider in the near future. The International Energy Agency estimates that thin-film technologies will represent 40% of the PV market by 2030 [5], and the European Photovoltaic Industry Association forecast that CdTe alone will occupy about 12% of the global PV market by 2020 [6]. Nevertheless, c-Si production costs are also quickly decreasing and these developments could impact on thin film and CdTe cost competitiveness. Other PV technologies (e.g. organic PV, concentrator PV, DSSC, multi-junction cells) [7][8] are also emerging and they must be considered as potential competitors.

As previously reported, the PV industry has changed dramatically over the last few years and the global market, which was dominated by Europe in the last decade, is gradually involving entrants from other countries (Figure 3). In fact, China has become the major manufacturing centre for solar cells and modules, followed by Taiwan, Germany and Japan. Among the 20 biggest PV manufacturers in 2013, only three had some of their production facilities in Europe, namely First Solar (USA, Malaysia), Hanwha Q CELLS (South Korea, Germany, Malaysia and China) and REC (Norway and Singapore) [1][9].
It is difficult to predict how the entrance of these new players will affect the future growth of the manufacturing industry and markets. On one hand, it is easy to anticipate the accelerated growth rates of PV markets, in particular if the new large solar cell companies guarantee a power output for over 30 years and with reasonable prices. On the other hand, this would mean tough competition for small and medium companies. These smaller companies will have to specialise with high value added products, with special solutions tailor-made for customers or they will need to offer technologically improved and cheaper solar cell concepts [11][12].

3. Why thin film solar cells technology?

Although the dominant technology in the PV market is crystalline silicon (c-Si), thin film technology has become competitive because the amount of material used is reduced, yielding lower production costs. Here is a summary of the advantages that attract investment in this technology.

- Deposition (growth) of layers on large areas
- High absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) which explains how a few microns of the absorber materials is sufficient to absorb a large amount of incident light
- Hetero-junction formation (between two different materials) gives the possibility of reducing optical absorption losses and improving device engineering
- Multi-junction (tandem) solar cells to absorb a wider range of the solar spectrum, improving efficiency
- Monolithic integration to minimise area losses
• Possibility of using flexible substrates such as metals or polymer foils allowing modules to be lightweight compared to the rigid and heavy glass substrates commonly used
• Possibility of roll-to-roll manufacturing to enhance the deposition speed and reduce energy payback time.

Another important aspect for this technology is the Life Cycle Analysis (LCA); the National Renewable Energy Laboratory (NREL) has developed a LCA Harmonization Project which is a systematic approach to review LCA literature from c-Si and Thin Film PV through a meta-analytical process called “harmonization”. According to this study, the harmonised median value for c-Si resulted to be 45 g CO₂ eq/kWh and for thin films PV-systems the life cycle greenhouses gas (GHG) emissions were estimated to be 20, 14, and 26 g CO₂ eq/kWh, for a-Si, CdTe and CIGS, respectively [13]. There are also drawbacks related to the thin films technology:

• In particular a-Si shows low efficiency and high cost equipment.
• CdTe is characterised by the presence of Cadmium which is highly toxic. Cd is one of the top 6 deadliest and toxic materials known. However, CdTe appears to be less toxic than elemental cadmium, at least in terms of acute exposure. Tellurium supply is another issue, while Cd is relatively abundant, this is not the case for Te. Tellurium is an extremely rare element (1-5 parts per billion in the Earth's crust). According to USGS (U.S. Geological Survey), global tellurium production in 2007 was 135 metric tons. Most of it results as a by-product of copper, with smaller by-product amounts from lead and gold. One gigawatt (GW) of CdTe PV modules would require about 93 metric tons (at current efficiencies and thicknesses)[14], so the availability of tellurium can represent a strong limit for the production of this material. Since CdTe is now regarded as an important technology in terms of PV’s future impact on global energy and environment, the issue of tellurium availability is significant. The disposal and long term safety of cadmium telluride is a known issue in the large-scale commercialization of CdTe solar panels. Serious efforts have been made to understand and overcome these issues. Researchers from the U.S. Department of Energy's Brookhaven National Laboratory [15] have found that large-scale use of CdTe PV modules does not present any risks to health and the environment, and recycling the modules at the end of their useful life resolves any environmental
concerns. During their operation, these modules do not produce any pollutants, and furthermore, by displacing fossil fuels, they offer environmental benefits. CdTe PV modules appear to be more environmentally friendly than all other current uses of Cd.

4. Solar cells overview and CdTe thin film technologies

Traditional solar cells are based on single crystal materials, such as crystalline silicon (c-Si) and crystalline gallium arsenide, c-GaAs, grown by costly processes such as the Czochralski method and molecular beam epitaxy (MBE). Because of the difficulty in processing, and cutting, single crystal ingots and due to the need to use high purity materials, these cells are subject to price fluctuations. As a result, the manufacturing cost of the ‘1st generation’ solar modules is relatively high compared with conventional sources of electricity in large-scale utility markets. Although due to the economy of scale brought about by volume manufacturing, this cost has recently reduced considerably [16].

Shockley-Queisser [17] studied the theoretical efficiency limit for an ideal homo-junction solar cell (also known as the Shockley-Queisser limit [18]) and found that, the maximum possible efficiency is 30% for a band gap of 1.1 eV (assuming only radiative recombination) if exposed to the sunlight of global air mass 1.5 (Figure 4). This value is relatively close to the most recent data published in Progress in Photovoltaics [19] which reports a crystalline silicon (Si) solar cell efficiency of 25% measured under the AM 1.5 spectrum at 25°C.

Figure 4: Maximum theoretical efficiency (Shockley–Queisser limit) for solar cells under AM1.5 illumination without concentration. The bandgaps of absorber materials (c-Si, CdTe, CIGS, CZTS) and window materials (CdS, ZnO) are shown for comparison. Note that the bandgap of the CIGS system can be tuned by controlling the In/Ga ratio [6].
Although mono-crystalline silicon cell technology currently dominates the market, accounting around 90% of the market [20], the main drawback with the Si solar cells is that it is an indirect band gap semiconductor and needs a thick layer around 20-100 μm to absorb photons [21]. The band gap of 1.1 eV for Si does not absorb more than 50% of the visible spectrum. Its low absorption cross section and high synthesis and processing costs mean that the Si is not considered a viable candidate for low cost thin film PV devices, although attempts have been made in the form of amorphous silicon, a-Si, cells, but these only exhibited efficiencies in the 10-12% range [22]. These films are made by vapour-depositing a layer of silicon material (~1 μm) on a substrate such as glass or metal. They can be deposited at low temperatures (~75ºC), which allows their deposition on plastic materials. One of the disadvantages of this technology is the low efficiency compared with mono- or polycrystalline solar cells. In addition, the major problem associated with the a-Si solar cells is the degradation of performance over time.

Other 2nd generation solar cells based on thin film materials, are cadmium telluride (CdTe), copper indium selenide (CIS), and copper indium-gallium diselenide (CuIn1-xGaxSe2 or CIGS). Thin film CIGS and CdTe have achieved cell efficiencies of 21.7% and 21.5%, respectively [23][24][25]. These solar cell materials are fabricated using simpler processes such as magnetron sputtering, close space sublimation (CSS), plasma enhanced chemical vapour deposition (PECVD), and multi-source evaporation which are all suitable for large scale automated production. The thicknesses of the films used in these solar cells are at least an order of magnitude smaller than those in c-Si cells. As a result, although thin film cells have lower conversion efficiencies, they can be manufactured at much lower cost. Additional details can be found in the following reports and literature; for example innovative, low-cost solutions for solar panels design have been developed by different companies [26][27] as novel designs to deliver more energy per watt and to be competitive with the conventional panels [28][29] Financial and environmental investments are dominating the modern market, offering solar power production systems for personal homeowners or business use [29][30]

Due to the direct band gap of the semiconductors used in thin film solar cells, they show much higher absorption coefficients compared to c-Si with its indirect band gap. Higher absorption coefficients allow a reduction in thickness to less than 10 μm, so that there is less requirement for long minority-carrier diffusion lengths and lifetimes allowing less pure polycrystalline or amorphous material to be used. For example, the absorber materials used for thin films solar cells have a range from 0.5 to 8 μm in thickness compared to the “thick”
c-Si generally in the range 80-150 μm of thickness. Figure 5 is an absorption coefficient graph, showing how the absorption coefficient is significantly higher for these materials compare to c-Si, especially at wavelengths close to the band gap of the material.

Figure 5: Absorption coefficients of different semiconductors. Materials commonly used in thin film solar cells have a much higher absorption coefficient compared to c-Si, allowing the use of thinner layers [31].

Chalcogenide–based thin film solar cells offer considerable cost reduction for solar energy production. Recently, First Solar LLC announced that the current cost of electricity produced by its CdTe solar panel was $0.63/W in 2013 and aims to develop solar cells at the cost of $0.35/W in 2018 [28] [32]. Although thin film materials for solar cells have obvious potential advantages including low cost, they also have a number of well-known drawbacks. The main issues are related to these materials when considered as pure and isolated elements before they are bonded to form compounds with a film. The scarcity, cost or toxicity associated with In, Ga, and Cd elements may compromise their sustainability in the future.

GaAs based solar cells have high efficiency, but the toxicity issues concerning arsenic and high substrate costs restrict their use. CIGS solar cells show promising potential, despite the scarcity and cost of indium and gallium, which ideally would be replaced by other elements. The quaternary compound semiconductor CZTS (Cu2ZnSnS4) [33] shows attractive optical properties, with a band-gap energy of about 1.5 eV and a large absorption coefficient in the order of 10⁴ cm⁻¹, but device efficiency must be improved to make it commercially viable. CdTe solar cells are also highly promising although cadmium toxicity and tellurium scarcity
are issues that need to be addressed. Research into new, cheap precursors and alternative low cost processes is necessary to improve the cost effectiveness of these devices.

Emerging technologies, known as “third-generation PV”, could become viable commercial options in the future [34], either by achieving very high efficiency or very low cost. Examples include dye-sensitised solar cells (DSSC) [35] and organic PV cells, which are based on a photo-electrochemical system with the semiconductor formed between a photo-sensitised anode and an electrolyte. This technology is relatively new but one of the most developed among third generation PV. Other examples of third generation devices include the use of quantum dots, plasmonic nanostructures, thermophotronics, intermediate band, multi-junctions and bio-inspired materials. Another recently developed PV technology is that of perovskite solar cells [36]. This technology is inspired from DSSC, but the electrolyte dye has been substituted with solid state material. Engineering of these solar cells such as changing the mesoporous TiO$_2$ layer with mesoporous Al$_2$O$_3$ leads to high performance, especially $V_{oc}$ values which are above 1.1 V. However, stability is one of the main issues with these cells, which is a common problem for devices based on organic material. All these technologies have promising theoretical potential which is being developed currently in many universities and research centres (Figure 6) [37][38].

Among thin film photovoltaics, CdTe is one of the promising technologies and as already stated is finding considerable market share. The relative competitiveness of CdTe versus
other technologies, and how fast these other emerging PV technologies will gain market share, are factors which will ultimately determine its long term future. CdTe production will certainly continue to grow, and the future demand for Te from the CdTe industry is actually one of the potential drawbacks of the technology, due to its relative low abundance. Research is moving towards more efficient use of Te in the production process, improving efficiencies whilst also reducing the thickness of the absorber layer (CdTe) and also increasing recycling of the material in the production process [36].

Another issue of concern with CdTe is that of regulation in its use, and this is currently under discussion in Europe, although the scientific community believes that the use of this material does not constitute a major environmental problem [37]. Research on thin film CdTe thus is focused on several challenges. The most important are increasing efficiency and lowering the cost. Other challenges include the introduction of novel manufacturing technologies and understanding, and minimising the degradation of these devices.

5. Thesis structure

One of the main objectives of this work was to develop a fast, inexpensive deposition method for high quality CdS and CdTe thin films, Pulsed DC Magnetron Sputtering (PDCMS). Since magnetron sputtering using RF power results in low deposition rates (for example a rate of 0.3 nm/s has been reported at 250 W [40]) and involves the use of complex matching circuits, the technique is not well suited to industrial deployment, although suitable for research purposes. The aim of the project was to study the advantages and disadvantages of solution based techniques compared to high throughput vacuum based technologies.

The ultimate goal was to devise an industrially relevant process for the deposition of high efficiency CdTe solar cells. In this work, a process based on pulsed DC power has been applied to sputter thin films of CdS and CdTe in process conditions which are highly stable. The major advantage is that the process produces high deposition rates suitable for use in solar module manufacturing. These rates are over an order of magnitude faster than those obtained by RF sputtering. In common with other applications it has also found that the energetics of the pulsed DC process produce favourable thin film properties and the power supply configuration avoids the need for matching circuits [41][42].

The structure of this thesis is as follows: Chapter 1 introduces the photovoltaic market, providing an historical overview through the last few decades up to the present day, as well
Chapter 1

as providing a general market overview. The motivation for developing, and improving, thin films photovoltaic is then outlined.

Chapter 2 provides an overview of solar cells, and in particular of CdTe thin films. An introduction to photovoltaics is provided with some basic physics, the general structure of a thin film solar cell and specifically that of the CdTe thin film solar cell.

Chapter 3 introduces the methods utilised for the deposition of CdS and CdTe thin films, starting with a general overview, analysing the critical issues related to these materials, describing the methods that were chosen for this study (these will be explained further with related results in the experimental section).

Chapter 4 is focused on the methods used in this study for the characterisation of thin films, starting with morphological and microstructural analysis by using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). There are also sections focused on the chemical compositional analysis of the surface with X-ray Photoelectron Spectroscopy (XPS) and analysis of the bulk material with Energy Dispersive X-ray Spectrometry (EDS), analysis of crystalline orientation using X-ray Diffraction (XRD). The basic concepts and principles of ellipsometry are analysed, including the generic structure of ellipsometers, the specific experimental apparatus, and the operational principles of ellipsometers. Data analysis strategies (modelling) used to describe film structure, optical and physical properties of materials deposited in this project are also explained in this chapter. It focuses on optical properties analysed using a spectrophotometer, Scanning White Light Interferometry (SWLI) and electrical measurements by studying the current-voltage (I-V) characteristics.

Chapter 5 provides a description of a plasma pre-treatment process for cleaning and activating the substrate before the thin film deposition. The condition of the surface free from contamination, organic compounds, native oxides, hydroxides, is a crucial step to ensure an optimised deposition and semiconductor device fabrication. Surface contaminants and native oxides can alter the growth mode and the optical, morphological properties of the deposited films. A functional plasma pre-treatment has been optimised which provides activation of the surface, leading to pinhole and void-free layers deposited after the treatment.

Chapter 6 introduces the low cost wet-chemical technique used for CdS films deposition: Chemical Bath Deposition (CBD). The deposition method is analysed, going through the experimental procedures applied in this work and the results achieved.

This conventional deposition methodology has been chosen as baseline to compare against Pulsed DC Magnetron Sputtering (PDCMS).
Chapter 1

The second part of this study focuses on using this process for high quality CdS and CdTe thin films. CREST is the first laboratory worldwide to show that pulsed DC power may be used to deposit CdS and CdTe thin films; this is a very promising process for eventual industrial deployment. In chapters 7 and 8 the PDCMS experimental process is described which has been developed and optimised to deposit thin films of CdS and oxygenated CdS (CdS:O), respectively.

Chapter 9 compares the structural properties of CdS thin layers deposited by CDB and PDCMS.

Chapter 10 introduces the experimental work on CdTe thin films, as well as CdS layers, a low cost technique has been selected as a baseline to compare against the PDCSM deposition process. The deposition method used to do this is electrodeposition (ED), the experimental procedures and results obtained for CdTe layers are presented and discussed in this chapter.

Chapter 11 focuses on CdTe deposited by PDCMS, describing the experimental process and the results achieved.

Chapter 12 introduces work on anti-reflective coatings for higher efficiency thin film CdTe photovoltaic devices by using PDCMS.

Chapter 13 summarises the conclusions drawn from the previous chapters and provides suggestions for future work.

The main objectives for this work were:

- optimisation of solution based techniques (Chemical Bath Deposition, CBD and Electrodeposition, ED) for the deposition of CdS and CdTe thin films
- optimisation of the high vacuum based technology, Pulsed DC Magnetron Sputtering (PDCMS) for the deposition of CdS and CdTe layers, used as a novel deposition technique applied to Photovoltaic field
- Characterisation of CdS and CdTe thin films to understand optical, morphological, structural, chemical properties of these layers
- Comparison between solutions based processes and high vacuum deposition system, understanding advantages and disadvantages of these techniques through chemical, optical, morphological, structural analyses.
- Test the real use and application of thin films deposited by PDCMS, including them into a final working device, CdTe solar cell.
Chapter 1

6. References

Chapter 1

1. Introduction to photovoltaics

When a material absorbs a photon, a localised electron-hole pair is formed. This charge-transfer state either dissociates into a free electron and a free hole, which requires overcoming the Coulomb interaction between the two charges, or recombines. To avoid recombination, the separation of these charges is the important step. Light with a photon energy $h\nu < E_g$ is not easily absorbed, while $h\nu > E_g$ is absorbed in the material (Figure 7).

![Figure 7: Schematic diagram for light absorbed and not absorbed when $h\nu < E_g$ and $h\nu > E_g$.](image)

The light intensity as a function of depth into the semiconductor is expressed by $I(x) = I_0 e^{-\alpha x}$, where $I_0$ is the initial light intensity (Figure 8), x the distance and $\alpha$ is the absorption coefficient measured in cm$^{-1}$.

![Figure 8: Schematic representation of the light intensity as a function of the depth in a semiconductor material.](image)
Doping is one of the main processes involved in making a solar cell. A material is an $n$-type semiconductor when it has a large electron conductivity compared to the hole conductivity, because of the large difference in electron and hole concentrations. This kind of material is also called the donor, the electrons are in fact the ‘majority carriers’ for current flow in this semiconductor (Figure 9 (a)). The opposite situation occurs for a $p$-type material, where the holes are mobile and responsible for the current flow (Figure 9 (b)). This type of semiconductor is called the acceptor, and holes can be considered as the ‘major carriers’. The doping process consists of the addition of impurities, which contribute to the electron and hole energy levels in the semiconductor band gap so that electrons can be easily excited into the conduction band for $n$-type and from the valence band for $p$-type materials.

![Figure 9: n-type (a) and p-type (b) materials, with $E_V$ valence band energy level, $E_C$ conduction band energy level, $E_D$ donor energy level and $E_A$ acceptor energy level.](image)

In equilibrium conditions, energy levels $E_D$ and $E_A$ are located closer to the conduction and valence bands, depending on the doping process. In non-equilibrium conditions, when bias is applied, both electron and hole density increases with a shift of Energy Fermi $E_F$ level (Figure 10).

![Figure 10: Schematic diagram showing equilibrium conditions and under bias conditions.](image)
The p-n junction consists of two semiconductor regions with opposite doping brought together. Across the junction, driving forces (dynamic equilibrium and electrostatic forces) act to move photo-generated charges from the place they are generated. In the n-type material, as a result of losing electrons to the other material, a positive charge builds up. The opposite occurs in the p-type material, where negative charge builds up. Diffusion processes caused by the carrier concentration gradient create an electric field to oppose further charge migration. This region is called the space-charge region or depletion region (shown in Figure 11 (a)).

Upon absorption of a photon with sufficient energy, an electron is able to cross the band-gap, $E_g$, leading to the formation of an electron-hole pair, which can be separated by the electric field at the space charge region. It can then be extracted to do useful work. The Figure 11 (b) shows a band diagram of a simple p-n junction.

![Figure 11: p-n junction and the potential difference across the junction (a) band diagram of a p-n junction (b).](image-url)
Chapter 2

The open circuit voltage, $V_{OC}$, of the system is determined by the difference between the n, ($E_{FN}$) and the p-type ($E_{FP}$) regions of the device, under illumination.

The short circuit current, $I_{SC}$, is given by the amount of photons with energy high enough to promote the movement of electrons across the band gap. The band gap of the absorber material is a crucial value for the efficiency of the final device. When $E_g$ is low, a large amount of photons can be converted into current, but the $V_{OC}$ will be low due to the close position of the $E_{FN}$ and $E_{FP}$. When the band-gap of a material is large, only a small proportion of photons can generate current, leading to a small $I_{SC}$, but with a high $V_{OC}$. Therefore, there is a compromise between the values of $I_{SC}$ and $V_{OC}$, and theoretical studies have determined that absorber layers with a band-gap around 1.4-1.5 eV will lead to the highest efficiency [7].

The p-n junction is called a homo-junction, when the two sides of the junction are made from the same material. It is called a hetero-junction when the two materials are different. In the case of CdTe solar cells, the p-n junction is hetero-junction type.

The equation used to determine the current flow ($J_n$) in response to the electric field and concentration gradient is:

$$ J_n = drift ~+~ diffusion = q\mu_n n \zeta + \mu_n kT \frac{\partial n}{\partial x} $$

Where $\mu_n$ is the mobility (cm$^2$V$^{-1}$s$^{-1}$), $n$ is the carrier concentration (cm$^{-3}$), $\zeta$ the electric field (Vm$^{-1}$) and $q$ the electronic charge (1.6 x 10$^{-19}$C)

$q\mu_n n \zeta$ is the drift component of the current and $\mu_n kT \frac{\partial n}{\partial x}$ the concentration gradient of the carriers.

The carrier concentration can be expressed as a function of the Fermi Energy ($E_F$):

$$ J_n = \mu_n n \frac{\partial E_F}{\partial x} $$

When equilibrium conditions are reached, the current flow reaches the zero value according to $\partial E_F/\partial x$ that goes to zero (no change in Fermi level position at equilibrium).

**Current generation**

When light intensity increases, it means that there are more photons, and more electrons, and as a consequence the short circuit current $I_{SC}$ increases. In dark conditions, the junction works as a diode, where two-terminal electronic component lets the current flow only in one
Chapter 2

direction. So the current I can flow under forward bias ($V>0$) but cannot flow under reverse bias ($V<0$). For an ideal diode the dark current density $J_{dark}(V)$ is given by:

$$J_{dark}(V) = J_0 \left(e^{qV/kt} - 1\right)$$

where $J_0$ is the reverse bias saturation current, $k$ is Boltzmann's constant and $T$ is temperature in degrees Kelvin.

When the device is illuminated, if the energy of the photons incident on the material is higher than the band gap $E_g$, electrons are excited and holes are created. Due to this process, if contacts are connected, a current flow is present, the so called photo-current ($J_L$), which flows in the opposite direction to the dark current ($J_{dark}$).

$J_L$ is defined as:

$$J_L = A \int b(E)SR(E)d(E)$$

where $A$ is the working area; $b(E)$ is the spectral irradiance and $SR(E)$ is the spectral response (SR). The spectral response is the ratio of the current generated and delivered to an external circuit to the power incident on the device. It depends on the absorption coefficient of the solar cell material. SR is a function of the energy and is limited at both long and short wavelengths. Any energy above the band gap energy is not utilised by the solar cell and instead causes it to heat. At long wavelength, low energy photons are not absorbed; the maximum value for SR is at intermediate wavelengths and it is limited by material reflectivity. The inability to fully utilise the incident energy at high energies and the inability to absorb low energies of light represents a significant power loss in solar cells. When the terminals are connected together the current developed is the short circuit current $J_{SC}$. When the terminals are isolated, the voltage developed is called open circuit voltage $V_{OC}$. For any intermediate load resistance $R_L$ the cell develops a voltage $V$ between 0 and $V_{oc}$ and delivers a current $I$ such that $V = IR_L$ and $I(V)$ is determined by the current-voltage characteristic of the cell under that illumination (Figure 12).

The photocurrent generated by a solar cell under illumination at short circuit is dependent on the incident light. To relate the photocurrent density, $J_{sc}$, to the incident spectrum we need to introduce another parameter, the cell’s quantum efficiency (QE). QE(E) is the probability that an incident photon of energy E will deliver one electron to the external circuit. Then

$$J_{sc} = q \int b(E) QE(E)dE$$
where \( bs(E) \) is the incident spectral photon density, the number of photons of energy in the range \( E \) to \( E+dE \) which are incident on a unit area in a unit time, and \( q \) is the electronic charge.

The overall current-voltage response of the cell can be approximated as the sum of photo- and dark current, with its conventional negative sign:

\[
J(V) = J_{SC} - J_{dark}(V) = J_{SC} - J_0 \left( e^{qV/kT} - 1 \right)
\]

The operating regime for a solar cell is in the bias range \( 0 - V_{OC} \), in which the cell delivers power. The cell power density is:

\[
P = JV
\]

The maximum power point \( P_m \) occurs at maximum voltage \( V_m \) with a corresponding current density \( J_m \) (Figure 13). The Fill Factor represents the area described by the maximum power rectangle divided by the product of the short-circuit current and open circuit voltage.

\[
FF = \frac{J_m V_m}{J_{SC} V_{OC}}
\]
The efficiency of a cell is the power density at the operating point as a fraction of the incident light power density, \( P_s \), dependent on the maximum power point:

\[
\eta = \frac{J_m V_m}{P_s} \tag{9}
\]

or it can be related to the fill factor:

\[
\eta = \frac{J_{SC} V_{OC} FF}{P_s} \tag{10}
\]

These parameters, \( J_{SC}, V_{OC}, FF \) and \( \eta \) are the key performance characteristics of a solar cell. All of these are defined for particular illumination conditions. The Standard Test Condition (STC) applied for solar cells are the Air Mass 1.5 spectrum, incident power density of 1000 W m\(^{-2}\), and temperature of 25°C [43].

### 2. General structure of a thin film solar cell and Cadmium Telluride (CdTe) solar cells

In general, these devices are deposited on a supporting substrate, commonly glass, although flexible substrates such as metal or polymer foils are currently of great interest. Firstly, a front contact is made in order to allow the efficient collection of photo-generated carriers onto which the p-n junction is deposited. The p-n junction usually consists of a thin n-type
layer with a thicker p-type absorber material. It is also possible to use p-i-n junctions, which utilise the “intrinsic” layer between the n and p type to improve photon absorption. Finally, the device is completed by a back/top contact.

Thin film cadmium telluride (CdTe) solar cells can be deposited in substrate and/or superstrate configuration (Figure 14). In substrate configuration the light goes through the transparent conducting oxide (TCO) electrode into the CdS and finally into the absorbing layer (CdTe). The superstrate configuration is the one used commercially, while the substrate configuration can be used for flexible cells [44].

A crucial step in cell design is the choice of an appropriate substrate material which must withstand the fabrication process temperatures and be transparent so to allow the incident light to pass through to the CdS/CdTe layers [45].

![Figure 14: A diagram showing the structure of a typical CdS/CdTe solar cell in superstrate and substrate configuration.](image)

The efficiency of a solar cell depends on the different deposition conditions used, the quality of materials, as well as the structure and morphology of the thin films. The uniformity of the deposited layer is also important to avoid spatial disparity in the electrical and optical properties of the materials [46].
Chapter 2

2.1. Solar cell structure of CdTe

A schematic diagram of a CdS/CdTe solar cell [47] structure is shown in Figure 15:

![Diagram of CdS/CdTe solar cell structure](image)

*Figure 15: Basic CdS/CdTe solar cell structure [47].*

The Glass superstrate is usually a simple glass or a soda-lime, borosilicate glass. Impurities in the glass can be crucial to the final performance of the cell. Antireflection coatings can be applied to the glass to improve the light transmission into superstrate configuration devices. Commonly the choice of substrate is either soda-lime glass or borosilicate glass because they are inexpensive, transparent and resistant to relatively high temperatures [48]. Depending on their properties, each type of glass substrate can affect the growth of the next layer.

**TCO:** Transparent Conducting Oxide is a coating, such as indium-tin oxide (ITO), In$_2$O$_3$:Sn, SnO$_2$, fluorine doped-tin oxide (FTO), SnO$_2$:F, or cadmium stannate, Cd$_2$SnO$_4$. In this study FTO has been used as the transparent conducting layer. In particular, TEC glass produced by NSG-Pilkington group has been used. It consists of three layers: tin oxide, silicon oxide and fluorine-doped tin oxide (Chapter 3). Its multilayer-structure provides chemical stability, transparency and a roughness level suitable for thin film PV applications. FTO is stable and does not change colour with time. It is resistant to abrasion and it can be processed at high temperature without degradation.
Chapter 2

**n-CdS window layer**: Cadmium sulphide (CdS) is an important semiconductor material widely used in thin film photovoltaics as a window layer [49], [23]. Cadmium sulphide is an n-type semiconductor with a direct band gap of 2.42 eV and a bulk refractive index (n) of 2.52 at wavelength 600 nm [50] which is well suited for its application in solar cells. The refractive index value is between the index of the absorber and the TCO contact, which allows light trapping by refractive index matching. This means that this material is suitable as a window layer. Thin film CdS has been used as a n-type material to form a heterojunction in a number of photovoltaic systems including copper indium selenide (CIS) [51], copper indium gallium (di)selenide (CIGS) [52][53][54], copper zinc tin sulphide (CZTS) [55][56] and cadmium telluride (CdTe) [1][57][58][59][60]. Although research is being conducted to evaluate alternatives to CdS in CIGS [7][53][10], the highest efficiency devices utilise a CdS window layer [2][8]. The CdS window layer is required to provide good transmission of light through to the absorber layer in a thin film photovoltaic (PV) stack. It is desirable to keep the CdS layer uniform to suppress shorting effects and as thin as possible (50-100 nm) to allow a high fraction of the photons with energy above its band gap to reach the CdTe absorber and hence produce a high photocurrent [61]. In addition, CdS has good photoconductivity properties, relatively easy doping and low resistive Ohmic contact. Furthermore, although still under development, a variety of deposition methods have been studied, which provide reproducible uniform, high quality films, with good adherence to different substrates.

To deposit a polycrystalline film of cadmium sulphide on a TCO different deposition methods can be used, including: Chemical Bath Deposition (CBD) [7][12][62], Electrodeposition (ED) [63], Close Space Sublimation (CSS) [13][64][65][66][67], Radio frequency (RF) sputtering [1][68][69][24][70] and High Vacuum Evaporation (HVE) [71][6][16][72]. Polycrystalline CdS films exist in two crystalline phases: a metastable cubic structure (Zinc blende), with the preferential orientation along the (111) direction and the stable hexagonal structure (Wurtzite) with (002) as the preferential orientation/reflection [73][74][75]. A mixture of hexagonal and cubic structure has been also reported in literature [76]. The structural transition from cubic to the hexagonal form caused by annealing or by other post deposition treatments has been investigated [76] [77]. The change in structure is accompanied by changes in the band gap energy of the annealed/treated films [78]. A detailed analysis of this is provided later in this thesis (Chapters 6, 7, 8). The typical grain size is in the range of 0.1 to 0.5 μm and it recrystallises after the CdCl₂ treatment [46]. CdS can help to
reduce reflection losses. An increase in both light absorption and carrier recombination also occurs. The morphology of CdS and its electrical performance depend on the parameters used during the deposition process and during any post-deposition treatments. The functionality of CdS/CdTe heterojunction solar cells is strongly influenced by the CdS/TCO substrates, since in the multi-stack structure of the cell, the physical and morphological properties of each layer play an important role in the resulting total efficiency.

*p-CdTe absorber layer:* CdTe is a p-type semiconductor which works as the absorber layer in this type of thin film solar cell. It forms the CdS/CdTe junction [79]. CdTe is a group II^B^-VI^A^ compound semiconductor, and it exhibits a direct optical band gap ($E_g = 1.5 \text{ eV}$) which optimally matches to the solar spectrum for photovoltaic energy conversion. Because of its high absorption coefficient (> $5 \times 10^4 \text{ cm}^{-1}$), and the nearly ideal optical band gap, a high quantum yield can be expected over a wide wavelength range, from the UV to the CdTe band gap, $\lambda \sim 825 \text{ nm}$. This means that the absorption near the CdTe surface occurs for photons with $E > E_g$, and the required absorber layer thickness to absorb >90 % of the light above the band gap is only about 1 μm [80] [81]. Other physical properties such as the high ionic nature, high melting point temperature, and large lattice parameter make this semiconductor an attractive absorber-layer material for thin-film solar cells [82].
Figure 16 shows the theoretical efficiency for a solar cell and the optical absorption coefficient as a function of the band gap for CdTe and other materials commonly used in PV cells for comparison.

![Figure 16: Theoretical solar cell efficiency (dotted line) for AM 1.5 spectral irradiance as a function of the band gap and absorption coefficient (solid line) as a function of energy for selected semiconducting photovoltaic materials [80].](image)

The phase diagram of CdTe (Figure 17) shows that above 500°C the stoichiometric compound is the stable solid phase [81]. According to the CdTe temperature-atomic % (T-x) phase diagram [81], there is a narrow window for stoichiometric composition $\sim 10^{-6}$ at. %, for temperatures lower than 500°C. CdTe can be Cd- or Te-rich depending on the deposition conditions. The CdTe melt temperature, $T_m=1092$°C is higher than that of the single elements, Cd, $T_m=321$°C and Te, $T_m=450$°C [83]. Due to the strong ionic behaviour (72 %) of the material, the photon energy in the solar spectrum is lower than the energy of CdTe (and also...
CdS) chemical bonds (>5 eV). This leads to the material being highly stable chemically and thermally, without degradation of performance.

![Figure 17: Cd-Te phase diagram](image)

Bulk single crystals of CdTe show the zinc blende structure. CdTe thin films can grow in both the stable cubic form and the metastable hexagonal form [85]. The hexagonal phase is more probable with increasing substrate temperature. The tetrahedral coordination of both Cd and Te species is favoured for CdTe in the zinc blende structure [86]. Polycrystalline CdTe films show the most intense reflection along the (111) direction together with (220) and (311) reflections as shown in the PDF card (Figure 18) [87] [88] [89] [90]. A thickness of a few microns results in 99% of the light entering the layer, being absorbed [91]. CdTe is the only compound in the Cd-Te system; it has a highly negative formation enthalpy; the vapour pressures of both Cd and Te are much higher than that of CdTe and for this reason the annealing process can be carried out whilst maintaining the integrity of the compound [92]. CdTe can be deposited by RF Sputtering, CBD [93], ED [36], CSS [37], Physical Vapour Deposition (PVD) [94] followed by CdCl₂ treatment and annealing in air.

The CdCl₂ treatment process greatly enhances efficiency, increasing the conductivity of p-CdTe. This step is important to change the structural and electrical properties of the absorber layer, increasing grain size, removing planar defects and passivating grain boundaries [95].
Chapter 2

The grain size is in the range of 0.5 to 2 μm, which increases to 5 μm after recrystallisation, with irregular morphology and grain boundaries. Imperfections or defects can dramatically modify the electrical conductivity of the semiconductor, as they add states in its band gap. Depending on the location of their energy states relative to the conduction or valence band edge, it is possible to distinguish them as shallow defects and deep states. Shallow defects have energy levels within a few tens of meV from the respective band edges and are relatively close to the conduction or to the valence band. Deep states can be found typically within the middle third of the semiconductor energy band gap [96][97]. In particular, cadmium vacancies (V_{Cd}) are shallow acceptor states, cadmium substitution for tellurium sites (Cd_{Te}) and interstitial cadmium (Cd_{i}) are shallow donor states, while interstitial tellurium (Te_{i}) is a deep state [80].

Figure 18: PDF card for CdTe in the cubic crystalline structure with 20 values of the characteristic reflections, with their intensity and hkl indices [87].
One interesting electrical property for CdTe is its amphoteric semiconducting behaviour, which makes it possible to dope intrinsically and extrinsically $n$ and $p$-type [47][98]. In general high efficiency CdTe solar cells are based on a $p$-type CdTe and $n$-type CdS structure. The required electrical properties are obtained by activation treatments which allow the introduction of specific impurities into CdTe and CdS thin layers (such as CdCl$_2$, O$_2$, Cu) to activate or passivate native defects [99]. However, the presence of imperfections or defects disrupts the periodic structure introducing localised electronic states within the band gap $E_g$. The types of defect which control the electronic properties include native defects, and/or chemical impurities and they can occur as a substitution of one element or as interstitial defects.

$Cu/Au$ or different types of back contact, and are usually annealed. These provide an electrical connection to the CdTe, which is a difficult material to produce an Ohmic contact to, due to its high electron affinity and high energy band gap.

### 2.2. Critical issues with CdS and CdTe: thickness, pinholes formation and annealing treatment

When considering all the properties of CdS and CdTe thin films, there are some aspects that are considered as critical to the performance of the CdTe/CdS solar cell. Firstly, film uniformity and the thickness of the CdS layer affects the cell efficiency [100]. The CdS layer can limit current generation by light absorption and this problem can be mitigated by using thinner films. Thinner films allow most of the light to pass through, but the layer thickness has a lower limit below which it becomes ineffective. As the layer becomes thinner, there are other aspects to consider, such as non-optimal electric field distribution and a possible increase in non-uniformity. The goal is to minimise the reduction of $V_{OC}$ and $FF$ values, due to the presence of pinholes, leakage along grain boundaries and maximise the transmission of the light through the layer. According to the literature, CdS layers have an optimum thickness around 100 nm [8]. Reducing the thickness further (lower) than 80 nm, results in severe losses in $V_{OC}$ and $FF$, due to non-uniformity (loss of continuity) of the CdS.

Another important issue for both CdS and CdTe film deposition is the formation of pinholes. Therefore, substrate cleaning and post-deposition treatments also have a significant influence on the material properties and performance. Different attempts have been made to overcome
these problems, as the deposition of a thin layer of CdS with a second layer of small grains in order to fill pinholes (~80 nm), generating a bi-layer structure can improve the short circuit current of the cell [101]. In addition, during post-deposition treatments, interdiffusion between S (from CdS) and Te (from CdTe) generally occurs, which results in CdS consumption. Therefore, this method could be useful as a protection of the junction properties and conservation of the CdS layer integrity. By using a bi-layer structure, pinhole formation is reduced, maintaining a relatively thin CdS layer. Other studies have been performed by post-deposition treatments of the films.

Thermal treatment of CdS and CdTe films promote changes in morphology and grain orientation. The heat treatment can be carried out in a different atmosphere or an additional post-deposition treatment can be performed using CdCl₂ [102]. Post-deposition treatments can be performed on films which have been deposited using different deposition processes. Depending on the deposition process employed, the as-deposited film can be amorphous, metastable cubic, mixed cubic/hexagonal. The treatments are carried out at temperatures above ~300°C to allow rearrangement of the neighbouring atoms. These processes lead to good crystallinity of the CdS and influences the growth of the subsequent CdTe layer [103]. The effect of post deposition treatments, depends on the deposition conditions of the as-deposited CdS [104]. The cadmium chloride (CdCl₂) treatment, also known as the ‘activation process’ is a vital process to dramatically improve the efficiency of CdS/CdTe devices. The benefits of CdCl₂ treatment are well established. They involve change in the surface morphology of the films, grain growth and coalescence, recrystallisation, reduction in optical losses, enhancement of CdTe p-type conductivity, passivation of interface defects, reduction in planar defects, randomisation of CdTe film orientation, change in concentration and distribution of trapping states, enhanced charge separation increasing hole depletion near grain boundaries and enhanced carrier collection [61].

Mismatch is important at the SnO₂ (substrate)-CdS interface, but interdiffusion effects and lattice match are much more important at the CdS-CdTe interface. Depending on the deposition technique [105], the amount of oxygen in the CdS film plays a role in the interdiffusion process between the two semiconductor layers. Several effects at the two interfaces have to be considered and a good compromise between them has to be reached during device engineering.
A number of these critical issues have been investigated in this thesis and the results are reported in the following chapters.
3. References


Chapter 2


Chapter 2

3. Thin Film processing methods for CdTe solar cells

1. Plasma Cleaning

The presence of contaminants and native oxides can affect the growth mode and the properties of the deposited film and the subsequent performance of electronic devices and solar cells [106]. Plasma cleaning is an effective, environmentally safe, economical method for treating surfaces. It is used to remove surface contaminants by low energy ion bombardment and by ultra-violet light generated in the plasma which is able to break down organic bonds and carbon residues.

The first step in processing CdTe solar cells in this thesis focused on studying the activation of the surface of the FTO substrate by applying a plasma pre-treatment to the sample. This was found to be an important processing step to avoid the presence of pinholes in subsequent layers.

1.1. What is a plasma?

A plasma is considered to be the fourth state of matter because its properties are similar to those of the gas and liquid phase, but it cannot be defined as either of them. Plasma is a partially, or wholly, ionised gas with an equal number of positive and negative charged particles. Electrons and ions as free electric charges make the plasma electrically conductive and responsive to electromagnetic fields.

Some of its many features make it attractive for applications in chemistry and other disciplines. The temperatures (electron temperature) of some plasma components and their energy density can reach values that greatly exceed those in conventional chemical technologies. Electrons, ions, atoms and radicals, in excited states, and photons at different wavelengths, are obtained in high concentrations as energetic active species. The plasma is far from thermodynamic equilibrium, keeping the bulk temperature as low as room temperature [107].
In a typical plasma system, the glow discharge is created by evacuating a vacuum vessel, made from an inert material, usually quartz, stainless steel or aluminium and refilling it with a low-pressure gas. It is possible to use different power supplies including radio frequency (RF), microwave (MW) and alternating or direct current (AC or DC). More recently pulsed DC and High-power Impulse Magnetron Sputtering (HIPIMS) supplies have also become available. The surfaces in contact with the gas plasma are bombarded by activated energetic species and their energy is transferred from the plasma to the material [108].

Plasma treatments are used to clean surfaces of metals, plastics, glass or polymers to remove contaminants and impurities. These can exist in the form of residues, anti-oxidants, carbon residues and other organic contaminants. It is important to choose the correct plasma gas, as gases react in different ways to remove contaminants on surfaces. For example, to remove organic contaminants, an oxygen plasma followed by an argon plasma is commonly used. In this way, the oxygen plasma is responsible for cracking the organic hydrocarbon molecule (i.e., C–H, C–C, C=C, C–O, and C–N). Oxygen species created in the plasma (O$_2^+$, O$_2^-$, O$_3$, O, O$^+$, O$^-$, ionised ozone, metastable excited oxygen, and free electrons) react with the organic residues to form H$_2$O, carbon monoxide (CO) and carbon dioxide (CO$_2$). Any other remaining oxide layer is removed from the surface by argon plasma bombardment. These compounds have high vapour pressures and are evacuated from the chamber during processing, leaving the surface perfectly clean (Figure 19).
Figure 19: Schematic diagram showing a plasma surface treatment reactor.

A wide range of parameters can affect the chemical and physical characteristics of the plasma and the chemistry of the treated surface. These include reactor design, gas inlet and vacuum, electrode location, power, temperature, gases ratio, pressure and treatment time.

Experimental details for plasma cleaning

For this study the substrate was treated using 20 sccm O₂ / 30 sccm Ar plasma, for 5 min, in a Glen100-P AE Advanced Energy parallel plate plasma reactor, prior to the CdS film growth. The plasma power was set at 100 W and at a pressure of between 335 and 273 mTorr. Electrodes and sample trays are 406.4 mm x 406.4 mm in area using perforated aluminium of thickness 3.175 mm. The parallel electrodes are used to provide uniform plasma across the sample area. All substrate surfaces are treated to the same degree, irrespective of their position on the sample tray. The plasma treatment reactor was a parallel plate system using AC plasma power source with potential for three gas admittance lines. The system was
pumped to a pre-process pressure of 332 mTorr using a rotary pump (details are provided in chapter 5).

2. CdS thin films

The functionality of CdS/CdTe heterojunction solar cells is determined by the CdS/TCO substrate utilised, since in the multi-stack structure the physical and morphological properties of each layer play an important role in the resulting total efficiency of the cell.

A wide range of techniques have been used to deposit CdS layers, including Close Spaced Sublimation (CSS), Chemical Bath Deposition (CBD), vacuum evaporation, spray deposition, Electrodeposition (ED), RF sputtering and Chemical Vapour Deposition (CVD). The deposition technique used will affect the grain size, orientation and crystallographic phase of the material.

Closed-space sublimated (CSS) CdS films generally show the hexagonal crystalline structure. While CBD CdS usually results in the cubic phase, which transforms into the more stable hexagonal structure after an annealing treatment [112]. CBD CdS films are characterised by the presence of oxygen in the coatings, which affects the interdiffusion process between CdS and CdTe [105]. Controlling the interdiffusion between CdS and CdTe layers is useful to overcome the lattice mismatch between CdS and CdTe which is ~ 10% with high defect density at the interface [113].

The common vacuum-based techniques used to deposit CdS window layers are RF Sputtering and Physical Vapour Deposition (PVD) [114]. According to the literature RF sputtered as-deposited films develop a hexagonal structure with preferential orientation in the <002> direction and a grain size dependent on film thickness [109]. Similar to CSS-deposited CdS, for PVD CdS films, the crystalline phase is hexagonal with preferential orientation in the <002> direction. The deposition temperature is another crucial parameter, the higher the temperature the more intense the preferred orientation. Also the band gap is affected by the deposition and annealing temperature. After annealing the film has been observed to be more textured.

Alternative non-vacuum, atmospheric pressure techniques used to deposit CdS are electrodeposition and Metal-Organic Chemical Vapour Deposition (MOCVD). After annealing, the electrodeposited CdS possesses a hexagonal structure. MOCVD deposition
also occurs at atmospheric pressure, using organometallic precursors such as dimethyl cadmium (DMCd) and ditertiarybutylsulphide (DTBS). The CdS layer is generally doped with nButylChloride (nBuCl). The resulting CdS layer results in epitaxial growth of the deposited CdTe layer [110].

2.1. Chemical Bath Deposition

Among the various deposition methods available for this study, it was decided to investigate the use of a non-vacuum and low cost technique, Chemical Bath Deposition (CBD). This is considered to be one of the most promising methods, which produces high quality films, with a few defects and a good stoichiometry. Furthermore, it is a low cost process that is scalable for large-area processing [115].

The CdS film growth is created by the reaction between Cd$^{2+}$ and S$^{2-}$ ions in an alkaline solution. Usually the solution contains Thiourea (CS(NH$_2$)$_2$) and a cadmium salt (see reactions below), as the main reactants. Many studies have focused on the optimisation of the reaction conditions to produce CdS films suitable for solar cells. The literature includes a wide variety of recipes in which different parameters have been changed to test their effect on the film properties [13] [14] [15] [16] [17].

CBD can be used to deposit any compound that satisfies four basic requirements:

- the material must be prepared by simple precipitation,
- the compound is highly insoluble in the solution,
- the compound is chemically stable in the solution,
- the reaction should proceed with a free anion that is generated slowly [62].

Most CBD reactions are carried out in alkaline solution. To prevent the precipitation of metal hydroxides, a complexing agent (ligand) is added to the Cd salt to form a cadmium complex species in the solution [116]. The complexing agent also reduces the concentration of free metal ions, leading to the slow release of Cd$^{2+}$ ions, which helps to prevent rapid bulk precipitation of the desired product. The S$^{2-}$ ions are supplied by the decomposition of Thiourea [61][117].
2.1.1. Chemical mechanisms proposed in literature

Chemical deposition has been in use for a long time and the reactions involved are straightforward, even if the mechanism of the process is often unclear. There are several proposed mechanisms and they can be divided into four different types.

- Ion-by-ion mechanism:

  (dissociation of complex to free Cd\(^{2+}\) ions)
  1. \(Cd(NH_3)_4^{2+} \leftrightarrow Cd^{2+} + 4NH_3\)

  (formation of sulphide ions)
  2. \((NH_2)_2CS + 2OH^- \rightarrow S^{2-} + CN_2H_2 + 2H_2O\)

  (CdS formation by ionic reaction)
  3. \(Cd^{2+} + S^{2-} \rightarrow CdS_{(s)}\)

- Cluster (hydroxide) mechanism

  (formation of a solid Cd(OH)\(_n\) cluster)
  4. \(nCd^{2+} + 2nOH^- \leftrightarrow [Cd(OH)_2]_n\)

  (exchange reaction)
  5. \([Cd(OH)_2]_n + nS^{2-} \text{ (from reaction 2.)} \rightarrow nCdS + 2nOH^-\)

- Complex decomposition ion-by-ion mechanism

  6. \((NH_2)_2CS + Cd^{2+} \leftrightarrow [(NH_2)_2CS - Cd]^{2+}\)

  7. \([(NH_2)_2CS - Cd]^{2+} + 2OH^- \rightarrow CdS + CN_2H_2 + 2H_2O\)

- Complex decomposition cluster mechanism
Chapter 3

8. $[Cd(OH)_2]_n$ (from reaction 4.) + $(NH_2)_2CS \leftrightarrow [Cd(OH)_2]_{n-1}(OH)_2CdSC(NH_2)_2$

9. $[Cd(OH)_2]_{n-1}(OH)_2CdSC(NH_2)_2 \rightarrow [Cd(OH)_2]_{n-1}CdS + CN_2H_2 + 2H_2O$

This reaction will continue until conversion of all the $Cd(OH)_2$ into CdS [118]:

The first two mechanisms involve free sulphide and cadmium ions, whilst the last two mechanisms involve carbon-chalcogen bonds but no free chalcogenides. It is also possible that more than one mechanism occurs at the same time and that other conditions change during the process thereby modifying the deposition mechanism.

The most commonly considered mechanism for the CdS growth is by ion-by ion, in a solution consisting of ammonia $(NH_3)$, Thiourea $CS(NH_2)_2$ and a cadmium salt (CdSO$_4$ or Cd(CH$_3$CO$_2$)$_2$) [119][120].

$S^{2-}$ ions are products of the alkaline hydorolysis of $CS(NH_2)_2$ and Cd$^{2+}$ ions are produced by the dissociation of the amino complex. The coordination number $(n)$ of this cadmium-ammonia complex is in the range 1 to 6 depending on the ammonia concentration [62]. When the product of $S^{2-}$ and Cd$^{2+}$ ion concentration is higher than the solubility product of CdS, $k_s = \sim 10^{-25}$, CdS starts to precipitate in the solution.

According to this classical model, an homogeneous mechanism occurs, with the formation of the CdS precipitate dominating the CdS thin film formation on the surface of the substrate immersed in the reaction solution (see below). Two kinds of precipitation occur: homogeneous and heterogenenous. The first one is a reaction in the bulk solution, where colloidal CdS or cluster aggregates are produced. The heterogeneous precipitation occurs on the substrate surface.

The mechanism proposed by Ortega-Borges and Lincot [121] for this is as follows:

1. Reversible adsorption of hydroxo-cadmium species:

$$Cd(NH_3)_2^{2+} + 2OH^- + site \leftrightarrow Cd[(OH)_2]_{ads} + nNH_3$$ \hspace{1cm} 11

2. Adsorption of thiourea by formation of a metastable complex:

$$Cd[(OH)_2]_{ads} + SC(NH_2)_2 \rightarrow [Cd(OH)_2SC(NH_2)_2]_{ads}$$ \hspace{1cm} 12
3. Formation of CdS by the metastable complex decomposition:

\[
[Cd(OH)_{2}SC(NH_{2})_{2}]^{\text{ads}} \xrightarrow{k_{3}} CdS + CN_{2}H_{2} + 2H_{2}O + \text{site}
\]

In this mechanism the rate-determining step is the metastable complex decomposition, so the metastable complex species adsorption (eq. 2) is responsible for the CdS film formation on the substrate [122].

According to Y.J.Chang et al. the CBD growth mechanisms appears to be similar to those in CVD, and the processes involved are mass transport of reactants, adsorption, surface diffusion, reaction, nucleation and growth [123].

Figure 20 shows a schematic diagram of the CdS growth mechanism based on two major reactions: homogeneous particle formation and heterogeneous surface reaction.

In the bulk solution the Cd\(^{2+}\) ions complex with ammonia, producing tetra-amino-cadmium complex ion \(Cd(NH_{3})_{4}^{+}\). Free sulphide ions, S\(^{2-}\), are released from CS(NH\(_2\))\(_2\) by a hydrolysis reaction and then CdS particles are obtained in the bulk solution from the reaction between Cd\(^{2+}\) and S\(^{2-}\).

Simultaneously, the complex ions on the surface react with hydroxide ions to form the adsorbed complex \([Cd(OH)_{2}SC(NH_{2})_{2}]^{\text{ads}}\) [62], this reacting with CS(NH\(_2\))\(_2\), forms the
metastable species $[Cd(OH)_2(NH_3)_2SC(NH_2)_2]_{ads}$, which finally decomposes to form CdS [124].

*Kaur et al.* suggested *ion-by-ion growth* in which the presence of colloidal particles will impact the film quality, promoting loose and powdery CdS films [125].

Their mechanism starts with the formation of Cd$^{2+}$ ions in solution, originated from salts, such as CdSO$_4$, Cd(NO$_3$)$_2$, Cd(CH$_3$CO$_2$)$_2$ and CdCl$_2$. In alkaline solution ammonium hydroxide provides ammonia in the solution:

$$\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O}$$

Cadmium ion complexes reacting with the ammonia and sulphide ions released by CS(NH$_2$)$_2$ produce CdS. Free Cd$^{2+}$ and S$^{2-}$ ions can react either through an homogeneous or an heterogeneous process. The more likely mechanism is that of the homogeneous nucleation process rather than heterogeneous [26]. They identified three main deposition regimes. The first one is called the *induction or coalescence regime* with nucleation centre formation, with a slow reaction rate. The second is the *compact layer growth regime* through the surface reactions which provides high quality films with good adhesion. The last one is a *porous layer regime* due to colloidal sticking caused by homogeous CdS particle formation.

*Mazon-Montijo et al.* suggested a similar mechanism based on nucleation, particle growth and final growth. [126] The first step leads to the formation of particles on the substrate. The growth of the film depends on the different deposition conditions chosen, it may occur by a condensation mechanism called *ion-by-ion*, by adsorption of colloidal particles, called *cluster-by-cluster* or by both mechanisms, known as *mixed growth*.

Various studies performed on the CdS growth mechanism, have also led to theories relating to the process, the role of chemical species involved and how they act to form the film on the substrate. Some of them agree on the necessary presence of cadmium hydroxide, Cd(OH)$_2$, to allow the CdS film growth and adhesion to the substrate. Others use the hypothesis that once CS(NH$_2$)$_2$ hydrolysis occurs, the Cd(OH)$_2$ layer is replaced with a layer of CdS; hence there are more free sulphide ions in the solution [120].

$$(\text{NH}_2)_2\text{CS} + 2\text{OH}^- \rightarrow \text{CH}_2\text{N}_2 + 2\text{H}_2\text{O} + \text{S}^{2-}$$
Chapter 3

Kaur et al. [127] found solution conditions under which CdS films were formed in the absence of Cd(OH)\textsubscript{2} precipitate, where NH\textsubscript{3} plays a major role in determining the quality of the films [128].

A wide range of parameters are involved in this process, and the literature reveals [125], that it is possible to modify the reaction system, changing the reactants, choosing for example different cadmium salts, like CdCl\textsubscript{2}, Cd(CH\textsubscript{3}COO)\textsubscript{2}, CdSO\textsubscript{4} or Cd(NO\textsubscript{3})\textsubscript{2} [120][129] or different sources for sulphide ions like CS(NH\textsubscript{2})\textsubscript{2}, thioacetamide, sodium thiosulphate or sodium sulphide [126][130].

Another parameter investigated is the ligand used. In general ammonia is used, but due to its high volatility, ethylenediamine has been used as an alternative [131]. Various studies have investigated different deposition temperatures, deposition times, thicknesses of the film, morphological, structural, optical and electrical properties, or adding ultrasonication during the deposition (it will be discussed further in this chapter) [62][116][132][133][134].

Ouachtari et al. [135] tested different initial solutions to grow CBD-CdS films, prepared from anhydrous cadmium chloride (CdCl\textsubscript{2}), CS(NH\textsubscript{2})\textsubscript{2}, NH\textsubscript{3} as a complexing agent, and ammonium chloride (NH\textsubscript{4}Cl). CdCl\textsubscript{2} has been used as a source for Cd\textsuperscript{2+} and Thiourea for S\textsuperscript{2-}. During CdS film deposition, the formation of Cd(OH)\textsubscript{2} occurred as a competing process in the bath. NH\textsubscript{3} is a source of OH\textsuperscript{-} ions. A true complexing agent was needed to control the slow release of metal ions and sulphur ions in order to improve homogeneity of the thin films as well as the growth rate. This study found that good quality CdS thin films, with a wurtzite structure, could be grown by using cadmium chloride and Thiourea as sources of cadmium and sulphur ions, respectively.

Some researchers have investigated different Cd sources (e.g. CdCl\textsubscript{2}, Cd(NO\textsubscript{3})\textsubscript{2}, CdI\textsubscript{2}/Cd(CH\textsubscript{3}COO)\textsubscript{2} and CdSO\textsubscript{4}) in order to study their influence on the electrical/optical/structural properties and surface morphology of CdS films deposited by CBD [129][136].

It has been shown that CdCl\textsubscript{2}-based films have better optical transmission, greater uniformity and a smoother surface compared with films prepared with other Cd salts [119]. The optical band gap was found to increase in the order CdCl\textsubscript{2}, Cd(NO\textsubscript{3})\textsubscript{2}, CdI\textsubscript{2}/Cd(CH\textsubscript{3}COO)\textsubscript{2} and CdSO\textsubscript{4}, whereas the thickness increases in the order CdI\textsubscript{2}, CdCl\textsubscript{2}, Cd(NO\textsubscript{3})\textsubscript{2}/Cd(CH\textsubscript{3}COO)\textsubscript{2}, CdSO\textsubscript{4}. For all Cd sources the films were found to be cubic in structure regardless of the Cd salt used. All the films exhibit high transmittance ~75%, low absorbance and low reflectance in the region from ~500 nm onwards [136].
The grain size decreases in the order CdSO$_4$ CdCl$_2$ Cd(CH$_3$COO)$_2$ CdI$_2$. The use of CdCl$_2$ and CdI$_2$ results in highly stoichiometric films (S:Cd=1:1). Literature reports [73][137][74][138] that the stable structure for CdS is the hexagonal phase, while the cubic structure is metastable [139][140]. The most common crystalline structure obtained by CBD is cubic but it changes into hexagonal by annealing at around 300ºC [75][77][73][137]. Nevertheless some authors [133][141][142] report that the as-grown CBD-CdS film (from a basic aqueous bath) is characterised by the hexagonal structure [143]. There are also studies [144][127] that infer the existence of both hexagonal and cubic phase as a mixed structure depending on the deposition conditions (Figure 21).
2.2. Growth mechanism

A growth mechanism for CdS thin films has been assumed from the literature, and the experimental work presented in this thesis. The layer deposition can be divided into three steps:

1. Induction period

Consisting of ion formation by the reactions:

\[ Cd(NH_3)_4^{2+} \leftrightarrow Cd^{2+} + 4NH_3 \]

\[ SC(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CN_2H_2 + 2H_2O \]

Through these reactions it is possible to have the ions \( Cd^{2+} \) and \( S^{2-} \) in the solution by decomposition of \( Cd(NH_3)_4^{2+} \) complex ions and thiourea hydrolysis in alkaline medium. This last reaction consumes hydroxide ions tending to decrease the starting pH value (12) of the reaction mixture.

2. Layer growth period by “ion by ion” mechanism

The ions formed are absorbed on the substrate, followed by chemical reaction between these species and the ion by ion mechanism starts to work. This growth is enhanced by the hydrophilic surface, where Cd(OH)\(_2\) nuclei are formed by absorption of OH\(^-\) ions from the solution. The Cd(OH)\(_2\) then reacts to form CdS [120].

\[ Cd^{2+} + S^{2-} \rightarrow CdS_{(s)} \]

Two kinds of precipitation occur during this process, one is the heterogeneous precipitation which takes place on the substrate. This has been tested during the present experimental work, this is the first type of precipitation that occurs in the chemical bath. The substrate changes colour, from transparent to pale-yellow, after a few minutes from the starting point of the experiment. The second type of precipitation is the homogeneous one which occurs in the bulk solution, where CdS colloids or aggregates are produced.

3. Layer growth period by “cluster by cluster” mechanism
Once the CdS colloids are formed in the bulk, they adhere to the substrate or over the layer previously deposited. The result is a porous less adherent layer on the top surface. It has been assumed that this third step of the process takes place at higher concentrations and for long reaction times. The non-adherent clusters precipitate on the bottom of the reaction beaker and it is possible to observe them directly in the solution.

For hetero-epitaxy, which means that the film and substrate are different materials, there are three main thin films growth modes, which are shown in the Figure 22, and which are determined by the surface free energies not only of the substrate but also of the materials deposited.

**Frank-van der Merwe**  \[\text{Volmer-Weber} \quad \text{Stranski-Krastanov}\]

![Figure 22](image-url)  

*Figure 22: A schematic diagram showing three growth modes for thin films.*

The *Frank van der Merwe or layer by layer* mode shows how a new layer is nucleated only after completion of the layer below, this growth occurs over long distances in the ideal case.

In general it yields the highest crystalline quality, and it occurs when film atoms are more strongly bound to the substrate than to each other.
The Volmer Weber or island growth consists of a first phase of a large number of surface nuclei followed by a second phase where they spread, forming three dimensional islands. Here, film atoms are more strongly bound to each other than to the substrate.

Finally the Stranski-Krastanov or mixed growth is considered as intermediate of the previous ones; initially it is a layer by layer growth followed by the appearance of three dimensional islands.

**Experimental details for CdS thin films deposited byCBD**

In this study CdS thin films were deposited by CBD, the reaction occurs in a beaker immersed in a water jacket to ensure constant temperature (70ºC). The bath solution was made of 200 ml of de-ionized water, 15 ml of Cd(CH$_3$COO)$_2$ 0.01 M, 25 ml of NH$_4$OH 25%, and 10 ml of CS(NH$_2$)$_2$. A magnetic bar was used to stir the solution to accelerate the reaction kinetics. After, the stirrer was replaced by the ultrasonic probe. (Details are in chapter 5 and 6).

3. **Pulsed DC Magnetron Sputtering of CdS**

A novel vacuum-based process has been chosen for the deposition of CdS thin films for this thesis, Pulsed DC Magnetron Sputtering (PDCMS).

Deposition of films by sputtering was first observed in 1852 by Grove [146], it was used through the 1920s for depositing reflective coatings and thin films samples. The implementation of this technique has changed dramatically since the introduction of magnetron systems in 1970s [147]. Magnetron sputtering has become the process of choice for the deposition of a wide range of coatings such as low friction coatings, corrosion-resistant coatings, coatings with specific electrical or optical properties [148]. The reason behind the development of this process has been the increasing demand of high quality functional films in a variety of sectors and application areas.

The basic sputtering process is characterised by a target plate, called the cathode, which is bombarded by energetic ions generated by the glow discharge plasma in front of the target. Free ions and electrons are attracted to opposite electrodes producing a discharge. However, in order to obtain a self-sustained discharge, regeneration of the electrons by the positive ion
bombardment of the cathode is required. This produces secondary electrons and enhances ionization. This bombardment is responsible for the removal of target atoms (from which the term ‘sputtering’ derives), either individual atoms, clusters of atoms or molecules. These neutral particles once ejected, travel until they then condense on a substrate, making a thin film [149] [150]. The basics of the sputtering process have been known and used for many years [151]. Generally, in sputtering there are different ways of operation: DC (diode and triode) and AC (radio-frequency, RF). However, low deposition rates, low ionisation efficiencies in the plasma, high substrate heating effect are limitations for this process.

To overcome all these negative issues, magnetron sputtering has been highly developed [152] [153]. This technology has resulted in higher plasma density, an arc suppression process and high deposition rates.

Magnetrons are important because the magnetic field, being parallel to the target surface, constrains secondary electrons motion near the target. The common features of magnetrons are shown in the cylindrical geometry in Figure 23. One magnetic pole is positioned at the central axis of the target and the second one is made by a ring of magnets placed at the outer edge of the target. In this way the electrons are trapped, increasing the ionising electron-atom collisions. In fact the combined effect of the electric field and the orthogonal magnetic field is to confine the electrons in cycloid paths around the target, while they are free to move parallel to the target surface along the magnetic field lines [147] [154]. Therefore, the path of the trapped electrons is significantly longer than the distance between the electrodes. This means that the trapped electrons are forced to make many more collisions with the working gas while trapped in front of the target. Consequently, the increased number of collisions between the working gas and the secondary electrons produce more electrons for sputtering. This is the reason why the use of magnetrons provides dense plasmas in the target region. This causes the increased ion bombardment of the target, increasing the ionisation probability and thus the plasma density also in regions far from the target. This results in higher sputtering rates at the target and higher deposition rates at the substrate. The increased ionisation efficiency allows the discharge to be maintained at a lower operating pressure ($10^{-3}$ mbar, instead of $10^{-2}$ mbar) and also at a lower operating voltage (-500 V instead of -2, -3 kV) than in the basic sputtering mode.
Figure 23: Schematic cross section of a cylindrical magnetron with the magnetic field, $B$, parallel to the axis of the cylinder. The electric field, $E$, is radial, with the voltage drop across the dark space which is typically less than 5 mm thick.

More recently the development of unbalanced magnetron sputtering has further improved the technology. In conventional magnetron sputtering (Figure 24 (a)), the plasma is totally confined to the target region. In this way, substrates locate within a range of ~60 mm from the target surface can be affected by the dense plasma, while those placed outside this region are affected by a low plasma density [155]. Due to the high concentration of electrons trapped in the region above the target, the ionisation of the carrier gas is more heavily concentrated in the same region. This causes the depletion of the source material over the target area, where the magnetic field is parallel to the target face, a highly non uniform plasma density, which results in simultaneous material removal and eventually re-deposition in adjacent target regions [156].

The energy of the bombarding ions depends not only on the working gas pressure, the voltage, the current and the magnetic field configuration, but also on the negative bias applied to the substrate and the distance between substrate and target. To increase the energy of the bombarding ions, it is possible to increase the negative bias on the substrate. Increasing the energy of the sputtered material can increase the probability of defects and increased film stress. To deposit dense films, avoiding excessive intrinsic stress, a high flux ($> 2$ mA/cm$^2$) of low energy ($< 100$ eV) ions is required [157]. These are the conditions provided by
unbalanced magnetrons, where the field lines are not totally closed between the central and the outer poles in the magnetron, but some are directed towards the substrate. Some of the secondary electrons follow these field lines. As a consequence, the plasma is not confined to the target region, but it is allowed to spread out towards the substrate [41]. Most of the electrons are confined in the so called magnetic-trap, close to the target, approximately within the dark space distance (typically <5 mm), while ions are accelerated to the target for sputtering [147] [158].

With this unbalanced field configuration (Figure 24 (b)), the ion current at the substrate is directly proportional to the target current, and the deposition rate is also directly proportional to the target current.

Unbalanced magnetron DC sputtering is a useful configuration: for the same applied voltage, the typically drawn current is one to two orders of magnitude more than with magnetron sputtering with simple DC discharges. This leads to higher deposition rates (in the range of 1 nm/s to 10 nm/s), or alternatively, lower applied voltage compare to conventional DC and RF sputtering. Other advantages of magnetron sputtering are the coating uniformity, the possibility to scale up the process, growing dense and well-adherent coatings, availability of a wide range of film materials and the tunability of film properties [42] [70].
3.1. Pulsed DC magnetron sputtering

Pulsed DC magnetron sputtering (PDCMS) is a recently developed process that overcomes those limitations encountered when operating in reactive sputtering mode. It has industrial applications for coatings and thin films. In particular, this process has been useful for the production of insulating films such as oxides. Oxide coatings can be deposited by reactive magnetron sputtering and also by direct RF (radio frequency 13.56 MHz) sputtering of an oxide target. However, both of these processes have limitations. RF sputtering can provide high quality films but with the drawbacks of low deposition rates (typically in the range of ~0.3 nm/s) and the use of complex matching circuits. The main problem associated with reactive magnetron sputtering is caused by arcing events. Generally, the atoms in proximity to the target are in two physical states: gaseous or plasma. The plasma state is originated by the ionisation of the gas and it is the source of the sputtering ions. The plasma density is determined by the electron density, which in turn is dependent on the magnetic field. Due to, for example, a field emission from the target, or a breakdown of the target because of electric forces, electrons at high rate populate the plasma, attracting ions, which form a sheath around the incoming electrons. So that a thread of ions and electrons bridges the cathode gap, forming what is called an ‘arc’. Arcing appears mainly on the portion of the target surface which is strongly bombarded by positive ions and where dielectric coatings are deposited. When depositing dielectric thin films, there is the high possibility of coating the inside surfaces of the deposition chamber with non-conductive layers. These accumulate electric charges from the plasma. These are then responsible for the formation of mini- or macro- arcs which cause the ejection of material from the target surface. This ejected material, in turn, causes defects in the growing films, altering properties such as composition and structure. Arcing can also damage the power supply. They can even become a source of further arc discharges. The use of pulsed DC plasmas based on the medium frequency range (10-200 kHz), can drastically reduce the formation of arcs and consequently the defects in the growing thin films. This process enables high deposition rates and is attractive for industrial and commercial applications.

Pulsed sputter processes work with two modes of operation: unipolar pulsed sputtering, where the voltage is pulsed between the operating voltage and ground; and bipolar pulsed sputtering, where the target voltage is reversed, during the pulse–off period. Hereinafter the bipolar mode is explained in detail.
The Pulsed Magnetron Sputtering (PMS) uses pulsed DC power. Figure 25 shows a typical voltage sequence; the voltage applied to the target is typically -400 to -500 V for an ‘on-time’ \( \tau_{on} \). At the end of this negative voltage pulse, the power is either switched off an ‘off-time’ \( \tau_{off} \), or it is reduced to a small positive value (around 20 V). This part of the cycle is also called \( \tau_{rev} \) ‘reverse time’. This off-time removes traces of compounds from the target before it accumulates making the target irreversibly poisoned. To promote an arc-free process, the ‘on-time’ cycle should be short enough to avoid the charge build-up and the ‘reverse time’ sufficiently long to completely discharge the surface. In practice, the ‘reverse time’ is about 1/10 of the ‘on-time’ [170].

![Figure 25: A schematic diagram showing the ideal voltage sequence for a bipolar pulsed sputtering of dielectrics.](image)

The full cycle, \( \tau_{cycle} \), is the sum of the ‘on time’ and ‘reverse time’, defines the critical frequency, \( (f_c = 1/\tau_{cycle}) \), which is the lowest pulsing frequency and also the highest duty cycle for the pulsed DC sputtering process [167].
Table 1 shows some parameters used to compare the main representative techniques for the deposition of CdS thin films.

**Table 1**

Comparison between main deposition techniques for CdS thin films

<table>
<thead>
<tr>
<th></th>
<th>CBD</th>
<th>CSS</th>
<th>PVD</th>
<th>RF</th>
<th>ED</th>
<th>MOCVD</th>
</tr>
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<tbody>
<tr>
<td><strong>High Vacuum</strong></td>
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<tr>
<td></td>
<td>10 Torr</td>
<td>10^6 Torr</td>
<td>10^4 Torr</td>
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<tr>
<td><strong>Alternative non-vacuum</strong></td>
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<td>atmospheric Pressure</td>
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<tr>
<td><strong>Crystalline structure</strong></td>
<td>Cubic-mixture of cubic/hexagonal</td>
<td>Hexagonal</td>
<td>Hexagonal</td>
<td>Hexagonal</td>
<td>Cubic</td>
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**Experimental details for CdS thin films deposited by PDCMS**

In this work, CdS films were sputtered on TEC15 and TEC10 coated glasses using the following deposition parameters: 10 sccm Ar, 500 W, 150 kHz, 2 s (ramp time), 2 μs (reverse time) by PDCMS, using the ‘PV Solar’ sputtering system (Power Vision Ltd., Crewe UK) (details are provided in chapter 7).
4. Thin film deposition technologies for CdTe

There are numerous deposition technologies employed to deposit CdTe thin films for solar cells. These can be arranged into three main process categories [171]:

1) Condensation/reaction of vapours (Cd and Te$_2$) on a substrate (PVD) Physical Vapour Deposition, VTD (Vapour Transport Deposition), CSS (Close Spaced Sublimation), and sputter deposition) [16][17][18][19][20] [44-48] (Figure 26).

![Figure 26: A schematic diagram of some high vacuum deposition techniques used to deposit CdTe thin films.](image)

2) Galvanic reduction of ions (Cd and Te) at a surface (ED) [172] (Figure 27)
Chapter 3

Figure 27: A schematic diagram of the Electrodeposition technique.

3) Reaction of precursors at a surface (Metal Organic Chemical Vapour Deposition (MOCVD), screen printing, spray deposition). [173][174][175] (Figure 28 and Figure 29)

Figure 28: A schematic diagram of MOCVD technique.
Chapter 3

By using a high vacuum evaporation technique as outlined in category 1, CdTe films have been deposited by evaporation from a heated crucible and subsequent condensation of Cd and Te vapours on a heated substrate. For substrate temperatures above 446.85ºC re-evaporation from the substrate can occur. This can lead to the deposition rate decreasing with the substrate temperature, at low chamber pressures, and is one of the limitations for the PVD technique. PVD CdTe films are generally deposited at a substrate temperature about 300ºC, after the CdS is deposited in the same chamber without breaking the vacuum [71]. PVD differs from the CSS technique because the substrate temperature is lower (~300ºC), and because of the greater distance between the substrate and source. The process is also different because the source changes from the solid to liquid state and then turns into vapour. The evaporated CdTe layers appear columnar and highly orientated when deposited, following the morphology of the underlying CdS film. However when recrystallized, the CdTe grains change orientation and morphology [176]. When the substrate temperature is much lower, CdTe layer forms a different crystalline structure (zinc blende) compared to the standard deposition condition, and the grains have a preferential orientation along <111> direction [177].

To avoid re-evaporation; a background pressure is needed, which means that a small distance source-substrate is required. Both CSS and VTD, satisfy these conditions. One of the main advantages of the CSS method is the high quality of the as-deposited material, characterised by large grain size (5-10 μm). Large grain size and columnar morphology are useful to reduce transverse grain boundaries, responsible for the recombination of the charge carriers [178].

Figure 29: Schematic diagram of spray and screen printing deposition techniques. (In the graphs are shown the typical film thicknesses, d, deposition rates and deposition temperatures.)
However, this increase in grain size causes an increase in the dimensions of voids between the grains; which means that the film has to be thicker to avoid the presence of pinholes. This issue can still persist even with increased thickness. A possible solution is to use a higher pressure of a non-reactive gas (up to 100 mbar (~75 Torr)), usually Ar, and a higher temperature of the CdTe source. As-deposited CSS films above 550ºC show a nearly random orientation. VTD is the other method that combines high substrate temperature with high deposition rate [177]. While CSS works by diffusion, VTD works by convection. This method has been developed by the Institute of Energy Conversion and is utilised by First Solar, LLC [179].

RF Sputter deposition takes place at a lower substrate temperature (380ºC) but with only a relatively small deposition rate (0.1 μm/min) [70]. The sputtering technique will be analysed elsewhere in this thesis (chapter 7).

MOCVD is an atmospheric pressure and low temperature technique, which uses organometallic precursors, which react to deposit the CdTe thin film. The deposition is the result of a chemical reaction, so it is possible to change the stoichiometry of the compound. In some cases, the CdCl₂ treatment can be avoided by controlling the process conditions and adding arsenic as a dopant [180].

Electrodeposition, and also screen printing of CdTe have been used for commercial cells by BP Solar and Matsushita Batteries [181] by depositing material at room temperature followed by annealing. BP Solar claimed an 11% module efficiency, the company dropped CdTe in the early 2000s. The simplicity of the screen printing process and equipment makes this technique suitable for manufacturing. It provides the growth of large-grained films but with the main drawback of the high film thickness, which needs to be above 10 μm, causing losses in photocurrent and high series resistance inside the active layer. As a consequence, the efficiency of devices obtained with these methods is in the range 8-11%. The process involves several hours of heat treatment to produce high quality films. High quality substrates are needed [182] [183].

Chemical spray pyrolysis is another low-cost manufacturing process, which had previously been used for CdS/Cu₂S thin film solar cells [81]. Here the liberated solvent (water) limits the deposition rate; the individual droplets evaporate and react quickly, leading to small grain sizes, usually less than 100 nm, which is a disadvantage for most semiconductor applications. It is sensitive to temperature because the deposition efficiency decreases with the temperature
An industrial process has been developed by Golden Photon Inc. with modules reaching efficiencies of around 9% [185]. The morphology depends on the deposition conditions, with films generally showing a porous back surface and severe CdS consumption [80], as a result of CdCl$_2$ presence as carrier in the deposition process. The screen printing method involves Cd, Te and a suitable binder, followed by baking at high temperatures (~700°C) [186].

### 4.1. Electrodeposition (ED) of thin film CdTe

In this study, electrodeposition was chosen as a non-vacuum and low cost technique for depositing CdTe thin films. Electrodeposition enables deposition of thin films on a conducting substrate using a conducting solution containing the ionic species of the material of interest. The deposition occurs by submersion of the substrate in the solution, along with one or two electrodes (counter and reference electrode) and applying a potential difference to initiate a reaction of the ionic species on the substrate surface. This reaction can occur in anodic (positive voltage applied on the substrate) or cathodic (negative voltage applied on the substrate) mode [187].

Electrodeposition has the advantage compared to the standard vacuum processes such as evaporation or sputtering that it is an atmospheric process, which employs simple inexpensive equipment; and it works at relatively low temperatures, below 100°C. The electrolyte lifetime is indefinitely long there is minimal waste of materials. However, there are also a number of drawbacks for this process since it is more substrate sensitive than vacuum-based techniques. This means that a non-conductive defect on the substrate surface causes defects in the electroplated film. In general, the chemical composition of the surface affects the whole process. In a plating solution each material has its own surface potential; which means that for different chemical compositions, different process parameters are required. The chemical and electrochemical properties of materials must be studied to prepare the plating bath and in particular to form film stacks (electrodepositing materials on the top of each other). It is also possible that the substrate surface may dissolve in the solution during the electrodeposition process if the potentials applied are more positive than the plating potential of the species on the surface in a given electrolyte. Alternatively, the electrolyte may chemically attack and dissolve the substrate surface. Finally, one of the major drawbacks for this process is the low deposition rate.
4.1.1. The mechanisms of Electrodeposition

The Electrodeposition experiments performed for this thesis were carried out in an electrochemical cell consisting of a reaction vessel with two or three electrodes, immersed in an electrolyte solution. The Working Electrode (WE) is the electrode for which the potential is controlled, and where the current is measured. It acts as a surface on which the electrochemical reaction takes place. The Reference Electrode (RE) is used to measure the working electrode potential. It should have a constant electrochemical potential as long as no current flows through it. The most commonly used Reference Electrodes are the Saturated Calomel Electrode (SCE) and the Silver/Silver Chloride (Ag/AgCl) electrodes. The Counter, or Auxiliary, Electrode (CE) is a conductor that completes the cell circuit. The Counter Electrode in laboratory cells is generally an inert conductor such as platinum or graphite. The current that flows into the solution via the Working Electrode leaves the solution via the Counter Electrode [188] (Figure 30).

![Figure 30: A schematic diagram of a conventional three electrode electrochemical cell.](image)

The reaction in the aqueous medium is governed by Faraday’s laws [189]. In 1834 Michael Faraday published the First and the Second law of Electrolysis. Faraday’s First law states that the chemical deposition due to the flow of electric current through an electrolyte solution is directly proportional to the quantity of electricity passed through it, measured in Coulombs.
Chapter 3

Faraday’s Second law states that the mass of substances deposited, passing through the electrolyte, is proportional to their respective chemical equivalent weights.

These laws can be summarised by:

\[ m = \left( \frac{Q}{F} \right) \left( \frac{M}{z} \right) \]

Where \( m \) is the mass of the substance deposited in grams, \( Q \) is the total electric charge passed through the substance, \( F = 96485 \text{ C mol}^{-1} \) is the Faraday constant, \( M \) the molar mass of the material, \( z \) the electrons transferred per ion (\( M/z \) is the equivalent weight of the material deposited).

The cell potential \( E \) is related to the Gibbs free energy (\( \Delta G \)), in thermodynamics. This expresses the chemical potential that is minimised when a system reaches equilibrium at a constant temperature and pressure.

\[ \Delta G = -nFE \]

Where, \( E \) is the electrochemical cell potential and \( n \) the number of electrons. If \( E > 0 \), the process is spontaneous, in contrast when the free energy is positive, at negative potential, the reaction must be forced. The Nernst equation is used to measure the potential of an electrochemical cell (\( E \)) and it provides information about how far from the equilibrium the redox reaction is. It is given by:

\[ E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_{ox}}{a_{red}} \right) \]

Where \( E^0 \) is the standard reference potential measured vs SHE, \( R \) is the gas constant (8.31 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the temperature, and \( a_{ox}, a_{red} \), activity of products and reactants, respectively.

### 4.2. Pourbaix Diagram

The Pourbaix Diagram, also known as potential/pH diagram or pE/pH diagram, is an indication of stable (equilibrium) phases of an aqueous electrochemical system. It is an isothermal phase diagram, used to evaluate the effects of pH, oxidation potentials, and corrosion. In Figure 31 the Pourbaix diagram of CdTe-H\(_2\)O system [190] is shown. Line 5 represents the thermodynamic equilibrium between Te-enriched surface of the CdTe electrode and Cd\(^{2+}\) ions. The stability limits of solid CdTe are represented by lines 1 and 4.
(lower limit) and 5, 11, and 12 (upper limit). In acidic, neutral, and basic solutions at potentials above the lower stability limit, the only process accompanying cathodic CdTe polarisation is hydrogen evolution. Therefore, in the region of cathodic potentials, CdTe is stable from an electrochemical point of view and this Voltage range is commonly used for CdTe deposition. The experiments have been performed using the same voltage range as in the literature.

Figure 31: A Pourbaix diagram of the CdTe-H₂O system [190].

4.3. ED CdTe from literature

Several review papers and books deal with the electrodeposition of semiconductors [191][192][193], this part of the project focused on films of semiconducting II-VI compounds. In principle, both anodic and cathodic deposition can be performed. However, the use of the anodic method leads to difficulty in controlling the films’ stoichiometry.
Anodic deposition involves negatively charged ions moving towards a positively charged substrate, the cathodic method works in the opposite way. According to previous studies reported in the literature, it has been found that CdS has been made by anodic deposition of sulphur from a solution of $S^{2-}$ ions onto a cadmium anode [194]. On the other hand, by using a cathodic method, it is possible to deposit Cd and Te, from different precursors but with both elements being present in the same aqueous solution. For this reason this study has concentrated on cathodic deposition [195][196][197].

Electrodeposition consists of the galvanic reduction of Cd and Te from Cd$^{2+}$ and HTeO$_2^+$ ions in acidic aqueous electrolyte. The first research on the cathodic electrodeposition of CdTe for solar cells was performed and reported by Monosolar Inc. in 1976, in collaboration with the University of Southern California (USC) and focused on developing and understanding the cathodic electrodeposition of CdTe [198][199][200].

The reactions and the corresponding equilibrium electrode potentials for Cd and Te according to Pourbaix vs Normal Hydrogen Electrode (NHE) are shown below [201]. The potentials are related to the activities of ions in solution and on the activities of the component in the deposit. From the table, reactions a. and d. are the important ones; in particular reaction d. shows the dependence of the potential on the pH.

Reactions:  \( E \) vs NHE (V)

a. 

\[
Cd(s) = Cd^{2+} + 2e^{-}
\]

\[
E_{Cd}^0 + \frac{RT}{2F} \ln\left(\frac{a_{Cd^{2+}}}{a_{Cd}}\right) = -0.403 + 0.0295 \log\left(\frac{a_{Cd^{2+}}}{a_{Cd}}\right)
\]

b. 

\[
Te(s) = Te^{2-} + 2e^{-} \quad (pH > 11)
\]

\[
E_{Te}^0 + \frac{RT}{2F} \ln\left(\frac{a_{Te^{2-}}}{a_{Te}}\right) = -0.94 + 0.0295 \log\left(\frac{a_{Te^{2-}}}{a_{Te}}\right)
\]

c. 

\[
Te(s) = Te^{4+} + 4e^{-} \quad (pH < -0.5)
\]

\[
E_{Te}^0 + \frac{RT}{4F} \ln\left(\frac{a_{Te^{4+}}}{a_{Te}}\right) = 0.568 + 0.0148 \log\left(\frac{a_{Te^{4+}}}{a_{Te}}\right)
\]
Typically, the electrolyte contains Cd ions from an aqueous solution of CdSO₄ and Te ions from a solution of TeO₂ in H₂SO₄ and /or HF or water [201][199].

In order to deposit Cd and Te in similar quantities, the preparation of an electrolyte with a high concentration of the less noble component, Cd, and a low concentration of the more noble component, Te, is required. The rate of Te deposition is diffusion controlled. The concentration of HTeO₂⁺ in the electrolyte is approximately zero during the deposition, compared to the larger CdSO₄ concentration which remains unchanged. Since the Te deposition rate is diffusion controlled, the rate of CdTe deposition should be limited by Te deposition and should therefore be increased by, for example, stirring the solution.

Considering the reactions a. and d.:

\[
Te(s) + 2H_2O = HTeO_2^+ + 3H^+ + 4e^- (0 < pH < 5)
\]

\[
E_0^0 + \frac{RT}{4F} \ln \left( \frac{a_{HTeO_2^+}}{a_{Te}} \right) + \frac{RT}{4F} \ln C_H^+ = 0.551 + 0.0148 \log \left( \frac{a_{HTeO_2^+}}{a_{Te}} \right) - 0.0443 pH
\]

In Figure 32 current density against potential curves are shown considering each element from their corresponding (acidic) solutions. In the lower part of the figure the curve represents the deposition from a solution containing both cadmium and tellurium species [193].

In Figure 32 the dotted line shows that stoichiometric CdTe can be deposited in a wide potential range (V/NHE). In fact, taking into account the free energy of CdTe formation
Chapter 3

\( \Delta G_f^0 = -98 \text{KJ/mol} \), then the following reaction \( \text{Cd}^{2+} + \text{Te} + 2e \rightarrow \text{CdTe} \) takes place at a potential more positive than the potential of \( \text{Cd} \) (-0.4V) by an amount of \(-\Delta G_f^0 / 2F = 0.5 \text{ V} \).  

![Current density (a.u.) against Potential graph of CdTe electrodeposited in a wide potential range (V/NHE).](image)

In theory, following this window for the stoichiometric deposition, the mechanism turns out to be highly site selective, leading to good quality crystalline materials [187] [202] [203] [204].
Table 2 shows some parameters used to compare the main representative techniques for the deposition of CdTe thin films.

**Table 2**

Comparison between main deposition techniques for CdTe thin films

<table>
<thead>
<tr>
<th></th>
<th>VTD</th>
<th>CSS</th>
<th>PVD</th>
<th>RF</th>
<th>ED</th>
<th>MOCVD</th>
</tr>
</thead>
<tbody>
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<td><strong>High Vacuum</strong></td>
<td>$10^{-6}$ Torr</td>
<td>10 Torr</td>
<td>$10^{-6}$ Torr</td>
<td>$10^{-4}$ Torr</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alternative non-vacuum</strong></td>
<td></td>
<td></td>
<td></td>
<td>atmospheric Pressure</td>
<td>atmospheric Pressure</td>
<td></td>
</tr>
<tr>
<td><strong>Deposition temperature</strong></td>
<td>600°C</td>
<td>600°C</td>
<td>400°C</td>
<td>200°C</td>
<td>80°C</td>
<td>200-400°C</td>
</tr>
<tr>
<td><strong>Deposition rate</strong></td>
<td>0.1-1 μm/min</td>
<td>1-5 μm/min</td>
<td>0.01-0.5 μm/min</td>
<td>~0.1 μm/min</td>
<td>0.01-0.1 μm/min</td>
<td>0.01-0.1 μm/min</td>
</tr>
</tbody>
</table>

**Experimental details**

Thin films of CdTe were prepared by electrodeposition in aqueous solution with CdSO$_4$ (3.8x10$^{-2}$ M) and TeO$_2$ (10$^{-3}$ M) as precursors in the bath, the pH solution was in the range 1-2 with the addition of H$_2$SO$_4$ >95%, without stirrer agitation. The experiments were performed at room temperature, ~23°C, using a PARSTAT 2273 potentiostat (Advanced Electrochemical System) for 4 hours. The electrodeposition system designed for this work consisted of a bespoke three electrode reaction cell (a working electrode, CdS/FTO, a counter electrode, Pt foil and a reference electrode [http://www.chinstruments.com/], saturated KCl silver/silver chloride electrode (Ag/AgCl) [Ag/AgCl +0.199 V vs standard hydrogen electrode (SHE)]) placed inside a glass tube.
5. References


Chapter 3


[62] F. Adibi, I. Petrov, G. J.E., L. Hultman, Effects of high flux low energy (20–100 eV) ion irradiation during deposition on the microstructure and preferred orientation of Ti0.5Al0.5N alloys grown by ultra-high vacuum reactive magnetron sputtering, Journal of Applied Physics. 73 (1993).
Chapter 3


Chapter 3

Chapter 4

Characterisation of thin films

1. Methods of thin film characterisation

Characterisation of thin films is carried out using a variety of methods to determine their optical, electrical, structural properties.

The following sections describe the main techniques used in this thesis.

1.1. Microstructural analysis: Scanning and Transmission Electron Microscopy

Physical, structural and microstructural analyses are important to understand the material properties of thin films used in photovoltaic devices. These analyses allow us to understand the material properties such as grain size, surface morphology, composition, defects inside the grains and at the interfaces, interdiffusion between the layers and other features. For this work two important techniques were used for characterising CdS and CdTe thin films: Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) [205].

Scanning Electron Microscopy (SEM)

The instrument used for this work was a Leo 1530 VP Field Emission Gun (FEG)-SEM. Low voltage SEM is typically used in a FEG-SEM because of its high spatial resolution (~2 nm), and the possibility to operate at low accelerating voltages (typically at 5 kV), using in lens detectors. With this instrument it is also possible to perform chemical analysis by using the Energy Dispersive X-ray analysis (EDX) which also provides information on the spatial distribution of elements. Electron Backscatter Diffraction (EBSD) provides information on texture and grain orientation. Plan view and cross-sectional images were taken using the Leo 1530 VP FEG-SEM. Samples were positioned on flat metallic stubs and glued with conducting silver paste connecting the stub to the surface of the sample to avoid charging issues. In addition, the surface was coated with a 5-10 nm sputtered gold-palladium layer to achieve better conductivity, and hence better imaging. Cross-section samples were mounted on apposite stubs which allowed them to be studied in a vertical orientation. The samples
were previously cut using a diamond tip roller and the sample surface was coated with gold-palladium.

**Transmission Electron Microscopy (TEM)**

This technique enables high-resolution (<<1 nm) images of the microstructure of samples from ultrathin materials. It can produce images with higher magnification and greater resolution than those produced by SEM. A dual beam FEI Nova 600 Nanolab was employed to prepare the TEM samples using a Focused Ion Beam (FIB). A standard in situ lift off method was used to prepare cross-sectional samples through the coating into the glass substrate. A platinum over-layer was deposited to define the surface of the samples and homogenise the final thinning of the samples. Combined electron and ion beams are used respectively to image and cut the sample (as shown in Figure 33) [206].

![Figure 33: Images showing the FIB procedure to prepare TEM samples: 1) cross-section to expose the sample surface; 2) second cross-section and cuts to isolate the sample; 3) sample after attachment to a TEM half-grid and final thinning.](image)

TEM images were obtained using a Jeol JEM 2000FX operating at 200 kV, with an integrated camera above the phosphor screen to obtain digital images. The TEM technique provides morphological analysis of grain structure across the whole multilayer thin film CdTe device.

2. **X-ray Diffraction (XRD)**

The electrical (and optical) properties of thin films are also dependent on the material crystalline structure. X-ray diffraction (XRD) is a commonly used method to probe the preferred orientation of crystalline samples.
In this work, measurements were made using a Bruker D2 Phaser bench-top XRD system using X-rays generated with a Cu anode with a 1.542 nm wavelength. A 3 mm anti-scatter grid and a 1 mm divergence slit were inserted during the analyses. The two-theta (2θ) start and stop angles were 17º and 60º, with a step size of 0.02º and a dwell time of 0.1 s, in order to pick up the range of peaks of interest. The scan was run for almost 15 hours and the sample holder was in constant rotation during the scan to provide accurate and precise data to detect the correct phase structure of CdS and CdTe thin films [207].

2.1. XRD analysis to measure residual stress in CdTe thin films

It is known that the physical properties of thin-film layers depend on their microstructure. In fact parameters like crystallinity, crystallographic orientation, grain size and so on, are crucial for the design of thin films devices. The XRD-based techniques play an important role for the determination of residual stress/strain values. During the deposition and subsequent processing of thin films residual stresses and strains are inevitably introduced into the films. Stresses can be intrinsic to the films, caused by the presence of impurities, voids or defect incorporation within the film, either due to partial recrystallisation in the film during the deposition or subsequent treatments. Residual stresses (generally defined as thermal stresses) can also be extrinsic. They derive from changes in material properties across the film/substrate interface such as different coefficients of thermal expansion in the film and in the substrate or differences in the atomic plane spacing near the film-substrate interface.
In general for diffraction measurements it is more common dealing with micro stresses, where the average of these measurements is taken over the diffracting volume of material. The measured quantity is the average micro stresses within a finite number of grains [208]. With the XRD measurement it is possible to measure the distance or spacing (known as ‘d-spacing’) between parallel crystalline lattice planes in the film. The crystallite atoms can diffract the incident X-ray beam into different specific orientations [209]. The measurement of the angle and intensities of the diffracted beams produce a diffraction pattern. The XRD analysis is based on Bragg’s law [210]:

\[ n\lambda = 2d_{hkl} \sin \theta_{hkl} \]

where \( \lambda \) is the X-ray wavelength, \( d_{hkl} \) is the lattice plane spacing of a family of crystallographic planes \((hkl)\) responsible for the Bragg peak, \( \theta_{hkl} \) is the diffraction angle of X-ray incidence with lattice plane, \( n \) is an integer and normally it is 1 (shown in Figure 35). The peak will be observed at an angle of \( 2\theta_{hkl} \) from the incident beam.

![Figure 35: X-ray beam of wavelength \( \lambda \), incident on the crystal at an angle \( \theta \) with respect to equidistant hkl lattice-planes, with interplanar distance \( d_{hkl} \).](image)

If a specimen is elastically strained, the lattice spacing is changed. Therefore any elastic strain will be revealed as a shift in the value of \( 2\theta_{hkl} \) for a particular reflecting plane illuminated by a fixed wavelength. By differentiating Bragg’s law,

\[ \Delta \theta_{hkl} = -\left(\frac{\Delta d}{d_0}\right) \tan \theta_0 \]

where \( \Delta d \) is the change of lattice spacing, and \( d_0 \), the lattice spacing of a stress-free sample of the material. So, the strain in the \((hkl)\) set of planes can be calculated with
\[ \varepsilon = \left( \frac{\Delta d}{d_0} \right) = \Delta \theta \cot \theta_0 \]

The direction in which strain is measured is along the scattering vector and is perpendicular to the diffracting planes [211].

From the CdTe diffraction pattern, the highest peak, with (111) orientation, is the preferred peak for the analysis. In addition, a sharp peak indicates a crystalline grain structure in the sample [3]. For CdTe samples completely free from stress (powder), according to the database, the main (111) peak corresponds to the 20 value of 23.76° and the d-spacing is 3.74 Å [212][213]. This is considered to be the standard baseline. For this study another reference point was used. This was taken from a CdTe sample deposited by closed-space sublimation (CSS) and then treated by using a CdCl₂ activation process which showed a (111) peak and d-spacing values respectively of 23.75° (2θ) and 3.74 Å.

Both baselines were compared with the results from the sputtered CdTe samples. The d-spacing can be calculated by using Bragg’s Law. As the changes in d-spacing are caused by strain, and the strain is created by internal stress, according to Poisson’s effect [7], if

- the d-spacing value of the untreated sample is larger than the baseline (stress-free state), the distance between atomic lattice planes parallel to substrate surface is expanded and there is compressive stress dominating in the film (Figure 36).

![Figure 36: A schematic diagram showing the situation when compressive stress dominates in a thin film.](image)

- the d-spacing value of untreated sample is smaller than the baseline; this means that there is tensile stress in the films and it contracts the distance between lattice planes [7] (Figure 37).

![Figure 37: A schematic diagram showing the situation when tensile stress dominates in a thin film.](image)
Depending on these changes in d-spacing, the (111) peak in the X-ray pattern is subject to a shift caused by changes in the internal stress in the film [3].

3. X-ray Photoelectron Spectroscopy (XPS)

Surfaces and interfaces play an important role in coatings and semiconductor materials. They define the boundary between a material and its surrounding environment. The properties of surfaces and interfaces can be completely different to those of the bulk.

It is important to study and analyse the chemical composition of the surface of thin films. XPS, also known as ESCA (Electron Spectroscopy for Chemical Analysis), is the most widely used technique. The technique utilises the photo-ionisation and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of the sample. From the binding energy (or kinetic energy) and intensity of photoelectron peaks, the elemental identity, chemical state and concentration of an element is determined. The process of photo-ionisation follows the conservation of energy. The kinetic energy, KE of the emitted photoelectrons is expressed by the formula:

\[ KE = h\nu - BE - \phi \]

Where, \( BE \) is the binding energy of the electron, which is the difference between the ionised and neutral atoms or the energy required to remove the electron from its initial level to the vacuum level. In solids, \( BE \) is conventionally measured with respect to the Fermi level (highest occupied level), rather than the vacuum level (the last binding level of the system).

For semiconductors, the Fermi level is positioned between the valence and the conduction bands. This is why the formula includes the term \( \phi \), the work function of the electron spectrometer used. The common x-ray sources used are Mg K\( \alpha \) radiation \( h\nu = 1253.6 \) eV and Al K\( \alpha \) radiation \( h\nu = 1486.6 \) eV (this anode with a beam diameter of 200 μm, was used in this work). The most common analysis with XPS is the Surface Scan, where energy peaks in the survey scan identify the elemental composition of the uppermost 20 to 50 Å of the analysed surface. All elements, except hydrogen and helium, are detected. Detection limits are approximately 0.1 atom percent for most elements. The High Resolution Multiplex Scan is used to evaluate the chemical state(s) of each element through its core electron binding energies. Precise determination of binding energies is made through the use of curve fitting routines applied to the peaks in the multiplex scan. Shifts in the binding energy can result from the atom’s oxidation state, chemical bonds, or crystal structure. A NIST database is
available to identify binding energies with specific compounds. The concentrations of the elements identified in the survey scan are determined by integrating the area under a characteristic peak for each element.

For this work, a Thermo Scientific K-Alpha Surface Analysis system, with Al Kα radiation used as X-ray source, has been used. Every analysis was preceded by a light ion etching (Ar ion surface etching at 1 eV for 30 s) performed in situ prior to measurements to remove atmospheric surface contamination such as adventitious carbon and oxidised layers [214].

4. Spectroscopic Ellipsometry (SE)

Ellipsometry is an optical technique used for surface and thin film analysis. It is based on the measurement of the change in state of polarisation of a light beam caused by the reflection on the sample surface (or the transmission through the sample). If the surface is covered by a film, or a stack of films, the entire optical system of film and substrate affects the change in polarisation. Hence it is possible to extract information about the film properties, especially the film thickness. The name “ellipsometry” derives from the concept that polarised light often becomes ‘elliptical’ upon light reflection (as explained in the next section).
4.1. Polarised light

Light is defined as being polarised when electric fields of light waves are oriented in specific directions. If the oscillating direction is completely random, the light is called unpolarised light (or natural light). Light in the form of a plane wave in space is said to be linearly polarised. If light is composed of two plane waves of equal amplitude but differing in phase by 90°, then the light is circularly polarised. Alternatively, if two plane waves of different amplitude are out of phase by 90° or if the relative phase difference is something other than 90°, then the light is said to be elliptically polarised (Figure 39 and Figure 40).

![Classification of polarisation of the light](Image)

Figure 39: Classification of polarisation of the light (a) Circular polarisation (b) and Elliptical polarisation (c) [14].

4.2. Fundamental equations of ellipsometry

The measured parameters are the so-called ellipsometric angles; $\Delta$ and $\Psi$. These represent the amplitude ratio $\Psi$ and phase difference $\Delta$ between light waves known as p- and s- polarised light waves. They are related to the ratio of the complex Fresnel reflection coefficient $r_s$ and $r_p$, where $r_s$ is the reflection coefficient for light polarised perpendicular to the plane of incidence and $r_p$ is the reflection coefficient for light polarised parallel to the plane of incidence. This is expressed by the fundamental equation of ellipsometry [215]:

Chapter 4

\[ \rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta} \]

Where \( \tan \Psi = \frac{|r_p|}{|r_s|} \)

\( 0^\circ \leq \Psi \leq 90^\circ \)

And \( \Delta = \delta_p - \delta_s \)

\( 0^\circ \leq \Delta \leq 360^\circ \)

Figure 40: Schematic view of an ellipsometric measurement in reflection configuration. On the right side the incident polarized beam. After reflection, on the left side the polarization state of the beam has changed [15].

In spectroscopic ellipsometry (\( \Psi, \Delta \)) spectra are measured by changing the wavelength of light. In general, the measurements are carried out in the ultraviolet/visible range, but analysis in the infrared region has also been widely performed [216].

4.3.Optical elements

The ellipsometric instrument used for this thesis was the Horiba Jobin Yvon UVISEL iHR320FGAS Horiba; (Figure 41) it consists of:

- Light source, Xe high pressure lamp (75 Watt) with filters to pass only the desired wavelength;

- Optical fibres, used to couple the light beam from the output of the light source to the input of the polariser and from the output of the analyser to the input of the monochromator. In general they have 1mm core diameter and there are two types: UV fibres (range 190-880 nm) and NIR fibres (range 260-2100 nm)

- Polariser (P) which defines the state of polarisation before the light strikes the sample;
Chapter 4

- Sample holder (stage);

- Analyser (A), which is similar to the polariser and is located after the sample holder;

- Monochromator, which separates the light into its components before reaching the detector;

- Detector (D), made by photomultipliers for the UV and visible spectral range and InGaAs detector for the IR spectral range;

- Acquisition interface, apart from the sample displacement, the ellipsometer is completely automated.

Figure 41: A schematic diagram of an ellipsometer.

The measurements are performed in external configuration for standard ellipsometers. This means that the light beam propagating in air (or vacuum) is reflected or transmitted through a sample, and then it goes back through the air (or vacuum) to reach the detector. The measurement is a simultaneous acquisition of the moduli and phases of the polarisation components of the light. The interferometric effect is the basis of this technique. Considering a multilayer sample, once the light has been reflected by the first interface of a layer, it interferes with the light reflected by the second layer and similarly for all the other layers. Therefore, the maximum film thickness that can be measured with ellipsometry must be less than the coherence length of the light source to avoid depolarisation.
4.4. Analysis of Ellipsometric data

The ellipsometric data were processed using the following procedure:

- The ellipsometer measurement yields the ellipsometric angles, $\Delta$ and $\Psi$.

- A model of the sample is then created to determine the sample parameters. To provide an example of the optical model, Figure 42 shows a model consisting of an air/thin film/substrate structure. An optical model is represented by the complex index, $N = n - ik$ (with $n$, refractive index and $k$, extinction coefficient) and thickness of each layer, so $N_0$, $N_1$ and $N_2$ represent the complex refractive indices of air, thin film and substrate, respectively. The transmission angles ($\theta_1$ and $\theta_2$) are calculated from the incident angle $\theta_0$ by applying Snell’s law [217]. The two ellipsometric parameters ($\Psi$, $\Delta$) are defined by $\rho \equiv \tan \Psi \exp (i\Delta)$; in the optical model $\rho$ is expressed by the following equation: $\tan \Psi \exp (i\Delta) = \rho (N_0, N_1, N_2, d, \theta_0)$.

Knowing $N$ it is possible to obtain the dielectric constant $\varepsilon$ and absorption coefficient $\alpha$, by $\varepsilon = N^2$ and $\alpha = 4\pi k/\lambda$.

- Once the model is built, calculated data (the output of the model) must be fitted to the experimental data (measured values $\Psi$ and $\Delta$) and the best match between the two sets is found.

- The user then evaluates the best-fit model to decide if the predicted model is physically reasonable.
Chapter 4

The quality of the fit is usually evaluated with a figure of merit which guides the numerical algorithm searching for the best-fit values of the model parameters. One of the most commonly used figures of merit is based on the mean square deviation between simulated and measured data.

$$\chi^2 = \frac{1}{N-M-1} \sum \left( \frac{(\psi_{Th}-\psi_{Exp})^2}{\sigma^2_{\psi}} + \frac{(\Delta_{Th}-\Delta_{Exp})^2}{\sigma^2_{\Delta}} + \frac{(R_{Th}-R_{Exp})^2}{\sigma^2_{R}} \right)$$

Where N indicates the total number of data points, M is the total number of fitted parameters; Th and Exp, as superscripts, are related to the theoretical and experimental data respectively. The summation considers all the spectral data points, and the sigmas in the denominators are the estimated uncertainties of the experimental values. Once the figure of merit has been defined, the automatic process of parameter fitting is carried out by computer which searches for the minimum value for the figure of merit.

5. Spectrophotometer

The optical properties of thin films are of vital importance since they affect the generation of photo-current in the absorber. The optical properties of CdS, CdTe layers and the entire device were obtained using a Cary 5000 (Agilent Technologies, USA) spectrophotometer (Figure 43).

This instrument is equipped with an integrating sphere and set of gratings which allow optical transmission measurements to be performed from 185 nm to 3300 nm [218].

Transmission and reflection measurements were carried out using an integrating sphere, with wide spectrum sensitivity (for these experiments in the range 200 nm to 1400 nm). The instrument used for this work is a double beam spectrophotometer; the light source, before reaching the sample, is split into two separate beams. One beam passes through the sample and the second one is used for reference. This is advantageous as long as the reference and sample readings take place at the same time. In transmission measurements, the spectrophotometer quantitatively compares the amount of light passing through the reference and test sample. This also occurs for reflection measurements. For transmission measurements, samples were placed over the entrance port of the integrating sphere with the glass side of the sample facing the incoming light. This configuration is the most practical for
a superstrate solar cell, since in a device, the film encounters the light after it has passed through the glass substrate and so any changes due to the different refractive indices of the glass and film are considered. A reference reflectance disk (pressed PTFE) was placed at the reflectance port, and all transmission measurements included direct and diffuse transmission. For reflectance measurements, samples were placed over the reflectance port, with the glass side again facing the incoming light and the reflectance spectra (both specular and diffuse) were recorded. In all cases a baseline correction was performed to remove measurement artefacts.

![Figure 43: A schematic diagram of the Spectrophotometer [18].](image-url)
Using the conservation of energy principle for a single thin film, then it is possible to estimate absorption and reflectance of thin films by using the formula \(1 = R + T + A\) (where \(R\)=reflectance, \(T\)=transmittance and \(A\)=absorption), as shown in Figure 44.

![Schematic diagram showing the principle of conservation of energy (1=R+T+A).](image)

Figure 44: A schematic diagram showing the principle of conservation of energy (1=R+T+A).

6. Coherence Correlation Interferometry (CCI)

Coherence correlation interferometry (CCI) [219] is a scanning white light interferometry technique which uses light interference patterns (set of interference fringes) from a white light source (Xenon). Two beams are produced by splitting the main beam from the source; one is reflected by a reference mirror, while the other one scans the surface. The light is reflected locally by the surface and the reflected beam is correlated to the reference and an interference pattern is created. The signal is detected by a high resolution digital CCD camera (Figure 45). Three-dimensional topographical maps are created by measuring the position of the lens which is moved in the vertical direction to obtain the maximum constructive interference. Use of white light allows only one peak as maximum. Each pixel acts as single interferometer, combining them together allows the accurate measurement of a relatively large surface area. The accuracy of the measurement is highly dependent on the efficacy of the coherence correlation algorithm used.

This is a non-contacting technique and there is no risk of damaging the surface with a stylus. The CCI provides accurate measurements for transparent and semi-transparent materials. The technique provides two and three-dimensional images of the surface together with a range of quantitative analysis routines for roughness, waviness and form. Measurements include root mean square roughness (Sq), average roughness (Sa), maximum peak height (St), step height,
groove width and depth, etc. CCI is capable of combining sub-nanometre thin film thickness measurements with quantitative three-dimensional metrology and imaging from the same thin film sample area. The measurements are taken over a relatively large and hence representative area of the surface. The scan area is defined by the magnification of the lens used and it ranges between 165 µm x 165 µm for a 100x objective lens to 6.6 mm x 6.6 mm for a 2.5x objective lens.

It is necessary to provide the refractive index (n) for the film material; n can be measured by using ellipsometric spectroscopy or it is often assumed to be the same as the bulk material. A ‘pattern measurement’ can be performed by taking thickness measurements at different points of the sample [220].

Thin film thickness measurements, thin film uniformity and the detection of voids and pinholes were carried out using a Coherence Correlation Interferometer: Sunstar HD CCI instrument from Taylor Hobson Ltd [221].

7. **Current-voltage (IV) curves**

Current-voltage characterisation is the main electrical measurement for solar cells. The parameters used to define a cell performance are short circuit current (I_{sc}) or current density (J_{sc}), open circuit voltage (V_{oc}), Fill Factor (FF) and combining these parameters, cell efficiency (η). The instrument used to test the solar cell performance is a solar simulator.
which works as an artificial sun, recreating the solar spectrum. The current-voltage curve is
generated by measuring the current as a function of the input Voltage. The intercepts with the
y- and x- axis are then obtained and, correspond to the $I_{sc}$ and $V_{oc}$ respectively. The shape of
the curve gives information on the FF, shunt and series resistances and roll-over effect. The
electrical measurements are generally carried out using a Keithley electrometer [222].

In this study, CdTe solar cells were deposited in superstrate configuration. For this reason,
issues on contacting modality occur. These have been overcome by building a suitable
bespoke solar simulator which allows the cell to be contacted from the top using Kelvin
probes and indium patches to avoid scratching, and consequent shorting of the active cell. A
schematic diagram of the arrangement used is shown in Figure 46.

A 1000 W Newport Xenon lamp was used as the light source. The light was reflected
upwards using a 45° optical mirror. The light beam was then passed through an AM 1.5 filter
and an optical array, which included an iris to control the intensity of light, two multi lens
arrays, one co-focal and a focal lens which projected onto a relative small area of the sample
stage. Due to the dimension of the cells ~ 0.25 cm$^2$, the aperture in the sample stage was only
2 cm diameter to provide a sufficient degree of light uniformity. The light intensity was calibrated before each set of measurements using a reference diode.

The cell area was defined during the back contact deposition of 50 nm of gold which was applied using a Quorum Q150T ES sputtering system. Prior to this process a mask was applied onto the sample(s), consisting of a sequence of equally spaced square holes 0.5 cm x 0.5 cm in dimension. This provided a consistent active area allowing comparison of measurements obtained from various samples processed using various conditions.

8. Water Contact Angle (WCA)

The contact angle measurement is a macroscopic representation of microscopic phenomena [223] which include surface roughness, surface energy of materials and surface coatings. All these play a role in the wettability of the material investigated for a given fluid. Quantitatively, this technique measures the ability of a liquid to spread on a surface. The angle is measured between the outline tangent of a drop deposited on a solid and the surface of this solid. The intersection of the three surfaces, liquid, air and solid represents the interior angle, contact angle, $\theta$, as shown in Figure 47.

When a liquid drop is on a flat surface, the static contact angle is defined by the Young Equation that explains the relation between the three interfacial surface tensions: solid and liquid, $\sigma_{\text{SL}}$, solid and vapor, $\sigma_{\text{SV}}$, and liquid and vapor, $\sigma_{\text{LV}}$.

\[
\sigma_{\text{LV}} \cos \theta = \sigma_{\text{SV}} - \sigma_{\text{SL}}
\]

![Figure 47: Young's model representing the contact angle, $\theta$ and the three interfacial tensions (solid and liquid, $\sigma_{\text{SL}}$, solid and vapor, $\sigma_{\text{SV}}$, and liquid and vapor, $\sigma_{\text{LV}}$) [23].](image-url)
Figure 48 shows that low values of $\theta$ mean that the liquid has spread and there is a strong affinity for the solid. High values of $\theta$ indicate poor wetting. If $\theta$ is less than 90º the drop wets the solid. A contact angle of zero corresponds to total wetting. If the angle is greater than 90º it corresponds to non-wettability [224].

![Diagram showing contact angles](image)

**Figure 48: Contact angles $\theta > 90^\circ$, indicating non-wettability, $\theta < 90^\circ$ indicating wettability, and $\theta = 90^\circ$ [25].**

The contact angle measurement gives information about the affinity of a liquid to a solid surface; if water is used as the liquid, it is possible to distinguish the hydrophobic ($\theta > 90^\circ$) and the hydrophilic ($\theta < 90^\circ$) behaviour of the surface investigated. If several liquids are used, the surface energy of a material can be determined discriminating between polar and dispersive components.

There are several methods used to determine contact angles. The most common is Goniometry. It provides a video-based contact angle, the measurements obtained by fitting a mathematical expression to the shape of the drop and then calculating the slope of the tangent to the liquid drop at the interface line between liquid-solid-vapour (LSV) phases. Computer software analysis provides the correct contact angle.

Figure 49 shows a common contact angle goniometer. Older systems used a microscope optical system with a back light, while current generation systems use high resolution cameras and software to capture and analyse the contact angle.
There are several different methods to measure the contact angle such as: static sessile drop, dynamic sessile drop, dynamic Wilhelmy, Single-fiber Wilhelmy and powder contact angle method.
Chapter 4

9. References

Chapter 5

Plasma pre-treatment

1. Introduction

Plasma cleaning is an effective and environmentally safe method for surface preparation which has been reported to be a useful process tool for more than 30 years in a broad range of applications spanning from microelectronics and photovoltaics (PVs) to automotive, textiles, medical, plastics, etc. [225] [226]. Activation of the surface of a material is important for the growth of thin films since surface contaminants and the native oxide can alter the growth mode and thin film adhesion. It can also affect the properties of the deposited films and therefore the performance of the PV devices [106][227].

The surface properties of transparent conducting oxides (TCOs) have an influence on the quality of the other films comprising the cell. In particular, sputter treatments have been shown to reduce carbon contamination and modify the resulting interface between the SnO₂ and the CdS layers [228]. Poor growth regions, appearing as pinholes, can form in the n-type CdS layer, allowing a shunt path to develop between the front contact and the p-type CdTe film [229]. Pinholes are particularly troublesome when a thin CdS layer is deposited on TCO-coated glass that has been cleaned using industry-standard techniques [230].

Plasma treatments have previously been applied to TCOs such as indium tin oxide (ITO) [1], aluminium-doped zinc oxide (AZO) [231] and zinc oxide (ZnO) [232] with different gas combinations such as argon, hydrogen, or oxygen. These treatments have been shown to change the properties of the TCO surfaces.

In this chapter the plasma treatment of commercially available fluorine doped tin oxide (FTO) transparent conducting oxide NSG TEC 15, which is used as a superstrate in CdTe solar cell devices, is studied.
Chapter 5

As previously described, a thin film CdTe solar cell consists of a multi-layer stack material system, with layers having specifically defined properties. Thin film CdTe solar cells are grown in a superstrate configuration as shown in Figure 50 on a FTO coated glass substrate [47]. The light transmits through the TCO coated glass before reaching the p-n heterojunction, consisting of the n-type CdS layer and a p-type CdTe layer.

Plasma pre-treatment of the TEC 15 glass was performed to activate the surface prior to the chemical bath deposition (CBD) of the thin CdS film. Good surface wettability of the TCO coated substrate is required to avoid the presence of the pinholes and ensure continuity in the deposited CdS thin films. Fluorine doped tin oxide is deposited on an industrial scale using an atmospheric pressure CVD process that results in a relatively rough surface. This roughness can increase the probability of pinhole formation. The aim of this study is to develop a plasma treatment process to produce pinhole-free CdS thin films on TEC 15 glass.

2. Experimental

TEC 15 glass supplied by NSG-Pilkington was used as the substrate material. TEC 15 is a multilayer stack of materials deposited on a 3.2 mm thick glass. The stack consists of a 25 nm SnO₂ layer, a 25 nm SiO₂ layer, and a 280 nm thick conducting layer of fluorine doped tin oxide (SnO₂:F). TEC 15 has a sheet resistance of 15 Ω/□ and a relatively good transparency, ∼82% light transmittance. These properties are a good compromise between the electrical and the optical requirements of a PV device substrate. The substrate was treated using 20 sccm O₂/30 sccm Ar plasma, for 5 min, in a Glen100-P AE Advanced Energy parallel plate plasma reactor, prior to the CdS film growth. The plasma power was set at 100 W and at a pressure of between 335 and 273 mTorr. Electrodes and sample trays are 406.4 mm x 406.4 mm in...
area using perforated aluminium of thickness 3.175 mm. The parallel electrodes are used to provide uniform plasma across the sample area. All substrate surfaces are treated to the same degree, irrespective of their position on the sample tray. The plasma treatment reactor was a parallel plate system using AC plasma power source with potential for three gas admittance lines. The system was pumped to a pre-process pressure of 332 mTorr using a rotary pump. A 50 nm CdS thin film was deposited by CBD, the reaction occurs in a beaker immersed in a water jacket to ensure constant temperature (70ºC). The bath solution was made of 200 ml of de-ionized water, 15 ml of Cd(CH\textsubscript{3}COO)\textsubscript{2} 0.01 M, 25 ml of NH\textsubscript{4}OH 25%, and 10 ml of CS(NH\textsubscript{2})\textsubscript{2}. A magnetic bar was used to stir the solution to accelerate the reaction kinetics.

2.1. Substrate surface modification

Plasma treatment activates the substrate surface by increasing the surface energy. The surface energy of the material was tested by measuring the water contact angle before and immediately after the treatment. Figure 51 shows the effect of the plasma treatment on the FTO coated glass surface. The equilibrium contact angle that the drop makes with the surface was 54.3º before the treatment and 12.3º after the plasma treatment. This indicates that the treatment increased the hydrophilic nature of the surface.
Figure 51: Water contact angle images (a) prior and (b) post plasma treatment.

The increased surface energy is beneficial for adhesion and the continuity of the thin film. It is possible that the increase in surface energy may change the thin film growth kinetics. However, there was only a marginal difference in thin film thickness (~50 nm) for films deposited on the treated and untreated surfaces as measured by spectroscopic ellipsometry. This hydrophilic behaviour corresponds to the removal of contaminants from the surface, as confirmed by X-ray photoelectron spectroscopy (XPS) analysis. Table 3 reports the atomic percentage of Carbon (C1s), Oxygen (O1s), and Tin (Sn3d) for the untreated and the plasma treated substrates, indicating carbon contamination reduction without altering the Sn/O ratio.
Table 3  
Atomic% composition as determined by XPS

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>Plasma treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s%</td>
<td>24.5</td>
<td>11.9</td>
</tr>
<tr>
<td>O1s%</td>
<td>46.3</td>
<td>55.2</td>
</tr>
<tr>
<td>Sn3d%</td>
<td>27.3</td>
<td>31.4</td>
</tr>
</tbody>
</table>

2.2. Impact of substrate plasma treatment on the CdS films

Scanning white light interferometry (SWLI) is a powerful tool for the metrology of surfaces. A variant of SWLI called Coherence Correlation Interferometry (CCI) developed by Taylor Hobson, Ltd, as already described in chapter 4, was used to analyse the surface morphology of the CdS films and detect pinholes in the CdS. Pinholes appear as spikes in the CCI surface image as shown in Figure 52 (a). In this case the CdS was deposited on the untreated substrate; pinholes were detected with a mean depth of 55 nm and a width of 0.65 μm as shown in Figure 53. The spatial resolution of the CCI is determined by the wavelength of light and the numerical aperture of the lens used is typically ~0.3 μm. The vertical resolution is typically <1 nm. The CCI analysis shows that the pinhole density was dramatically decreased and virtually eliminated for the film grown on the plasma treated substrate (Figure 52 (b)); the thin film also has a smoother surface.
Chapter 5

Figure 52: Three dimensional CCI images of CdS deposited on (a) untreated and (b) plasma treated substrates (20 sccm O₂/30 sccm Ar).

Figure 53: Mean depth and width of pinholes in CdS observed on the surface of the untreated samples. The thickness of the CdS layer was 50 nm.

Scanning Electron Microscopy (SEM) images were obtained to study the surface morphology of the grown CdS films. Figure 54 shows the comparison between the surface of the untreated (a) and the plasma treated (b) samples. The CdS films exhibit a crystalline structure with
small crystallites (~10-20 nm) that agglomerate in bigger grains; their size increased from ~100 nm to ~130 nm following plasma treatment of the substrate. The grain size was calculated using ‘AxioVision SE64 Rel.4.9.1’ software, estimating a mathematical average over 20 different measurements. The treated samples generally showed more uniform coverage of the surface with a more compact deposited film.

Figure 54: SEM images of CdS films grown on (a) untreated and (b) plasma treated (20 sccm O₂/30 sccm Ar) FTO coated glass.

XPS analysis was also performed on the CdS films to analyse their stoichiometry. Figure 55 shows the XPS spectra of Cd3d and S2p photoelectron core levels for the untreated and the plasma treated samples. The position of the peak at 405.8 eV for Cd orbital 3d5/2 and the shape and binding energy of 161.6 and 162.8 eV for S2p3/2 and S2p1/2, match the theoretical CdS values [126], indicating that CdS was not incorporating oxygen into the films.
The optical properties of the CdS films were measured using spectroscopic ellipsometry. Transmission and reflection measurements were obtained using a spectrophotometer. The Tauc- Lorentz model [233] was used to parameterise the spectral dependence of the CdS refractive index, n, and extinction coefficient, k. The derived optical properties are shown in Figure 56.

The CdS film deposited on the plasma treated substrate showed increased refractive index, n, (Figure 56 (a)). The film also showed a slight increased extinction coefficient, k (Figure 56 (b)). This is consistent with the increased grain size, increased compactness and density, and reduced pinhole density observed for the film deposited on the plasma treated substrate.
Figure 56: \( n \) (a) and \( k \) (b) dispersions measured for CdS films deposited on the untreated substrate and the plasma treated substrate (20 sccm of \( O_2 \)).

Figure 57 shows the transmittance and reflectance spectra of the CdS thin films deposited on the untreated and on the plasma treated substrates. The transmittance of the thin films reaches a maximum of \(~80\%\) and it decreases near the absorption edge at 500 nm; this confirms that the CdS has good crystallinity [234].

The CdS deposited on the plasma treated substrate shows lower transmission compared to the film deposited on the untreated substrate, consistently with the higher \( k \) measured by ellipsometry. The transmittance is lower due to the higher optical density of the CdS film as shown by the SEM measurements and the removal of pinholes as shown by the CCI.
metrology measurements. The Urbach equation can be used to obtain the optical bandgap from the absorption coefficient [235] through the formula

$$\alpha = \frac{A(h\nu-E_g)^p}{h\nu}$$

where $A$ is a constant, $E_g$ is the band gap energy, $\nu$ is the frequency, $h$ is the Plank’s constant, $p$ is the numerical coefficient. In Figure 58, $[\alpha h\nu]^2$ is shown as a function of the energy (eV), $p$ in this case is 0.5. The single slope in the curve explains the direct transition of electrons between the valence band and the conduction band. Extrapolating the linear region of $[\alpha]^2$ up to the value $\alpha = 0$, the band gap energy ($E_g$) is determined to be 2.34 eV.

Figure 57: Transmission and reflection spectra for CdS thin films deposited on TEC 15, comparing the untreated and the plasma treated surface, with 20 sccm O$_2$/30 sccm Ar.
The band gap decreased from 2.4 eV to 2.3 eV as a result of the substrate plasma cleaning due to the increased density of the film or the small grain size [236].

3. Conclusions

Plasma cleaning of FTO-coated glass prior to the deposition of the CdS/CdTe solar cell strongly affected the TCO surface, and improved the density and compactness of the subsequently deposited CdS thin film. Specifically, the plasma cleaned FTO exhibited increased hydrophilic behaviour, due to a reduction or elimination of surface contamination. This corresponds to a reduction in water contact angle and increased surface energy. When CdS thin films were deposited on to a plasma cleaned FTO surface it has been shown that the pinhole density was greatly reduced and virtually eliminated compared with CdS films deposited on substrates treated using standard wet cleaning techniques. The plasma treatment improved the wettability of the substrate as demonstrated using water contact measurements. This improved the optical and morphological properties of the deposited CdS thin films, resulting in a higher refractive index related to the increased film density and increased grain size of CdS film. The pinhole removal and the increased density allow the use of a much thinner CdS layer. Use of a thinner CdS layer actually reduces absorption of blue spectrum photons thereby increasing the efficiency of the thin film CdTe.
cell. All further experiments have incorporated the plasma cleaning process into a full cell deposition process to assess the improvement to device performance.
4. References


Chapter 5

Chapter 6

Chemical Bath Deposition (CBD) of CdS thin films

1. CdS as an n-type window layer
The performance of CdS/CdTe heterojunction solar cells is dependent on the quality of the underlying CdS/TCO layers. Each layer in the multi-stack structure plays an important role in the overall device efficiency.

Thin film CdS is an n-type semiconductor that works as a window layer. It is desirable that the CdS layer is uniform and continuous to suppress short circuit effects [237]. It should also be as thin as possible (50-100 nm) to allow a high fraction of the photons with energy above its band gap to reach the CdTe absorber and hence produce a high photocurrent [61]. CdS thin films have been deposited by using Chemical Bath Deposition (CBD). The deposition process has been optimised and CdS layers have been characterised to understand their morphological, structural and optical properties. Sonochemical bath deposition (sonoCBD) has also been used and the optical, morphological and structural properties of these films have been compared to those deposited using the conventional chemical bath.

2. Experimental
The experimental work in this work used TEC 15 Fluorine doped Tin Oxide (FTO) coated glass as the substrate for the Chemical Bath Deposition (CBD). According to the theory of the process, a variety of parameters play a role in the deposition. In this study, the effect of the concentrations of chemicals in the bath, the use of different magnetic stirrers (shape and speed), and the use of an ultrasonic probe have been investigated. Furthermore, a comparison between CBD and sonochemical bath deposited films was performed. The influence of different substrates (TEC10/TEC15) on the morphological and optical properties of CdS layers was also tested.

The first objective was the optimisation of the CdS deposition; investigating the influence of parameters such as:
• **Concentration of chemicals used**

The concentration of Cd(CH$_3$COO)$_2$ (cadmium acetate) was varied from 0.01 M to 0.05 M and from 0.1 M to 0.5 M for SC(NH$_2$)$_2$ (thiourea). A much higher concentration was also studied as well (0.3 M) for Cd(CH$_3$COO)$_2$ and 4 M for SC(NH$_2$)$_2$.

• **Stirrer shape and speed**

A magnetic stirrer has been used, testing a circular and a cylindrical geometry, with speeds varied between 300 rpm and 500 rpm.

• **Deposition time**

The deposition time has been varied from 20 min, 30 min, 40 min and 60 min,

-Substrates used

• TEC15/TEC10

Transparent Electrical Conductive glass (TEC) 15 and 10 provided by NSG-Pilkington Ltd were used as substrate (Chapter 5). TEC 15 and TEC 10 have a slightly different sheet resistance of 15 and 10 Ω/□, respectively, a relatively good transparency and a smooth surface. Their properties provide a practical compromise between the electrical and the optical requirements for PV devices and in particular for CdS/CdTe solar cells.

These materials have slightly different properties, determined by the thickness of the top tin oxide layer. The general structure is as follows: a 3.2 mm glass substrate, coated with 25 nm SnO$_2$, 25 nm SiO$_2$ and a top layer doped with fluorine SnO$_2$:F, (Figure 55) using an atmospheric CVD process. The top SnO$_2$ thickness is varied to modify the sheet resistance. In general the doped top layer is 450 nm for TEC10 and 350 nm for TEC15.
Figure 59: A schematic diagram of a multi-layer TEC 15 /10 glass: glass/SnO₂/SiO₂/SnO₂:F.

The surface morphologies are only slightly different as TEC10 shows slightly larger grains, approximately 50-100 nm, with the roughness of the FTO surface less apparent than the other TEC15 glass.

-Deposition process

The deposition process occurs in a beaker immersed in a water jacket to ensure constant temperature (70°C).

The solution used for the process is made from Cd(CH₃COO)₂ (cadmium acetate), CS(NH₂)₂ (thiourea), NH₄OH (ammonium hydroxide), in de-ionized water. The solution is alkaline with a pH of approximately 12.

The starting point of this process shows a transparent phase of the solution and the substrate; after a few minutes the solution changes in colour to pale-yellow, transforming through yellow pale-orange and for longer deposition time it finally turns orange, and opaque (Figure 60).
Figure 60: Pictures showing Chemical Bath Deposition processing steps: from the starting point of the process, with the transparent phase, to the orange phase of the solution and the substrate, for longer deposition times.
2.1. CdS deposition at different molarity

The first parameter investigated was the concentration of chemical reagents used.

The SEM images show how the morphology of the deposited films changed from lower to higher concentrations (0.01-0.3 M for Cd(CH$_3$COO)$_2$ and 0.1-4 M for SC(NH$_2$)$_2$) and from shorter to longer deposition times (20-60 min).

- **0.01 M Cd(CH$_3$COO)$_2$ /0.1 M SC(NH$_2$)$_2$**

  Initial depositions used the lowest concentration for the chemical bath of 0.01 M for Cd(CH$_3$COO)$_2$ and 0.1 M of SC(NH$_2$)$_2$ using a thin circular stirrer rotating at a speed of 500 rpm; different deposition times were used to deposit CdS on to TEC15 TCO coated glass previously cleaned using the method described in chapter 5. The thickness of the CdS film was found to increase linearly with deposition time.

  After a deposition time of 20 min the CdS film appears homogeneous and the surface is totally covered. The thickness of this layer was measured to be 25 nm and the film conforms to the morphology of the FTO coated substrate. An image of a TEC15 surface is shown in Figure 61, as a reference. The similarity in the grain size of the FTO and the image of the CdS coated surface supports the observation that the CdS is conformal. An image of TEC10 is shown in the same Figure 61 (b) as a comparison with TEC15.

Figure 61: SEM image of TEC 15 (a) and TEC10 (b).

SEM images of CdS thin films deposited for 20 min on TEC15 are shown in Figure 62.
Experiments were then performed by increasing the deposition time to 30 min, and then 60 min. Increased deposition time resulted in thicker CdS films of 50 nm, and 90 nm respectively, as measured by spectroscopic ellipsometry.

The shape of the stirrer has been found to be very important in the deposition. When a larger cylindrical stirrer bar was used, the surface of the TEC15 was not uniformly covered by the
CdS layer, as shown in Figure 65. Individual grains of CdS can be observed. The thin film of CdS was not conformal or continuous on the TEC 15 surface and defects in the coverage are clearly visible in the images.

**Figure 65: SEM images deposition time of 60 min of CdS on TEC15, using a larger cylindrical stirrer bar.**

- **0.02 M Cd(CH$_3$COO)$_2$/0.2 M SC(NH$_2$)$_2**

Depositions were then conducted using a higher concentration for the chemical bath of 0.02 M for Cd(CH$_3$COO)$_2$ and 0.2 M of SC(NH$_2$)$_2$ using the thin circular magnetic stirrer rotating at a speed of 500 rpm; different deposition times were used to deposit CdS on to TEC15 TCO coated glass previously cleaned with de-ionised water and in oxygen/argon plasma (chapter 5). The thickness of the CdS film increased with deposition time. The deposition times investigated were 20, 30 and 60 minutes.

The deposition of CdS for 20 minutes resulted in a much thicker layer of 60 nm. The coverage of the TEC 15 substrate was uniform and conformal as shown in Figure 66.

However, when the deposition time was extended to 30 minutes, voids appeared in the film and the resultant film was discontinuous. Figure 67 shows SEM images of the inhomogeneous film after 30 minutes of deposition.
Further depositions were conducted for 60 minutes. The SEM images of the film are shown in Figure 68. These images show further deterioration of the quality of the film. Voids were clearly visible and the surface coverage was even more inhomogeneous. The film deposited at 60 minutes was much thicker and individual grains of diameter ~200 nm were visible. However due to the voids and roughness of the film, accurate ellipsometric measurements of thickness were not possible.
Figure 68: SEM images for deposition time of 60 min of CdS on TEC15.

- **0.03 M Cd(CH$_3$COO)$_2$ / 0.3 M SC(NH$_2$)$_2$ $\rightarrow$ 0.05 M Cd(CH$_3$COO)$_2$ / 0.5 M SC(NH$_2$)$_2$**

Depositions were then conducted using higher concentrations from 0.03 M to 0.05 M for Cd(CH$_3$COO)$_2$ and from 0.3 M to 0.5 M of SC(NH$_2$)$_2$ using the thin circular magnetic stirrer rotating at a speed of 500 rpm, for deposition times of 20, 30 and 60 minutes. The CdS film thickness increased with deposition time.

Using these higher concentrations, the quality of the films further deteriorated. For this reason only the depositions conducted for 20 minutes are shown here. In general, the higher concentrations resulted in poor thin film growth. Figure 70 and 71 reveal the appearance of clusters and aggregates of grains on the TEC 15 surface. This increased deterioration in quality is more evident by comparing Figure 69, Figure 70 and Figure 71.
Chapter 6

Figure 69: SEM images for deposition time of 20 min of CdS on TEC15 0.03 M/0.3 M.

Figure 70: SEM images for deposition time of 20 min of CdS on TEC15 0.04M/0.4M. The red arrows point out clusters and aggregates of grains on the surface.

Figure 71: SEM images for deposition time of 20 min of CdS on TEC15 0.05M/0.5M. The red arrows point out clusters of grains on the surface.

- \( 0.3 \text{ M Cd(CH}_3\text{COO)}_2 / 4 \text{ M SC(NH}_3\text{)}_2 \)
In this experiment the highest concentrations, 0.3 M for Cd(CH₃COO)₂ and 4 M for SC(NH₂)₂, was investigated, with a lower speed of rotation 300 rpm for the thin circular stirrer. CdS film thickness increased with deposition time. The deposition times studied were 20, 30 and 60 minutes. However, since the morphology of the deposited films was poor, only the 60 minute deposition is presented in Figure 72.

The grains of CdS appeared round and they coalesced with the formation of clusters and aggregates on the surface. These films were extremely rough and inhomogeneous and were not suitable for use as a window layer in thin film photovoltaics.

Figure 72: SEM images for deposition time of 60 min of CdS on TEC15 0.3M/4M.

According to these experiments, it was concluded that the lowest concentration 0.01 M of Cd(CH₃COO)₂ and 0.1 M of SC(NH₂)₂ for 30 minutes of deposition time, at a rotation speed of 500 rpm produced the highest quality CdS thin film. These conditions allowed the deposition of a uniform, thin (~50 nm), pinhole-free and void-free CdS film (as shown in chapter 5).

It was decided to use this set of parameters for the deposition of the thin CdS window layer in the CdTe solar devices.
3. Results and Analysis

3.1. Optical properties and band gap characterisation

The graphs show transmittance curves (T%) against wavelength (nm) for CdS films deposited on to TEC10 glass substrates obtained for different concentrations (0.01 M/0.1 M, 0.02 M/0.2 M and 0.3 M/4 M) of Cd(CH$_3$COO)$_2$ and SC(NH$_2$)$_2$, respectively. For each of these concentrations, different deposition times have been investigated (20, 25, 30, 40, 60 min).

In Figure 73 Transmission (T%) curves for 0.01 M acetate /0.1 M thiourea, CdS thin films deposited on TEC10 are reported. Increasing the deposition time, and, therefore, the film thickness, the average T% decreased, as expected.

![Figure 73: Transmittance curves (T%) against wavelength (nm) for (0.01 M acetate/0.1 M thiourea) CdS thin films deposited on TEC10 for different deposition times.](image)

For a slightly higher concentration, 0.02 M acetate /0.2 M thiourea, Figure 74 shows the T% curves for different deposition times. Here, the T% rose towards higher values for the lowest deposition times, while it plateaued for the others. This shows that after 30 minutes of
deposition the film thickness did not change and the quality of the coverage became even worse.

Figure 74: Transmittance curves (T%) against wavelength (nm) for (0.02 M acetate/0.2 M thiourea) CdS thin films deposited on TEC10 for different deposition times.

For the highest concentration, 0.3 M acetate/4 M thiourea, the minimum values of transmittance were reached at deposition times of 15 minutes. For longer times, the uniformity of the film was lost. The transmittance (%) increased due to the presence of voids, clusters and aggregates.
Chapter 6

These transmission results, shown in Figure 75, are consistent with SEM images shown in Figure 75.

![Figure 75: Transmittance curves (T%) against wavelength (nm) for (0.3M acetate/4M thiourea) CdS thin films deposited on TEC10 for different deposition times.](image)

From an optical analysis, the band gap has been calculated, and for 30 minutes of deposition, for the lowest concentration, it was found to be 2.38 eV which is close to the literature value 2.42 eV [111] [238] [131].

The Urbach equation has been used to calculate the absorption coefficient, defined by the formula shown in equation 30 [235]

\[
(\alpha h\nu)^2 = C h\nu
\]

The estimated band gap from the plot of \((\alpha h\nu)^2 \) versus \(h\nu\) is shown in Figure 76.
Figure 76: CdS band gap, 2.38 eV, calculated from optical measurements, extrapolating the linear region of $\alpha^2$ up to the value $\alpha$.

$\alpha h \nu$ is shown as a function of the energy (eV). The single slope in the curve explains the direct transition of electrons between the valence band and the conduction band. Extrapolating the linear region of $\alpha^2$ up to the value $\alpha=0$, the band gap energy ($E_g$) is determined to be 2.38 eV.

### 3.2. Reaction time

The reaction time was studied using six different solution colours, from transparent to intense-orange:
The graph in Figure 77 shows the change in solution colour for each concentration (0.01-0.05 M, 0.3 M) with also the reaction performed without a substrate. For lower concentrations there was a direct proportionality with increasing time, step by step, there was a change in colour of phase. However it was found that for higher concentrations this proportionality was lost and a plateau was reached, as shown in the graph in Figure 77. This is in agreement with the theory of growth mode explained in section (4.3) where, for lower concentrations used, CdS films followed the Volmer-Weber mode, whereas at higher concentration and higher reaction time their growth moved to the Stranski-Krastanov mode [41].

These results have confirmed the advantage of using lower concentrations to take advantage of a proportional growth of the deposited film in terms of thickness and uniformity of the layers.
3.3. Optical properties and thickness by Spectroscopic Ellipsometry

Ellipsometry was used to obtain the optical constants and thickness of CdS thin films deposited by chemical bath deposition [240]. The model used for the analysis of data is shown in Figure 78. It comprises a substrate, TEC15 in this case, an interface layer, the CdS layer, and where necessary, a top layer with surface roughness.

![Figure 78: A schematic diagram of the CdS ellipsometric model.](image)

This optical model was applied to study the optical properties, namely the refractive index, \( n \), and the extinction coefficient, \( k \), of the ~50 nm thick CdS layer deposited under the optimised conditions of 0.01 M Cd\((CH_3COO)\)_2, 0.1 M SC\((NH_2)\)_2, as shown in Figure 79.
The dispersion law used for modelling these samples is Tauc-Lorentz2, which is often used for semi-absorbing dielectrics and semiconductors. When more oscillators are considered, \( N > 1 \), as in this case, \( N = 2 \), the expression is:

\[
\varepsilon_i \begin{cases} 
1 \sum_{i=1}^{N} \frac{1}{E} \times \frac{A_i E_i C_i (E - E_g)^2}{(E^2 - E_i^2)^2 + C_i^2 E^2} & \text{for } E > E_g \\
0 & \text{for } E \leq E_g
\end{cases}
\]

for \( E > E_g \) and for \( E \leq E_g \)

where \( A_i \) is the Tauc coefficient, \( E \) the photon energy, \( E_i \) the transition energy of the oscillator of highest order, \( C_i \) the broadening term of the peak, and \( E_g \) the optical band gap.

\( \varepsilon_r \) is written as the following sum:
$$\varepsilon_r(E) = \varepsilon_r(\infty) + \sum_{i=1}^{N} \frac{2}{\pi} \cdot P \cdot \int_{E_g \xi^2 - E^2}^{\infty} \frac{\xi \varepsilon_i(\xi)}{d\xi}$$

4 parameters describe the imaginary part of the dielectric part:

- $A_i$ (eV) is related to the strength of the $i$:th absorption peak. The subscript “$i$” is referred to the number ($i=1, 2$ or $3$) of oscillators. As $A_i$ increases, the amplitude of the peak increases and the Full Width at Half Maximum (FWHM) of that peak gets slightly larger. Generally $10 < A_i < 200$.

- $C_i$ (eV) is the broadening term; the higher that peak becomes and at the same time the smaller its amplitude is. In general, $0 < C_i < 10$.

- $E_g$ (eV) is the optical band gap energy.

- $E_i$ (eV) is the energy of maximum transition probability or the energy position of the peak of absorption. The subscript “$i$” refers to the number ($i=1, 2$ or $3$) of oscillators. Always, $E_g < E_i$.

The graph in Figure 80 shows the thickness (nm) against time (min) for CdS films deposited on TEC 15 using the lowest concentrations (0.01 M of Cd(CH$_3$COO)$_2$ and 0.1 M of SC(NH$_2$)$_2$ in the chemical bath.
Figure 80: Thickness values against time (min) of deposition for the two lowest concentrations used.

3.4. Chemical composition and stoichiometry by X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed on CdS films deposited using the lowest concentration to analyse their stoichiometry. Figure 81 shows the XPS spectra of Cd3d and S2p photoelectron core levels for chemical bath deposited films. The position of the peak at 405.8 eV for Cd orbital 3d_{5/2} and the shape and binding energy of 161.6 and 162.8 eV for S2p_{3/2} and S2p_{1/2}, match the theoretical CdS values [126], indicating that CdS was not incorporating oxygen into the films. This is also supported by a fitting analysis which showed only the CdS component.
Figure 81: XPS spectra of Cd3d and S2p photoelectron core levels for chemical bath deposited films.

This confirms that the thin film deposited on TEC TCO coated glass is pure CdS.
4. CdS thin films by Sonochemical bath

4.1. Ultrasonic probe

Further experiments were performed replacing the magnetic stirrer with an ultrasonic probe, to test if the homogeneity of the solution could be improved by the use of the ultrasonic waves and how this would affect the CdS film deposition.

Sonication consists of applying sound energy to agitate particles in a sample. Ultrasonic frequencies are higher than 20 kHz. The field of study related to sonication is called Sonochemistry. It investigates how the chemical system can be affected and/or altered by sonic waves. It is not a direct interaction with molecular species, there is no direct coupling of an acoustic field with chemical species. Sonochemistry is related to the acoustic cavitation which is the formation, growth and implosive collapse of bubbles in a liquid. There are three main areas of chemical effect: homogeneous sonochemistry, heterogeneous sonochemistry and sonocatalysis [241]. Physical effects of ultrasound result in the improvement of mass transport from turbulent mixing and acoustic streaming, emulsification, bulk thermal heating and different effects on solids [242]. Choi et al. [132] investigated the influence of ultrasonication on the CdS deposition studying the change in film properties. They considered the process as an ion-by-ion deposition, where CdS was deposited as a transparent, uniform adherent film, but as a late stage of the deposition, CdS colloidal particles, which precipitate homogeneously in the bulk solution, absorb randomly on the growing film, leading to an opaque, non-uniform and poorly adherent film, called ‘B-quality’ film [243]. These two reactions (ion by ion and colloid-by-colloid) usually occur at the same time, even under proper control of conditions [244]. The use of the ultrasonic agitation in the bath acts as an external force, which might eliminate the ‘B-quality’ component in the CdS films. They finally observed that films grown under sonication where compact, uniform; and the deposition rates were reduced by suppressing the formation of the B-quality component and the growth of CdS grains. The grain size reduced to 3-5 nm from 12-15 nm size observed without sonication. The transmittance of these films at long wavelengths (≥520 nm) was higher due to the ultrasonication effect and the band gap increased from 2.37 eV to 2.39 eV [132].
A similar study has been performed in this project. The ultrasonic probe used for the present experimental work was a Microson XL 2000 ultrasonic liquid processor, the probe was dipped in the solution and the output power settled at 4 W (RMS).

Figure 82: Ultrasonic probe used in the CdS chemical bath.
Chapter 6

Sonochemical bath deposited layers of CdS have been characterised by CCI (chapter 4). A totally uniform, smooth, pinhole and void free coverage has been observed for a 50 nm thick film, as shown in the Figure 83.

Figure 83: 3D and 2D CCI images of 50 nm thick CdS film deposited by sonochemical bath.

While 30 min of deposition by CBD resulted in a 50 nm thick film, a ~ 70 nm thick film was obtained by the sonochemical bath in the same time indicating an increased deposition rate.
Transmittance measurements show that 30 min of deposition by CBD on TEC15 are comparable with 20 min of sonochemical deposition on the same substrate TEC15 (Figure 84).

\[\begin{figure}
\centering
\includegraphics[width=\textwidth]{transmittance_curves.pdf}
\caption{Transmittance curves of 50 nm thick CBD and sonochemical deposited CdS layers on TEC15.}
\end{figure}\]

Sonochemical bath deposited films showed slightly higher transmittance in the long wavelength range (over 550 nm), whilst in the short wavelength region the CBD film showed higher transmittance values. According to the literature, crystalline defects such as grain boundaries or dislocations are responsible for the absorption of light in the longer wavelength region \((\lambda \geq 520 \text{ nm})\) [132][245]. Therefore, it is assumed that sonochemical deposited films have a lower defect density, which may lead to better electrical properties.
Additionally, transmission of light in the shorter wavelength range may result from thin films or layers without a perfectly uniform thickness, i.e. with voids or pinholes. As a consequence, the lower transmittance values observed for the sonochemical bath deposited films indicated a denser and more uniform structure.

Figure 85: (a) Transmittance curves of CBD and Sonochemical CdS deposited films on TEC10, for 30 and 60 min of deposition. (b) Comparison of T% curves between (~100 nm thick) CBD and Sonochemical deposited layers on TEC10 in the range 300-800 nm.
The chemical XPS analysis showed the Cd peaks at 405.8 eV and 412.3 eV for Cd3d5/2 and Cd3d3/2 respectively, and the shape and the binding energy of 161.6 eV and 162.8 eV measured for S2p3/2 and S2p1/2 matched the theoretical values for CdS [126] indicating that the deposited CdS films were stoichiometric and no oxygen was incorporated into the film.

Figure 86: (a) and (b) shows the XPS spectra of Cd3d and S2p photoelectron core levels measured for CdS films chemical bath and sonochemical both deposited at 70ºC with Cd(CH3COO)2 0.01 M, NH4OH 25% and CS(NH2)2, 0.1 M.
The two peaks show different intensity. This might be related to the different film density which is higher for the sonochemical deposited CdS film than for the chemical bath deposited films. This is supported by the transmittance analysis discussed above.

The band gap ($E_g$) has been extrapolated by using the Tauc plot (as explained in chapter 4) for 50 nm CdS thin films deposited by CBD and sonochemical bath. The graph shows a comparison between the $E_g$ for both of the films, and the extrapolated energy band gap which lead to the same value, 2.38 eV.

![Figure 87: Band gap ($E_g$) of 50 nm CdS thin films deposited by CBD and Sonochemical bath on TEC10 extrapolated by Tauc plot.](image-url)
The SEM analysis showed that the top surface morphology and the grain size is similar for both CB and sonochemical depositions as shown for the CBD and sonochemical CdS layers, 50 and 100 nm thick, deposited on both TEC10 and TEC 15 substrates.

Figure 88: 50 nm thick CBD (a) and sonochemical deposited CdS (b) on TEC15. Grain size in the range of 133 nm.

Figure 89: 50 nm thick CBD (a) and sonochemical deposited CdS (b) on TEC10. Grain size in the range of 160 nm.

Figure 90: 100 nm thick CBD (a) and sonochemical deposited CdS (b) on TEC10. Grain size in the range of 200 nm.
The ellipsometric analysis shows that the use of ultrasonics in the deposition bath promoted the growth of films with higher optical density with higher refractive index (Figure 91).

Figure 91: Ellipsometric analysis with $n$ and $k$ values for 50 nm thick CdS films deposited by CBD and Sonochemical bath on TEC15 (a) and TEC10 (b).

5. Conclusions

Chemical bath deposition of CdS thin films on TEC glass has been performed and optimised by testing several of the parameters involved in this deposition including the concentration of chemical reagents used in the bath, shape and size of magnetic stirrers, and deposition times. It has been found that using the lowest concentration 0.01 M of Cd(CH$_3$COO)$_2$ and 0.1 M of SC(NH$_2$)$_2$ a deposition time of 30 minutes produced the highest quality CdS thin films. These
process conditions allowed the growth of uniform, thin (~50 nm), pinhole and void-free CdS layers.

This set of parameters was then used for the deposition of the thin CdS window layer in the CdTe solar device.

Replacing the magnetic stirrer with the ultrasonic probe resulted in CdS films with higher optical density, higher refractive index, pinhole and void-free, more compact and uniform along the surface and through the thickness of the deposited material. These optical and morphological properties have been established for CdS films deposited on both TEC15 and TEC10. A higher refractive index and more uniform distribution of grains were obtained for films grown on TEC10. For this reason the ultrasonic probe was used in all subsequent experiments.
Chapter 6

6. References


Chapter 7

Pulsed DC Magnetron Sputtering of CdS thin films

The main topic of this thesis is the study of the novel process of Pulsed DC Magnetron Sputtering to deposit CdS and CdTe thin films. This chapter is focused on the optimisation of the deposition conditions for CdS thin films by analysing the effect of different process parameters such as the working gas flows, deposition power, and the deposition temperature. The study includes an analysis of how these parameters affect the deposition rate, crystal structure, chemical composition, morphology and optical properties of CdS layers.

1. Experimental

CdS thin films were deposited by pulsed DC magnetron sputtering using a ‘PV Solar’ sputtering system (Power Vision Ltd., Crewe UK). The pumping system consists of a turbomolecular pump backed by a rotary pump. The machine has two vacuum chambers; a main chamber and a smaller load lock chamber. The load lock enables faster loading and unloading of samples (Figure 92 (b)). Efficient water cooling is required to prevent overheating and this is provided by an external 3.2 kW recirculating water chiller. The system is equipped with four six inch diameter circular magnetrons mounted vertically, with an option to replace one of the magnetrons with a plasma source for reactive sputtering. The samples were mounted vertically on a rotatable carrier, designed for 5 cm x 5 cm substrates. The target to substrate distance is typically 10 cm. During the deposition process the carrier is typically rotated at 120 rpm, as shown in the Figure 92 (c). This provided excellent uniformity in the horizontal direction. Uniformity in the vertical direction was achieved by using disposable masks mounted in front of the magnetron target. The CdS thin films were sputtered using a pulsed DC power supply (Advanced Energy Inc. Pinnacle plus, 5 kW) using argon as the working gas [246].
Figure 92: A schematic diagram of the PV Solar® sputtering system (Power Vision Ltd., Crewe UK) used for this work (a) The main chamber and the lower load lock to allow loading and unloading of the substrates (b) The carrier can rotate at typically 120 rpm (c).

The CdS thin films were deposited on NSG-Pilkington (http://www.pilkington.com/) TEC15 and TEC10 Fluorine doped tin oxide (FTO) coated glass substrates. Prior to the CdS deposition, the substrates were externally cleaned following the procedure already described in chapter 5. The chemical composition, microstructure and optical properties of the CdS thin films were investigated (details are described in chapter 4). The Electron Backscattered Diffraction (EBSD) was used for crystal analysis to measure the structure and orientation in the solid crystalline phase. Transmission Electron Back-Scatter Diffraction (t-EBSD) was used because it offers the superior resolution suitable for the characterisation of
the small grains of the sputtered CdS material. t-EBSD was carried out using a dual beam FEI Nova 600 equipped with an ultra-high speed Hikari, Electron backscattering diffraction (EBSD) camera, using a beam current of 6.7 nA and an acceleration voltage of 30 kV.

2. Results and Discussion

2.1. CdS composition, structure and morphology

Figure 104 shows the XPS spectra of Cd3d and S2p photoelectron core levels measured for CdS films deposited at different Ar gas flows. The position of the Cd peaks was 405.8 eV and 412.3 eV for Cd3d5/2 and Cd3d3/2 respectively, the shape and the binding energy of 161.6 eV and 162.8 eV measured for S2p3/2 and S2p1/2 matched the theoretical values for CdS [20]. This indicated that the deposited CdS films are stoichiometric and no oxygen was incorporated into the film. This is also supported by a fitting analysis which showed only the CdS component.

The XPS analysis of CdS films deposited at different values of Ar gas flow, deposition power and temperature showed that the chemical composition of the sputtered film CdS was unaffected by the deposition parameters, reason why only one spectrum has been shown in Figure 93. The other spectra acquired at different gas flows, deposition power and temperature are not shown in the figure.

![Figure 93: XPS spectra measured for pulsed DC deposited CdS, showing photoelectron core levels of (a) Cd3d5/2 and Cd3d3/2 and (b) S2p for CdS thin films deposited at 10 sccm Ar, 500 W and 150 kHz. For (a) the fitting is achieved with a single Gaussian peak due to CdS and for (b) the fitting shows the splitting of S2p3/2 and S2p1/2. The green line below shows the error fitting function.](image-url)
Figure 94 shows the XRD spectra obtained from a CdS sample sputtered with Ar flow of 10 sccm on a TEC15 glass substrate. Diffraction peaks due to the (002), (100), (101), (102), (110) and (103) reflections indicate the hexagonal phase for the CdS thin film.

![Figure 94: (a) XRD pattern, (b) Kikuchi pattern from EBSD in SEM and (c) indexed Kikuchi pattern of a CdS film sputtered on TEC15 coated glass for 3600 s, 10 sccm Ar, 500 W, 150 kHz, 2 s (ramp time), 2 μs (reverse time). The * in (a) indicates peaks due to the TEC 15 glass substrate.](image)

The hexagonal phase was also found in t-EBSD analysis carried out on various grains. Each Kikuchi line, in the Kikuchi diffraction pattern collected in transmission electron back-scattered diffraction from a cadmium sulphide grain, is associated with Bragg diffraction from one side of a single set of lattice planes and they can be labelled with the same Miller indices that are used to identify diffraction spots. Figure 94 (b-c) shows a large number of bands overlaid on a typical diffraction pattern obtained from the CdS sputtered sample, which provides evidence that each grain has a hexagonal crystal structure.

The relative (and absolute) orientation of individual grains within the coating is shown in the inverse pole figure (IPF) map shown in Figure 95. The inverse pole figure (IPF) maps uses a basic RGB colouring scheme to display absolute orientation relative to a stereographic triangle. The transmission electron back-scatter diffraction map in Figure 95 (a) shows local preferred growth directions of the columnar grains. Furthermore, the high resolution transmission electron back-scattered diffraction phase/confidence index map in Figure 95 (b) shows that within the grains there is a high degree of indexing, while at grain boundaries the Kikuchi pattern quality is reduced and therefore they are shown as darker regions, highlighting the columnar structure of grains, also confirmed by the TEM cross section and SEM fracture cross section images of a 1.6 μm thick CdS film deposited on TEC10 glass shown in Figure 95 (c) and 91 (d), respectively. The TEM image in 91 (d) shows the
grain size is typically ~50 nm and the onset of grain coalescence is observed from the SEM surface images, shown in Figure 96 and 97.

Figure 95: (a) Transmission electron back-scatter diffraction derived map overlaid with inverse pole figure of a sputtered CdS sample. Different colours represent different orientations for grains as shown in the inverse pole figure (IPF) map. (b) Transmission electron back-scatter diffraction derived phase/Confidence index map from a CdS sputtered sample; the dark parts are related to the grain boundaries. (c) SEM fracture cross section of 1.6 μm thin film of CdS sputtered with 10 sccm Ar for 3600 s, 500 W. TEM image (d) of the same sample. The film shows a structure with thin columnar grains.
The SEM images in Figure 96 show the surface morphology of the deposited CdS film, measured for films deposited at different gas flows and deposition powers. The surface morphology appeared to be mostly unaffected by the Ar gas flow and the deposition power. The substrate temperature was ambient, a few degrees above room temperature due to the interaction with the magnetron plasma. The thickness was maintained at ~270 nm for the set of experiments.

Figure 96: SEM images of CdS films deposited at 600 s, 150 kHz, 2 s, 2.5 μs, by changing (a) the Ar gas flow from 10 sccm to (b) 20 sccm and power from 500 W to (c) 1500 W.
Figure 97 (a-c) shows SEM images of 100 nm thick CdS thin films deposited at different temperatures (250ºC, 300ºC and 400ºC). Increasing the deposition temperature from 250ºC to 400ºC resulted in morphology changes of the deposited CdS films. The grains of the films deposited at 250ºC appeared to have a round shape. The thin films deposited at higher temperature (300ºC and 400ºC) were more compact and showed a more uniform grain size.

Figure 97: SEM images of 100 nm thick CdS films deposited at 150 kHz, 2 s, 2.5 μs, 500 W by changing the deposition temperature (a) 250ºC (b) 300ºC (c) 400ºC.
Figure 98 shows a typical surface profile obtained using SWLI for samples deposited using an Ar flow of 5 sccm and 20 sccm. The analysis showed that films deposited at Ar flows below 20 sccm had a smooth uniform surface, but when the Ar flow was increased to 20 sccm voids appeared in the SWLI image of the film surface. The voids appear as deep pits in the surface, a 2D cross section across recorded voids shows that the detected pinholes were 174 nm deep. The thin film was 270 nm thick, therefore, these pits were voids in the deposited film but no pinholes were detected.

![Figure 98: SWLI surface maps of CdS films deposited at different Ar flows: 5 sccm (a) and 20 sccm (b). 2D cross section across recorded voids in the surface of CdS deposited at 20 sccm Ar flow(c). The thickness of the CdS layer was 270 nm.](image)

### 2.2. Optical properties of the deposited CdS films

To analyse SE data and derive the energy band gap and refractive index of films, a three-layer model was used consisting of TEC-substrate/interface/CdS-film/surface-roughness/air;
for the TEC substrate, the SE experimental file recorded just before starting the deposition, was used without any assumption; the interface was a Bruggeman effective medium (BEMA) [28] mixture of the top layer of the TEC substrate (SnO\textsubscript{2}:F) and CdS; the CdS optical properties were parameterised using a double Tauc Lorentz dispersion formula [226] (equations 31 and 32). The surface roughness was a BEMA mixture of 50% CdS and 50% voids. The fit parameters were the Tauc parameters and layer thicknesses.

Figure 99 shows the derived optical properties of the CdS film deposited at 10 sccm of Ar flow and 500 W deposition time for 600 s. The peak at 2.7 eV is the $E_0$ inter-band transition [233] and is consistent with the absorption edge of hexagonal CdS [31], while the $E_1$ inter-band transition at 4.9 eV is just at the end of the experimental measurement range.

The uniformity of the optical properties and thickness of the deposited films was verified by ellipsometric mapping; Figure 99 shows the distribution of the refractive index (c) and thickness (d) on a 5 mm x 5 mm area. Typically the refractive index changed in the range 2.50-2.54, with a standard deviation of $\sigma < 0.01$.

![Figure 99: Refractive index spectra of a 400 nm CdS thin film, (a) real (n) and (b) imaginary part (k), with marked $E_0$ and $E_1$ inter-band transitions points; (c) shows a map of refractive index at 550 nm, area of 5 mm x 5 mm outlined by 25 different points; (d) shows a thickness map of CdS layer 400 nm thick on a 5 mm x 5 mm area outlined by 25 different points.](image)
Chapter 7

The transmittance of this film reaches a maximum of ~80% and decreases to 0% near the absorption edge at 500 nm (Figure 100). From the Tauc plot, an energy band gap ($E_g$) of 2.31 eV has been determined.

Figure 100: Energy Band Gap, 2.31 eV and Transmittance curve, as inset, for CdS film deposited at 600 s, 500 W, 150 kHz, 2 s, 2.5 $\mu$s with 10 sccm of Ar on TEC15 and soda lime glass.

Figure 101 shows refractive index, extinction coefficient, and transmittance measured for films deposited at different gas flows. The measurement showed that, while the extinction coefficient and band gap do not change significantly, the increase in the gas flow resulted in a lower refractive index. This is consistent with the SWLI results where for higher Ar flows, voids were present in the surface of the CdS films. Voids are known to reduce refractive index of material because the optical density is affected by the presence of these defects in the material. Consequently, the transmittance changed slightly in the range 75% - 80%.
Figure 101: (a) refractive index, \( n \); (b) extinction coefficient, \( k \). for thin film CdS deposited using different argon gas flows.

Figure 102 shows that the deposition power affected the refractive index of films, as shown by the spectra for CdS films deposited at 5 sccm Ar flow at different deposition powers of 500, 1000, 1250 and 1500 W.

Figure 102: Refractive index (a) and extinction coefficient (b) of CdS films sputtered at different deposition powers: 500, 1000, 1250 and 1500 W.
2.3. The effect of deposition parameters on the deposition rate

The influence of deposition power and gas flow on the deposition rate was studied. The results are shown in Figure 99 and Figure 100. The deposition rate increased linearly with the deposition power. The deposition rate was affected by the argon flow rate and working gas pressure with rate increasing from 4.26 nm/s at a flow rate of 5 sccm to 5.33 nm/s at 20 sccm, as shown in the inset. Increasing the amount of argon gas flow (higher than 20 sccm) the deposition rate decreased. Therefore, the investigated range of gas flow was between 5 and 20 sccm of argon.

Figure 103: Deposition rate as a function of argon gas flow at 500 W deposition power.
Chapter 7

Figure 104: Deposition rate as a function of deposition power (150 kHz, 10 sccm Ar).

The effect of substrate temperature on the deposition rate was also investigated. Figure 105 shows the measured deposition rates for different substrate temperatures up to 400°C. The deposition rate decreased with increasing substrate temperature [126].

Figure 105: Deposition rate as a function of deposition temperature. The first point on the x-axis represents the deposition processed without heating.
3. Conclusions

Pulsed DC magnetron sputtering, at 150 kHz, resulted in a highly stable process with no plasma arcing. It allowed close control of film thickness using time only. There was no requirement for feedback using quartz crystal monitoring. These conditions were used to deposit CdS films.

A comprehensive analysis of the micro-structural and optical properties of the CdS films as a function of argon gas flows, power, temperature, and deposition time showed that CdS films deposited by pulsed DC sputtering were uniform, columnar and smooth, and in all cases the films were stoichiometric and this was unaffected by gas flow, deposition power or temperature. All the films were in the preferred hexagonal structure even at room temperature. The films exhibited a high level of texture in the <001> direction. The grain size was typically ~50 nm. Pinholes and voids could be avoided by reducing the working gas pressure using gas flows below 20 sccm.

The mapping of the refractive index showed that the deposited CdS thin films were very uniform to ±0.8%. The band gap was measured to be 2.31 eV while refractive index (n) was measured to be 2.52 +/- 0.02. Increase in the gas flow lead to a reduction in the refractive index, while increasing the deposition power resulted in an increase of the refractive index. Pulsed DC magnetron sputtering allowed close control of the thickness by changing the gas flows, deposition power and deposition temperature. By increasing substrate temperature up to 400°C, the morphology of the thin film changed, leading to a more compact layer.

The deposition rate achieved using pulsed DC magnetron sputtering is of particular note. Using 1500 W of deposition power at the magnetron target (corresponding to a power density of ~ 8.5 Wcm⁻²) at 150 kHz pulsing frequency and 10 sccm argon gas flows, the deposition rate was measured to be 1.33 nm/s. However, this rate is achieved on a 5 cm x 5 cm substrate located on a 180 mm diameter rotating carrier. In this configuration, the substrate is exposed to the deposition flux only for a fraction of each revolution. The equivalent deposition rate for a static substrate is 8.66 nm/s, which is significantly faster than that which can be achieved using a chemical bath deposition or RF magnetron sputtering. As an example, the typical thickness of the CdS window layer in a thin film CdTe device is ~100 nm and this could be deposited in less than 12 seconds. The high deposition rate makes the process highly attractive for industrial scale-up. Although target utilisation is poor with the planar magnetrons used in this study, this limitation could be overcome in a manufacturing environment by using rotating magnetrons.
4. References


Chapter 8

**Pulsed DC Magnetron Sputtering of CdS:O thin films**

1. **Introduction**

The optical properties of the CdS layer limit the short circuit current density and efficiency of thin film CdTe TF-PV. The main drawback of CdS is its band gap (2.45 eV) which causes absorption losses below 500 nm and therefore limits the photocurrent of thin film CdTe device. One solution to this problem is to deposit a thinner window layer to reduce these losses [247]. Alternatively, the transmission can be improved by engineering the band gap of the CdS layer [248]. It has been shown previously that by adding oxygen to the working gas pressure in an RF sputtering deposition process it is possible to deposit an oxygenated CdS (CdS:O) layer with an improved band gap [249][250]. An increase of the band gap of CdS thin films can lead to improve carrier collection due to extra carriers generated. Wu et al. [24] have developed a process for depositing oxygenated amorphous CdS window layers (a-CdS:O) at room temperature by RF sputtering. These materials showed a higher optical band gap (2.5-3.1 eV) compared to poly-CdS film, with an amorphous structure, due to the high atomic concentration of oxygen incorporated in the film. They showed that the presence of oxygen suppressed the Te diffusion from CdTe layer into the window layer and the CdS$_x$Te$_{1-x}$ alloy formation. Testing the full device (depositing CdTe by CSS), with the integration of the amorphous layer in the cell, gave an improvement in $J_{sc}$ (25.85 mA/cm$^2$), while $V_{oc}$ and FF were also higher, achieving a total-area efficiency of 15.4%. Gupta et al. [251] studied the oxygenated CdS layer sputtered at room and high temperature. They observed a red shift of the absorption edge (from 2.35 to 1.94 eV) when the deposition temperature was 250ºC, compared to a blue shift which was observed for depositions performed at room temperature (from 2.26 to 3.28 eV). The presence of oxygen promoted the formation of an amorphous structure. QE measurements, after the deposition of CdTe by CSS, showed improved current collection from blue region with CdS:O layers. RF magnetron sputtering deposition of CdS layers in an argon/oxygen environment with oxygen flow varying from 0 % to 3 % of argon has also been performed by the CSU group [252]. They also found higher transmission in
spectral region at higher oxygen incorporation, leading to higher device current and also increased quantum efficiency at wavelengths below 500 nm.

Unfortunately, RF magnetron sputtering is not well suited to volume manufacturing due to its low deposition rate and the complexity of matching circuits. In this study, the properties of thin film oxygenated cadmium sulphide CdS:O deposited at high rates using pulsed DC magnetron sputtering have been investigated.

2. Experimental

The thin film layers of CdS:O were deposited by pulsed DC magnetron sputtering (PDCMS) using a “PV Solar” deposition system manufactured by Power Vision Ltd., (Crewe, UK). The layers of CdS and CdS:O were sputtered at ambient temperature using a pulsed DC power supply (Advanced Energy Inc. Pinnacle Plus 5 kW) in an argon/oxygen environment. The 99.999% CdS 150 mm circular target was sputtered at 500 W using a 150 kHz pulsing frequency. The pulse reverse time was set to 2.5 µs. At these deposition conditions, the plasma arcing was minimal during the film growth. The CdS:O films were deposited with oxygen supplied to the chamber through a computer controlled mass flow controller. The films were first deposited on 1 mm thick soda lime glass slides to allow the measurement of the optical properties of the materials deposited and to establish their deposition rates. Once the process conditions had been optimised, ‘TEC10’ TCO coated glass substrates (NSG-Pilkington) were used. The use of pulsed DC magnetron sputtering to deposit CdS has been reported elsewhere [253].

The microstructure, composition and optical properties of the deposited CdS:O films have been investigated using techniques described in chapters 4 and 7.

3. Results and discussion

Figure 106 shows a composite image of a range of CdS:O films deposited using different oxygen gas flows (2 sccm – 10 sccm). The films were deposited on to a 1 mm thick soda lime glass substrate. A direct comparison between the deposited thin films on glass shows that the colour of the deposited film changed from orange to almost completely transparent as the oxygen gas flow was increased.
Figure 106: Photographs of CdS:O films deposited using increasing oxygen gas flows.

A BF-TEM image of a CdS cross section deposited by pulsed DC magnetron sputtering is shown in Figure 107. The BF-TEM image shows that the material had a structure consisting of grains extending through the thickness of the material and crystallites with a semi-amorphous structure which coalesced forming columnar structures which extended through the thickness of the CdS layer.

Figure 108 shows BF-TEM cross section images of CdS:O films deposited using increasing oxygen flows. The addition of oxygen to the deposition plasma resulted in the growth of amorphous films. The types of crystallites which were present in the BF-TEM image of the CdS film (Figure 108) are only visible in the image of the film deposited using 2 sccm flow of oxygen.
Figure 109 shows a BF-TEM cross section image of a CdS:O film grown on TEC10 using a 10 sccm oxygen flow. The thin film was completely amorphous. The influence of incorporating oxygen in the CdS film is clear by comparing the images in Figure 107 and Figure 109.

Figure 108: BF-TEM cross section images of CdS:O films deposited on TEC10 using increasing O₂ gas flows during the deposition.
The cross section also shows that the films were compact and that they provided uniform coverage of the TEC 10 substrate surface. No voids were detected at the interface and no voids or pinholes were present in the deposited material.

Figure 109: BF-TEM image of a 200 nm thick CdS:O thin film cross section on TEC10. The film was grown at 10 sccm oxygen flow during the deposition.

Figure 110 shows SEM surface images of the CdS:O films deposited by pulsed DC magnetron sputtering at various oxygen gas flows. The BF-TEM analysis shows that the oxygenated films were amorphous. The SEM images and BF-TEM cross sections show that the morphology of the surface was affected by the morphology of the underlying TEC10 substrate but it is also dependent on the deposition conditions used. The analysis shows that when the oxygen flow rate was increased, the average feature size at the surface increased from ~170 nm to ~230 nm for the film deposited at 10 sccm O₂ flow rate.
Figure 110: SEM images of the CdS:O films deposited on TEC 10 fluorine doped tin oxide coated glass using different O₂ gas flow rates.

Spectroscopic ellipsometry measurements of the deposited samples were carried out to measure the thickness and the dispersion of the refractive index. Figure 111 shows the dispersion measured for each of the deposited films. The spectra of the films deposited using lower oxygen gas flows showed two distinct peaks. The two peaks gradually merged into one broader peak as the oxygen flow was increased during the deposition. This is caused by the initial decrease and thereafter the removal of the thin film crystallinity [254]. The refractive index of the films decreased as a result of increasing the addition of oxygen to the deposition plasma as shown in Figure 112.
Figure 111: The measured refractive index (n) dispersion of CdS:O films deposited using different O\textsubscript{2} flows.

![Graph showing refractive index dispersion](image1)

Figure 112: The refractive index at 550 nm for films deposited using different oxygen flow rates during the sputter-deposition process.

![Graph showing refractive index at 550 nm](image2)

The deposition rates were calculated from the film thickness measurements obtained by spectroscopic ellipsometry. Figure 113 shows the deposition rates measured for films deposited using different O\textsubscript{2} flows. The deposition rate of the films decreased as the oxygen flow rate was increased. The deposition rate varied from \(~2.44\) nm/s to \(~1.49\) nm/s as the
flow of oxygen was increased from 0 sccm to 10 sccm. The power supplied to the magnetron during the depositions was fixed at 500 W for these experiments.

![Figure 113: The measured deposition rates for CdS:O films deposited using different O₂ gas flow rates (0-10 sccm).](image)

The optical transmission of the films was measured using a spectrophotometer. Figure 114 shows the transmission measured for films deposited at increasing O₂ flow rates. The thickness of the deposited films was kept constant for all samples. However, due to the change of refractive index as a result of the oxygen addition into the film, the dispersion characteristics were changed. The oxygen flow also affected the transmission of the films. The transmission data shows a strong blue shift of the absorption edge as the oxygen gas flow rate was increased during the film growth. The absorption edge shifted from ~500 nm down to ~350 nm for the thin film deposited using a 10 sccm oxygen flow.
The band gap of the deposited material was calculated from the transmission data using the Tauc’s plot method [40]. The band gap calculations are shown in Figure 115. The band gap of the deposited CdS:O films increased from 2.38 eV to 3.1 eV as more oxygen was incorporated in the thin films during the deposition. The relationship between band gap and the oxygen gas flow used is shown in Figure 116. Therefore, the band gap of the deposited material can be accurately controlled during the deposition through control of the oxygen flow.

Figure 117 shows calculated values of current loss in a window layer as a function of band gap. The current loss was calculated assuming full absorption in the window layer and that the entire AM1.5g spectrum was transmitted into the window layer. The values were calculated as the current available from the AM1.5g spectrum between 350 nm and the absorption edge defined by the band gap. The analysis shows that for material with a 2.38 eV band gap the absorption could cause losses up to 8.4 mA/cm². The current losses reduced to only 1.9 mA/cm² when material with a band gap of 3.1 eV was used. For thinner layers the losses would be reduced much further. A band gap of 2.38 eV was measured for a pulsed DC sputtered layer of CdS and 3.1 eV was measured for CdS:O film deposited at 10 sccm O₂ flow. The film deposited at 6 sccm O₂ flow had a band gap of 2.65 eV and this would limit the losses to 5 mA/cm² which is a reduction of 3.4 mA/cm² compared to using CdS. Using CdS:O deposited at 8 sccm O₂ flow would limit the losses to 3.8 mA/cm². However, further
work is required to evaluate the possible corresponding detrimental effects of cadmium sulphate in the films.

Figure 115: The band gap extraction using Tauc’s plot method from the measured transmission data.

Figure 116: The band gap of deposited CdS:O films as a function of oxygen flow rate used during the deposition.
Figure 117: Maximum photocurrent loss due to absorption in the window layer as function of the window layer’s band gap.

Figure 118 shows a sequence of XRD spectra measured for the range of deposited CdS:O films. The structure of the thin films sputtered with and without oxygenation was found to be in the more stable hexagonal crystalline structure. The intensity of the peaks decreased as a result of adding O$_2$ to the deposition plasma and the films became amorphous for higher oxygen flow rates. This is similar to behaviour reported for the RF sputtered CdS:O films [249]. The XRD spectra of the CdS:O thin film deposited at 10 sccm O$_2$ flow shows a peak at $2\theta$: 27.16°. This indicates a formation of orthorhombic crystalline structure of CdSO$_4$ with $<$002$>$ orientation. The XRD spectrum of a CdS film deposited using the same conditions but without O$_2$ flow is plotted for reference in (a).
Figure 118: (a) XRD spectra of a CdS thin film deposited without oxygen provided for reference (b) XRD Spectra of CdS:O deposited at different oxygen flow rates.
XPS was used to measure the composition of the deposited films. The surface of the sample was etched with a low current ion beam for 30 seconds prior to the measurements to remove ~20 nm of atmospheric contamination and to expose the deposited thin film.

Figure 119 shows how the atomic composition of the deposited films changed with the oxygen flow rate used. The oxygen concentration increased up to 33% when the oxygen was added to the deposition plasma using a flow rate of 10 sccm. The cadmium level was constant for all the samples at ~50% and the sulphur concentration decreased as the oxygen flow rate was increased during the deposition.

![Figure 119: Atomic concentrations (XPS) of Cd, S and O in the deposited CdS:O films as function of O₂ gas flow used.](image)

A chemical shift occurs in the XPS sulphur peak which depends on its bonding. The cadmium sulphide peak occurs at ~161.5 eV and the sulphate peak is found at ~168.8 eV [255][256]. An XPS sulphur spectrum for a film deposited with 2 sccm of oxygen is shown in Figure 120 and the spectrum shown in Figure 121 corresponds to a film deposited using 10 sccm of oxygen in the plasma.

The XPS spectrum for the CdS:O film deposited using a 10 sccm flow rate shows two distinct peaks related to the formation of cadmium sulphate. The peak located at 168.5±0.01 eV corresponds to the formation of a CdSO₄ in the deposited film. The sulphur in the film deposited at 6 sccm was 9% in sulphate form and 91% as sulphide. With increased oxygen at
10 sccm, the percentage in the sulphate form increased to 27%. Cadmium sulphate was detected in all CdS:O films deposited using O₂ flow rates above 2 sccm.

Figure 120: An XPS spectrum of the sulphur peaks measured for a CdS:O sample deposited using a 2 sccm O₂ flow rate.

Figure 121: An XPS spectrum of the sulphur peaks measured for a CdS:O sample deposited using a 10 sccm O₂ flow rate showing the presence of cadmium sulphate.
Conclusions

4. Conclusions

Oxygenated CdS films for CdTe TF-PV applications were successfully deposited by using pulsed DC magnetron sputtering. The process was highly stable using a pulse frequency of 150 kHz and a 2.5 µs pulse reverse time. No plasma arcing was detected. A range of CdS:O films were deposited by using O₂ flows from 1 sccm to 10 sccm during the deposition process.

TEM analysis was used to analyse the crystalline structure of the deposited films. The films showed the presence of small crystallites for the lower oxygen flows similar in appearance to those observed in CdS films [5]. The films were amorphous at higher O₂ flow rates.

The SEM analysis of the surface of films deposited on TEC10 shows that surface features are present reflecting the original morphology of the FTO coated glass substrate. The BF-TEM analysis shows that these extended through the thickness of the material. The feature size increased from 170 nm to 230 nm as the oxygen flow was increased.

Transmission measurements showed that the addition of oxygen results in a blue shift of the absorption edge from 500 nm to 350 nm due to the widening of the band gap of the deposited material. Detailed Tauc’s plot analysis showed that the incorporation of oxygen into the deposited films caused the band gap to be widened from 2.38 eV to 3.1 eV thereby eliminating absorption losses that would otherwise occur in the CdS window without oxygenation. This results in a useful increase in photocurrent [249][257].

The spectroscopic ellipsometry analysis showed that the refractive index of the deposited film decreased from 2.57 to 2.17 at λ=550 nm as the O₂ flow was increased. The deposition rate of the CdS:O decreased as the O₂ flow was increased. The refractive index dispersion measured for the films deposited at lower oxygen flows showed two distinct peaks. The peaks gradually merged into one broader peak as the oxygen flow increased as the films become amorphous.

The XRD measurements showed that the deposited films are hexagonal at low O₂ flow rates but the peak diminished as more oxygen was added to the deposition plasma. The formation of CdSO₄ was observed for films with O₂ flow rates above 2 sccm.

The XPS analysis showed that the oxygen content in the film increased up to 33% as more oxygen was added to the deposition plasma. The concentration of cadmium was unaffected at 50% and the concentration of sulphur was reduced. Cadmium sulphate formation was detected for films deposited using O₂ flow rates above 2 sccm. XPS measurements showed that for the film deposited at the 10 sccm O₂ flow approximately 27% of the sulphur was present as cadmium sulphate. This gradual change in chemical structure from cadmium
sulphide to cadmium sulphate as oxygen is added to the film will impose a limit on the increase in transparency available using this process.

The deposition process using pulsed DC power was stable and led to the deposition of the films at high deposition rates. The addition of O\textsubscript{2} to the deposition plasma allows precise control of the film properties including refractive index and band gap.

Importantly, the deposition rates achieved using pulsed DC magnetron sputtering with only 500 W of power to the magnetron target were in the range \(\sim 1.49 \text{ nm/s} \sim 2.44 \text{ nm/s} \), depending on the oxygen flow rate used. This is a high rate of deposition and much faster than can be achieved using RF sputtering (for example a rate of 0.3 nm/s has been reported at 250 W [163]). It could be increased further by simply increasing the power to the magnetron. This makes pulsed DC magnetron sputtering a viable process for the deposition of an improved oxygenated CdS window layer for high efficiency CdTe devices. The combination of tight control of the band gap and associated increases in photocurrent together with the high rate of deposition makes the use of pulsed DC magnetron sputtering a commercially attractive process for high volume manufacturing of thin film CdTe photovoltaic modules.
5. References


Chapter 9

The structural properties of CdS deposited by Chemical Bath Deposition and Pulsed DC Magnetron Sputtering

Once the depositions of CdS films by CBD and PDCMS had been optimised, the morphological, structural and optical properties of each film were analysed and compared to understand which deposition method is the most suitable for use in efficient solar cell devices.

1. Experimental

Transparent Electrically Conducting (TEC 10) glass supplied by NSG-Pilkington (http://www.pilkington.com/) was used as the substrate (superstrate) material. The substrates were cleaned in a two-step ultrasonic bath process followed by a plasma surface treatment prior to the CdS film growth [258]. CdS thin films of ~ 100 nm thickness were deposited by pulsed DC magnetron sputtering in a ‘PV Solar’ magnetron sputtering system (Power Vision Ltd., Crewe UK), details of the system have been provided elsewhere [259]. The deposition conditions were set using the following process parameters: 10 sccm of Ar gas flow, 500 W, 150 kHz, 2 s (ramping time), 2.5 μs (reverse time).

Thin films of CdS of ~ 100 nm thickness were also deposited by chemical bath deposition (CBD); the reaction occurred in a beaker immersed in a water jacket to ensure constant temperature (70°C). The bath solution consisted of 200 ml of de-ionised water, 15 ml of Cd(CH$_3$COO)$_2$ 0.01 M, 25 ml of NH$_4$OH 25% and 10 ml of CS(NH$_2$)$_2$, 0.1 M. An ultrasonic probe was immersed in the solution to accelerate the reaction kinetics [1].

The chemical composition, microstructure and optical properties of CdS thin films prepared by CBD and PCDMS were investigated and compared using techniques previously described in chapter 4.
2. Results and Discussion

Figure 122 (a) and (b) shows the XPS spectra of Cd3d and S2p photoelectron core levels measured for CdS films deposited by PDCMS sputtering and chemical bath deposited at 70ºC with Cd(CH$_3$COO)$_2$ 0.01 M, NH$_4$OH 25% and CS(NH$_2$)$_2$, 0.1 M, respectively. The binding energies of 405.8 eV and 412.3 eV for Cd3d$_{5/2}$ and Cd3d$_{3/2}$, respectively, and 161.6 eV and 162.8 eV for S2p$_{3/2}$ and S2p$_{1/2}$ matched the theoretical values for CdS [126]. This indicates that the deposited CdS films are stoichiometric and no oxygen was incorporated into the films. This is also supported by fitting analysis, which showed only the CdS component.

![XPS spectra](image)

Figure 122: The XPS spectra measured for pulsed DC and chemical bath deposited CdS films, were not affected by the deposition conditions, showing photoelectron core levels of (a) Cd3d$_{5/2}$ and Cd3d$_{3/2}$ and S2p for CdS thin films deposited at 10 sccm Ar, 500 W and 150 kHz and (b) Cd3d$_{5/2}$ and Cd3d$_{3/2}$ and S2p for CdS thin films deposited using a chemical bath. For Cd3d$_{5/2}$ and Cd3d$_{3/2}$, the fitting is achieved with a single Gaussian peak due to CdS and for S2p the fitting shows the splitting S2p$_{3/2}$ and S2p$_{1/2}$. The green line at the bottom shows the error fitting function.
The XRD analysis (Figure 123) is complicated by the coincidence of the TEC substrate and CdS film peaks; nevertheless, some analysis can be performed by examining the intensity of the peaks and the different attenuation of the TEC peaks. Specifically, the very intense \(<002>\) reflection for the PDCMS CdS indicates the hexagonal structure with a preferential orientation \(<001>\), whereas the CBD CdS films exhibit a cubic structure. The XRD analysis was referred to JCPDS database cards (http://www.icdd.com/).

Figure 123: XRD spectra of CBD and PDCMS CdS films. The peaks due to the hexagonal and cubic structure are indicated by H and C, respectively. The peaks due to the substrate are indicated with *.

Figure 124 compares the surface morphologies of PDCMS (a) and CBD (b) deposited CdS thin films. The CBD deposited films have smaller crystallites compared to the PDCM sputtered films. Both show the onset of grain coalescence.
Figure 124: SEM surface images of CdS films deposited by PDCMS (a) and CBD (b).

BF-STEM cross-sectional images of a 100 nm thick CdS film deposited on TEC10 glass by PDCMS and CBD are shown in Figure 125 (a) and (b), respectively. The grains expand through the thickness of the film deposited by PDCMS with a columnar structure (a) while small grainy crystallites grow through the thickness of CBD CdS film (b), consistent with the SEM images and XRD data. In both cases, the grains grow by following the structure of the substrate surface beneath (TEC10 glass) and voids are not observed at the interface.

Figure 125: TEM images of the sputtered CdS film (a) and CBD CdS film (b) both deposited on TEC10 coated glasses.
Figure 126 shows the derived optical properties, dispersion of the refractive index, n, and extinction coefficient, k, of the CdS films deposited on TEC10 by PDCMS and CBD. The PDCMS CdS film shows a higher refractive index and a slightly higher absorption at 500 nm with sharper interband transition $E_1$ [233] (Figure 126 (b)). This can be explained by the increased grain size, increased density, and higher crystallinity observed for the films deposited by PDCMS compared to the CBD deposited CdS.

![Figure 126: Refractive index dispersion a of 100 nm CdS thin films, (a) real (n) and (b) imaginary part (k).](image)

The transmittance of the thin films reaches a maximum of ~75% (this includes the effect of absorption in the TEC10 substrate) and decreases near the absorption edge at 500 nm, confirming the crystallinity of the CdS thin films (Figure 127, inset). The PDCMS CdS has a lower transmission than the CBD deposited CdS, due to its higher optical density, in agreement with the ellipsometric analysis. Figure 127 shows the band gap ($E_g$) determined from the Tauc plot. The PDCMS CdS has a band gap of $2.34 \pm 0.01$ eV compared to $2.38 \pm 0.01$ eV measured for the CBD CdS.
Figure 127: Energy Band Gap, 2.34±0.01 eV and 2.38±0.01 eV for PDCMS and CBD thin films, respectively. Transmittance curve, as inset, for CdS films on TEC10 glass (the sample in the spectrophotometer is positioned letting the light pass through the glass/TCO/CdS layers).

The deposition rate for CdS obtained using pulsed DC magnetron sputtering was 0.44 nm/s using only 500 W power on a six inch circular magnetron target. This rate is achieved on a 5 cm x 5 cm substrate located on a 180 mm diameter-rotating substrate carrier. The equivalent deposition rate for a static substrate is ~2.86 nm/s. The deposition rate using CBD is much slower (0.027 nm/s); to deposit a 50 nm thick film of CdS required about 30 minutes, and a thickness of 150 nm needed one hour.

3. Conclusions
The properties of CdS thin films deposited by pulsed DC magnetron sputtering and chemical bath deposition have been studied and compared. The pulsed DC magnetron sputtering process produced CdS thin films with the preferred hexagonal <001> oriented crystalline structure. TEM analysis shows evidence of columnar grain growth. Conversely, the CBD deposited films were polycrystalline with a cubic structure, showing small grainy crystallites throughout the thickness of the films. CBD deposited films exhibited comparatively poor thickness uniformity while the pulsed DC sputtered films were highly uniform. The
spectroscopic ellipsometry analysis showed higher refractive index and slightly higher absorption at 500 nm for the PDCMS deposited CdS films, confirming the increased grain size, increased density, and higher crystallinity compared to the CBD CdS films. The films deposited by both techniques were pinhole and void-free, with an optical band gap of 2.34±0.01 eV for the PDCMS deposited films and 2.38±0.01 eV for CBD.

It has been found that the deposition rate for CdS obtained using pulsed DC magnetron sputtering was 2.86 nm/s using only 500 W power on a six inch circular target. This is a high deposition rate compared to other methods available. Moreover, the process stability could be maintained using 1.5 kW of power which produced a proportionate increase in deposition rate without affecting film quality (chapter 7). In comparison, deposition with RF sputtering is much slower. For example, deposition rates of 0.2 to 0.3 nm/s have been reported for powers in the range 50 W to 250 W. This is approximately an order of magnitude slower than using pulsed DC power [18] and similar to CBD, which is also comparatively slow. In this work, it required 30 minutes to deposit a 50 nm thick film of CdS and one hour for a 150 nm thick film. The comparative quality of the CdS thin films together with high rates of deposition show that the pulsed DC magnetron sputtering process has the potential for application in high throughput and low cost manufacturing of solar modules.
4. References


Chapter 10

**Electrodeposition (ED) of CdTe thin films**

The deposition of the absorber layer, CdTe, is an important topic in this thesis. As mentioned already in chapter 3, there is a wide spectrum of deposition techniques available for CdTe thin film growth. For this thesis, electrodeposition has been chosen as a conventional low cost technique, and this has been compared to Pulsed DC magnetron sputtering, which is a high vacuum process (and unique for PV applications).

The electrodeposition of CdTe thin films on CdS/TEC10 coated glass has been investigated and the resultant films characterised to define their morphology, structural and chemical composition. Moreover, to study the influence of the underlying layer of CdS on the CdTe growth, a set of experiments electrodepositing CdTe on both pulsed DC magnetron sputtered and chemical bath deposited CdS layers has been performed. Sonochemical bath deposition was used in this section of work as it had been found beneficial for CdS compared to standard CBD (chapter 6). The morphological, structural and optical properties of the resultant electrodeposited CdTe thin films were compared in order to understand which would be the most suitable candidate for a final device.

1. **Experimental**

CdS films were deposited on TEC10 glass substrate, (a transparent conducting fluorine doped tin-oxide (FTO)) coated glass supplied by NSG-Pilkington (http://www.pilkington.com/). The glass substrate was initially cleaned in a two-step ultrasonic bath process (IPA and rinse), followed by a plasma surface treatment in a mixture of O$_2$ and Ar (chapter 5) [116]. Initially, thin films of CdS were grown by sonoCBD, details are available elsewhere in this thesis (chapter 6) [1], [117] and onto these films, the optimum conditions required to obtain good electrodeposited films were determined. Once these conditions had been determined, the
influence of the way the CdS film was grown on the subsequent electrodeposited CdTe film was investigated.

Thin films of CdTe were prepared by electrodeposition in aqueous solution onto the CdS films. The experiments were performed at room temperature, ~23ºC, using a PARSTAT 2273 potentiostat (Advanced Electrochemical System). The electrodeposition system designed for this work consisted of a bespoke three electrode reaction cell (Figure 128) with a working electrode, CdS/FTO, a counter electrode, Pt foil and a reference electrode (http://www.chinstruments.com/), saturated KCl silver/silver chloride electrode (Ag/AgCl) [Ag/AgCl +0.199 V vs standard hydrogen electrode (SHE)] placed inside a glass tube (Figure 128), which was left open in order to prevent the back diffusion in the solution of O₂ formed during the process.

Figure 128: The electrodeposition system designed for this work.

The solution used for electrodepositing CdTe was an acidic aqueous solution containing CdSO₄, TeO₂, H₂SO₄ [260]. The depositions were performed at a constant potential of -0.3 V, at room temperature (RT), for a deposition time of 4 hours, in order to get a film thickness of ~1μm. The source of Cd²⁺ ions was CdSO₄ (3.8x10⁻² M) and TeO₂ (10⁻³ M) was the precursor for HTeO₂⁻ ions, the pH solution was adjusted to 1-2 with the addition of H₂SO₄, >95 %.
Chapter 10

Figure 129: CdTe thin film was applied by electrodeposition in 4 hours.

Two steps represent the deposition process [261], [2]:

1) Tellurium reduction

\[ \text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- \rightarrow \text{Te} + 2\text{H}_2\text{O} \]  \hspace{1cm} \text{[1]}

2) The tellurium reacts rapidly with Cd\(^{2+}\) ions in solution due to the free energy gain in CdTe formation, \(\Delta G = -103.7 \text{kJ/mol}\):

\[ \text{Te} + \text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{CdTe} \]  \hspace{1cm} \text{[2]}

The deposition potential, \(E\), for each, is given by

\[ E = E^0_{\text{Te}} + RT/4(a_{\text{HTeO}_2^+} + a_{\text{Te}}) + 3RT/4Flna_{\text{H}^+} \]  \hspace{1cm} \text{[3]}

\[ E = E^0_{\text{Cd}} + RT/2Fln \left( \frac{a_{\text{Cd}^{2+}}}{a_{\text{Cd}}} \right) \]  \hspace{1cm} \text{[4]}

with \(a_{\text{HTeO}_2^+}, a_{\text{Cd}^{2+}}\), the activities of the species in the electrolyte during the deposition and \(a_{\text{Te}}, a_{\text{Cd}}\) the activities of the species in the deposit.
From cyclic voltammetry (Figure 130) the region for the formation of CdTe was found to commence at around -0.3V.

![Cyclic voltammogram](image)

Figure 130: Cyclic voltammogram of a CdTe film deposited from acidic solution (CdSO4 (3.8x10^{-2} M) and TeO2 (10^{-3} M), H2SO4, >95 %).

The techniques used to characterise CdTe films were described in chapter 4.

2. Results and Discussion

Figure 131 shows a TEM cross section image of electrodeposited CdTe films deposited using the conditions previously described. The film is dense and compact throughout the layers.

![TEM cross section](image)

Figure 131: TEM cross section image of a CdTe film deposited at RT.
CdTe thin films were also electrodeposited at 60ºC and compared with those deposited at RT. As shown in Figure 132, the quality of the resultant films at the elevated temperature was similar to RT with compact, dense and void-free layers, both at the interface and through the depth of the deposited film.

![Figure 132: TEM cross section image of a CdTe film deposited at 60ºC.](image)

Figure 133 shows SEM images from the top surface of the CdTe films electrodeposited, at room temperature and at 60ºC. The morphology of the films reveals round features, with an average size of ~300 nm, measured by using Axiovision SE64 software.

![Figure 133: SEM images from the top surface of the CdTe films electrodeposited without stirring the solution, at room temperature and at 60ºC.](image)

These experiments showed that compact, dense, homogeneous void-free layers of electrodeposited CdTe could be obtained from the use of a solution containing CdSO₄.
(3.8x10^{-2} M) and TeO_2 (10^{-3} M) as precursors in the bath, the pH solution was in the range 1-2 with the addition of H_2SO_4, >95%. The bath deposition temperature did not appear to greatly affect the film quality of CdTe thin films, and so subsequent experiments were performed at RT.

2.1. Electrodeposition of CdTe films on CdS layers deposited using magnetron sputtering and chemical bath deposition

Utilising the conditions optimised in the preceding experiments, an investigation of how the preparation of the underlying CdS film (CBD or sputter deposited) affected the electrodeposited CdTe film was performed. The working electrode was made of a CdS thin film (~100 nm) deposited either by sonochemical bath deposition (sonoCBD) [1] or by Pulsed DC Magnetron sputtering [9] on TEC 10 glass. Depositions were performed with the optimised parameters previously described, under potential control, the ( -0.3 V) and the exposed area was 6cm^2 for a deposition time of 4 h [260]. The chemical composition, microstructure and optical properties of the resultant CdTe films were investigated.

The first observation from these experiments was that the CdTe film grew at different rates, depending on the underlying CdS film. The CdTe film deposited on sonoCBD grown CdS was ~340 nm thick compared to almost a 1μm thick film grown on the Pulsed DC magnetron sputtered CdS. This is clearly shown in the TEM cross section images in Figure 134. Despite the difference in thickness, the cross-sectional view of both samples showed a compact and dense CdTe film (Figure 134) for both samples. However, some differences in the films were observed.
Figure 134: TEM cross sections of CdTe films electrodeposited for 4h at -0.3V on CdS CBD deposited on TEC 10 (a), CdS deposited by Pulsed DC magnetron sputtering (b) XPS CdTe on CBD CdS.

The CdTe deposited on the sonoCBD CdS initially grew small crystals following the underlying film, but once it had grown to 50 nm, larger grains started to form (up to 50 nm in diameter). The CdTe deposited on the sputtered CdS showed small crystallites across the entire thickness, (Figure 134 (b)). The surface morphology of the deposited films is shown in Figure 135.
Figure 135: SEM images of CdTe electrodeposited on CdS deposited by chemical bath (a), and Pulsed DC magnetron sputtered CdS (b).

Figure 136 shows an XRD spectrum, taken from a CdTe thin film electrodeposited on TEC10. EDS analysis showed the composition of the film, consisting of 57 % of Te and 43 % of Cd (inset).

Figure 136: XRD spectrum of CdTe ED on TEC10. Inset: EDS spectrum.
Chapter 10

Optical analysis was performed on the two prepared samples. Figure 137 shows the transmittance spectra measured for the CdTe films deposited on sputtered and sonoCBD CdS films. Both spectra showed a high absorption of light. The higher transmittance of the CdTe on sonoCBD CdS, around 13%, is a result of the reduced thickness of the film.

Figure 137: Transmittance curves of an electrodeposited CdTe on sputtered and sonoCBD CdS.
Chapter 10

The Tauc plot analysis showed that the energy gap ($E_g$) for CdTe grown on sonochemical bath deposited CdS was 1.46 eV, compared to 1.41 eV for the CdTe film grown on sputtered CdS (Figure 138).

Figure 138: Energy band gap, transmittance and reflectance curves, as inset, for CdTe electrodeposited on chemical bath deposited (a) and Pulse DC sputtered (b) CdS.
3. Conclusions

CdTe thin films were grown on CdS films prepared by sonoCBD and Pulsed DC magnetron sputtering. The results showed that the deposition technique used for the CdS layer affected the growth and properties of the CdTe film. The CdS film not only affected the structural and morphological properties of the CdTe film but also determined the deposition rate of CdTe, being 3 times faster on the sputtered CdS. The CdTe films initially grow in a similar way forming small crystallites but once 50-100 nm had been deposited the film deposited on the sonoCBD CdS grew much bigger crystallites. It seems that the growth of the new layer follows the underlying material (CdS) up to a certain thickness, after that point the layers have a different resistivity and this affects the subsequent material growth.

Transmission measurements showed that the films deposited on the sonoCBD CdS had a wider band gap of 1.46 eV compared to 1.41 eV measured for the films deposited on CdS films prepared by pulsed DC magnetron sputtering.

Further experimental work is needed in order to test these materials. Analysing their properties, CdTe electrodeposited on the top of CdS films appear promising for a final working device. More work should be done on the electrodeposition process, optimising the deposition conditions and testing these materials during and after the activation treatment (CdCl₂). It would be interesting to determine how final devices, with different CdS films, compare knowing that films deposited by different methods can affect the deposition, and properties of the CdTe absorber layer.
Chapter 10

4. References


**Chapter 11**

**Pulsed DC Magnetron Sputtering of CdTe**

A CdTe thin film deposition process using Pulsed DC magnetron sputtering has been studied. The CdTe thin films have been deposited on CdS/TEC10 coated glass. The effect of Ar gas flow and deposition temperature has been investigated to optimise the deposition process. A study of the residual stress in CdTe thin layers has been developed.

1. **Experimental**

CdTe thin films were deposited by pulsed DC magnetron sputtering (PDCMS) in a ‘PV Solar’ sputtering system. The system has been described in previous chapters (chapter 7-8) and the deposition of CdTe was performed over a sputtered layer of a CdS previously deposited by PDCMS (chapter 7). The CdTe/CdS thin films were deposited on NSG-Pilkington TEC10 Fluorine doped tin oxide (FTO) coated glass substrates. Prior to the CdS deposition, the substrates were cleaned following the procedure previously described in chapter 5.

The CdTe layer was deposited at ambient temperature using the following process parameters, 500 W, 2.9 μs, 10 s, 150 kHz. The microstructure, composition and optical properties of the deposited CdTe films have been investigated using techniques described in chapter 4 and 7. Initial studies optimised the deposition parameters used in PDCMS, focusing on testing different argon gas flows, deposition temperatures and annealing post-deposition treatment to study their effect on the structure and morphology of CdTe thin films.

2. **Results and Discussion**

Figure 139 (a) shows a surface image of the sputtered CdTe layer, with a thickness of approximately 2 μm. The layer appeared uniform and smooth with a grain size less than 100 nm. Figure 139 (b) is a cross-section which shows the columnar morphology of the grains and the smoothness of the film. The SEM images show that sputter deposition of cadmium
telluride results in highly compact layers and the morphology is dominated by columnar grain growth.

Figure 139: (a) An in lens SEM image of the surface morphology of PDCMS deposited CdTe and (b) cross section SEM image of a thick CdTe cell with thin through thickness columnar grains

Figure 140 shows the XRD spectra of the sputtered CdTe film at room temperature with a dominating (111) peak. The grain size was typically ~50 nm in diameter through the whole thickness of the coating, ~2 µm. The CdTe grain morphology followed that of the sputtered CdS layer, which was also columnar with a grain size of ~50 nm in a thin film thickness of 100 nm.

The study has also revealed that sputtering resulted in highly uniform thin film thicknesses both for individual layers and for multilayer stacked structures. This uniformity was important since it means that the CdTe absorber thickness could be accurately controlled and optimised. This may lead to a cost reduction and to the production of consistent device performance.
2.1. The Effect of Argon Gas Flow on CdTe Thin films

The Ar working gas pressure is known to have an impact on the deposition rate and properties of thin films. At higher Ar sputtering pressures, the sputtered and reflected neutral atoms, arriving at the substrate, have lower energies. This is due to the increased number of collisions that occur before they reach the substrate. As a consequence the atoms arriving at the substrate have a lower surface mobility. This has an effect on the growth kinetics of the depositing film, and therefore on its structural, morphological and crystallographic properties. Conversely, at low Ar pressures the sputtered and reflected neutral atoms have much higher energies than the plasma gas between the target and substrate and these species arrive at the substrate with high energy due to undergoing fewer collisions before their arrival. Therefore the sputtered atoms in low Ar pressure conditions have a high surface mobility when they reach the substrate surface. The Ar pressure also affects the stress in the deposited film [262]. Windischmann [4] showed strong correlation between residual stress and Thornton’s structure zone model (SZM) [263][264] for sputtered thin films. Low density thin films deposited at high argon pressure and low temperature (regime Zone I) have almost zero residual stress [265]. Decreasing argon pressure develops tensile stress and a further decrease in pressure leads to a dramatic change from tensile to compressive stress, finally forming a dense thin film (regime Zone T). In order to deposit low stress thin films, the working
pressure should be set between the tensile and compressive stress transition regions. This process window is very narrow and it is challenging to find a perfect combination of working parameters which result in a stable low stress thin coating [266]. Therefore, a set of experiments was performed to investigate the effect of the change in gas flows on the structure of the CdTe films by using TEM and XRD analysis. 20 sccm (with and without post-deposition annealing at 400ºC for 20 min), 50 sccm, 70 sccm and 100 sccm of Ar were used, keeping the other deposition parameters fixed. Depositions of ~1 μm thick CdTe films were performed at ambient temperature on ~100 nm thick CdS layer.

Figure 141: BF-STEM images of CdTe thin films deposited at 20 sccm (a), 50 sccm (b) and 70 sccm (c) of Argon on CdS/FTO coated glass.

BF-STEM images show the presence of small crystallites clearly visible through the whole thickness of CdTe layer deposited by using 20 sccm of Ar. It appeared slightly different from 50 sccm Ar (Figure 141 (b)) and 70 sccm Ar (Figure 141 (c)) CdTe layers. Specifically, the image shows a very dense CdTe layer, with small polycrystalline grains, with size less than 10 nm. Planar defects were observed perpendicular to the growth direction. Figure 141 (b)) shows a sample obtained using an argon deposition flow of 50 sccm, this appeared less dense than the sample deposited with 20 sccm (Figure 141 (a)) of Ar and the grains seemed to arrange in nodules, with pore channels between nodules. The presence of
these channels might be due to the roughness of the underlying TCO, the window layer CdS was conformal to this uneven surface and consequentially also the next layer (CdTe) was also affected. In particular pore channels appeared where the underlying layers (CdS/TCO) show some hollows (valleys). The same occurred with samples deposited at higher deposition gas flows (Figure 141 and Figure 142 (a)) these pore channels are thin voids between each nodule of grains.

The samples deposited with 50, 70 and 100 sccm of Ar appeared to have a similar grain size of ~30 nm. This suggests that there should be a critical point between 20 and 50 sccm Ar gas flow where the maximum grain size is reached. The pore channels size was between 100-150 nm for all three samples; all the samples appear to have a very high density of stacking faults running perpendicular to the growth direction (Figure 142 (a)).

The stress measurements were performed on the CdTe layers deposited at room temperature (20, 50, 70, 100 sccm Ar).

Figure 142 (a) shows the STEM images obtained from CdTe layers deposited with 20-50-70-100 sccm Ar and the (111) peak of cubic CdTe for each was scanned by XRD analysis in the range 22.8°-24.2°. The 2θ value (23.76°) for the unstressed CdTe film was reported as a reference from the PDF card [ICCD database] Figure 142 (b). The XRD analysis showed that the highest film stress was found for the sample deposited with 20 sccm Ar, due to the greatest peak shift. This sample also showed a much broader peak due to the smaller grain size, as shown in the TEM images in Figure 142 (a). The sample deposited at 20 sccm has grains < 15 nm, whereas the other three samples had larger grain sizes (~30nm) and showed also similar peak shapes. A slight peak shift from the PDF database angle was registered for the samples deposited with 50 and 70 sccm Ar, but with higher gas flow (100 sccmAr) the film showed more stress.

The stress analysis was also performed on CdTe layers deposited at 20 sccm of Ar and annealed at 400°C for 20 minutes in air, after deposition. A peak shift was observed for the annealed CdTe film compared to the sample deposited with the same gas flow (sccm) of Ar without annealing, showing reduced stress in the layer (Figure 142 (b)).
Scherrer’s equation [267] was used in order to calculate grain sizes of the four samples, as shown in Table 4.

\[
\tau = \frac{K\lambda}{\beta \cos\theta}
\]

where: \( \tau \) is the calculated mean grain size, \( K \) is the dimensionless shape factor (constant=0.9), \( \beta \), the line broadening at half the maximum intensity (FWHM), \( \theta \), the Bragg’s diffraction angle and \( \lambda \) is the x-ray wavelength (1.5406 Å).
## Table 4

CdTe films sputtered at different gas flows with $\theta, \beta, \lambda$ values respectively used to calculate $\tau$, mean grain size by Scherrer’s equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$ (degrees)</th>
<th>$\beta$</th>
<th>$\lambda$ (Å)</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 sccm</td>
<td>23.50</td>
<td>0.59</td>
<td>1.540</td>
<td>15 nm</td>
</tr>
<tr>
<td>50 sccm</td>
<td>23.85</td>
<td>0.28</td>
<td>1.540</td>
<td>30 nm</td>
</tr>
<tr>
<td>70 sccm</td>
<td>23.80</td>
<td>0.28</td>
<td>1.540</td>
<td>30 nm</td>
</tr>
<tr>
<td>100 sccm</td>
<td>23.70</td>
<td>0.28</td>
<td>1.540</td>
<td>30 nm</td>
</tr>
<tr>
<td>20 sccm annealed</td>
<td>23.70</td>
<td>0.34</td>
<td>1.540</td>
<td>25 nm</td>
</tr>
</tbody>
</table>

The XRD showed that for CdTe films deposited using gas flows over 50 sccm of Ar, the grain sizes are similar, ~30 nm. The sample deposited with the lowest gas flow (20 sccm, Ar) showed a much smaller grain size of ~15 nm. These results are in good agreement with the TEM analysis. As previously mentioned, magnetron sputtered thin films deposited under low gas pressure are often subjected to compressive stress due to the high mobility of the atoms during the deposition process. A possible way to reduce the stress in the film is the annealing post-deposition treatment [268]. Figure 142 (b) also shows the peak shift for the annealed sample deposited with 20 sccm Ar. After 20 min of annealing at 400ºC, the coating showed a large reduction in stress, as the peak shifted closer to the PDF reference value. This shift can be correlated to a change in the lattice parameter, as the latter increased; the stress in the film is relieved.

### 2.2. Effect of Deposition Temperature on CdTe Thin films

The temperature of the substrate during the deposition process can also have a large impact on the morphology and crystal properties of the PDCMS film. Stress can be induced in the thin film if the thermal expansion coefficient of the substrate and the film are dissimilar. An
increase in deposition temperature will also increase the surface mobility of the arriving atoms, ultimately altering the morphology of the growing film. The samples analysed in this section were deposited using 100 sccm Ar gas flow and different deposition temperatures (ambient temperature, 250, 300 and 400°C) for CdTe thin films. The CdS films were deposited at ambient temperature using the same deposition parameters (500 W, 2.5 μs, 2 s, 150 kHz) for all the samples. The STEM images in Figure 143 show the cross section of the deposited CdTe films.

For the deposition at ambient temperature, the substrate was at a few degrees above room temperature due to the interaction with the magnetron plasma. The thickness of CdTe layers was varied between ~1 and ~2.5 μm for this set of experiments. The thickness of CdS layers was maintained at ~100 nm. The layers were deposited onto Pilkington TEC10 FTO coated glass, as this substrate was used throughout this study.

Figure 143 (a) shows the morphology of the cell after deposition of CdTe at 250°C, the change in grain size is evident. It increased from around 30 nm, for deposition at room temperature, to over 250 nm when higher deposition temperatures were used. The grains became larger at the top of the coating compared to their size at the bottom of CdTe layer. All grains appeared to contain defects extended perpendicular to the growth direction and terminating at the grain boundaries. BF-STEM (a) and (b) images show the top and the bottom of CdTe layer at the interface with CdS layer, respectively. Image (c) shows the presence of voids between some grains. As previously described, these voids are caused by the roughness of the underlying layers; CdS grew conformal to the uneven surface FTO substrate. Because of the small CdS grain sizes, CdTe grains initially showed a small diameter at the CdS interface. The layers appeared columnar through their whole thickness.
Figure 143: BF-STEM images of sample of CdTe deposited at 250ºC showing (a) top of the CdTe /CdS/FTO interface. The presence of voids between some grains is shown in the BF-STEM of the same CdTe sample (c).

The images in Figure 144 show a ~2.5 μm thick layer of CdTe, deposited at 300ºC, 150 kHz, 10 s, 2.9 μs, with a columnar structure extended through the whole thickness of the film. The grains seemed to enlarge as the film became thicker. Towards the top surface of CdTe, the grain size was measured to be ~300 nm, while on the bottom of the columnar structure, up to a few nanometres above the interface with the window layer, the grains became smaller, ~50nm. This means that the CdTe layer initially grew following the structure of the layer underneath. In fact PDCM sputtered CdS thin films showed a typical grain size around ~50 nm, as reported in Chapter 7. Once CdTe had grown to ~400 nm thickness, the grains started to enlarge. It is possible to observe voids running between grains.
Figure 144: TEM images of sample T 300°C showing (a) top of the CdTe (b) CdTe/CdS/FTO interface.

Figure 145 shows the ~2.5 μm thick CdTe layer deposited at 400°C, keeping the other parameters the same as the previous experiments. The grains size was ~50 nm at the CdS interface (up to ~400 nm), and the grains widened (~450 nm) towards the top surface.

Figure 145: BF-STEM images of ~2.5 μm thick CdTe layer deposited at 400°C.

Figure 146 shows the cross section of CdTe layer deposited at ambient temperature. The columnar structure showed the different growth of the film; in this case the grains followed
the underlying CdS layer, small crystals of ~50 nm extended through the whole thickness of the layer (~1 μm). Stacking faults and defects were observed also in these films.

Figure 146: BF-STEM images with the cross section of CdTe layer deposited at ambient temperature.

This set of experiments showed good agreement with the theory of structural zones (the zone model) of film deposition [269], where the film morphology is a function of the substrate temperature. The transition between zones is not sharp and sometimes zones are difficult to identify; this study pointed out the transition between Zone T and Zone 2, increasing the temperature from ambient temperature to 400ºC, as shown in Figure 147.
Therefore, the change in deposition temperature had an effect on the microstructure of CdTe thin films. With the increase in temperature, the grain growth increased up to ~600 nm. However, the initial growth of CdTe film for all the samples was characterized by small grains, visible at the bottom part of the layer, due to a continuation of grain boundaries from the underlying CdS layer. All the samples showed a high density of stacking defects within the CdTe grains.

2.3. Residual stress in CdTe thin films

The residual stress/strain values were determined by using the XRD-based technique. The X-ray source used for this study was Cu K$_\alpha$ with a wavelength of 1.5 Å. The power setting was 30 kV and 10 mA. The scanning mode was continuous PSD fast with a scanning range of 20° ~ 90° (20). The matched scanning step size was 0.02° and the speed was 0.1 s/step. In addition, 23.2° ~ 24.2° (20) range was further scanned during the XRD experiment in order to collect more accurate data for (111) peak analysis with a 0.01° step size and 1 s/step speed. Each sample was measured three times in order to minimise the measurement errors.
2.4. Stress Analysis before Annealing Treatment

Table 5 and 6 show the XRD results (θ values and d-spacing) obtained for PDCMS CdTe samples deposited at different deposition temperatures (100-200-300-400ºC) and at room temperature with different gas flows (30-50-70 sccm Ar). The measurement error reported for the d-spacing values of (111) peak was ± 0.001 Å.

Table 5
CdTe thin films deposited at various substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>100ºC</th>
<th>200ºC</th>
<th>300ºC</th>
<th>400ºC</th>
<th>Stress free state (baseline)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°) [(111) oriented peak]</td>
<td>23.709</td>
<td>23.749</td>
<td>23.698</td>
<td>23.657</td>
<td>23.658</td>
</tr>
<tr>
<td>θ (°)</td>
<td>11.854</td>
<td>11.875</td>
<td>11.849</td>
<td>11.829</td>
<td>11.879</td>
</tr>
<tr>
<td>Sinθ</td>
<td>0.205</td>
<td>0.205</td>
<td>0.205</td>
<td>0.205</td>
<td>0.205</td>
</tr>
<tr>
<td>d-spacing (Å)</td>
<td>3.749</td>
<td>3.743</td>
<td>3.751</td>
<td>3.758</td>
<td>3.742</td>
</tr>
</tbody>
</table>

Table 6
CdTe thin films deposited at various argon flow rates.

<table>
<thead>
<tr>
<th>Argon rate</th>
<th>Flow rate</th>
<th>Stress free state (baseline)</th>
<th>CSS treated sample (baseline)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°) [(111) oriented peak]</td>
<td>30 sccm Ar</td>
<td>23.688</td>
<td>23.709</td>
</tr>
<tr>
<td>θ (°)</td>
<td>11.844</td>
<td>11.854</td>
<td>11.869</td>
</tr>
<tr>
<td>Sinθ</td>
<td>0.205</td>
<td>0.205</td>
<td>0.206</td>
</tr>
<tr>
<td>d-spacing (Å)</td>
<td>3.753</td>
<td>3.749</td>
<td>3.745</td>
</tr>
</tbody>
</table>

The d-spacing value of the (111) peak for each CdTe sample was found to be higher than the reference stress-free state and the CSS sample (used as baseline) values. Compressive stress was developed during the sputtering process.
Chapter 11

For CdTe samples deposited at 200°C the d-spacing value was the closest to the baseline value as represented in Figure 148 and corresponded to the minimum strain. These deposition conditions correlate to the point of minimum compressive stress.

![Graph showing d-spacing variation at various substrate temperatures.](image)

Figure 148: A graph showing d-spacing variation at various substrate temperatures.

By testing different argon flow rates, it was found that CdTe deposited with high Ar flow (70 sccm Ar), showed the minimum deviation from the baseline d-spacing value (as shown in Figure 149). This means that the internal stress also became smaller. Therefore, the main conclusion from this study was that it was possible to grow CdTe thin films with low stress by setting the deposition temperature around 200°C and using high argon flow ~ 70 sccm Ar.

![Graph showing d-spacing variation at various argon flow rates.](image)

Figure 149: A graph showing d-spacing variation at various argon flow rates.
3. Conclusions

PDCMS CdTe layers were deposited at ambient temperature, deposition power 500 W, reverse time 2.9 μs, deposition time 10 s, deposition frequency 150 kHz, with a thickness of approximately 2 μm. The layer appeared uniform and smooth with a grain size less than 100 nm. SEM analysis showed the columnar morphology of the grains and smoothness of the film, resulted in highly compact layers and the morphology dominated by columnar grains. XRD spectra of the sputtered CdTe films at room temperature showed a dominating (111) peak. The CdTe grain morphology (with grain size typically ~50 nm in diameter through the whole thickness of the coating) followed that of the sputtered CdS layer, which was also columnar with a grain size of ~50 nm in a thin film thickness of 100 nm.

The use of different Ar gas flows was tested: 20 sccm (with and without post-deposition annealing at 400ºC for 20 min), 50 sccm, 70 sccm and 100 sccm of Ar were used, keeping the other deposition parameters fixed. This study suggested that there should be a critical point between 20 and 50 sccm argon gas flows where the maximum grain size is reached. High density of stacking faults was found perpendicularly to the growth direction.

The stress measurement was performed on the CdTe layers deposited at room temperature and different gas flows. Magnetron sputtered thin films deposited under low gas pressure are often subject to compressive stress due to the high mobility of the atoms during the deposition process. A possible way to reduce the stress in the film is the annealing post-deposition treatment. As the lattice parameter increased; the stress in the film is relieved.

Furthermore, the change in deposition temperature had an effect on the microstructure of CdTe thin films. Increasing the deposition temperature, the grain growth was apparent up to ~600 nm. However, the initial growth of CdTe film for all the samples was characterized by small grains, visible at the bottom part of the layer, following the underlying CdS layer. All the samples showed a high density of stacking defects within CdTe grains.

The main conclusion from this study was that it was possible to grow CdTe thin films with low stress by setting the deposition temperature around 200ºC and using high argon flow, ~70 sccm Ar.
Chapter 11

4. References


Chapter 12

Multilayer Broadband Antireflective Coatings for more efficient thin film CdTe solar cells

1. Introduction

Thin-film CdTe cells with an efficiency of \( \sim 12\% \), have a short-circuit current density of \( \sim 21 \text{ mA/cm}^2 \). However, in principle, the AM1.5G spectrum (between 350 and 850 nm) allows current densities of up to 31.2 mA/cm\(^2\), to be obtained. The current density losses, in CdTe devices, are mainly due to optical effects. Two of the loss mechanisms are the optical absorption in the n-type CdS window layer and the reflection losses from the glass substrate used. The absorption losses in the CdS can be controlled by minimising the thickness of the CdS layer. The most commonly used techniques to reduce the reflection include texturing of the glass surface and the application of an antireflective coating (ARC) to this surface. The simplest ARC consists of a single layer of refractive index matching material [2]. The problem is the availability of material with a refractive index lower than glass \( (n = 1.52) \). The champion NREL device, with efficiency of 16.5\%, utilised a single layer magnesium fluoride (MgF\(_2\)) ARC coating with a thickness of \( \sim 110 \text{ nm} \) [3]. However, a single-layer coating is designed to reduce reflection at a single wavelength and is not effective over the spectral range used by the solar cell. In addition, a MgF\(_2\) coating is not durable and therefore not suitable for use on modules used in outdoor environments.

Multilayer antireflection (MAR) coatings are widely used in the ophthalmic industry to reduce the reflection and glare on spectacle lenses [4], [5]. They are also used in precision optics for a variety of applications including increasing the transmission on camera lenses. These MAR coatings are designed based on high/low refractive index materials pairs. The low index material is usually silicon dioxide (SiO\(_2\)). The high index material is usually chosen from a range of metal oxides including zirconium dioxide (ZrO\(_2\)), hafnium dioxide (HfO\(_2\)), titanium dioxide (TiO\(_2\)), niobium pentoxide (Nb\(_2\)O\(_5\)), and tantalum pentoxide (Ta\(_2\)O\(_5\)). The choice is dictated by the level of antireflection required, lifetime, durability, and cost.
Careful design of the thickness of each layer in a multilayer stack allows the interference of light to be controlled and used to reduce the reflection losses. These dielectric metal-oxide materials are hard and scratch resistant and adhere well to glass surfaces. Their durability and environmental stability is exceptional and already well proven in the ophthalmic and precision optical applications even on plastic substrates [6].

1.1. Multilayer antireflection coating design

A MAR coating utilises interference to control the reflection. The interference occurs due to the change of refractive index at a medium boundary. As a result of a change of medium, part of the energy is reflected and some is transmitted. The amplitude of the transmitted and the reflected waves can be calculated using Fresnel equations. MAR coatings, based on a thin-film multilayer design, utilise destructive interference at medium boundaries to reduce the reflection. In a multilayer thin-film stack system, the waves reflected between different medium boundaries can interfere, provided that the thickness is less than the coherence length. Depending on a phase difference (Δ) two coherent waves will interfere as described by the following equation:

\[ A = A_1 \sin(\omega t) + A_2 \sin(\omega t + \Delta) \]

At a phase difference of \( \Delta = k\pi \) (where \( k \) is any integer), destructive interference occurs, and thus, the amplitude of light is reduced to a minimum (equal to 0 for \( A_1 = A_2 \)). The phase difference between waves, as a result of propagation through a medium, can be controlled by adjusting the thickness of the layer. The phase change as a function of distance travelled is given by the following equation:

\[ \Delta = \frac{dc}{n} \cdot \frac{1}{\lambda \cdot T} \]

where \( d \) is the distance travelled, \( c \) is the speed of light in vacuum, \( n \) is the refractive index of the medium in which the wave propagates, \( \lambda \) and \( T \) are the wavelength and the period of the wave, respectively. In a single-layer ARC, this interference mechanism is used by depositing a layer with thickness equal to a quarter wavelength, \( \lambda/4 \). Destructive interference occurs between the light reflected from the substrate/coating interface and the ARC coating surface.
This enables the reflection to be reduced at a chosen wavelength. This type of coating is referred to as a “V” coating since the reflection rises rapidly at each side of the chosen wavelength. In an MAR coating, coupled medium boundaries are present; therefore, the efficacy of the antireflection effect can be greatly improved and extended across a wavelength range. This is known as a broadband MAR coating. Another advantage of this approach is that the material is no longer required to have a refractive index lower than the substrate. The performance of the MAR is adjusted by tuning the thickness of each layer and selecting materials with a wide difference in refractive index.

The coating designs used in ophthalmic and most precision optical applications are purely for the visible range 400–700 nm. An extended broadband performance is required for the application to solar modules. In principle, the performance of the MAR can be improved by increasing the number of layers in the multilayer stack. However, increasing the number of layers increases the materials usage and the thin-film deposition process time. Cost is an important consideration; therefore, this part of the thesis has focused on the development of a four-layer broadband design.

The MAR coating was designed using the “Essential Macleod” optical modelling software package [7]. The software models the performance of an optical coating by considering propagation of the electromagnetic wave using the transfer matrix method. In this study, zirconia (ZrO₂) was chosen as the high refractive index material, with silica (SiO₂) chosen as the low index material. Zirconia is a relatively low-cost material. The design was optimised to minimise reflection for wavelengths in the range between 400 and 850 nm. Narrowing the bandwidth allows the performance of the coating to be increased in the spectral range. The 850 nm limit is set by the band gap of CdTe (1.45 eV), no photons with longer wavelength contribute to the photocurrent. The 400 nm lower wavelength was chosen as a compromise to improve the design for the Vis-IR region, since the external quantum efficiency (EQE) of thin-film CdTe devices is low in that spectral region due to absorption in the CdS window layer. Attempts reported in this thesis to increase the transmission of the CdS layer and improvements in the 300–400 nm wavelength range could be accommodated easily in the design [8].

The design of the MAR coating optimised for a thin film CdTe solar cell is shown in Table 7, the total thickness is 277 nm and 153 nm of zirconia is included. Modelling this four layers design shows that light reflection from the front surface is reduced from 4.5% to below 1% in the 400 – 850 nm wavelength range.
Figure 150 shows the modelled performance of the MAR on a 1 mm-thick glass slide. The solid line shows reflection from the front surface only and the dotted line shows the total reflection which is including in the back reflection.

Table 7

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Refractive index</th>
<th>Extinction Coefficient</th>
<th>Thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium</td>
<td>Air</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SiO2</td>
<td>1.45</td>
<td>0.0</td>
<td>94.12</td>
</tr>
<tr>
<td>2</td>
<td>ZrO2</td>
<td>2.13</td>
<td>0.0</td>
<td>133.99</td>
</tr>
<tr>
<td>3</td>
<td>SiO2</td>
<td>1.45</td>
<td>0.0</td>
<td>30.40</td>
</tr>
<tr>
<td>4</td>
<td>ZrO2</td>
<td>2.13</td>
<td>0.0</td>
<td>18.81</td>
</tr>
<tr>
<td>Substrate</td>
<td>Glass</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 150: Modelled performance of the coating (dotted red line includes the back reflection from the glass/device interface).
A weighted average reflection (WAR) is a more representative measurement of the reflection loss for a solar cell, since it includes the importance of the photon flux $\Phi$ in the AM1.5G solar spectrum. WAR is calculated using the following equation:

$$\text{WAR} (\lambda_{\text{min}}, \lambda_{\text{max}}) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \frac{\Phi R}{R} \, d\lambda$$

The model shows that the WAR (400-850) for reflection from the front surface of a glass slide is reduced from 4.22 % to 1.24 % after applying the MAR coating. The uncoated WAR = 4.22 % imposes a limit on the short-circuit current density of 30.19 mA/cm$^2$, and at 1.24 %, it increases the current density obtainable to 31.13 mA/cm$^2$. Hence, the model indicates that the four layers MAR provides scope for an improvement in current density of 0.96 mA/cm$^2$ for a $\sim$ 12 % efficient device.

Figure 151 shows the modelled reflection from an uncoated glass surface, one with a 110 nm MgF$_2$ single-layer ARC and one with the four layer broadband MAR used in this study. Only the reflection from the front surface of the glass was considered in these simulations.
The MgF₂ AR coating enables a value of WAR (400-850) = 1.76 % to be obtained. The model shows a clear advantage for the transmission performance obtained by using the broadband MAR coating.

2. Experimental

The thin-film layers required for the MAR were deposited by using magnetron sputtering already described in chapters 4 and 7. The system allows deposition of multilayer stacks, with the option to replace one of the magnetrons with a plasma source for reactive sputtering. The carrier rotates typically at 120 rpm during the deposition process. Two magnetrons were fitted with 6-inch diameter silicon and zirconium planar metallic targets (details are described in chapter 7). A thin layer of metal ~1 nm is deposited in each pass of the carrier. Oxygen plasma is available from a 800 V DC plasma source located at a third position allowing the metal films to be converted into the optical quality metal-oxides required for the MAR design. The layers were sputtered using a pulsed DC power supply in an argon/oxygen environment. The zirconium was sputtered at 1 kW using a 1.5 μs reverse time, while the silicon was deposited at 1.5 kW and 2.5 μs reverse time. The frequency of the pulse was set to 150 kHz for both materials. The strategy of separating metal deposition from the oxidation process in separate zones avoids reactive sputtering hysteresis effects as well as allows high deposition rates to be obtained [9], [10]. Since the sputtering rate of metals is stable, the layer thickness can be controlled accurately using time only under computer control; therefore, a quartz crystal monitor is not required. The films were first deposited on 1 mm thick soda lime glass slides to allow measurement of the optical properties of the materials deposited and the establishment of their deposition rates. The complete MAR coating was then deposited on a glass slide to assess its performance against the model and before depositing on the NSG-Pilkington TEC10 superstrate and then finally on a complete thin-film CdTe solar cell. The glass slides were cleaned using the RCA cleaning procedure to ensure a good quality clean surface for the thin-film deposition [11].

The antireflection performance of the MAR coating deposited on a glass slide was tested by measuring the light reflection spectrum using the spectrophotometer (details are described in chapter 4). Finally, the MAR coating was deposited on the front surface of a 1 cm-diameter round thin-film CdTe solar cell with the CdTe absorber layer deposited using CSS. The
efficiency of the cell was measured before and after applying the broadband MAR coating. The efficiency of the cell was measured at STC.

3. Results

Measurements using spectroscopic ellipsometry of the test samples deposited on glass substrates provided information about the refractive index for the deposited ZrO$_2$ and the SiO$_2$ layers. The dispersion of the refractive indices measured for the deposited films are presented in Figure 152. The deposited ZrO$_2$ films have a refractive index of $n = 2.12$ at 550 nm. The SiO$_2$ films have a refractive index of $n = 1.46$ at 550 nm. The deposition rates measured for ZrO$_2$ and SiO$_2$ were: 0.7 and 0.66 nm/s, respectively. The substrate carrier has positions for several substrates and has a diameter of 20 cm and a circumference of 62.8 cm.

The reflection spectra of the broadband MAR deposited coatings on 1 mm soda lime glass that were measured using a spectrophotometer are shown in Figure 153. The measured reflection spectra show that the shape and performance is very close to the values predicted by the modelled designed values; however, measured reflectance is higher than modelled due to absorption in the glass which is not considered in the model.
Figure 152: Refractive index dispersion of (a) ZrO$_2$ and (b) SiO$_2$ materials used for the broadband MAR deposition.
Figure 153: Reflection from the broadband MAR-coated glass surface (black line) and the uncoated glass (red line) of the measured values against design values are listed in Table 7.

Figure 154 shows the reflection spectrum measured for an uncoated TEC10 and an MAR-coated TEC10 glass superstrate. The MAR coating on the TEC10 superstrate confirms the reduced reflection losses across the entire wavelength range of interest (400–850 nm). The spectra show a clear reduction of the reflection for the sample with the MAR coating compared with the uncoated TEC10 glass slide. The TEC10 is a textured glass substrate coated with a thin-film stack which is including buffer layers and transparent conductive oxide. The thin-film stack is on the other side of the substrate than the MAR coating; it consists of thin layers of SnO$_2$, SnO$_2$:F, and SiO$_2$ the stack create interference fringes, which dominated the spectrum and the MAR peaks are not as clearly visible. The MAR coating deposited on the TEC10 superstrate was measured by spectroscopic ellipsometry to verify the thickness of each layer and verify the design. The results of the comparison of the measured values against design values are listed in Table 8.
Figure 154: Reflection spectra measured for the uncoated and MAR-coated TEC10 superstrate.

Table 8

Comparison of designed and measured

<table>
<thead>
<tr>
<th>Layer</th>
<th>Designed [nm]</th>
<th>Measured [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>94.1</td>
<td>98.9</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>133.9</td>
<td>133.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>30.4</td>
<td>31.0</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>18.8</td>
<td>19.0</td>
</tr>
</tbody>
</table>

The comparison shows good agreement between the deposited MAR coating and the design. The effect of the MAR coating on the efficiency of the cell measured before and after the application of the coating is summarised in Table 9. The deposition of the broadband MAR coating on the thin film CdTe solar cell increased the short-circuit current density by 0.65 mA/cm$^2$ (3.1 % relative increase). As a result, the efficiency of the device was increased from 10.55 % to 10.93 %, an absolute increase of 0.38% and a 3.6 % relative increase.
Table 9

J–V parameters of solar cell before and after applying the coating

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>$I_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>10.55</td>
<td>20.98</td>
<td>65.6</td>
<td>24.5</td>
</tr>
<tr>
<td>MAR</td>
<td>10.93</td>
<td>21.63</td>
<td>65.5</td>
<td>24.7</td>
</tr>
</tbody>
</table>

The J–V characteristics of the solar cells measured before and after the application of the broadband MAR coating are compared in Figure 155.

Figure 155: J–V performance of the thin-film CdTe solar cell before and after applying the broadband MAR coating.

4. Conclusion

Broadband multilayer ARCs using alternate high and low refractive index dielectric thin films are commonly used to improve the transmission and reduce the reflection of spectacle
lenses in the visible wavelength range. They are also used in a variety of precision optical applications. However, broadband coatings have not previously been used to improve the light transmission into solar cell devices by reducing the reflection of the glass in the extended wavelength range utilised by thin-film CdTe devices. Some work has been reported using an MAR coating design with a reducing index by oblique angle deposition, but these have been applied direct to GaAs and polycrystalline silicon devices and not to a glass surface [12],[14]. MAR coatings in ophthalmic and most precision optical applications are designed to operate in the visible range of wavelengths. In this study, a four-layer multilayer stack has been designed and tested, which operates across the wavelength range used by thin-film CdTe PV devices (400–850 nm). This is of particular interest because in the superstrate configuration, the light enters the cell through the glass and the reflection of light from the outer glass surface represents an immediate optical loss. Optical modelling predicts that the MAR coating reduces the WAR (400-850) from the glass surface from 4.22 % down to 1.22 %. The application of the MAR coating on a thin-film CdTe solar cell increased the efficiency from 10.55 % to 10.93 % or by 0.38 % in absolute terms. This is a useful 3.6 % relative increase in efficiency. The increased light transmission leads to an improvement of the short-circuit current density produced by the cell by 0.65 mA/cm². For wavelengths below 500 nm, the optical improvement was limited by the low internal quantum efficiency (IQE), due to light absorption in the CdS window layer. A relative increase in efficiency of 3.6 % is an attractive increase in performance. The performance of the coating could be improved even further by increasing the number of layers in the stack design and by choosing a material such as tantalum pentoxide which has a much higher refractive index ($n = 2.275$). However, cost is an important issue and this is minimised by reducing the number and thickness of the layers and by using a low cost and abundant material such as zirconium dioxide. The cost of such a broadband MAR coating for solar modules could be dramatically reduced if deposited at high volumes using high material utilisation rotating magnetrons by a glass manufacturer. The sputtering process developed in this work is capable of scaling to an industrial level. The durability and environmental stability of multilayer dielectric coatings is well established and will not be an issue for manufacturing warranties even when modules are subject to regular cleaning cycles.
5. References


Chapter 13

Conclusions and Suggestions for Future Work

The objective of this thesis has been to evaluate various methodologies for enhancing CdS/CdTe solar cell technology. In this context, various deposition processes for thin films within the CdTe solar devices have been investigated and compared. A novel technique, Pulsed DC Magnetron Sputtering (PDCMS) has also been developed for photovoltaic applications, since it is has been discovered that sputtering thin films of CdS and CdTe can be achieved in highly stable process conditions. The processes have been optimised. Despite the wide range of deposition techniques which are currently available for use for photovoltaic applications, (metal-organic vapour phase epitaxy, chemical bath deposition, close space sublimation, vacuum evaporation, Radio Frequency (RF) magnetron sputtering), each technique has drawbacks. Consequently, this research developed using PDCMS is relevant, since it promises the development of a new process to manufacture cells. Although a previous study using pulsed DC magnetron sputtering of CdS has been reported [168], this work focused only on the wavelength and lifetime of transient species. The work reported in this thesis is the first time PDCMS has been investigated for PV devices. The main results achieved are summarised as follows:

- The major advantages of PDCMS are the high deposition rates, making the process suitable for use in solar module manufacturing. It also allows nanometre control of thin film thickness using time only. The rates obtained are over an order of magnitude faster than those obtained by RF sputtering. In common with other applications the present study has found that the energetics of the pulsed DC process produce favourable thin film properties and the power supply configuration avoids the need for complex matching circuits [259] [270].

Another processing step that has been shown to have significant advantages is plasma cleaning of FTO-coated glass prior to the deposition of the CdS/CdTe thin films for solar cells. The plasma treatment improved the wettability of the substrate and the optical and morphological properties of the deposited CdS thin films. This results in higher refractive index due to the increased film density and increased grain size of the CdS films. Following the surface treatment, the layers did not contain
pinholes [258]. This allows the use of a much thinner CdS window layer which then produces greater photocurrent.

Chemical bath deposition of CdS thin films on TEC glass has also been performed and optimised by a systematic investigation of the several parameters involved in this type of deposition. These parameters include the concentration of chemical reagents used in the bath, the shape and size of magnetic stirrers, and the deposition times. Replacing the magnetic stirrer with an ultrasonic probe resulted in CdS films with higher optical density, higher refractive index, pinhole and void-free, more compact and uniform both along the surface and through the deposited material. This deposition method was used as a baseline. The properties of CdS thin films deposited by pulsed DC magnetron sputtering and chemical bath deposition have then been compared. The comparison of the pulsed DC magnetron sputtering process and the CBD process revealed that PDCMS CdS thin films have the preferred and more stable hexagonal crystalline structure. Conversely, the CBD deposited films were polycrystalline with a cubic structure. Furthermore, PDCMS CdS showed columnar grain growth and high uniformity compared to the CBD films, which showed small grainy crystallites throughout the thickness of the films and poor thickness uniformity. PDCMS films also showed increased grain size, increased density, and higher crystallinity compared to the CBD CdS films. PDCMS also had higher deposition rates which were more than an order of magnitude faster, than the chemical bath deposition technique [271]. Therefore, this comparative study showed that PDCMS could deposit high quality films at high deposition rates making the technique a potentially attractive candidate for application in high throughput and low cost manufacturing of solar modules.

A parallel study has been performed for CdTe layers. Electrodeposition is considered as a viable and conventional low cost technique. CdTe thin films were grown on CdS films prepared by both sonoCBD and PDCMS. It was found that the deposition technique used for the CdS layer affected the growth and properties of the CdTe film. The CdS film not only affected the structural and morphological properties of the CdTe film but also determined the deposition rate of CdTe [272]. Indeed, further experimental work is needed to test these films, making a full PV device and measuring the efficiency.

CdTe films have been deposited by PDCMS. The study was focused on the optimisation of the deposition process, understanding the influence of each deposition
parameter and analysing the optical, morphological, structural and chemical properties of the absorber layer. Further work is needed to complete the optimisation of the full PV device. As final step the deposition of broadband Multilayer Anti-reflection coatings (MARs) to improve the efficiency of thin film CdTe solar cells has also been developed. Reflection losses limit the efficiency of all types of photovoltaic devices. Since the first reflection loss occurs at the glass-air interface of the photovoltaic module, about 4% of the solar energy is lost at this surface. The most commonly used techniques to reduce the reflection include texturing of the glass surface and the application of a single layer antireflective coating (ARC). An important issue is the availability of material with a refractive index lower than glass \((n = 1.52)\). Furthermore, a single-layer coating is designed to reduce reflection at a single wavelength and is not effective over the spectral range used by the solar cell. To minimise the losses, a broadband multilayer thin-film coating has been designed in this study, and deposited onto the glass surface of a thin-film CdTe solar cell. The coating consisted of four dielectric layers of alternating thin films of ZrO\(_2\) and SiO\(_2\). The layers were deposited by using high-rate-PDCMS. Spectrophotometer measurements confirm that the transmission increased by between 2% and 5% over the spectrum utilised by the thin-film CdTe solar cell. The weighted average reflection reduced from 4.22% to 1.24%. Standard test conditions (STC) solar simulator measurements confirmed a 0.38% increase in absolute efficiency and a 3.6% relative increase in efficiency [246]. This is a significant breakthrough and it is expected that the use of broadband MAR coatings will be adopted by module manufacturers world-wide.

The experimental work reported in this thesis demonstrates that PDCMS has significant advantages for PV applications. The technique deposits high quality thin films, with very high deposition rates and highly stable processes. The performance and the high deposition rates make the PDCMS process highly attractive for industrial scale-up.

Furthermore, CREST has established a close relationship with the National Science Foundation Industry and University Cooperative Research Program on Next Generation Photovoltaics at Colorado State University (CSU). The deposition technology used at CSU is mainstream close spaced sublimation (CSS) which is complementary to the techniques used
in this study. This has allowed us to produce hybrid devices by mixing the layers developed at CREST with those from CSU.

In particular, a working device has been made with efficiency ~13%. A CdS layer, 100nm thick, was deposited by PDCMS on TEC10 coated glass with the optimised deposition conditions (chapter 7). The cell has been finished by the CSU group, with the CdTe absorber layer deposited by CSS (around 500°C), treated with CdCl₂ (~ 400°C) and then Cu doped using a CuCl₂ compound treatment (around 200°C) [273], for the back contact formation [67].

![IV test confirmed the efficiency of the cell ~ 13% with FF = 71% for a hybrid device, CdS window layer deposited and CREST and cell finished at CSU.](image)

\[ \eta = 13.2\% \]
\[ J_{sc} = 23.38\text{mA/cm}^2 \]
\[ V_{oc} = 797\text{mV} \]
\[ FF = 71\% \]

This test showed and confirmed the good quality of CdS thin film deposited by PDCMS and the result is highly promising for the future work planned to fabricate the entire device at CREST using PDCMS. This work is already in progress.
Chapter 13

This study satisfied the all objectives that were supposed to be achieved, as they were established and mentioned at the beginning of the thesis (chapter1).
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**The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering**, Thin Solid Films. (2014) 2–6 –In press
Pinhole free thin film CdS deposited by chemical bath using a substrate reactive plasma treatment

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Achieving a pinhole-free CdS layer is necessary to produce high performance thin film CdTe solar cells. Pinholes in the CdS layer can compromise the efficiency of a CdTe solar cell by causing shunts. We have investigated the use of a plasma treatment of a fluorine doped tin oxide coated glass substrate (NSG TEC 15) and its effect on pinhole reduction in thin film CdS layers grown by Chemical Bath Deposition. CdS films, <100 nm thickness, were deposited on both O$_2$/Ar plasma cleaned and conventionally cleaned substrates. We show that the O$_2$/Ar plasma treatment of the TEC 15 substrate reduced the water contact angle from 55° to less than 12° indicating a substantial increase in the surface energy. The CdS deposited on the plasma treated TEC 15 was pinhole free, very smooth and homogenous in morphology and composition. Scanning electron microscopy images show that the O$_2$/Ar plasma treatment is effective in increasing film density and grain size. Corresponding spectroscopic ellipsometry measurements show an increase in the refractive index from 2.18 to 2.43 at 550 nm wavelength.

I. INTRODUCTION

Surface treatment by plasma cleaning has been reported to be a useful process tool for more than 30 yr in a broad range of applications spanning from microelectronics and photovoltaics (PVs) to automotive, textiles, medical, plastics, etc.1,2 Plasma cleaning is an effective and environmentally safe method for surface preparation. Activation of the surface of a material is important for the growth of thin films since surface contaminants and the native oxide can alter the growth mode and thin film adhesion. It can also affect the properties of the deposited films and therefore the performance of the PV devices.3,4

The surface properties of transparent conducting oxides (TCOs) have an influence on the quality of the other films comprising the cell. In particular, sputter treatments have been shown to reduce carbon contamination and modify the resulting interface between the SnO$_2$ and the CdS layers.5 Poor growth regions, appearing as pinholes, can form in the n-type CdS layer, allowing a shunt path to develop between the front contact and the p-type CdTe film.6 Pinholes are particularly troublesome when a thin CdS layer is deposited on TCO-coated glass that has been cleaned using industry-standard techniques.7

Plasma treatments have previously been applied to TCOs such as indium tin oxide (ITO),1 aluminium-doped zinc oxide (AZO),8 and zinc oxide (ZnO)9 with different gas combinations such as argon, hydrogen, or oxygen. These treatments have been shown to change the properties of the TCO surfaces.

In this paper, we discuss the plasma treatment of a commercially available fluorine doped tin oxide (FTO) transparent conducting oxide NSG TEC 15, which is used as superstrate in CdTe solar cell devices.
A thin film CdTe solar cell consists of a multi-layer stack material system, with layers having specifically defined properties. Thin film CdTe solar cells are grown in a superstrate configuration as shown in Figure 1 on a FTO coated glass substrate. The light transmits through the TCO coated glass before reaching the p-n heterojunction, consisting of the n-type CdS layer and a p-type CdTe layer.

The plasma pre-treatment of the TEC 15 glass was performed to activate the surface prior to the chemical bath deposition (CBD) of the thin CdS film. Good surface wettability of the TCO coated substrate is required to avoid the presence of the pinholes and ensure continuity in the deposited CdS thin films. Fluorine doped tin oxide is deposited on an industrial scale using an atmospheric pressure CVD process that results in a relatively rough surface. This roughness can increase the probability of pinhole formation. Here we report on the use of a plasma treatment process to grow pinhole-free CdS thin films on TEC 15 glass.

II. EXPERIMENTAL

TEC 15 glass supplied by NSG-Pilkington was used as the substrate material. TEC 15 is a multilayer stack of materials deposited on a 3.2 mm thick glass. The stack consists of a 25 nm SnO₂ layer, a 25 nm SiO₂ layer, and a 280 nm thick conducting layer of fluorine doped tin oxide (SnO₂:F). TEC 15 has a sheet resistance of $15 \Omega/\square$ and a relatively good transparency, ~82% light transmittance. These properties are a good compromise between the electrical and the optical requirements of a PV device substrate. The substrate was treated using 20 sccm O₂/30 sccm Ar plasma for 5 min prior to the CdS film growth. The plasma power was set at 100 W and at a pressure of between 335 and 273 mTorr. Electrodes and sample trays are 406.4 mm x 406.4 mm in area using perforated aluminium of thickness 3.175 mm. The parallel electrodes are used to provide uniform plasma across the sample area. All substrate surfaces are treated to the same degree, irrespective of their position on the sample tray. The plasma treatment reactor, Glen100-P AE Advanced Energy, was a parallel plate system using AC plasma power source with potential for three gas admittance lines. The system was pumped to a pre-process pressure of 332 mTorr using a rotary pump.

A 50 nm CdS thin film was deposited by CBD, the reaction occurs in a beaker immersed in a water jacket to ensure constant temperature (70 °C). The bath solution was made of 200 ml of de-ionized water, 15 ml of Cd(CH₃COO)₂ 0.01 M, 25 ml of NH₄OH 25%, and 10 ml of CS(NH₂)₂. A magnetic bar was used to stir the solution to accelerate the reaction kinetics.

III. RESULTS AND DISCUSSION

A. Substrate surface modification

Plasma treatment activates the substrate surface by increasing the surface energy. The surface energy of the material was tested by measuring the water contact angle before and immediately after the treatment. Figure 2 shows the effect of the plasma treatment on the FTO coated glass surface. The equilibrium contact angle that the drop makes with the surface is $54.3^\circ$.
before the treatment and 12.3° after the plasma treatment. This indicates that the treatment increases the hydrophilic nature of the surface. The increased surface energy is beneficial for adhesion and the continuity of the thin film. It is possible that the increase in surface energy may change the thin film growth kinetics. However, there was only a marginal difference in thin film thickness (~50 nm) for films deposited on the treated and untreated surfaces as measured by spectroscopic ellipsometry. Hence a valid comparison was possible between their properties.

This hydrophilic behaviour corresponds to the removal of contaminates from the surface, as confirmed by X-ray photoelectron spectroscopy (XPS) analysis. Table I reports the atomic composition as determined by XPS.

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>Plasma treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s %</td>
<td>24.5</td>
<td>11.9</td>
</tr>
<tr>
<td>O1s %</td>
<td>46.3</td>
<td>55.2</td>
</tr>
<tr>
<td>Sn3d %</td>
<td>27.3</td>
<td>31.4</td>
</tr>
</tbody>
</table>

FIG. 2. Water contact angle images (a) prior and (b) post plasma treatment.
percentage of Carbon (C1s), Oxygen (O1s), and Tin (Sn3d) for the untreated and the plasma treated substrates, indicating carbon contamination reduction without altering the Sn/O ratio.

B. Impact of substrate plasma treatment on the CdS films

Scanning white light interferometry (SWLI) is a powerful tool for the metrology of surfaces. We use a variant of SWLI called Coherence Correlation Interferometry (CCI) developed by Taylor Hobson, Ltd. The CCI technique was used to analyse the surface morphology of the CdS films and detect pinholes in the CdS. Pinholes appear as spikes in the CCI surface image as shown in Figure 3(a). In this case the CdS was deposited on the untreated substrate; pinholes were detected with a mean depth of 55 nm and a width of 0.65 μm as shown in Figure 4. The spatial resolution of the CCI is determined by the wavelength of light and the numerical aperture of the lens used and is typically ~0.3 μm. The vertical resolution is typically <1 nm.

The CCI analysis shows that the pinhole density was dramatically decreased and virtually eliminated for the film grown on the plasma treated substrate (Fig. 3(b)); the thin film also has a smoother surface.

Scanning Electron Microscopy (SEM) images were obtained to study the surface morphology of the grown CdS films. Figure 5 shows the comparison between the surface of the untreated (a) and the plasma treated (b) samples. The CdS films exhibit a crystalline structure with grain size increasing from ~108 nm to ~175 nm following plasma treatment of substrate.

FIG. 3. Three dimensional CCI images of CdS deposited on (a) untreated and (b) plasma treated substrates (20 sccm O2/30 sccm Ar).
The treated samples generally showed more uniform coverage of the surface with a more compact deposited film.

XPS analysis was also performed on the CdS films to analyse their stoichiometry. Figure 6(a) shows the XPS spectra of Cd3d and S2p photoelectron core levels for the untreated...
and the plasma treated samples. The position of the peak at 405.8 eV for Cd orbital 3d_{5/2} and the shape and binding energy of 161.6 and 162.8 eV for S_{2p_{3/2}} and S_{2p_{1/2}}, match the theoretical CdS values, indicating that CdS was not incorporating oxygen into the films.

The optical properties of the CdS films were measured using spectroscopic ellipsometry. Transmission and reflection measurements were obtained using a spectrophotometer. The Tauc-Lorentz model was used to parameterise the spectral dependence of the CdS refractive index, n, and extinction coefficient, k. The derived optical properties are shown in Figure 7. The CdS film deposited on the plasma treated substrate showed increased refractive index (Figure 7(a)). The film also showed increased absorption and a red-shift of the absorption edge (Figure 7(b)). This is consistent with the increased grain size, increased compactness, and reduced pinhole density observed for the film deposited on the plasma treated substrate.

Figure 8 shows the transmittance and reflectance spectra of the CdS thin films deposited on the untreated and on the plasma treated substrates. The transmittance of the thin films reaches a maximum of ~80% and it decreases near the absorption edge at 500 nm; this confirms that the CdS has good crystallinity.
The CdS deposited on the plasma treated substrate shows lower transmission compared to the film deposited on the untreated substrate. The transmittance is lower due to the higher optical density of the CdS film as shown by the SEM measurements and the removal of pinholes as shown by the CCI metrology measurements. The Urbach equation can be used to obtain the absorption coefficient,\textsuperscript{14} it is defined by formula

\[
\alpha = A \left( \frac{\hbar \nu}{E_g} \right)^p,
\]

where \( A \) is a constant, \( E_g \) is the band gap energy, \( \nu \) is the frequency, \( h \) is the Plank’s constant, \( p \) is the numerical coefficient. In Figure 9, \( [\alpha h \nu]^2 \) is shown as a function of the energy (eV), \( p \) in this case is 0.5. The single slope in the curve explains the direct transition of electrons between the valence band and the conduction band. Extrapolating the linear region of \( [\alpha]^2 \) up to the value \( \alpha = 0 \), the band gap energy \( E_g \) is determined to be 2.3 eV.

FIG. 7. n (a) and k (b) dispersions measured for CdS films deposited on the untreated substrate and the plasma treated substrate (20 sccm of O\textsubscript{2}).
The band gap decreased from 2.4 eV to 2.3 eV as a result of the substrate plasma cleaning due to the increased density of the film or the small grain size.\textsuperscript{15}

\section*{IV. CONCLUSIONS}

Plasma cleaning of FTO-coated glass prior to the deposition of the CdS/CdTe solar cell strongly affects the TCO surface, and improves the quality of the subsequently deposited CdS thin film. Specifically, the plasma cleaned FTO exhibits increased hydrophilic behaviour, due to a reduction or elimination of surface contamination. This corresponds to a reduction in water contact angle and increased surface energy. When CdS thin films are deposited on a plasma cleaned FTO surface we have shown that the pinhole density is greatly reduced and virtually eliminated compared with CdS films deposited on substrates treated using standard wet cleaning techniques.

The plasma treatment improves the wettability of the substrate as demonstrated using water contact measurements. This improves the optical and morphological properties of the deposited CdS thin films, resulting in a higher refractive index and a higher absorption coefficient related

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig8}
\caption{Transmission and reflection spectra for CdS thin films deposited on TEC 15, comparing the untreated and the plasma treated surface, with 20 sccm of O\textsubscript{2}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9}
\caption{Energy band gap ($E_g$) of the untreated and plasma treated sample, estimated from the ($\alpha h \nu$)$^2$ = $f(\nu)$, by using the Urbach equation.}
\end{figure}
to the increased film density and increased grain size of CdS film. The pinhole removal and the increased density allow the use of a much thinner CdS layer. Use of a thinner CdS layer actually reduces absorption of blue spectrum photons thereby increasing the efficiency of the thin film CdTe cell. Further experiments are now planned to incorporate the plasma cleaning process into a full cell deposition process to assess the improvement to device performance.


High rate deposition of thin film cadmium sulphide by pulsed direct current magnetron sputtering

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1. Introduction

Cadmium Sulphide (CdS) is an important n-type semiconductor widely used as a window layer in thin film photovoltaics Copper Indium Selenide, Copper Indium Gallium (di)Selenide, Copper Zinc Tin Sulphide and Cadmium Telluride (CdTe). Cadmium Sulphide has been deposited using a number of techniques but these techniques can be slow (chemical bath deposition and Radio Frequency sputtering) or the uniformity and the control of thickness can be relatively difficult (close space sublimation). In this paper we report on the development of a process using pulsed Direct Current magnetron sputtering which allows nanometre control of thin film thickness using time only. The CdS thin films deposited in this process are highly uniform and smooth. They exhibit the preferred hexagonal structure at room temperature deposition and they have excellent optical properties. Importantly, the process is highly stable despite the use of a semi-insulating magnetron target. Moreover, the process is very fast. The deposition rate using 1.5 kW of power to a 6-inch circular magnetron was measured to be greater than 8 nm/s. This makes the process suitable for industrial deployment.

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conditions which are highly stable. The major advantage is that the process produces high deposition rates suitable for use in solar module manufacturing. These rates are over an order of magnitude faster than those obtained by RF sputtering. In common with other applications we also find that the energetics of the pulsed DC process produce favourable thin film properties and the power supply configuration avoids the need for matching circuits [26,27].

2. Experimental details

CdS thin films were deposited by pulsed DC magnetron sputtering in a ‘PV Solar’ sputtering system (Power Vision Ltd., Crewe UK). The system is equipped with four six-inch diameter circular magnetrons mounted vertically, with an option to replace one of the magnetrons with a plasma source for reactive sputtering. The samples are mounted vertically on a rotatable carrier, designed for 5 cm × 5 cm substrates. The target to substrate distance is typically 10 cm. During the deposition process the carrier rotates at typically 120 rpm. This provides excellent uniformity in the horizontal direction. Uniformity in the vertical direction is achieved using disposable masks mounted in front of the magnetron target. The CdS thin films were sputtered using a pulsed DC power supply (Advanced Energy Inc. Pinnacle plus, 5 kW) using argon as the working gas [28].

The CdS thin films were deposited on NSG-Pilkington Transparent Electrically Conducting (TEC15 and TEC10) Fluorine doped tin oxide (FTO) coated glass substrates. Prior to the CdS deposition, the substrates were cleaned in a two-step ultrasonic bath process consisting of a 5 min
bath in a solution of Isopropanol and de-ionised water (1:10), followed by a second ultrasonic bath in de-ionised water for 5 min. Following the cleaning, the substrates were subjected to a plasma surface treatment in a mixture of 20 sccm of O₂ and 30 sccm of Ar using a plasma discharge power of 100 W and a pressure ~40 Pa to activate the surface [29,30]. The plasma treatment was carried out in a Glen100-P AE Advanced Energy system. The reactor is a parallel plate system with an AC plasma power source connected to substrate shelves which act as electrodes. The samples were then transferred to the deposition system. The chamber was evacuated to a pressure of 5 × 10⁻³ Pa before admitting pure Ar gas at flows in a range between 5 sccm and 20 sccm. The depositions were performed using the following process conditions: 150 kHz (pulsing frequency), 2 s (ramping time), and 1.5 μs (pulse reverse time). The effects of increasing the Ar gas flow (5 sccm, 10 sccm, 15 sccm and 20 sccm), the deposition power (250 W–1500 W) and the deposition temperature (250, 300 and 400 °C) on the film properties were investigated. At these deposition conditions, the plasma arcing was minimal during the film growth and the working pressure was measured to be 1 Pa.

The chemical composition, microstructure and optical properties of the CdS thin films were investigated. The microstructure was studied with a high resolution field emission gun scanning electron microscope (FEGSEM), Leo 1530 VP FEG-SEM, which provides the ability to visualise surface features of the material with nanometer resolution.

An X-ray Photoelectron Spectroscopy (XPS) surface analysis tool was used to obtain the chemical composition of the layers. The analysis was performed using a Thermo Scientific K-Alpha XPS. An electron flood gun was used to reduce any charging that would cause peak shifts to occur. An argon ion surface etch at 1 keV for 30 s, was carried out prior to analysis to remove surface contamination. The X-ray source used was Al Kα, radiation \( h\nu = 1486.6 \) eV with a beam diameter of 200 microns. The High Resolution Multiplex Scan was used to evaluate the chemical state(s) of each element through its core electron binding energies. Precise determination of binding energies was made through the use of curve fitting routines applied to the peaks in the multiplex scan and sensitivity factors were taken into account to determine elemental composition. A dual beam FEI Nova 600 Nanolab was employed to prepare the transmission electron microscopy (TEM) samples. A standard in situ lift off method was used to prepare cross-sectional samples through the coating into the glass substrate. A platinum over-layer was deposited to define the surface of the samples and homogenize the final thinning of the samples. TEM images were obtained using a Jeol JEM 2000FX operating at 200 kV, with an integrated camera above the phosphor screen to obtain digital images. The TEM technique provided morphological analysis of the grain structure of the sputtered CdS films on FTO coated glass substrates. The X-ray diffraction analysis (XRD) was performed, using a Bruker D2 Phase bench-top XRD using Copper X-rays with a 1.542 nm wavelength, to investigate the crystalline structure of the material. Each sample was scanned using an angular range of 20–90° with a step size of 0.02° and a dwell time of 0.1 seconds. Electron Backscattered Diffraction (EBSD) was used for crystal analysis to measure the structure and orientation in the solid crystalline phase. Transmission Electron Back-Scatter Diffraction (t-EBSD) was used because it offers superior resolution suitable for the characterisation of the small grains of the sputtered CdS material. t-EBSD was carried out using a dual beam FEI Nova 600 equipped with an ultra-high speed Hikari Electron backscattering diffraction (EBSD) camera, using a beam current of 6.7 nA and an acceleration voltage of 30 kV. Scanning White Light Interferometry (SWLI) (Sunstar CCI, Taylor Hobson Ltd.) was used to measure sample surface roughness and to detect the presence of pinholes. Pinholes are a known problem for thin films CdS in PV devices [28]. Pinholes are microscopic imperfections in the coating which appear as pits in the interferometer surface image. The spatial resolution of the interferometer is determined by the wavelength of light and the numerical aperture of the lens used, and is typically ~0.3 μm. The vertical resolution is typically ~1 nm. The transmission, reflection and energy band gap \( E_g \) measurements were carried out using a spectrophotometer (Varian Cary® UV–Vis 5000). The instrument is equipped with an integrating sphere and set of gratings which allow the collection of transmission information from wavelengths in the range from 185 nm to 3.3 μm. The energy band gap \( E_g \) was calculated as a graphic extrapolation by using the Tauc plot [31].

\[
a = \frac{A(h\nu-E_g)^{\frac{1}{2}}}{h\nu}
\]

with \( A \) is the absorption coefficient, \( E_g \)– the band gap energy, \( \nu \)—the frequency, \( h \)– the Plank’s constant,
p—numerical coefficient ($p = 0.5$ for direct band gap material and $p = 2$ for indirect band gap material).

The optical properties of the thin films were also measured using spectroscopic ellipsometry (SE) (Horiba, Jobin Yvon, UVISEL); which provided information about the thickness and refractive index (and uniformity) of the deposited films. The dispersion of the real and imaginary part of the refractive index was measured in a wavelength range between 248 nm and 2100 nm. To analyse SE data and derive the energy band gap and refractive index of films, we used a three-layer model consisting of TEC-substrate/interface/CdS-film/surface-roughness/air; for the TEC substrate, the SE experimental file recorded just before starting the deposition, was used without any assumption; the interface was a Bruggeman effective medium (BEMA) [28] mixture of the top layer of the TEC substrate (SnO$_2$:F) and CdS; the CdS optical properties were parameterised using a double Tauc Lorentz dispersion formula [29]:

\[
\varepsilon_i \begin{cases} 
\sum_{i=1}^{N} \frac{A_i \cdot E_0 \cdot C_i \cdot (E-E_g)^2}{(E^{2}-E_0^{2})^2 + C_i^{2} \cdot E^2} & \text{for } E > E_g \\
0 & \text{for } E \leq E_g
\end{cases}
\]
where $A_i$ is the Tauc coefficient, $E$, the photon energy, $E_i$, the transition energy of the oscillator of highest order, $C_i$, the broadening term of the peak, and $E_g$, the optical band gap. $\varepsilon_r$ is written as the following sum:

$$
\varepsilon_r(E) = \varepsilon_r(\infty) + \sum_{i=1}^{N} \frac{2}{\pi} \cdot \frac{E_g - E}{E_g - E_i^2} \, dE_i
$$

The surface roughness was a BEMA mixture of 50% CdS and 50% voids. The fit parameters were the Tauc parameters and layer thicknesses.

### 3. Results and discussion

#### 3.1. CdS composition, structure and morphology

Fig. 1 shows the XPS spectra of Cd3d and S2p photoelectron core levels measured for CdS films deposited at ambient temperature using different Ar gas flows. The position of the Cd peaks was 405.8 eV and 412.3 eV for Cd3d_{5/2} and Cd3d_{3/2} respectively; the shape and the binding energy of 161.6 eV and 162.8 eV measured for S2p_{3/2} and S2p_{1/2} matched the theoretical values for CdS [30]. This indicated that the deposited CdS films are stoichiometric and no oxygen was incorporated into the film. This is also supported by a fitting analysis which showed only the CdS component. The XPS analysis of CdS films deposited at different values of Ar gas flow, deposition power and temperature showed that the chemical composition of the sputtered film CdS was unaffected by the deposition parameters.

Fig. 2 shows the XRD pattern measured for a CdS sputtered at ambient temperature, at an Ar flow of 10 sccm on a TEC15 glass substrate. Diffraction peaks due to the (002), (100), (101), (102), (110) and (103) reflection peaks indicate the hexagonal phase for the CdS thin film.

The hexagonal phase was also supported by t-EBSD analysis carried out on various grains. Each Kikuchi line, in the Kikuchi diffraction pattern collected in transmission electron back-scattered diffraction from a CdS grain, is associated with Bragg diffraction from one side of a single set of lattice planes and they can be labelled with the same Miller indices that are used to identify diffraction spots. Fig. 2 (b–c) shows a large number of bands overlaid with the hexagonal phase map, which provide a clear indication that each grain is of the hexagonal phase.

Additional information on the crystalline structure of individual grains was obtained by the inverse pole figure (IPF) map shown in Fig. 3. Inverse pole figure (IPF) orientation component uses a basic RGB colouring scheme, fit to an inverse pole figure. Euler angles are a set of three angles used to describe the crystallographic orientation of crystals relative to a reference co-ordinate system (usually defined by the primary SEM stage axes). Here, the value of each Euler angle is individually set to a colour scale (normally red, green, and blue), and the three are combined into a single RGB colour. Intermediate orientations are coloured by an RGB mixture of the primary components. The transmission electron back-scatter diffraction map in Fig. 3a shows that the sputtered grains have a high level of texture in the $<111>$ direction, consistent with the XRD pattern (Fig. 2). Furthermore, the high resolution transmission electron back-scattered diffraction phase/confidence index map in Fig. 3b shows that within the grains there is a high degree of indexing, while at grain boundaries the Kikuchi pattern quality is reduced and therefore they are shown as darker regions, highlighting
the columnar structure of grains, also confirmed by the TEM cross section and SEM fracture cross section images of a 1.6 μm thick CdS film deposited on TEC10 glass shown in Fig. 3c and d, respectively. The TEM image in Fig. 3d shows that the grain size is typically ~50 nm and the onset of grain coalescence is observed from the SEM surface images, shown in Figs. 4 and 5.

The SEM images in Fig. 4 show the surface morphology of the deposited CdS film, measured for films deposited at different gas flows and deposition powers. The surface morphology appeared to be mostly unaffected by the Ar gas flow and the deposition power. The substrate temperature was ambient, a few degrees above room temperature due to substrate interaction with the magnetron plasma. The thickness of each thin film was maintained at ~270 nm for this set of experiments.

Fig. 5 (a–c) shows SEM images of 100 nm thick CdS thin films deposited at different temperatures (250 °C, 300 °C and 400 °C). Increasing the deposition temperature from 250 °C to 400 °C resulted in morphology changes of the deposited CdS films. The grains of the films deposited at 250 °C appeared to have a round shape. The thin films deposited at higher temperature (300 °C and 400 °C) were more compact and showed more uniform distribution of the grain size.

The uniformity of the optical properties and thickness of deposited CdS films

3.2. Optical properties of the deposited CdS films

Fig. 7 shows the derived optical properties of the CdS film deposited at 10 sccm of Ar flow and 500 W deposition time for 600 s. The peak at 2.7 eV is the E<sub>0</sub> inter-band transition [32] in good agreement with the absorption edge of hexagonal CdS [31], while the E<sub>1</sub> inter-band transition at 4.9 eV is at the end of the experimental measurement range. The uniformity of the optical properties and thickness of deposited CdS films was assessed using SWLI for samples deposited using an Ar flow of 5 sccm and 20 sccm. The analysis showed that films deposited at Ar flows below 20 sccm had a smooth uniform surface, but when the Ar flow was increased to 20 sccm voids appeared in the SWLI image of the film surface. The voids appear as deep pits in the surface; a 2D cross section across recorded voids shows that the detected pinholes were 174 nm deep. The thin film was 270 nm thick; therefore, these pits were voids in the deposited film but no pinholes were detected.
films was verified by ellipsometric mapping; Fig. 7 shows the distribution of the refractive index (c) and thickness (d) on a 5 mm × 5 mm area. Typically the refractive index changed in the range of 2.50–2.54, with a standard deviation of σ < 0.01.

The transmittance of this film reaches a maximum of ~80% and decreases to 0% near the absorption edge at 500 nm (Fig. 8). From the Tauc plot, an energy band gap (Eg) of 2.31 eV has been determined.

Fig. 9 shows refractive index, extinction coefficient, and transmittance measured for films deposited at different gas flows. The measurement showed that, while the extinction coefficient and band gap do not change significantly, the increase in the gas flow resulted in a lower refractive index. This is consistent with the SWLI results where for higher Ar flows, voids were present in the surface of the CdS films. Voids are known to reduce refractive index of material because the optical density is affected by the presence of these defects of the material. Consequently, the transmittance changed slightly in the range of 75%–80%. Fig. 10 shows that the deposition power affected the refractive index of films, as shown by the spectra for CdS films deposited at 5 sccm Ar flow at different deposition powers of 500, 1000, 1250 and 1500 W.

3.3. The effect of deposition parameters on the deposition rate

The influence of deposition power and gas flow on the deposition rate was studied. The results are shown in Figs. 11 and 12. The deposition rate increased linearly with the deposition power. The deposition rate was affected by the argon flow rate and working gas pressure with rate increasing from 4.26 nm/s at a flow rate of 5 sccm to 5.33 nm/s at 20 sccm, as shown in the inset. The deposition rate was observed to decrease once the argon gas flow rate was higher than 20 sccm possibly caused by scattering. The effect of changing the gas flow rate was investigated in the range between 5 and 20 sccm. The effect of substrate temperature on the deposition rate was also investigated. Fig. 13 shows the measured deposition rates for different substrate temperatures up to 400 °C. The deposition rate decreased with increasing substrate temperature [33].

4. Discussion

Thin film CdS is an important component of several thin film photovoltaic device systems including thin film CdTe, CIS, CIGS and CZTS. It is used as an n-type window layer to form the device heterojunction. Layers of thin film CdS are often deposited using a chemical bath method but this process is slow and is prone to the formation of...
The deposition rate achieved using pulsed DC magnetron sputtering is of particular note. Using 1500 W of deposition power at the magnetron target (corresponding to a power density of ~8.5 W m$^{-2}$) at 150 kHz pulsing frequency and 10 sccm argon gas flows, the deposition rate was measured to be 1.33 nm/s. However, this rate is achieved on a 5 cm $\times$ 5 cm substrate located on a 180 mm diameter rotating carrier. In this configuration, the substrate is exposed to the deposition flux only for a fraction of each revolution. The equivalent deposition rate for a static substrate is 8.66 nm/s, which is high and much faster than can be achieved using a chemical bath deposition or RF magnetron sputtering. As an example, the typical thickness of the CdS window layer in a thin film CdTe device is ~100 nm and this could be deposited in less than 12 s. We will investigate the properties of these thin layers in devices in future work. The high deposition rate makes the process highly attractive for industrial scale-up. Although target utilisation is poor with the planar magnetrons used in this study, this limitation could be overcome in a manufacturing environment by using rotating magnetrons.

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The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering

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Chemical bath deposition
Cadmium sulphide
Thin films
Film uniformity
Pinhole free films
Void-free films

A B S T R A C T
Cadmium sulphide (CdS) thin films were deposited by two different processes, chemical bath deposition (CBD), and pulsed DC magnetron sputtering (PDCMS) on fluorine doped tin oxide coated glass to assess the potential advantages of the pulsed DC magnetron sputtering process. The structural, optical and morphological properties of films obtained by CBD and PDCMS were investigated using X-ray photoelectron spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, spectrosopic ellipsometry and UV–Vis spectrophotometry. The as-grown films were studied and comparisons were drawn between their morphology, uniformity, crystallinity, and the deposition rate of the process. The highest crystallinity is observed for sputtered CdS thin films. The absorption in the visible wavelength increased for PDCMS CdS thin films, due to the higher density of the films. The band gap measured for the as-grown CBD–CdS is 2.38 eV compared to 2.34 eV for PDCMS–CdS, confirming the higher density of the sputtered thin film. The higher deposition rate for PDCMS is a significant advantage of this technique which has potential use for high rate and low cost manufacturing.

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1. Introduction
Cadmium sulphide (CdS) is an important II–VI compound semiconductor material with applications in several heterojunction photovoltaic systems including cadmium telluride (CdTe), copper indium diselenide/sulphide and copper indium gallium diselenide/sulphide (CIGS) solar cells [1]. It has also applications in various electro-optic and infrared devices [2]. There are several deposition techniques used for the deposition of thin film CdS including RF sputtering [3,4], chemical bath deposition (CBD) [5], thermal evaporation [6], chemical vapour deposition [7], close space sublimation (CSS) [8], molecular beam epitaxy [9] and spray pyrolysis [10]. Each deposition process produces different structural, electrical and optical properties of the CdS thin films. In most heterojunction devices, high efficiency cells utilise a CdS window layer [11,12]. For example, First Solar has reported CdS deposited high-rate vapour transport deposition (HRVTD) [13]. A 14.2% efficient thin film CdTe solar cell with CdS deposited by CSS has been reported [14]. Use of RF sputtered CdS in CdTe solar cells resulted in an efficiency of 15.8% [15,16]. Interestingly, an efficiency of 21.7% has been reported for CIGS devices with CdS layers grown by CBD [17].

We have developed a process using pulsed DC magnetron sputtering (PDCMS) [18] to sputter thin films of CdS in highly stable process conditions. In this paper, we report on the differences in the properties of CBD and PDCMS deposited CdS thin films. The major advantage of the PDCMS process is that it produces high deposition rates which are much higher than those obtained using RF sputtering [19]. This makes the use of pulsed DC sputtering suitable for high throughput solar module manufacturing [18]. We also find that the energetics of the pulsed DC process produce favourable thin film properties. In addition, the use of pulsed DC power supplies avoids the need for complex matching circuits necessary when using radio frequency power supplies.

2. Experimental details
Transparent electrically conducting (TEC 10) glass supplied by NSG-Pilkington (http://www.pilkington.com/) was used as the substrate (superstrate) material. The substrates were cleaned in a two-step ultrasonic bath process followed by a plasma surface treatment prior to the CdS film growth [20]. CdS thin films of ~100 nm thickness were deposited by pulsed DC magnetron sputtering in a ‘PV Solar’ magnetron sputtering system (Power Vision Ltd., Crewe UK); details of the system have been provided elsewhere [18]. The deposition conditions were set using the following process parameters: 10 sccm of Ar gas flow, 500 W, 150 kHz, 2 s (ramp time), 2.5 μs (reverse time).

Thin films of CdS of ~100 nm thickness were deposited by chemical bath deposition (CBD); the reaction occurred in a beaker immersed in a water jacket to ensure constant temperature (70 °C). The bath solution consisted of 200 ml of de-ionised water, 15 ml of Cd(CH3COO)2 0.01 M. A sputtering chamber was used for the deposition of CdS using a mixture of 300 ± 15 mTorr Ar gas flow, 500 W, 150 kHz, 2 s (ramp time), 2.5 μs (reverse time). The substrates were cleaned with ethanol, acetone, and deionised water in an ultrasonic bath and dried with N2. The samples were sputtered for a period of 10 min with a current density of 100 A/m2. The initial thickness of the CdS layers was assessed using a Dektak 3030 profilometer.

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25 ml of NH4OH 25\% and 10 ml of CS(NH2)2, 0.1 M. An ultrasonic probe was immersed in the solution to accelerate the reaction kinetics[20].

The chemical composition, microstructure and optical properties of CdS thin films prepared by CBD and PCDMS were investigated and compared. The microstructure was studied with a high-resolution field emission gun scanning electron microscope (FEGSEM), Leo 1530 VP FEG-SEM, which provides the ability to visualise surface features of the material with nanometre resolution, operating at 5 kV. X-ray photoelectron spectroscopy (XPS) was used to obtain the surface chemical composition of the layers. The analysis was performed using a Thermo Scientific K-Alpha XPS surface analysis tool. An electron flood gun was used to reduce charging that would cause peak shifts to occur. An argon ion surface etch at 1 keV, for 30 s, was carried out prior to analysis to remove surface contamination. The X-ray source used was Al Kα radiation $\nu = 1486.6$ eV with a beam diameter of 200 microns. The High Resolution Multiplex Scan was used to evaluate the chemical state(s) of each element through its core electron binding energies. Precise determination of binding energies was made through the use of curve fitting routines applied to the peaks in the multiplex scan and sensitivity factors were taken into account to determine elemental composition. A dual beam FEI Nova 600 Nanolab was employed to prepare the transmission electron microscopy (TEM) samples. A standard in situ lift off method was used to prepare cross-sectional samples through the coating into the glass substrate. A platinum over-layer was deposited to define the surface and homogenise the final thinning of the samples. TEM images were obtained using a Jeol JEM 2000FX operating at 200 kV, with an integrated camera above the phosphor screen to obtain digital images. The TEM technique provided morphological analysis of the grain structure of the sputtered and CBD CdS films on fluorine doped tin oxide (FTO) coated glass substrates (TEC 10). Scanning transmission electron microscopy (STEM) was carried out using a FEI Tecnai F20 (S) TEM, equipped with a silicon drift detector, in the common imaging mode for the STEM bright field imaging (BF). The X-ray diffraction analysis (XRD) was performed, using a Bruker D2 Phase bench-top XRD using copper X-rays with a 1.542 nm wavelength, to investigate the crystalline structure of the materials. Each sample was scanned using an angular range of 20–90 ° with a step size of 0.02 ° and a dwell time of 0.1 s. The transmission, reflection and energy gap (Eg) measurements were carried out using a spectrophotometer Varian Cary® UV–Vis 5000. The energy band gap Eg was calculated by a graphic extrapolation by using the Tauc plot [21].

The optical properties of the thin films were measured using spectroscopic ellipsometry (SE) (Horiba, Jobin Yvon, UVISEL); which provided information about the thickness and refractive index (and uniformity) of the deposited films. The dispersion of the real and imaginary part of the refractive index was measured in a wavelength range between 248 nm and 2100 nm. The transparent electronic conductive (TEC 10) glass has a complex multilayer structure, being coated with successive layers of undoped SnO2, SiO2 and F-doped SnO2, to achieve the desired sheet resistance. The optical properties of each component layer have been reported.
The overall properties of the TEC 10 glass optical structure were measured by spectroscopic ellipsometry prior to CdS deposition. This data was then used as a fixed optical structure for the substrate in the ellipsometric model. The model consisted of a TEC-substrate/interfacedCdS-film/surface-roughness/air structure to analyse SE data and derive the energy gap and refractive index of the CdS thin films. The CdS optical properties were obtained using a double Tauc Lorentz parameterisation. The surface roughness was a Bruggeman Effective Medium Approximation (BEMA) mixture of 50% CdS and 50% voids. The fit parameters were the Tauc parameters and layer thicknesses.

### 3. Results and discussion

Fig. 1(a) and (b) shows the XPS spectra of Cd3d and S2p photoelectron core levels measured for CdS films deposited by PDCMS sputtering and chemical bath deposited at 70 °C with Cd(CH3COO)2 0.01 M, NH4OH 25% and CS(NH2)2 0.1 M, respectively. The binding energies of 405.8 eV and 412.3 eV for Cd3d5/2 and Cd3d3/2, respectively, and 161.6 eV and 162.8 eV for S2p3/2 and S2p1/2 matched the theoretical values for CdS. This indicates that the deposited CdS films are stoichiometric and no oxygen was incorporated into the films. This is also supported by fitting analysis, which showed only the CdS component.

The XRD analysis (see Fig. 2) is complicated by the coincidence of the TEC substrate and CdS film peaks; nevertheless, some analysis can be performed by examining the intensity of peaks and the different attenuation of the TEC peaks. Specifically, the very intense <002> reflection for the PDCMS CdS indicates the hexagonal structure with a preferential orientation <001>, whereas the CBD CdS films exhibit a cubic polycrystalline structure. The XRD analysis was referred to JCPDS database cards (http://www.icdd.com/).

Fig. 3 compares the surface morphologies of PDCMS (a) and CBD (b) deposited CdS thin films. The CBD deposited films have smaller crystallites compared to the PDCM sputtered films. Both show the onset of grain coalescence.

BF-STEM cross-sectional images of a 100 nm thick CdS film deposited on TEC10 by PDCMS and CBD are shown in Fig. 4(a) and (b), respectively. The grains expand through the thickness of the film deposited by PDCMS with a columnar structure (a) while small grainy crystallites grow through the thickness of CBD CdS film (b), consistent with the SEM images and XRD data. In both cases, the grains grow by following the structure of the substrate surface beneath (TEC10 glass) and voids are not observed at the interface.

Fig. 5 shows the derived optical properties, dispersion of the refractive index, n, and extinction coefficient, k, of the, CdS films deposited on TEC10 by PDCMS and CBD. The PDCMS CdS film shows a higher refractive index and a slightly higher absorption at 500 nm with sharper interband transition E1 [23] (Fig. 5(b)). This can be explained by the increased grain size, increased density, and higher crystallinity observed for the films deposited by PDCMS compared to the CBD deposited CdS.

The transmission of the thin films reaches a maximum of ~75% (this includes the effect of absorption in the TEC10 substrate) and decreases near the absorption edge at 500 nm, confirming the crystallinity of the CdS thin films (Fig. 6, inset). The PDCMS CdS has a lower transmission than the CBD deposited CdS, due to its higher optical density, in agreement with the ellipsometric analysis. Fig. 5 shows the band gap (Eg) determined from the Tauc plot. The PDCMS CdS has a band gap of 2.34 ± 0.01 eV compared to 2.38 ± 0.01 eV measured for the CBD CdS.

The deposition rate for CdS obtained using pulsed DC magnetron sputtering was 0.44 nm/s using only 500 W power on a six inch circular magnetron target. This rate is achieved on a 5 cm × 5 cm substrate located on a 180 mm diameter-rotating substrate carrier. The equivalent deposition rate for a static substrate is ~2.86 nm/s. The deposition rate using CBD is comparatively much slower. To deposit a 50 nm thick film of CdS required about 30 min and a thickness of 150 nm needed 1 h.
4. Conclusions

We have deposited and compared the properties of CdS thin films deposited by pulsed DC magnetron sputtering and chemical bath deposition. The pulsed DC magnetron sputtering process produced CdS thin films with the preferred hexagonal -001 > oriented crystalline structure. TEM analysis shows evidence of columnar grain growth. Conversely, the CBD deposited films were polycrystalline with a cubic structure, showing small grainy crystallites throughout the thickness of the films. Cbd deposited films exhibited comparatively poor thickness uniformity while the pulsed DC sputtered films were highly uniform. The spectroscopic ellipsometry analysis showed higher refractive index and slightly higher absorption at 500 nm for the PDCMS deposited CdS films, confirming the increased grain size, increased density, and higher crystallinity compared to the CBD CdS films. The films deposited by both techniques were pinhole and void-free, with an optical band gap of 2.34 ± 0.01 eV for the PDCMS deposited films and 2.38 ± 0.01 eV for CBD.

We have found that the deposition rate for CdS obtained using pulsed DC magnetron sputtering was 2.86 nm/s using only 500 W power on a six inch circular target. This is a high deposition rate and much more than an order of magnitude faster than the chemical bath deposition technique. Moreover, we found that we could maintain process stability using 1.5 kW of power which produced a proportionate increase in deposition rate without affecting film quality. In comparison, deposition with RF sputtering is much slower. For example, deposition rates of 0.2 to 0.3 nm/s have been reported for powers in the range of 50 W to 250 W. This is approximately an order of magnitude slower than using pulsed DC power [18]. CBD deposition is also comparatively slow. In our case, it required 30 min to deposit a 50 nm thick film of CdS and 1 h for a 150 nm thick film. The comparative quality of the CdS thin films together with high rates of deposition shows that the pulsed DC magnetron sputtering process has the potential for application in high throughput and low cost manufacturing of solar modules.

Acknowledgements

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References

[5] F. Ouachtari, In Energy band gap, 2.34 ± 0.01 eV and 2.38 ± 0.01 eV for PDCMS and CBD thin films, respectively. Transmittance curve, as inset, for CdS films on TEC10 glass (the sample in the spectrophotometer is positioned letting the light pass through the glass/TEC10/CdS layers).


Oxygenated CdS window layers for thin film CdTe Photovoltaics by pulsed DC magnetron sputtering

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Abstract: Absorption in the CdS window layer limits the photocurrent obtained from thin film CdTe solar cells. These absorption losses can be avoided by tailoring the band gap of the CdS material to improve the light transmission at shorter wavelengths. This can be achieved by adding oxygen to the CdS to create Oxygenated Cadmium Sulphide films (CdS:O). In this paper we report on a new process in which oxygen is incorporated into the thin film CdS during deposition by pulsed DC magnetron sputtering. Spectrophotometric measurements of transmission show that the absorption edge is shifted from 500nm to 350nm by incorporating the oxygen into the deposited films. In this way, light absorption in the window layer of the solar spectrum utilised by the CdTe solar cells was significantly reduced. Ellipsometric measurements showed that the refractive index of the CdS decreased from 2.45 to 2.1 at \( \lambda = 632.8 \text{nm} \) and the band gap shifted from 2.38eV to 3.1eV as a result of incorporating the oxygen into the film. The refractive index dispersion profiles suggest that the oxygenated films are amorphous/semi-amorphous and this was confirmed by X-ray Diffraction measurements and TEM cross-section images.

Index terms : CdTe, CdS, CdS oxygenated, window layer

I. INTRODUCTION

Thin film CdTe is currently the lowest cost photovoltaic (PV) technology with further reductions possible through increasing the conversion efficiency and improvements in module manufacturing techniques. CdS is an important semiconductor material for CdTe thin film PV (TF-PV). It is an n-type material and it is used to form a heterojunction solar cell with the CdTe absorber layer. The optical properties of the CdS are currently limiting the short circuit current density and efficiency of thin film CdTe TF-PV. The main drawback of CdS is its bandgap (2.45eV) which causes absorption losses below 500nm and therefore limits the photocurrent of thin film CdTe devices. One solution to this problem is to deposit a thinner window layer to reduce the losses [1]. Alternatively, the transmission can be improved by engineering the band gap of the CdS layer [2]. It has been shown previously that by adding oxygen to the working gas pressure in an rf sputtering deposition process it is possible to deposit an oxygenated CdS (CdS:O) layer with an improved band gap [3], [4]. Unfortunately, rf magnetron sputtering is not well suited to volume manufacturing due to its low deposition rate and the complexity of matching circuits. In this paper, we report on the properties of thin film oxygenated cadmium sulphide CdS:O deposited at high rates using pulsed dc magnetron sputtering.

II. EXPERIMENTAL

A. Sample preparation

The thin film layers of oxygenated Cadmium sulphide were deposited by using pulsed DC magnetron sputtering (PDCMS) using a “PV Solar” deposition system manufactured by Power Vision Ltd., (Crewe, UK). The system was designed for multilayer thin film deposition and is equipped with up to four 6 inch circular magnetrons mounted vertically around a cylindrical chamber. The system allows deposition of multi-layer stacks under computer control. There is an option to replace one of the magnetrons with a plasma source for reactive sputtering. The samples are mounted vertically on a rotatable carrier, designed for mounting up to four 5cm x 5cm substrates. The carrier rotates typically at 120rpm during the deposition process to provide horizontal uniformity. Vertical uniformity is achieved by placing a detachable mask in front of the magnetron target. Two of the magnetrons are fitted with 6 inch diameter CdS and CdTe planar magnetron targets. The layers of CdS and CdS:O were sputtered at ambient temperature using a pulsed DC power supply (Advanced Energy Inc. Pinnacle Plus 5kW) in an argon/oxygen environment. The 99.999% CdS 150mm circular target was sputtered at 500W using a 2.5us reverse time. The pulsing frequency was set to 150 kHz. At these deposition conditions, the plasma arcing was minimal during the film growth. The CdS:O films were deposited with oxygen supplied to the chamber through a computer controlled mass flow controller. The films were first deposited on 1 mm thick soda lime glass slides to allow the measurement of the optical properties of the materials deposited and the establishment of their deposition rates. Once the process conditions had been optimised, ‘TEC10’ TCO coated glass substrates (NSG-Pilkington) were used.

B. Characterization

The microstructure, composition and optical properties of the deposited CdS:O films have been investigated. STEM was used to investigate the crystalline structure of the deposited films. The STEM imaging was carried out using a FEI Tecnai F20 (S) TEM. The images were obtained using a Bright Field detector at 200 kV. The TEM samples were prepared by Focused Ion Beam (FIB) milling using a dual beam FEI Nova 600 Nanolab. A standard in situ lift out method was used to prepare cross-sectional samples through the coating into the glass substrate. A platinum over-layer was deposited to define the surface of the samples and
homogenize the final thinning of the samples, down to 75nm.
A high resolution field emission gun scanning electron microscope (FEGSEM) Leo 1530 VP FEG-SEM, was used to investigate the microstructure of the deposited thin films. The refractive index, extinction coefficient and thickness of the deposited films were measured using a Horiba Jobin Yvon UVISEL iHR320FGAS spectroscopic ellipsometer. The transmission of the deposited CdS:O thin films on a glass slide was measured using a Varian Cary 5000 UV-Vis-NIR spectrophotometer.
The crystalline structure of the sputtered films was measured using X-ray diffraction (XRD). The XRD measurements were performed using a Bruker D2 Phase bench-top XRD system.
X-ray Photoelectron Spectroscopy (XPS) surface chemical analysis was performed using a Thermo Scientific K-Alpha XPS system. The XPS measurements provided information about the chemical composition of the sputtered thin films of CdS:O.

III. RESULTS
A range of CdS:O films were deposited using different oxygen flow rates during the deposition. Fig. 1 shows a composite image of a range of CdS:O films deposited using different oxygen gas flows (2sccm - 10sccm). The films were deposited on to a 1mm thick soda lime glass substrate. A direct comparison between the deposited thin films on glass shows that the colour of the deposited film changes from orange to almost completely transparent as the oxygen gas flow is increased.

![Fig. 1 Images of CdS:O films deposited using increasing oxygen gas flows.](image1)

**A. TEM analysis**

![Fig. 2 BF-TEM image of thin film CdS cross section deposited on TEC 10 without the addition of oxygen at 750W and 10sccm Argon flow.](image2)

A BF-TEM image of a CdS cross section deposited by pulsed DC magnetron sputtering is shown in Fig. 2. The use of pulsed dc magnetron sputtering to deposit CdS has been reported elsewhere [5]. The BF-TEM image shows that the material has a structure consisting of grains extending through the thickness of the material and crystallites with a semi-amorphous structure which coalesce forming columnar structures which extend through the thickness of the CdS layer.

Fig. 3 shows BF-TEM cross section images of CdS:O films deposited using increasing oxygen flows. Addition of oxygen to the deposition plasma resulted in the growth of amorphous films. The types of crystallites which were present in the BF-TEM image of the CdS film (Fig. 2) are only visible in the image of the film deposited using 2 sccm flow of oxygen.

![Fig. 3 BF-TEM cross section images of CdS:O films deposited on TEC10 using increasing O2 gas flows during the deposition.](image3)

Fig. 4 shows a BF-TEM cross section image of a CdS:O film grown on TEC10 using a 10 sccm oxygen flow. The thin film is amorphous. The influence of incorporating oxygen in the CdS film is clear by comparing the images in Fig. 2 and Fig. 4. The cross section also shows that the films are compact and that they provide uniform coverage of the TEC 10 substrate surface. No voids were detected at the interface and no voids or pinholes were present in the deposited material.
Fig. 4 BF-TEM image of a 200nm thick CdS:O thin film cross section on TEC10. The film was grown at 10 sccm oxygen flow during the deposition.

B. SEM analysis

Fig. 5 presents SEM surface images of the CdS:O films deposited by pulsed DC magnetron sputtering at various oxygen gas flows. The BF-TEM analysis showed that the oxygenated films were amorphous. However, the SEM images of the surface show that the material coalesces and forms a granular structure. The size of these grains increased when the oxygen flow rate used during the film growth was increased. The SEM images and BF-TEM cross sections show that the morphology of the surface is affected by the substrate but it is also dependent on the deposition conditions used. The analysis shows that when oxygen flow rate is increased, the average grain size at the surface increased from ~170nm to ~230nm for the film deposited at 10sccm O2 flow rate.

C. Spectroscopic Ellipsometry

Spectroscopic ellipsometry measurements of the deposited samples were carried out to measure the thickness and the dispersion of the refractive index. Fig. 6 shows the dispersion measured for each of the deposited films. The films deposited using lower oxygen gas flows showed two distinct peaks in the refractive index dispersion. The two peaks gradually merged into one broader peak as the oxygen flow was increased during the deposition. This is caused by the decrease in the thin film crystallinity [6]. The refractive index of the films decreased as result of the addition of oxygen to the deposition plasma as shown in Fig. 7.

Fig. 6 The measured refractive index (n) dispersion of CdS:O films deposited using different O2 flows.

Fig. 7 The refractive index at 550nm for films deposited using different oxygen flow rates during the sputter-deposition process.

The deposition rates were calculated from the film thickness measurement obtained by spectroscopic ellipsometry. Fig. 8 shows the deposition rates measured for films deposited using different O2 flows. The deposition rate of the films decreased as the oxygen flow rate was increased. The deposition rate varied from ~2.4nm/s to ~1.4 nm/s as the flow of oxygen was increased from 0sccm to 10sccm. The power supplied to the magnetron target was fixed for these measurements at 500W.

Fig. 5 SEM images of the deposited CdS:O films using different O2 gas flow rates. The grain size increased with increasing oxygen gas flow.
D. **UV-Vis-NIR Spectrophotometer**

The optical transmission of the films was measured using a spectrophotometer. Fig. 9 shows the transmission measured for films deposited at different O$_2$ flow rates. The thickness of the deposited films was kept constant for all samples. However, due to the change of refractive index as a result of the oxygen addition into the film the dispersion characteristics changed. This, in turn, affected the transmission of the films. The transmission data shows a strong blue shift of the absorption edge as the oxygen gas flow rate was increased during the film growth. The absorption edge shifted from ~500nm down to ~350nm for the thin film deposited using a 10sccm oxygen flow.

The band gap of the deposited material was calculated from the transmission data using the Tauc’s plot method [7]. The band gap calculations are shown in Fig. 10. The band gap of the deposited CdS:O films increased from 2.38eV to 3.1eV as more oxygen was incorporated in the thin films during the deposition. The relationship between band gap and the oxygen gas flow used is shown in Fig. 11. The graph shows that the band gap of the deposited material can be accurately controlled during the deposition through simple control of the oxygen flow through the mass flow controller.

E. **XRD**

The XRD spectrum of a CdS film deposited using the same conditions but without O$_2$ flow is plotted for reference in Fig. 12.
Fig. 13 XRD Spectra of CdS:O deposited at different oxygen flow rates.

Fig. 13 shows a sequence of XRD spectra measured for the range of deposited CdS:O films. The structure of the thin films sputtered with and without oxygenation was found to be in the more stable hexagonal crystalline structure. The intensity of the peaks decreases as a result of adding O₂ to the deposition plasma and the films became amorphous for higher oxygen flow rates. This is a similar to behaviour reported for the rf sputtered CdS:O films [3].

XPS was used to measure the composition of the deposited films. The surface of the sample was etched with a low current ion beam for 30 seconds prior to the measurements to remove ~20nm of atmospheric contamination and to expose the deposited thin film. Fig. 14 shows how the atomic composition of the deposited films changed with the oxygen flow rate used. The oxygen concentration increased up to 33% when the oxygen was added to the deposition plasma using a flow rate of 10 sccm. The cadmium level was constant for all the samples at ~50% and the sulphur concentration decreased as the oxygen flow rate was increased during the deposition. A chemical shift occurs in the XPS sulphur peak which depends on its bonding. The cadmium sulphide peak occurs at ~161.5eV and the sulphate peak is found at ~169eV [8]. An XPS sulphur spectrum for a film deposited with 2sccm of oxygen is shown in Fig. 15 and the spectrum shown in Fig. 16 corresponds to a film deposited using 10sccm of oxygen in the plasma.

Fig. 14 Atomic concentrations (XPS) of Cd, S and O in the deposited CdS:O films as function of O₂ gas flow used.

Fig. 15 An XPS spectrum of the sulphur peaks measured for a CdS:O sample deposited using a 2 sccm O₂ flow rate.

Fig. 16 An XPS spectrum of the sulphur peaks measured for CdS:O sample deposited using a 10 sccm O₂ flow rate showing the presence of cadmium sulphate.

The XPS spectrum for the CdS:O film deposited using a 10sccm flow rate shows two distinct peaks related to the formation of cadmium sulphate. The film deposited at 10 sccm had a sulphur concentration of 24%. Approximately 6.5% of this sulphur was in form of cadmium sulphate. Cadmium sulphate was detected in all CdS:O films deposited using O₂ flow rates above 2 sccm.
Oxygenated CdS films for CdTe TF-PV applications were successfully deposited by using pulsed DC magnetron sputtering. The process was highly stable using a pulse frequency of 150 kHz and a 2.5 μs pulse reverse time. No plasma arcing was detected. A range of CdS:O films were deposited by using O₂ flows from 1 sccm to 10 sccm during the deposition process. STEM analysis was used to analyse the crystalline structure of the deposited films. The films showed the presence of small crystallites for the lower oxygen flows similar in appearance to those observed in CdS films [5]. For higher O₂ flow rates, the films were amorphous. The SEM analysis of the surface of deposited films showed that the crystallites coalesce to form a granular structure at the surface. The BF-TEM analysis shows that these extend through the thickness of the material. The grain size increased with the oxygen flow from 170 nm to 230 nm. Transmission measurements showed that the addition of oxygen results in a blue shift of the absorption edge from 500 nm to 550 nm due to the widening of the bandgap of the deposited material. Detailed Tauc’s plot analysis showed that the incorporation of oxygen into the deposited films caused the band gap to be widened from 2.38 eV to 3.1 eV thereby eliminating absorption losses that would otherwise occur in the CdS window without oxygenation. This results in a useful increase in photocurrent [3], [4]. The spectroscopic ellipsometry analysis showed that the refractive index of the deposited film decreased from 2.57 to 2.17 at λ=550 nm as the O₂ flow was increased. The deposition rate of the CdS:O decreased as the O₂ flow was increased. The refractive index dispersion measured for the films deposited at lower oxygen flow showed two distinct peaks. The peaks gradually merged into one broader peak as the oxygen flow increased as the films become more amorphous. The XRD measurements showed that deposited films are hexagonal and the peak diminishes as more oxygen was added to the deposition plasma. The XPS analysis showed that the oxygen content in the film increased up to 33% as more oxygen was added to the deposition plasma. The concentration of cadmium was unaffected at 50% and the concentration of sulphur was reduced. Cadmium sulphate formation was detected for films deposited using O₂ flow rates above 2 sccm. The deposition process was stable and allows deposition of the films at high deposition rates. The addition of O₂ to the deposition plasma allows precise control of the films properties such as refractive index and band gap. Importantly, the deposition rates achieved using pulsed dc magnetron sputtering with only 500W of power to the magnetron target were in the range ~1.4 nm/s ~2.4nm/s, depending on the oxygen flow rate used. This is a high rate of deposition and much faster than can be achieved using rf sputtering. It could be further increased by simply increasing the power to the magnetron. This makes a pulsed DC magnetron sputtering process feasible for the deposition of an improved oxygenated CdS window layer for high efficiency CdTe devices. The combination of tight control of the band gap and associated increases in photocurrent together with the high rate of deposition makes the use of pulsed DC magnetron sputtering a commercially attractive process for high volume manufacturing of thin film CdTe photovoltaic modules.

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