Solution processing of thin films for solar cell applications: Culn(S,Se)₂, Cu(In,Ga)(S,Se)₂ and ZnO:Al

by

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Abstract

Cu(In,Ga)(Se,S)₂ (CIGS) solar cells have attracted a lot of attention due to their high performance and the prospect for lower manufacturing costs over conventional crystalline silicon solar cells. All recent record efficiency CIGS absorbers have been deposited using vacuum processing which introduces high manufacturing costs. CIGS can also be compatible with low cost, atmospheric processing which can significantly reduce manufacturing costs.

Recently, there has been some progress in developing atmospheric solution-based processes for CIGS. Among different solution approaches, deposition of molecular precursors can be advantageous in terms of simplicity and straightforward compositional control. Nonetheless, the developed methodologies involve highly toxic reagents or large impurity content in the device, limiting the potential for commercialisation.

This thesis describes the development of a novel solution-based approach for the deposition of CIGS absorber layers. Metal chalcogenides are used as the starting precursors, which are free from detrimental impurities. These compounds contain strong covalent bonds and, consequently, they are insoluble in common solvents. Until recently, hydrazine, which is highly toxic and explosive, was the only solvent to effectively dissolve these types of precursors, limiting the feasibility of this approach for industrial applications. In this work, metal chalcogenides are dissolved in a safer solvent combination of 1,2-ethanedithiol and 1,2-ethylenediamine, completely eliminating hydrazine from the process. By using this solvent system, optically transparent solutions are formed which exhibit long-term stability. The precursor solutions are decomposed cleanly and they are converted to single phase CIGS upon selenisation.

Culn(S,Se)₂ solar cells with power conversion efficiencies up to 8.0% were successfully fabricated by spray depositing the precursor solution, followed by a selenisation step. This progress has been made by continuously optimising the deposition, drying, and especially the selenisation configuration. Among other parameters, the working pressure during selenisation was found to have a dramatic

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effect on the material crystalline quality. Rapid thermal processing was also explored as an alternative selenisation configuration to tube furnace annealing and it was shown to improve the back contact/absorber interface.

It has been demonstrated that Ga can easily be incorporated in the absorber for band-gap tuning and, consequently, for V_{OC} enhancement of the solar cells. The structural properties of the films were investigated with Ga content, as well as the opto-electronic characteristics of the corresponding solar cells. The band-gap of the material was conveniently varied by simply adjusting the precursor ratio, allowing for fine compositional control. By using this technique, Cu(In,Ga)(Se,S)₂ solar cells with conversion efficiencies of up to 9.8% were obtained.

The solar cell performance in this work is limited by the porosity of the absorber and the back contact quality. Despite a significant improvement during the course of this work, the remaining porosity of the absorber causes selenium to diffuse towards the back forming a thick MoSe₂ layer and causing a high series resistance in the device.

A low cost, solution-based technique was also developed for the deposition of aluminium-doped zinc oxide films that can be used as the transparent conductive oxide layer in thin film solar cells. This methodology involves the use of an ultrasonic spray pyrolysis system, which is a very versatile and easily controlled deposition technique. Although the presence of oxygen makes the film closer to stoichiometric (fewer oxygen vacancies) good electronic and optical properties have been obtained by process optimisation. Films deposited with optimum conditions exhibited a sheet resistance of 23 Ω /sq, which can be further reduced by increasing the thickness with minimal transmittance losses.

The simplicity, low toxicity and straightforward control make the proposed methodologies extremely potential for low cost and scalable deposition of thin film solar cells.

Keywords: thin film solar cells, solution processing, CIGS, low cost, aluminium doped zinc oxide, spray deposition.

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List of publications

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- C.S. Cooper, P. Arnou, L. Wright, S. Uličná, J.M. Walls, A. V. Malkov, J.W. Bowers, A novel approach for fabrication of Cu₂ZnSnSe₄ absorber layers using solutions of elemental metal powders, Submitted to: Thin Solid Films (2016).

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Nomenclature

AM	Air Mass
AR	Anti-reflective
AZO	Aluminium-doped zinc oxide
CBD	Chemical bath deposition
CGI	Cu/(Ga+In) ratio
CIGS	Copper indium gallium diselenide
c-Si	Crystalline silicon
CVD	Chemical vapour deposition
DC	Direct current
DMSO	Dimethyl sulfoxide
EA	Ethyl acetate
EDA	1,2-ethylenediamine
EDS	Energy dispersive X-ray spectroscopy
EDT	1,2-ethanedithiol
Eg	Band-gap
EQE	External quantum efficiency
FF	Fill factor
FTO	Fluorine doped tin oxide
FWHM	Full width at half maximum
GGI	Ga/(Ga+In) ratio
HR	Highly resistive
ICDD	International Centre for Diffraction Data
lo	Saturation current
I _{ph}	Photocurrent
JCPDS	Joint committee on powder diffraction standards
J _{mpp} / V _{mpp}	Current density / Voltage at maximum power point
J _{sc}	Short circuit current density
JV	Current density-voltage
LPM	Litres per minute
MEK	Methyl ethyl ketone
ODC	Ordered defect compounds

PCE	Power conversion efficiency	
PID	Proportional integral derivative	
P _{in}	Incident power	
PL	Photoluminescence	
PTFE	Polytetrafluoroethylene	
PV	Photovoltaics	
PVD	Physical vapour deposition	
QE	Quantum efficiency	
R2R	Roll-to-roll	
RF	Radio frequency	
R _p	Shunt resistance	
rpm	Revolutions per minute	
Rs	Series resistance	
R _{sheet}	Sheet resistance	
RTP	Rapid thermal processing	
SEM	Scanning Electron Microscopy	
SLG	Soda lime glass	
STC	Standard test conditions	
тсо	Transparent conducting oxide	
ТЕМ	Transmission Electron Microscopy	
TFPV	Thin film photovoltaics	
TFSC	Thin film solar cells	
TGA	Thermogravimetric analysis	
THF	Tetrahydrofuran	
USP	Ultrasonic spray pyrolysis	
v/v	Volume to volume ratio	
V _{oc}	Open circuit voltage	
XPS	X-ray photoelectron spectroscopy	
XRD	X-ray diffraction	
α	Absorption coefficient	

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Chapter 1 Introduction

The increasing global energy demand and climate change caused by greenhouse gas emissions is now a widespread concern [1]. The prime source of electricity comes from fossil fuels, the use of which has had severe consequences on the environment. The combustion of fossil fuels is the principal contributor to greenhouse gas emissions, which accelerate global warming [2,3].

Renewable energy resources have the potential to meet the global energy demand as well as mitigate our contribution to global warming. Renewable energy technology is steadily maturing and its share of energy generation has been increasing in the last few years [1]. Among the different renewable energy resources, solar energy is the largest and the most abundant source. Fortunately, the solar radiation reaching the Earth's surface far exceeds the energy demand of the entire planet [4], which shows the huge potential that photovoltaics (PV) possess as a solution to the high energy demand.

Interest in PV technology has increased rapidly through time. It was predicted that solar electricity will contribute about 20% of the global electricity supply by 2050 and over 60% by 2100 [5]. The worldwide growth of this technology is based on the increasingly favourable economics, since solar cell costs have been decreasing in the past few years. Also, efficiencies for commercial PV modules are continuously increasing, leading to a lower cost-per-watt ratio, which is an important factor for stabilising this technology [1].

Polycrystalline Si solar cells are the market-leading PV technology to date, although thin film solar cells (TFSC) are approaching their efficiency [1]. TFSC serve as a promising alternative to the wafer-based cells, as they can be compatible with low cost manufacturing processes.

The following sections of this chapter will provide an introduction to the PV operating principles and the common PV technology. The concept of TFSC will be introduced

as an alternative PV technology with the potential to overcome the limitations of the existing wafer-based systems. Finally, this section will include an overview of copper indium gallium diselenide (CIGS) solar cells, which is one of the most promising thin film technologies to date.

1.1 Introduction to Photovoltaics

Converting the abundant solar energy directly into electricity is a very attractive option for sustainable production of electrical energy. The sun is an enormous energy source and the challenge is to utilise this energy as much as possible. Based on the estimated solar irradiance of about 1370 W/m^2 [6] and considering the energy losses due to reflection and absorption by the atmosphere, the energy delivered by solar radiation at the surface of the Earth is equivalent to more than 10000 times the current global energy demand [4]. In order to effectively use this colossal amount of energy, sunlight harvesting needs to be optimised. As such, it is essential to develop an understanding of the solar spectrum and the spectrum that eventually reaches the ground level of the Earth.

The sun is an energy source with a radiation spectrum comparable with the spectrum of a black body at about 6000 K [7]. However, the spectrum of light that arrives at the Earth's surface is different due to atmospheric attenuation. The spectrum at the ground level also varies with location, time of day and local environmental conditions [6]. This makes the optimisation of energy harvesting and yield prediction highly complex and as a result, most systems are optimised for the standard AM1.5G spectrum.

Air Mass 1.5 Global (AM1.5G) is a standard reference spectrum (Figure 1) used for the evaluation of PV technologies, according to the standard test conditions (STC), as defined by the IEC Standard 60904-3:2008 [8]. STC assume an irradiated power density of 1000 W m⁻² with an AM1.5G spectrum at 25 °C [7].

The AM initials stand for air mass, which is indicative of the mass of air between the surface and the sun. Since the spectral distribution and intensity of sunlight is affected by the thickness of the atmosphere through which light travels, this value is associated with the light intensity. Longer optical paths result in more light deviation

due to higher absorption and reflection in the atmosphere. The length of the distance that the light travels through in the atmosphere (given as a multiple of average atmospheric thickness) is indicated by the x coefficient of AMx, which is defined as [7]:

$$Air Mass = \frac{I}{\cos\theta_z} \tag{1.1}$$

Where θ_z is the angle of the sun with reference to the zenith (when the sun is positioned directly overhead). The larger the value of x, the longer the optical path and subsequently the greater the air mass between the sun and the surface of the Earth. AM1.5G corresponds to the solar spectrum with a solar angle of $\theta_z = 48.19^{\circ}$. Here, the path of the sunlight equals to $1/\cos(48) \sim 1.5$, which means that it is 1.5 times longer than the path at normal incidence. Similarly, when the sun is directly overhead, the Air Mass is denoted as 1 (or AM1) and the extra-terrestrial solar spectrum is denoted as AM0, since the light does not pass through the Earth's atmosphere [7].



Figure 1: Reference solar spectral irradiance (AM1.5G) [8].

Over the last few decades, the performance of PV technology has improved, whilst associated costs have decreased significantly. The starting point for the development of solar cells was the discovery of the photovoltaic (PV) effect, which dates back to Becquerel's paper in 1839 [9]. This discovery triggered the

development of materials which exhibit the PV effect, with the first solar cell produced in 1877 [10]. Research on PV continues until today, with the efficiency constantly increasing, resulting in a decreased cost per watt ratio. As a result, over the last few decades the use of solar cells as a means of energy generation has increased dramatically. It is expected that this exponential growth of the solar cell market will continue for the coming decades [5], taking into account the strongly increasing demand for electrical power. PV cells provide an energy source with continuously improving technology and growing relevance in the global energy scene.

1.1.1 Photovoltaic operating principles

Solar cells are semiconductor devices which absorb photons and convert them into electric current. The PV effect involves the formation of a potential difference at the junction of two different materials, in response to radiation. The cell typically consists of a metallic back contact, a semiconductor p-n junction to absorb light and the top contact, which is transparent for most of the solar spectrum [11]. The basic structure of p-n junction solar cell is shown in Figure 2 (a). The p-n junction is formed by two semi-conductors being in close contact with each other, one being an n-type and the other p-type material. P-type materials are altered so that they contain a significant number of holes available for conduction and conversely, n-type materials to contain electrons. This is done by introducing specific impurities (dopants) to the material, called donors and acceptors [12]. For example, silicon is made as p-type when doped with group three elements of the periodic table (such as boron) or n-type when doped with group five elements (such as phosphorous) [12]. Doping a semiconductor changes the average electron energy, known as Fermi level [12].

In thermal equilibrium there is no net current flow [12]. However, the difference in the concentration of holes and electrons between the two semiconductors causes a thermodynamically unstable situation, while the Fermi level of each semiconductor is different. As a result, electrons from the n-type material and holes from the p-type material flow in opposite directions [12]. Once the Fermi level is equal on both sides of the junction, the flow of charge carriers ceases. The two charged regions around the junction are known together as the "space charge region" or the "depletion region", since they are effectively depleted of holes and electrons at the n-type and

the p-type side, respectively [12]. The formation of the depletion region is depicted in Figure 2 (b).



Figure 2: (a) Basic structure of a p-n junction solar cell, (b) Diagram of a p-n junction, showing the formation of the depletion region.

The band-gap energy (E_g) of a semiconductor is the minimum energy required to excite an electron from the valence band to the conduction band. Consequently, band-gap defines how many charge carriers are generated from photons with energy equal or higher than the band-gap. A low band-gap maximises the number of photons contributing to the short-circuit current density (J_{sc}) of the solar cell, however, this is counter-balanced by the lower voltage of the solar cell [13]. Wide band-gap absorbers only utilise a small proportion of the solar spectrum, thereby the J_{sc} is small and the voltage is high. Therefore, there should be an optimum band-gap value for maximum power conversion efficiency [13]. This is described by the Shockley-Queisser (SQ) limit, according to which the optimum band-gap energy is in the range of 1.1-1.45 eV, resulting in maximum conversion efficiencies of around 33% with un-concentrated sunlight [14].

The current density-voltage (JV) characteristics of a crystalline silicon (c-Si) solar cell measured at STC are shown in Figure 3, along with the main parameters used for describing them. The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), current density and voltage at the maximum power point (J_{mpp} and V_{mpp} , respectively) are indicated on the curve. The maximum power point defines a

rectangle whose area, given by $P_{mpp} = V_{mpp}$. I_{mpp}, is the largest on the JV curve [12]. The most important figure of merit for a solar cell is its power conversion efficiency, η , which is defined as [12]:

$$n = \frac{P_{MPP}}{P_{in}} = \frac{FF V_{OC} I_{SC}}{P_{in}}$$
(1.2)

P_{in} is the incident power and FF is the fill factor, which is described by [12]:

$$FF = \frac{P_{MPP}}{V_{OC}I_{SC}} = \frac{V_{MPP}I_{SC}}{V_{OC}I_{SC}}$$
(1.3)

The fill factor, FF, is a measure of the "squareness" of the JV curve and it always equals less than one [12].



Figure 3: An example of a JV curve of a c-Si solar cell (AM1.5G illumination, 1000 W m⁻²).

The electrical properties of solar cells are described by an equivalent circuit, shown in Figure 4 and described by Equation 1.4. The equivalent circuit is described by a current source, (I_L), a diode and two resistors in series and in parallel, respectively [13]. The resistor in parallel with the diode represents the shunt resistance (R_p), which accounts for the shunts which can occur in a real solar cell, at pinholes in the p-n junction or at grain boundaries. The series resistance (R_s) accounts for all the voltage drops across the solar cell [15]. An approximation of the magnitude of the series and parallel resistances may be calculated from the slope of the I-V curve at open and short circuit, respectively.



Figure 4: Equivalent circuit of a pn-junction solar cell.

$$I = I_0 \left(exp\left(\frac{V + IR_s}{k_B T}\right) - 1 \right) + \frac{V + IR_s}{R_p} - I_{ph}$$
(1.4)

1.2 PV technologies

PV technology undoubtedly has a valuable contribution to the challenges of carbon emission mitigation and energy security. The PV industry has in fact experienced a dramatic growth, achieving a global market size of 31 GW in 2012 with an average increase rate of 48% per year [16]. Wafer-based technologies and specifically c-Si dominate the PV market, with a share of over 85% [17].

Although a significant cost reduction has already been achieved to date compared to the last decade, wafer-based PV is still a relatively expensive choice for power generation. The manufacturing costs for this technology are high, due to the poor silicon feedstock utilisation and the high energy requirements associated with processing discrete wafers [17]. Also, silicon is an indirect band-gap material with a low infrared optical absorption coefficient, and as such large substrate thicknesses on the order of >25 µm are required to absorb a high number of photons [17]. Further cost reductions are required for PV electricity to be cost-competitive with the established grid electricity rates, and reach "grid parity". It was estimated that the cost of c-Si modules needs to be reduced to as low as US\$0.50/watt peak (Wp) for subsidy-free utility-scale adoption [16]. Despite the price decrease in the past few years, the current PV module costs still exceed this figure [18]. In order to further reduce the manufacturing cost, silicon utilisation needs to be increased, the

manufacturing processes streamlined and the efficiency improved further, which requires ongoing research and development. Nevertheless, the high purity, the high crystalline quality of silicon and the robust research and development on these systems have led to record cell and module efficiencies of 25.6% [19] and 22.9% respectively [20].

Using materials which require a significantly lower energy input can potentially result in further cost savings. Direct band-gap materials can be much thinner, leading to lower material costs. Solar cells that fit these criteria are called "thin film" solar cells and they are characterised by a thickness ranging from 10 nm to about 10 µm [21]. An additional market opens up when thin film photovoltaics (TFPV) are not only deposited on rigid substrates but on flexible substrates as well, such as plastic or stainless steel foils. These lightweight structures can further reduce the cost per watt of the module since the price of the glass substrate (in the case of rigid modules) accounts for a large proportion of the overall module cost [22]. Also, this type of PV can be building-integrated and is consequently very attractive from a manufacturing viewpoint.

TFPV are also associated with a reduced number of processing steps and interconnect materials, which translates to further cost savings. In contrast to the processing of Si wafers into individual solar cells, TFSC are formed from a stack of layers coated onto a substrate and then patterned into cells and modules, a process called "monolithic integration".

Long-term stability is another important factor for commercialisation. While less studied, CIGS [23] and cadmium telluride (CdTe) thin film modules were shown to have equivalent long-term stability to that of c-Si, with a very constant output over a period time [24]. TFPV technology is therefore a very promising alternative to c-Si, offering a comparable reliability and durability [25].

TFPV accounted for 12% of the total PV market in 2010, an increase from 6.5% in 2005 [26]. Among the TFPV market share, more than 70% is represented by First Solar Inc., who produces CdTe modules. The remaining portion of the market is divided between the other two main commercial TF technologies: amorphous silicon and CIGS [26].

TFPV are generally considered to have a significant potential for cost reductions, provided that the production facility sizes and efficiencies are increased. It is anticipated that the share of TFPV production capacity in the PV market will increase to 30% by 2020 [26]. Cell and module efficiencies have also been improving over recent years. The champion module efficiencies of CdTe and CIGS are both currently at 17.5%, bridging the efficiency gap between wafer based crystalline-Si PV and TFPV technologies [20]. The average module prices have been decreasing from about \$2.75/Wp in 2005 to \$1.35/Wp in 2010 and are currently approaching a cost of \$0.75/Wp (for CdTe) [26]. The target cost of around US\$0.50/Wp is believed to be achievable across TFPV technologies [26].

TFPV have the potential to be a major source of electricity at competitive prices; however, they do suffer from some limitations. Firstly, they still exhibit lower energy conversion efficiencies than the wafer based technologies, although the efficiency gap is closing. Secondly and most importantly, there is a lack of turn-key production lines for thin film materials [26]. This prevents the PV manufacturers from rapidly setting up a factory with a proven process, as is the case for c-Si PV. The success of companies like First Solar with CdTe-based modules and Solar Frontier with ClGS-based modules, however, suggests that marketing will not be a problem [27].

In addition, concerns over scarcity (and consequently high price) of some TFPV component materials have been increasingly highlighted as potential barriers to further market expansion and cost reductions of TFPV. In particular, major concerns have been raised for indium (In) and tellurium (Te) availability and potential risks for the TFPV technologies that utilise them, i.e. CdTe and CIGS [26]. It has been estimated, however, that the availability of In and Te is sufficient to supply a significant proportion of future PV market growth, at least in the next couple of decades. This is based on the continuous reduction of the amount of indium that is needed, in combination with recycling of these materials [26].

Lastly, despite the cost benefits, the fabrication process of TFPV still utilises high vacuum-based deposition equipment, which requires a high capital investment [28]. But as will be seen in later sections, TFPV are actually compatible with low cost, atmospheric processing and are therefore very promising in terms of low cost PV manufacturing.

1.3 CIGS solar cells

There is a wide range of materials that can be used to form a solar cell, including binary, ternary or quaternary compounds which can be produced using different techniques [29]. Among TFSC, the most commonly used materials are a-Si:H, CdTe and CulnSe₂ along with its alloys, commonly referred to as CIGS. CIGS thin-film solar cells have been investigated in the present thesis. Of all thin-film solar cells, CIGS devices have yielded the highest energy conversion efficiencies to date, up to 22.3% (on a 0.5 cm x 0.5 cm cell) [30]. In the following sections, a brief introduction to the CIGS material system alongside a description of the state-of-the-art CIGS solar cell will be given.

1.3.1 Material and solar cell properties

Descriptions of the Cu(In, Ga)(S, Se)² system in the literature are often based on pure CuInSe₂. The ternary phase diagram of the Cu–In–Se system has been extensively studied [31,32]. The phase diagrams of the other ternary compounds leading to the pentenary alloy Cu(In, Ga)(Se, S)₂ are qualitatively similar to that of CuInSe₂ and so they will not be discussed here [33–35].

Among the ternary phase diagram of the Cu–In–Se system, the required phase for a solar cell is the tetragonal chalcopyrite phase, which is closely related to the cubic zincblende structure. The unit cell of the chalcopyrite is shown in Figure 5. The ratio of the lattice parameters c/a, is close to 2. Cu–Se and the In–Se (or Ga–Se) bonds differ in length and therefore there is a deviation from c/a = 2 in CuInSe₂. This is known as tetragonal distortion [23].



Figure 5: The unit cell of the chalcopyrite lattice structure [23].

Of all the phases of the Cu–In–Se system, the ones that are of interest for solar cell applications have compositions that fall on the tie-line between Cu₂Se and In₂Se₃ [23]. A phase diagram along the Cu₂Se–In₂Se₃ pseudobinary section is shown in Figure 6 [36]. The chalcopyrite CuInSe₂ phase is located on this line as well as a number of phases called ordered defect compounds (ODC). ODC have a lattice structure described by the chalcopyrite structure with an ordered insertion of intrinsic defects. Here, α is the chalcopyrite CuInSe₂, δ is a high-temperature (HT) phase with the sphalerite structure, and β is an ODC phase [23]. Interestingly, the single phase field for the chalcopyrite CuInSe₂ phase at low temperatures is relatively narrow and does not contain the composition 25 at. % i.e., the CIGS alloy is non-stoichiometric. On the Cu-rich side of the phase diagram, α -CuInSe₂ exists as a mixture with Cu₂Se. It was reported that a slight solubility exists between these two phases [37], though segregated mixtures are more often observed, with Cu₂Se present on the surface of the CuInSe₂ layer [38].

CuInSe₂ can be alloyed in any proportion with CuGaSe₂, thus forming Cu(In, Ga)Se₂. In high-performance devices, Ga/(Ga+In) ratios are typically varied from 0.2 to 0.3 [23]. One of the beneficial characteristics of CIGS is its ability to accommodate large variations in composition without appreciable differences in optoelectronic properties. In particular, when alloying CuInSe₂ with CuGaSe₂ for the formation of Cu(In,

Ga)Se₂, the existence range of the chalcopyrite phase is enlarged [39]. Similarly, the increase in the chalcopyrite phase was also reported with the addition of Na [23].



Figure 6: Cu-In-Se ternary phase diagram along the In_2Se_3 -Cu₂Se pseudobinary tie line, for compositions around the CuInSe₂ chalcopyrite phase, denoted as α [36].

CulnSe₂ has attracted a lot of interest as an absorber material, due to its very high absorption coefficients of about 10^5 cm⁻¹ over most of the visible solar spectrum which allows the utilisation of low absorber thicknesses for sufficient collection [23]. The band-gap of this material can also be controlled by alloying with S or Ga [40]. Although the band-gap of pure CulnSe₂ (1.04 eV) is lower than the optimal band-gap energy for a single junction solar cell, alloying this material can tune the band-gap to the optimum value. Of the ternary materials in the Cu-In-Ga-Se-S system, CuGaS₂ has the widest direct band-gap at nearly 2.5 eV and therefore sets the upper limit for the band-gap of CIGS [40]. The band-gap of the alloy does not vary linearly with the composition, due to band-gap bowing [41].

In the current high efficiency solar cells, there is a band-gap grading in the absorber by varying the Ga content as a function of depth in the CIGS films. The Ga/(Ga+In) ratio varies approximately from 20 to 35 at.% and it normally increases towards the back of the film [42]. In some cases, there is also an enhanced Ga concentration at the surface of the CIGS layer [43]. It has been shown that varying the composition in this manner increases the V_{oc} compared with non-graded CIGS cells, probably due to reduced back contact recombination [43].

The doping of CIGS is largely determined by intrinsic point defects. CIGS with an excess of Cu is always p-type but In-rich films can be made p-type or n-type. By annealing in a selenium (Se) overpressure, n-type material can be converted to p-type, and conversely, by annealing in a low Se pressure, p-type material becomes n-type. Device-quality CIGS films grown with excess Se, are p-type with a typical carrier concentration of about 10¹⁶ cm⁻³ [23].

1.3.2 State-of-the-art chalcopyrite solar cells

CIGS devices have yielded the highest energy conversion efficiencies to date, among TFSC materials. The record efficiency for a TFSC was obtained by ZSW with 21.7% (for a cell area of 0.5 cm^2) [44]. 22.3% was very recently reported by Solar Frontier, and while its characteristics have not yet been published, the following section will describe the previous record cell. The highest efficiency obtained for a submodule (30×30 cm² size) is 17.8% [45].

The state-of-the-art CIGS solar cell, shown in Figure 7, consists of a stack of thin-film layers deposited on a substrate, e.g. soda-lime glass substrate. The substrate is covered with a thin film of sputtered molybdenum (500-900 nm) which serves as the electrical back contact. The p-n junction of the solar cell is formed by a p-type CIGS absorber and an n-type semiconductor window layer, in this case CdS. The CIGS semiconductor layer (2.5–3.0 µm) is deposited by co-evaporation with a multi-stage process, followed by an alkali treatment. The CdS layer is deposited by chemical bath deposition. The front contact layer is then applied, which is a combination of intrinsic ZnO (50–100 nm) and Al-doped ZnO (150–200 nm) as the conductive layer. Both these layers are deposited by RF sputtering. Finally, a Ni-Al grid is deposited on top of the i-ZnO/ZnO:AI window layer to increase the charge collection. An antireflective (AR) coating on top of the whole cell stack is also evaporated (MgF₂, 105-115 nm). This CIGS solar cell is in the so-called "substrate configuration" and it is illuminated from the ZnO side. The top three layers are therefore collectively referred to as the "window layer". The device characteristics of this record device are summarised in Figure 7 [44].



Figure 7: Left: The standard configuration of a CIGS solar cell. Right: Device characteristics of a world record CIGS solar cell.

The preferred substrate for chalcopyrite-based solar cells is soda lime glass (SLG). The benefits of using SLG as the substrate are manifold. Firstly, SLG has a similar expansion coefficient to that of CulnSe₂ in the temperature of interest for material growth. This eliminates tensile stresses in the film and micro-cracks that could be formed, in the case where a substrate with a lower expansion coefficient is used [23]. Additionally, and most importantly, SLG supplies sodium to the growing chalcopyrite material. The sodium diffusion from the glass into the absorber is believed to improve the grain growth and the cell performance, although the exact effect is not entirely understood yet [29]. It was suggested that sodium improves the solar cell performance by promoting the incorporation of the chalcogen component, by supporting the growth of the MoSe₂ at the back contact and by reducing the diffusion of metals [11].

The sodium diffuses through the back contact, which means that the properties of the back contact should also be carefully controlled. The preferred back contact for CIGS devices is sputtered molybdenum (Mo), because it is stable under the high temperatures needed for the chalcopyrite deposition [29] and it does not add any n-type dopants to compensate p-type doping of CIGS [46]. Mo forms an ohmic contact with the absorber via the formation of an intermediate MoSe₂ layer. The presence of this intermediate layer provides a lower resistance contact for holes and reduces the recombination of electrons at the back contact [47]. A thick MoSe₂ layer, however, can induce an excessive high series resistance in the device [48].

CIGS thin-film solar cells are formed by combining the p-type CIGS absorber with a wide band-gap n-type semiconducting window layer. This window layer is composed of three layers, the first of which is called the "buffer layer". The buffer layer is typically CdS with band-gap energy of about 2.4-2.5 eV. This layer is kept thin (~50 nm) in order to minimise its absorption. The buffer layer has an important effect on the device quality. The use of a chemical bath for the buffer layer deposition contributes to the effect the buffer layer has on the cell performance. Specifically, it was suggested that the use of ammonium hydroxide in the bath during chemical bath deposition (CBD) cleans the chalcopyrite surface of native oxides that might be formed during sample handling in air. Also, Cd is incorporated into the chalcopyrite surface during CBD which creates an effective n-type inversion layer in the near-junction region of the absorber layer [23]. This type inversion is believed to reduce the interface recombination [49].

On top of the buffer layer, a transparent conducting ZnO window layer is deposited which consists of a i-ZnO/ZnO:Al bilayer. The doping of ZnO by Al results in a very high n-doping (in the order of 10²⁰ cm⁻³). This layer is the transparent conducting oxide (TCO) layer and it provides a low resistivity electrical contact for the cell. The highly resistive (HR) intrinsic ZnO layer (sometimes called HR layer or buffer layer [29]) is deposited directly on top of the buffer layer and it typically has a thickness of about 50 nm. The intrinsic layer was shown to improve the quality of the junction and to protect the interface from sputter damage during the deposition of the TCO layer [23]. Both zinc oxide layers are deposited by RF sputtering from ceramic targets.

A current collection grid is commonly deposited on top of the TCO layer in order to contact laboratory test cells. This is a highly conductive Al/Ni bilayer grid which minimises the series resistance of the device. This grid should have a minimum shadow area in order to allow as much light as possible into the device. In order to prevent the Al coming into contact with ZnO and forming a resistive Al₂O₃ interfacial layer, a thin layer of Ni is evaporated first, followed by the evaporation of Al.

For the absorber layer, a p-type chalcopyrite film with a thickness of 2-3 μ m is typically used, although it was shown that high performing devices can be prepared with a thickness of as low as 0.4 μ m [50]. Among the different combinations within the Cu(In, Ga)(S,Se)₂ system, CuInS₂ has a band-gap of 1.53 eV which is close to

the optimum band-gap value for maximum conversion efficiencies for a single junction solar cell. Nevertheless, the best absorber layers to date are typically sulphur (S)-free. This can be partly justified by the fact that the control of S is difficult during deposition and that CuInS₂ is very sensitive to impurities [29]. Cu(InGa)Se₂ has therefore attracted most of the attention for solar cells, with a band-gap of around 1.1-1.3 eV and compositional ratios of 0.88<Cu/(In+Ga)<0.95 and Ga/(In+Ga)~0.3 [23]. It was also reported that for high band-gap devices such as CuInS₂, there is lack of gain in V_{oc} due to unfavourable conduction band offset of the CdS/CIGS layers [51].

Usually, a Cu-depleted surface is attempted, since Cu-rich compositions contain a Cu_xSe phase in addition to $Cu(InGa)Se_2$. Cu_xSe is a conductive material and it can cause serious shunt paths in the device, deteriorating its performance [52]. Segregations of these phases on the surface can be selectively removed by a KCN etch, but this is not desirable because of the high toxicity of the cyanide.

In terms of the deposition technique, high deposition rates, high reproducibility and high compositional uniformity over large areas are required for commercial manufacturing of modules. The most promising approaches that have already been applied in industry can be roughly categorised in two types: vacuum co-evaporation and two step approaches.

Most of the recent record efficiency CIGS absorbers have been deposited using the co-evaporation process. For this approach, all constituents (Cu, In, Ga, and Se) are delivered to a heated substrate (at 400-600 °C) and the CIGS film is formed in a single growth process. This typically involves thermal evaporation from the elemental sources at temperatures greater than 1000 °C for Cu, In and Ga. Different deposition variations have been explored with co-evaporation, using varied elemental fluxes.

The second approach is a two-step process that separates the delivery of the metals from the reaction to form device-quality films. Typically, the Cu, Ga, and In are deposited using low-cost and low temperature methods that facilitate uniform composition. Then the films are annealed in a Se atmosphere at high temperatures (also at 400-600 °C). Although this approach often takes longer than co-evaporation, it is amenable to batch processing and high process rates can be achieved by handling many substrates in parallel [23]. Whilst most of the recent record efficiency

CIGS solar cells have the absorber deposited by co-evaporation process, a simpler methodology like a two-step approach might be advantageous for large scale production of CIGS solar cells.

TFPV have high potential for low cost manufacturing as opposed to c-Si. However, they still lack the huge production volumes and the professional manufacturing that c-Si has gained as a more mature technology. Nonetheless, high volume manufacturing has started within the last decade and the PV market is fast growing. The success of companies such as Solar Frontier with manufacturing capacities at the Gigawatt per year scale, demonstrate the potential CIGS material has for mass production [27].

The low cost potential of CIGS can only be achieved with a deposition technology that meets the necessary criteria; namely low material costs, high throughput and high yield [25]. In-line continuous processing would be ideal for volume production and could further reduce the manufacturing costs [25]. This is difficult to implement for such a complicated system as CIGS, comprising multiple layers and interfaces with several elements involved. Despite the technological innovations in this field, turn-key production lines are still absent, which requires the companies to develop custom-made deposition methodologies and equipment [53]. This adds significantly to the start-up costs for a new CIGS company and it might be an important factor for the low market share of CIGS among the other PV technologies to date. Further research and development is required to improve the fabrication processes and to successfully transfer into high volume manufacturing. A low cost, high throughput and highly reliable fabrication process needs to be developed in order for CIGS to be more competitive with c-Si technologies.

Reductions in the CIGS production costs could be achieved by reducing material consumption, process temperatures and process times, and by decreasing the capital costs [25]. A reduction in the capital costs is of utmost importance as it will lower the risks of starting a new business. By substituting the conventionally used vacuum-based deposition technologies with low cost atmospheric-based equipment, the capital investment can be reduced dramatically, and the real cost potential of CIGS can be realised. Low cost approaches will be introduced in the next chapters of this thesis.

1.4 Scope of this thesis

Research and technical development of CIGS is rapidly approaching a sufficient level to allow this solar cell technology to enter mass production. New manufacturing methods are continuously being developed, and are now becoming established processes for large-scale production. Although this material already has great potential for low cost manufacturing of solar cells, it has not yet been extensively exploited. For the development of a truly successful large-scale manufacturing process, the capital costs need to be further decreased and the production yields improved. This is possible by substituting high vacuum processing with atmospheric, solution-based approaches. The development of a low cost and reliable fabrication method would be a significant achievement for the production of CIGS.

The main objective of this thesis is to develop a low cost, solution-based approach for CIGS deposition. This will be fulfilled by:

- 1. Development of molecular precursor solutions for CIGS deposition.
- 2. Deposition of CIGS layers using a low cost, atmospheric technique.
- 3. CIGS device fabrication and optimisation.
- 4. Material and solar cell characterisation.

The present thesis is therefore structured in the following way. Chapter 2 will provide a literature review on non-vacuum CIGS deposition approaches, along with the key challenges of each approach. Chapter 3 will briefly describe the principal characterisation methods used during this work and the methodologies followed for device processing. Chapter 4 will present the development of a novel, solution-based deposition method for CIGS absorbers. Implementation of this approach in solar cell devices will be shown in chapters 5 and 6. Chapter 7 will present an atmospheric based deposition technique for transparent conducting layers in TFSC. Finally, concluding remarks and an outlook will be given in chapter 8.

Chapter 2 Non-vacuum processing of Cu(In,Ga)(Se,S)₂ thin film solar cells

2.1 Introduction

It has been proven that TFSC can compete favourably with c-Si, especially in large scale installations [25]. In order to commercialise new TFSC plants, however, a combination of factors needs to be taken into account such as the yield, efficiency, materials cost, process robustness, energy consumption and safety. All these factors have a significant impact on the end price [25]. Non-vacuum techniques have important advantages compared to vacuum-based approaches and hence are of significant commercial interest. Some of the main advantages are stated below:

- Non-vacuum deposition equipment is extremely inexpensive in comparison to vacuum-based equivalents. The absence of high vacuum parts such as vacuum chambers, load locks, pumps and power units decreases the capital costs of the manufacturing equipment significantly.
- Solution-based approaches such as printing, doctor blade coating and stamping can reach very high deposition rates [54]. High deposition rates make these processes high-throughput and compatible with roll-to-roll (R2R) processing of flexible substrates [54]. Vacuum-based approaches are typically more time consuming due to pumping down and venting procedures.
- Module production costs are dominated by the efficiency of material utilisation, especially for large scale production [25]. High vacuum based deposition methods typically have low material utilisation because of the unintentional deposition on the vacuum chamber walls. For instance, even relatively high efficiency vacuum techniques such as dual rotatable magnetron sputtering can only achieve materials utilisation efficiencies of 75–80% [53]. In contrast, for

atmospheric-based techniques such as printing, the material can be precisely placed to the desired location on the substrate surface allowing for higher utilisation efficiencies (close to 100%).

- It is easier to obtain a uniform composition throughout a large area using nonvacuum based techniques. This is because the final film composition is directly related to the composition of the starting material. Vacuum-based techniques on the other hand, typically involve multiple evaporation/sputtering sources which can result in composition variations.
- Atmospheric-based approaches have the capability of performing with a lower energy input. In some cases a solution-based method can be performed at room temperature, followed by a short post-deposition heat treatment such as rapid thermal processing (RTP) to form the desired material phase. RTP has in fact been applied to highly performing (over 13%) Cu(InGa)Se₂ modules [25]. Vacuum-based processes are typically more energy intensive since the evaporation or sputtering of a material typically requires a high energy input. These processes often occur on a heated substrate, especially when forming chalcopyrite-structured material directly during deposition.

Vacuum techniques introduce challenging issues for low-cost production of large area modules due to processing complexities. Ideally, low cost techniques should be applied to all stages of the cell deposition, thereby enabling these advantages to be fully realised. A considerable amount of work has been conducted for laboratory scale CIGS devices involving one or two functional layers deposited by low-cost methods. Preparation of a fully solution-processed device has been challenging however, especially in relation to the back and front contact layers [55]. Only two groups have managed to successfully fabricate fully solution deposited CIGS devices with a power conversion efficiency (PCE) of greater than 10% [55,56]. In both cases, all the layers of the stack were solution processed apart from the Mo back contact, which was deposited by magnetron sputtering.

Nonetheless, replacing even just the CIGS formation step with a non-vacuum process would yield significant cost-savings. The CIGS absorber layer embodies the highest material costs among the active layers in the solar cell and so the greatest

achievable cost savings will be obtained through increases in the material utilisation efficiency for the deposition of this layer.

Despite the advantages of non-vacuum manufacturing, an additional increase in PCE is needed in order to further reduce the cost of generated electricity and make TFSC more competitive with c-Si. Recent research in CIGS solar cells has been focused on lowering the production costs, as well as increasing the PCE. Various atmospheric approaches have already been demonstrated with efficiencies approaching the equivalent of vacuum-based devices.

The atmospheric-based approaches can be categorised based on the scale of mixing of the starting precursors. These techniques can be divided into two categories (particle-based and solution-based) depending on the presence or absence of solid particles in the precursor ink. Both categories are particularly attractive for large-scale manufacturing due to their compatibility with high throughput deposition techniques such as printing and casting, which are already established in industry [54]. The electrodeposition/electroplating method is an example of a solution-based approach and is a well-established route for high quality chalcopyrite solar cells [57]. Although this technique is highly promising in terms of high deposition rates, low cost and low toxicity (use of water as the solvent); compositional control is challenging due to the different redox potentials and reduction kinetics of the elements involved [58]. The remaining of this chapter will investigate alternative low cost techniques which can further simplify large scale fabrication. Each deposition approach has different benefits, shortcomings and complexities which will be addressed in the following sections.

Figure 8 shows the record PCE obtained so far with each deposition approach for CIGS solar cells. PCEs of 15-17% are achievable using low cost atmospheric-based techniques, which makes these techniques very attractive as low cost alternatives to the conventionally used vacuum methods.

CONVENTIONAL DEPOSITION TECHNIQUES				
High vacuum co-evaporation	22.3%	[30]		
LOW COST DEPOSITION TECHNIQUES				
PARTICLE-BASED APPROACH				
Screen printing	17.1%	[67]		
Spray pyrolysis	4.6%	[61]		
SOLUTION-BASED APPROACH				
Use of metal salts				
Spray pyrolysis	10.7%	[82]		
Doctor blading	7.7%	[73]		
	14.7%	[76]		
Spin coating	13.0% Culn(S,Se) ₂	[76]		
Molecular based approach				
	15.2%	[68]		
Hydrazine route	12.2% Culn(S,Se) ₂	[28]		
Non-hydrazine route	10.1%	[90]		

Figure 8: The record PCE of CIGS solar cells for each deposition approach.

2.2 Non-vacuum Cu(In,Ga)(Se,S)₂ formation

2.2.1 Particulate methods

The particulate-based approaches typically involve the synthesis of sub-micron powders of individual constituents or alloys. The powder is then deposited on a substrate by a simple non-vacuum technique, forming thin and porous particulate layers. This is followed by a thermal treatment, usually sintering, which typically converts the porous layers into dense and polycrystalline films. Particles with a well-defined structure, high degree of purity and tuneable optical and electrical properties can be synthesised [58].

The synthesis of these particles can however be very complicated, especially when a uniform size and composition are required [58,59]. An additional drawback is the layer porosity. In order to obtain a dense and compact film, post-deposition annealing is typically required at temperatures close to the melting point of the material. CIGS alloys have a high melting point, hence annealing has to be done at high temperatures, typically above the working temperature of ordinary SLG [59]. Implementation of organic ligands in the precursor ink is also often required, which makes the densification of the layer even more challenging. Organic ligands (such as oleylamine) are added for colloidal stability but are typically insulating, as they consist of long chain molecules. These bulky organic ligands should therefore be removed to allow carrier transport within the layer. The removal of the ligands often causes further cracking and discontinuities in the film.

The use of ternary or quaternary particles of CIGS would be ideal because it can provide a greater degree of control compared to binary phases. By using CIGS nanoparticles as the precursor, the composition of the nanoparticles can be transferred directly to the film [60]. As a result, any inhomogeneities would only affect the thickness and not the film stoichiometry. Furthermore, for a pure CIGS precursor, no additional treatment would be required to remove by-products. This approach was followed by researchers at the National Renewable Energy Laboratory (NREL), who deposited amorphous CIGS by spray pyrolysis followed by a selenisation step under vacuum [61]. As sintering of such materials is challenging however, there was lack of grain growth, limiting the PCE to 4.6% [61]. The most successful approach to date using CIGS nanoparticles involves oleylamine (OLA) as the capping agent and alkanethiol as the solvent, and gave a PCE of 12% [62].

Efforts were made to substitute OLA with alternative capping agents in order to improve the transport properties of the layers. Metal chalcogenide complexes (MCCs) were used as capping agents instead, through a ligand exchange process which however did not show any improvement compared to the OLA-capped particles [63].

Binary phase nanoparticles can also be used for the preparation of CIGS. These particles typically have a lower melting temperature compared to ternary/quaternary particles, which could facilitate film densification. Metal oxides, metal selenides and
elemental metal particles have all been used as precursors, followed by annealing in Se vapour [64]. Films obtained with metal oxide and selenide precursors exhibited voids and micro cracks. The use of metal particles instead has led to better densification and grain growth, but In_2O_3 was detected as an impurity phase, and was still present after selenisation [64,65].

A more successful approach was followed by the International Solar Electric Technology, Inc. (ISET), involving mixed oxide particles and an aggressive twostage reduction/selenisation treatment [66]. Devices obtained with this technique have a PCE of 13.6%. Another (now defunct) company, Nanosolar, was a leader in the development of particle-based techniques for CIGS. Nanosolar's approach involved mixed selenide nanoparticles and a single-stage annealing treatment. This method resulted in a PCE of 17.1%, which is the highest PCE obtained so far for a CIGS solar cell with the absorber deposited by an atmospheric technique [67].

2.2.2 Solution-based methods

Similar to the particulate methods, solution-based methods involve the deposition of the ink first, followed by a post-deposition thermal treatment. The use of true solutions instead of suspensions simplifies the process, as it eliminates the complicated nanocrystal synthesis or the use of additives. In a real solution, the components are mixed on a molecular scale. The resulting precursor homogeneity allows for a more uniform composition and consequently, a reduced risk of defects [68].

There are, however, many other factors which also need to be considered in order to obtain a high quality material through solution processing. For example, the solvent has to be carefully selected in terms of polarity, reactivity and toxicity [69]. Water is a cheap and environmentally friendly solvent, but unfortunately introduces large oxygen impurities in the film. Organic solvents on the other hand, can eliminate the oxygen but introduce residual carbon into the film [69]. Choice of solvent, precursor material and deposition technique is crucial for the deposition of high quality films and thus requires careful selection.

Solution-based processes can be broadly categorised based on the nature of the starting materials:

1. Metal salt precursors

- 2. Organometallic precursors
- 3. Molecular precursors

In some cases, metal salt based recipes can be considered molecular processes when sacrificial ligands are involved. In this framework, however, the molecular precursors will not include metal salt based techniques. The following sections will expand on each type of precursor.

2.2.2.1 Metal salt precursors

Metal salt precursors are widely used in non-vacuum deposition processes for CIGS. This might be the most straight forward way to introduce the desired elements into a solution because of the high solubility of salts in a wide range of solvents, particularly water [69]. A wide range of deposition techniques can be used depending on the viscosity of the solution [69]. For solutions without a binding agent (i.e. low viscosity), spraying techniques such as ultrasonic or pneumatic spray are more suitable. The viscosity can be increased by adding binders or chelating agents. In this case, techniques such as doctor blading, screen printing or spin coating can be used instead. A simplified diagram for these techniques is shown in Figure 9. Figure 9 (a) shows the doctor blading technique, with a blade moving over the substrate surface, at a certain distance from the surface. Figure 9 (b) shows the screen printing process. This involves a screen that is filled with the ink and brought to the substrate. The screen is first filled with an emulsion that is impervious to the coating ink, with some areas kept open to allow the deposition of the ink [54]. Figure 9 (c) shows the spin coating process, i.e. the application of a liquid to a substrate followed by acceleration of the substrate up to a specified rotational speed. While doctor blading and screen printing are easily transferred to R2R processing, spin coating is not.



Figure 9: Schematic diagram of the doctor blading (a), screen printing (b) and spin coating (c) techniques.

The doctor blading technique is often used in the literature [65]. For this approach, a binder is typically used to adjust the viscosity of the starting solution. The addition of such a compound normally introduces carbon impurities to the device, often in the form of a dense carbon layer between the absorber layer and the Mo back contact [70]. One of the most successful approaches using this technique involves the dissolution of metal nitrates in methanol and the addition of ethyl-cellulose for viscosity adjustment. A PCE of 6.7% was obtained after a post-deposition selenisation step. A carbon layer was formed in the structure, however, resulting in poor adhesion of the absorber on the Mo layer [71]. In an attempt to overcome this problem the binder was replaced by polymethyl methacrylate (PMMA) which is known to decompose at low temperatures [72]. The formation of a carbon-rich layer was avoided, but the performance was limited by film inhomogeneities and traces of parasitic oxide phases [72]. A similar approach was followed without the addition of a binder, using carboxylic chelate complexes and an alcoholic solvent, resulting in a PCE of 7.7% [73]. This still resulted in the formation of a carbon-rich layer, however.

The spin coating technique has also been applied, resulting in CuInGaS₂ solar cells with PCEs of over 8% [74]. This approach involves the use of nitrate salts and polyvinyl acetate (PVA) as an organic binder. A thermal treatment was performed through an oxidation/sulphurisation step for carbon removal [74].

Spraying techniques typically require low viscosity solutions, hence there is no necessity of a binding agent [69]. The spray pyrolysis deposition of CIGS typically involves metal chlorides and a chalcogen compound, such as thiourea or N-dimethyl

selenourea as the S or Se source, respectively. The precursor is deposited on a preheated substrate (~300-400°C) to allow decomposition. The drawback of this technique is the formation of impurity phases, such as binary oxides, secondary chalcogenide phases or impurities from reaction by-products, such as chlorine and carbon [75]. An alternative approach has recently been proposed to involve a combination of dimethyl sulfoxide, thiourea and chlorides. This methodology has led to the highest obtained PCE to date, for solution processed CIS and CIGS absorber (13.0 and 14.7% respectively) from metal salt precursors [76].

Fully-sprayed devices have also been successfully deposited. For CulnS₂, solar cells have been made with a PCE of ~7% using nanocomposites of n-type TiO₂ and p-type CulnS₂, and with In₂S₃ as the buffer layer. The device configuration was TCO/TiO₂/In₂S₃/CIS [77]. A device with a sprayed absorber and buffer layer was also fabricated using a modified superstrate configuration of ITO/CulnS₂/In₂S₃/Ag which gave a PCE of 5.9% [78]. An improved PCE of 9.5% was reported after the complete optimisation of the deposition parameters [79]. This is the highest PCE obtained to date for a CulnS₂-based Cd-free solar cell by spray pyrolysis. For CulnSe₂, a fully sprayed device was prepared with an ITO/CdS/CulnSe₂/Au configuration, resulting in a PCE of about 3% [80].

The typical substrate temperature for the spray pyrolysis approach varies from 300 to 400°C. At lower temperatures, an excessive amount of impurities from the precursor (i.e. C, Cl, N) remains in the film [75]. Higher temperatures can cause the loss of S and Se and the formation of secondary phases, mostly oxides [75]. A substrate temperature of 300-400°C eliminates these problems, but is not sufficient for obtaining a highly crystalline material. Consequently, a post-deposition annealing treatment in a reducing or chalcogen atmosphere is often required. The highest PCEs for sprayed CIGS materials are obtained when a post-deposition thermal treatment is implemented. A PCE of 10.5% was obtained by spray deposition of aqueous solutions of metal chlorides and thiourea and selenising the film in a tube furnace [81]. Almost simultaneously, another group reported a PCE of 10.7% using an aqueous solution of metal nitrates and thiourea and a selenisation treatment in a glass ampule with Se powder [82]. The device configuration was the same for both these approaches (SLG/Mo/CIGSSe/CdS/i-ZnO/AZO). Only the absorber layer of the solar cell stack was spray-deposited.

2.2.2.2 Organometallic precursors

Organometallic precursors are often used for depositing semiconductors, primarily using the metal organic chemical vapour deposition (MOCVD) technique. The metal alkyls or hydrides which are typically used in these processes; however, tend to be pyrophoric and/or toxic. The precursors can also vary considerably in terms of volatility and thermal reactivity. Control of the product composition is therefore very challenging, especially when a large imbalance in the molar ratios of the materials is required [83].

In order to overcome these challenges, single source precursor (SSP) materials have been developed for the deposition of ternary CulnS₂ and CulnSe₂ thin films [84]. SSPs are metal-organic molecules that contain all the desired elements for the growth of a compound material and ideally have the film stoichiometry "built in" (I-III-VI₂ in the case of CIGS) [83]. The use of SSPs could make the process more controllable and could lower the deposition temperature which is beneficial for the application of flexible substrates. Lastly, the formation of impurity phases can be avoided, since the synthesis is controlled on a molecular level [85]. The synthesis of the SSP compound (PPh₃)₂Culn(SEt)₄ was reported for the preparation of the ternary CulnX₂ (X = S or Se) semiconductors [84]. The non-uniformity of the resulting films and the small grain size of the as-grown material limited the performance of these devices [86]. The use of this SSP compound as the precursor resulted in a PCE of 6.7% when physical vapour deposition (PVD) was used, but only 1% by using atmospheric-based techniques [85].

2.2.2.3 Molecular precursors

A molecular-based approach involves the preparation of a soluble molecular complex. These techniques typically involve thermally degradable precursors. A mild thermal treatment is used to convert the precursor to the desired phase and removes any residual organic species. The bulkiness and volatility of the sacrificial ligands significantly influence the quality of the final film. When large ligands are involved, cracks are formed in the film during drying/partial decomposition. Aside from the drying step, a post-deposition annealing treatment in S or Se atmosphere is typically required for the formation of highly crystalline films with the desired phase [58].

The primary example of this type of approach uses hydrazine as the solvent, and holds the record PCE for solution deposited CIGS. The use of hydrazine results in high quality chalcogenide thin films. Hydrazine easily dissolves metal chalcogenides such as Cu₂S and In₂Se₃, which are insoluble in common solvents due to the strong covalent bonds of these compounds [87]. Metal chalcogenides are the preferred starting material for CIGS, since they are free from impurities (i.e. C, O, CI) that typically originate from other precursors and can cause deterioration of the device performance [88]. Hydrazine has melting and boiling point temperatures similar to those of water (1.4 °C and 113.5 °C under standard atmospheric pressure) and is a strong reducing agent [88]. Additionally, it is a small and volatile molecule and hence decomposes at fairly low temperatures without the formation of cracks and voids in the film [87]. Lastly, all the desired components can be contained in the starting solution (including S and Se), which enables the formation of the chalcopyrite phase with the desired stoichiometry without requiring a high temperature annealing step in S/Se ambient. A clean annealing step is therefore sufficient for the formation of CIGS, which is the major advantage of this approach as opposed to other solution-based CIGS deposition techniques [87].

Both CulnSe₂ and Cu(In, Ga)Se₂ devices have been fabricated from hydrazine precursors resulting in 12.2% [28] and 15.2% [68] respectively. Although this is the highest performance obtained so far for solution processed CIGS, this methodology is difficult to implement industrially because hydrazine is highly toxic, explosive and carcinogenic. The increased transport, handling and storage requirements that would be necessary for hydrazine-based solar-cell manufacturing might prevent the production of cost-effective modules [87]. In order to avoid these requirements, research into alternative solvents is being conducted with the goal of making the process safer whilst still compatible with atmospheric processing.

A similar approach has been proposed using alternative solvents, but the use of hydrazine was still required in the precursor preparation step [89]. Initially the hydrazinium precursors were prepared by dissolving Cu_2S and In_2Se_3 in hydrazine. These precursors were then dried and re-dissolved in ethanolamine (EA) and dimethylsulfoxide (DMSO). The obtained PCE by this method (3.8%) was limited by the lower degree of crystallinity and the smaller grains of the films, as compared to the hydrazine-based method [89].

A few non-hydrazine molecular based approaches have very recently been reported for the deposition of CIGS, with the most successful being reported by Pan et al [90]. The suggested approach involves a butyldithiocarbamic acid based ethanol solution of metallic oxides. The selenisation of these films resulted in high quality Culn(SSe)₂ with a PCE of 10.1% [90]. Although this technique seems very promising, the use of a post-deposition annealing step in Se atmosphere is still required.

Interestingly, most of the work published on molecular-based techniques for CIGS involves spin coating, despite the limitations of this deposition technique. Spin coating produces a large amount of waste and is incompatible with R2R processing, hence viable alternatives are needed. Spray deposition, which is a high throughput technique, can make the process much more applicable to large scale manufacturing. Development of a low cost, hydrazine-free molecular based technique which can easily be adopted industrially would have significant benefits. Such a methodology will be presented in later sections of this thesis.

2.3 Non-vacuum TCO deposition techniques

In order to realise the true low cost potential of atmospheric processing, vacuumbased deposition techniques should ideally be eliminated from all stages of the solar cell fabrication process. Although the absorber is conventionally associated with the highest production costs, considerable attention has been given to atmospheric processing of the TCO layer of the solar cell.

As mentioned in the previous chapter, the window layer in a standard CIGS solar cell consists of an intrinsic oxide (i-ZnO) and TCO layer (AZO). Conventionally, both layers are deposited by RF sputtering, which has high equipment cost and low deposition rates [91]. The substitution of this technique by low cost alternative approaches could therefore be extremely beneficial for large scale PV manufacturing.

Low-cost deposition of the TCO layer is typically more challenging compared to the intrinsic oxide. The requirements for the intrinsic layer are mainly a high resistivity, high transparency and a controlled thickness [92]. Therefore, optimisation of i-ZnO is relatively straightforward, provided that the deposition occurs in an oxygen containing atmosphere and that high temperatures are used for complete pyrolysis of the

precursor. AZO, however, has to be carefully optimised. As a TCO material, a low resistivity and high transparency in the UV-Vis spectrum is required. Additionally, there should be a good matching of the electronic bands and the lattice constants to the underlying absorber/buffer layers for optimum performance [91].

An alternative deposition approach for AZO in industry would ideally have high deposition rates, high process stability and controllability as well as producing homogeneous coatings [91]. A few approaches have been investigated such as MOCVD, sol–gel and spray pyrolysis. Spray pyrolysis offers some additional advantages including uniform coverage of the substrate and simple and cheap instrumentation used.

2.3.1 AZO deposited by spray pyrolysis

As a solar cell TCO material, AZO thin films must correspond to specific requirements. Low sheet resistance R_{sheet} <10 Ω /sq and maximal transmittance T> 80% in the visible part of the spectrum is desirable [93]. It is challenging, however, to achieve these characteristics using atmospheric-based approaches such as spray deposition. In order to obtain sprayed AZO films comparable to vacuum-deposited films, the spray deposition process has to be carefully optimised.

The spray pyrolysis of AZO thin films typically involves metal salts of AI and Zn, dissolved in water or alcoholic solvents. In particular, the use of chlorides or acetates can result in films with high crystalline quality and good opto-electronic properties [94]. Each deposition parameter needs to be optimised if a high quality TCO layer is to be obtained. For instance, the doping level needs to be carefully controlled by varying the atomic ratio of AI relative to Zn. The doping ratio significantly affects the sheet resistance of the film and, to a lesser extent, the band-gap [95]. Excessive doping can result in the formation of crystal defects and a large quantity of ionised impurities which cause scattering of photons and consequently, a reduced transmittance [95,96]. Parameters such as the pH of the starting solution also have an effect. If the pH is outside the optimum range, Zn^{2+} can precipitate in the form of $Zn(OH)_2$, which is an insulator [97].

The fact that these processes are performed in air introduces additional complexities. The presence of oxygen during deposition causes the formation of a more stoichiometric ZnO matrix (fewer oxygen vacancies) and thus highly resistive films. The spray flux density can be controlled in such a way that a shorter time is required for deposition. The lower availability of oxygen with a shorter deposition time has been shown to result in an enhanced carrier concentration [98].

Substrate temperatures significantly affect the final film quality. Low temperatures can be insufficient for complete pyrolysis of the precursors. As a result of insufficient thermal energy, two separate layers are formed: the unpyrolysed precipitate on the surface and the pyrolysed material underneath [99]. Excessive temperatures on the other hand result in highly resistive films because of the more pronounced oxygen adsorption at the surface [100].

A post-deposition annealing step in vacuum can be implemented to improve the film quality. The annealing step has been shown to increase the film density by reducing the content of the hydrated species. Some of the adsorbed oxygen is also removed resulting in a higher density of the oxygen vacancies [95].

Most literature sources on sprayed AZO give a resistivity of the order of 10^{-1} - 10^{-2} Ω cm, hence films unsuitable for solar cell applications [95,98–100]. As a result, little work has been done implementing sprayed AZO films in devices. Nevertheless, a PCE of 12.1% has been achieved in a CdTe solar cell using a sprayed AZO film of 3 µm thickness [101].

2.4 Discussion and prospects

A variety of atmospheric approaches for deposition of the absorber have been demonstrated showing rapid progress and, as a result, the efficiency gap between vacuum and atmospheric processed CIGS is continuously decreasing. The record efficiencies obtained using the hydrazine approach and particle based approaches (e.g., Nanosolar) are very encouraging for the implementation of low cost technologies [67,68].

Figure 10 shows a brief summary of the most successful low-cost deposition approaches to date, indicating the main processing steps and challenges.



Figure 10: The main processing steps of the most successful low-cost deposition routes for CIGS.

Atmospheric-based methods are typically sequential processes. They usually consist of two separate steps: a low temperature precursor deposition step and a thermal treatment at higher temperature. High quality and highly crystalline material is normally obtained after the post-deposition thermal treatment, which can be in the form of clean or reactive annealing (in the presence of S/Se vapour) [69].

The use of metal salts is a straightforward way to prepare CIGS. Printing methods, such as doctor blading, can be used for high viscosity inks. Apart from the postdeposition selenisation, an additional pre-treatment step is required for elimination of the carbon species that are used for viscosity adjustment [58]. Alternatively, low viscosity inks do not require an additive for viscosity adjustment and can be spray deposited. Spray pyrolysis differs in principle from the sequential approaches [69]. The solvent is typically evaporated upon contact with or close to the substrate surface and the film growth can take place during the actual deposition step. Although this technique is extremely attractive from a manufacturing viewpoint, the as-deposited material is often of low crystalline quality and typically contains a large impurity content. A post-deposition selenisation treatment considerably improves the material quality and results in better PCE [65]. The use of metal-organic precursors could potentially avoid the problem of impurities remaining in the film due to a cleaner decomposition pathway, but additional complexities appear in terms of compositional control.

The particle-based approaches on the other hand, typically require an additional pretreatment step to remove the binder material or to reduce oxides that might be formed during the process [58]. This additional step makes the technique even more complicated, thereby increasing the process cost.

Among the molecular-based approaches, the hydrazine approach has the benefit of process simplicity. All the desired elements (including S/Se) are present in the solution and therefore a clean annealing step is sufficient to form the chalcopyrite phase, without secondary phases or impurities being present. This is a significant advantage, since a selenisation/sulphurisation step would significantly raise the complexity of the process, as well as the cost. In addition, the implementation of a selenisation step typically results in poor reproducibility due to the different volatilities of S/Se during selenisation [102]. There has been some success on hydrazine-free molecular based approaches, but complex post-treatment and high temperature steps are still required [90]. These approaches also typically involve spin coating, despite the limitations of this deposition technique.

The development of a technique with the advantages of the hydrazine approach but with less or non-toxic reagents could potentially offer significant cost reductions. The precursor solution should ideally involve all of the desired components, thereby rendering reactive annealing redundant. A simple and safe technique with a minimum number of processing steps would be extremely beneficial, especially when combined with an appropriate deposition technique. The ideal deposition technique should have high material utilisation efficiency and should be applicable to large scale manufacturing.

A novel, hydrazine-free molecular based deposition technique is presented in chapters 4 to 6 as a promising alternative for safe, low cost production of CIGS.

Chapter 3 Solar cell processing and characterisation

3.1 Production of CIGS solar cells

3.1.1 Molybdenum back contact deposition

The substrates used for the majority of this work consist of molybdenum (Mo) coated soda lime glass (SLG) and were provided by AimCore Technology Co., Ltd. The substrates have a Mo thickness of ~600 nm with a resistivity of ~ $2.6 \times 10^{-5} \Omega$ cm.

Towards the end of this work, different Mo substrates were used in order to improve the CIGS/Mo interface of the devices. These Mo substrates have been deposited inhouse by DC (direct current) sputtering.

The material properties of sputtered Mo are altered by changing the sputter power and working pressure, which results in the sputtered Mo atoms arriving at the substrate with different kinetic energies. Mo deposited at a high sputter power has a better adhesion to the SLG substrate compared to low-power deposited Mo [103]. Continuous sputtering at high sputter power however may cause delamination of undesired flakes from the deposition chamber walls [104]. Also, Mo films deposited at high power exhibit a larger resistivity compared to those deposited at low power. A Mo bilayer is therefore typically applied as the back contact in CIGS TFSC in order to combine good adhesion and electrical properties [103].

Mo was deposited on SLG substrates of 5cm x 5cm size by DC sputtering in a Nordiko DC magnetron sputtering system. Three separate layers were deposited with 2, 4 and 8 SCCM of Ar, respectively. The power used for the first two steps was 1180 W and for the last one was 880 W, corresponding to a power density of 3.9 and 2.9 W/cm², respectively. The base pressure varied from 3 to $6x10^{-7}$ Torr and the working pressure varied from 0.9 to 1.5 mTorr. The total Mo thickness was about

600 nm and the obtained resistivity was $3.3 \times 10^{-5} \Omega$ cm. The target (300 mm x 100 mm size and 99.99% purity) was supplied by Testbourne Ltd. The SLG substrates were mounted on a sample holder ~10 cm away from the target and were rotated at 4 revolutions per minute (rpm).

3.1.2 Deposition of the absorber and post-deposition treatments

During the initial stages of this work, the absorber was deposited using the spin coating technique; however, spray deposition was subsequently used for the majority of this work.

For the sprayed CIGS material, the thin films were deposited in ambient atmospheric conditions within a fume hood, using a GlasKeller glass chromatography atomiser with air as the carrier gas. The solution is atomised pneumatically, by the interaction of the air with the liquid. A gas stream is injected across a solution-filled capillary, as depicted in Figure 11. Following Bernoulli's principle [105], there is a reduced pressure at the top of the tube and the pressure differential causes the liquid to move from the reservoir up the capillary and into the moving stream of air, where atomisation occurs. The nozzle is manually operated with a tuber ball, as in the case of an unpressurised perfume atomiser.



Figure 11: Schematic diagram of the chromatography atomiser used in this work.

The deposition was performed manually, and involved spray coating a Mo coated glass substrate placed on a preheated hot plate. An intermediate drying step was performed between the spray runs. The atomiser was held at ~15 cm distance from the hot plate and at an angle of ~45° to the horizontal plane. The number of sprays per run was varied based on the spray spot size. The spot size was found to be

dependent on the solvent properties, as well as on the concentration of the solution. The deposition was carried out in a way that the entire surface area was covered. Bare glass substrates were placed around the Mo-coated glass substrate in order for the spray spot to be more visible and for a more homogeneous temperature distribution along the hot plate.

A post-deposition selenisation treatment was employed using various approaches during the course of this work. A Lenton two-temperature zone tube furnace controlled with PID controllers was used for the selenisations. Se pellets were used as the Se source. During the early stages of this work, the Se pellets and the samples were placed in different zones and the temperature of each zone was independently controlled. The pellets were placed inside a quartz crucible and the Se vapour was continuously transported to the substrate using nitrogen as a carrier gas. A constant nitrogen flow rate was kept, resulting in a constant working pressure.

An alternative method involved placing the Se pellets and the sample inside a graphite box, which was then placed in the high temperature zone. Similar to the first configuration, there was a continuous nitrogen flow and a constant working pressure during selenisation.

A similar approach was also followed using a graphite box. Instead of using flowing nitrogen as the carrier gas however, the tube was initially charged with nitrogen until a certain pressure was reached. The tube was then sealed off prior to the heating run.

RTP was also used as an alternative route to the tube furnace selenisation. The RTP selenisation runs were performed at NREL, USA.

Each of these approaches is analysed more extensively later in this thesis.

3.1.3 CdS buffer layer deposition

No chemical etching was performed on the absorber films prior to the CdS deposition. The CdS layer in this work was deposited by CBD. The samples (selenised absorbers of 2.5 x 2.5 cm size) were immersed into an aqueous solution of ammonium hydroxide (28-30% NH_4OH), cadmium sulphate (0.015 M CdSO₄) and thiourea (1.5 M NH_2CSNH_2) with the same concentrations and volumetric ratios as in

previous work [106]. The samples were first placed in preheated water, followed by the sequential addition of $CdSO_4$ and ammonia. Thiourea initiated the reaction and was added 5 minutes after the addition of ammonia in order to allow a partial electrolyte treatment [106]. The bath was controlled at 70°C and the total deposition time was 10 minutes. The mixture was stirred throughout the procedure using a magnetic bar. A typical thickness of the CdS layer was 50-70 nm.

The overall reaction can be described as [107]:

$$Cd(NH_3)_4^{2+} + SC(NH_2)_2 + 2 OH^- \rightarrow CdS + CH_2N_2 + 4NH_3 + 2H_2O$$

3.1.4 Window layer deposition

The most common window layer in CIGS solar cells consists of two layers [91]. The first layer is a thin intrinsic ZnO (i-ZnO) film with a thickness of ~50 nm. The second layer is aluminium-doped ZnO (ZnO:AI) that serves as the front contact of the device with a thickness of ~500 nm. Both layers are deposited by RF magnetron sputtering.

ZnO:Al and i-ZnO films were deposited using an AJA Orion 8 HV sputter system at a base pressure of ~3 x 10^{-7} Torr. The power used for the deposition was 180W (3.95 W/cm²) and the working pressure was 1 mTorr. The gas flow rates were 5 SCCM of Argon and 6 SCCM of 1% O₂ in Ar mixture for the deposition of i-ZnO and 5 SCCM of Ar for the AZO deposition. For AZO, a target with 0.5% by weight Al₂O₃ dopant concentration was used. Both sputtering targets have a purity of 99.99% and were supplied by Plasmaterials Inc. Unless otherwise stated, no metal grid or AR coating was deposited on the front contact of the device.

3.2 Methods of characterisation

3.2.1 Structural characterisation

3.2.1.1 X-ray diffraction

X-ray diffraction (XRD) is based on the interaction between the crystal lattice and an X-ray beam. The obtained XRD pattern can give information on the material crystal structure.

The XRD patterns shown in the present thesis were acquired using a Bruker D2 Phaser benchtop XRD system equipped with a Cu K_{α} X-ray source and LynxeyeTM detector. The divergence slit was set at 1 mm and the antiscatter plate at 3 mm. The sample was rotated at 15 rpm. The results were compared to powder diffraction patterns from the International Centre for Diffraction Data database.

Many of the binary phases that can be found in the Cu-In-Se-S system, such as the Cu_xSe phases, show a degree of overlap with the CIGS chalcopyrite structure [108]. Therefore, in some cases, additional characterisation techniques such as Raman spectroscopy were used in combination with the XRD measurements.

3.2.1.2 Raman spectroscopy

Raman spectroscopy is an optical, non-destructive tool based on the inelastic scattering of photons with elemental vibrational excitations in a material [13]. This technique can provide information on the crystal structure and the chemical composition of a material. Raman was used in combination with XRD to facilitate the distinction between binary and multinary phases with similar diffraction patterns. Specifically, the distinction between the Culn(S,Se)₂/Cu(In,Ga)(Se,S)₂ and binary copper selenide phases is relatively straight forward as they are both strongly Raman active and have well separated active phonon modes.

A Jobin-Yvon LabRam HR system was used to collect un-polarised micro-Raman spectra using a x50 objective lens and a He-Ne laser (λ = 632.817 nm) in backscattering configuration, as described in the literature [109]. For the x50 objective (NA 0.55), the estimated laser spot size is 1.5 µm. All spectra were calibrated with respect to the silicon Raman mode at 520.7 cm⁻¹.

3.2.1.3 Electron microscopy

Electron microscopy is based on the interaction of a beam of accelerated electrons with a specimen and it can involve bulk samples as in the case of Scanning Electron Microscopy (SEM), or thin specimens as in the case of Transmission Electron Microscopy (TEM). These techniques provide the capability of imaging at very high resolutions as well as analysing microstructures, compositions and properties of individual layers or interfaces [13].

SEM was used to investigate the surface morphology and cross sections of samples. The images presented in this work were obtained using a Carl Zeiss 1530 VP field emission gun scanning electron microscope (FEGSEM). The aperture size was 30 µm and the operating voltage was 5 kV. For the cross sections, the samples were scribed at the back side of the film and then fractured by hand. In some cases, there is some debris on the cross section due to non-ideal fracture. A few nanometres of gold/palladium were sputtered on top of the samples prior to imaging, in order to prevent charging of the glass substrates. A Hitachi TM3030 Tabletop SEM was also used for imaging at lower magnifications, which did not require any sample preparation.

TEM was used to investigate the micro-structure of the films. The TEM measurements were performed using a FEI Tecnai F20 scanning TEM system. The system is equipped with a silicon drift detector and has an operating voltage of 200 kV. The TEM samples were prepared by Focused Ion Beam (FIB) milling using a FEI Nova 600 Nanolab dual-beam system where, a standard in situ liftout procedure was used. This involved depositing a layer of platinum onto the sample surface above the area to be analysed, using the ion beam [110].

3.2.2 Composition analysis

The compositional analysis of CIGS solar cells can be rather complicated, since the cell is comprised of multiple layers, interfaces and impurities. Each technique has its own advantages as well as limitations and therefore a combination of various techniques needs to be employed. In this work, Energy Dispersive X-Ray Spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) techniques were used for compositional analysis.

3.2.2.1 Energy dispersive X-ray spectroscopy

EDS is a chemical microanalysis technique that is used in conjunction with SEM. It is probably the most commonly used tool for the chemical analysis of thin films because of the very quick measurements and simple sample preparation. EDS measurements are performed by recording the X-rays that are emitted from the specimen upon electron-beam irradiation. The energy of the x-rays is equal to the difference in potential energy between atomic electronic states, and hence is

characteristic to a specific element. Consequently, EDS gives information on the chemical composition of the samples [13].

EDS is a technique well suited to homogeneous samples. This is often not the case for CIGS, as there can be a compositional grading through the film. As a result, EDS analysis can produce serious inaccuracies, particularly when measuring crosssections. Because of the large specimen size, there is a comparably large interaction volume of the electron beam with the sample which results in a substantially high spatial resolution [13]. Consequently, elemental mapping can be superimposed on electron microscope cross sections. In this work, EDS was used in combination with TEM for cross section elemental mapping. Elemental mapping with TEM rather than SEM gives more reliable results, as the specimen thickness is very small and the spatial resolution is therefore much lower [13].

EDS analysis was also used for top surface analysis despite its drawbacks. These include an insufficiently high detection limit for light elements such as Na or C, and the occurrence of a peak overlap in some elements of interest for CIGS (S and Mo). EDS point analysis was used for the majority of the samples, primarily for a comparison between samples of similar thicknesses and also for an estimation of the Cu/In ratio.

The EDS analysis on top surface samples was performed in conjunction with the FEGSEM, with an accelerating voltage of 20 keV.

3.2.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique used for analysing the surface composition of a material. The technique involves illuminating a sample with soft (50-1500 eV) X-rays [13]. This causes emission of electrons as a result of the photoelectric effect. The kinetic energy of the emitted electrons is probed. A typical spectrum records the intensity of the emitted electrons as a function of kinetic energy (E_{kin}), which is then converted into "binding energy", E_{B} .

The holes created by the excitation process are filled by Auger transitions. These transitions can reveal information about the chemical state of the atom. Auger and XPS techniques therefore complement each other and can provide some useful insight into the chemical properties of the material.

Although XPS is a surface technique, it can also be used to obtain a compositional depth profile of the sample. Depth profiling gives information on the bulk composition of the film, which often strongly deviates from the surface composition, especially in a complicated multinary phase material such as CIGS [11]. Depth profiling is achieved by repeatedly measuring the surface composition in-between etching the surface using an Ar^+ ion beam. Nevertheless, the results need careful interpretation. Firstly, any compositional grading throughout the film would affect the sputter rate and thus the data points collected are not necessarily evenly distributed throughout the layer. Secondly, XPS is a very sensitive technique and will therefore show a high carbon and oxygen content at the surface because of exposure of the sample to air during handling.

XPS was performed using a Thermo Scientific K-Alpha XPS system equipped with an Al-K_α X-ray source and 180^o hemispherical analyser. Depth profiling data were obtained through a repetitive, sequential process of XPS measurements followed by a 100 sec low power Ar⁺ etch (200 eV beam energy). Peaks were identified and fitted using the Thermo Scientific[™] Avantage Software, using Smart (a Shirley variant) background subtraction.

3.2.3 Device characterisation

3.2.3.1 Current-voltage characteristics

JV measurements were carried out under both dark and illuminated conditions. JV characterisation was performed under AM1.5G simulated sunlight using a Wacom dual source solar simulator under 1000 W m⁻² with a calibrated Si reference cell. The simulator design combines light from a xenon arc lamp and a halogen lamp. A series of filters is used to match the source with the AM1.5G spectrum.

Samples (2.5 x 2.5 cm) were mechanically scribed into cells with a total area of 0.25 cm². No grids or anti-reflective coatings were applied to the device. For JV measurements the devices were contacted using a 4-wire configuration. The probes were typically placed at the centre of each cell, despite this causing partial shading. The lack of a metal grid resulted in a change in the shape of the JV curve. Altering the probe position was found to have an impact, with R_s being particularly affected. These effects have been reported previously [111]. The series and shunt resistances

for each device were extracted using a curve fitting algorithm written in MATLAB based on the single diode equivalent circuit, as described in chapter 1 [112].

3.2.3.2 Quantum efficiency

In addition to the JV measurements, quantum efficiency (QE) analysis was carried out on the best performing solar cells. Quantum efficiency (QE) is the ratio of the number of charge carriers generated to the number of incident photons as a function of wavelength. Consequently, QE is related to the solar cell's response to each wavelength in the measured spectrum.

EQE measurements can give useful information about each layer of the stack. The band-gap energy of the absorber layer can be calculated from the long wavelength cut-off of the EQE curve. In addition, the shape of the curve indicates problems that might be present in the devices. Some of these are commonly found in solution-processed CIGS, e.g. gradual weakening of the response at longer wavelengths. This typically indicates a loss of deeply absorbed photons due to poor minority carrier diffusion length and/or insufficient penetration of the depletion width into the absorber [113].

EQE spectra were acquired with chopped light using a Bentham PVE300 system with both Si and Ge reference diodes. Measurements were performed at 0V bias with a spectral resolution of 5 nm.

3.2.4. Characterisation techniques for TCOs

The electrical characterisation of TCOs was mainly performed using a four-point probe and a Hall Effect measurement system. The four-point probe was used for an initial measurement of the film sheet resistance. Hall Effect measurements were performed to cross check the resistivity value and to determine the mobility and carrier concentration. Sprayed TCO films deposited in early stages of this work were highly resistive and were measured solely using the four-point probe as the resistivity was too high for the Hall Effect system to measure accurately.

3.2.4.1 Four-point probe

Resistivity (ρ) is the most important parameter for a TCO material. One of the most common techniques used to measure resistivity is the four-point probe method. Four

point contacts are placed onto the surface, with the probe tips arranged in a straight line with equal spacing (S), as shown in Figure 12. A current (I) is applied between the two outer probes and the potential difference (ΔV) across the two inner probes is measured.

When the sample is considered semi-infinite (i.e. the thickness, width and length of the sample are greater than the contact spacing) then the resistivity can be calculated using Equation (3.1) [114].

$$Rsheet = \frac{\pi}{\ln 2} \left(\frac{V}{I} \right)$$
(3.1)

Otherwise, a correction factor, α , is added to the equation to correct for the sample geometry.

The sheet resistance measurements in this work were performed using a Jandel four-point probe with a probe spacing of 1 mm and a tip radius of 100 μ m, in combination with a Keithley 2460 current-voltage source meter.



Figure 12: Diagram of the four point probe setup showing the equally spaced probes.

3.2.4.2 Hall Effect

Hall Effect measurements were performed to cross check TCO resistivity and to measure carrier concentration and mobility.

The first step in determining carrier mobility is to measure the Hall voltage (V_H) by placing a magnetic field perpendicular to the sample and applying a current through the sample. The combination of the current (I) and the magnetic field (B) causes a

transverse current, which in turn generates a transverse voltage which is perpendicular to both the magnetic field and the applied current. The measurements are then repeated with the reversed magnetic field. The fundamental principle is called the Lorentz force, and the voltage induced by carrier deflection is the Hall voltage.

The resulting potential (V_H) is measured across the device. Accurate measurements of both the sample thickness (t) and its resistivity (ρ) are also required.

The resistivity can be determined using the van der Pauw measurement technique. The V_H is given by the Equation (3.2) [114]:

$$V_H = \frac{IB}{q N_S} \tag{3.2}$$

where Ns is the sheet carrier concentration of the film. This is converted to the bulk carrier concentration, N, by dividing over the film thickness. The Hall mobility is calculated by the Equation (3.3) [114]:

$$\mu = \frac{1}{q} N_S R_{sheet} \tag{3.3}$$

Figure 13 illustrates the configurations for the Hall Effect voltage and resistivity measurements. These two measurement configurations are very similar in that they both use four contacts and involve application of a current whilst measuring the resulting voltage. In the Hall mobility configuration, the current is applied to opposing contacts and the voltage is measured across the other set of opposing contacts. In contrast, for the resistivity measurement configuration the current is applied on adjacent contacts and the voltage is measured on the opposing set of adjacent contacts. No magnetic field is applied for resistivity measurements.

The Hall Effect measurements were performed with an Ecopia HMS-3000 system using the Van der Pauw method. 1cm x 1cm square samples were placed in a holder with spring-loaded probes contacting the four corners of the sample. Each corner was ultrasonically soldered prior to the measurement for better contacting. Each measurement was repeated 4-5 times and the results were averaged.



Figure 13: Measurement configurations of the Hall Effect voltage (left) and the resistivity measurements (right).

3.2.4.3 Spectrophotometry

A UV-Vis-NIR spectrophotometer was used in this work for measuring the optical properties of the TCO layers. The transmission of the TCO films has a direct effect on the photo-current generation of the solar cell and is therefore crucial for the optimisation of this material. Although this technique was mostly used for the TCO layers, it can be applied in a similar manner for the absorbers.

The transmission (T) and the reflection (R) measurements were performed using an integrating sphere for a range of wavelengths from 200 to 1800 nm. For the transmission measurements, the sample was placed over the entrance port of the integrating sphere, whilst a reference reflectance disk is placed at the reflectance port. For the reflection measurements, the entrance port was left uncovered and the TCO film was placed at the reflectance port. A baseline correction was performed by keeping the opening in front of the integrating sphere uncovered (air as the baseline) for the 100% baseline and by blocking the opening for the 0% baseline. The transmission and reflection spectra were measured using a Varian Cary 5000 spectrophotometer.

The absorption spectrum can be calculated using the measured transmission and reflection spectra using Equation (3.4):

$$A(\lambda) = 1 - T(\lambda) - R(\lambda)$$
(3.4)

The optical band-gap is estimated using Tauc plots, by taking into account the transmission and reflection spectra [115]. First, the material absorption coefficient is calculated using Equation (3.5):

$$\alpha = -\frac{\ln\left(\frac{T}{1-R}\right)}{d} \tag{3.5}$$

Where T and R are transmission and reflection, respectively (as a percentage) and d is sample thickness in centimetres.

For direct band-gap materials, the band-gap is calculated by plotting $(\alpha hv)^2$ against hv values and extrapolating the linear portion to the horizontal axis. This estimation is based on the assumption that the film is uniform. This is often not the case however, particularly for solution-deposited films, and therefore the results should be carefully assessed.

Chapter 4 Deposition of CuIn(S,Se)₂ thin films from metal chalcogenide solution precursors

4.1 Scope

This chapter outlines the development of a hydrazine-free molecular based solution approach for Culn(S,Se)₂ (CIS) thin film absorbers. The proposed methodology is very attractive as it involves metal chalcogenide precursors which so far have only been dissolved in hydrazine. Hydrazine is substituted with safer solvents, making this process more easily applicable to solar cell manufacturing.

The molecular based solutions investigated are discussed, as well as the relevant initial deposition approaches. Characterisation of the obtained absorbers will be presented which verifies the presence of the CIS chalcopyrite phase with good crystal growth.

4.2 Introduction

The chalcopyrite-structured semiconductor CIS along with the related alloy Cu(In,Ga)(S,Se)₂ (CIGS) is a high performance PV material for TFSC. This material has attracted considerable attention in the solar community with a record PCE of 22.3% recently recorded by Solar Frontier [30].

High efficiency CIGS thin films are conventionally fabricated using vacuum-based co-evaporation or sputtering [30,44]. Since vacuum processing introduces high manufacturing costs however, recent research into high efficiency CIGS solar cells has been more focused on development of low-cost atmospheric deposition techniques [69]. Various low cost techniques are under investigation (see chapter 2)

which depending on the nature of the precursor can be categorised as either solution or particle based processes [69]. Considering the two routes, solution-based approaches are more favourable as they involve simpler synthesis and purification processes compared with the nanoparticle route [116].

Various types of precursor compounds can be used for solution processing of CIGS thin films, including metal–organics [117,118], metal salts [73,113] and metal chalcogenides [68]. Metal chalcogenides are the ideal precursors, as they are free of undesirable elements (such as carbon, oxygen, or chlorine) which can remain in the film and consequently result in a deterioration in device performance [69]. Whilst these precursors are not easily dissolved in common solvents due to their strong covalent bonds, they can be effectively dissolved in hydrazine in the presence of excess chalcogen [68]. Despite the success of this approach for CIGS, the highly toxic and explosive nature of hydrazine renders the process unsuitable for large scale manufacturing.

Substitution of hydrazine for a safer solvent could enable large-scale industrial exploitation of the chalcogenide solution approach for the manufacture of high efficiency CIGS devices. This work therefore aims to develop a safer procedure for the deposition of the absorber layer in CIGS solar cells, whilst still involving the use of metal chalcogenide precursors.

4.3 Background

4.3.1. Hydrazine-based approach

The dissolution of chalcogenide compounds (namely As_2S_3 , As_2S_2 , As_2Se_3 and As_2Te_3) in amines dates back to 1982 [119]. The actual dissolution mechanism was reported later, where the solubility effect of ethylenediamine was justified by the weakening of the dimensionality of the As_2S_3 ring network [120]. Likewise, metal chalcogenides can be dissolved in hydrazine in the presence of excess chalcogen via "dimensional reduction" [88].

Dimensional reduction is a solid state reaction which incorporates an ionic component A_aX into a covalent structure MX_x to form a child compound $A_{na}MX_{x+n}$. The added anions serve to terminate the M-X-M bridges, resulting in a less tightly

connected framework [121]. Specifically for the case of hydrazine (as proposed by David B. Mitzi), the dissolution occurs due to the formation of metal chalcogenide anions accompanied by hydrazinium cations [88]. Excess chalcogen added into the precursor solution facilitates the disruption of the metal chalcogenide framework by breaking up M–X–M linkages, in analogy to the dimensional reduction [88].

This approach has been applied for the preparation of CIS and CIGS devices, resulting in the highest PCEs (12.2% and 15.2%, respectively) obtained for solutionprocessed CIGS solar cells [28,68]. This methodology consists of the solution preparation, film deposition, an intermediate low-temperature drying/partial decomposition step and a high temperature post-deposition heat treatment. The low temperature drying step is performed after each deposition cycle before applying the next layer. The deposition and the drying steps are repeated to build up film thickness [88]. For the preparation of CIS absorbers the starting precursors are Cu₂S and In₂Se₃, dissolved in hydrazine in the presence of excess S/Se [28]. For CIGS deposition, Ga is also included by dissolving Ga in hydrazine in the presence of excess Se [68]. The presence of excess Se in the starting solution eliminates the necessity for a post-deposition selenisation step and a clean annealing step is performed instead. The avoidance of a complex instrumentation and toxic gaseous reactions with H₂S/H₂Se that would otherwise be used for selenisation simplifies the process, which is beneficial from a manufacturing perspective [122].

4.3.2. Non-hydrazine-based approaches

Research on hydrazine-free approaches has recently been stimulated due to the highly toxic and explosive nature of the solvent. For example, a molecular-based approach was proposed by Pan and co-workers, which involved а butyldithiocarbamic acid based ethanol solution of Cu_2O and $In(OH)_3$. The selenisation of these films resulted in CIS with a PCE of 10% [90]. The same methodology, including Ga(acac)₃ as well as Cu₂O and In(OH)₃ and with subsequent selenisation, resulted in CIGS devices with a PCE of 8.8% [116]. Another group used the same starting precursors, with thioacetic acid as the solvent and a suitable S source [123]. Ammonia was added to the mixture to assist with the dissolution of the compounds. The dissolution of Cu₂O and In(OH)₃ in thioacetic acid was attributed to the strong coordination ability of S and is described by the following reaction [123]:

$$H_3C - C - SH \xrightarrow{NH_3} H_3C - C - S^- \xrightarrow{MO} M \left(S - C - CH_3 \right)_x$$

The addition of a base is required to deprotonate the SH in the thioacetic acid. This enables exploitation of the strong coordination ability of S. CIGS cells with PCEs of 8.6% were obtained with this approach [123].

A very similar set of methodologies were developed for Cu₂ZnSn(S,Se)₄ absorbers, starting from metal oxides in an aqueous ammonium thioglycolate solution [124], a combination of thioglycolic acid and ethanolamine [102] or 1,2-ethanedithiol and ethanolamine [125]. These approaches involve a combination of thiols under basic conditions. The solution is typically deposited by spin coating and a subsequent selenisation treatment is performed after the deposition step to form the desired phase [102,124,125]. Although the above mentioned solvents were successfully used for the dissolution of metal oxide precursors, S/Se components are still insoluble. As a result, a post-deposition selenisation step is still required, which significantly raises the complexity of the process [122]. The implementation of a selenisation step in the process also results in poor reproducibility of the film composition (and hence PCEs). The control of the S/Se ratio is very difficult, arising from the volatilities of S and Se [102]. Development of a solution-based approach for CIGS solar cells that does not require a post-deposition selenisation step would thus result in improved reproducibility as well as significant cost reductions. Finally, even the most recently proposed approaches typically involve metal oxides and/or salts as the precursors, which contain impurities. Therefore, the most effective route would be to identify effective alternatives to hydrazine for dissolution of metal chalcogenides instead.

In a recent publication of Webber et al. it was reported that nine V_2VI_3 chalcogenides (where V=As, Sb, or Bi and VI=S, Se, or Te) were easily dissolved at ambient conditions in a solvent mixture comprised of 1,2-ethanedithiol (EDT) and 1,2ethylenediamine (EDA) [126]. This group subsequently found that the same binary solvent can effectively dissolve hexagonal grey Se and Te at room temperature and ambient pressure [127]. The use of combinations of thiols and amines dates back to 1967 for dissolution of elemental S [128]. The proposed dissolution mechanism involves the deprotonation of the thiol followed by the formation of a thiolate. The

thiolate opens the sulphur ring by a series of nucleophilic attacks [128]. The work reported by Webber et al. showed that the 1,2-chelating dithiol and 1,2-chelating diamine were both essential for maximum solvent power, and that the stabilisation of the thiolate anions by H-bonds was contributing to the solvent power [126]. It has also been found that the same molecular complex was obtained by dissolution of Sn, SnO, and SnS in EDT-EDA, despite the different material compositions and oxidation states (Sn⁰ and Sn²⁺) [129]. The suggested complex was the four coordinated bis(1,2-ethanedithiolate)tin(II), hence EDA is not coordinated to tin [129]. This approach opens a new path in terms of CIGS solution processing, since metal chalcogenides as well as S/Se components can be rapidly dissolved, forming stable solutions. All the desired elements can be conveniently included in the starting precursor, which significantly simplifies the CIGS fabrication process.

The next section will show the development of a molecular-based approach for CIGS, using the EDT-EDA solvent combination. It is shown that the same solvent mixture can be used for the dissolution of Cu_2S , Cu_2Se , In_2S_3 and In_2Se_3 and that single phase CIS films can be obtained with good crystal growth after the selenisation treatment of a spin-coated thin film. Spin coating is applied as a starting point for this work, due to the simplicity and the repeatability of the technique. Although it is the most widely used deposition technique for solution processed thin films on a research scale, spin coating has low throughput, low material usage and is incompatible with flexible substrates [54]. These characteristics inhibit large scale applications. Whilst spin coating has been applied in this chapter, alternative deposition methods will be presented in chapters 5-6.

4.4 Development of a molecular based technique for Culn(S,Se)₂

4.4.1. Experimental details

CIS thin films were deposited by spin coating using the EDT-EDA solvent mixture as described by Webber et al. [126]. The process of the precursor preparation and the deposition procedure is illustrated in Figure 14. The procedure consists of four stages: precursor preparation, deposition of the precursor, drying, and post-deposition selenisation. Other than the annealing step, all processing steps were performed in ambient atmospheric conditions in a fume hood.



Figure 14: Schematic diagram of the absorber preparation procedure, including the solution preparation, deposition, drying and post-deposition selenisation step.

4.4.1.1 Precursor preparation

Each individual solution of metal chalcogenide (or a mixture of chalcogenide and chalcogen) was prepared separately by mixing the corresponding compound with the solvent combination and stirring overnight at room temperature in air. Then the two component solutions (Cu and In precursors) were mixed together in certain ratios, depending on the targeted film composition. Cu_2S or Cu_2Se can be used for the Cu precursor and similarly, In_2S_3 or In_2Se_3 for the In precursor. Any combination of these precursors can be used for preparation of CIS according to the final desired film composition. The results reported here were obtained solely using the sulphide precursor combination (Cu_2S and In_2S_3) due to a higher solubility limit and improved storage stability of the corresponding solution.

The two solvents were added to each component sequentially in a vial. First, EDA was added, followed by the addition of EDT, while stirring. Upon the addition of the dithiol, a coloured suspension was formed which was then converted to a transparent solution after stirring overnight in a sealed vial. Figure 15 shows a snapshot of different precursor combinations, demonstrating that true solutions were obtained. Each metal chalcogenide precursor can be dissolved separately, as well as mixed. Unlike hydrazine, dissolution does not require the presence of excess chalcogen [88]. The chalcogen (elemental S or Se) can instead be dissolved

separately, which would allow for a more straightforward control of the chalcogen incorporation in the film.

The standard concentration used in this work was 0.1 M. The solutions were mixed together targeting a copper poor Cu/In ratio of 0.8. The mixed precursor solution was stirred for a few hours and was then diluted immediately prior to the deposition step.



Figure 15: Snapshots of separate precursor and chalcogen solutions, demonstrating that they are optically transparent.

4.4.1.2 CIS precursor dilution

The CIS precursor solution was prepared with a target concentration of 0.1 M. It was then diluted immediately prior to the deposition in a 2:1 ratio (solution to solvent). The precursor was diluted in an effort to eliminate any residual carbon in the dried films which could be present due to incomplete decomposition of the molecular species, and to improve the packing density of the films. The diluting solvent was selected based on a number of solvent characteristics such as polarity, surface tension, boiling point, vapour pressure, viscosity, reactivity and toxicity. Ideally, the diluting solvent should be a good wetting agent for a Mo substrate and should also preserve the stability of the solutions without causing the complex to precipitate. It was found that only polar, aprotic and coordinating solvents could effectively be used for dilution, without precipitation. The use of tetrahydrofuran (THF) or acetone gave a stable solution, but poor wetting on the Mo surface.

EDA, ethyl acetate (EA), dimethyl sulfoxide (DMSO) and methyl ethyl ketone (MEK) were used in this work, resulting in stable solutions with desirable wetting properties.

The physical properties of these solvents are summarised in Figure 16. Among these solvents, the use of EA resulted in the most densely packed films and hence EA was used as the diluting solvent for the majority of this work. Also, the low boiling point of EA could facilitate the decomposition of the organic species in the film, thereby eliminating any residual carbon that would otherwise be present at moderate drying temperatures.

Physical properties of the solvents				
at 20°C	EDA	EA	DMSO	MEK
Boiling point (°C)	117	77	189	80
Dielectric constant	13.3	6	47	18.5
Density (g/ml)	0.9	0.9	1.1	0.8
Vapour pressure (mmHg)	10.4	73	0.4	80
Viscosity (cP)	1.8	0.4	2.0	0.4
Surface tension (dyn/cm)	42	23.9	43.5	24.6

Figure 16: Summary of the physical properties of the solvents used for dilution.

The dilution of the CIS precursor solution with EA is depicted in Figure 17. EA is immiscible with the precursor solution right after mixing, but a homogeneous and transparent solution is obtained after stirring the mixture for ~30 minutes at room temperature.



Figure 17: Snapshot images of the precursor solution after addition of EA (2:1 solution to EA). (a) immediately after mixing, (b) after 15 min of stirring and (c) after 30 min stirring at room temperature.

4.4.1.3 Deposition of the precursor

The precursor solution was spin coated on Mo-coated SLG substrates. The solution was first coated at a low rotation speed of 500 rpm, followed by a faster rotation at 1000 rpm. Between each coating, the film was dried for 5 minutes on a preheated hot plate maintained at 250 °C. The coating and the drying steps were repeated until the desired thickness was obtained. The thickness of each coating depends on the precursor concentration. For 0.1 M which was the standard concentration used in this work, five runs of precursor resulted in a film thickness of ~500 nm. The deposition and the drying steps both took place in air, inside a fume hood.

4.4.1.4 Post-deposition selenisation

The dried sample was selenised in nitrogen in a dual temperature-zone tube furnace. Se pellets were used for the selenisation process. The temperature of the Se source was controlled at 350-400 °C. The pellets were placed inside a crucible made of quartz glass. The sample was placed in the centre of a quartz plate in the second temperature zone, which was controlled independently from the first. The Se vapour was transported to the substrate using nitrogen as the carrier gas, and at a constant working pressure of ~7.5 Torr. Annealing was performed at a range of temperatures, durations, ramping and nitrogen flow rates. The heating duration used for the results presented here was 50 minutes with a ramping rate of ~35 °C/min. The final annealing temperature was 550 °C.

4.4.1.5 Characterisation

The grain size was measured offline on the SEM images using AxioVision software (release 4.9.1, Zeiss). Film thickness was determined using cross sectional SEM images of fractured samples. Thermogravimetric analysis (TGA) scans were performed using a TA Instruments Q5000IR system under a flowing nitrogen atmosphere with a ramp rate of 5 °C/min in a covered unsealed platinum pan.

4.4.2. Results and discussion

The following results were obtained solely using the sulphide precursor combination. The selenide combination can be applied in a similar manner. The XRD pattern of a selenised sample deposited using Cu_2S and In_2S_3 is shown in Figure 18. The

spectrum verifies the presence of CuInSSe chalcopyrite phase, in accordance with the JCPDS file 36–1311. XRD analysis of the as-deposited sample prior to annealing is also shown for comparison. Three peaks with low intensity are evident which either correspond to the (112), (220) and (312) peaks of CuInS₂ (JCPDS 15-0681), or to a Cu_xS phase. It is evident that the crystallinity of the dried film is very low, but annealing in Se vapour at 550 °C causes significant crystallisation.



Figure 18: XRD pattern of a sample (before and after selenisation) deposited using the sulphide precursor combination (Cu_2S and In_2S_3).

TGA analysis was performed in order to investigate the precursor properties during the thermal decomposition process and consequently, to define the optimum range for the drying temperature. TGA was carried out on the undiluted precursor residue, after the evaporation of the prepared solution using a rotary evaporator at 60 °C. For the precursor preparation, a solution of Cu_2S with excess S and a solution of In_2S_3 with excess S were mixed in an equimolar ratio, resulting in a final concentration of 0.14 M.

The thermal decomposition pattern of the precursor is shown in Figure 19 and consists mainly of two steps in the weight loss regime. The first step at around 120 °C is associated with residual solvent evaporation from solvent still present in the not fully dried sample. The amount of weight loss is affected by how well the bulk precursor has been dried. The second step in the weight loss curve occurs at around 200 °C and can be attributed to the dissociation of the molecular complexes formed

between the diamine/dithiol and the metal chalcogenides. This weight loss can also be partly related to the loss of excess chalcogen, as has been reported previously for the hydrazine-based procedure [130]. The TGA analysis shows that the precursor is mostly decomposed at fairly low temperatures (200 °C), in agreement with what has been reported for the hydrazine route [87,130]. A very small weight loss is evident at ~500°C, which could be related to the loss of organic ligands, thereby a small amount of residual carbon could be present in dried films. 250 °C was identified as the optimum drying temperature, as it is sufficiently high for removal of the majority of the organic species whilst also being low enough to eliminate molybdenum oxidation in air during the drying step.



Figure 19: TGA data of the precursor mixture of sulphides evaporated using a rotary evaporator. The first derivative of the weight loss curve is also shown. No precursor dilution was performed prior to the evaporation.

SEM analysis of film morphology shows that the material exhibits good crystallinity with grains approaching 500 nm in size after annealing, as shown in Figure 20 (a). The SEM image was obtained from a selenised sample with a thickness of ~500 nm. The film is not sufficiently uniform and fully compact however, with major cracks and voids present. The voids are present in the film after the deposition/drying step and are retained after selenisation. The formation of cracks can be explained by the high volume contraction due to rapid evaporation of the solvent during the drying step. Cracks are typically formed during the thermal decomposition of the molecular complexes [63]. The difficulty in growing a thick and dense absorber layer and the

poor layer morphology has recently been observed in a molecular-based approach for CIGS, which involves Cu_2Se , $In(OAc)_3$ and $Ga(acac)_3$ dissolved in the same solvent combination [131].

The crystal growth of the material is also evident in the cross-sectional TEM image, shown in Figure 20 (b). The crystalline CIS layer is shown on top of the Mo layer with a grain size approaching 500 nm. The final surface layer is the platinum over-layer. The intermediate layer at the Mo/CIS interface was identified to be molybdenum oxide, using EDS mapping (Figure 21). The Mo layer was partly oxidised due to a leak in the selenisation furnace.



Figure 20: (a) SEM image and (b) cross-sectional TEM image of a selenised sample.



Figure 21: EDS mapping on the cross-sectional TEM image of a selenised sample.
4.4.2.1 Investigation of the drying step

Based on the previous results, it was shown that single phase CIS material can be obtained with good crystal growth. However, a considerable amount of cracks and voids are present in the film. Consequently, these films are not ideal for incorporation in a solar cell device as the voids would result in significant shunting paths. The presence of cracks also results in the underlying Mo layer being directly exposed to the Se vapour. This can result in the excessive formation of MoSe₂, as has been reported previously [64]. The presence of voids can be attributed to the rapid evaporation of the solvent during the drying step. The formation of cracks normally occurs during the thermal decomposition of the molecular complexes into an inorganic phase because of the high volume contraction [63]. This problem is not present in the hydrazine-based approach due to hydrazine being a small molecule; hence the volume contraction is significantly smaller.

The drying method was further investigated with a view to reducing the solvent evaporation rate and thereby minimising the volume contraction. Instead of drying the film on the preheated hot plate between each spin coating step, the film was dried in the tube furnace using a controlled temperature profile. The drying step consisted of a slow ramp from room temperature to 400 °C in 35 minutes (Figure 22 a) which corresponds to a heating rate of less than 16 °C/min. A snapshot of a dried film deposited on glass can be seen in Figure 22 (b) which shows the uniformity of the film at this scale.



Figure 22: a) heating ramp rate of a slow drying step in the furnace and (b) a snapshot of a film deposited on glass using the slow heating step.

Figure 23 shows the top surface SEM images of two representative samples, one dried on a preheated hot plate and the other in the tube furnace. It is evident that the slow ramp rate causes the film to be denser, but the degree of porosity is still significant. Film quality can be improved to a greater extent by further reductions in ramp rate during drying, or by using less solution per coated layer.

In an effort to reduce the volume contraction and improve the layer density, higher spin coating rotational speeds and further precursor dilution were investigated. A lower precursor concentration (0.05 M) and a higher rotational speed (1500 rpm) were used, and it was found that the film thickness was limited to ~100-200 nm after 6 coated layers, which highlights the difficulty in building up layer thickness by spin coating, using this solvent system.



Figure 23: Top surface SEM images of two representative samples, (a) dried on a preheated hot plate and (b) with the slow ramp in the furnace.

Lower drying temperatures were also attempted in an effort to obtain thicker asdeposited films. Figure 24 shows the SEM top surface and cross section of an asdeposited sample with the intermediate drying step performed at 200 °C (a, b) and the same film after selenisation (c, d). Although the as-deposited film was thicker, there was a significant volume loss after selenisation. It is evident that at lower drying temperatures the solvent gets trapped in the film, which is then released at the high temperature selenisation step, ultimately resulting in pore formation.

Overall, the spin coated films are highly porous, despite the drying temperature used. Small improvements can be obtained by further slowing down the drying step or by increasing the rotational speeds; which however, limit the absorber thickness and make the process much slower and less practical. The high porosity and the

difficulty in building up thick films limit the applicability of this process. The quality of the films obtained with this solvent system is limited to a significant extent by the deposition technique used. Substitution of spin coating with spray deposition results in a significant improvement of the film quality, as will be seen in later chapters.



Figure 24: SEM top surface and cross section of an as-deposited film (top) and the same film after selenisation (bottom), with low drying temperature.

4.4.2.2 Comparison with the hydrazine-route

The high absorber quality obtained with the hydrazine-based route is mostly attributed to the solvent characteristics of hydrazine. Hydrazine coordinates weakly; as such it is decomposed cleanly and it does not contain carbon or oxygen. It is also a strong reducing agent which prevents any metal oxidation [132].

EDA was used in this work as the main solvent (90% v/v of the solvent mixture). The boiling point, vapour pressure and surface tension of EDA are 117 °C, 1.4 kPa and 40.8 mN/m respectively, which are close to those of hydrazine (113 °C, 1.9 kPa and 66.7 mN/m). Considering that it is significantly less toxic, EDA is a very promising solvent for the fabrication of CIGS TFSC, especially if a comparable performance to the hydrazine-processed devices is obtained.

In comparison to the hydrazine route, the complexes formed in this work are expected to be bigger, due to the larger molecule size of EDA and EDT in comparison to hydrazine. Consequently, there is a high volume contraction during the drying step resulting in the formation of cracks and voids. The voids can act as shunting paths, which are deleterious to the device performance.

As opposed to other solvents that have been used for low cost deposition of CIGS, the EDT-EDA solvent mixture can easily dissolve S/Se, in a similar manner to hydrazine [90,123]. The post deposition sulphurisation and/or selenisation processes can thus potentially be avoided, thereby significantly simplifying the process. Elemental S/Se can be dissolved separately and the incorporation of chalcogen in the final film can be directly associated with the quantity of solution used. This can provide a higher degree of S/Se control in the film and more flexibility in terms of solution preparation.

4.5 Conclusions

A novel methodology for the deposition of CIS solar cells was developed as a safer and low cost alternative to the hydrazine-based approach. Metal chalcogenides are dissolved at room temperature in a safer solvent combination comprised of EDT and EDA, forming optically transparent solutions with long term stability. The use of a safer solvent combination simplifies the process from a safety perspective and, consequently, the process can be performed in air. Although the selenisation step has yet to be eliminated, it was shown that excess Se can be incorporated into the starting solution which could further simplify the methodology.

The precursor solution is spin coated and the films are selenised, resulting in crystalline CIS films. The spin coated films are not of sufficiently high quality to be implemented in solar cells because of the considerable number of cracks and voids present. Small improvements can be obtained by applying a slow ramp rate for drying or by increasing the rotational speeds. Both options can reduce the volume contraction during film decomposition, thereby minimising the formation of cracks and voids. This would however make the process much slower and less practical.

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The high porosity and the difficulty in building up the film thickness are the main drawbacks of this approach. These drawbacks will be eliminated by modifying the deposition technique, as will be shown in the next chapters. Regardless of the non-optimal film morphology, the straightforward precursor preparation and the simplicity of this approach make it highly potential as a safer and low cost molecular based deposition technique for TFSC.

Chapter 5 Culn(S,Se)₂ solar cell processing

5.1 Scope

The previous chapter presented the development of a molecular-based technique for the preparation of $Culn(S,Se)_2$ (CIS) absorbers, starting from metal chalcogenide solution precursors. This chapter will show the extension of this work and the application of the solution-processed absorbers in TFSC.

A brief overview will be given on the incremental increase of the PCEs from 0.3% to 8.0% obtained during the course of this work. However, detailed characterisation will be reserved for the best performing devices obtained.

5.2 Introduction

The use of vacuum-based deposition techniques for the preparation of chalcogenide absorber layers has resulted in highly efficient CIGS PV devices [44]. Nevertheless, the high capital cost associated with vacuum technologies is a major obstacle to the commercialisation of CIGS. As a consequence, recent research on CIGS solar cells has been focused mostly on developing solution-based approaches, where the deposition occurs under atmospheric conditions.

Chapter 4 presented a hydrazine-free molecular-based technique for obtaining CIS thin films with the chalcopyrite structure. This chapter will present the extension of this methodology and the implementation of the absorbers in solar cell processing. During the course of this work, an incremental increase in PCE has been obtained through process optimisation. The PCE increase will be presented along with the varied parameters that caused the corresponding improvement. The remainder of the chapter will focus on the characterisation of the highest performing devices. Among the varied parameters, the selenisation procedure was found to have the most dramatic effect on the absorber quality. Figure 25 shows the incremental

increase in PCE during the course of this work, broadly categorised by the selenisation configuration that was followed. For each configuration, the Se partial pressure evolves differently during selenisation.



Figure 25: Progression chart showing the incremental increase in the PCE of CIS solar cells during the course of this work. The PCE milestones are categorised based on the selenisation method used.

The first selenisation method is an "open vessel" approach, where a continuous carrier gas flow and constant working pressure are maintained. An alternative "closed vessel" approach was also used, allowing for higher Se pressures which resulted in better quality absorbers. A "closed vessel" approach has previously been used for electrodeposited CIS films, resulting in more uniform films compared with films processed with flowing gas [133]. Finally, RTP was explored as an alternative selenisation method to the tube furnace annealing in an effort to reduce the thermal treatment time, which is desirable from a production point of view. RTP was also attempted in an effort to improve the crystallisation of the films and the quality of the back contact/absorber interface. It has been reported that the use of RTP results in improved crystal growth and that detrimental phases can be avoided by passing intermediate formation temperatures rapidly [134].

Aside from the selenisation approach, it was found that the deposition technique has a significant effect on the absorber quality. Substitution of spin coating with the spray deposition technique has resulted in significantly denser films. A thinner layer of the material is deposited per spray deposition pass which minimises the volume contraction and the formation of cracks that occur during thermal decomposition of the molecular complexes [63]. The as-sprayed material has a better packing density, which facilitates crystallisation during the selenisation step. It was also found that spraying requires a smaller amount of starting solution for obtaining the same film thickness compared to spin coating. This enables the thickness of the film to be built up easily and quickly. Spray deposition is a high-throughput and scalable technology and is very attractive from a manufacturing process viewpoint.

5.3 Experimental details

The precursor preparation process and the deposition procedure are illustrated in Figure 26. In comparison to the methodology described in chapter 4, this approach involved spray coating instead of spin coating. Also, the intermediate drying step was integrated into the deposition step which occurred on a heated substrate. Metal sulphides were solely used as the starting precursors, although metal selenides can be used in a similar manner. Besides selenisation, all processing steps were performed in ambient atmospheric conditions within a fume hood.



Figure 26: Schematic diagram of the absorber preparation procedure, including the precursor preparation, the deposition and the post-deposition selenisation step.

5.3.1. Precursor preparation

The precursor preparation was performed using two different approaches. The precursors were dissolved separately, or as a "one pot" mixture.

For the first approach, In_2S_3 and Cu_2S were dissolved separately by mixing the corresponding powder with the solvent combination and stirring overnight at room temperature. The solvents were added sequentially to the powder, into a vial. First, 10 ml of EDA was added, followed by the addition of 1 ml of EDT while stirring. Upon addition of the solvents, coloured suspensions were formed, which converted to optically transparent solutions with overnight stirring at room temperature. Each component solution was prepared with a target concentration of 0.2 M. After dissolution, the two solutions were mixed together targeting a copper-poor (Cu/In) ratio of 0.8. For this targeted Cu/In ratio, 2.5 ml of the In_2S_3 solution (0.5 mmol) and 2ml of the Cu_2S solution (0.4 mmol) were mixed in a separate vial. The solution mixture was left stirring for a few hours and was then diluted with ethyl acetate (2:1 v/v). The diluted solution was filtered (0.45 µm PTFE) right before the deposition step.

Alternatively, the precursor was prepared as a "one pot" approach. In_2S_3 (0.326 g, 1 mmol) and Cu_2S (0.127 g, 0.8 mmol) were placed in a vial together, and the solvents were sequentially added to the mixed powder. Similar to the other approach, 10 ml of EDA was added first, followed by the addition of 1 ml of EDT while stirring. The solution was left stirring overnight at room temperature in a fume hood and was diluted with ethyl acetate (2:1 v/v) before the deposition. Similar to the other approach, the diluted solution was filtered before the deposition step. Unless otherwise stated, the "one-pot" approach was followed.

It should be noted that during the dissolution process for both approaches, the vial was purged with nitrogen (using a nitrogen filled balloon) and that the solutions were transferred using syringes, in order to eliminate exposure with air. Finally, all the reagents were used without any purification processes.

5.3.2. Deposition of the precursor

CIS thin films were sprayed using a chromatography atomiser, as described in chapter 3. The solution was atomised by a gas stream (using a tuber ball) injected

across a solution-filled capillary. The solution was sprayed on Mo-coated SLG substrates. The substrates were placed on a preheated hot plate, controlled at 310 °C. The deposition run was repeated 10 times, with a 3-minute drying step inbetween each layer. Finally, a 10-minute drying step was performed after the last deposition at the same temperature to evaporate any excess solvent.

5.3.3. Post-deposition selenisation

5.3.3.1 Open vessel approach

A two-temperature zone tube furnace was used for this selenisation approach, which allows the independent temperature control of the substrate and the Se source.

A quartz crucible (shown in Figure 27 a) was filled with Se pellets and then placed in the low temperature zone, controlled at 350-400 °C. The as-deposited samples were positioned on a quartz plate placed in the high temperature zone, controlled at 550 °C. The tube was purged with nitrogen three times before setting the working pressure to ~7.5 Torr. The Se vapour was transported to the samples using a continuous nitrogen flow, while maintaining a constant working pressure. The reactor is kept "open" in this configuration; so that Se can diffuse out of the reactor. Consequently, this setup does not allow a high Se partial pressure. The heating period lasted for 50 minutes including a ramping rate of ~35 °C/min (Figure 28). This setup allowed the selenisation of multiple substrates at a time. Typically, a set of four 2.5 x 2.5 cm samples were selenised per run.

Selenisation was also performed using a graphite box, which contained both the substrates and the Se source. As a result, a single temperature zone was used and the Se source temperature could not be independently controlled. A digital photograph of the graphite box used for this selenisation approach is shown in Figure 27 (b). The graphite container contained two 2.5 x 2.5 cm samples and Se pellets evenly distributed at the six openings. The diameter of the box was ~65 mm and the volume was ~9 cm³ (with the lid on). A small hole (1 mm) was placed at the centre of the lid, hence the box was partially closed.



Figure 27: Snapshots of (a): the quartz crucible used for the Se source for the "open vessel" approach, (b): the graphite box, (c): the Pyrex enclosure used for the RTP selenisation.



Figure 28: Heating profile of the high temperature zone (sample side) and the low temperature zone (Se source) for the "open vessel" selenisation approach.

5.3.2.2 Closed vessel approach

A similar procedure was followed using the graphite box but with the tube sealed during selenisation, allowing a higher Se partial pressure. The tube was first purged with nitrogen three times before setting the starting pressure to 160 Torr and remained sealed for the duration of the selenisation step. The working pressure increased during selenisation from a starting pressure of 160 Torr to a final pressure of ~240 Torr at the end of the heating run. Before each selenisation run, ~300 mg of Se pellets were placed inside the graphite box and were evenly distributed at the 6 openings (1 pellet at each opening). The same 50 minute heating profile was used as in the "open vessel" approach for the high temperature zone, with a ramp rate of ~35 °C/min. This temperature profile resulted in the evaporation of the entire Se amount in the box. Figure 29 shows diagrams for each selenisation configuration,

indicating the open values for the "open vessel" approach and the closed values for the "closed vessel" approach.



Figure 29: Diagrams showing each selenisation configuration: (a) "open vessel" approach with two temperature zones, (b) "open vessel" approach with a single temperature zone and the use of a graphite box and (c) "closed vessel" approach in a single zone, using a graphite box. In the open vessel configuration (a, b) Se vapour can escape from the tube furnace.

5.3.3.3 Rapid thermal processing

RTP was performed as an alternative selenisation route to tube furnace annealing. For this approach, a 2.5 x 2.5 cm sample was placed inside a Pyrex enclosure with Se pellets. A digital photograph of the enclosure is shown in Figure 27 (c). An insulating spacer separated the two Pyrex plates approximately 5 mm apart, resulting in a volume of ~25 cm³. The selenisation was performed with flowing nitrogen (5 litres per minute) at atmospheric pressure.

The RTP furnace was controlled using PID controllers, with the capability of independently controlling the top and bottom lamps of the oven. The heating profile (shown in Figure 30 a) was power-controlled using multiple steps. The heating period of the RTP selenisation process was 8 minutes including a ramping rate of $4 \, ^{\circ}\text{C} \, \text{s}^{-1}$ and a dwell time of 3 minutes, at approximately 550 °C. The profile started with a short dwell step at lower temperatures in order to assure a more repeatable heating profile. The heating profiles of the RTP oven and the tube furnace are plotted together in Figure 30 (b) to allow comparison of the ramp rates.

For the temperature measurements, a sister sample (1 cm x 1 cm) was placed near the sample to be selenised. A wire thermocouple was used, with the tip attached to the centre of the sister sample. The thermocouple was placed into two grooves through the Pyrex plate.



Figure 30: a) Heating profile of the RTP oven and b) comparison of the heating profiles between the RTP oven and the tube furnace.

5.3.4. Device fabrication

Unless otherwise stated, the solar cells had a standard configuration of AZO/iZnO/CdS/CIS/Mo/SLG. The CdS layer (~80 nm thickness) was deposited by chemical bath deposition [106]. The intrinsic ZnO and AI doped ZnO layers (~80 nm and 500 nm respectively) were both deposited using RF sputtering. Lastly, mechanical scribing was performed to isolate each cell of ~0.25 cm² area. The devices processed in the RTP oven were completed in a different configuration: IZO/ZTO/CdS/CIS/Mo/SLG. The amorphous Zn-Sn-O (ZTO) and amorphous In-Zn-O layers (IZO) had a thickness of 50 nm and 150 nm, respectively, and were

deposited by reactive DC sputtering as described in the literature [135,136]. Unless otherwise stated, the Mo substrates were provided by AimCore Technology Co. Ltd.

5.3.5. Characterisation

The grain size and thicknesses indicated on SEM images were measured offline using AxioVision software (release 4.9.1, Zeiss). The full width at half maximum (FWHM) of the XRD peaks was calculated with the DIFFRAC.SUITE[™] Eva software. Prior to the JV measurements, the cell area was measured using a digital microscope. Photoluminescence (PL) imaging was performed using an excitation wavelength of 808 nm with an exposure time of 30 sec.

5.4 Champion efficiencies – Milestones

During the course of this work, an incremental increase in the PCE was obtained (Figure 31) by optimising the deposition, selenisation and device processing steps. The effect of the most important variables on the material quality (where possible) will be investigated here. It should be noted that the reported PCEs were the best-case results and not average.



Figure 31: PCE milestones during the course of this work, showing the incremental improvements that will be investigated.

(A): 0.3% - Spin coating of precursor solution

As shown in chapter 4, single phase CIS thin films were obtained by spin coating the precursor solution, followed by subsequent selenisation. A substantial amount of cracks and voids were present in the films which impeded their application in solar cells. Cracks are typically formed during the thermal decomposition of the molecular complexes into an inorganic phase because of high volume contraction [63]. As suggested in chapter 4, the discontinuities in the film during drying were caused by the large size of the molecular complexes.

The volume contraction per deposition run can be reduced by implementing a slower drying step or a lower precursor concentration. Using a combination of the two, the first performing solar cell was obtained, which exhibited a PCE of 0.27%. The intermediate drying step was performed using a slow ramp rate to 400 °C in 35 minutes. The dark and light JV curves for this device are shown in Figure 32. Despite the slow ramp rate, the film porosity was still significant, as shown in the cross-sectional SEM image at Figure 32. The high porosity of the absorber layer coincides with the low FF of the device. The voids act as serious shunting paths, causing the poor quality of the p-n junction.





Figure 32: Left: Light and dark JV curves of a spin coated device. Right: Cross section SEM image of an as-deposited sister sample on a SLG substrate, showing that voids are present prior to the selenisation step.

(B): 1.5% - From spin coating to spray deposition

In an effort to minimise film porosity, spin coating was substituted by the spray deposition technique. The same precursor solution in terms of concentration and Cu/In ratio was sprayed using a chromatography atomiser. The first sprayed sample was applied in a solar cell, which exhibited a PCE of 1.48%. Figure 33 shows the dark and light JV curves, as well as a cross-sectional TEM image of the same device. The improvement in the performance of this device is attributed to the as-sprayed material being denser compared to the spin coated films. Also, it was found that denser films were crystallised to a greater extent during the selenisation step, resulting in a better material quality.

Figure 34 shows the same cross sectional TEM image at two magnifications. The absorber layer consists of a crystallised and a non-crystallised part, which indicates that crystallisation initiates from the top of the film. The crystalline part has a thickness of ~0.5 μ m and the non-crystallised (or fine-grain layer) consists of individual layers (appear with different contrast) formed by multiple spray runs and subsequent film drying. The formation of a MoSe₂ layer is also evident at the interface between the Mo back contact and the absorber.

Despite the improved packing density, the sprayed film was still mesoporous, which suggests that the deposition and drying steps could be further improved. The remaining porosity causes electrical shunting, which is evident by the low FF of the device. Also, the absorber layer could be too thick for optimum collection, as the typical absorber thickness for high performing CIGS is limited to 2-3 μ m [44]. These results suggested that there was large room for improvement in terms of material quality and device performance.

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Figure 33: Left: Light and dark JV curves of the first sprayed device. Right: Cross section TEM image of the solar cell.



Figure 34: Cross sectional TEM image of the first sprayed device, at two different magnifications.

(C): 1.9% - "Open vessel" selenisation approach – optimisation

The "open vessel" selenisation approach was performed during the early stages of this work. The initial optimisation of the selenisation treatment was performed in terms of sample temperature, pressure and gas flow rates. Following this, the selenisation duration and the Se source temperature were varied.

Three different selenisation times were used; 50, 80 and 100 minutes including a ramp rate of ~35 °C/min, for a constant Se source temperature of 360 °C. The temperature of the Se source was also varied at 280, 360 and 440 °C, for a constant duration of 100 minutes. Figure 35 shows the SEM images of sister samples selenised with each set of conditions, as well as the corresponding as-deposited sample. The presence of micro-cracks on each sample suggests that the solvent evaporation was too rapid and that the drying step could be further improved. Formation of grains is evident on each sample; however, the grains do not entirely cover the film surface. Two different grain morphologies are shown; grains of up to 500 nm and a few larger grains of several μ m size. The smaller grains were identified as Cu_xSe (Figure 36) [137]. The SEM images show that for this selenisation approach, a long dwell time and a selenisation temperature of 360 °C might be optimum; but crystallisation is poor overall. Also, Cu_xSe phases are formed despite the Cu-poor stoichiometry of the precursor.

XRD measurements were also performed to investigate the effect on the crystalline quality of the films. The XRD patterns of all the samples correspond to CuInSSe with the chalcopyrite structure (JCPDS 36–1311). Figure 37 shows the XRD pattern of the sample selenised for 100 minutes at 360 °C. A comparison of the XRD patterns of the samples is also shown for a narrower 2θ range. It is evident that the annealing duration does not affect the position of the XRD peaks. In terms of the Se source, however, the peaks of the sample selenised at low temperatures (280 °C) are shifted to higher 20 angles. This suggests that S/Se ratio is higher for this sample, which indicates that Se displaced S to a lesser extent during selenisation [138]. The Se consumption for this run was also significantly lower compared to the other combinations (Figure 37). Lastly, the FWHM of the (1 1 2) peak for each sample is also shown in the table of Figure 37. The FWHM value of a diffraction peak gives an indication of the material crystalline quality. The mean size of the crystalline domains is defined by Debye–Scherrer's formula t= $0.9\lambda/\beta.\cos\theta$, where t is the average crystalline domain size, λ is the X-ray wavelength, θ is the diffraction angle and β is the FWHM. Since the FWHM is inversely proportional to the domain size, a decrease in FWHM indicates a larger domain size and, consequently, a better crystal quality.

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The samples selenised at higher temperatures and longer annealing times have, therefore, a better crystalline quality.



Figure 35: Top surface SEM images of absorber films selenised with different duration at a fixed temperature of 360°C and with different Se source temperature at a fixed duration of 100 minutes. The SEM image of the corresponding as-deposited film is also shown.



Figure 36: Raman spectra for two spots on the sample, indicating the presence of Cu_xSe secondary phases, in addition to the CulnSe₂ chalcopyrite structure.



Figure 37: XRD patterns of the samples selenised for different durations and different Se source temperature, for a narrow range of 20 angles. XRD pattern of the sample selenised for 100 minutes and at 360 °C. Summary of the FWHM of the (1 1 2) peak and the Se consumption for each selenisation run.

The selenised films were implemented in solar cell devices and the JV curves are shown in Figure 38. The lowest FF was obtained for a Se source temperature of $^{\circ}C$, suggesting that this temperature was too low for effective selenisation. Overall, these devices are of poor quality, with the low FF attributed to the presence of Cu_xSe secondary phases, acting as shunting paths in the device [52].



Figure 38: JV curves and PV parameters for absorbers selenised with different duration (left) and different Se-source temperature (right).

(D): 5.0% - Use of graphite box with "open vessel" selenisation configuration

The open vessel approach was performed in a similar manner, but in a single temperature zone instead of two zones. The working pressure, gas flow rate and heating profiles were kept constant. In this approach, however, both substrates and Se source were contained in a graphite box. The downside of this method is the fact that Se evaporation cannot be controlled independently from the samples. The use of a partly closed graphite box caused a higher Se overpressure which facilitated crystallisation of the films. This is in line with previous work suggesting that high Se pressures assist the grain growth of CIS [133].

The use of the graphite box with the same heating profile as previously, resulted in significantly improved solar cell performance. This is shown with the light JV curves of two devices processed in each way (Figure 39). The first sample was selenised in the two-temperature zone configuration without the box, as depicted in Figure 29 (a). The second sample was selenised in a single temperature zone using the graphite

box, as depicted in Figure 29 (b). Overall, V_{OC} is almost constant but the Jsc is almost doubled when the box is used, resulting in a PCE of 5.0%.



Figure 39: JV curves of samples selenised with the open reactor approach, with and without the graphite box.

SEM imaging was performed on the two devices to investigate the difference in the solar cell performance. Figure 40 shows the cross section SEM images of the device processed without the graphite box. No significant crystal growth is evident, with the absorber consisting of fine grains of up to 100 nm size. Similarly, Figure 41 shows the cross section SEM images of the device processed in the graphite box. The absorber of this cell consists of larger grains of up to 240 nm at the top part and a fine-grain layer underneath. The increased grain growth explains the better junction quality for the sample selenised inside the box. The use of the graphite box and, consequently, the higher Se partial pressure resulted in the formation of a thicker MoSe₂ layer. A thick MoSe₂ layer causes a high series resistance in the device [48]. It should be noted that the Mo deposition recipe used for each device was slightly different, but a comparison can still be made in terms of the back contact quality.



Figure 40: Cross sectional SEM images of the device processed without the graphite box.



Figure 41: Cross sectional SEM images of the device processed with the graphite box.

(E): 7.3% - "Closed vessel" selenisation approach – effect of pressure

The selenisation step was modified in order to further increase the Se partial pressure. Similar to the last approach, two samples were placed inside the graphite box along with Se pellets. In this approach, however, the tube remained sealed during selenisation, resulting in a pressure increase during heating.

Four sister samples were selenised with the same heating run but with varied starting pressure, in order to investigate the effect of the staring pressure on the crystallisation. Figure 42 shows the top surface and cross sectional SEM images of these samples. The crystal size was shown to increase with pressure, with all the samples incompletely crystallised throughout the absorber thickness. Figure 43 shows the same cross sectional SEM images at a higher magnification. The crystalline layer thickness increases with pressure, while a highly sintered top crust was obtained with a starting pressure of 240 Torr. Despite crystallisation being most significant at this pressure, Mo layer was delaminated from the SLG substrate. Delamination problems can be caused by excessive MoSe₂ formation [60]. The crystal size measured from the top and from the cross section SEM images, respectively, are summarised in Figure 43. The enhanced grain growth with pressure has previously been shown for solution processed CIGS films [108]. It has been reported that a high Se vapour pressure was required in order to ensure a sufficient Se supply throughout the entire absorber film [108].

XRD analysis was also performed (Figure 44) showing that all the patterns correspond to the CuInSSe chalcopyrite phase (JCPDS 36–1311). No significant peak shift is evident with pressure. The low intensity ratio of the Mo/MoSe₂ peaks suggests that Mo has fully reacted with Se, regardless of the pressure. The XRD comparison is shown in Figure 45 for a narrower 20 range. The decrease in the FWHM of the (2 2 0)/(2 2 4) peak with pressure confirms the improved crystallisation.



Figure 42: Top surface and cross section SEM images of sister samples selenised with different starting pressures (10, 80, 160 and 280 Torr), showing the effect of the pressure on the crystallisation.



Figure 43: Cross section SEM images of sister samples selenised with different starting pressures (10, 80, 160 and 280 Torr). Summary of the crystalline layer thickness and the grain size measured from the cross sectional and top surface SEM images, respectively.



Figure 44: XRD patterns of sister samples selenised with different starting pressures (10, 80, 160 and 280 Torr) indicating that there is no noticeable peak shift with pressure.



Figure 45: (a) XRD patterns for a narrower range of 2θ indicating higher peak intensity with pressure. (b) The influence of the starting pressure on the FWHM of the (2 2 0)/(2 2 4) peak.

Overall, it was shown that higher pressures improve crystallisation, but excessive pressures can cause delamination problems. The film selenised with a starting pressure of 160 Torr was applied in a device, which exhibited a PCE of 7.3%. The dark and light J–V curves for this device are shown in Figure 46. Despite the significant improvement in the crystalline quality, there is still room for further optimisation, especially in terms of the back contact quality.



Figure 46: Light and dark JV curves of the device selenised with a starting pressure of 160 Torr.

(G): 8.0% - Rapid thermal processing

RTP was explored as an alternate selenisation method to tube furnace annealing in an effort to reduce the thermal treatment time and to improve the crystallisation of the film. This section shows the optimisation of the RTP process in terms of the dwell time of the last step; however, a more in-depth characterisation of the best performing device will be presented in later sections.

Figure 47 demonstrates a comparison of the XRD patterns of sister samples selenised in the RTP oven with a different dwell time of: 50, 200 and 500 sec. The final temperature is kept constant (~550 °C) for all the selenisation runs. The broad peaks at 20 ~32° and 56° (noted with circles) indicate the presence of MoSe₂ and are evident in each spectrum. The main difference between the three spectra is the intensity ratio of the Mo/MoSe₂ peaks (at 20 ~ 40° and 32°). Assuming that this intensity ratio is correlated with the thickness of the MoSe₂ layer, the MoSe₂ layer seems to be thicker at longer dwell times [48].

These samples were implemented in solar cells devices with a configuration of In,Zn:O/ZTO/CdS/CIS/Mo/SLG. The light JV curves are plotted together in Figure 48. The V_{OC} and J_{SC} values are similar, whilst the FF is considerably different. The device with the longest dwell time has the thickest $MoSe_2$ layer formed, causing a high series resistance and a low FF. A dwell time of 200 sec has resulted in the highest FF, with a corresponding PCE of 8.0%.



Figure 47: XRD patterns of the selenised samples with varied dwell time of the last step of RTP. The spectra have been shifted by 1000 and 3000 counts to allow comparison.



Figure 48: JV curves of samples selenised with varied dwell time of the last step of RTP.

(F): 8.0% - Absorber thickness and back contact improvement

Despite the rapid progress in terms of solar cell performance, there are still some major problems in terms of device quality. For example, the sprayed absorbers might be too thick for optimum collection. It has previously been observed that the fine-grain sub-layer in Cu₂ZnSn(S,Se)₄ solar cells did not affect the device performance, provided that the large-grain layer thickness was constant [139]. The effect of the absorber thickness on the performance was investigated in this work in order to see if a similar phenomenon is observed for sprayed CIS devices.

Figure 49 shows the SEM cross section images of four samples, processed with identical conditions but with varied target absorber thicknesses. The samples were completed into devices; hence the cross sections show the entire solar cell stack.



Figure 49: Cross sectional SEM images of devices with varied absorber thickness. The finegrain sub-layer of the CIS absorber is indicated on each image with an arrow. Overall, the large-grain layer has a similar thickness in each sample; however, the sample with the thinnest absorber (denoted as d) has slightly larger grains and a thicker MoSe₂ layer. It is assumed that Se diffuses to a greater extent from the top to the bottom of the film for thinner absorbers, causing excessive MoSe₂ formation. The MoSe₂ formation can potentially be controlled by implementing a thin barrier layer (such as MoN_x) as an intermediate layer in the back contact to minimise the Se diffusion. This layer has previously been used for CIGS, but no solar cells were fabricated [140].

Separate cells of ~ 0.25 cm² area were defined on each sample by isolating the multi-layered film from adjacent areas via mechanical scribing. Figure 50 shows the distribution of photovoltaic parameters of a set of 6 adjacent cells on each of the four samples. The samples are denoted in a similar manner as in Figure 49 with "A" being the thickest and "D" being the thinnest. The solar cell devices of sample C have the highest FF (and PCE), which suggests an optimum absorber thickness in the order of 1-2 µm. The PV parameters vary significantly with absorber thickness, despite the similar thickness of the large-grain layer. The strong dependence of the device performance on the absorber thickness highlights the necessity of absorber thickness control. However, this is very difficult to control using the hand-held spraying method, due to the manual nature of the technique. It should be noted that these solar cells were measured using a different simulator compared to the one used for the rest of the devices presented in this thesis. This simulator has been calibrated to 1000 W m⁻² illumination, but the light spectrum (using a warm white LED) significantly differs from the AM1.5G. Nonetheless, these results are still meaningful for statistical analysis purposes only.

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Figure 50: Box plots showing variation of the photovoltaic parameters with absorber thickness. Sample A has the thickest absorber layer and sample D the thinnest.

Based on these results, the targeted absorber thickness was limited to 2 μ m, resulting in the next PCE milestone. The selenisation step for this sample was performed in the tube furnace with the "closed vessel" approach. The selenisation step and the Mo deposition were both modified for improved crystal growth and better back contact quality, respectively.

It was shown that the absorber crystalline quality is improved with selenisation pressures. As such, the starting pressure for this sample was increased to 530 Torr, resulting in a final pressure of 760 Torr at the end of the heating run. The selenisation temperature was decreased from 570 to 540 °C and the Mo was deposited using the 3-layer approach, as described in chapter 3. These modifications were implemented in the process in order to avoid delamination problems which would otherwise occur at high pressures.

Figure 51 shows the top surface and the cross section SEM image of a CIS film that was processed with these conditions. Figure 52 shows a cross sectional TEM image on the same sample, as well as EDS mapping on the same area. It is shown that the absorber layer is still incompletely crystallised. In this case, however, the top layer seems to be highly sintered with larger grains, whilst the fine-grained layer is thinner. The formation of the MoSe₂ layer is also evident at the interface between the Mo back contact and the absorber, but it is less pronounced than in the previous cases. Finally, EDS mapping on the cross section TEM image indicates that some Cu is present in the MoSe₂ layer, which suggests that Cu diffuses from the absorber layer to the back contact. This effect will be discussed more in chapter 6.



Figure 51: Top surface and cross section SEM image of the sample selenised in the tube furnace with a starting pressure of 530 Torr.

These process conditions resulted in a PCE of 8.0%. The dark and light JV curves for this solar cell are shown in Figure 53. In comparison to the champion device processed in the tube furnace (Figure 46), this device has a slightly better V_{OC} and FF, hence a higher PCE.

Overall, it is shown that PCEs of 8% can be obtained with different selenisation approaches, using this molecular deposition technique. Compared to the previous champion solar cell processed in the tube furnace, the working pressure was increased for improved crystallinity and the Mo deposition process was modified in order to withstand the new selenisation conditions. Despite the significant progress in the material quality and device performance, room for improvement remains. Further optimisation of the device processing is required for fully crystallising the absorber layer and for further controlling the MoSe₂ layer formation.



Figure 52: (Top): Cross sectional TEM image on the absorber film selenised in the tube furnace with a starting pressure of 530 Torr. (Bottom): EDS mapping on the cross section TEM image.



Figure 53: Light and dark JV curves for the device selenised in the tube furnace with 530 Torr starting pressure.

5.5 Characterisation

This section will provide a more in-depth characterisation on the best performing devices, which will elucidate the benefits and shortcomings of this approach.

The previous sections of this chapter showed that the CIS material quality can be significantly improved by altering the selenisation conditions in the tube furnace, with high pressures facilitating crystallisation. RTP was also explored as an alternative selenisation method in an effort to reduce the thermal treatment time and to further improve crystallisation. The two highly performing devices obtained by each selenisation approach will be characterised here. Whilst a direct comparison between devices is difficult to make due to different TCOs and buffer layers used, the merits of each selenisation process are highlighted, in terms of crystal growth and MoSe₂ formation. It should be noted that the two samples have comparable Mo substrate and as deposited CIS film.

SEM and XRD were used to evaluate the surface morphology and crystal structure of the absorber. Figure 54 (a) shows an SEM image of the absorber surface, which was selenised in the tube furnace and deposited from a mixture of Cu_2S and In_2S_3 , targeting a copper poor ratio (Cu/In=0.8) of the precursor. The selenisation step was performed using the "closed vessel" approach and a starting pressure of 160 Torr. The SEM image indicates that the films are homogeneous and crack-free, with the surface comprising of large grains of 1-1.5 µm size. Figure 54 (b) shows the XRD pattern of the same sample which verifies the presence of a single-phase chalcopyrite material. Compared to the (112), (220)/(204) and (312)/(116) reflections of the CulnSe₂ chalcopyrite phase that are expected at $2\theta = 26.58^{\circ}$, 44.23°, and 52.39°, respectively, (JCPDS 40-1487), the peaks are slightly shifted towards higher 2θ angles ($2\theta = 26.83^\circ$, 44.48° , and 52.63° respectively). This is indicative of the decreasing d-spacing, as would be expected with increasing S substitution in the crystal lattice [138]. This shift indicates that only a small amount of S is present in the film and that S is mostly displaced by Se during the selenisation step. The broad peaks at $2\theta \sim 32^{\circ}$ and 56° (noted with circles) correspond to the MoSe₂ layer which is located between the Mo and the absorber.



Figure 54: (a) SEM image of the top surface and (b) XRD pattern of a CIS film, selenised in the tube furnace.

Similarly, Figure 55 (a) shows the SEM image of the absorber top surface of a sister sample, selenised in the RTP oven. The sample was selenised as described previously in this chapter, with a 200 sec dwell time for the last step (Figure 30 a). The SEM image indicates that the films are homogeneous and crack-free, with grains of up to 1 μ m size. Figure 55 (b) shows the XRD pattern of the sample, which verifies the presence of a single-phase chalcopyrite material. The MoSe₂ peaks are evident, as in the case of the sample selenised in the tube furnace. The intensities of the MoSe₂ (100) and Mo (110) diffraction peaks can be related to the thickness of the MoSe₂ layer [48]. Here, the intensity ratio of the Mo/MoSe₂ peaks (at 20 ~ 40° and 32°) is higher for the RTP-processed sample (6.1 compared to 3.5). This suggests that the MoSe₂ layer is thinner for the RTP-processed sample.

The XRD pattern of the as-deposited sample is shown in Figure 56. The XRD of the RTP-processed sample is also plotted to allow comparison. The spectrum of the asdeposited film consists of two low intensity peaks at 2θ ~28° and 46.7° which correspond either to the (112) and (220) peaks of CulnS₂ (JCPDS 15-0681), or to a Cu_xS phase. It is evident that the crystallinity of the dried film is very low, but there is significant crystallisation after selenisation at 550 °C. In combination with the EDS analysis (Figure 57), these results suggest that CulnS₂ is formed during spraying, with Se displacing S during selenisation. EDS analysis shows that the Cu/In ratio remains approximately constant for the as-deposited and selenised samples, for both selenisation approaches.
Raman was performed in combination with XRD to confirm the absence of secondary phases (Figure 56). A peak at ~175 cm⁻¹ is identified as the A1 peak of chalcopyrite structured CIS and a double peak is identified as the B2 or E mode [141]. No peaks are observed at 260 cm⁻¹ showing that Cu_xSe phases are absent at the surface of the samples [137]. Nonetheless, the presence of the Cu_2Se phase cannot be discarded, as it exhibits very weak Raman features [142].



Figure 55: a) SEM image of the top surface and b) XRD pattern of a CIS film, selenised in the RTP oven.



Figure 56: Left: XRD pattern of the as-deposited sample and the sample processed in the RTP oven. Right: Raman spectra of the two selenised samples.

	EDS analysis - at.%						
	Cu / In	Se / In	(S or Mo) / In				
As-dep	0.82	0.00	1.61				
Tube	0.84	2.05	0.04				
RTP	0.86	2.03	0.04				

Figure 57: Elemental composition the as-deposited and selenised samples for each selenisation approach, measured with EDS. A significant S and Mo peak overlap in the EDS spectrum precluded the quantitative elemental analysis of each element separately, therefore the S and Mo content is shown as the sum of the two.

Figure 58 (a) shows the JV characteristics of the device processed in the tube furnace, measured under dark and simulated AM1.5G illumination. These results are for the highest performing cell of the sample. The configuration of the device was AZO/iZnO/CdS/CIS/Mo/SLG, as described in earlier sections. A PCE of 7.3% was obtained, with a V_{oc} of 432 mV, a J_{sc} of 31.1 mA cm⁻² and a FF of 54%. The V_{oc} and J_{sc} of this device are comparable to that of a hydrazine-processed Culn(S,Se)₂ solar cell with low S content (n = 10.7%, V_{oc} = 440 mV, J_{sc} = 35.9 mA cm⁻², FF = 67.5%) [28]. In comparison to the hydrazine-based device, our cell is limited by the low FF, which is mainly attributed to a high series resistance of 3.5 Ω cm². The high series resistance can be related to excessive MoSe₂ formation and the incomplete crystallisation of the absorber throughout its thickness [48]. It is expected that further improvement of the selenisation step, the TCO deposition, as well as the evaporation of current collecting grids can significantly increase the FF of the device.

Figure 58 (b) shows the EQE measurement of the same device. The observed decrease in EQE at wavelengths below 550 nm corresponds to the absorption of the CdS buffer layer. The EQE data shows good collection efficiency from 550 to 700 nm, but the collection is gradually reduced at longer wavelengths. The drop in EQE at wavelengths >700 nm indicates that there is high recombination towards the back of the absorber. This suggests that the device is not fully recrystallised throughout the thickness and that the selenisation step should be further improved. The bandgap was estimated from the EQE curve, by plotting $[E.ln(1-EQE)]^2$ versus E [143] (shown in the inset of Figure 58 (b), where band-gap was extracted from the band edge by extrapolating to the horizontal axis intercept. The estimated band-gap of 1.06 eV corresponds to Culn(S, Se)₂ with low S content. Based on previous work

that associates the S/Se ratio with the band-gap (assuming a linear relationship between the band-gap values of $CulnSe_2$ and $CulnS_2$) [87,138], the estimated band-gap from the QE data corresponds to a S content of 4 at. %. This result suggests that S is mostly displaced by Se during selenisation, in agreement with the XRD data and EDS analysis.



Figure 58: Electrical characteristics of the device processed in the tube furnace. a) Light and dark JV curves (AM1.5G illumination, 1000 W m⁻²). b) EQE spectrum. Inset: estimation of the band-gap by extrapolation from the EQE data.

Figure 59 (a) shows the dark and light JV curves for the device processed in the RTP oven. The configuration of the device was: IZO/ZTO/CdS/CIS/Mo/SLG. It should be noted that these two devices were completed in different laboratories; therefore different configurations were employed according to the respective lab standard process (between Loughborough and NREL). The highest performing cell of the sample area (2.5 x 2.5 cm) has a PCE, V_{oc} , J_{sc} and FF of 8.0%, 452 mV, 31.4 mA cm⁻² and 56%, respectively. In comparison to the 7.3% cell, the RTP-selenised device has a slightly improved V_{oc} and a lower series resistance, which results in a better FF. The lower series resistance could be attributed to the shorter annealing time which results in a thinner MoSe₂ layer formed at the interface. This is in agreement with the XRD pattern and the cross sectional SEM images shown in Figure 60. The cross sectional images show a similar crystallisation, with a crystalline layer thickness of ~600 nm for the cell processed in the tube furnace and ~500 nm for the RTP-processed cell. This suggests that the small difference in the

series resistance could be solely attributed to the different MoSe₂ thickness, which is indicated in the images.

Figure 59 (b) shows the EQE measurement of the RTP processed device. In comparison with the previous device, there is a decrease in the collection below 550 nm, good collection efficiency from about 550 to 700 nm and a reduced collection at longer wavelengths. This indicates that the absorber is not fully recrystallised throughout its thickness, which is also confirmed in the cross sectional SEM images of Figure 60. In comparison to the EQE of Figure 58 (b), this cell has a slightly better collection at longer wavelengths, which could be attributed to a slight improvement in the absorber quality or the use of a different TCO layer combination.

The estimation of the band-gap is shown in the inset of Figure 59 (b) and equals to 1.03 eV, which corresponds to pure CulnSe₂ [41,138]. This verifies that S is mostly displaced by Se during the selenisation process, within the accuracy of this calculation.



Figure 59: Electrical characteristics of the device processed using the RTP approach. a) Light and dark JV curves (AM1.5G illumination, 1000 W m⁻²). b) EQE spectrum. Inset: estimation of the bandgap by extrapolation from the EQE data.

Overall, the EQE data shows that both devices have good collection but room for improvement remains. Specifically, further optimisation of the selenisation process should result in the complete crystallisation of the absorber, which will improve the EQE at longer wavelengths and consequently the J_{sc} of the device.



Figure 60: Cross sectional SEM images of (a): the solar cell processed in the tube furnace, (b): the solar cell processed in the RTP oven, (c): the as-deposited film before selenisation.

Further analysis was performed in order to investigate the uniformity within the samples. PL imaging was carried out in order to identify inhomogeneities in the optoelectronic properties. This technique can give useful information on the distribution of efficiency limiting structural defects and is a suitable tool for quality assessment [144]. An excitation wavelength of 808 nm was used in order to excite electrons across the band-gap of CIS. Figure 61 (top) shows the PL imaging on the 2.5 x 2.5 cm sample processed in the tube furnace and Figure 61 (bottom) shows the sample processed in the tube furnace. The finished cells isolated by mechanical scribing are visible. The brightness variation is probably related to a variation in the material quality due to unintentional gradients during growth, such as a non-uniform Se distribution inside the box during selenisation or temperature inhomogeneities. The PL image also shows dark defect-related spots, which could be structural defects from the absorber or the buffer deposition stage. Pinholes are also evident, which appear as bright spots. These pinholes are caused by contacting the cells during the JV measurements, due to the absence of grids. The presence of these pinholes might accelerate humidity absorption, which could increase the rate of degradation of the solar cell performance with time. Lastly, a dark area is shown in the bottom left part of the image for the sample processed in the tube furnace. This area was masked during CdS deposition in order to mount the sample. Hence, it is shown that the diode is very weak in the absence of the buffer layer. The scribe lines appear bright due to reflection of the back contact, which is a measurement artefact.

The different brightness pattern in the two samples originates from the different device processing procedures. For example, different compositional gradients could be caused during selenisation, due to the dissimilar container dimensions. In addition, the CdS deposition for the RTP-processed sample was performed without masking the sample; hence there is no masking area. Finally, it should be noted that no spectral PL was measured, which could be useful for identification of the type of defects.

The box plots in Figure 62 display the distribution of the photovoltaic parameters (n, FF, J_{SC}, V_{OC}) for a set of 6 adjacent cells on the RTP-processed sample. The calculated standard deviation for n, FF, Jsc, Voc equals to 0.8%, 4.5%, 1.1 mA/cm² and 4.6 mV, respectively. It should be noted that these measurements were performed without light soaking, whilst the reported efficiencies (7.3% and 8.0%) were obtained after a 5 min light soak. The box plots show that there is variation on the cell parameters, especially for the case of V_{oc} and FF values. This result is in line with the PL image and suggests that there is a compositional or thermal variation in the box during selenisation. Further investigation is required to verify this reasoning.

The solar cells devices prepared in this work exhibit reversible metastability under light soaking, which is common for CIS/CIGS devices [145]. Figure 63 shows the effect of the 5 min light soaking step on the JV curve of the best performing cell. This short light soaking produced ~12% improvement in efficiency.



Figure 61: PL imaging on (top): the device processed in the tube furnace and (bottom): the device processed in the RTP oven.



Figure 62: Box plots showing the variation of the photovoltaic parameters in 6 adjacent cells of the RTP-processed device.



Figure 63: The effect of a 5 minute light soaking on the JV curves of the best performing solar cell.

5.6 Conclusions

This chapter presented the application of the molecular solution approach developed in this work. Sprayed CIS thin films are incorporated in solar cell devices. CIS solar cells with PCEs of up to 8.0% were obtained by optimisation of the deposition and selenisation procedures.

Substitution of spin coating with spray deposition has resulted in denser films, which are crystallised to a greater extent during selenisation. The most significant part of this progress was, however, related to the selenisation configuration. It was found that high Se pressures improve the crystalline quality of the absorber but can also cause delamination problems and excessive MoSe₂ formation. RTP was explored as an alternative selenisation technique to tube furnace annealing in an attempt to improve the back contact/absorber interface. Despite being reduced, the MoSe₂ layer thickness was still relatively large, causing a high series resistance in the device. It was suggested that the remaining porosity of the material causes Se to diffuse towards the back, forming a thick MoSe₂ layer.

A more controlled spraying technique, such as ultrasonic spray pyrolysis, could greatly improve the material quality. For example, the narrower droplet size distribution obtained with ultrasonic atomisation can improve the packing density of the material [146]. Se will therefore diffuse to a lesser extent to the back contact, minimising the MoSe₂ formation. Also, an automated process would result in more reproducible film thicknesses which were shown to affect dramatically the device properties. In terms of the MoSe₂ formation, a thin barrier layer (such as MoN_x) could be applied as an intermediate layer in the back contact to minimise the MoSe₂ layer formation [140].

Finally, it is anticipated that higher device performance can be obtained with further process optimisation or by alloying CIS. Specifically, Ga can be incorporated in the absorber in order to increase the bandgap of the device and consequently, the V_{OC} . The addition of Ga and the processing of Cu(In,Ga)(S,Se)₂ TFSC will be presented in chapter 6.

Chapter 6 Cu(In,Ga)(S,Se)₂ solar cell processing

6.1 Scope

The previous chapter presented the device processing of sprayed Culn(S,Se)₂ solar cells and showed the progress in terms of PCE milestones. This chapter investigates the effect of adding Ga to the film with the aim of fine-tuning the band-gap. It will be shown that Ga content can be controlled in a straightforward manner, allowing for synthesis of optimised material and hence improved solar cell properties. CIGS solar cells with active area PCEs of up to 9.8% were obtained.

6.2 Introduction

One of the most promising thin film technologies is the chalcopyrite-based semiconductor CuInSe₂ and its alloys, commonly referred to as CIGS. CIGS has a broad single-phase composition range, and by alloying CuInSe₂ with S or Ga, a tuneable band-gap [59]. Most of the best performing devices are nonetheless S-free with a bandgap of around 1.1-1.3 eV, corresponding to a Cu to Ga+In ratio (CGI) of 0.88-0.95 and a Ga to Ga+In ratio (GGI) of ~0.3 [23]. Usually, a graded bandgap as a function of film thickness is desirable, with higher Ga content towards the back of the absorber [147]. Such a bandgap grading normally results in an enhanced V_{oc} and increased collection efficiency compared to non-graded CIGS due to the suppression of back contact recombination [43,148].

The most promising solution-based approach for CIGS in terms of PCE involves the dissolution of metal chalcogenides (Cu_2S and In_2Se_3) and Ga metal in hydrazine [68]. The toxic and explosive nature of the solvent, however, makes scale-up and commercial use of this process difficult.

Chapter 5 presented the development of a hydrazine-free molecular solution-based approach for CIS films. TFSC with PCEs of up to 8% were fabricated using this

approach (chapter 5, [149]). In this chapter the potential of this approach is further explored for CIGS deposition, by adding Ga in the starting precursor. The Ga content is varied, in an effort to investigate the effect of Ga content on the material and device properties.

A repeatable and easily controlled methodology is presented that allows fine adjustment of the absorber composition. A champion PCE of 9.8% is obtained for a graded bandgap of GGI 0.2-0.3.

6.3 Experimental details

The precursor preparation and deposition procedure is illustrated in Figure 64. In comparison to the methodology described in Chapter 5, a Ga precursor was added, as well as the Cu and In precursors.



Figure 64: Schematic diagram of the absorber preparation procedure, including the solution preparation, the deposition, the drying and the post-deposition selenisation step.

6.3.1 Preparation of CIGS precursor solution

The solutions were prepared targeting a Cu-poor film stoichiometry with varied Ga content. Each individual component solution (i.e., In_2S_3 , Cu_2S , Ga) was prepared by dissolving the corresponding powder in a mixture of EDT and EDA (v/v = 10:1) with a targeted concentration of 0.2 M. Precursor preparation was performed inside a fume hood, using a nitrogen-purged vial during dissolution.

350 mg of Cu₂S (2.2 mmol), 717 mg of In_2S_3 (2.2 mmol), and 153 mg of Ga metal mixed with 345 mg of Se (2.2 and 4.4 mmol respectively) were each dissolved in 11 ml of the solvent mixture. Solvents were added to the solid precursors sequentially under continuous stirring, starting with 10 ml of EDA and followed by 1 ml of EDT. The three inks are left stirring overnight at room temperature, after which they become optically transparent solutions which exhibit long-term stability of the order of several weeks or more. Mild heating of the Ga precursor mixture at ~50 °C for a few hours is required in order for the Ga metal to melt, and dissolve easily. The three component solutions were then mixed in predetermined ratios to form the CIGS precursor solution, depending on the targeted CIGS film composition. For example, for a targeted composition of Cu_{0.9}In_{0.9}Ga_{0.1}S_{1-v}Se_v, 2.25 ml, 2.25 ml and 0.25 ml were taken from the Cu₂S, In₂S₃ and Ga stock solution, respectively, and mixed together in a new vial. Unlike the hydrazine approach, no excess chalcogenide is required for metal sulphide dissolution in EDT-EDA solvent system [68]. Elemental Se is therefore only added to the Ga stock solution. The dissolution of Ga has also been attempted in the presence of S instead of Se, but the solubility limit was considerably lower.

Cu₂S stock solution is brown, Ga solution is dark orange and In_2S_3 solution is colourless. The mixed precursor solution is further diluted with ethyl acetate (2:1 v/v) and is filtered (0.45 µm PTFE) prior to the deposition step. After dilution, the precursor solution has a bright orange colour. Snapshots of each stock solution, as well as the CIGS precursor solution after mixing and dilution are shown in Figure 65.



Figure 65: Snapshots of each stock solution and the CIGS precursor solution (from mixing the three stock solutions and subsequently diluting), showing that all the solutions are optically transparent.

6.3.2 Film preparation and selenisation

Precursor spray deposition is performed in ambient atmospheric conditions within a fume hood using a glass chromatography atomiser. The films were sprayed onto Mo coated glass substrates placed on a hot plate, controlled at 310 °C. In between each spray run a 90 sec drying step was performed at the same temperature. After the final deposition/drying cycle, a post-deposition selenisation step was performed in the tube furnace. Unless otherwise stated, there was no intentional band-gap grading in the films and the same solution was used for all the spray cycles. Band-gap grading was attempted by first spraying 3 layers of the solution with GGI=0.3, followed by two layers of the solution with GGI=0.2.

For the selenisation, two 2.5 x 2.5 cm samples were placed inside a graphite box with Se pellets. The tube was first purged with nitrogen, after which the pressure was set to 400 Torr. Heating was maintained for 50 min at 550 °C and with a ramping rate of ~35 °C/min. This typically resulted in the evaporation of all of the Se in the box (~300 mg).

6.3.3 Fabrication of CIGS solar cells

The devices prepared in this work were completed using a standard device configuration of AZO/iZnO/CdS/CIGS/Mo/SLG. The CdS layer (~60 nm thickness) was deposited by chemical bath deposition. The intrinsic ZnO and AI doped ZnO layers (~80 nm and 500 nm respectively) were both deposited using RF sputtering. Finally, a top contact grid and MgF₂ AR coating were evaporated at Nanoco Technologies plc (UK). Mechanical scribing was performed to define and electrically isolate individual cells of ~0.25 cm² area. The top contact grid (0.05 cm²) shades about 20% of the device area. The results presented here represent the first devices in this work to use both AR coatings and current collection grids. Results presented in previous chapters were based on grid-less cells.

6.3.4 Characterisation

Prior to the JV measurements, the cell area was measured using a digital microscope. The fitting program Fityk was used for secondary phase identification on XPS spectra using Gaussian functions [150].

6.4 Results and discussion

6.4.1 Structural Properties

EDS analysis was performed on as-deposited and selenised samples. The chemical composition of the film is determined by averaging the data collected from 2 random points. Figure 66 summarises the composition of each film, as the concentration of each element in relation to the (In+Ga) content. The targeted film composition for the as-deposited films was Cu_{0.9}In_{1-x}Ga_xS_{1-y}Se_y, with a constant CGI ratio and a GGI varied from 0 to 0.4. The desired ratio for cations was controlled by mixing the stock solutions in certain ratios, as described in the experimental section. In terms of the S/Se content, it was assumed that S will only be incorporated from the metal sulphide compounds (and not the solvent) and Se from the Se powder (present in the Ga stock solution). Overall, it is shown that the atomic ratios of the cations in the as-deposited films are retained, which shows that there is no major cation loss during the deposition/drying steps.

Composition											
Ga/In+Ga		As-deposited				Selenised					
		Cu	In	Ga	S	Se	Cu	In	Ga	S	Se
0.0	Targeted	0.90	1.00	0.00	1.95	0.00	0.90	1.00	0.00	0.00	2.00
	Film	0.82	1.00	0.00	1.56	0.00	0.86	1.00	0.00	0.11	2.19
0.1	Targeted	0.90	0.90	0.10	1.80	0.20	0.90	0.90	0.10	0.00	2.00
	Film	0.93	0.91	0.09	1.46	0.13	0.88	0.92	0.08	0.08	2.41
0.2	Targeted	0.90	0.80	0.20	1.65	0.40	0.90	0.80	0.20	0.00	2.00
	Film	0.86	0.79	0.21	1.29	0.26	0.93	0.81	0.19	0.72	3.57
0.3	Targeted	0.90	0.70	0.30	1.50	0.60	0.90	0.70	0.30	0.00	2.00
	Film	0.85	0.73	0.27	1.19	0.32	0.88	0.72	0.28	0.19	2.04
0.4	Targeted	0.90	0.60	0.40	1.35	0.80	0.90	0.60	0.40	0.00	2.00
	Film	0.81	0.60	0.40	1.29	0.44	0.90	0.61	0.39	0.17	2.30

Figure 66: The targeted film composition (based on the precursor solution) and the actual composition of each as-deposited and selenised CIGS sample, estimated with EDS analysis. The composition noted is the ratio of each element (in at.%) in relation to the (In+Ga) content.

Similarly for the selenised films, the targeted composition was $Cu_{0.9}In_{1-x}Ga_xSe_2$. With regards to the S/Se content it is assumed that S is fully displaced by Se, as seen in in pure $Culn(S,Se)_2$ devices from Chapter 5. It is shown that the atomic ratios of the

cations (at least within the interaction volume of the electron beam) are retained in both, the as-deposited and the selenised films. Also, it was confirmed that S is mostly displaced by Se during the selenisation process, as previously seen for CIS films in chapter 5.

The effects of the Ga content on the CIGS structural properties were investigated with XRD and Raman analysis. The XRD patterns of all the films show the same distinct peaks which correspond to the chalcopyrite phase of Culn_{0.5}Ga_{0.5}Se₂ (JCPDS 40-1488). This indicates that the films grow mainly with the chalcopyrite structure, despite the composition. The XRD pattern of the sample with GGI=0.3 is shown in Figure 67 (a). It was found that the (112), (220)/(204) and (312)/(116) peaks shift toward higher 2 θ angles with increasing GGI, which indicates the reduction in the lattice constants caused by Ga substituting In [81]. The shift in the (220/204) diffraction peak to higher 2 θ values with GGI, is shown in Figure 67 (b). Finally, the peak split for GGI=0 appears due to the tetragonal distortion, which represents a high crystallite quality [151]. Interestingly, the well-split peak shape is only evident for the pure CulnSe₂ film which might suggest a small degradation in the crystalline quality with Ga addition [130].



Figure 67: (a) XRD pattern of a selenised sample with GGI=0.3. (b) XRD patterns showing the shift in the (220)/(204) diffraction peak with GGI, denoted as x. The peaks were normalised to facilitate comparison.

The Raman spectra of the as-deposited CIGS samples with varying GGI are shown in Figure 68 (a). No noticeable peaks are observed in these spectra which show that

there is no significant crystallisation prior to the selenisation step. The spectrum with x=0, however, shows two weak peaks at ~300 and 340 cm⁻¹, which could be associated to CulnS₂ or Culn₅S₈ phases [77,152].

Figure 68 (b) shows the Raman spectra of the corresponding selenised films. The most intense Raman peak for CulnSe₂ and Culn_{1-x}Ga_xSe₂ films is the A1 zonecentre phonon of the chalcopyrite structure [137]. As anticipated, the frequency of the A1 mode varies slightly with increasing x (GGI ratio) from 170 cm⁻¹ (for x=0) to 176 cm⁻¹ for (x=0.4). This anticipated trend was also previously observed for an aqueous spray-pyrolysis approach [81]. The peaks assigned to B2/E vibrational modes of the chalcopyrite are weakened with GGI, with the pure CulnSe₂ phase having the strongest peaks. An additional peak is evident in the film with GGI=0 at about 350 cm⁻¹ and is probably associated to the spinel Culn₅S₈ phase (observed in Cu-poor CulnS₂) [137]. Secondary phases associated with Se-rich composition, such as elemental Se and Cu_xSe are absent in these films [153]. Nonetheless, the presence of the Cu₂Se phase cannot be discarded, as it exhibits very weak Raman features [142].



Figure 68: Raman spectra of (a) the as-deposited and (b) selenised samples with varying GGI.

6.4.2 Solar cell properties

The sprayed CIGS films were completed into devices and the opto-electronic properties were investigated with EQE and JV analysis. The EQE spectra in Figure

69 (a) show a shift in the long-wavelength cut-off to shorter wavelengths, with GGI. This is indicative of the increased band-gap with Ga content. The drop in EQE at longer wavelengths suggests that the sample is not fully recrystallised throughout its thickness, which is in agreement with the work presented in chapter 5. Figure 69 (b) shows the band-gap values calculated from the EQE data by plotting $[E.ln(1-EQE)]^2$ versus E and extrapolating the band edge to the x-axis intercept [154]. The estimated band-gap values are close to the values calculated with the empirical formula for α -Culn_{1-x}Ga_xSe₂: $E_g = 1.65x + 1.01(1-x) - 0 + 151(1-x)x$ [41]. The calculated band-gap values are slightly higher than the theoretical values, which could be attributed to the presence of a small amount of S in the film.

The EQE spectrum and the light JV curve of the highest performing cell are shown in Figures 69 (c) and (d), respectively. A champion PCE of 9.8% (active area) was obtained with a targeted graded bandgap, with a GGI of 0.2 towards the front and 0.3 towards the back of the absorber. The bandgap grading will be further discussed in later sections of this chapter. The EQE spectrum of the graded device has the same long-wavelength cut-off compared to the non-graded cell with GGI of 0.2. The collection at the long wavelengths, however, is slightly higher. The improved collection could be associated to the back surface field provided by Ga grading [148].

The PV parameters for the best cell on each sample are summarised in Figure 70. The anticipated trend of increasing V_{OC} and decreasing J_{SC} with GGI is observed. Based on these results, it is shown that Ga can be conveniently and controllably incorporated in sprayed CIGS films for optimised solar cell properties.

Figure 71 shows the cross section SEM images for these devices. It is shown that the absorber and the MoSe₂ layer thicknesses are varied to some extent within these devices. It is evident that the device with the graded band-gap has the best morphology, with largest grains. Consequently, the improved collection of the champion device could be related to a better material morphology, rather than the band-gap grading itself. The improved crystallisation in the champion device could be related to small variations in the selenisation or the deposition procedure, and particularly to thickness variations. As described in chapter 5, the difficulty in controlling the absorber thickness is a limitation of the deposition technique used in this work.



Figure 69: (a) EQE spectra of CIGS devices with varying GGI, showing a shift in the longwavelength cut-off. The difference in the short wavelength region of the sample with x=0.4 is due to a small thickness variation in the CdS layer. (b) Correlation of the calculated bandgap values (from EQE) with the theoretical values. (c) EQE spectrum and (d) light JV curve of the best performing device, with a graded bandgap (GGI=0.2/03). The PCE, V_{oc}, J_{SC} and FF equal to 9.8% (active area), 528 mV, 30.7 mA cm⁻² and 60%, respectively.

	Photovoltaic Parameters						
Ga/In+Ga	V _{oc} (mV)	Active Area J _{sc} (mA/cm ²)*	FF (%)	Active Area Eff (%)*	Total Area Eff (%)		
0.0	466	31.1	49.5	7.18	5.81		
0.1	478	29.2	46.5	6.48	5.21		
0.2	521	28.4	57.2	8.47	6.83		
0.3	416	26.5	51.4	5.68	4.59		
0.4	575	19.2	55.2	6.10	4.91		
0.2/0.3	528	30.7	60.2	9.76	7.86		

Figure 70: JV characteristics of the best performing cell of each sample, with varying GGI.



Figure 71: Cross section SEM images of the CIGS solar cells with varying GGI. The images show the entire solar cell stack.

6.4.3 Depth Profiling

XPS analysis was performed on a CIGS film, which was representative of the record device. The depth profile was obtained through repetitive, sequential XPS measurements in-between 100 sec Ar^+ ion etching. The sample has a targeted graded E_g , with a GGI of 0.2 towards the front and 0.3 towards the Mo back contact.

Figure 72 (a) shows the elemental depth profile of the as-deposited sample. The CIGS/Mo film was etched until the glass surface, indicated by the increase in the O and decrease in the Mo signal. Carbon is only evident on the film surface due to air exposure during storage and handling and is therefore omitted from the profile. The low carbon content in the as-deposited sample is in agreement with the TGA analysis in chapter 4. It was shown that the majority of the organic species was removed during the drying step through a clean decomposition pathway, without leaving carbon impurities in the film. Figure 72 (b) shows the composition of Cu, Ga, S and Se in relation to the (In+Ga) content through the absorber thickness. In terms of the GGI ratio, there is a gradual increase from 0.2 to 0.3, as intended. This implies that the band-gap gradient can be accurately controlled within this technique. It is also shown that the absorber surface is Cu depleted, whereas in the bulk of the absorber the CGI ratio is 0.8, as intended. A non-intentional Cu depleted surface is typically observed for CIGS and it has been shown to reduce recombination at the CIGS/CdS interface [148].

Lastly, there is relatively high O content throughout the thickness of the as-deposited film and especially towards the surface. This implies that some of the precursors are oxidised during the deposition/drying steps which take place in air. Air is also used as the carrier gas for the spray deposition, which facilitates oxidation reactions.



Figure 72: (a) Elemental depth profile of the as-deposited CIGS sample on a Mo-coated glass substrate. (b) Relative composition of the elements through the absorber thickness.

Figure 73 shows the high-resolution scans of the peaks corresponding to Cu2p, In3d, Ga3d, and O1s measured at different depths in the absorber. The Cu2p peak position is constant, whilst the In3d and Ga3d peaks are slightly shifted through the etch levels. The peaks for In3d and Ga3d are positioned at a slightly higher binding energy for the first etch levels (200 and 300 sec), which indicates a contribution from the corresponding oxides near the film surface [155]. The In $3d_{5/2}$ peak is shifted to 445.2 eV near the surface, compared to 444.8 eV in the bulk of the sample. Similarly, the Ga $3p_{3/2}$ peak is shifted to 1118.0 eV compared to 1117.8 eV in the bulk. It is shown from the depth profile in Figure 72 (a) that at the same depth levels (200 and 300 sec) there is increased In and O content. These results, combined with the low FWHM of the O1s peak, suggest that Ga and In oxide phases, such as Ga₂O₃ and In₂O₃, are segregated at the surface. The presence of these oxides has previously been reported in the literature for CIGS [155,156].



Figure 73: High-resolution scans of the Cu2p, In3d, Ga3d, and O1s peaks measured at different depths in CIGS films.

Similarly, Figure 74 (a) shows the elemental depth profile of the selenised sample and Figure 74 (b) shows the composition of the elements in relation to the (In+Ga) content. The presence of a thick $MoSe_2$ layer at the CIGS/Mo interface is evident by the lower Mo and high Se content at 5000-13000 etching times.

In terms of the GGI ratio, it is shown that the gradient built into the absorber at the deposition stage is removed with selenisation. A GGI ratio of 0.2 is homogeneous throughout the depth of the absorber. This finding differs to what is typically reported for CIGS. Specifically, Ga tends to segregate towards the back contact due to the slower selenisation kinetics of Ga relative to In, resulting in separate CuInSe₂ and CuGaSe₂ phases [157]. No such phase separation is evident in this work. The homogeneous Ga distribution suggests that the slightly improved collection efficiency of the champion solar cell (compared to the corresponding non-graded cell) is not associated with the Ga grading, as would be anticipated based on the literature [148]. The higher performance could be solely related to the improved material morphology, as shown in the cross section SEM images of Figure 71. This can be caused by small variations in the selenisation or the deposition procedure, and particularly to thickness variations.

Surprisingly, the depth profile shows a significant Cu diffusion into the $MoSe_2$ layer, resulting in a Cu-poor stoichiometry towards the back of the absorber. It has been reported that $Cu_{2-\delta}S$ and $Cu_{2-\delta}Se$ compounds are superionic conductors in which Cu can diffuse easily [41]. Although the addition of In minimises this effect, Cu can still be highly mobile, even at room temperature [41].

The presence of Cu in the $Mo(S,Se)_2$ layer has previously been reported for kesterites and it was suggested that there was a phase separation of Cu₂ZnSnS₄ at the interface with the Mo [158,159]. Nonetheless, the so called "Cu out-diffusion" in kesterites was recently considered to be a measurement artefact induced by the TEM sample preparation [160]. The Cu diffusion to the back contact in our case was, however, obtained using a different analysis technique. Although the presence of voids in the film or potential chemical reactions caused by the ion bombardment could slightly affect the depth resolution, the Cu gradient in the $MoSe_2$ layer seems to be well defined, which makes it unlikely to be a measurement artefact [161].



Figure 74: (a) Elemental depth profile of the selenised CIGS sample on a Mo-coated glass substrate. (b) Relative composition of the elements through the absorber thickness.

Figure 75 shows the high-resolution scans of the peaks corresponding to Cu 2p, In 3d, Ga 3d and Se 3d, measured at different depths in CIGS films. The first three depth levels (900, 1300, 1700 sec) correspond to the absorber layer and the last depth level (10500 sec) corresponds to the MoSe₂ layer with a high Cu content. The increased FWHM and the shift in the Cu 3p_{3/2} peak to lower binding energy at this etch level could be related to the presence of the Cu₂Se phase [38]. This assumption is further supported by the fact that there is no In or Ga present in the MoSe₂ layer, which suggests that the Cu compound is different compared to the bulk of the absorber.

The Cu diffusion into the MoSe₂ layer and the resulting deviation to a Cu poor stoichiometry of the absorber layer might be the reason for the incomplete crystallisation though the absorber thickness, by inhibiting the formation of CIGS. Nevertheless, further investigation is needed in order to verify this reasoning. The application of a barrier layer on the Mo coated substrates could potentially minimise the Cu migration. Such a layer has been previously applied in Cu₂ZnSnSe₄ solar cells to inhibit decomposition reactions [159].



Figure 75: High-resolution scans of the Cu2p, In3d, Ga3d, and Se3d peaks measured at different depths in CIGS films deposited on a Mo-coated SLG substrate.

Overall, the bulk of the samples contain mainly the CIGS phase; however, peak fitting (Figure 76) suggests that secondary phases might be present. For the case of Cu 2p peak there is a Cu₂Se secondary phase in the MoSe₂ layer, identified at ~932.4 eV binding energy. An additional peak is present at ~934.1 eV, which could be related to the presence of a Cu-Mo-O alloy. This reasoning could not be confirmed, however, due to the difficulty in the deconvolution of the O1s peak. Similarly, peak fitting of the Ga 3d peak at the 1700 sec depth level suggests that Ga₂Se₃ is present as a secondary phase in the bulk of the absorber.

Finally, no O is present in the bulk of the selenised film, despite the high O content of the as-deposited film. This finding suggests that the oxides formed during the deposition/drying steps are reduced during selenisation. This is a surprising result since the reduction of the oxides is not thermodynamically favoured, as Ga and In oxides have lower enthalpies of formation than their selenide analogues [162].

Nonetheless, the approach followed by ISET uses a H₂/N₂ gas mixture, which makes the reduction of these metal oxides to be kinetically favourable [66]. The precursors in our films are partly oxidised due to the deposition and drying steps being performed in ambient atmospheric conditions. Also, air is used as the carrier gas during spray deposition. Side reactions could be avoided by performing these steps under inert conditions instead. The elimination of the oxidation side reactions is anticipated to facilitate the crystallisation step.



Figure 76: Peak fitting of the Cu2p and Ga3d peaks indicating the presence of secondary phases in the selenised film. Cu2p peak fitting shows the presence of Cu_2Se as a secondary phase, with an additional peak that could not be identified. Ga3d peak fitting shows the presence of Ga_2Se_3 .

6.5 Conclusions

This chapter presented a molecular solution-based approach for CIGS deposition, starting from metal chalcogenide precursor solutions. In comparison to the previous chapter, Ga was added in the starting solution for band-gap adjustment. CIGS thin films were spray deposited with varying GGI ratios and were implemented in solar cells. It was shown that Ga content can be conveniently controlled using this methodology, simply by modifying the composition of the starting solution. The effect of the Ga addition on the structural properties of the material was investigated with XRD and Raman analysis.

The fine adjustment of the Ga content can be used for optimising the material and solar cell properties. EQE and JV analysis confirmed the increase in the band-gap

with Ga content, with the anticipated trend of increasing V_{OC} and decreasing J_{SC}. A champion PCE of 9.8% (active area) was obtained with a graded E_g , with a GGI of 0.2 towards the front and 0.3 towards the back of the absorber. It was found that the improved collection of the champion device could be related to a better material morphology, rather than reduced back contact recombination caused by the band-gap grading. This reasoning was further supported with XPS analysis, which showed that the Ga gradient built into the absorber at the deposition step is removed with selenisation.

Despite this improvement, the devices are still non-ideal in terms of the back contact quality and incomplete absorber crystallisation. It was shown that there is a significant Cu diffusion into the MoSe₂ layer, causing a Cu deficiency towards the back of the absorber. The resulting Cu-poor stoichiometry could be the reason for the incomplete crystallisation though the absorber thickness, by inhibiting the formation of CIGS. The application of a barrier layer on the Mo coated substrates could potentially minimise the Cu migration [159]. Lastly, XPS analysis showed that the Ga and In precursors are partly oxidised during the deposition/drying steps in air, with oxide phases segregated at the absorber surface. Substitution of air with an inert gas as the carrier gas for spray deposition, and the use of a more controlled environment (i.e. glove box) could eliminate oxidation reactions. The absence of oxide secondary phases could facilitate selenisation, so that a milder selenisation (lower Se partial pressure) could be sufficient for the formation of highly crystallised CIGS films. Selenisation at lower pressures will minimise the MoSe₂ formation at the CIGS/back contact interface, which is still a limiting factor for the device quality in this work.

Further optimisation of the process is anticipated to result in better device performance. Nonetheless, the simplicity of this method and the potential for a fine compositional adjustment and optimised solar cell properties, make this process highly promising for CIGS fabrication.

Chapter 7 Non-vacuum processing of transparent conducting oxides

7.1 Scope

This chapter reports the development of a low cost, atmospheric deposition technique for aluminium-doped zinc oxide (AZO) films that can be used as the transparent conductive oxide (TCO) layer in TFSC. An ultrasonic spray pyrolysis system is used, which is a very versatile and easily controlled deposition technique. An introduction to the experimental setup will be given, followed by the optimisation of the deposition process for high quality TCO thin films. Finally, the characterisation of the obtained sprayed material will be presented, which shows good opto-electronic properties for TCO applications.

7.2 Introduction

Ultrasonic spray pyrolysis (USP) is a low cost, atmospheric deposition technique and is a viable alternative process to vacuum based systems. Spraying techniques are typically material-efficient and allow for high-throughput, thus they are very attractive from a manufacturing point of view [163].

TCO films are used in an increasing number of optoelectronic devices, such as displays and smartphones, as well as solar cells [164]. At present, the most commonly used TCO is tin-doped indium oxide (ITO), as it offers a combination of high transparency and high electrical conductivity [164]. Recently, however, there has been an increased interest in alternative TCO materials as indium is a relatively scarce element [165]. Zinc oxide (ZnO) is increasingly being investigated as an alternative metal oxide because of its non-toxicity, high abundance and low material cost [165]. ZnO is an n-type semiconductor and its conductivity can be tuned by

controlling the doping level. Doping can be intrinsic due to oxygen deficiency and interstitial zinc atoms, or extrinsic by adding impurity dopants in the film [166]. Extrinsic impurities can be used as substitutional elements for Zn or O. In terms of n-type doping, various extrinsic dopants have been used in the literature, such as gallium, aluminium and boron [166]. Aluminium is one of the most commonly used dopants, resulting in high quality opto-electronic properties [91]. Aside from these excellent characteristics, aluminium-doped zinc oxide (AZO) can be easily texturised, which was proven to be beneficial for TFSC applications, by enhancing light scattering and consequently extending the optical paths in the device [167].

AZO is conventionally deposited by RF sputtering using high purity ZnO:Al₂O₃ targets, but it can also be deposited by a range of atmospheric deposition techniques, such as metal organic chemical vapour deposition (MOCVD), sol–gel or spray pyrolysis [168]. Despite the fact that AZO is a cheaper alternative to ITO, the true low cost potential of AZO as a TCO material can only be realised when it is combined with a low cost deposition method. Consequently, the aim of this work is to deposit high quality AZO films by USP for their use in TFSC.

AZO thin films were deposited on glass by USP, from metal salt precursors. The electrical and optical properties were investigated as a function of the deposition parameters and the optimum conditions were defined.

7.2.1 Ultrasonic spray pyrolysis

Spray coating is a simple and cost-effective deposition technique, especially with regards to the equipment costs. As a solution-based method it can be easily controlled, for obtaining optimum material properties. The composition and the film properties can be adjusted, simply by modifying the precursor solution and the deposition parameters [69]. Spraying is a very versatile technique and can be used for the deposition of dense or porous films, and for powder production [169].

Compared to normal spray deposition which was presented in the previous chapters for CIGS deposition, spray pyrolysis (SP) technique requires more precise process control [69]. The SP technique for thin film deposition usually involves the spraying of a metal salt solution onto a heated substrate. The precursors undergo a pyrolytic decomposition, hence the process requires high temperatures [170]. By comparison, the spray process which is often used for the deposition of thin film absorbers is a sequential liquid coating approach [69]. This means that the process usually involves a separate thermal treatment which is performed in a precisely controlled gas atmosphere after the deposition step. As such, the high quality material is obtained after the thermal treatment and the deposition parameters do not significantly affect the final film quality [69]. SP, however, needs to be precisely controlled and the full process optimisation is necessary for a high quality material that is applicable as the TCO layer in a TFSC.

During the spraying process, the droplets reach the substrate surface, spread into a disk-shaped structure, and undergo thermal decomposition [169]. The shape and size of the disk depends on the momentum and volume of the droplet, as well as on the substrate temperature [169]. Many processes occur simultaneously when a droplet hits the surface of the substrate such as evaporation of residual solvent, spreading of the droplet, and salt decomposition [169]. Among the different spraying parameters, the substrate surface temperature is the most critical as it is affects all these processes. When the temperature is too low, the droplet splashes onto the substrate and decomposes. An increase in the temperature causes the complete evaporation of the solvent during the flight of the droplet and dry precipitate hits the substrate, followed by decomposition. At even higher temperatures the solvent is again completely evaporated before the droplet reaches the substrate. Then, the solid precipitate melts and evaporates without decomposition and finally the vapour diffuses to the substrate to undergo a chemical vapour deposition (CVD) process. At excessive temperatures the precursor is evaporated before it reaches the substrate and solid particles are formed upon a chemical reaction in the vapour phase [169]. At too low or too high temperatures, the deposited material has low quality; hence the temperature should be carefully optimised [169]. Figure 77 illustrates each case with increasing deposition temperature. It has been suggested that only a CVD process can give high quality films by SP [169].



Increased deposition temperature



There are different types of atomisation, such as pneumatic (the liquid is exposed to a stream of air), ultrasonic (use of ultrasound for fine atomisation) and electrostatic (use of a very high voltage electric field) [169]. Of these, ultrasonic spray pyrolysis (USP) offers additional advantages such as narrow droplet size distribution and precise process control [146]. Ultrasonic nozzles can be used for fine and lowvelocity aerosols, while for pneumatic spraying, a high velocity gas is needed to atomise the spray solution [69]. In the case of USP, the carrier gas is only used to transport the droplets to the substrate and not for the atomisation itself, which means that the gas flow rate is independent of the aerosol flow rate [171]. An inert gas can be used as the carrier gas, which means that the atomised solution can be directed onto the substrate by a clean gas stream [163]. This can be very important, particularly if there are side reactions taking place, such as the oxidation of the precursors.

Unlike absorber films, where sequential direct liquid processes can be used, precise control of the spray parameters is required for deposition of TCOs [69]. USP allows the fine adjustment of the deposition parameters, such as the carrier gas flow, solution flow rate, nozzle movement etc. in a reproducible manner and is therefore a well suited technique for this application.

7.3 Experimental details

7.3.1 Experimental setup

The USP deposition of thin films was conducted using a home-made system placed into a self-contained enclosure equipped with air extraction. The system consists of the precursor solution, a syringe pump for the liquid delivery, an ultrasonic generator, the spray nozzle and a substrate heater with a temperature controller. The heater is fixed on a table that is moved on the x axis, while the nozzle is moved on the y axis, to cover the entire area of the substrate. The x-y movement is controlled using a stepper motor driver. The ultrasonic nozzle used in this work was manufactured by Sonotek (NY, USA) with an operating frequency of 120 kHz. Figure 78 shows a simplified diagram of the spray setup with the main components of the system and a close-up snapshot of the spray nozzle.

The solution precursors are atomised into a fine mist spray, with the use of high frequency vibrations. The ultrasonic generator delivers the electrical energy required for the atomisation, which is then converted into kinetic energy in the form of vibrations, by piezoelectric transducers. The operating frequency of the nozzle (120 kHz) results in a median droplet size of 18 µm for water, as reported by the nozzle manufacturer. In this system, unlike pneumatic spray, there is no need for pressurised liquid or air for the atomisation process. A carrier gas is used in this system, which focuses the stream of droplets onto the sample, thereby increasing the material utilisation. A syringe pump is used for the liquid delivery, to control the flow of the precursor solution. Finally, a flow of cooling gas is applied in the nozzle housing, in order to prevent elevated temperatures that can cause degradation of the piezoelectric oscillators. The cooling gas ports are also shown in Figure 78.

Initial tests were inconclusive due to chemical attack of the titanium alloy front horn by the precursors, causing poor atomisation. After the replacement of the front horn and the microbore with new parts made from cobalt, the atomisation was significantly improved. It is expected, however, that the optimum conditions remain the same, as the nozzle is basically identical in terms of frequency, atomisation area, orifice size etc.



Figure 78: Left: Schematic diagram of the spray setup with the main components. Right: Close-up snapshot of the spray nozzle.

7.3.2 Precursor preparation

The starting precursors for AZO deposition were aluminium chloride and zinc acetate. The precursors were chosen based on their high solubility in alcoholic solvents and water. Zinc acetate was preferred among other salts, as it can be effectively decomposed to volatile molecules [172]. In terms of the aluminium source, aluminium chloride was found to be superior compared to other salts, in terms of the obtained film uniformity [173]. It has been suggested that chlorine impurities result in the creation of zinc vacancies (V_{Zn}) which act as compensating acceptors [174]. More recent work, however, shows that chlorine is actually an effective n-type doping element for ZnO, by substitutional doping of oxygen sites [166,175]. Consequently, Cl impurities originating from aluminium chloride are not anticipated to be detrimental for the film quality. Hydrated compounds were also found to be more stable compared to their anhydrous counterparts. In this work, precursor solutions of the anhydrous salts were occasionally starting to precipitate a few hours after dissolution, with Zn(OH)₂ formed as a by-product of hydrolysis [101].

Anhydrous $(Zn(CH_3COO)_2, AlCl_3)$ and hydrated compounds $(Zn(CH_3COO)_2.2H_2O, AlCl_3.6H_2O)$ were dissolved in methanol, water or a mixture of the two. The Al precursor was added as the dopant by altering the atomic percent of aluminium in relation to zinc. The doping ratio was varied from 0 (intrinsic material) to 8 at. %. The

corresponding volume of a 0.2 M Al precursor solution in methanol was added to the starting solution to vary the doping concentration. The final concentration of the Zn precursor varied from 0.05 to 0.2 M, in order to obtain the optimum deposition rate and material quality.

7.3.3 Substrate pre-treatment

AZO was deposited on a clean, bare SLG substrate, or on a SLG substrate coated with AZO nanoparticles, which served as a seed layer. The size of the SLG substrates was 5 x 5 cm with a thickness of 1 mm. The substrates were cleaned prior to the deposition using a simplified "RCA Standard Clean" process, which is a wet chemical treatment conventionally used in industry for cleaning silicon wafers [176]. The RCA process involves the immersion of the substrates in an alkaline mixture (water, hydrogen peroxide and ammonium hydroxide) and then in an acidic mixture (water, hydrogen peroxide and hydrochloric acid) in order to remove organic and inorganic contaminants from the surface [176].

AZO nanoparticles were spin coated on SLG substrates for the application of a seed layer. The nanoparticles were suspended in methanol in a concentration of 16.3 mg/ml. 1ml of the suspension was spin coated at 3000 rpm for 30 sec, with an acceleration speed of 500 rpm/s. After the deposition, the film was dried on a preheated hot plate controlled at 300 °C for 3 minutes. The deposition and the drying steps were repeated twice. A similar procedure has been used for an aqueous solution deposition approach for ZnO, where the use of a seed layer was proven to be essential for layer nucleation [177]. The AZO nanoparticles used here were synthesised by detonation of an emulsion containing Zn and Al metal precursors and were provided by the Portuguese company Innovnano S. A. [178].

7.3.4 Deposition of the precursor

For the spraying conditions, a large number of process parameters were optimised in parallel in order to obtain good electronic and optical properties. Key parameters included the atomisation power, the flow rate of the precursor solution and the carrier gas flow rate. The required atomisation power is correlated with the solution flow rate and they both have to be controlled in parallel in order to obtain a fine mist of droplets. Additional parameters such as the distance between the nozzle and the heater and the deposition temperature were also investigated.

7.3.5 Post-deposition annealing

Although the optimisation was based on as-deposited samples, a post-deposition annealing step in vacuum was occasionally performed. The annealing treatment was carried out in a Plasma Quest Ltd HiTUS RF sputtering system at 400°C for 1 hour and with a 4% hydrogen in argon gas mixture. The working pressure was $3x10^{-3}$ Torr and the base pressure was in the order of 10^{-7} Torr. Unless otherwise stated, annealing was performed with an argon/hydrogen flow. Occasionally, a 100% argon gas flow was used instead, for 1 hour and at 500°C.

7.3.6 Characterisation

The resistivity of the films was determined by Van der Pauw Hall Effect measurements on 1 cm² samples. Sheet resistance measurements were taken using a four-point probe with the corresponding resistivity values cross checked with the Hall Effect measurements. The thickness of the samples was measured using an Ambios XP2 stylus profilometer after etching the sample with zinc powder and hydrochloric acid. Prior to the XPS analysis, the samples were etched for 30 seconds. Depth profiling data have been obtained through a repetitive, sequential process of XPS measurements followed by a 30 sec etch. The grain size from the SEM was measured offline using AxioVision software (release 4.9.1, Zeiss). Coherence Correlation Interferometry (CCI) was performed for analysing the film surface topography using a Sunstar HD CCI instrument from Taylor Hobson Ltd [179].

7.4 Results and Discussion

7.4.1 Optical properties

The optical properties and specifically the transmittance did not vary significantly with the variation of each deposition parameter, but were indirectly associated with the parameters that affect the thickness of the samples. The optimisation process was therefore mainly carried out based on the obtained electrical properties. It was found, however, that the use of a seed layer has an effect on the transmittance of the films.

Figure 79 shows the transmittance and reflectance spectra from three representative samples deposited using the optimum parameters, as defined according to the obtained electrical properties. All sprayed films have high transmission in the visible range. AZO samples deposited on bare glass gave an average transmission of 78% and 82% for films with a thickness of 1.8 µm and 1.2 µm, respectively. The loss in transmittance due to increased thickness is not significant, allowing for the deposition of thicker films for improved electrical properties without sacrificing optical transparency. The interference fringes at wavelengths longer than the band-gap have a different spacing and magnitude, which are mainly dependent on the film thickness [180]. Figure 79 also shows the transmittance spectrum of a sample deposited with the same conditions but grown on the seed layer of nanoparticles, instead of on bare glass. The implementation of nanoparticles as a seed layer results in increased transmission compared to a sample deposited directly on glass with a comparable thickness. The absence of interference fringes for the film deposited using the seed layer is an indication of a rough surface [181]. Textured TCOs can be beneficial in certain thin film applications, such as ultra-thin CIGS or amorphous silicon solar cells [167]. Overall, it is shown that the transmittance of sprayed AZO can be increased by using a seed layer on the substrate, due to the subsequent surface roughness.

The band-gap was estimated using Tauc plots. The presence of a linear part in the plot of $(\alpha hv)^2$ against hv shows that the material is a direct band-gap semiconductor. An example of the band-gap determination is shown in Figure 80 for the sample of 1.8 µm thickness. The spread in the values of Figure 80 could originate from unintentional sample thickness variations and consequently, an error in the absorption coefficient calculation. Therefore, this method allows only a rough estimation of the band-gap. Nonetheless, the band-gap of the material is estimated to be 3.32 eV, which corresponds to the zinc oxide [182].



Figure 79: Transmission and reflection spectra of three representative samples; (blue): AZO on bare glass (1.8 μ m thickness), (red): AZO on bare glass (1.2 μ m thickness), (black): AZO seeded (2.6 μ m thickness).



Figure 80: Estimation of the band-gap by Tauc plot, for a sprayed AZO film deposited with optimum conditions. The linear portion to the horizontal axis is extrapolated to the horizontal axis, for band gap estimation.

7.4.2 Electrical properties

The optimisation process was focused on the electrical properties of the films, as these are dramatically affected with each deposition parameter. The deposition parameters do not materially affect the optical properties in the visible spectrum, provided that the thickness, the nature of the substrate and the solvent used are the same.
Each deposition parameter was varied while keeping the remaining parameters constant in order to analyse the effect on the film quality. A four-point probe was used for the optimisation based on the sheet resistance values. Part of the optimisation based on the sheet resistance is shown in Figure 81. For all depositions, the same volume of solution (20.4 ml) was used to deposit similar thicknesses of ~250-300 nm. This thickness was used to speed up and simplify the optimisation process. However, thicker films show improved electrical properties due to higher carrier concentration and carrier mobility which result from increased grain growth [183]. The following subsection describes the optimisation of each process parameter.

Atomisation power:

The atomisation power can be adjusted by changing the output of the power generator. The power generator sends the electrical input to the piezoelectric transducers, converting it to vibrations. The vibrational amplitude of the atomising surface and thus the input power should be carefully controlled, in order to obtain a fine and low velocity mist. A narrow range of input power (1.3-1.4 W) to the spray head is ideal for the formation of a fine mist. At lower input power, the atomisation of the drops is inefficient, while higher power leads to cavitation (rapid collapse of bubbles) inside the nozzle causing a disturbed mist flow [184]. Partly atomised drops and cavitation bubbles can both result in poor surface quality and deterioration of the film electrical properties. Figure 81 (a) shows the effect of the atomisation power on samples deposited as follows: 4% doping level, hydrated compounds dissolved in 100% methanol at a concentration of 0.2 M, a deposition temperature of 475 °C, a precursor flow rate 0.6 ml/min and nitrogen flow rate of 7 LPM.

Doping level:

Conductivity can be increased with the generation of additional free charge carriers. This can be achieved through increased doping, such that AI^{3+} ions substitute the Zn^{2+} site, consequently creating one extra free carrier [166]. There is, however, a limit on the doping level. Excess doping leads to saturation in crystal grains and grain boundaries. Films with excessive doping levels tend to have an increased ionised impurity scattering, which limits the carrier transport in the material [96]. Figure 81 (b) shows the effect of the atomisation power on samples deposited as

follows: use of hydrated compounds dissolved in 100% methanol, a concentration of 0.2 M, deposition temperature 475 °C, precursor flow rate 0.6 ml/min, nitrogen flow rate of 7 LPM and atomisation power of 1.2 W. The lowest sheet resistance values are obtained for a 2% doping ratio. It should be noted that the resistivity of the film with 0% doping was outside the measurement range of both the 4-point probe and Hall Effect system.

Carrier Gas Flow:

High flow rates of carrier gas cause cooling of the heated substrate and, consequently, the incomplete pyrolysis of the precursors. Conversely, low flow rates do not deliver the droplets efficiently to the substrate surface and as a result, the deposition rate is reduced. An optimum rate of 6 LPM was determined, as shown in Figure 81 (c). For the optimisation of the carrier gas flow, the following parameters were kept constant: the use of hydrated compounds in 100% methanol, a concentration of 0.2 M, deposition temperature of 475 °C, precursor flow rate 0.6 ml/min, 4% doping and atomisation power of 1.3 W.

Precursor flow rate:

High precursor flow rates cause the formation of bigger droplets and therefore thicker and more conductive films. Very high flow rates, however, cause incomplete atomisation and a low quality material, with the non-atomised droplets forming separate domains on the surface and causing inhibited carrier transport [185]. For the optimisation of the precursor flow rate shown in Figure 81 (d), the parameters kept constant were: the use of hydrated compounds and 100% methanol, a concentration of 0.2 M, deposition temperature of 475 °C, 2% doping and 1.2 W atomisation power.

Precursor concentration:

The optimum concentration of the solution is in the range of 0.1-0.2 M. At higher concentrations, there is a limited solubility of zinc acetate in methanol; whilst at lower concentrations the deposition rate is very low, making the process very slow and, therefore, less practical.

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Figure 81: Optimisation of (a) atomisation power, (b) doping level, (c) carrier gas flow and (d) solution flow rate based on the sheet resistance values of the films.

Carrier Gas:

Nitrogen and compressed air were used as the carrier gas. The use of compressed air gave highly resistive films, probably because of the presence of excess oxygen making the ZnO film closer to stoichiometric. A more stoichiometric ZnO will have a low density of oxygen vacancies and will therefore be more insulating [186].

Temperature:

High deposition temperatures compensate the cooling effect from the carrier gas, therefore facilitating pyrolysis. At very high substrate temperatures (>475 °C), however, the droplets dry too quickly forming separate domains at the surface. At even higher temperatures (>500 °C) there is rapid solvent evaporation inside the spray head which causes the nozzle to become clogged. The formation of separate

domains makes the film resistive, because the charge transport across the domain boundaries is impeded [185]. A deposition temperature of 475 °C was found to be the optimum in terms of sheet resistance and material quality.

Annealing:

The sheet resistance of the films is significantly decreased by implementing a postdeposition annealing step in vacuum. It was reported that vacuum annealing removes some of the adsorbed oxygen on the as-deposited film, which is present as a result of the oxygen-containing deposition atmosphere [187]. Similarly in this work, annealing in reducing conditions increases the conductivity of the films by reducing the excess oxygen species.

Other parameters:

The combined effect of the type of precursor, solvent mixture and the deposition temperatures are shown in Figure 82. A small amount of water was occasionally added in the starting solution in order to investigate the effect of the solvent on the obtained electrical properties. In addition, anhydrous compounds could only be fully dissolved in the presence of water. Addition of water (5% v/v) results in considerably more resistive films for the same precursor type and concentration. The higher surface tension and viscosity of the water compared to methanol cause the formation of bigger droplets and thus poor film quality [185]. Additionally, the higher resistivity in the case of water-containing solution could be related to the presence of hydrated zinc species and excess oxygen in the film [95].

The use of anhydrous compounds compared to hydrated compounds dissolved in the same solvent mixture results in more resistive films, as shown in Figure 82. Nonetheless, the sheet resistance values for hydrated and anhydrous compounds are comparable at higher deposition temperatures or after post-deposition annealing in vacuum. The difference in the film conductivity with the precursor type could be related to insulating hydroxides Zn(OH)₂ precipitating from solution in the case of the anhydrous salts.

Lastly, the conductivity is improved with post-deposition annealing in reducing conditions for all the samples. The improvement in conductivity with annealing is

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more pronounced at low deposition temperatures. This could be related to a more obvious change in crystal quality or to a more pronounced oxygen removal.



Figure 82: The effect of the type of precursor, solvent and deposition temperature on the sheet resistance. Solid lines: as deposited samples, dotted lines: annealed films in vacuum after deposition.

7.4.3 Structural properties

The XRD pattern of a sample deposited with optimum conditions before and after annealing is shown in Figure 83. The XRD pattern verifies the hexagonal wurtzite structure of the ZnO, according to the International Centre for Diffraction Data (ICDD) reference pattern (00-036-1451). No noticeable difference is observed between the patterns of the as deposited and annealed sample in terms of shift, peak sharpness and intensity. This suggests that the conductivity improvement with annealing is related to composition (reduction of oxygen species) rather than crystal quality improvement.

The surface morphology of the samples deposited with optimum conditions is shown in the top-view SEM images in Figure 84. The top two images correspond to a sample deposited on bare glass. The material is polycrystalline, comprised of grains ~300 nm in size. The bottom two images correspond to the representative AZO sample, but deposited on a seed layer of AZO nanoparticles on a SLG substrate. The two films have a comparable thickness, with 1800 nm and 1920 nm for the film on bare glass and the seeded sample, respectively. The nucleation seems to be significantly affected by the presence of the seed layer, with the surface morphology of the seed layer being exhibited at the film surface. Large coalesced grains are present 1.5-2 μ m in size, which comprise of smaller grains of 200-290 nm size. There is a clear increase in surface roughness in the seeded films, which is in line with the optical transmission spectra in Figure 79.

Figure 85 shows a snapshot of the seed layer on an SLG substrate. The presence of the seed layer makes the film look hazy, but it is still highly transparent, as shown in the transmittance spectrum of the seeded sample in Figure 79. The SEM top surface image is also shown for the same sample.

The microstructure of the sample deposited on bare glass was also investigated with a cross section TEM image, shown in Figure 86. The film is composed of small crystals of 20 to 100 nm with some voids present on the order of 10 nm across.



Figure 83: XRD pattern of AZO deposited on glass, before and after annealing. The XRD pattern of the annealed sample was shifted for clarity. Both XRD patterns correspond to the hexagonal wurtzite structure of ZnO.



Figure 84: SEM images of two AZO films for comparison, at two different magnifications. 1(a, b): AZO on bare glass, 2(a, b): AZO on the nanoparticle seed layer.



Figure 85: (Left): Snapshot of the seed layer, deposited by spin coating on a SLG substrate. (Right): Top surface SEM image of the same sample.



Figure 86: TEM cross section image of a sample showing small grains with <100 nm size.

7.4.4 Compositional analysis

XPS was performed for compositional analysis of a representative sample. Figure 87 (a) shows the elemental depth profile of an as-deposited sample on bare glass, deposited with optimum conditions. The surface of the sample is zinc deficient and there is excess oxygen as a result of the sample being deposited in an oxygen-containing atmosphere. Aluminium is not detected at the surface, whilst it is around 2% through the depth of the sample. By etching the sample, the oxygen concentration is decreased and the material becomes oxygen deficient, which is beneficial for the material properties since oxygen vacancies make ZnO more conductive [186]. The elemental composition remains almost constant through the remainder of the depth profile.

The high resolution scan for the O1s peak is shown in Figure 87 (b). Fitting analysis shows that the peak consists of two separate peaks. The lower energy peak at around 531 eV corresponds to the Zn-O bond, while the higher energy peak corresponds to hydrated oxide species [95]. It has been suggested that the second peak corresponds to chemisorbed oxygen or to OH– groups on the surface of samples, such as the absorbed O_2 and H_2O [95]. Interestingly, the composition of the chemisorbed oxygen on the sample remains constant through the film. Carbon and chlorine were not included in the depth profile for clarity, but were less than 1%.



Figure 87: (a) Elemental depth profile of the sample. (b) High-resolution scan of the oxygen peak, indicating the presence of two types of oxygen.

7.4.5 Summary of results

The electrical properties of the films deposited with optimum conditions are given in Table 1.

Sample	Thickness (nm)	Resistivity Hall Effect (Ω cm)	Carrier Concentration (/cm³)	Mobility (cm²/Vs)	R _{sheet} (Ω/ _{sq})
AZO	1800	2.31 x 10 ⁻²	-9.03 x 10 ¹⁹	2.99	67.50
AZO annealed (400°C Ar/H ₂)	2200	9.11 x 10 ⁻³	-1.57 x 10 ²⁰	4.37	42.20
AZO seeded	1920	4.64 x 10 ⁻²	-5.89 x 10 ¹⁹	2.28	121.43
AZO seeded	2601	2.02 x 10 ⁻²	-7.32 x 10 ¹⁹	4.22	73.48
AZO seeded annealed (500°C Ar)	2675	9.66 x 10 ⁻³	-1.02 x 10 ²⁰	6.33	23.31

Table 1: Summary of the electrical properties of the best samples, before and after the annealing treatment.

It is shown that there is a decrease in the resistivity and an increase in the carrier concentration with increasing thickness and annealing treatment (Ar/H₂ in vacuum at 400°C or Ar only at 500°C). The increase in the mobility of the seeded samples could be related to the more pronounced crystal growth or to inaccuracies within the Hall Effect system, given that the values are close to the minimum that the system is capable of measuring accurately. More analysis is required to adequately control the mobility, transmittance and resistivity of the film. It was demonstrated, however, that the nanoparticle seed layer is a useful addition to the sprayed AZO process for adjusting the film properties.

7.4.6 Implementation of sprayed AZO films in a solar cell device

In order to show the applicability of the sprayed films as the TCO layer in TFSC, a non-seeded sprayed AZO sample deposited with optimum conditions was implemented in a CdTe device. The film was applied in a CdTe solar cell, as it is easier to decouple the effect of the TCO in CdTe devices compared to CIGS. CdTe solar cells are typically prepared in a superstrate configuration and as such, the TCO layer is deposited first. This prevents elemental interdiffusion which would otherwise occur in a substrate configuration (like in CIGS) due to the high deposition temperatures of sprayed AZO films.

The CdTe device was processed according to a standard close-space sublimation (CSS) process at Colorado State University, with a TEC-12D/CdS/CdTe/back contact structure and a CdCl₂ and Cu treatment [188]. Two devices were made for comparison. The first was prepared as a reference according to the standard process used, with FTO-coated glass (TEC-12D, Pilkington) as the TCO layer. For the second device, the TCO layer was replaced with the sprayed AZO film. The AZO film was deposited on a bare 1 mm borosilicate glass (Corning Eagle XG^{TM}) substrate, due to the lower sodium content of these substrates, as sodium has shown to be a detrimental dopant in CdTe [189].

Figure 88 shows the JV characteristics of the two devices. The device with the sprayed AZO has a decreased performance compared to the reference device, mainly due to the decreased FF. The lower FF is mainly attributed to the higher series resistance and the slightly lower shunt resistance of the device, caused by the higher TCO sheet resistance (40 Ω /sq as opposed to 12 Ω /sq) and poorer junction

quality, respectively. The poor junction quality originates from the absence of a thin intrinsic oxide buffer layer on the TCO (referred to as high resistance transparent layer) in the stack. Application of a buffer layer could further improve the shunt resistance and FF of the device [190]. The layer thickness and the sheet resistance should be optimised in order to reduce the optical and the electrical losses.



Figure 88: JV curves of CdTe devices with the sprayed AZO and with a standard configuration.

Overall, it was shown that sprayed AZO can be used effectively as the TCO layer in TFSC. Further device optimisation is needed for higher performance CdTe devices; however this was not within the scope of this thesis.

7.4.7 Investigation of the poor atomisation at non-optimum conditions

The precise control of each deposition parameter during SP is very important for the obtained film quality. At non-optimum conditions the atomisation is poor, resulting in non-optimal electrical properties for the TCO. For example, at too high flow rates or at too low atomisation power, the droplets are not sufficiently atomised. Deposition temperatures which are outside the optimum range also result in bad morphology. As a result, the non-atomised droplets or the droplets that were dried too quickly (prior to reaching the substrate) form separate domains on the surface which cause inhibited carrier transport.

An example of bad atomisation is shown in the SEM images of Figure 89. This is for a sample deposited at a too high deposition temperature (550 °C) resulting in rapid

drying of the droplets. The SEM images show the formation of separate domains on the surface with a higher magnification image on the edge of one of the dried droplets. EDS point analysis was also performed for elemental composition. The composition is determined by averaging the data collected from 2 random points, measured on the dried droplet and outside the droplet (denoted as bulk), respectively. There is increased AI content on the droplet, which could be aluminium oxide segregated at the surface. The difference in the composition suggests that the structural inhomogeneity is not the sole parameter diminishing the film conductivity, but compositional inhomogeneity could have an effect as well.



Figure 89: SEM images of a sample, deposited at 550°C. Left: Stacking of dried droplets. Right: The image was magnified on the edge of the droplet. EDS composition analysis on the sample, of the dried drop and in the bulk of the film.

In order to further investigate the poor atomisation, CCI was used. CCI is a noncontacting surface metrology tool and is capable of analysing the surface topography of a relatively large area [179]. It can give information on the surface roughness and step height measurements [179]. Figure 90 shows a two dimensional "false colour" image of one of the samples, with the height information represented by colour changes. This is for a sample deposited when the microbore of the nozzle was not placed at the optimum position inside the nozzle housing. It is evident that there are dried drops on the surface of the sample, caused by the poor atomisation. A threedimensional CCI image of the same sample after etching is also shown in order to give a more visible representation of the surface topography. Figure 91 shows the cross section profile of one of the dried droplets on the surface. It is shown that the dried droplet leaves a coffee ring pattern at the micron scale. The solids are in the order of 10 µm and result in deterioration of both the optical and electrical properties of the films. This analysis shows that in order to obtain high quality and homogeneous sprayed TCO films, an in-depth optimisation of the process is required.



Figure 90: Left: 2-D 'false colour' image for one of the samples. The height information is represented by colour changes. Dried droplets are present on the surface of the sample. Right: 3-D CCI image of the etched sample.



7.5 Conclusions

The development of low cost deposition techniques such as SP is challenging, as there are a large number of parameters that can affect the thin film properties. By fully optimising the spray deposition process, however, AZO layers of sufficiently good electronic and optical properties were deposited which can be used as the TCO layer in TFSC. It was shown that the sprayed films can be effectively used as the TCO layer in TFSC by implementing a sprayed TCO film in a CdTe device. AZO can also be deposited on a nanoparticle seed layer for adjusting the optical properties of the films. Thin films deposited with optimum conditions exhibit ~80 % transparency and a resistivity in the order of $2x10^{-2} \Omega$ cm. Lastly, it was demonstrated that the electrical properties can be further improved by implementing

a post-deposition annealing in vacuum, or with increase in thickness which causes insignificant transmission losses.

Even after the optimisation of the process, the properties of the resulting films are not as ideal as those deposited using high vacuum techniques, like sputtering. The solution processing of AZO films introduces a source of contamination, such as chlorine and carbon which cannot be removed completely, even after a high temperature annealing step. The incorporation of chlorine and carbon impurities was however detected at a level of <1 at% and so the contribution of these impurities to the electrical and optical properties of AZO films remains unclear.

The deposition occurs in an oxygen-containing environment, with the excess oxygen causing the film to be more stoichiometric and therefore more resistive. This source of contamination is eliminated in sputtering, as sputtering occurs in ultra-high vacuum and as a result, a sheet resistance of <10 Ω /sq can be obtained. The excess oxygen in the sprayed films can be partly reduced, by implementing a post-deposition annealing step, especially in a reducing atmosphere. Even with the annealing treatment the samples are still not ideal, with the lowest obtained sheet resistance of 23 Ω /sq. Alternatively, an improvement could be obtained by performing the depositions inside an air-tight enclosure (e.g. glove box) using an inert gas, which would allow a highly controlled environment.

Chapter 8 Conclusions and suggestions for further research

Substitution of high vacuum processing with atmospheric-based deposition techniques for CIGS can potentially result in significant cost savings. Aside from the low costs, a truly successful large-scale manufacturing process should ideally be combined with high production yield, high power conversion efficiency, low energy consumption and safety.

During the course of the present thesis, a solution-based deposition approach was developed for CIGS. In the following section, a summary of the conclusions and suggestions for further studies is given.

An atmospheric-based deposition technique was developed for aluminium-doped zinc oxide (AZO) films that can be used as the transparent conductive oxide (TCO) layer. AZO films were deposited using an ultrasonic spray pyrolysis system, which is easily controlled and scalable to large-areas. The deposition occurs in air, thus in an oxygen-containing environment, with excess oxygen causing the film to be closer to stoichiometric and, therefore, more resistive. After process optimisation, a sheet resistance of ~23 Ω /sq was obtained which can be further improved by increasing the thickness with minimal transmittance losses. The limiting factor in this approach is the excess oxygen in the film, which is still present (although to a lesser extent) after a post-deposition annealing step in a reducing atmosphere. Further improvements could be obtained by performing the depositions inside an air-tight enclosure (e.g. nitrogen-filled glove box), which would allow a highly controlled environment.

In terms of the CIGS absorber layer, a hydrazine-free, molecular-based approach was developed using metal chalcogenides starting precursors. As shown in chapter 4, metal sulphides are effectively dissolved in 1,2-ethanedithiol/1,2-ethylenediamine, forming optically transparent solutions with long-term stability. It was also shown that

the majority of the organic species were decomposed during the drying step without leaving carbon impurities in the film. The clean decomposition pathway, together with the simple precursor preparation and the straightforward compositional control make this approach extremely attractive from a manufacturing perspective.

Chapters 5 and 6 show the device processing for Culn(S,Se)₂ (CIS) and Cu(In,Ga)(S,Se)₂, respectively. For CIS, an overview was given on the incremental increase of the power conversion efficiency up to 8.0% and it was shown that the selenisation step conditions have a dramatic effect on material quality. Rapid thermal processing (RTP) was explored as an alternative selenisation technique to tube furnace annealing and it was found to improve the back contact/absorber interface. Gallium was effectively incorporated into the absorber for band-gap adjustment, resulting in CIGS solar cells with PCEs of up to 9.8%.

Nonetheless, there is still room for improvement in terms of absorber porosity and back contact quality. As shown in chapter 5, sprayed films are much denser than spin coated films, although they are still mesoporous. The remaining porosity of the absorber causes Se to diffuse towards the back forming a thick MoSe₂ layer which causes a high series resistance in the device. The porosity could be further reduced by implementing a soaking step in the cation precursor solution prior to selenisation (as in [131]). Denser films are anticipated to minimise the Se diffusion to the back of the absorber, thereby resulting in a more controlled MoSe₂ formation. The use of RTP as an alternative selenisation approach resulted in a thinner MoSe₂ layer, although still relatively thick. The device performance was also found to be significantly dependent on the absorber thickness, since the latter affects the extent of Se diffusion and consequently the MoSe₂ formation. It is challenging, however, to control the absorber thickness with hand-held spraying, due to the manual nature of this deposition technique.

Aside from the excessive MoSe₂ formation, the high series resistance is also attributed to the incomplete crystallisation throughout the absorber thickness. XPS analysis on CIGS films in chapter 6 showed that there is a significant Cu diffusion into the MoSe₂ layer, causing a Cu-poor stoichiometry towards the back of the absorber. The Cu diffusion and the resulting deviation to Cu-poor stoichiometry could justify the incomplete crystallisation, although further analysis is required to verify

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this assumption. A barrier layer could potentially be applied on the Mo coated substrates to minimise Cu migration at the back contact (as in [159]). Also, a thin MoN_x barrier could be applied as an intermediate layer in the back contact to minimise the $MoSe_2$ layer formation (as in [140]).

XPS analysis on the as-deposited films showed that the Ga and In precursors are partly oxidised after the deposition/drying steps in air, with oxide phases segregated at the absorber surface. Substitution of air with an inert gas as the carrier gas for spray deposition, and the use of a more controlled environment, such as a nitrogenfilled glove box, could eliminate oxidation reactions, which would make the selenisation reaction more thermodynamically favourable.

In addition, a more controlled spraying technique should be implemented, instead of the hand-held chromatography atomiser. Ultrasonic spray pyrolysis, for example, which was used for the TCO deposition, allows precise process control and has a narrower droplet size distribution, which is expected to improve the packing density of the material [146]. Moreover, the use of an inert carrier gas can eliminate side reactions such as oxidation, which otherwise occur in air. The use of a more controlled deposition system will result in highly uniform samples with reproducible thicknesses and consequently, photovoltaic properties.

No sodium or antimony dopants have been used intentionally in this process. These dopants have been shown to improve the electronic properties and enhance the grain growth of CIGS, respectively [191,192]. Sodium was only supplied from the glass substrate through diffusion. A SiO₂ barrier layer could be applied on the soda lime glass substrate to prevent sodium diffusion and the doping can instead be performed externally, in a controllable manner. For example, sodium can be added by evaporating a sodium compound, such as NaF [193]. Alternatively, sodium can be supplied by dissolving a sodium containing compound in the precursor solution, or by dip coating the as-deposited film in an alkali solution [82,194].

Lastly, it was shown that excess chalcogenide (S, Se) can be successfully dissolved in the starting solution. A clean annealing process can therefore be sufficient for the formation of high quality absorbers, provided that sufficient amount of Se is added in the starting solution.

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