LASER CHEMICAL PROCESSING (LCP) OF POLY-SILICON THIN FILM

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LASER CHEMICAL PROCESSING (LCP) OF POLY-SILICON THIN FILM

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DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in

its entirety.

I have duly acknowledged all the sources of information which have been used in the

thesis.

This thesis has also not been submitted for any degree in any university previously.

S. Viras

SIGNATURE 12th May 2015

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Abstract

Laser chemical processing (LCP), developed by Fraunhofer Institute for Solar Energy Systems was successfully applied in fabricating *n*-type selective emitters and *p*-type local back surface fields for bulk crystalline silicon wafer solar cells. In this thesis, LCP is demonstrated as a straightforward technique for laser doping of poly-silicon (poly-Si) thin films, thereby overcoming the process complexity related to laser doping on thin films as well as supplying a practically infinite amount of dopants during the doping process. Using a frequency-doubled (532 nm) tunable nanosecond Nd:YAG laser coupled inside a phosphoric acid jet, LCP was successfully applied in fabricating an *n*-type active layer for poly-silicon thin film solar cells on glass.

Different LCP parameters such as pulse energy, pulse overlap and pulse length were investigated for *n*-type doping of boron-doped poly-Si films. The sheet resistances (R_{sh}) and active dopant concentration were assessed by four-point-probe and electrochemical capacitance-voltage (ECV) profiling. The peak doping concentrations and doping depth were influenced by the melt lifetime and number of melt cycles per unit area, which were dependent upon the LCP conditions. Below the ablation threshold, a longer melt lifetime increases impurity diffusion inside the poly-Si until the liquid jet dominates the melt flow above a characteristic melt expulsion time.

Dopant activation was performed by post-LCP annealing in a nitrogen-purged oven using different temperatures and durations or by a rapid thermal process (RTP) at 1000 °C for 1 min. The best structural quality and lowest R_{sh} were obtained under RTP conditions. LCP was then applied to fabricate an *n*-type emitter on a p^{-}/p^{+} poly-Si thin film layer structure on glass. After dopant activation, the sheet resistances were about 2-5 k Ω/\Box and the active dopant concentration was about 8 x 10¹⁸ cm⁻³ to 1 x 10¹⁹ cm⁻³ at a doping depth of less than 350 nm (as measured by ECV). Selected samples were then passivated by hydrogenation in a low pressure chemical vapor deposition tool with an inductively-coupled remote plasma source. The R_{sh} was further reduced due to improved carrier mobility from passivation of defects. Furthermore, the device performance was evaluated by quasi-steady-state open-circuit voltage (Suns- V_{oc}) measurements before and after hydrogenation. A major improvement in open-circuit voltage (V_{oc}) (> 400 mV) and pseudo-fill factor (*pFF*) (> 65%) was realized through hydrogenation whereby the best cell had an average V_{oc} of (446 ± 7) mV and a *pFF* of (68.3 ± 0.9)%. It was found that the post-LCP anneal was the limiting factor for better device performance.

A detailed investigation of the electrically-active defects also indicated that the V_{oc} and *pFF* of the fabricated cells were limited by intra-grain defects generated from excessive hydrogenation as well as recombination within the space-charge region. It is expected that device performance can be improved by a rapid thermal processing step (e.g. 1000 °C for 1 min) after LCP and by using optimized hydrogenation conditions. Overall, this research has shown that LCP is practical for doping poly-Si thin films and is further amenable towards other thin film technologies.

List of Publications

- 1. <u>S. Virasawmy</u>, N. Palina, S. Chakraborty, P.I. Widenborg, B. Hoex and A.G. Aberle, "Laser Chemical Processing (LCP) of Poly-Silicon Thin Film on Glass Substrates", *Energy Procedia*, vol. 33, pp. 137-142, 2013.
- 2. <u>S. Virasawmy</u>, N. Palina, P.I. Widenborg, A. Kumar, G.K. Dalapati, H.R. Tan, A.A.O. Tay and B. Hoex, "Direct Laser Doping of Poly-Silicon Thin Films Via Laser Chemical Processing," *IEEE J. Photovoltaics*, vol.3, pp.1259-1264, 2013.
- S. Virasawmy, P.I. Widenborg, N. Palina, C. Ke, J. Wong, S. Varlamov, A.A.O. Tay and B. Hoex, "Laser Chemical Processing of *n*-type Emitters for Solid Phase Crystallised Poly-silicon Thin Film Solar Cells", *IEEE J. Photovoltaics*, vol. 4, pp. 1445-1451, 2014.
- 4. <u>S. Virasawmy</u>, N. Palina, P.I. Widenborg, A.A.O. Tay and B. Hoex, "Investigation of the structural properties of poly-silicon thin films doped by Laser Chemical Processing (LCP)", in preparation.
- 5. S. Chakraborty, C. Ke, <u>S. Virasawmy</u>, A. Kumar, P.I. Widenborg and A.G. Aberle, "Investigation of isotropic plasma etching processes for interdigitated metallisation of poly-Si thin film solar cells", submitted to *Semiconductor Science and Technology*, 2014.

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Nomenclature

- a-Si amorphous silicon
- ABF ammonium bi-fluoride
- AIT aluminium-induced texturing
- BSF back surface field
- C-V capacitance-voltage
- CVD chemical vapour deposition
- EBSD electron backscatter diffraction
- ECV electrochemical capacitance-voltage
- HYD hydrogenation
- PECVD plasma-enhanced chemical vapour deposition
- Poly-Si polycrystalline silicon
- RTP rapid thermal processing
- SEM scanning electron microscopy
- SIMS secondary ion mass spectroscopy
- SPC solid phase crystallisation
- TEM transmission electron microscopy
- XTEM- cross-sectional transmission electron microscopy

CHAPTER 1

INTRODUCTION

1.1 Thin film solar cells

Today's commercially available bulk crystalline silicon wafer cells have solar cell efficiencies in the range of 15% - 25%. At the forefront lies the notable SunPower silicon solar cell - an all back-contact *n*-type silicon wafer solar cell with efficiency ~25% [1] followed by the Sanyo HIT cell featuring a thin mono-crystalline wafer sandwiched between ultra-thin amorphous silicon layers, with a cell efficiency over 22% [1]. Despite these strong achievements, photovoltaic (PV) electricity is still far behind other forms of green electricity such as hydroelectricity. The Renewable Energy Policy Network for the 21st Century (REN21) 2013 reports that only ~19% of our global energy consumption consists of renewable energy – out of which, wind/solar/geothermal/biomass power generation altogether form a mere 1.1%. Nevertheless, given these low numbers, the annual growth rate for PV is a staggering 42%, more so than any other forms of renewable technologies such as wind power which is only about 19%. This is primarily due to economies of scale and constant technological advancements that continuously drive down the price of PV manufacturing [2].

The cost of modern-day PV module manufacturing is around US\$ 0.5/Wp, and there is still continuing effort to drive down the price by either decreasing production cost or by increasing the efficiency of the solar cell. The cost of a silicon substrate makes up ~50% of the overall fabrication cost [4]. One way to lower costs is to move towards larger and thinner wafers to scale up production but at some stage the wafer

breakage rate will limit the minimum achievable thickness [4]. Another consideration is that the relative fraction of silicon loss due to sawing (kerf loss) increases as the wafer gets thinner. Similarly, the fractional loss due to saw damage etch is likely to increase. Thus, one possible way to decrease the dollar per watt and yet overcome these issues is through thin film technology.

Thin film PV technology combines the advantages of using small amounts of material with scalability. The thin film material is deposited by physical [4] or chemical vapor deposition [3, 5] and by solution-based processing [6]. In addition, batch scale manufacturing can be expanded towards larger and/or flexible substrates. Leveraging off semiconductor technology, production time and cost can be decreased significantly through monolithic integration and novel interconnection methods involving laser scribing and inkjet printing.

To date, various thin film technologies have already found their way to the market. For instance, First Solar is a leading industrial manufacturer of cadmium telluride (CdTe) PV modules with average efficiency in the range of 12% - 13%. Additionally, copper indium gallium selenide (CIGS) PV modules with efficiencies in the range of 13% - 14% are already being commercialized [7]. Even though these technologies seem promising, they rely heavily on scarce elements such as indium and telluride and thus, may potentially limit their growth in the near future. Additionally, cadmium is toxic and in this respect, CdTe PV is not quite symbolic for 'green energy'. In contrast, silicon-based thin film PV technologies are non-toxic and sustainable. Amorphous silicon (a-Si) solar cells have already been on the market for years and can be found in calculators and watches, amongst others. Nevertheless, one barrier to industrial production is the relatively low PV efficiency of amorphous silicon. The latter technology also suffers from light-induced degradation (Staebler-

Wronski effect) which decreases the efficiency by up to 30% of its initial value [8]. Thus, one effective way to exploit a-Si technology is to combine it with other siliconbased material (e.g. micro-crystalline silicon) to form tandem solar cells. For example, the team from Neuchatel, Switzerland demonstrated stable efficiencies (~12%) with triple junction solar cells using this technology [9].

Another silicon-based technology is poly-silicon thin film. Poly-silicon (polycrystalline silicon or poly-Si) thin film is a common semiconductor material driving numerous applications in the semiconductor industry (e.g. thin film transistor (TFT) circuitry in active matrix liquid crystal display (AMLCD) [10]). Poly-Si can be formed or deposited in multiple ways – for instance, by laser crystallisation of a-Si, solid phase crystallisation of a-Si [11], physical vapor deposition methods such as ebeam evaporation or chemical vapor deposition techniques as in low pressure chemical vapor deposition (LPCVD) [12] or plasma-enhanced chemical vapor deposition (PECVD) of poly-Si [4]. Depending upon the deposition conditions, amorphous, poly- or micro-crystalline silicon may be formed for chemical vapor deposition techniques such as PECVD. These three materials are typically classified according to their grain size and range order. Amorphous silicon (a-Si) has no long range order while poly-Si has relatively long range order and consists of grain sizes varying between 1 and 1000 micrometers. In contrast, micro-crystalline silicon consists of amorphous tissue and poly-Si altogether and is typically made up of grain sizes less than 1 micrometer [4].

In the late 1980s, Sanyo Electric pioneered the first poly-Si solar cells made by the solid phase crystallisation approach. Those were made on quartz substrates and had solar cell efficiencies around 8.5% [13]. More details about this layer structure will be described in Chapter 2. Despite these encouraging results, this type of solar cell structure has slowly phased out to evolve into their present-day silicon heterojunction solar cell (called HIT). In 2007, CSG Solar demonstrated the first *commercial* poly-Si thin film PV technology on glass (fabricated by solid phase crystallization (SPC) of PECVD amorphous silicon) by manufacturing a 10.4% minimodule with an aperture area of 94 cm² [14]. The structural and device properties of the poly-Si were further enhanced by post-SPC processes such as rapid thermal processing (RTP) and hydrogenation. More details about this cell structure will be discussed in Chapter 2.

At the Solar Energy Research Institute of Singapore (SERIS), a similar layer structure to CSG Solar is adopted on borosilicate glass (the fabrication details are described in Chapter 2) and is being scaled up for higher efficiencies. Realistically, through the use of industrially viable technologies, a module efficiency of 13% is within reach for poly-Si thin film solar cells on glass. A schematic of a metallised poly-Si thin film solar cell on planar glass is illustrated in Figure 1.1.



Figure 1.1: A schematic of a metallised poly-silicon thin film solar cell on planar glass in superstrate configuration [i.e. light enters the solar cell through the supporting structure]

1.2 Doping of poly-silicon thin films

To date, numerous techniques exist for doping poly-Si thin films. Some of these include thermal diffusion [15], in-situ deposition followed by epitaxy [4], laser doping, ion beam implantation and so forth. Each technique is characterized by its process temperature, cost, throughput, material quality, grain size, dopant concentration and doping depth. Some of the main doping technologies available for poly-Si are described below:

- Thermal diffusion [15] this process is similar to creating a *p*-*n* junction on a silicon wafer and involves diffusing a doping gas at relatively high temperatures between 700 °C 900 °C. This solid-state diffusion is relatively slow (in hours) because the diffusion coefficient of the dopant is low under these conditions. In addition, the diffusion profile may be hard to control due to enhanced diffusion along crystallographic defects such as grain boundaries etc.
- Spin-on-dopant (SOD) [16] this form of doping is typically performed using a commercially available diffusion source. This technique does not require expensive infrastructure as in thermal diffusion and requires a drive-in step typically achieved through a furnace or by a laser. However, there are also risks of contamination from impurities in the SOD.
- In-situ methods followed by epitaxy [4] this is the most convenient way to grow a *p*-*n* junction and is very well established in industry. CVD methods can also decouple the formation of the seed layer from the growth rate and the crystallographic orientation. Therefore, subsequent layers can be deposited at higher deposition rates.

- Ion beam implantation [17] this technique is commonly used in industry to achieve high doping levels at shallow diffusion depths (tens of nanometers). A thermal anneal is necessary to activate dopants and anneal defects either in the form of a flash or a laser anneal. The diffusion profiles of ion-implanted samples depend upon the ion energy, the sample thickness and the subsequent annealing conditions.
- Metal-induced crystallisation Some metals do not form silicides but instead act as acceptors (i.e. *p*-type doping) upon annealing. At the same time, they also lower the crystallisation threshold of amorphous silicon such that crystallisation occurs at significantly lower temperatures. Processes such as aluminum-induced crystallisation (AIC) simultaneously dope and crystallise amorphous silicon into poly-silicon. The doping levels are relatively high (~10¹⁹ atoms/cm³) [18]. However, there are also significant amounts of metal contaminants in the crystallised layers.
- Laser doping excimer laser has been applied to SOD on amorphous silicon or SOD on poly-Si [19, 20]. High doping concentrations can be achieved at shallow diffusion depths but a significant amount of contaminants is also incorporated into the film. On the other hand, Nd:YAG laser is applied mostly for crystallising and scribing thin films. Studies about Nd:YAG laser doping on silicon wafers reported high doping levels (~10¹⁹ atoms/cm³) at depths of 1000 nm [21].

1.3 Application of Nd:YAG laser – a literature review

This Section describes the studies that form the understanding that laser-induced interaction on silicon lead to melting of the solid and solidification of the molten silicon. Also it was established that the temperature threshold for laser doping coincided with the silicon melting threshold and hence laser doping was basically liquid phase diffusion. It also gives the reader a broad picture of the application of Nd:YAG laser on silicon over the years.

By the late 1960s, lasers were already being investigated for semiconductor applications such as in laser annealing of ion-implanted silicon. The fundamental findings were that laser melting of the surface layer removed crystallographic defects and that the silicon solidified epitaxially from the underlying substrate. During this solidification process, impurity atoms were incorporated into the lattice with concentrations that could well exceed the equilibrium solubility limit and the doping concentration and segregation coefficients were dependent upon the resolidification velocities [22]. A few examples of such studies are described below.

In 1968, Fairfield reported a solid-state diode fabricated by laser irradiation of a phosphorus-coated silicon wafer with a ruby laser (694 nm). The doping depth was about 1 μ m [23]. Around the same year, Harper and Cohen realised a *p-n* junction by irradiating an aluminium-coated *n*-type silicon wafer with a pulsed Nd:YAG laser (1064 nm). They measured the rectifying behavior of the diodes and concluded that the diodes exhibited satisfactory electrical behavior [24].

In subsequent years, several studies were performed with Nd:YAG laser using various precursors and system (e.g gas immersion systems). Those studies seemingly showed that a threshold laser fluence existed for the onset of laser doping and that it coincided with the silicon melting threshold. It was also observed that the depth of the diffused layers increased linearly with laser fluence and that the doping depth was equivalent to the melt depth. Thus, it was established that laser doping was essentially liquid phase diffusion and the high dopant concentrations in short processing times was due to the high temperature prevailing at the reaction site. Lastly, it was observed that infinite doping precursors could only be realised with gaseous systems while predeposited precursors, being exhaustive, eventually lead to a decrease in the peak doping concentration [22]. For example, in 1978, Affolter [25] fabricated ohmic and rectifying (*p*-*n* junctions) contacts on silicon with a Nd:YAG (Q-switched) and a CO₂ laser using precursors from SOD. The diffusion depth was about 0.5 μ m. Bentini [26] doped GaAs substrates with silicon using a Nd:YAG laser (pulsed, 532 nm) in a silane atmosphere. The doping concentration was about 10²⁰ Si atoms/cm³ at a doping depth of 100 nm. Besi-Vetrella and co-authors [20] achieved selective doping on silicon using a two-step process involving Rapid Thermal Diffusion (RTD) on SOD followed by Nd:YAG (pulsed, 532 nm) laser irradiation of the doped regions. The diffusion depth was about 2-3 μ m.

A comparative work between Nd:YAG laser doping (continuous wave and pulsed mode with wavelength of 1064 nm) and excimer doping for *n*-type doping (using N₂ precursors) and *p*-type doping (using Al precursors) in different background gases was also performed on silicon carbide substrates by Tian [27]. Lien *et al.* [28] demonstrated a one-step laser crystallisation and doping process of amorphous silicon (100 nm thick) on glass. The authors employed a Nd:YAG laser (pulsed, 355 nm) on phosphorus-doped TiO₂-coated a-Si on glass. However, they performed a dehydrogenation step at low laser fluence before the doping/crystallisation process. They revealed SIMS concentration of about 2 x 10^{19} atoms/cm³. Palani *et al.* [29] performed laser doping and crystallisation of amorphous silicon with a Nd:YAG laser

(pulsed, 355 nm) of Nd:YAG. The authors utilized a thin antimony layer for doping and crystallising the amorphous silicon. They also carried out a two-step laser irradiation process to first crystallise the amorphous silicon and diffuse the dopants and lastly to activate the dopants. Barhdadi *et al.* [22] compared the defect level introduced by solid-state laser [Nd:YAG (pulsed, 530 nm) and ruby] and excimer laser irradiation on silicon. They concluded that for fluence above the melting threshold value (the value of which depends upon the type of laser), the active defects measured by deep level transient spectroscopy (DLTS) are somewhat similar for all three lasers. They claimed that the defects are due to a fast melt cooling and resolidification velocity of the irradiated layer. Those defects can act either as charge carrier traps or as recombination centers. More recently, Li *et al.* [30] demonstrated the application of Nd:YAG (pulsed, 532 nm) laser in chalcogen doping and microstructuring of silicon. By irradiating silicon in a background gas of SF₆, they demonstrated increased absorption of the irradiated silicon.

Since then, the demands from the semiconductor industry have evolved significantly due to device miniaturization and thus, Nd:YAG laser is mostly used for crystallisation of doped and undoped amorphous silicon. As such, Nd:YAG lasers have slowly phased out due to the laser specifications and are increasingly being replaced by excimer lasers for doping and crystallisation applications on thin films. Nevertheless, depending upon the application, Nd:YAG is still widely popular due to its cost and flexibility. For example, some laser crystallisation studies have been carried out using Nd:YAG on thin amorphous silicon layers. Notable examples are the works by Fereira *et al.* [31] who crystallised ~200 nm thick PECVD a-Si film (doped and undoped) using a pulsed Nd:YAG laser (532 nm). Similarly, Shibata *et al.* [32] reported Nd:YAG (pulsed, 1064 nm and continuous wave) laser annealing on 180 nm

thick a-Si deposited by LPCVD. The a-Si was implanted with phosphorus prior to the annealing/ activation process.

1.4 Laser Chemical Processing (LCP)

Laser chemical processing (LCP), based on the patented LaserMicroJet technology by Synova® S.A, was originally introduced by Fraunhofer Institute for Solar Energy Systems ISE, as a novel approach for micro-structuring and wafering applications. Hence, the technique was initially called laser chemical etching (LCE). The technology was explored as an alternative to a low-cost damage-free wafering process for the PV industry. Due to the emergence of thinner silicon wafer solar cells, it became increasingly important to cut down the silicon loss during PV manufacturing for e.g. kerf loss during sawing and post-damage etch processes. Hence, a laser wafering process that could potentially saw wafers at relatively high cutting speeds without a subsequent cleaning/polishing process (i.e. a damage-free wafering process) would meet such requirements [33]. During the experimental phase, different carrier fluids such as water and potassium hydroxide (KOH) were experimented using pulsed and continuous Nd:YAG laser. It was found that LCP could indeed lead to an improved surface quality due to *in-situ* etching from KOH. Eventually, in 2001, Fraunhofer explored this technology for a novel doping application for bulk crystalline solar cells. Subsequently, the first results were published using LCP for *n*type doping in selective emitter applications. Since then, the technique was called LCP to encompass both micro-structuring and doping applications.

LCP features a laser light (pulsed or continuous) coupled inside a highly pressurised hair-thin liquid jet (~50-80 μ m) by total internal reflection. Essentially, the liquid jet acts as an optical waveguide. The laser beam is transported from the

laser source through an optical fibre cable and coupled through a quartz window into the jet through the Synova Microjet-Minihead[®]. Laminarity inside the liquid jet is maintained by using either compressed dry air (CDA) or helium (He) gas. The focal spot is determined by the focusing optics inside the LCP head as well as the jet output diameter from the nozzle. Technical capabilities allow the focal point to be between 20 mm and 70 mm from the nozzle exit (in SERIS focal point is about 30 mm inside the jet and focal spot is ~30 μ m).

Therefore, according to the type of chemistry, LCP can be targeted for different applications such as doping, grooving or both. Figure 1.2 illustrates the laser/jet coupling inside the Synova Microjet-Minihead[©].



Figure 1.2: Laser/jet coupling inside one of the Synova Microjet-Minihead[©]

So far, LCP has shown successful results for damage-free wafering applications using potassium hydroxide (KOH) as carrier fluid. More importantly, Fraunhofer ISE has demonstrated successful results in n-type and p-type doping: n-type doping for

fabricating selective emitters in high efficiency solar cells (i.e. the simultaneous ablation of passivating layers and localized doping for making ohmic contacts) [34, 35] and *p*-type doping for making local back surface fields (LBSF) in silicon wafer solar cells [36].

1.5 Motivation

Earlier, it was shown that lasers are promising for a multitude of thin film applications such as crystallisation, doping and annealing, amongst others. They are fast, versatile (in terms of spot size and pulse modifications etc.), capable of spatial patterning and can easily outcompete other forms of processing such as tube diffusion and photolithographic patterning. For example, lasers can be applied either at an early stage during the cell fabrication process (for e.g. laser crystallization [37], laser annealing [38] and laser doping [39]) or towards the end of the metallization/module fabrication process (for example in laser-fired contacts [40], cell isolation [41, 42] etc).

Within the realm of laser doping on poly-Si, excimer and Nd:YAG lasers have been commonly employed on pre-doped layers such as silicates and spin-on dopants or by gas immersion laser doping (GILD) to yield high dopant concentrations (~10²⁰ atoms/cm⁻³). However, there are few limitations to these methods such as the number of required pre-process steps, cost and supply of the doping precursors. For instance, SODs are exhaustible doping sources that generally require a few additional steps (for example spin coating and solvent removal) before a drive-in step in a furnace or laser activation. In contrast, GILD is a more straightforward technique that features a practically infinite doping source. As a result, homogenous doping profiles can be achieved from GILD. However, GILD requires a specialized infrastructure which is relatively expensive and potentially hazardous due to the poisonous doping gases. Additionally, GILD requires adsorption of dopants onto the film (performed by lower laser fluences before the actual doping step). Therefore, it seems that there is no report of a laser doping process that avoids the complexity of using pre-doped layers and yet provides a continuous flux of doping precursors.

In this case, LCP is a unique approach for laser doping of poly-Si thin films. Being laser-based, it derives all the benefits imparted by laser processing. It is also a 'direct' doping procedure with the additional capability of supplying a practically infinite amount of dopant atoms throughout the doping process. Previously such feature was only available from specialized techniques such as GILD. Furthermore, the process can be localized or extended to large area substrates. In this respect, several jet heads can be fitted within the LCP system for doping or grooving several wafers simultaneously. Lastly, as discussed in the earlier Sections, there has not been much doping work carried out with Nd:YAG laser except in the earlier days. Even then, most of the work was carried out mostly on bulk crystalline silicon using predeposited precursors or a background doping gas. As such, there has not been a single step laser doping process except for the published work by Lien *et al.* [28]. To the best of the author's knowledge, there has also been no prior LCP work on poly-Si except for the work investigated in this thesis.

1.6 Aim of the current work

This thesis focuses on two main aspects of LCP. First, it demonstrates that LCP can be successfully applied for doping poly-Si thin films. In this case, the optimum LCP parameters for *n*-type doping of poly-Si thin films are investigated systematically. Second, this work targets the fabrication of an LCP-doped active layer for poly-Si thin

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film solar cells on glass. The basic structure of a poly-Si thin film solar cell is similar to that of a conventional wafer solar cell. It consists primarily of a relatively low doped layer (absorber) sandwiched between two layers of higher dopant concentration namely an emitter and a back surface field (BSF) [more details about the layer structure are described in Chapter 2]. Fabricating an active layer by LCP entails a few salient features. These are the dopant concentration, the doping depth, the structural and electronic quality of the films.

1) Dopant concentration

Depending upon the device architecture (e.g. substrate or superstrate), LCP can be applied to fabricate an emitter or a back surface field. A relatively high dopant concentration (e.g. 10^{19} cm⁻³) is desirable as it yields a reasonably low sheet resistance which minimises series resistance losses in the solar cell. On the other hand, if the layer is very heavily doped (e.g. 10^{21} atoms/cm³), carrier recombination is high and the diffusion length becomes rather short. Hence, a trade-off is necessary between the electronic quality and the sheet resistance.

2) Doping depth

The doping depth is another important factor that determines the collection efficiency of the solar cell. In the case of an emitter, a shallow doped layer is highly desirable to improve the blue response of the cell. In this way, the carriers are generated close to or within the absorber layer. The diffusion length of the carriers is higher in the absorber layer due to a lower defect density and thus, the collection efficiency of the solar cell is increased.
3) Structural quality

The structural quality of the LCP-doped layer is another factor that determines the overall device performance. Grain boundaries and other structural defects act as carrier traps and influence the carrier lifetime. A study by Wong *et al.* [43] showed that clean dislocations lead to shallow band recombination and charged dislocations lead to deep level defects, both of which are detrimental to the performance of the solar cell. The structural quality of the LCP-doped layer is assessed against that of float-zone (FZ) silicon which possesses the best structural quality.

4) Electronic quality

The electronic quality of a solar cell determines the overall device performance. Despite possessing satisfactory material quality, the electronic quality of the solar cell may be rather poor, thus making the device impractical. The fabricated devices in this thesis are compared to the 'baseline' poly-Si thin film solar cells fabricated in SERIS to assess the relative device performance. To further enhance the device properties of the LCP-doped layers, the fabricated poly-Si thin film solar cells are hydrogenated in a LPCVD reactor.

1.7 Organization of thesis

This thesis is organized into eight chapters. Below is a brief description of each chapter:

Chapter 1 summarizes the current technologies available for doping poly-Si with particular attention to laser doping of poly-Si. LCP is proposed to overcome the shortcomings of laser doping process on thin films namely process complexity, cost

and a continuous supply of doping precursors. The research scope and motivation behind the current study are stated and the aim is to fabricate an active layer for poly-Si thin film solar cells using LCP.

Chapter 2 describes the laser-induced physical and chemical interactions occurring at each step during LCP. These include physical models detailing the optics, thermodynamics and hydrodynamics of LCP in order to give the reader a better understanding of LCP. A summary of the physical parameters/ models relevant to the LCP conditions used in this thesis is provided. Those parameters are later used for the simulations of melt depth and melt lifetime using the SLIM (simulation of laser interaction with materials) software.

Chapter 3 covers the fabrication process of poly-silicon thin film solar cells on glass made by the solid phase crystallisation (SPC) method. The SPC approach is utilized to form the poly-Si samples before *n*-type doping by LCP. The characterisation techniques for assessing the structural and electrical integrity of the LCP-doped layers are also outlined.

Chapter 4 summarizes the LCP doping experiments performed on *p*-type poly-Si on glass. The experimental procedures for LCP optimization and annealing conditions are detailed therein. Melt depth and melt lifetime simulations are performed using the laser modeling software SLIM (simulation of laser interaction with materials) for a qualitative assessment of the LCP process parameters on the sheet resistance and doping profiles. An analytical model is introduced for calculating the sheet resistances of the LCP-doped layers.

Chapter 5 describes LCP doping experiments on p^{-}/p^{+} poly-Si on glass. The first poly-Si thin film solar cells featuring an active layer by LCP are presented. The device performance is assessed by *Suns-V_{oc}* measurements and hydrogenation is

carried out to enhance the device performance. These results are compared to our baseline solar cells and areas for further improvement are indicated. The solar cell modeling software, PC1D is used to model the solar cells and to compare the theoretical and measured V_{oc} values.

Chapter 6 deals with the investigation of the structural properties of the LCPdoped layers. The experimental procedures for assessing the structural integrity of the LCP-doped films are described. The influence of the annealing conditions on the structural properties of the films is also studied.

Chapter 7 investigates the electrically-active defects in LCP-doped solar cells. The dominant recombination behaviour in LCP-doped solar cells is identified. Hydrogenation-induced defects are also studied by Raman spectroscopy. The performance-limiting factors affecting the solar cells are discussed and suggestions are given to increase device performance.

Chapter 8 summarizes the essential findings from the work carried out in this thesis. Possible areas for further improvement on the existing work are suggested. Future studies towards a better understanding of LCP doping mechanisms on polysilicon are highlighted.

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CHAPTER 2

LASER CHEMICAL PROCESSING (LCP)

2.1 Introduction

This chapter details the laser-induced physical and chemical interactions occurring at each step during LCP. Despite the complexity associated with the laser/jet coupling in LCP, the laser-silicon interactions are similar to that of dry laser doping and therefore most of the physical models are relevant for LCP. In the first Section, the physical models pertaining to the optics and thermodynamics of LCP are described to give the reader a better understanding of LCP. Lastly a summary of the physical parameters/ models relevant to the LCP conditions used in this work is provided. Those parameters are later used for the simulations of melt depth and melt lifetime using the SLIM (simulation of laser interaction with materials) software.

2.2 Laser chemical processing

LCP couples a laser beam (pulsed or continuous) into a highly pressurised liquid jet and the laser-induced, physical and chemical interactions between the substrate and doping medium lead to micro-structuring, doping or both. The liquid jet acts as an optical waveguide and through total internal reflection, the laser is transported to the surface of the material for the desired application.

During LCP, the laser-induced physical and chemical interactions are highly complex. Therefore, the number of parameters is rather significant and precise mathematical models are required to evaluate the effect of each parameter on LCP process quantitatively. Prior work on LCP revealed that there was no existing algorithm or commercial software that could couple the physical, chemical and hydrodynamic effects altogether. Additionally, at high temperature scales, some of the physical models may not be completely valid and material parameters measured under such conditions cannot be found in literature. Nevertheless, the laser-material interactions during dry laser doping of silicon are still relevant for LCP. In the following Sections, the models and governing equations were taken from Ref. [1] and available literature [2-15]. Only the physical models reflecting the LCP conditions used in this thesis are detailed. Additionally vapor dynamics were not considered in the mathematical models because the laser intensities were in the low to mid-range.

a) Laser-jet coupling

A high pressure pump is used to force a liquid (water or a suitable doping medium) across a nozzle to generate a hair-thin liquid jet of diameter about 50 μ m. The laser light is then coupled through a quartz window into the jet. At this stage, the liquid jet absorbs energy from the laser and is heated up. If the liquid jet contains a low reactive solvent, photochemical reactions may already occur within the liquid jet. It is important to note that initially, Fell *et al.* [1, 2] assumed a uniform intensity distribution across the liquid jet. However, they later found out that the liquid jet was essentially a multi-mode waveguide and that the laser intensity showed interference peaks dependent upon the nozzle diameter and the coupling optics.

b) Interactions at the reaction spot

During a laser interaction with silicon, part of the laser light is reflected by the silicon while the remaining light is absorbed by the silicon. The melting temperature of silicon is reached. At this stage, a phase transition from solid to liquid occurs. The melt time (ns-µs) of the silicon (i.e. liquid silicon) is longer than the nanosecond laser pulse length (less than 80 ns in the experiments within this thesis) used during LCP [1] and thus, even when the laser is off, the silicon is still in its molten state. The contact of the liquid jet with the hot silicon melt results in a small vapor layer that acts as a thermal insulating layer and reduce the viscous forces between the silicon melt and the liquid jet. Therefore melt expulsion does not occur instantaneously but depends on a characteristic melt expulsion time influenced by the hydrodynamics of the liquid jet such as the jet velocity etc. [1]. Further heating causes the melt to reach its evaporating temperature. Fast evaporation rates result in the formation of a dense vapor plume that exerts a recoil pressure onto the melt possibly shielding it from the impinging jet.

c) Melt solidification

Lastly, the silicon temperature drops down rapidly to about room temperature in only a few microseconds [1]. During this process, the melt solidifies (dopants are incorporated into the lattice if a doping medium is used as liquid jet) until the onset of the next laser pulse.

2.3 Optics

After absorption inside the liquid jet, the remaining laser intensity becomes available for melting the silicon. The complex refractive index, n^* is given by:

$$n^* = n + ik \tag{2.1}$$

where k is the extinction coefficient and determines the attenuation of light in the material. Using a wavelength of 532 nm, the data for solid Si is taken from literature [3].

$$n = 3.95 + 5.68 \times 10^{-4} \, T \tag{2.2}$$

$$k = 2.1252 \times 10^{-2} \exp(\frac{T}{430}) \tag{2.3}$$

where *T* is the absolute temperature (K).

The Drude model is used to calculate the refractive index of liquid silicon since it essentially behaves as a metal (free electron gas) at this temperature and the photons are mainly absorbed by free carriers. The frequency-dependent complex permittivity of a free electron gas is given by:

$$\varepsilon^*(\mathbf{f}) = 1 - \frac{\omega_{pl}^2}{\omega^2 + \gamma^2} + i \frac{\gamma \omega_{pl}^2}{\omega(\omega^2 + \gamma^2)}$$
(2.4)

where the plasma frequency ω_{pl} is a material-dependent constant value and the collision rate γ is a temperature-dependent value given by Equation (2.6). T_m is 1683 K.

$$\omega = \frac{2\pi c}{\lambda} \tag{2.5}$$

$$\gamma = \gamma_m \frac{T}{T_m}$$
(2.6)

The refractive index is then calculated by:

$$(n^*)^2 = \varepsilon_1 + i\varepsilon_2 \tag{2.7}$$

Assuming parameters $\omega_{pl} = 2.50 \text{ x } 10^{16} \text{ s}^{-1}$ and $\gamma_m = 4.717 \text{ x } 10^{15} \text{ s}^{-1}$ from Ref. [4], the refractive index of liquid silicon is then calculated as a function of temperature.

For photons of energy above the band gap, the laser energy is absorbed through electronic excitation (that is electrons moving from valence band to conduction band) within the silicon. These electrons then interact with phonons and transfer this energy to the lattice on a picosecond timescale. At high laser intensities (i.e. high photon densities), multi-photon absorption may result whereby more than one photon is absorbed by an electron and during the process creates more free electrons. At even higher laser intensities, more laser light is absorbed until it results in avalanche ionization (optical breakdown) whereby all the light is absorbed. For a 532 nm laser, a minimum pulse length of roughly one nanosecond is desired to prevent optical breakdown in the liquid jet [1].

After passing through the liquid jet, the laser light is still highly directional. The absorption of light in silicon can be approximated by a one dimensional Beer-Lambert equation along the depth axis *Z*:

$$I(z) = I_o \exp(-\alpha z) \tag{2.8}$$

where I_o is the laser intensity (W/m²) at depth (z = 0). The intensity I_o is determined by the peak power, P_{peak} (W) over the effective area (m²) by:

$$I_o = \frac{P_{peak}}{\pi \left(\frac{d_{spot}}{2}\right)^2} \tag{2.9}$$

where peak power is given by:

$$P_{peak} = \frac{Pulse \, energy}{t_p} = \frac{P/Rep}{t_p} \tag{2.10}$$

where P is average power in Watt (W), t_p is the pulse length in seconds (s) and *Rep* is the pulse repetition rate in Hertz (Hz). Since a square pulse is used, the peak power refers to the average power across the jet.

The absorption coefficient α is related to the extinction coefficient by:

$$\alpha = \frac{4\pi k}{\lambda} \tag{2.11}$$

For solid Si, it is given by [5]:

$$\alpha = 5.02 \times 10^3 \exp\left(\frac{T}{430}\right) \tag{2.12}$$

As can be seen in Equation (2.11), the absorption coefficient is both wavelength and material dependent. In LCP, the laser beam is not directly coupled into the liquid but rather at an angle determined by the optics and the liquid. Thus, an effective path enlargement (δ) exists whose angle is limited by the critical angle to ensure total internal reflection. This path enlargement factor is accounted into the absorption coefficient by calculating an effective absorption coefficient [1]:

$$\alpha_{eff} = \delta \alpha \tag{2.13}$$

At the reaction spot, part of the incident laser light is reflected and the rest is absorbed by the silicon. The reflectivity is calculated by Fresnel equation and is given by [1, 6]:

$$R = \frac{(n_{env} - n_{Si})^2 + k_{Si}^2}{(n_{env} + n_{Si})^2 + k_{Si}^2}$$
(2.14)

where n_{Si} is the refractive index of silicon and n_{env} is the refractive index of the surrounding medium. In the current work, 42.5% phosphoric acid was used during doping and therefore, the refractive index was calculated from Ref. [7]. It is assumed that the refractive index of phosphoric acid is temperature independent.

$$n_{acid} = 0.000792 \times concentration in \% + 1.3346$$
 (2.15)

Replacing n_{Si} , K_{Si} and n_{env} by their corresponding values, R is given as a function of temperature. Therefore,

$$I(z) = (1 - R)I_0 \exp(-\delta\alpha z)$$
(2.16)

2.4 Thermodynamics processes during LCP

The thermodynamics occurring during the LCP process are described by heat transport, phase changes as well as species transport through evaporation or diffusion. The heat transport is solved by the general partial differential equation which includes a transient, a convection term, a conduction term and a source term as described by Equation (2.17) [8]:

$$\frac{d(\rho C_p T)}{dt} + \vec{v} \nabla (\rho C_p T) = \nabla (K \nabla T) + S$$
(2.17)

where $S = \alpha_{eff} I(z)$

Assuming that the temperature distribution across the cross-sectional area of the jet is constant, Equation (2.17) can be reduced to a one dimensional heat equation along the depth axis (z). This assumption is valid because the jet length is about 3 cm and the diameter of the jet is about 50 μ m. Therefore, the aspect ratio of the jet is relatively high such that the temperature is homogenized across the cross-sectional area of the jet. Furthermore, since the heat capacity C_p , density ρ and heat conductivity K are assumed to be constant, Equation (2.17) can be further simplified to:

$$\rho C_p \frac{dT}{dt} + \rho C_p v_z \frac{dT}{dz} = \mathbf{K} \frac{\mathbf{d}^2 \mathbf{T}}{\mathbf{dz}^2} + S$$
(2.18)

Grigoropoulos *et al.* [9] described the laser-induced melting of silicon using an enthalpy scheme. During a phase change, the enthalpy is steadily rising while the temperature remains constant. Assuming no melt flow (i.e. no movement of silicon), the enthalpy is given by:

$$\frac{dH}{dt} = \nabla(K\nabla T) + S \tag{2.19}$$

where $H(T) = \int_0^T \rho C_p \, dT$

For solid Si, the temperature dependent heat capacity (in $J/cm^{3}K$) is obtained as in Ref. [10]:

$$C_p = \frac{\rho}{M} [23.698 + 3.305 \times 10^{-3}T - 4.354 \times 10^{-5}T^{-2}]$$
(2.20)

where ρ is density of silicon in g/cm³ and *M* is molar mass of silicon (g/mol).

The heat capacity is dependent upon the temperature and was defined in a stepwise manner using the temperature-enthalpy relation, as seen in Reference [11]. To define the enthalpy relation for each phase, a polynomial fit based on available data from literature was used. In the case of solid silicon, Equation (2.21) was derived [11]:

$$T_s = -2.375x \, 10^{-17} H^2 + 5.512 \times 10^{-7} H + 98.06 \tag{2.21}$$

For liquid Si, the specific heat capacity was assumed to be a constant at $2.432 \text{ J/cm}^3\text{K}$ [11]. The temperature-enthalpy relation for liquid Si is given by Equation (2.22):

$$T = dH + e \tag{2.22}$$

Where
$$d = \frac{1}{\rho c_p}$$
 and $e = T_{melt} - \frac{(H_{melt} + L_{melt})}{\rho c_p}$

a) Surface cooling

Surface cooling may occur either by radiation, by convection or by conduction. Neglecting incoming radiation, the radiative heat loss (J_{surf}) is given by Stefan-Boltzmann law as in Equation (2.23):

$$J_{surf} = \varepsilon_T \sigma (T_{surf}^4 - T_{env}^4)$$
(2.23)

where ε_T is the emissivity of silicon, T_{surf} is surface temperature of the silicon, T_{env} is the surrounding temperature and σ is Stefan's constant.

For both conductive and convective cooling, the surface heat transfer was assumed to be linearly dependent upon the temperature difference of the two materials and was described by a heat transfer coefficient *ht*. In this case it is given by [6],

$$J_{surf} = ht(T_{surf} - T_{env}) \tag{2.24}$$

However, *ht* is dependent upon both the thermal properties of the material and the velocity of the cooling fluid in the case of convective cooling. This parameter needs to be derived empirically for each setup [1].

If the near-surface temperature distribution of the fluid/solid (in this case, liquid jet /silicon) is known, *ht* can be calculated by the temperature gradient and conductivity of the fluid K_{fluid} as in Equation (2.25) [8]:

$$K_{fluid} \frac{dT}{dn} = ht (T_{surf} - T_{env})$$
(2.25)

The heat loss by radiation was considered to be negligible according to the simulations performed at Fraunhofer [1]. Nevertheless, the cooling effect induced by the liquid jet can be considerable because the heat transfer coefficient of the pressurised liquid jet is in the order of $10^6 \text{ W/m}^2\text{K}$. However, since the heat transfer coefficient in the silicon is much higher or on the same magnitude (in the range of $10^7 \text{ W/m}^2\text{K}$) as that of the liquid jet, the heat is dissipated in the silicon very fast. As a result, only a fraction of the absorbed heat is transferred to the liquid jet. Using short pulse length during LCP processing leads to short melt lifetime and thus, the heat loss

to the liquid jet is even smaller. Additionally, the contact of the liquid jet with the silicon melt leads to a small vapor film being formed above the molten silicon and acts as a thermal insulating layer.

b) Phase transition from solid to liquid silicon

The speed of the solid-liquid interface (v_{sl}) is dependent upon the temperature difference (T_{sl}) between the interface and the melting temperature, as shown in Equation (2.26) [12]:

$$v_{sl} = KT_{sl} \left(1 - exp \left(-\frac{L_m}{K_B T_m} \frac{T_{sl} - T_m}{T_{sl}} \right) \right)$$
(2.26)

where *K* is a kinetic rate constant for either melting or solidification, L_m is latent heat of melting and T_m is melting temperature.

In this case, K is higher for solidification because the activation energy is higher for crystallisation. Therefore, the phase change does not occur exactly at the melting temperature but some superheating or undercooling is required. However, the undercooling was estimated to be around 75 K and the superheating was estimated at even lower value. Therefore, it is feasible to assume that the phase change occurs at the melting temperature.

During the phase change, the temperature is constant while the enthalpy either increases or decreases until the latent heat of melting has been overcome. In the case of Si, the latent heat L_m is reported to be 50 kJ/mol. To maintain consistency in the units, L_m is converted into units of energy per volume by:

$$L_m = L_{mol} \frac{\rho}{M}$$
(2.27)
= 4158 J/cm³K

For liquid Si, the temperature enthalpy relation is derived according to Equation (2.28).

$$T = \frac{1}{\rho C_p} H + T_m - \frac{(H_m + L_m)}{\rho C_p}$$
(2.28)

Where H_m is calculated by inserting T_m in Equation (2.21).

c) Evaporation of liquid silicon

For high laser intensities (particularly when using pulse length in the nanosecond scale), significant superheating occurs and therefore no specific boiling point exists. The evaporation is then considered using the Hertz-Knudsen evaporation model. It is assumed that above the melt surface, a layer of pure vapor exists. Thus, the evaporation rate of atoms is set to the effusion rate calculated from statistical thermodynamics [1].

$$\dot{n} = \frac{P_{sat}}{\sqrt{2\pi m_a K_B T}}$$
(2.29)

where m_a is mass of a silicon atom, K_B is Boltzmann constant, P_{sat} is saturation vapor pressure and *T* is the surface temperature.

The evaporation speed can be calculated by the difference in saturation pressure of the vapor and partial pressure of the environment P_{env} . Additionally, this externally calculated partial pressure can take into account the pressure distribution

caused by the impinging liquid jet. Therefore, the evaporation velocity, v_{lv} is calculated by dividing Equation (2.30) by the atom density of the liquid ρ_{melt}/m_a [11, 13].

$$v_{lv} = \frac{P_{sat} - P_{env}}{\rho_{melt} \sqrt{\frac{2\pi K_B T_{lv}}{m_a}}}$$
(2.30)

Since no measured data exists for the saturation pressure of silicon above the boiling temperature, the Clausius-Clapeyron equation is used to calculate a temperature dependent saturation pressure as in Equation (2.31) [11]:

$$p_{sat} = p_0 \exp\left(-\frac{L_{mol,v}}{R} \left(\frac{1}{T} - \frac{1}{T_b}\right)\right)$$
(2.31)

where p_0 is the atmospheric pressure, T_b is boiling temperature and R is the gas constant. Here, the evaporation causes some cooling and should be accounted by a heat flux given by $-v_{lv} \times L_v$. Assuming a constant molar latent heat of vaporization, $L_{mol,v}$ is calculated to be 400 kJ/mol at the boiling temperature.

The Knudsen evaporation model is still a simplification of the overall vapor dynamics occurring during LCP. This is because in practice, at high laser intensities, the vapor plume generates a recoil velocity onto the melt that influences the evaporation speed. For an accurate modeling, gas dynamics should be coupled into the modeling.

d) Species transport

Species transport combines light-induced radical generation and transport through the liquid jet as well as diffusion of impurity atoms into the silicon (e.g. during a doping process). The general diffusion equation includes a transient, a convection term, a conduction term and a source term which can be described by Equation (2.32) [13]:

$$\frac{dC}{dt} + v\nabla C = D\nabla C + S \tag{2.32}$$

The diffusion coefficient D is orders of magnitude higher in liquid phase than in solid phase. However, in solid phase, the diffusion coefficient is temperature dependent. On the other hand, in liquid phase, D is instead related to the size of the impurity atom and is temperature independent. Hence, it can be assumed to be constant in the liquid phase.

Since convection is not considered and there is no actual source of dopants within a molten volume, Equation (2.33) can be simplified to a one dimensional Fick's law:

$$\frac{dC}{dt} = D\nabla C \tag{2.33}$$

The boundary conditions are then implemented to solve the concentration. In the case of LCP, an infinite source is assumed at the liquid jet and reaction spot. The analytical equation as a function of (z) is [1]:

$$C(z) = C_{surf} \left[1 - erf\left(\frac{z}{\sqrt{Dt}}\right) \right]$$
(2.34)

Since thermal atomization of the dopant was not considered in this work, the surface concentration is a free parameter that is dependent upon the setup.

2.5 Fluid dynamics

a) Fluid flow

Fluid dynamics simulations are handled by the software Ansys Fluent. Since the flow within the simulation model occurs on a micrometer scale and the Knudsen number is below 1, Navier Stokes equations consisting of momentum and mass conservation (continuity equation) apply and are solved by Equation (2.35) and (2.36) respectively [1, 8]. The properties of the mixture are defined by a volume fraction and mass and momentum conservation is solved for each phase.

$$\frac{d}{dt}(\rho_{mixture}\vec{v}) + \nabla (\rho_{mixture}\vec{v}\vec{v}) = -\nabla p + \nabla (\bar{\bar{\tau}}) + \overrightarrow{S_{mom}}$$
(2.35)

$$\frac{d\rho}{dt} + \nabla \left(\rho_{phase} \vec{v}\right) = \overrightarrow{S_{mass}}$$
(2.36)

 $\overrightarrow{S_{mom}}$ represents the momentum sources due to surface tension and the melting/solidification process and *p* denotes the pressure.

During melting and solidification, the phases are further solved by introducing a temperature dependent liquid fraction β that solves the phases within a mushy region around the melting temperature. This parameter also provides numerical stability during the simulations. While it is possible that turbulence occurs during LCP due to the high pressure liquid jet, turbulence effects were not considered in the simulation model. The silicon melt is treated as an incompressible fluid, optionally with a temperature dependent density. Furthermore, as mentioned earlier, a recoil pressure acts on the melt but it is not considered within the model because vapor dynamics are not implemented into the mathematical model. In the case of short pulse length, this recoil pressure is relatively high, in the order of 1 GPa which is much higher than the liquid jet pressure. However, since the liquid jet exerts pressure far longer than the recoil pressure which occurs only during the evaporation stage, it can be assumed that the liquid jet dominates the melt flow particularly when using relatively long pulse lengths (> 1 μ s) and low pulse energies.

The interaction of the liquid jet with the silicon melt is modeled using multiphase flow corresponding to the Euler-Euler model [1]. The liquid and the silicon melt are treated as two immiscible liquids and thus, a sharp interface and surface tension exists. In the simulation model, all the phases occupy a volume fraction that sum up to unity at any arbitrary point in space. Therefore, the algorithm can track each phase independently. Surface tension effects are also included within the model.

In this thesis, the nanosecond pulse lengths result in relatively high laser intensities. Therefore, the melt lifetime is much smaller than when using long pulse length (> 1 μ s) or a continuous wave (CW) laser. As a result, the melt flow induced by the liquid jet is small and does not affect the doping quality of the poly-silicon considerably. However, during laser ablation processes, where a CW laser or long pulse length are being used, melt expulsion by the liquid jet is significant and depends

on a characteristic melt expulsion time determined by the hydrodynamics of the liquid jet.

b) Radical generation and chemical reactions

Depending upon the absorption coefficient of the molecules within the liquid medium, laser energy may be absorbed to generate radicals within the jet. In addition, at the reaction spot, other interfacial reactions may occur. In the model the reaction kinetics were not considered for doping. However, LCP was previously employed for wafering using a chlorine and potassium hydroxide media. Some of the reaction kinetics are described in Ref. [14].

2.6 Laser-material parameters used in the current work

A large number of parameters used during LCP cannot be calculated directly by analytical equations. These have to be determined empirically as some of those parameters are setup-dependent. In this thesis, some of these values are borrowed from literature or the work by Fell [1] and are therefore not exactly representative of the setup and process conditions in this thesis. Hence, some discrepancies are expected due to the following reasons:

a) The intensity of the laser beam across the jet is unknown in the LCP system used in the current work. It is known that the liquid jet acts as a multi-mode waveguide and therefore the intensity profile shows a speckled distribution across the jet [2]. Even though the side-effects of this intensity profile can be reduced by using a flat pulse and relatively high pulse overlap, it was shown in previous work that local melting and evaporation of the silicon starts at much lower fluences than expected. Fell *et al.* [2] carried out LCP simulations based on the measured intensity profile across the liquid jet. The profile was monitored in real time using a glass plate and a CCD camera. Afterwards, the exact profile was used to calculate the laser intensity profile. In this work, the intensity profile is assumed to be flat and uniform across the laser jet.

- b) To correctly model the absorption of the laser light in the liquid jet, the path enlargement requires measurement as it is dependent upon the coupling optics. At Fraunhofer, the laser intensity distribution across a water jet was measured at varying distances from the nozzle outlet and the path enlargement was estimated to be about 1.3 [1]. Additionally, the absorption in the liquid jet was not empirically determined. Nevertheless, in this thesis, the effect of absorption and path enlargement of the laser inside the jet has been accounted by assuming a constant power loss of about 30%.
- c) To date, LCP work focused mainly on bulk silicon. It is assumed that the thermal and optical properties of bulk silicon are similar to those of poly-crystalline silicon. However the thermal conductivity of poly-Si is influenced by the phonon mean free path length. The phonon mean free path is dependent upon deposition conditions, grain size and shape as well as doping [15]. Therefore, the heat transport is different in poly-Si. Furthermore, the defect levels in poly-Si are subjective to the fabrication process and may differ across the samples. In this thesis, the thermal properties are assumed to be same as those of bulk crystalline silicon.

The software, SLIM (simulation of laser interaction with materials) is employed in Chapter 4 to calculate the time-dependent thermal effects of the laser parameters through an implicit finite-difference scheme [16]. The software is used to identify the influence of the LCP parameters qualitatively and to improve the understanding of LCP on poly-Si thin films. In this Section, the parameters used for simulating the melt depth and the melt lifetime carried out in Chapter 4 are listed in Table 2.1. Unless otherwise stated, the physical constants assumed the values of silicon. Wavelength-dependent parameters were estimated based on a 532 nm laser.

| Parameters | Solid Si | Liquid Si |
|--|-----------------------------------|---------------------------|
| Melting temperature [K] | 1685 | - |
| Evaporation temperature [K] | - | 3540 |
| Thermal conductivity [W/cmK] | 2.99 x 10 ² / (T - 99) | - |
| | - | 0.56 |
| Specific heat capacity [J/cm ³ K] | Equation (2.20) | - |
| | - | 2.432 |
| Reflectivity | Equation (2.2) and (2.14) | - |
| | - | Equation (2.4) and (2.14) |
| Absorption coefficient [cm ⁻¹] | Equation (2.3) and (2.11) | - |
| | - | Equation (2.7) and (2.11) |

Table 2.1: Parameters used for the simulations in the current work

2.7 Conclusion

In this Chapter, the main physical interactions occurring at each stage during LCP were described to give the reader a better understanding of the dynamics of the process. LCP is a complex laser-based process due to the significant number of parameters related to the optics, thermodynamics and hydrodynamics during the process. Therefore it is hard to model the influence of each of those parameters quantitatively, partly due to unavailable literature under those process conditions and

also due to the high computational effort for undertaking this task. Nevertheless, the laser-silicon interactions occurring during dry laser doping still apply for LCP. Therefore, physical models available from literature can be used to model LCP. Those physical models/parameters were modified according to the LCP conditions used in this thesis and will serve as input for the simulations of melt lifetime and melt depth using the SLIM software.

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CHAPTER 3 EXPERIMENTAL AND CHARACTERISATION METHODS

3.1 Introduction

This chapter describes the fabrication process of poly-silicon thin film solar cell on glass made by the solid phase crystallisation (SPC) method. The SPC approach is utilized to form the poly-Si samples before *n*-type doping by LCP. In the second Section, the relevant characterisation techniques for assessing the structural and electrical integrity of the LCP-doped layers are outlined. The electrical and material properties of the LCP-doped films are compared to those from standard poly-Si thin film solar cells (i.e. baseline solar cells) to evaluate the material and electronic quality of the LCP-doped films.

3.2 Poly-Si thin film on glass PV technology

Poly-silicon (poly-Si) thin film solar cells on glass have significant potential to compete against the well-proven bulk silicon wafer counterparts. They are based on silicon which is abundant, cheap and non-toxic. In addition, the poly-Si thin film growth/deposition process can leverage off the semiconductor industry for technological and process innovation [1-4]. For instance, thin film PV technology benefits largely from processes and equipment originating from the semiconductor industry such as plasma-enhanced chemical vapor deposition (PECVD) and

sputtering, amongst many others. Furthermore, through advanced light-trapping mechanisms, only a small amount of semiconductor material (~2 μ m thick) is sufficient to fabricate a poly-Si thin film solar cell with reasonable efficiency (e.g. ~9 %) as compared to a typical silicon wafer solar cell which is about 180 μ m thick [4, 5]. Such large difference in the required material significantly cuts down the manufacturing costs.

The first prototype poly-Si thin film solar cell fabricated by the SPC approach goes back to the late 1980s to early 1990s and was developed by Sanyo Electric [6]. The team pioneered a bi-layer crystallisation method in which a bi-layer amorphous stack, consisting of a thin n^+ layer and a thicker lightly-doped or undoped layer was deposited on metal substrates by plasma-enhanced chemical vapor deposition (PECVD). During the SPC process, the n^+ layer acted as the nucleation layer and crystal growth originated from this layer into the much thicker lightly-doped or undoped layer. The high doping levels lowered the crystallisation threshold (particularly for *n*-type films) and thus, the heavily doped layer crystallised much faster than the less heavily doped layer [5]. Excellent quality poly-Si films were reported using such technique. In 2007, by using a comparable layer structure on glass, (Crystalline Silicon on Glass) CSG Solar commercialized a world record 10.5% efficient poly-Si thin film module on a 94 cm² aperture area via the SPC method [9]. This record efficiency has remained unbroken since then.

Doped poly-Si layers have sufficient lateral conductance and novel interconnection schemes can be devised from this desirable feature. For instance full area expensive transparent conductive oxides (TCO) can be substituted by aluminium during metallisation. It is worth noting that TCOs cannot be used for poly-Si on glass PV technology. This is because TCOs are thermally unstable at high temperatures (> 600 °C) and hence are incompatible with the process temperatures of poly-Si on glass. Additionally, since doped poly-Si layers have relatively low sheet resistances, the TCOs will shunt the solar cells once they are in contact with oppositely doped poly-Si layers.

While other thin film PV technologies such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) have module efficiencies in the range of 13%, it is relatively hard to foresee long term growth of such technologies due to the toxicity of cadmium and scarcity of indium. On the other hand, while amorphous silicon PV technology is a seemingly cheaper and better alternative than CIGS and CdTe, it suffers from light induced degradation due to the Staebler-Wronski effect [11]. As such, the stabilized efficiency is only about 85% of its initial value. In contrast, poly-Si PV technology does not suffer from any light induced degradation [8] and is a cheap and durable technology.

Glass is highly favorable as a superstrate (i.e. light enters the solar cell through the supporting material) because:

a) It is cheap, transparent to visible light, mechanically robust and easily scalable towards large scale production.

b) Additionally, glass possesses excellent moisture barrier properties for long term outdoor conditions [2, 4, 5].

c) Another benefit of using glass as a supporting material is that the overall module fabrication cost can be substantially reduced by using glass as the front cover. Typically, for silicon wafer PV, the cost of a bulk crystalline silicon wafer costs nearly 40-50% of the overall module production cost [4]. Additionally the module fabrication process includes a series of intricate steps such as stringing and tabbing of the solar cells followed by the lamination of an encapsulant [ethylene-vinyl acetate

(EVA)], a rear back sheet and a protective front glass cover over the solar cells to protect them against outdoor conditions. In poly-Si thin film on glass PV technology, the glass supporting material inherently takes over the role of this protective cover. d) Last but not least, glass can be textured using a variety of techniques to increase optical absorption in the thin film solar cells. For instance, sand blasting [12], aluminium-induced texturing (AIT) [4] and the glass-beaded technology [13] from CSG Solar are common examples of glass texturing.

However, the common challenges with glass are the maximum processing temperature and impurities that can potentially diffuse from the glass to contaminate the poly-Si layers during the solar cell fabrication process. Fortunately, such concerns have been successfully addressed by using intermediate temperature processing technologies such as SPC and by using barrier layers such as silicon nitride to prevent diffusion of impurities from the glass to the thin films [1-4]. Additionally, more advanced glass materials such as Borofloat®33 from SCHOTT with a strain point above 520 °C have now appeared on the market, making them ideal for low-cost PV.

Since poly-Si can be formed by a multitude of techniques, the structural and electronic quality can be vastly different. One way to classify poly-Si is to use the temperature stability of the supporting material as a classification criterion. These are the low temperature methods (< 450 °C), intermediate temperature approaches (450 °C - 700 °C) such as SPC and high temperature methods (> 700 °C) [4]. So far, there has been no appreciable efficiency from solar cells made by low temperature methods [4]. Therefore, present poly-Si technologies focus mainly on intermediate and high temperature methods.

High temperature (high-T) approaches utilize thermally stable supporting materials such as alumina. For instance, the research team in IMEC, Belgium

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fabricated a high-*T* poly-Si solar cell using a p^+ poly-Si layer first formed by aluminium-induced crystallisation (AIC) method, followed by the epitaxial growth of a p^+ back surface field and an absorber layer via thermal CVD. To improve the light trapping properties of the device, the poly-Si stack was textured before an *n*-type amorphous silicon emitter was deposited over the layer structure to form a heterojunction solar cell. With such process, solar cells with 8% efficiency have been achieved with an open-circuit voltage (V_{oc}) of about 534 mV, a short-circuit current density (J_{sc}) of 20.7 mA/cm² and a fill factor (*FF*) of 73 % [15]. A schematic of the cell structure using this high temperature approach is shown in Figure 3.1 below.



Figure 3.1: Schematic of cell structure using the high temperature approach [15].

On the other hand, the intermediate temperature methods have mostly been investigated by researchers at the University of New South Wales (UNSW). The group deals mainly with poly-Si on glass (in superstrate configuration). The poly-Si device architecture features a homojunction that is a junction made from the same material (in this case poly-Si) and encompasses an emitter, an absorber and a back surface field. A schematic of this cell structure is shown in Figure 3.2.

To date, poly-Si thin film solar cells on glass at UNSW [16] have been made by the:

- a) Deposition of hydrogenated amorphous silicon by PECVD followed by solid phase crystallisation (SPC) or solid phase epitaxy (SPE) to form poly-Si. This is similar to the cell structure investigated in this thesis.
- b) Evaporation of amorphous silicon on glass followed by SPC to form poly-Si. In this case, doping is performed using effusion cells. Evaporation has the advantages of lower setup cost and much faster material deposition rates (~1 µm/min) as compared to PECVD with deposition rate in the range of tens of nanometers/min. Therefore, the cell fabrication process is faster, more economic and yet still scalable.
- c) A seed layer on glass formed by the AIC method followed by the evaporation of amorphous silicon for the subsequent absorber and back surface field layers. The layers are then crystallised by SPC.
- d) Lastly, a seed layer made by AIC followed by poly-Si grown directly by ionassisted deposition (IAD) technique to form a complete poly-Si thin film solar cell structure.



Figure 3.2: A schematic of a metallised poly-silicon thin film solar cell on planar glass using the intermediate temperature approach

Amongst these methods, the best solar cell efficiency was achieved by the deposition of a-Si via PECVD followed by SPC, with a solar cell efficiency of 9.3% on a 4 cm^2 area [17].

A similar layer structure on glass was implemented by CSG Solar using commercial scale-up equipment. The standard process by CSG Solar starts with a bead-textured glass substrate, deposition of barrier layers (e.g. silicon oxide and silicon nitride) followed by the deposition of $n^+/p^-/p^+$ hydrogenated amorphous silicon layers via PECVD. Then, the entire layer structure undergoes a SPC process to convert the amorphous silicon into poly-Si. Afterwards, point defect annealing and passivation of electrically-active defects are performed by a rapid thermal process (RTP) and a remote in-line hydrogenation process respectively. The final stages of the module fabrication process comprise of the formation of grooves by either inkjet printing or laser scribing. Then a few micron-thick insulating and optically nonabsorbing resin is applied using a proprietary inkjet printing process. This process occurs in two separate stages whereby the first stage comprises of opening up the 'crater' regions to contact the n^+ poly-silicon layer while the second stage creates the vias for the p^+ layer (i.e. the 'dimple' region). Aluminium is then blanket deposited over the entire device and patterned into strips by either laser isolation or inkjet printing. In this way, the cells are automatically connected in series in one another forming the module [10]. Figure 3.3(a) shows a schematic representation of the layer structure of a CSG Solar poly-Si thin film solar cell on glass while Figure 3.3(b) illustrates the metallisation scheme employed by CSG. The crater and dimple openings are clearly visible along the conducting strips.



Figure 3.3: (a) Schematic representation of the layer structure of a CSG Solar poly-Si thin film solar cell on glass technology (b) CSG Solar metallisation scheme using their proprietary inkjet technology to open contact vias [10]

3.3 Poly-Si thin film solar cell fabrication process

At the Solar Energy Research Institute of Singapore (SERIS), a structure similar to that of CSG Solar is being developed on borosilicate glass utilising proprietary and less expensive processes such as AIT glass texturing [18] and an inter-digitated metallisation scheme [19]. The aim is to produce higher efficiency solar cells on a large scale.

The cell fabrication starts with a 3.3 mm borosilicate glass (Schott Borofloat® 33) of size 30 cm by 40 cm that has been thoroughly cleaned and dried with nitrogen gas. Borosilicate glass is chosen because it has a relatively high glass transition temperature (~560 °C) and is closely matched to the coefficient of thermal expansion (CTE) of silicon [20]. In this way, the thermal stress on the glass/silicon structure is minimized. The glass is then loaded into a PECVD tool (MV Systems, USA) where an ~70 nm thick anti-reflective and barrier silicon nitride (SiN_x) layer is deposited over the sample. The SiN_x prevents impurities from the glass from contaminating the poly-Si during the subsequent SPC process and also couples more photons into the solar cell during device operation. Subsequently, doped amorphous silicon layers (a-Si:H) are deposited inside separate chambers within the PECVD machine by

flowing silane (SiH₄) with doping gases such as phosphine (2% PH₃:H₂) and diborane (100 ppm B₂H₆:H₂) for depositing *n*-type and *p*-type layers respectively. The deposited amorphous precursor stack typically comprises of ~100 nm n^+ emitter layer (> 10¹⁹ cm⁻³), ~1.9 µm p^- absorber layer (~10¹⁵-10¹⁶ cm⁻³) and ~100 nm p^+ BSF layer (~10¹⁸ cm⁻³). Before SPC, a 100 nm capping silicon oxide (SiO_x) layer is deposited over the entire layer structure to prevent contamination during the subsequent SPC and RTP process.

At this stage, the layer structure consists of glass/70 nm SiN_x/100 nm n^+ a-Si:H/~1.9 µm p^- a-Si:H/100 nm p^+ a-Si:H/100 nm SiO_x. The sample is subsequently annealed in a nitrogen-purged furnace (Nabertherm, model N 120/65HAC, Germany) in a two-step process – first at 450 °C for one hour to remove the hydrogen (this step prevents cracking of the films during the subsequent SPC step) and then at 610 °C for about 10 hours to crystallise the amorphous silicon. After the SPC process, the sample is slightly warped due to the different thermal contraction/expansion of the poly-Si and glass. Additionally the poly-Si contains a high density of defects. Hence, the sample undergoes a rapid thermal process (RTP) in a RTP tool (CVD Equipment Corporation, USA) at 1000 °C for 1 min to activate the dopants, to anneal the point defects and to flatten the glass sheet [21].

After RTP, the poly-Si layers contain a large number of electrically-active defects such as dangling bonds which are detrimental to the device performance. Thus the solar cell undergoes a hydrogenation process in a hydrogenation reactor (AK800, Roth & Rau, Germany) at 450 °C for 15 min [22]. The system is equipped with a linear microwave plasma source (LMPS) capable of handling substrate sizes up to 30 cm by 40 cm. Prior to the hydrogenation process, the capping silicon oxide is removed by a 5% hydrofluoric acid (HF) dip.
It is important to note that the above fabrication processes are primarily for poly-Si thin film solar cells on planar glass (i.e. non-textured glass). Generally, high efficiency poly-Si solar cells on glass utilise a textured glass to increase optical absorption into the cells. This is usually done by texturing the glass prior to the diode deposition process and adding a SiO₂ back surface reflector (BSR) after the hydrogenation step. The glass texturing is carried out by aluminum-induced texturing (AIT), initially developed in UNSW by Widenborg et al. [23]. Subsequently a 100 nm thick silicon oxide BSR is deposited over the samples after the hydrogenation process. This layer serves to couple photons back into the solar cell once they reach the rear side of the device. Figure 3.4 shows a textured solar cell illustrating the inter-digitated metallisation scheme developed at UNSW. The emitter fingers are the thin light grey lines contacting the n^+ emitter layer (glass side of the solar cell) while the air side fingers are in contact with the p^+ back surface field (BSF). In both cases, the grey areas represent aluminium that has been deposited by thermal evaporation. The different shades of grey are due to the SiO₂ back surface reflector (BSR) that is deposited at the rear of the device, i.e. on the p^+ layer.

Since the experiments investigated in this thesis deal only with poly-silicon thin film solar cells fabricated on planar glass substrates, only the relevant fabrication processes for these devices are described. Figure 3.5 summarizes the fabrication process flow for poly-Si thin film solar cells on planar glass substrates.



Figure 3.4: A textured solar cell illustrating the inter-digitated metallisation scheme developed at UNSW. The emitter fingers are the thin light grey lines contacting the n^+ emitter layer (glass side of the solar cell) while the air side fingers are in contact with the p^+ back surface field (BSF).



Figure 3.5: Process details for fabrication of poly-Si thin film solar cells on planar glass substrates at SERIS.

3.4 Characterisation methods

3.4.1 Electrical characterisation

3.4.1.1 Four point probe

A manual four point probe (Jandel Engineering Ltd equipped with a RM3-AR test unit, Bedford, U.K.) was used to measure the resistivity (or in this case, the sheet resistance) of the LCP-doped layer. By driving a voltage at the two outer probes and measuring the current with the two inner probes, the resistivity of the sample is determined without considering parasitic voltage drops. The probe location, the probe diameter, the sample thickness and the temperature are important factors for accurately measuring the sheet resistance.

For thin film samples, if the thickness t of the poly-Si layers is much smaller than the diameter of the probes (in our case 1.59 mm), then the resistivity simplifies to [24]:

$$\rho = \frac{\pi}{\ln(2)} t \frac{V}{I} \tag{3.1}$$

where ρ is the resistivity (Ω cm), *t* is the thickness of the film (cm), *V* is the voltage (V) and *I* is the current (A).

For a sample of finite geometry (e.g. rectangular sample of width d and length a), a correction factor f is required and thus, the resistivity equation becomes:

$$\rho = \frac{\pi}{\ln(2)} t \frac{V}{I} f \tag{3.2}$$

The sheet resistance is a measure of the resistivity averaged over the sample thickness and is given by:

$$R_{sheet} = \frac{\rho}{t} = 4.532 \frac{V}{I} \tag{3.3}$$

The Jandel four point probe head comprises of four conductive pins, each of diameter 40 µm and spaced 1.59 mm apart in a linear fashion. Due to the finite geometry of the LCP-doped samples, it was necessary to insert a correction factor to calculate the sheet resistance accurately. The correction factor was calculated according to the method by Smits [25]. For the LCP-doped area (length 40 mm by 7 mm), the correction factor is ~ 0.755 for a width/probe spacing (d/s) of 4.4 and a rectangle width d with length $\geq 4d$. This correction factor was also experimentally verified by the author by cutting a doped poly-Si sample (about 10 cm by 10 cm) to a size of 7 mm by 40 mm (similar to that of the LCP-doped area) and comparing the sheet resistance of the original structure to that of the final poly-Si test structure. It was found that the sheet resistance of the cut sample was about 0.8 times that of the larger sample and in good agreement with the calculated correction factor. The sheet resistance was measured at several locations across the samples ensuring that the probes were aligned in the middle of the sample to prevent any edge effects. The sheet resistance measurements were acquired in both forward and reverse bias with different driving currents and the average sheet resistance was calculated based on those measurements.

3.4.1.2 Electrochemical capacitance-voltage (ECV)

ECV is a depth profiling technique that determines the active dopant concentration in a semiconductor by means of repetitive etching and measuring the capacitancevoltage (C-V) at an electrolyte-semiconductor interface. From the C-V measurements, the active doping concentration at the edge of the depletion region below the electrolyte-semiconductor interface can be determined.

Depth profiling is achieved due to the presence of holes. If the semiconductor is *p*-type, holes are already present and etching is performed by forward biasing the electrolyte-semiconductor junction. In the case of a *n*-type semiconductor, holes are created by illuminating the electrolyte-semiconductor interface (typically done with an ultra-violet (UV) light) and reverse biasing the junction. The etch depth (X_{etch}) is controlled by the applied current at the junction and is calculated by Faraday's law of electrolysis according to [26, 27]:

$$X_{etch} = \frac{QM_{mol}}{eValN_A\rho A}$$
(3.4)

where Q is the total measured charge (C), e is the charge of an electron (C), *Val* is the number of valence electrons per atom (in this case it is silicon), M_{mol} is the molar mass of silicon (28 g/mol), N_A is the Avogadro constant (6 x 10²³ mol⁻¹), ρ is the density of Si (2.33 g/cm³) and A is the etched area (cm²).

The semiconductor-electrolyte interface is characterized by a depletion region in the semiconductor with an interface barrier height known as the Schottky barrier. The width of this depletion region ($X_{depletion}$) can be changed by applying an external voltage to the system. In this way, the C-V measurement is performed with a fixed reverse DC bias and a small superimposed AC signal (typically in the range of 1-50 kHz). As a result of this varying AC signal (AC current), the depletion region width changes accordingly. This changing width is similar to that of a parallel-plate capacitor model with a variable plate gap. Therefore, the capacitance of the depletion region is expressed by:

$$C = \left| \frac{dQ}{dV} \right| = \frac{\varepsilon_0 \varepsilon_r A}{X_{depletion}}$$
(3.5)

where Q is the total charge, V is the applied voltage, ε_o is the permittivity in vacuum (F/cm), ε_r is the relative permittivity of silicon (11.7), A is the area of the diode and $X_{depletion}$ is the width of the depletion region.

In the case of an abrupt junction, the relationship between the capacitance C and the applied voltage V is given by the Mott-Schottky equation [24]:

$$\frac{1}{C^2} = \frac{-2}{q\varepsilon_0 \varepsilon_r A^2 N} \left(V - V_{fb} \right)$$
(3.6)

where V_{fb} denotes the flat-band potential and N is the carrier concentration. Plotting $1/C^2$ against V yields a linear relationship whereby the slope gives the active doping concentration N and the y-intercept is V_{fb} .

For evaluating a non-uniform doping profile with depth, differentiating equation (3.6) yields the majority doping concentration N as a function of the capacitance [26, 27]:

$$N = -\frac{2}{e\epsilon_{o}\epsilon_{r}A^{2}}\frac{1}{d(\frac{1}{C^{2}})/dV}$$
(3.7)

where *N* is the majority carrier concentration (cm⁻³). Thus, the overall depth (X_{total}) measured by ECV is:

$$X_{total} = X_{etch} + X_{depletion} \tag{3.8}$$

Therefore, assuming a constant area and measuring the doping concentration as a function of depth, the active doping profile of the semiconductor can be plotted. The area is determined by the geometry of the sealant ring during ECV measurements.

In this work, a commercial ECV profiler (CVP21 ECV Profiler, WEP Control, Germany) was utilized to measure the active dopant profiles of the LCP-doped films. The electrolyte solution was prepared by dissolving 2.89 g of ammonium bifluoride (ABF) [NH₄F.HF] into 500 ml of DI water to achieve a 0.1 M solution. The etched area was defined by the area of the sealant ring and was equivalent to 0.095 cm². Figure 3.6 illustrates a schematic of the ECV measurement technique.



Figure 3.6: Schematic of the ECV measurement technique (not drawn to scale)

Throughout the etching process, the applied voltage was 1.5 V with respect to the saturated calomel electrode (SCE). C-V measurements were performed across an applied voltage between -0.65 V to -0.30 V with respect to the SCE. The error in the measurement of the active doping concentration was calculated from the non-linearity of the $1/C^2$ curve [26]. High contact resistance and non-uniform etching can be the main sources of error during ECV measurements. A gallium indium eutectic paste was spread at the probe contact areas to decrease the contact resistance prior to measurements. It is important to note that ECV doping profiles are dependent upon numerous factors such as ring geometry, surface area factor (in the case of textured samples, this factor is increased), etched depth and the material being etched, amongst many others [28]. Each of these factors has a significant influence over the doping profile. Therefore, for accurate analysis, ECV measurements require other complementary techniques such as secondary ion mass spectroscopy (SIMS).

3.4.1.3 Quasi-steady state open-circuit voltage (Suns- V_{oc}) measurements

Introduced by Sinton and Cuevas [29, 30], Suns- V_{oc} is a fast (takes less than 2 seconds per measurement), non-destructive measurement procedure that is very popular in the photovoltaic industry. By simultaneously illuminating a reference solar cell and the device under test (DUT) with a slowly decaying flash light (from a Xenon lamp), the open-circuit voltage (V_{oc}) is measured as a function of the light intensity. Since the V_{oc} of a silicon solar cell is influenced by its temperature (typically a 1 °C increase in cell temperature leads to a 2.2 mV decrease in V_{oc}), the flash decay is chosen to be fast enough (within 10 ms) such that temperature effects during the measurements can be neglected. Furthermore, the V_{oc} is corrected with the temperature coefficient of the sample under test (-0.0022 V/°C for crystalline Si solar cells). In this work, Suns- V_{oc} measurements were acquired using a customized thin film Suns- V_{oc} tester [31]. Since our standard poly-Si thin film solar cell is fabricated on glass, a fast hassle-free method of contacting the rear of the devices was devised during the Suns- V_{oc} setup. The contact probes enable the n^+ and p^+ layer to be contacted from the rear side of the solar cell while the front side (glass side) faces the transparent glass stage. The Suns- V_{oc} system is equipped with a Xenon flash lamp directly underneath the glass stage. The flash is fitted with filters and a wide angle diffuser to uniformly distribute the light over the glass stage. On top of the glass stage, there are transparent plastic foils that have been printed with dotted patterns of different density to achieve good spatial uniformity of the light intensity over the glass stage. In this way, large area samples (25 x 35 cm²) can be measured with good uniformity. More details about the setup and demonstration of the capabilities of this tester can be found in Ref. [31].

The light intensity of the Suns- V_{oc} flash tester is calibrated against the shortcircuit current (I_{sc}) flowing across a calibrated silicon wafer reference solar cell (area 1 cm²), which is located at a fixed distance from the light source. The short circuit current is measured by passing it through a small load of 1 Ω and measuring the voltage drop across the resistor. This voltage drop is then amplified using a gain amplifier for measurement accuracy. The light intensity is then calculated by dividing the I_{sc} across the silicon reference cell by the I_{sc} at 1 Sun (the value of which was measured independently by a calibrated I-V tester). An example of the illumination against time during a Suns- V_{oc} measurement is shown in Figure 3.7 below [27]:



Figure 3.7: Illumination (from the Xenon lamp) against time and the measured open-circuit voltage during a Suns- V_{oc} measurement [27]

The resulting Suns- V_{oc} curves on a log and linear scale are plotted as in Figure 3.8 [27].



Figure 3.8: Illumination (from the Xenon lamp) against measured open-circuit voltage (V_{oc}) [on the left the scale is a logarithmic plot] and illumination against the measured open-circuit voltage [on the right the scale is a linear plot].

Assuming that the measured current varies linearly with the light intensity, the Suns- V_{oc} curve can be converted into a light I-V curve. However, since there is no actual current flowing out of the device under test (the raw measurement is open-circuit voltage), the measured light intensity (Suns) can instead be converted into current density (mA/cm²). Therefore the y-axis (originally in Suns) is converted to J_{sc} by using the formulation below [29]:

$$J_{implied} = J_{sc}(1 - Suns) \tag{3.9}$$

A reasonable short-circuit current density (J_{sc}) (in this case, a J_{sc} of 30 mA/cm² is used in the calculations). This value is the highest current density achieved for our baseline poly-Si solar cells on textured glass. Since this current is not the 'actual' current flowing through the device, the I-V curve is known as a 'pseudo-IV' curve. The resulting I-V curve then shows up as in Figure 3.9, after which the I-V curve is downshifted from the first quadrant to the fourth quadrant to extract relevant parameters.



Figure 3.9: An example of the 1-Sun pseudo-IV curve extracted from the Suns- V_{oc} data

Typically, the fill factor (FF) (%) of a metallised solar cell is the ratio of the maximum power output of the solar cell to the product of V_{oc} and J_{sc} . It is essentially a measure of the squareness of the *I-V* curve and is given by:

$$FF = \frac{V_{oc}(MPP) \times J_{sc}(MPP)}{V_{oc} (1 Sun) \times J_{sc} (1 Sun)}$$
(3.10)

The maximum power output (W) by a solar cell is calculated by:

$$P_{max} = V_{oc} (1 Sun) \times J_{sc} (1 Sun) \times FF$$
(3.11)

The efficiency (η) of a solar cell is then calculated by the ratio of output power to input power:

$$\eta = \frac{V_{oc} (1 Sun) \times J_{sc} (1 Sun) \times FF}{\text{Input power}}$$
(3.12)

Where the input power is AM1.5G spectrum, that is 1000 W/m^2 or 100 mW/cm^2 .

From the Suns- V_{oc} curve, the pseudo-fill factor (*pFF*) which represents the upper limit of fill factor excluding series resistance (R_s) can be calculated. It is given by [32]:

$$pFF = \frac{v_{oc}(MPP) \times J_{norm}(MPP)}{v_{oc} (1 Sun)}$$
(3.13)

where $V_{oc}(1 \text{ Sun})$ is the open-circuit voltage at 1 Sun, $V_{oc}(\text{MPP})$ and $J_{norm}(\text{MPP})$ is the open-circuit voltage and normalized current density at maximum power point (MPP) respectively. The normalized current density is due to the hypothetical short-circuit current density of 30 mA/cm².

Generally, before metallisation, the shunt resistance (R_{sh}) remains unaffected during the diode fabrication process and the series resistance does not have significant effect on the Suns- V_{oc} measurements. Thus, the *pFF* represents the actual fill factor without the effect of R_s and R_{sh} . When both R_s and R_{sh} have negligible effects, the fill factor is given by [33]:

$$FF = pFF = \frac{v_{oc} - \ln (v_{oc} + 0.72)}{v_{oc} + 1}$$
(3.14)

where v_{oc} is the normalized open-circuit voltage given by:

$$v_{oc} = \frac{q}{nKT} V_{oc} \tag{3.15}$$

where n is the diode ideality factor and K is the Boltzmann constant.

However, it is worth noting that the extraction of V_{oc} and *pFF* becomes unstable at very high series resistance and can impact the Suns- V_{oc} curve. This procedure will be addressed in more details in Chapter 5. Figure 3.10 shows the inhouse Suns- V_{oc} thin film tester. The glass stage holds the reference sample, the device under test and a thermocouple for temperature measurements.



Figure 3.10: Customized thin film Suns- V_{oc} tester for measuring poly-Si solar cells. The glass stage holds the reference sample, the device under test and a thermocouple for temperature measurements.

Since the Suns- V_{oc} method does not require a metallised solar cell, measurements can be performed on a solar cell at various stages during the fabrication process. Furthermore, the shunt and series resistance can be evaluated before and after metallisation providing further opportunity to optimize the process. In this work, the V_{oc} of the non-metallised samples are measured with the in-house thin film Suns- V_{oc} . In Chapter 6, the effective ideality factor (n_{eff}) is used to evaluate the electronic quality of LCP-doped poly-Si thin film solar cells before and after hydrogenation process.

3.4.2 Crystal characterisation

3.4.2.1 Ultra-violet (UV) reflectance

Hemispherical reflectance measurements were performed using a UV-VIS-NIR (ultraviolet-visible-near infrared) spectrometer equipped with an integrating sphere (Perkin Elmer UV/VIS Lambda 950) to measure both specular and diffuse reflectance from the LCP-doped samples. Crystalline silicon (c-Si) yields two prominent maxima in the UV range, more specifically at 280 nm and at 365 nm. These peaks are the result of optical interband transitions occurring along the I-L axis of the Brillouin zone [34]. Imperfect crystallinity in the near-surface region typically causes broadening and attenuation of those peaks. Thus, UV reflectance can be used as a measure of assessing the crystalline quality of silicon. Additionally it is a fast, contactless and non-destructive method that has been widely employed to investigate the crystalline quality of poly-Si thin films. The crystallinity of the LCP-doped layers was investigated by comparing the average reflectance of the LCP-doped films to that of a double-sided polished boron-doped float zone (FZ) Si wafer which arguably possesses the best crystalline quality. This method is described in Ref. [35].

3.4.2.2 Raman spectroscopy

Raman spectroscopy involves the inelastic scattering of a monochromatic light (typically a laser beam) by the atomic vibrations in a medium (e.g. silicon). Such lattice vibrations are collectively described by a wave vector q and frequency ω . Those are quantized and in the absence of perturbations (e.g. doping and stress), they are degenerate and have the same frequency value. In silicon, due to translational symmetry, momentum is conserved (q = 0) and the Raman spectrum is represented by a single transverse-optical (TO) phonon mode and two longitudinal-optical (LO) phonon modes. Therefore the Raman spectrum is distinguished by a narrow line (full width half maximum (FWHM) ~3.5 cm⁻¹ at room temperature) and is located at around 521 cm⁻¹. This value is somewhat subjective to setup, calibration and is measured relative to the frequency of the laser. The optical phonon mode (OPM) of crystalline silicon (c-Si) is characterised by its peak frequency ω , FWHM, intensity of the scattered signal and peak symmetry. Due to disturbances in the crystal structure

(e.g. imperfect crystallinity, doping, stress etc.), the phonon correlation length decreases and momentum is no longer conserved. Hence, the TO phonon peak in the Raman spectra is either shifted (usually known as Raman shift) or broadened [36]. For instance, in the presence of tensile stress, the peak shifts to lower frequency and vice-versa. Additionally, structural defects in the crystal (e.g. dislocations, doping, crystal disorder) lead to broadening or peak asymmetry. There are numerous studies in literature dealing with stress, doping and defects in poly-silicon thin films by Raman spectroscopy. Some of these studies focus on low pressure chemical vapour deposition (LPCVD) poly-Si films [37], laser-crystallised poly-Si films [38] and laser-annealed poly-Si films [39], amongst many others.

In this work, micro-Raman spectroscopy was used to investigate the stress and structural quality in LCP-doped films. Raman spectroscopy was also used to identify electrically-active defects in the LCP-doped poly-Si thin film solar cells – for example dangling bonds before and after hydrogenation. More details are found in the respective chapters.

3.4.2.3 Electron backscattered diffraction (EBSD)

EBSD is a specialised characterisation technique that is used in conjunction with a scanning electron microscope (SEM). It provides quantitative microstructural information about the grain boundary character, texture and grain size, amongst many others. An electron beam is directed on a sample tilted at a shallow angle (e.g. 20 °). Usually the SEM stage is used to tilt the sample and thus, the stage tilt is equivalent to 70 °. Typical acceleration voltages are in the range of 10-30 kV and beam currents are in the order of 1-50 nA. At the point of incidence on the sample's surface, an EBSD pattern originates spherically from this point. Upon interaction with the sample, low

energy backscattered electrons are channeled and subjected to path differences resulting in constructive or destructive interference. These diffraction patterns are captured by a phosphor screen linked to a CCD camera, positioned a close distance from the sample (~15 mm). The phosphor screen converts the diffracted electrons into light such that the EBSD patterns can be recorded on the CCD camera [40, 41].

EBSD patterns depend upon the lattice parameters of the material, its orientation in space, the acceleration voltage of the scanning beam and proximity of the detector. A special software then detects the Kikuchi bands using a Hough transform and indexes all the possible grain orientations within each phase. In this work, EBSD measurements are carried out using a Bruker CrystAlign 200 system attached to a Carl Zeiss Auriga SEM. Information from EBSD is used to quantify the average grain size and to identify any geometrically-necessary dislocations (GNDs) in the LCP-doped samples.

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CHAPTER 4 LASER CHEMICAL PROCESSING OF *P*-TYPE POLY-SILICON THIN FILM ON GLASS

4.1 Introduction

In this chapter, LCP is investigated for *n*-type doping of poly-Si thin film on glass substrates. The poly-Si was lightly doped with boron (~ 10^{16} cm⁻³) such that a *p*-*n* junction was formed at the surface of the poly-Si during LCP. The first Section investigates LCP and annealing conditions required for dopant activation. Therein, the LCP-doped layers were characterised by four point probe, secondary ion mass spectrometry (SIMS) and electrochemical capacitance-voltage (ECV) measurements. Melt depth and melt lifetime simulations were then performed using the laser modeling software SLIM (simulation of laser interaction with materials) for a qualitative assessment of the LCP process parameters on the sheet resistance and doping profiles. An analytical model was introduced for calculating the sheet resistances of the LCP-doped layers and the theoretical and measured data were compared. From the findings in this Chapter, the optimum doping conditions of poly-Si thin film on glass were identified and used for future processing.

4.2 Experimental details

An approximately 1.5 μ m thick *p*-type amorphous silicon layer (a-Si:H) was deposited by plasma-enhanced chemical vapour deposition (PECVD) (MV Systems, USA) onto a borosilicate glass sheet (Borofloat33, Schott AG, Germany) of size 30 cm x 40 cm x 3.3 mm. The glass was pre-coated with a 70 nm thick silicon nitride which acts as an anti-reflective and barrier layer against impurities from the glass. Before solid phase crystallization (SPC), a 100 nm capping silicon oxide layer was deposited *in situ* over the 1.5 μ m *p*-doped a-Si:H to prevent contamination during the subsequent thermal treatments. The sample was then crystallized by the SPC process at 610 °C for 10 hours in a nitrogen-purged oven (Nabertherm, model N120/65HAC, Germany). Rapid thermal anneal (RTP) was performed in a RTP tool (CVD Equipment Corporation, U.S.A) at 1000 °C for 1 min to flatten the glass sheet and to anneal point defects. The capping oxide layer was later removed by a HF dip (10%) after RTP. A 20 cm x 20 cm sample was then cut out for LCP. Figure 4.1 shows the sample preparation steps before LCP doping.

Borosilicate glass is deposited with ~ 70 nm SiN_x and ~ 1.5 μ m a-Si:H through plasma-enhanced chemical vapor deposition (PECVD) + 100 nm capping SiO_x layer

> Solid Phase Crystallisation (SPC) process at 610 °C for 10 hours to form poly-Si

Rapid Thermal Process (RTP) to flatten the glass sheet and provide defect removal

Removal of oxide layer by HF dip before LCP

Figure 4.1: Sample preparation before LCP doping

Before the doping experiments, the LCP equipment (SelectDop, RENA, Germany) was switched to run mode. Under this configuration, the doping medium (in this case phosphoric acid) was pumped at high pressure (120 bars) through one of the jet heads. From experience, it was found that the commercial grade phosphoric acid (85%) caused random clogging of the jet head due to its high viscosity. Therefore, a 42.5% phosphoric acid solution was used in the experiments. Before LCP, the laser source (PyroFlexTM 25 Series) was also turned on for about 20-30 min before operation such that the laser output remained stable throughout the doping experiments. The laser unit featured a Q-switched, frequency-doubled solid state Nd:YAG laser (wavelength 532 nm).

Then, the 20 cm by 20 cm poly-Si sample was inserted into a custom-made Teflon chuck. The latter was milled according to the geometry of the glass sample (i.e. 20 cm by 20 cm by 3.3 mm) such that the glass remained securely held within the chuck during LCP operation. Furthermore the chuck was fitted with leveling screws that allowed independent adjustment at each edge and corner for proper sample positioning. An allowance of about 3 cm between the nozzle and the poly-Si was necessary to maintain the laminar flow of the jet and to prevent the nozzle head from striking the sample during LCP operation. During LCP, the jet head remained stationary while the stage (i.e. chuck) moved along the X and Y translational directions. LCP parameters (jet pressure, number and width of lines forming the busbar-like patterns etc.) as well as other setup variables such as chuck speed served as input to the equipment through the touch-sensitive computer screen. Figure 4.2 shows a screenshot of the parameter input window.

| Login User | PLC1 Manual PLC | 2 | | | PLC3 | | | - 0 | Semi E10 States Unknown |
|--------------------|---|---------------|------------------|----------------|---------|---------|-----------------------------|-----------------------|--|
| Level | Date Time No | Message | | IState | | | | | |
| Logout Supervisors | 12/16/2011 9.22:33 AM 5023 Lassifiead LCP Jet 2 pressure | e below limit | | | | | | | Quit All Buzzer Off |
| Machine Overview | and the second se | | | | | | _ | and the second second | And in case of the local division of the loc |
| Middanne Overview | Laser | r System LUI | P - Licneral La: | ser System LCI | ~ | | | | |
| Module List | Picture Setting | Statebit | | lγO | | States | | | |
| - Main Screen | Type Parameter | | | | | | | Module State | Manual |
| E-Laser System LCP | Parameter | Unit | Current Value | New Value | Min | Max | Default | | |
| Media Supply LCP | I - 1 - Fingers | | | | | | | | |
| - Axis LCP | Number Fingers | | 71 | 71 | 0 | 200 | 144 | | |
| - Chuck LCP | Finger pitch | mm | 0.000 | 0.000 | 0.000 | 0.500 | 0.000 | | |
| - Laser Unit LCP | Number finger fiber | | 1 | 1 | 1 | 20 | 1 | | |
| | - 2 - Busbars | | | | | | | | |
| | Busbar pitch | mm | 0.010 | 0.010 | 0.000 | 0.200 | 0.200 | | |
| | Number busbar section | | 1 | 1 | 1 | 2000 | 1 | | |
| | Busbar 1 active | | Yes | Yes | No | Yes | Yes | | |
| | Busbar 1 Y position | mm | 26.000 | 26.000 | 0.000 | 300.000 | 26.000 | | |
| | Busbar 2 active | | Yes 70.000 | Yes | No | Yes | Yes | | |
| | Busbar 2 y position | mm | 78.000 | 78.000 | U.UUU | 300.000 | 28.000 | | |
| | Dusbar 3 active Dushay 2 V assister | | 105 | 130,000 | 110 | 165 | 100 000 | | |
| | Busbar 5 Y position | trirri | Ne. | 130.000 | Nie. | - Xee | 130.000 | | |
| | Bushard V position | 00100 | 15,000 | 15 000 | 0.000 | 200,000 | 0.000 | | |
| | Bushar 5 active | | No | No | No | Yes | Nn | | |
| | Busbar 5 Y position | mm | 75.000 | 75.000 | 0.000 | 300.000 | 0.000 | | |
| | Busbar 6 active | | No | No | Na | Yes | No | | |
| | Busbar 6 Y position | mm | 145.000 | 145.000 | 0.000 | 300.000 | 0.000 | | |
| | Busbar 7 active | | No | No | No | Yes | No | | |
| | Busbar 7 Y position | mm | 97.000 | 97.000 | 0.000 | 300.000 | 0.000 | | |
| | Busbar 8 active | | No | No | No | Yes | No | | |
| | Busbar 8 Y position | mm | 0.000 | 0.000 | 0.000 | 300.000 | 0.000 | | |
| | Busbar 9 active | | No | No | No | Yes | No | | |
| | Busbar 9 Y position | mm | 0.000 | 0.000 | 0.000 | 300.000 | 0.000 | | |
| | Busbar 10 active | | No | No | No | Yes | No | | |
| Machine Overview | Busbar 10 Y position | mm | 140.000 | 140.000 | 0.000 | 300.000 | 0.000 | | |
| | 📕 – 3 - Wafer type (0 - square, 1 - pseudo square | e, 2 - grey) | | | | | | | |
| GDS | Wafer type | | 0 | 0 | 0 | 2 | 0 | | |
| | Image: A - Camera system | | | | | | | | |
| Alarm Messages | Active | | No | No | No | Yes | Yes | | |
| | | | | | | | | | |
| Quality Matrix | | | | | | | | | |
| | | | | | | | | | |
| System Settings | | | | | | | | | |
| | Onen Save | | No | w f | ownload | | Help | | |
| Help Desk | | | | | | | | | |
| | | | | | | | Production Engineering Sche | eduled | Unsche |
| RENA | Start Start S | stop | Sto | p | time | 3 | NICI | IUCI | aervice UFF |

Figure 4.2: Screenshot of the parameter input window

Before starting the doping experiments, a laser power output was first monitored at the laser/optical fibre entry point located inside the laser cabinet and subsequently at the laser/jet output situated in the processing chamber. This procedure was performed to determine the loss in laser power after passing through the optics and inside the liquid jet. Since high pressure phosphoric acid flowed out of the nozzle, the power output was monitored by holding a plain glass piece towards the incoming jet while measuring the laser power with a photodiode. Since the glass was transparent at the laser wavelength (532 nm), the approach was feasible to verify the power losses between the laser source and the jet output. Typically, a 30% power loss between the laser source and the nozzle output was acceptable for LCP doping. This power loss originated from the coupling optics, absorption inside the laser jet and nonuniformities from the laser output. Any power loss higher than 40% necessitated the Synova Microjet-Minihead[©] alignment which entailed mounting the Synova jet head on a separate fixture for aligning purposes. However, a detailed description of this procedure is not treated here. Figure 4.3 depicts the LCP equipment and its process control.



Figure 4.3: LCP equipment and its process control

LCP doping was performed by scanning the sample under the coupled laser beam/acid jet in the X and Y translational directions. By overlapping a series of single lines, doping was achieved over a particular area. In this work, 7 mm wide lines (busbarlike structures) covering the entire length of a 20 cm square sample were *n*-type doped by the LCP process. Those busbars were raster scanned with a line pitch of 10 μ m (0.01 mm x 700 busbars) and were each spaced 2 cm apart to prevent any dopant smearing during the subsequent thermal treatments. At a repetition rate (*Rep*) of 100 kHz, the pulse overlap was calculated to be 80% and 90% for processing speeds (*s*) of 1000 mm/s and 500 mm/s respectively. The pulse overlap Δ was calculated according to Equation (4.1):

$$\Delta = \frac{D - D_1}{D}$$
(4.1)
where

$$D_1 = s * \frac{1}{\text{Rep}}$$

where *D* was the jet diameter (assumed to be the jet diameter exiting the nozzle i.e. 50 μ m) and *s* was the processing speed in m/s.

The pulse energy *P* in Joules (J) was calculated from the average measured power P_{laser} in Watts (W) after accounting for 30% power loss. The laser fluence, *F* (J/cm²) was determined by the pulse energy over the area *A* of the laser spot size (in cm²). The diameter of the laser spot was assumed to be 30 µm. The laser fluence was then determined by Equation (4.2):

$$F = \frac{P/Rep}{\pi \left(\frac{d_{spot}}{2}\right)^2}$$
(4.2)

The LCP parameters were investigated to determine the influence of the pulse energy and pulse overlap over the sheet resistance and doping depth of the samples. In this case, the LCP conditions were explored for two different pulse regimes (20 ns and 60 ns) and are listed in Table 4.1. The laser fluence reflects the actual laser energy available to the sample after accounting for laser losses within the jet and coupling optics (about 30%). Figure 4.4 shows a schematic illustration of the sample during LCP.



Figure 4.4: A schematic of the sample structure during LCP

Table 4.1: LCP parameters used for the experiments (pulse shape, repetion rate and jet pressure were set to square-shaped, 100 kHz and 130 bar respectively).

| Laser pulse length [ns] | Parameter optimisation | Sample number | Pulse energy [µJ] | Fluence [J/cm ²] | Pulse overlap [%] | Average surface roughness [nm] |
|----------------------------|---|------------------|-------------------------|---------------------------------|-------------------------|---|
| | Influence of pulse energy | E1 | 14 | 2.0 | 80 | 92 ± 34 |
| | | E3 | 12 | 1.7 | 80 | 50 ± 19 |
| 20 | | E5 | 10.5 | 1.5 | 80 | 12 ± 11 |
| 20 | Influence of pulse overlap | E2 | 14 | 2.0 | 90 | 135 ± 18 |
| | | E4 | 12 | 1.7 | 90 | 62 ± 24 |
| | | E6 | 10.5 | 1.5 | 90 | 28 ± 8 |
| | Influence of pulse energy Influence of pulse overlap | S 1 | 24.5 | 3.5 | 90 | 208 ± 44 |
| | | S2 | 21 | 3.0 | 90 | 150 ± 3 |
| 60 | | S 3 | 17.5 | 2.5 | 90 | 62 ± 7 |
| | | S4 | 17.5 | 2.5 | 80 | 37 ± 2 |
| | | S5 | 21 | 3.0 | 80 | 93 ± 12 |
| | | S 6 | 24.5 | 3.5 | 80 | 189 ± 16 |

For each experimental run, one sample was kept as control (hereafter labelled asdoped) while the remaining samples were subjected to different annealing conditions to study the effect of the annealing step on the sheet resistance and doping profiles. Prior to annealing, a 100 nm thick barrier silicon oxide layer was deposited on each batch of LCP-doped samples except for batch B1. Prolonged and short thermal annealing for dopant activation was carried out in a nitrogen-purged oven at different temperatures or in a RTP tool at 1000 °C for 1 min respectively. After a short 10% HF etch to remove any oxide layer, sheet resistance measurements were carried out on each LCP-doped sample. Based on the geometry of the samples, a correction factor was applied to the measured sheet resistances after the method of Smits [1]. The process step for each batch of samples is shown in Figure 4.5. After dopant activation, electrochemical capacitance-voltage (ECV) profiling was performed on the samples to assess the active phosphorus concentration. SIMS measurements were also conducted to determine the atomic concentration of phosphorus within the LCP-doped layers. Surface roughness measurements were conducted using a stylus profiler (Dektak 150 surface profiler). Lastly, scanning electron microscope (SEM) micrographs were acquired on an Auriga system from Carl Zeiss.



Figure 4.5: Process steps for each batch of samples after LCP processing. All samples were subjected to a 10% HF dip to remove any oxide layer prior to sheet resistance measurements.

In another round of experiments, the influence of the pulse length over the doping depth and the sheet resistances was studied. Due to a major fire occurring at the authors' research institute, the following study was performed through collaboration with Fraunhofer Institute of Solar Energy Systems (Fraunhofer ISE), Germany. The LCP equipment used in this investigation was similar to the one shown in Figure 4.3 except that the specifications of the laser were different. The repetition rate could not be varied independently from the pulse length. For instance, at 100 kHz, the pulse length was set at 40 ns and the pulse length was about 60 ns at 160 kHz and so forth. Sample preparation followed the process steps described in Figure 4.1. After LCP and sample cleaning, the samples were annealed in a nitrogen-purged oven at 610 °C for 30 min. Table 4.2 summarizes the LCP conditions used for the LCP experiments (pulse shape and jet pressure were set to square-shaped and 130 bar respectively).

| Sample number | Laser parameters | Fluence [J/cm ²] | Pulse overlap [%] | Average surface roughness [nm] |
|------------------|-------------------------|---------------------------------|-------------------------|-----------------------------------|
| D1 | [13 µJ, 160 kHz, 60 ns] | 1.8 | 88 | 41 ± 8 |
| D2 | [11 µJ, 160 kHz, 60 ns] | 1.5 | 94 | 27 ± 6 |
| D3 | [11µJ, 220 kHz, 80 ns] | 1.5 | 96 | 36 ± 3 |
| D4 | [11 µJ, 220 kHz, 80 ns] | 1.5 | 91 | 54 ± 17 |
| D5 | [10 µJ, 200 kHz, 70 ns] | 1.4 | 95 | 88 ± 8 |
| D6 | [10 µJ, 200 kHz, 70 ns] | 1.4 | 90 | 35 ± 2 |
| D7 | [12 µJ, 100 kHz, 40 ns] | 1.8 | 90 | 39 ± 6 |
| D8 | [13 µJ, 100 kHz, 40 ns] | 1.8 | 80 | 38 ± 16 |

Table 4.2: LCP parameters used for the LCP experiments (pulse shape and jet pressure were set to square-shaped and 130 bar respectively).

4.3 Results and Discussion

4.3.1 Sheet resistance measurements

A) Influence of pulse energy and pulse overlap

The sheet resistance of the as-doped LCP samples was very high with values close to $1 \text{ M}\Omega/\Box$ implying that the dopants were not activated directly after the LCP process. However it was found that a prolonged thermal anneal in a nitrogen-purged oven at 610 °C for 30 min or a RTP at 1000 °C for 1 min was sufficient to reduce the sheet resistance to values below 5 k Ω/\Box . This significant decrease in the sheet resistance was originally attributed to the formation of amorphous silicon (i.e. amorphisation) [2, 3]. Literature reports that amorphisation is dependent upon the resolidification velocity of the melt [4]. However, a detailed investigation of the structural quality through transmission electron microscopy (TEM), ultra-violet (UV) reflectance and Raman spectroscopy confirmed that the high sheet resistance was not due to amorphisation. More details about this study are reported in Chapter 6.

Figure 4.6 displays the sheet resistance measurements of the samples that were processed using a 20 ns pulse length and two different pulse-to-pulse overlap ratios (see Table 4.1 for LCP parameters) and anneal conditions B1-B3 (refer to Figure 4.5). The error bars reflect the standard deviation in the sheet resistance measurements conducted at various locations over the samples.



Figure 4.6: Sheet resistance of LCP samples processed using a 20 ns pulse length and LCP parameters from Table 4.1. The samples were annealed as described in Figure 4.5. Samples processed with 90% pulse overlap yielded lower sheet resistances due to increased dopant diffusion. Batches B1 and B2 showed almost similar sheet resistances. The error bars reflect the standard deviation in the sheet resistance measurements.

The batches B1 (without barrier oxide) and B2 (with barrier oxide) displayed somewhat similar sheet resistances indicating that the ambient annealing conditions did not contribute to dopant activation. From Figure 4.6, the samples processed using a 90% pulse overlap showed a lower sheet resistance than those processed with an 80% laser pulse overlap due to increased dopant diffusion. A 90% overlap implied that the number of pulses per unit area was doubled as compared to that of an 80% pulse overlap. Thus, the number of melt cycles per unit area was increased which resulted in a deeper doping depth. The RTP batch (B3) was expected to show the lowest sheet resistance for the same LCP conditions but the high thermal gradient during the RTP process caused cracking of the samples (e.g. refer to sample E4 from B3 in Figure 4.6). Sample E1 from B3 was processed with higher laser fluence (e.g. 2.0 J/cm² using 20 ns pulse length) and thus, the laser damage was higher causing

partial ablation of the poly-silicon. In addition, the sample was also cracked after the RTP process. Therefore it showed higher sheet resistance. From Figure 4.6, it appears that the optimum conditions for LCP processing using a laser pulse length of 20 ns lie within a range of 1.5-1.7 J/cm² at 90% overlap conditions. Those samples also showed a reasonably low average surface roughness (refer to Table 4.1) indicating low surface damage as a result of LCP.

Figure 4.7 depicts the sheet resistances of LCP samples processed using a 60 ns laser pulse length. The 90% pulse overlap conditions yielded the lowest sheet resistances due to improved dopant diffusion. It was also observed that longer anneals (e.g. 610 °C for 2 hours) or anneals at higher temperatures (e.g. 700 °C for 30 min) resulted in lower sheet resistances, possibly due to improved defect annealing and increased carrier mobility under these process conditions. At higher laser fluences (\geq 3.0 J/cm² using 60 ns pulse length), there was more significant material damage such as partial ablation of the poly-Si material and therefore there were large variations in the measured sheet resistances. From Table 4.1, those samples also showed higher surface roughness as a result of the laser damage from LCP.



Figure 4.7: Sheet resistance of LCP samples processed using a 60 ns laser pulse length and LCP parameters from Table 4.1. The samples were annealed as described in Figure 4.5. For LCP at lower fluence, the sheet resistance decreased upon annealing for longer durations or annealing at a higher temperature (refer to B5 and B6). Samples processed with 90% pulse overlap yield lower sheet resistances due to enhanced dopant diffusion. The error bars represent the standard deviation in the sheet resistance measurements.

The above experiments confirm that the incorporated phosphorus is not activated after LCP. Upon annealing, phosphorus diffuses into the substitutional site within the silicon lattice and becomes activated. This diffusion mechanism (e.g. kick-out, vacancy etc.) is thermally activated and requires an activation energy. Additionally, conduction in solids typically follows an Arrhenius behavior since they are thermally activated processes.

In this Section, the activation energy for dopant activation is evaluated by investigating the drop in sheet resistance as a function of the annealing temperature (up to 610 °C), for two as-doped LCP samples, E3 and S4 from Table 4.1 processed using different laser pulse lengths (20 ns and 60 ns respectively). These samples were subjected to an isochronal anneal (the duration was set to 30 min) in an argon

ambient. The same heating and cooling rate was applied for each experimental condition. After each anneal step, the samples were cooled down to room temperature and the sheet resistance was measured at different points across the samples. Figure 4.8 displays an Arrhenius plot as a function of annealing temperature.



Figure 4.8: Measured sheet resistance of two LCP samples (E3 and S4 processed using 20 ns and 60 ns laser pulse length respectively) as a function of annealing temperature during an isochronal anneal. All samples were annealed for 30 min and were subjected to the same heating and cooling rate.

The data from Figure 4.8 was fitted empirically in an Arrhenius form using Equation (4.3). It was observed that dopant activation required at least a temperature of 500 °C. Below this temperature, the sheet resistances were very high (in M Ω / \Box) indicating that the dopants were not activated.

$$\ln R_{sheet} = A - \frac{E_A}{KT} \tag{4.3}$$

where E_A is the activation energy in eV, *K* is the Boltzmann constant (8.62 x 10⁻⁵ eVK⁻¹) and *T* is the absolute temperature. The activation energy of the annealing process was calculated from the slope of the graph. From the Arrhenius fit line of each sample, the activation energy was calculated to be ~0.49 eV for both samples. This activation energy could be related to some diffusion mechanism (i.e. dopant activation) occurring at relatively low temperatures (~500 °C). The atoms become mobile at this temperature (~0.3 x melting point of silicon) and therefore, during atom re-arrangement, the phosphorus atoms occupy substitutional sites and become activated [5].

B) Influence of pulse energy and pulse length over the sheet resistance

Table 4.3 summarizes the measured sheet resistances of the LCP-doped samples annealed at 610 °C for 30 min in a nitrogen-purged oven. It is observed that for a relatively similar laser fluence and pulse overlap, an increase in pulse length resulted in lower sheet resistances (refer to samples D2 & D3 and D1 & D7). Since the sheet resistance is related to the carrier mobility and active dopant concentration within the LCP-doped layers, the sheet resistance decreased for samples with higher active dopant density. For example, sample D3 showed the lowest sheet resistance due to a slightly higher peak doping concentration (above 10^{19} cm⁻³) and a deeper doping depth as compared to sample D2 [refer to Figure 4.12(a)]. The same explanation applied for the lower sheet resistance of sample D1 as compared to sample D7. Even though sample D8 was processed using the same pulse energy as sample D7, it showed a much higher sheet resistance than sample D7. It is possible that sample D8

had a much higher defect density and thus, it can be considered as an outlier in this experiment.

Table 4.3: Sheet resistance of LCP samples processed using LCP parameters from Table 4.2. The samples were annealed at 610 $^{\circ}$ C for 30 min in a nitrogen-purged oven. The error bars represent the standard deviation in the sheet resistance measurements. A longer pulse length leads to lower sheet resistances due to increased phosphorus diffusion.

| Sample number | Laser parameters | Fluence [J/cm ²] | Pulse overlap [%] | Sheet resistance measurements [kΩ/□] LCP +oven anneal at 610 °C for 30 min |
|------------------|-------------------------|---------------------------------|-------------------------|---|
| D1 | [13 µJ, 160 kHz, 60 ns] | 1.8 | 88 | 3.5 ± 0.1 |
| D2 | [11 µJ, 160 kHz, 60 ns] | 1.5 | 94 | 2.0 ± 0.2 |
| D3 | [11µJ, 220 kHz, 80 ns] | 1.5 | 96 | 0.7 |
| D4 | [11 µJ, 220 kHz, 80 ns] | 1.5 | 91 | 1.3 ± 0.1 |
| D5 | [10 µJ, 200 kHz, 70 ns] | 1.4 | 95 | 6.5 ± 3.3 |
| D6 | [10 µJ, 200 kHz, 70 ns] | 1.4 | 90 | 3.7 ± 1.4 |
| D7 | [12 µJ, 100 kHz, 40 ns] | 1.8 | 90 | 4.1 ± 0.7 |
| D8 | [13 µJ, 100 kHz, 40 ns] | 1.8 | 80 | 10.9 ± 1.5 |

4.3.2 Doping profiles (ECV and SIMS)

Electrochemical capacitance-voltage (ECV) profiling [6] was performed on the annealed LCP samples to assess the active phosphorus concentration in the LCP-doped layers. Since the phosphorus in the as-doped samples was not activated, ECV measurements could not be conducted on this batch. Instead, SIMS measurements were carried out on a few representative samples from this batch.
A) Influence of pulse energy and pulse overlap over the active doping profiles

Figure 4.9 shows the ECV profiles of the LCP-doped samples from batches B2 (LCP + oven anneal at 610 °C for 30 min) and B3 (LCP + RTP at 1000 °C for 1 min). The LCP conditions are listed in Table 4.1.



Figure 4.9: Active dopant concentration of poly-Si samples that were oven-annealed at 610 °C for 30 min and RTP-annealed at 1000 °C for 1 min after LCP. The doping depth of the samples processed with 90% pulse overlap was deeper due to a higher number of melt cycles per unit area. Higher pulse energies lead to a deeper doping depth due to longer melt lifetime and molten volume. The doping profiles of the RTP-annealed samples were closely matched to the corresponding oven-annealed samples.

From Figure 4.9, one striking feature is the flat-top doping profile implying that the dopants were uniformly distributed across the doped layers. Using the same concentration of phosphoric acid (e.g. 42.5% in our present study), the peak doping concentration was observed to be quite similar for all of the samples. Therefore, it

appears that the junction depth is tailored by varying the laser parameters (mainly pulse energy and pulse overlap). For instance, increasing the pulse energy lead to an increased amount of energy available for melting the silicon (i.e. bigger molten volume) which then resulted in a deeper doping depth (refer to samples E1, E3 and E5 or E2, E4 and E6). On the other hand, changing the pulse overlap from 80% to 90% doubled the number of pulses per unit area. Therefore, the number of melt cycles per unit area was increased which lead to a deeper doping depth (e.g. samples E1 & E2, E3 & E4 or E5 & E6). As a result, the active dopant density within the samples increases and the sheet resistance decreases.

Another interesting feature was the relative similarity between doping profiles of samples processed under the same LCP conditions but annealed differently in either an oven or a RTP. This observation showed that the dopants did not smear significantly upon annealing. Additionally, the relative similarity between the ECV profiles of those samples showed that the lower sheet resistance of the RTP samples (refer to Figure 4.6) was the result of better carrier mobility from improved defect annealing.

B) Influence of annealing conditions over the active doping profiles

In order to investigate the influence of the annealing conditions over the active doping profiles, two selected LCP samples from Table 4.1 (for e.g. S3 and E5) were subjected to ECV profiling. Figure 4.10 shows the ECV profiles of those annealed LCP-doped samples. It is observed that the pulse length may have a significant influence over the doping depth. Using a 60 ns pulse length and a fluence of 2.5 J/cm², the melt lifetime was increased significantly thereby enabling dopants to diffuse deeper inside the silicon film. Additionally, samples processed under identical

LCP conditions displayed somewhat similar doping profiles despite being annealed under different conditions. For example, the set of doping profiles represented by S3 and E5 were quite comparable.



Figure 4.10: Active dopant profiles (as determined by ECV) of two selected LCP samples (E5 and S3). The doping profiles of each LCP sample were quite similar despite being annealed under different conditions.

In order to assess the chemical concentration (i.e. both active and inactive phosphorus) of phosphorus within the LCP-doped layers, SIMS measurements were carried out on an as-doped and a RTP sample (E5 from Table 4.1). The SIMS profiling was carried out from the *n*-type LCP-doped layer up to the silicon nitride layer. The background boron concentration for each sample was also measured to determine the location of the *p*-*n* junction within each sample. The measured SIMS profiles are shown in Figure 4.11. For comparison, the ECV data of sample E5 (RTP)

are also shown (refer to the blue open triangles in Figure 4.11(b)) to compare the active dopant concentration from the ECV data to the total atomic concentration from the SIMS data.



Figure 4.11: Measured SIMS profiles of phosphorus (P) and boron (B) for sample E5 from Table 4.1 for: (a) an as-doped sample (b) a sample processed at 1000 °C for 1 min (RTP). The junction depth was measured to be about 260 nm for the as-doped and 300 nm for the RTP sample respectively. Within the LCP-processed area (the first 350 nm of the film), the as-doped and RTP profile are relatively similar. The ECV data of sample E5 subjected to RTP (see open blue triangles) is included for comparison in Figure 4.11(b).

As observed in Figure 4.11, the SIMS doping profiles of the phosphorus in the asdoped and RTP samples were relatively similar within the LCP–processed area (the first 350 nm of the film). The boron spike close to the silicon nitride/ glass side most likely originated from the borosilicate glass. From the doping profiles, the junction depth was estimated to be ~260 nm for the as-doped sample and ~ 300 nm for the RTP sample. Comparing the active phosphorus peak doping concentration from the ECV data of sample E5_P (ECV) to the SIMS data of E5_P (RTP), it is found that the peak doping levels agree to within ~70%. This is a reasonably good agreement and can be attributed to various measurement artifacts affecting the ECV measurements on poly-Si. Firstly, the non-uniform etching of the test sample by the electrolyte may be a contributing factor during ECV profiling. Secondly, diffusion, being a defect-induced process, is also highly dependent upon the material quality of the boron-doped polysilicon. Therefore, the doping levels may differ according to the defect levels within the film. Thirdly, jet or laser instability during the LCP doping process may also lead to doping variations across each doped line. The beam intensity profile within the liquid jet is not completely uniform [7] and may give rise to doping inhomogeneities despite the high pulse overlap conditions within our work. In addition, the SIMS profiling could also be affected by numerous factors such as the sputtering rate, the material quality of the poly-silicon etc.

C) Influence of pulse length over the active doping profiles

Figure 4.12(a) and (b) shows the ECV and SIMS profiles of the samples processed with LCP conditions as listed in Table 4.2. Prior to ECV, the samples were annealed in a nitrogen-purged oven at 610 °C for 30 min for dopant activation.

From Figure 4.12, it is observed that one cannot draw a straightforward comparison amongst those samples. This is because the different laser system used at Fraunhofer ISE did not allow independent setting of the repetition rate and the pulse length. Since the repetition rate affects the pulse overlap and the pulse energy simultaneously, all three parameters varied at the same time.

Nevertheless, with some assumptions, it is still possible to make qualitative comparisons amongst these samples. Firstly, comparing samples D2 and D3 processed using same pulse energy but different pulse lengths, it is found that D3 has a higher peak dopant concentration and a deeper doping depth. Since the pulse overlap was also relatively similar, it can be argued that the longer pulse length (80 ns as compared to 60 ns) lead to a deeper doping depth and higher peak doping concentration. This is because using a longer pulse length, the melt lifetime and molten volume was increased [8] allowing increased dopant diffusion. Figure 4.12(b) shows the total phosphorus concentration of as-doped samples D2 and D3. For comparison purposes, the active phosphorus concentration of sample D2, annealed at 610 °C for 30 min was also included in Figure 4.12(b).





Figure 4.12: (a) Measured active phosphorus doping concentration of poly-Si samples that were ovenannealed at 610 °C for 30 min in a nitrogen-purged oven. The LCP conditions are listed in Table 4.2 (b) measured SIMS profiles of phosphorus (P) for as-doped samples D2 and D3 from Table 4.2. The ECV profile of sample D2 annealed at 610 °C for 30 min in a nitrogen-purged oven was included for comparison purposes.

The SIMS profiles of the samples (refer to Figure 4.12(b),) looked significantly different from the SIMS profiles in Figure 4.11. The peak phosphorus doping concentration of sample D3 and D2 was found to be $\sim 10^{19}$ cm⁻³ and $\sim 10^{20}$ cm⁻³ respectively. The peak doping concentration of sample D3 was higher most likely due to an increased melt lifetime that allowed more phosphorus atoms to diffuse into the films. It is also seen that for both samples, the doping profile was rather steep within the first 150 nm of the film. However, upon annealing and dopant activation, the

doping profile levels out across the LCP-doped layer [refer to the ECV profile of sample D2_P (ECV)]. Two possibilities were considered to explain this observation:

- a) Since the melt lifetime of the LCP-doped samples (from Figure 4.12) was significantly longer as a result of the longer pulse length, the evaporation velocity was lower and thus, the shielding effect from the evaporated layer was less pronounced, resulting in more significant melt expulsion by the liquid jet. Thus a fraction of the doped layer may have been removed during the doping process. However, since the pulse energy used for processing both samples was quite low (~11 μ J) and the average surface roughness was also rather insignificant (refer to Table 4.2), this possibility appeared unlikely. Additionally, except for the peak doping concentration, the doping profiles of samples D2 and D3 appeared relatively similar despite using different pulse lengths.
- b) Another possibility could be dopant segregation effect whereby a fraction of the diffused dopants are accumulated at the surface as a result of the fast solidification velocity in the melt. This occurrence is generally characterised by a segregation coefficient (K) and is less than unity in cases of dopant segregation. Additionally, the dopant may not be incorporated substitutionally if its concentration in the solid becomes higher than the solubility limit of the process. The latter is dependent upon the segregation coefficient as well as the thermal equilibrium solubility limit [9, 10]. From Figure 4.12(b), it is possible to conclude that samples D2 and D3 displayed dopant segregation effects where a fraction of dopant atoms were accumulated at the surface.

4.4 Simulations of melt depth and melt lifetime

The melt depth is largely influenced by the absorption depth and the laser parameters such as pulse energy and pulse length. For a 532 nm wavelength, the absorption depth in silicon is about 1 μ m [11]. During interaction with a nanosecond (ns) laser pulse, the solid silicon undergoes progressive phase transition into the liquid phase and if the laser energy is high enough, another phase transition from liquid to gaseous phase (i.e. evaporation) occurs. Although the melt lifetime varies from ns to a few μ s which is longer than the laser pulse length typically used in LCP, the temperature drops rapidly to room temperature within a few microseconds. For instance, Fell *et al.* [12] showed that using a 532 nm laser, 30 ns pulse length and a fluence of 5.0 J/cm², the time taken for the silicon to reach room temperature was less than 10 μ s. Therefore it can be assumed that the laser pulses are thermally independent. As a result, the influence of the laser parameters on the melt depth and melt lifetime can be investigated by studying the interaction of a single laser pulse.

In this work, the fluence used was less than 5.0 J/cm^2 and LCP was carried out at SERIS using a pulse length ranging from 20 ns to 60 ns. Therefore, the time taken for the silicon to reach room temperature was estimated to be less than 10 µs. Hence, the assumption of the laser pulse being independent is feasible. Simulations using the software SLIM [13] were carried out to investigate the influence of different LCP conditions over the melt depth and melt lifetime. The parameters used for the simulations are listed in Table 2.1 in Chapter 2. Those parameters have been modified to reflect the LCP conditions used in this work. However, the following simulation results are only meant to study the effect of the LCP parameters qualitatively. Additionally, due to the limitations of the SLIM software, parameters such as a temperature-dependent reflectivity and absorption coefficient of liquid Si could not be accounted during the simulations. Instead a constant value was assumed and the latter was calculated at the melting temperature of silicon. Moreover the thermal conductivity (K) of liquid silicon varied across a wide range in literature, from 0.56 W/cmK to 0.84 W/cmK [14, 15]. The influence of the thermal conductivity on the melt depth and melt lifetime was quite significant in the simulations - for example using a laser fluence of 1.5 J/cm², a pulse length of 20 ns and a square-shaped pulse, increasing K from 0.56 to 0.84 W/cmK resulted in an increased melt depth from ~700 nm to ~ 880 nm. The melt lifetime was also increased from ~250 ns to ~350 ns. In this work, we assumed a lower bound of 0.56 W/cmK .

It is important to distinguish between the melt depth and the junction depth. The junction depth is equivalent to the depth at which the donor doping concentration is equal to the acceptor doping concentration (N_A) and is thus subjective to N_A . Nevertheless, at low laser energies when the melt front velocity is low, the melt depth is approximately equal to the junction depth. In contrast, at high laser energies, the melt front advances faster than the dopants and in these cases, there is a clear distinction between the melt depth and the junction depth. Also, the junction depth depends not only on the absorption depth and laser parameters but also on the number of pulses per unit area (i.e. number of melt cycles per unit area). The melt depth is generally not influenced by the number of melt cycle because the silicon is assumed to be at room temperature at the end of each melt cycle [10]. For instance, using a repetition rate of 100 kHz, the time lapse between two successive pulses is 10 μ s. Figure 4.13 displays the influence of the laser fluence over the melt depth and melt lifetime for (a) a 20 ns pulse length (b) a 60 ns pulse length. The simulations were carried out using a square-shaped pulse.



Figure 4.13: Influence of the laser fluence over the melt depth and melt lifetime for (a) a 20 ns pulse length (b) a 60 ns pulse length. The simulations were carried out using a square-shaped pulse.

From Figure 4.13(a), as the laser fluence increases, the melt depth and the melt lifetime increase which results in a deeper doping depth (e.g. refer to the ECV profiles of samples E1, E3 and E5 in Figure 4.9). Also, the melt depth profiles show that the melt depth does not change significantly when the fluence is increased. This is in reasonable agreement with the ECV profiles where increasing the fluence increases the doping depth by < 75 nm (refer to Figure 4.8). In contrast, for the 60 ns pulse regime shown in Figure 4.13(b), the melt depth and the melt lifetime is increased more significantly. Therefore, the junction depth is considerably deeper than the samples processed with a 20 ns pulse regime (for e.g. refer to samples S3 and E5 annealed at 610 °C for 30 min in Figure 4.10).

Figure 4.14 shows the influence of the laser fluence and the pulse length over

the melt depth and the melt lifetime. The solid, dashed and dotted blue curves show the effect of the pulse length over the melt depth at the same laser fluence. The simulations were carried out using a square-shaped pulse.



Figure 4.14: Influence of the laser fluence and pulse length over the melt depth and melt lifetime. The solid, dashed and dotted blue curves show the effect of the pulse length over the melt depth at the same laser fluence. The simulations were carried out using a square-shaped pulse.

From Figure 4.14, the solid, dashed and dotted blue curves show that for the same laser fluence, a longer pulse length increases the melt lifetime. Since the phosphorus diffusion (liquid phase diffusion) is dependent upon the melt lifetime, more phosphorus diffuses into the liquid silicon, which explains the higher peak doping concentration when using a longer pulse length [refer to Figure 4.12(a)]. Furthermore, Fell *et al.* [8] showed through a simulative approach that longer pulse lengths results in increased melt lifetime and molten volume. Additionally, the speckled intensity distribution of the laser is significantly homogenized as a result of improved lateral

heat conduction thus leading to more uniform dopant distribution in the doped layers. The authors also explained that increasing the pulse length lead to lower thermal stress in the LCP-doped layers.

4.5 Sheet resistance modeling

The resistivity of the poly-silicon was calculated using the method of Lu *et al.* [16]. The details and derivations of the mathematical model can be found in Ref. [16]. A similar analysis was also performed on *p*-type poly-Si solar cells by considering the peak dopant concentration and doping depth of the absorber and back surface field [17]. The resistivity is given by:

$$\rho = \rho_b \left(\frac{2W}{L}\right) + \rho_c \left(1 - \frac{2W}{L}\right) \tag{4.1}$$

where W is the depletion width in cm, L is the grain size in cm, ρ_b is the grain boundary resistivity in Ω cm and ρ_c is the intra-grain boundary resistivity in Ω cm.

For an *n*-type film, ρ_b is given by:

$$\rho_b = \frac{1}{f} \frac{1}{2Wq^2 n(0)} \sqrt{2\pi m_e^* KT} exp\left(\frac{qV_B}{KT}\right)$$
(4.2)

where

$$V_B = \frac{qNW^2}{2\varepsilon} \tag{4.3}$$

where V_B is the potential barrier height in V, N is the doping concentration in cm⁻³, q is the electronic charge in C, ε is the permittivity of silicon in Fcm⁻¹, f is a dimensionless fit parameter, n(0) is the electron concentration (cm⁻³) in quasi-neutral region, m_e^* is effective electron mass, K is Boltzmann constant in JK⁻¹ and T is absolute temperature in K.

The depletion width W is calculated by Equation (4.4):

$$W = \frac{Q_T}{2N\left[1 + 2\exp\left(\frac{e_T + qV_B - E_f}{KT}\right)\right]}$$
(4.4)

where e_T is the trapping state energy with respect to the Fermi level, E_F is the Fermi energy level and Q_T is the trap density.

The intra-grain resistivity was calculated using mobility values determined from Arora's model. The mobility was estimated as a function of doping concentration and temperature.

The sheet resistance was then obtained using Equation (4.5):

$$R_{sheet} = \frac{1}{\int_0^t \sigma \, dt} \tag{4.5}$$

where σ is the conductivity of the film in $(\Omega \text{cm})^{-1}$ calculated by taking the inverse of Equation (4.1) and *t* is the thickness of the doped layer in cm (as measured by ECV).

The mathematical model assumes a uniform grain size, a single trap level and a constant trap density for calculating the sheet resistances. In this work, it was shown that LCP generated flat-top doping profiles across the doping depth. Therefore the sheet resistance was calculated using the measured peak dopant concentration and doping depth (from the ECV data) for each sample from Figure 4.9. The average grain size was measured by electron backscattered diffraction (EBSD) to be 1.1 μ m. Additionally a trap level of ~ 0.2 eV and a trap density of 10¹² cm⁻³ were used to calculate the sheet resistances. All other parameters assumed the default value for silicon and be found in Ref. [16]. The fit parameter, *f* is a dimensionless parameter that was adjusted to have a better fit between the measured and calculated sheet resistance. It was estimated to be around 0.05. Figure 4.15 compares the calculated and measured sheet resistances of the LCP-doped samples annealed at 610 °C for 30 min (refer to Figure 4.9) in a nitrogen-purged oven (i.e. from batch B2 in Figure 4.4). The LCP conditions are listed in Table 4.1.



Figure 4.15: Calculated and measured sheet resistances of LCP-doped samples annealed in a nitrogenpurged oven at 610 C for 30 min (refer to Figure 4.9).

As seen in Figure 4.15, it is observed that a reasonably good agreement was achieved between the theoretical and measured sheet resistances except for samples E1 and E2. The discrepancy between the data can be due to several factors. Firstly, despite using a high pulse overlap and a flat pulse shape, the speckled intensity distribution of the laser results in doping inhomogeneity. Secondly, intra-grain and grain boundary defects in the poly-Si also affect carrier mobility and contribute to higher sheet resistances. Laser damage from LCP could also create more point defects that increase the sheet resistances. Thirdly, the ECV measurements are subjective to non-uniform etching of the poly-Si as well as defects in the poly-Si. Lastly, the discrepancy between the data is due to the limitations of the mathematical model which assumed a uniform grain size, a single trap level and a constant trap density for calculating the sheet resistances.

4.6 Optical characterisation

SEM micrographs of selected samples from Table 4.1 were acquired to show the influence of the LCP conditions on the overall surface quality. Figure 4.16 shows the SEM micrographs (tilted at 45°) of the as-doped samples (E5 and S1 from Table 4.1) illustrating the doped and undoped areas. The images were taken at a magnification of 550X. The scale bar is 10 µm. The inset in the pictures illustrates a magnified view of the LCP-doped region at 2500X.

a) E1 [2.0 J/cm², 80% pulse overlap, 20 ns]

b) E2 [2.0 J/cm², 90% pulse overlap, 20 ns]



c) E3 [1.7 J/cm², 80% pulse overlap, 20 ns]

Mag = 550 X 10 μm WD = 14.9 mm



e) E5 [1.5 J/cm², 80% pulse overlap, 20 ns]



f) E6 [1.5 J/cm², 90% pulse overlap, 20 ns]





i) S4 [2.5 J/cm², 80% pulse overlap, 60 ns]

g) S6 [3.5 J/cm², 80% pulse overlap, 60 ns]



Figure 4.16(a)-(j): SEM micrographs of as-doped samples at a magnification of 550X. The scale bar is 10 µm. The inset in the pictures illustrates a magnified view of the LCP-doped region at 2500X. Figure 4.16(e) and (h) show the LCP-doped and undoped region (distinguished by the dashed white line) for a 20 ns pulse length and 60 ns pulse length.

From Figure 4.16, it is evident that using a lower laser fluence (e.g. sample E5), there is less surface damage to the doped poly-silicon as compared to LCP processing with higher laser fluence (e.g. sample S1). The surface roughness of sample E5 (12 ± 11 nm) is also lower than that of sample S1 (208 \pm 44 nm) (refer to Table 4.1). The micro-structuring of the doped region is the result of the melt-regrowth process from the laser-induced interaction. At higher pulse overlap (e.g. 90% as compared to 80%), the surface damage is slightly more pronounced due to the higher number of melt cycles per unit area and the average surface roughness of the samples is also increased. Lastly, using a combination of high laser fluence and long pulse length, it

h) S1 [3.5 J/cm², 90% pulse overlap, 60 ns]

j) S3 [2.5 J/cm², 90% pulse overlap, 60 ns]

is observed that the melt expulsion by the liquid jet is more apparent as shown in Figure 4.16(g) and (h). This is because the melt lifetime was significantly increased and the melt flow became dominated by the liquid jet.

4.7 Conclusion

In this chapter, LCP was applied to *n*-type doping of poly-Si thin film on glass. The influence of the pulse energy and the pulse overlap on the sheet resistance and doping profiles of the LCP-doped samples was studied. It was found that below the ablation threshold, increasing the pulse energy and pulse overlap lead to deeper doping depth and lower sheet resistances as a result of higher dopant density. The doping profiles were characterised by a flat-top profile implying that the dopants were homogenously distributed across the doping depth. It was also found that the dopants were not activated after LCP and that a thermal anneal was necessary for dopant activation, either through a rapid or a prolonged thermal anneal in a RTP tool or a nitrogenpurged oven. Further investigation revealed that the ambient conditions were not the cause of dopant activation, as demonstrated by the relatively similar sheet resistances between batches of samples annealed with and without a barrier silicon oxide layer. It was also showed that the annealing conditions did not smear the doping profiles significantly. The annealing conditions improved the carrier mobility of the LCPdoped samples whereby annealing at a higher temperature resulted in lower sheet resistances due to improved defect anneal and carrier mobility.

The influence of pulse length suggested that using a longer pulse length, the melt lifetime and doping depth was increased. As a result, the peak doping concentration also increased accordingly. The SIMS profiles of the as-doped samples with longer pulse length (> 40 ns) showed a steep dopant profile in comparison to the

SIMS profiles of the as-doped samples processed using a shorter pulse length (e.g. 20 ns).

It was speculated that dopant segregation effect could have caused accumulation of dopants near the surface of the LCP-doped layer.

SLIM simulations were carried out using the laser parameters employed in this work to assess the influence of the laser parameter qualitatively. Increasing the pulse energy resulted in a deeper melt depth and a longer melt lifetime as predicted by the simulation results. Therefore, more dopants diffused into the film during the liquid phase. Increasing the pulse length also showed a similar finding whereby the melt lifetime was significantly increased. Hence the peak doping concentration increased. The sheet resistances of the LCP-doped samples were determined using an analytical model from literature and good agreement was showed between the measured and calculated sheet resistances considering the limitations of the model and the factors affecting the measured sheet resistances.

Overall, it was established that LCP can be successfully applied for doping poly-silicon on glass. The sheet resistances and doping profiles are tailored according to the LCP conditions during the doping process. The pulse energy and the pulse length are critical for the overall doping quality. Higher pulse energy leads to increased surface damage causing partial ablation of the poly-Si. In contrast, long pulse lengths increase the melt lifetime until significant melt expulsion by the liquid jet is observed.

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CHAPTER 5 LASER CHEMICAL PROCESSING OF *P'/P*⁺ POLY-SILICON THIN FILM ON GLASS

5.1 Introduction

This chapter describes the first reported application of LCP in fabricating an active layer for poly-Si thin film solar cells on glass. The optimized LCP conditions detailed in Chapter 4 are used to make an *n*-type emitter on a p'/p^+ poly-Si thin film on glass. In this way, a complete solar cell was formed with an *n*-type emitter (on the air side of the device), a *p*-type absorber and a *p*-type back surface field (on the glass side of the device). After dopant activation in a nitrogen-purged oven, selected samples from each batch of annealed devices were then hydrogenated in a low pressure chemical vapor deposition (LPCVD) tool with an inductively-coupled remote plasma (ICP) source to passivate the electrical defects in the poly-silicon. Those devices were subsequently assessed by sheet resistance, Suns- V_{oc} and ECV measurements before and after the hydrogenation process. The 1-Sun open-circuit voltage (hereafter called V_{oc}) and pseudo-fill factor (*pFF*) from the Suns- V_{oc} data were used to evaluate the electronic quality of the films. Lastly, the solar cell modeling software, PC1D was used to model the solar cells and to compare the theoretical and measured V_{oc} values.

5.2 Experimental details

An approximately 1.9 μ m p^{-1} 100 nm thick p^+ amorphous silicon (a-Si:H) precursor layer was deposited on a silicon nitride coated borosilicate glass via plasma-enhanced chemical vapor deposition (PECVD) [PECVD, MV Systems, USA]. The glass size was 30 cm by 40 cm by 3.3 mm. After solid phase crystallisation (SPC) at 610 °C for 10 hours in an oven [Nabertherm, model N120/65HAC, Germany] and a rapid thermal process (RTP) at 1000 °C for 1 min in a RTP tool [CVD Equipment Corporation, USA], the sample was cut down to a size of 20 cm by 20 cm for LCP. Prior to the doping experiments, the barrier PECVD silicon oxide (SiO₂) layer was removed by a 10% hydrofluoric (HF) dip. More details about the sample preparation before LCP can be found in Chapter 4. LCP doping was then carried out using a Qswitched, frequency-doubled (532 nm) Nd:YAG laser coupled inside a 42.5% phosphoric acid jet (the doping medium was pressurized at 130 bars). Figure 5.1 illustrates a schematic of the sample structure used in LCP doping (not drawn to scale).



Figure 5.1: Schematic of the sample structure used in LCP doping (not drawn to scale).

After LCP doping, the sample was thoroughly cleaned with deionized (DI) water and dried with nitrogen gas. Then, a 100 nm thick PECVD capping SiO₂ layer was deposited over the samples to prevent any contamination during dopant activation in a nitrogen-purged oven. After the thermal anneal, the SiO₂ layer was removed by a 10% HF dip. Afterwards, samples of 4 cm length and 2 cm width, enclosing the strip-like cells (active area 40 mm by 7 mm) were cut out from the main sample for subsequent characterisation. One sample from each run was kept as a control (labelled as-doped) while the remaining samples were grouped into different batches according to their annealing conditions (refer to Table 5.2). The process parameters used during LCP doping are listed in Table 5.1.

| Parameter optimisation | Sample number | Laser parameters | Fluence [J/cm ²] | Pulse overlap [%] | Average surface roughness [nm] |
|---------------------------------------|------------------|-------------------------|---------------------------------|-------------------------|---|
| Influence of pulse energy | S 1 | [14 µJ, 100 kHz, 20 ns] | 2.0 | 80 | 16 ± 4 |
| | S 2 | [12 µJ, 100 kHz, 20 ns] | 1.7 | 80 | 14 ± 2 |
| Influence of pulse-to-pulse | S3 | [14 µJ, 100 kHz, 20 ns] | 2.0 | 90 | 32 ± 11 |
| overlap (as compared to S1 and S2) | S 4 | [12 µJ, 100 kHz, 20 ns] | 1.7 | 90 | 15 ± 1 |
| Influence of pulse length | S 5 | [14 µJ, 100 kHz, 40 ns] | 2.0 | 80 | 18 ± 1 |
| | S 6 | [24 µJ, 100 kHz, 60 ns] | 3.4 | 80 | 195 ± 18 |
| Influence of repetition rate | S 8 | [16 µJ, 150 kHz, 20 ns] | 2.3 | 87 | 66 ± 12 |
| | S 9 | [12 µJ, 200 kHz, 20 ns] | 1.7 | 90 | 21 ± 10 |

Table 5.1: LCP parameters used during LCP doping (pulse shape and jet pressure were set to square-shaped and 130 bar respectively).

The sheet resistance of the LCP-doped layers was measured by a manual four point probe (Jandel Engineering Limited, Bedford, U.K.). Based on the geometrical parameters of the sample, a correction factor of 0.755 was applied to the measured sheet resistances [1]. The active dopant concentration in the samples was determined by electrochemical capacitance-voltage (ECV) measurements using a commercial system (CVP21 ECV Profiler, WEP Control, Germany). A sealant ring of 3.57 mm diameter was used during ECV profiling.

The accuracy of ECV measurements depends upon the contact area of the sample with the electrolyte. Besides the geometrical area defined by the sealant ring, the surface texture of the samples also defines the contact area between the sample and the electrolyte. Typically, for very rough surfaces such as for poly-silicon thin film solar cells fabricated on textured borosilicate glass, a surface area factor is used to account for the area enhancement because the texture size is about 1.5 μ m [2]. In this work, the samples have an average surface roughness in the order of nanometers as measured by a stylus profiler (Dektak 150 surface profiler) and therefore do not require a surface area factor. The average surface roughness of each LCP-doped sample is listed in Table 5.1. The error bars show the standard deviation in the measurements.

Suns- V_{oc} measurements were performed using a customized thin film Suns- V_{oc} tester [2]. Before the measurements, the samples were wet etched (corner etched) in a mixture of 70% nitric acid/ 49% hydrofluoric acid /deionized water in a volume ratio of 1:1:1 to reveal the buried p^+ layer for the probe contacts.

Lastly, to study any improvements in the devices, a few selected samples from each batch were manually cleaved into two and one sample from each pair was subjected to a hydrogenation process at 600 °C for 30 min in a LPCVD tool with an inductively coupled remote plasma source. The remote plasma prevented surface damage to the samples as a result of ion bombardment during the process. Before inserting the samples into the LCPVD reactor, they underwent a HF dip to remove the native oxide layer. After the hydrogenation process, the samples were again analyzed by ECV, Suns- V_{oc} and four point probe measurements.

5.3 **Results and Discussion**

5.3.1 Sheet resistance measurements

Table 5.2 summarizes the average sheet resistances of the annealed samples measured at different locations over the samples. If applicable, the error bars reflect the standard deviation in the measurements. The as-doped samples showed very high sheet resistances because the dopants were not activated. Therefore, only the sheet resistances of the annealed samples are shown in Table 5.2.

The annealed samples yielded sheet resistances around 2-5 k Ω/\Box . A sheet resistance of ~2 k Ω/\Box is practical to reduce the resistive losses in a poly-Si thin film solar cell, particularly in a metallisation scheme where the poly-Si carries current laterally. S6 was processed with high laser fluence and suffered from material damage. Thus, most of the n^+ layer was removed and the sheet resistance was much higher than that of the other samples. Comparing S1 and S5, it is observed that a slightly higher sheet resistance is obtained for the same laser fluence, similar pulse overlap and a longer pulse length. Since the sheet resistance is related to the active dopant density in the samples, the higher sheet resistance is due to the decreased amount of dopants from using a longer pulse length [refer to the active doping profiles in Fig. 5.2(c)]. Prolonged annealing at the same temperature (e.g. 610 °C for 2 hours)

resulted in a higher sheet resistance. This could be due to dopant re-distribution across

the grains and grain boundaries which then lead to an increased sheet resistance.

Table 5.2: Sheet resistance measurements performed at several locations over the LCP-doped samples. If applicable, the error bars reflect the standard deviation in the measurements. All the samples were annealed in a nitrogen-purged oven at different temperatures and durations.

| | | | | Sheet resistance measurements | | | |
|------------------|-------------------------|---------------------------------|-------------------------|--|---|---|--|
| Sample number | Laser parameters | Fluence [J/cm ²] | Pulse overlap [%] | LCP +oven anneal at 610 °C for 30 min [kΩ/□] | LCP +oven anneal at 610 °C for 2 hrs [kΩ/□] | LCP + oven anneal at 700 °C for 30 min [kΩ/□] | |
| S 1 | [14 µJ, 100 kHz, 20 ns] | 2.0 | 80 | 1.9 | 4.2 ± 0.1 | 1.8 | |
| S2 | [12 µJ, 100 kHz, 20 ns] | 1.7 | 80 | 2.1 | 3.2 ± 0.1 | 2.0 ± 0.1 | |
| S3 | [14 µJ, 100 kHz, 20 ns] | 2.0 | 90 | 2.0 ± 0.1 | 3.1 ± 0.1 | 1.9 ± 0.1 | |
| S 4 | [12 µJ, 100 kHz, 20 ns] | 1.7 | 90 | 2.1 ± 0.2 | 3.4 ± 0.2 | 1.9 | |
| S5 | [14 µJ, 100 kHz, 40 ns] | 2.0 | 80 | 2.5 ± 0.1 | 4.5 ± 0.2 | 2.9 ± 0.2 | |
| S 6 | [24 µJ, 100 kHz, 60 ns] | 3.4 | 80 | 5.0 ± 0.5 | 10.0 ± 1.1 | 7.1 ± 0.4 | |
| S 8 | [16 µJ, 150 kHz, 20 ns] | 2.3 | 87 | 2.5 ± 0.1 | 5.1 ± 0.5 | 2.7 ± 0.3 | |
| S9 | [12 µJ, 200 kHz, 20 ns] | 1.7 | 90 | 2.1 | 3.6 ± 0.4 | 2.5 ± 0.1 | |

5.3.2 Electrochemical capacitance-voltage (ECV)

measurements

The doping concentration and the doping depth of the LCP-doped emitter layer are critical for the performance of the solar cell. The peak doping concentration should be sufficiently high such that it yields a low contact resistance. However, a very heavilydoped emitter layer is detrimental to the short wavelength response (i.e. blue response) in a solar cell because the electronic quality of heavily doped layers is compromised and the diffusion length within the layer becomes relatively short. Hence, there is a trade-off between the doping concentration and the electronic quality of the doped layer. In the case of poly-Si devices made on borosilicate glass, the glass is non-absorbing in the UV range, and thus the short wavelength response can be affected by high doping levels of the emitter layer. Additionally, the doping depth of the emitter determines the location of the p-n junction in the cell. If the latter is located too far away from the side of illumination (i.e. the side where carrier generation is the highest), minority carriers which are predominantly generated close to the glass side of the solar cell are more susceptible to recombination before they are collected at the space charge region.

To assess the active dopant concentration within the samples, ECV measurements were performed on a batch of LCP samples annealed at 610 °C for 30 min. Figure 5.2(a)–(d) displays the active dopant profiles of the samples processed using the LCP parameters shown in Table 5.1. The blue symbols represent the *n*-type dopant (phosphorus) while the corresponding red symbols refer to the *p*-type dopant (boron). From Fig. 5.2(a), the active dopant concentration in the absorber layer was about 2 x 10^{17} cm⁻³ and the peak doping concentration of the *p*⁺ layer was about 2 x 10^{18} cm⁻³. The peak phosphorus doping concentration was close to 10^{19} cm⁻³.

From Figure 5.2(b), an increase in pulse energy resulted in a deeper junction depth because a higher amount of energy was available to melt more material per unit volume and thus, the melt front moved deeper into the poly-silicon [refer to samples S1 and S2 processed with a laser pulse energy of 14 μ J and 12 μ J respectively]. On the other hand, an increase in pulse overlap also lead to a deeper junction depth due to a higher number of melt cycles per unit area [refer to samples S2 and S4 processed with a pulse overlap ratio of 80% and 90% respectively]. However, an increase in pulse energy has a more significant influence over the junction depth as shown by

samples S2 & S1 and S4 & S3. Figure 5.2(c) shows how the pulse length affects the active dopant profile. Using constant pulse energy and a longer pulse length, the peak power decreases and melting is achieved at a lower energy threshold [3]. It is also possible that a pulse length of 40 ns homogenized the intensity distribution across the jet and thus, the melt lifetime was not increased significantly despite the longer pulse length. Therefore the doping depth was shallower (refer to samples S1 and S5 processed with a pulse length of 20 ns and 40 ns respectively). Even though for longer pulse lengths, melting was achieved at a lower energy, S6 was processed with a much higher fluence resulting in significant material damage. Hence, most of the n^+ layer was removed. This is also reflected in the irregular doping profile. Figure 5.2(d) illustrates the doping depth as a function of the repetition rate. In this case the repetition rate affects both the incident energy and the pulse overlap. It is shown that for the same incident laser energy, a change in pulse overlap [achieved by altering either the chuck speed (e.g. S4) or the repetition rate (e.g. S9)] affects the number of pulses per unit area and the doping depth. As discussed above, S8 has a much deeper doping depth because the pulse energy has a more prominent influence over the doping depth as compared to the pulse overlap.



Figure 5.2: (a) Active dopant profiles throughout the cell structure. The background *p*-type (red symbols) dopant concentration was about 2×10^{17} cm⁻³ and the peak phosphorus (blue symbols) doping concentration was ~ 10^{19} cm⁻³ (b) Influence of pulse energy/overlap ratio over the doping depth. (c) Influence of pulse length over the doping depth (d) Influence of repetition rate and pulse overlap over the doping depth

5.3.3 Suns-V_{oc} measurements

Suns- V_{oc} essentially measures the excess minority carrier density at the edges of the depletion region. This technique is widely used for process optimisation in both bulk crystalline and thin film PV technology [4, 5]. In general, the V_{oc} of a poly-silicon thin film solar cell is influenced by numerous factors such as the doping concentrations/profiles within the active layers, the width of the space charge region, the location of the *p*-*n* junction and the defect density within the poly-silicon (intragrain and grain boundary defects) [6]. Since minority carrier transport is dominated by diffusion under low injection conditions, the diffusion length of these carriers in the absorber layer has a significant effect on the V_{oc} of the solar cell. Considering a simple one-diode model of a *p*-*n* junction and assuming that the thickness of the absorber significantly exceeds its diffusion length such that the surface recombination at the rear of the absorber does not influence the electrical parameters of the solar cell, it is found that a short diffusion length increases the diode's dark saturation current density (J_{0abs}) as shown by Equation (5.1) [7].

$$J_{0,abs} = \frac{qn_i^2}{N_{abs}} \frac{D_{abs}}{L_{abs}}$$
(5.1)

where $J_{0,abs}$ is the dark saturation current density, q is the elementary charge, n_i is silicon's intrinsic carrier concentration, D_{abs} is the diffusion constant of the minority carriers in the absorber layer, N_{abs} is the doping concentration in the absorber layer and L_{abs} is the diffusion length in the absorber layer.

If recombination in the emitter region and at the *p*-*n* junction is neglected, the increase in the diode's dark saturation current has a major implication on the V_{oc} according to Equation (5.2) [7]:

$$V_{oc} = \frac{nKT}{q} \ln \frac{J_{sc}}{J_0}$$
(5.2)

where *T* is the absolute temperature, *n* is the ideality factor of the diode, *K* is Boltzmann constant and J_{sc} is the short-circuit current density.

Suns- V_{oc} measurements were carried out in superstrate configuration using the customised Suns- V_{oc} thin film tester i.e. light was shone from the glass side of the solar cell. The measurements were conducted by placing a sharp probe on the emitter and the back surface field of the solar cell. Since poly-Si thin film solar cells have relatively large sheet resistances (in the range of $k\Omega/\Box$) as compared to conventional bulk silicon wafer solar cells (in the range of $< 100 \ \Omega/\Box$), the contact resistance is relatively high. Such large contact resistance can cause significant measurement errors when probing non-metallised samples with pulsed illumination. This is because a resistor-capacitor (RC) element is formed as a result of the contact resistance and parasitic external capacitance. This issue was overcome by coupling a buffer amplifier with unity gain into the electrical circuit. In this way, the amplifier ideally provides infinite input impedance and low output impedance such that the measurement draws negligible current [9].

The as-doped samples showed very poor V_{oc} between 30-60 mV and *pFF* of ~31%. This is because the low fraction of active dopants from the *n*-type emitter layer gives rise to a low built-in potential at the *p*-*n* junction. Figure 5.3 shows the average V_{oc} of the annealed samples in superstrate configuration.



Figure 5.3: Average V_{oc} of the oven-annealed samples in superstrate configuration. The error bars represent the standard deviation in the V_{oc} measurements.

As compared to the as-doped samples, the annealed samples displayed a moderately high V_{oc} (~177-225 mV) and *pFF* (~48-58%) because the dopants were activated after the thermal anneal. From Figure 5.3, the samples annealed at 610 °C for 2 hours displayed the lowest V_{oc} , possibly due to dopant re-distribution across the layers that may have shifted the *p*-*n* junction slightly. Hence, the light-generated current was lower and the V_{oc} decreased accordingly. In contrast, the samples annealed for shorter durations (e.g. 610 °C for 30 min) or at higher temperature (e.g. 700 °C for 30 min) showed higher V_{oc} .

5.4 Hydrogenation

Poly-silicon is a rather defective material with a high defect density - intra-grain and grain boundary defects (e.g. dangling bonds and dislocations) and oxygen-related

defects, amongst many others [10, 11]. Hydrogen effectively passivates electricallyactive defects such as dangling bonds in poly-Si and therefore, significantly alters the electronic properties of the material. During the fabrication of poly-Si thin film solar cells on glass, the SPC (~ 600 °C) and the RTP process (1000 °C) drives most of the hydrogen out of the films. Hence, a separate process is carried out to incorporate hydrogen into the poly-Si. A common way to passivate electronic defects in poly-Si is by exposure to hydrogen plasma, commonly known as a hydrogenation process. The improvement in the devices is remarkable – for example the V_{oc} can be increased by 2-3 times and the efficiency increase of the solar cells can be up to 4-5 fold [5]. The exposure of poly-Si thin film to hydrogen plasma is already well established in the thin film transistor [12] and the photovoltaic field. The three critical process parameters during hydrogenation are the process temperature, the hydrogenation time and the hydrogen concentration. Other factors such as the film thickness and presence of diffusion barriers also contribute to the overall hydrogen distribution in the poly-Si films [2, 5]. In this work, the LCP-doped samples were hydrogenated at 600 °C for 30 min in a LPCVD reactor with an inductively coupled plasma source.

5.4.1 Sheet resistance measurements after hydrogenation

Selected samples from the as-doped and annealed batches were hydrogenated and subsequently characterized by four point probe measurements. Table 5.3 lists the average sheet resistances of the LCP-doped samples after the hydrogenation process.

As observed in Table 5.3, the sheet resistances of the hydrogenated samples were in the order of ~2 k Ω / \Box while the non-hydrogenated samples were in the range of ~3 k Ω / \Box (refer to Table 5.2). This was primarily due to defect annealing and improved carrier mobility of the samples as a result of the hydrogenation process.

Literature reports that hydrogenation improves the carrier mobility as it reduces the grain boundary trap state density in poly-Si [11]. The above sheet resistance values are practical for low resistive losses in a solar cell. Furthermore, the "LCP + hydrogenation" batch was made to study the feasibility of omitting the annealing process in between the LCP and the hydrogenation process. The data shows that a higher sheet resistance was obtained for these samples due to lower dopant activation [e.g. refer to sample S2_(as-doped)_hyd in Figure 5.4(b)].

5.4.2 ECV profiling after hydrogenation

After the hydrogenation process, ECV measurements were carried out on some samples to investigate the active doping profiles throughout the cell structure. After cleaving the cells for hydrogenation, some of those samples became too small and could not be contacted properly for ECV profiling. Therefore, they were excluded from this investigation. A few non-hydrogenated annealed samples were included in the study to compare the influence of the annealing conditions over the doping profiles. Figure 5.4 shows (a) the ECV profiles after annealing under different conditions (i.e. "LCP + anneal") (b) the ECV profiles after the hydrogenation step (i.e. "LCP + anneal + hydrogenation").

| Sample number | LCP + hydrogenation [kΩ/□] | LCP + anneal at 610 °C for 30 min + hydrogenation [kΩ/□] | LCP + anneal at 610 °C for 2 hrs + hydrogenation [kΩ/□] | LCP + anneal at 700 °C for 30 min + hydrogenation [kΩ/□] |
|---|----------------------------------|---|--|---|
| S1 [14 μJ, 100 kHz, 20 ns, 80% overlap] | 1.5 ± 0.1 | 1.1 ± 0.1 | 1.5 ± 0.1 | 1.2 |
| S2 [12 μJ, 100 kHz, 20 ns, 80% overlap] | 1.6 ± 0.1 | 1.1 | 1.5 ± 0.1 | 1.3 |
| S3 [14 μJ, 100 kHz, 20 ns, 90% overlap] | 1.6 | - | - | - |
| S4 [12 μJ, 100 kHz, 20 ns, 90% overlap] | 1.5 | - | - | - |
| S5 [14 μJ, 100 kHz, 40 ns, 80% overlap] | 1.7 ± 0.1 | - | - | - |
| S6 [24 μJ, 100 kHz, 60 ns, 80% overlap] | 2.2 ± 0.1 | - | - | - |
| S8 [16 μJ, 150 kHz, 20 ns, 87% overlap] | 1.6 ± 0.1 | 1.0 | 1.5 ± 0.1 | 1.3 |
| S9 [12 μJ, 200 kHz, 20 ns, 90% overlap] | 1.5 | 1.0 | 1.7 ± 0.1 | 1.1 |

Table 5.3: Average sheet resistances of the LCP-doped samples after hydrogenation at 600 °C for 30 min in a LPCVD tool with an inductively coupled plasma source.


Figure 5.4: ECV profiles after annealing under different conditions (i.e. "LCP + anneal") (b) ECV profiles after the hydrogenation step (i.e. "LCP + anneal + hydrogenation").

From Figure 5.4(b), the active phosphorus doping profiles in the LCP-doped layer (blue symbols) are characterized by a flat-top profile indicating that the dopants remained homogenously distributed throughout the LCP-doped layer after hydrogenation. From the ECV profiles, the junction depth of sample "S2_(610_2hr)" and "S2_(700_0.5hr)" is ~316 nm and ~344 nm respectively whereas the junction depth of sample "S2_(610_0.5hr)" is ~260 nm. Also, there seems to be no further dopant activation when the sample was annealed at 700 °C for 30 min. Thus, it can be inferred that the lower sheet resistances were due to improved carrier mobility from defect annealing.

Similarly, the ECV profiles of the hydrogenated samples did not show significant dopant activation from the hydrogenation process [refer to Figure 5.4(b)]. The ECV profile of the non-hydrogenated sample "S1_(700_0.5hr)" was included to

show the relative comparison in active doping profiles between a non-hydrogenated and a hydrogenated counterpart "S1_(700_0.5hr)_hyd". Likewise, the lower sheet resistance of sample "S1_(700_0.5hr)_hyd" as compared to sample "S1_(700_0.5hr)" was also primarily due to increased carrier mobility. Sample "S2_asdoped_hyd" had a much lower peak doping concentration due to insufficient dopant activation. It is also possible that the defects may not have been passivated properly from the hydrogenation process. This sample did not undergo any thermal treatment after the LCP process and was instead directly subjected to a hydrogenation process at 600 °C for 30 min. Despite the low peak active doping concentration in this sample, the relatively low sheet resistance of that sample (~1.6 k Ω/\Box) further supports our argument that carrier mobility was greatly enhanced from hydrogenation. Interestingly, the junction depth was located at around 500 nm and was deeper than a sample that had undergone both an intermediate oven anneal and a hydrogenation process (for e.g. sample"S2_(610_0.5hr)_hyd").

The active doping concentration of conventional poly-Si thin film solar cells on glass (i.e. baseline poly-Si thin film solar cells) is affected by smearing of the n^+ layer during the RTP process carried out at 1000 °C for 1 min and a hydrogenation process performed at a temperature of ~480 °C for about 15 min [13]. This is because the effective diffusion coefficient of phosphorus is higher than that of boron and thus, phosphorus smears more than boron. This smearing effect is detrimental to the performance of the devices because the *p*-*n* junction is shifted and the collection efficiency of the devices is reduced. Figure 5.5 shows a typical example of dopant smearing effect encountered in non-metallised poly-Si thin film solar cells on planar glass (i.e. non-textured glass) after RTP and a hydrogenation step carried out at ~480 °C for about 15 min).



Figure 5.5: Example of dopant smearing effect encountered in our non-metallised poly-Si thin film solar cells on planar glass (i.e. non-textured glass) after RTP and a hydrogenation step carried out at ~ 480 $^{\circ}$ C for about 15 min (from Ref. [13]).

As shown in the graph [*n*-type (1000 °C)], the *p*-*n* junction shifts by about ~0.5 μ m from its original location (the thickness of the *n*-type emitter was about 100 nm). In contrast, our current work demonstrates that after a hydrogenation process carried out at a higher temperature of 600 °C for 30 min, the *p*-*n* junction shifted only by ~120 nm (for e.g. refer to sample "S2_(610_0.5hr)" and sample ""S2_(610_0.5hr)_hyd" from Figure 5.4). In samples "S1_(700_0.5hr)" and "S1_(700_0.5hr)_hyd", this shift in the junction shift was even lower, around 75 nm. Moreover, we showed in our earlier work (refer to Chapter 4) that the shift in the *p*-*n* junction between an "asdoped" and a "LCP + RTP at 1000 °C" sample was only about 40 nm [14]. Therefore, it can be inferred that using a combination of RTP at 1000 °C for 1 min and a hydrogenation process at 600 °C for 30 min, the shift in the *p*-*n* junction in LCP-doped poly-Si cells is at the most 200 nm, which is lower than that in our baseline solar cells (~500 nm). This is beneficial for carrier collection and for improving the light generated current during device operation. Furthermore, the smearing of the *n*⁺ layer during the hydrogenation process can be further reduced by decreasing the

process temperature to about 450 °C. The lower dopant smearing effect in LCP-doped devices could be due to the lower mobility of the dopants as a result of the large amount of impurities found in LCP-doped films (e.g. refer to Figure 7.6 in Chapter 7).

5.4.3 Suns-V_{oc} measurements after hydrogenation

After corner etching to access the p^+ layer, Suns- V_{oc} measurements were performed on the hydrogenated samples in superstrate configuration. Figure 5.6(a) and (b) show the average measured V_{oc} and pFF from the Suns- V_{oc} data. Table 5.4 displays the measured Suns- V_{oc} parameters from the batch "LCP + hydrogenation".

From Figure 5.6, the best V_{oc} (> 400 mV) and pFF (> 65%) were achieved for the samples that were annealed at 700 °C for 30 min prior to the hydrogenation process except for S2. For comparison purposes, Figure 5.7 shows the typical V_{oc} of non-metallised poly-Si thin film solar cells on glass fabricated by the process flow described in Chapter 3. The sample structure is glass/70 nm SiN_x/100 nm n^+ Si (emitter layer)/2 µm p^- Si (absorber layer)/100 nm p^+ layer (BSF layer). As can be seen, the V_{oc} values of LCP-doped hydrogenated solar cells are relatively close to those of non-metallised poly-Si thin film solar cells fabricated on non-textured glass (i.e. planar glass) which are in the range of 435-475 mV [13].



Figure 5.6: (a) Average V_{oc} (b) average *pFF* after a hydrogenation process performed at 600 °C for 30 min in a LPCVD tool with an inductively-coupled plasma. The measurement uncertainty reflects the standard deviation in the measurements. The best V_{oc} (> 400 mV) and *pFF* (> 65%) were achieved for the samples that were annealed at 700 °C for 30 min prior to the hydrogenation process.

In some cases, the large variation in the V_{oc} could be the result of nonhomogenous doping due to laser/jet instability from the LCP process or from defects within the poly-Si. The batch of samples annealed at 610 °C for 2 hours or at 610 °C for 30 min showed slightly lower average V_{oc} and *pFF* as compared to those annealed at 700 °C for 30 min. Lastly, the samples with the lowest V_{oc} and *pFF* were those that were directly hydrogenated after the LCP process (refer to Table 5.4). This could be due to incomplete passivation of defects from the hydrogenation process and lower dopant activation.



Figure 5.7: Average measured V_{oc} of non-metallised poly-Si thin film solar cells on glass fabricated by the process described in Chapter 3. The sample structure is glass/70 nm SiN_x/100 nm n^+ Si (emitter layer)/2 µm p^- Si (absorber layer)/100 nm p^+ layer (BSF layer) [13].

Comparing the average V_{oc} and *pFF* values from Figure 5.6, it appears that for the same hydrogenation parameters, the limiting factor for a higher V_{oc} and *pFF* was the intermediate annealing step (i.e. the dopant activation step). It is likely that a high temperature process such as RTP before hydrogenation can lead to much higher V_{oc} values than the ones obtained in the current work. Prior work by Rau *et al.* [15] demonstrated that the increase in open-circuit voltages after hydrogenation depended strongly upon the RTP conditions applied to the samples. They reported that the V_{oc} increased almost linearly with the RTP plateau temperature. Furthermore, the hydrogenation conditions can also be optimized for the LCP-doped samples since

hydrogenation is dependent upon multiple process parameters such as the hydrogenation temperature and the hydrogenation time, amongst others. Similarly, other studies showed that hydrogenation can also lead to detrimental effects such as de-activation of dopants, particularly *p*-type dopants [16], platelets [17] etc. For instance, a recent study by Qiu *et al.*[11] revealed that depending upon the hydrogenation temperature, platelets can be localized at different depths within the poly-Si thin film solar cells. Such hydrogen-induced defects have localized states within the band gap and can decrease V_{oc} and *pFF* significantly. Therefore, there is still possibility of improving the V_{oc} and the *pFF* of the LCP-doped samples.

| Sample number | Parameters | <i>V_{oc}</i> [mV] | pFF [%] | |
|---------------|---|-------------------------------|----------------|--|
| S1 | [14 µJ, 100 kHz, 20 ns, 80% overlap] | 348 ± 14 | 59.0 ± 5 | |
| S2 | [12 µJ, 100 kHz, 20 ns, 80% overlap] | 364 ± 7 | 65.7 ± 2 | |
| S3 | [14 µJ, 100 kHz, 20 ns, 90% overlap] | 365 ± 8 | 65.4 ± 3 | |
| S4 | [12 μJ, 100 kHz, 20 ns, 90% overlap] | 376 ± 5 | 66.5 ± 2 | |
| S5 | [14 µJ, 100 kHz, 40 ns, 80% overlap] | 353 ± 9 | 67.5 ± 0.9 | |
| S6 | [24 µJ, 100 kHz, 60 ns, 80% overlap] | 370 ± 20 | 68.2 ± 0.1 | |
| S8 | [16 µJ, 150 kHz, 20 ns, 87% overlap] | 344 ± 12 | 63.4 ± 0.6 | |
| S9 | [12 µJ, 200 kHz, 20 ns, 90% overlap] | 369 ± 4 | 63.9 ± 1 | |

Table 5.4: Measured Suns- V_{oc} parameters from the batch "LCP + hydrogenation".

An important consideration is that LCP was applied to fabricate *n*-type emitters on poly-Si thin film solar cells on glass. Generally, poly-Si thin film solar cells on glass in superstrate configuration (i.e. light is shone from the glass supporting material) feature a *p*-*n* junction close to the glass side. In this way, once light-generated electron-hole pairs are created, they can be readily collected by the *p*-*n* junction (provided that the absorber layer has a suitable diffusion length). The minority carriers are then swept across the *p*-*n* junction where they become the majority carrier. In this work, the *p*-*n* junction was located close to the surface of the solar cells, i.e. at the air-side of the solar cells. Hence, the light-generated electron-hole pairs have to diffuse a relatively long distance before their separation by the *p*-*n* junction. As a result, the light-generated current and the V_{oc} were relatively low. Figure 5.8 shows (a) a schematic illustration (not to scale) of carrier generation and subsequent separation by the *p*-*n* junction for a LCP-doped solar cell (in this work) and (b) for a conventional poly-Si thin film solar cell on glass superstrate respectively.

However, for poly-Si thin film solar cell in superstrate, a p-n junction that is close to the glass side cannot be directly fabricated by LCP because the latter is a surface doping technique. Instead, it is possible to use LCP in the following ways:

- a) If the device architecture is intended for superstrate, then LCP can be used to fabricate an *n*-type back surface field on a $n^{-}/p^{+}/\text{SiN}_x$ on glass or a *p*-type back surface field on a $p^{-}/n^{+}/\text{SiN}_x$ on glass.
- b) LCP can be potentially applied to fabricate a seed layer on a foreign substrate followed by epitaxial growth to fabricate the subsequent active layers. In this case, the focus on the seed layer is on grain size and structural quality while the epitaxial layers target the electronic quality. Chapter 7 describes the structural quality of LCP-doped films in more details.



Figure 5.8: Schematic illustration (not to scale) of carrier generation and subsequent separation by the p-n junction for (a) a LCP-doped solar cell (in this work) (b) a conventional poly-Si thin film solar cell on glass superstrate. The n-type carriers are represented by the red spheres while the p-type carriers are denoted by the green spheres.

5.4.4 Superstrate and substrate measurements

In order to study the influence of the location of the *p*-*n* junction over the collection efficiency of the fabricated solar cells, Suns- V_{oc} measurements were carried out in both superstrate (light was shone through the glass) and substrate (light was shone from the air side of the solar cell). First, Suns- V_{oc} measurements were performed on a reference poly-silicon thin film solar cell on planar glass (i.e. non-textured glass) in both superstrate and substrate. The cell was made by the standard processes as described in Chapter 3 and featured a *p*-*n* junction located close to the glass side. This

step was performed to verify experimentally whether there was any measurable change in V_{oc} using the Suns- V_{oc} setup.

Since our customized thin film Suns- V_{oc} tester is designed for thin film solar cells in superstrate configuration, the probe contacts can only be made at the rear side of the device because the glass side of the solar cell faces the glass stage during the measurements. Therefore, a specially designed fixture was used to contact the poly-Si solar cell from the rear side and yet measure the solar cell in both superstrate and substrate. The chuck consists of two spring-loaded probes (for *n* and *p* contacts) that were held firmly to the fixture by strong magnets. These probes could be moved manually across the chuck to contact the devices. The voltage output of the assembly was then connected to the input of the buffer/gain amplifier of the thin film Suns- V_{oc} system via an electrical cable.

Before starting the measurements, the solar cell (device under test) was secured by a sliding fixture on each side of the chuck. Suns- V_{oc} measurements in superstrate were conducted as usual, i.e. by shining light through the glass supporting material. For substrate measurements, the chuck/solar cell assembly was then flipped over towards the light source without moving the contact probes. It is important that the reference solar cell of the thin film Suns- V_{oc} tester be positioned at the same level as the device under test throughout this study. This procedure ensures that both cells receive the same light intensity. Figure 5.9 depicts the customized chuck used for the Suns- V_{oc} measurements in substrate and superstrate configuration.



Figure 5.9: Customized chuck used for the Suns- V_{oc} measurements in substrate and superstrate configuration.

Table 5.5 displays the average measured V_{oc} and *pFF* of the baseline solar cell. The average V_{oc} of the reference device was about 17 mV higher in superstrate than in substrate configuration. In superstrate configuration, the light is shone through the glass onto the n^+ emitter and thus, the light-generated current is higher and the V_{oc} is also higher. Additionally, in superstrate configuration, the anti-reflective silicon nitride layer couples more photons into the device whereas in the substrate configuration, this layer is absent.

Table 5.5: Average V_{oc} of the reference planar SPC sample measured in superstrate and substrate configuration with a customized chuck. The error bars reflect the standard deviation in the measurements

| Parameter | Superstrate configuration | Substrate configuration |
|----------------------|---------------------------|-------------------------|
| V _{oc} [mV] | 413 ± 3 | 396 ± 1 |
| <i>pFF</i> [%] | 71.7 ± 0.3 | 70.8 ± 0.1 |

Suns- V_{oc} measurements were subsequently carried out on a few non-hydrogenated samples from the annealed batches in both substrate and superstrate. Figure 5.10 displays the average V_{oc} of the oven-annealed samples in superstrate and substrate configuration. The error bars represent the standard deviation in the V_{oc} measurements.



Figure 5.10: Average V_{oc} of the oven-annealed non-hydrogenated samples measured in superstrate and substrate configuration. The error bars represent the standard deviation in the V_{oc} measurements.

From Figure 5.10, the average V_{oc} measured in superstrate and substrate configuration was relatively similar. The V_{oc} was slightly higher for those samples annealed at 700 °C for 30 min, most likely due to improved defect annealing at higher temperature. Furthermore, the standard deviation in the measured V_{oc} were up to about 30 mV for the samples annealed at 610 °C for 30 min, possibly due to defects in the poly-Si films or from doping inhomogeneities. Comparing the above results with those from Figure 5.3, it is found that even though the same samples were measured in superstrate with the same system, the V_{oc} was about 20 mV lower than measured previously. We speculate that the lower V_{oc} was due to the samples being damaged from repeatedly probing the n^+ and p^+ layers. Sample S9 was too small to fit inside the customized jig and thus, was excluded from this investigation. The samples annealed at 700 °C for 30 min had the highest V_{oc} .

The customized fixture was then utilized to measure the hydrogenated samples in superstrate and substrate configuration. The active area of some samples became rather small after sample cutting and the corner etch. As a result, they could either not be held securely inside the jig or the contact probes of the fixture would shadow part of the solar cell. Hence, such samples were excluded from the investigation. Table 5.6 summarizes the Suns- V_{oc} measurements for the batch "LCP + hydrogenation" in both superstrate and substrate configuration.

The average measured V_{oc} were relatively similar in both substrate and superstrate. On the other hand, the standard deviation in the V_{oc} measurements was rather significant ranging between 5-83 mV. Since the average V_{oc} , *pFF* and the standard deviation were roughly the same in both substrate and superstrate, it was likely that the samples were damaged due to probing.

| Sample | | Superstrate | | Substrate | |
|------------|---|--------------|--------------|--------------|----------------|
| number | Parameters | V_{oc} | pFF | V_{oc} | pFF |
| number | | [mV] | [%] | [mV] | [%] |
| S1 | [14 µJ, 100 kHz, 20 ns, 80% overlap] | 298 ± 59 | 60.8 ± 6 | 297 ± 69 | 59.9 ± 5 |
| S2 | [12 μJ, 100 kHz, 20 ns, 80% overlap] | 337 ± 17 | 65.6 ± 1 | 345 ± 10 | 65.2 ± 2 |
| S3 | [14 µJ, 100 kHz, 20 ns, 90% overlap] | 339 ± 35 | 63.6 ± 0.5 | 345 ± 29 | 63.3 ± 1 |
| S 4 | [12 μJ, 100 kHz, 20 ns, 90% overlap] | 355 ± 9 | 64.5 ± 0.5 | 356 ± 5 | 64.3 ± 0.7 |
| 85 | [14 µJ, 100 kHz, 40 ns, 80% overlap] | 262 ± 26 | 64.3 ± 3 | 287 ± 31 | 65.9 ± 2 |
| S 6 | [24 μJ, 100 kHz, 60 ns, 80% overlap] | 234 ± 63 | 65.7 ± 5 | 212 ± 83 | 64.4 ± 7 |
| S 8 | [16 μJ, 150 kHz, 20 ns, 87% overlap] | 307 ± 32 | 65.4 ± 0.7 | 308 ± 20 | 65.1 ± 0.7 |
| S 9 | [12 μJ, 200 kHz, 20 ns, 90% overlap] | 326 ± 18 | 65.8 ± 0.4 | 339 ± 32 | 65.2 ± 1 |

Table 5.6: Measured Suns- V_{oc} parameters for the batch "LCP + hydrogenation". Measurements were performed in superstrate and substrate using the customized jig.

Figure 5.11 (a) and (b) show the average measured V_{oc} and pFF of the oven-annealed hydrogenated samples in superstrate and substrate configuration. The error bars represent the standard deviation in the measurements. The batch of samples annealed at 610 °C for 30 min was too small to provide any reliable measurements and were excluded from this study.

From Figure 5.10, the average measured V_{oc} were again comparable in both substrate and superstrate. The standard deviation in the measurements was also higher than measured previously due to the samples being damaged from repetitive probing. Even though the V_{oc} values were lower than measured previously in superstrate [refer to Figure 5.6(a)], the trends remained somewhat similar with the hydrogenated samples annealed at 700 °C having higher V_{oc} than those annealed at 610 °C due to improved defect annealing.



Figure 5.11: Average measured (a) V_{oc} (b) pFF of the oven-annealed hydrogenated samples in superstrate and substrate configuration. The error bars reflect the standard deviation in the measurements.

5.5 Modeling of silicon solar cells using PC1D

A simple model of a non-metallised poly-Si thin film solar cell on non-textured (i.e. planar) glass was implemented into the solar cell simulator PC1D [18] to model the V_{oc} of the devices in superstrate and substrate. Since the absorber and the back surface field have similar electrical and structural properties as the ones made from the baseline solar cells, it can be argued that V_{oc} is mainly dependent upon the doping profile, as well as the electrical and material properties of the LCP-doped regions. As most of the samples were too small for ECV measurements after being cut for hydrogenation, only a few hydrogenated samples could be measured with ECV and subsequently modelled in PC1D.

Additionally the fabricated solar cells were not metallised and quantum efficiency measurements could not be acquired on the samples. Therefore, some of the modeling parameters (e.g. recombination velocity, refractive index of the silicon nitride etc.) were taken from conventional poly-Si thin film solar cells on glass.

Auger recombination was enabled in the model such that the minority carrier lifetime was influenced by the doping concentration. In PC1D, the emitter layer is at the top of the device by default. Therefore, the measured ECV profiles of the LCPdoped samples were re-adjusted for modeling the devices in superstrate such that the p^+ layer was at the front of the solar cell. The active area of the solar cell was defined by its LCP-doped region (7 mm by 20 mm). The AM1.5G spectrum was used as the illumination source. Unless otherwise mentioned, the parameters assumed the default value provided by PC1D or that of silicon. Table 5.7 lists the main parameters used in PC1D for a LCP-doped hydrogenated poly-Si solar cell measured in superstrate.

| Parameter | Value | Unit | |
|--|-----------------------|-----------------|--|
| Device area | 1.4 | cm ² | |
| Front surface optically coated | | | |
| Upper layer thickness (taken as air) | 0 | nm | |
| Upper layer refractive index | 1 | - | |
| Middle layer thickness (glass) | 3.3 | mm | |
| Middle layer refractive index | 1.47 | - | |
| Lower layer thickness (SiN _x) | 75 | nm | |
| Lower layer refractive index | 2.05 | - | |
| Internal reflectance – enabled | | | |
| Front surface (specular) | | | |
| First bounce | 20 | % | |
| Subsequent bounce | 20 | % | |
| Rear surface (specular) | | | |
| First bounce | 20 | % | |
| Subsequent bounce | 20 | % | |
| Cell thickness | 2 | μm | |
| Bulk recombination | Fit parameter used in | ns | |
| Minority carrier lifetime $\tau_{no} = \tau_{po}$ | the simulation | | |
| Front surface | 1×10^5 | cm/s | |
| Recombination velocity $\mathbf{S}_{no} = \mathbf{S}_{po}$ | 1 x 10 | | |
| Rear surface | $1 \ge 10^{7}$ | cm/s | |
| Recombination velocity $S_{no} = S_{po}$ | | | |

Table 5.7: Main parameters used in PC1D for a LCP-doped hydrogenated poly-Si solar cell measured in superstrate.

In the first scenario, light passes through air, glass, silicon nitride and then enters the solar cell through the p^+ layer. The recombination velocity of the front surface (p^+) was set to 1 x 10⁵ cm/s due to surface passivation provided by SiN_x. Since the rear surface (n^+) was exposed to air, the rear surface recombination velocity was set to a

high value of 1 x 10^7 cm/s. This model was synonymous with the device being measured in superstrate on the thin film Suns- V_{oc} tester.

In the second scenario, the model was modified for a poly-Si thin film solar cell being measured in substrate configuration. In this case, light goes through the LCP-doped emitter layer first and then exits the solar cell by passing through SiN_x , glass and air. Hence, the front surface recombination velocity was set to 1 x 10⁷ cm/s because it was exposed to air and the rear recombination velocity was set to 1x 10⁵ cm/s.

Only the hydrogenated samples were modelled to correlate the simulated V_{oc} to the experimental V_{oc} . This is because the electrically-active defects in the nonhydrogenated samples were not passivated and would affect the V_{oc} significantly. Additionally, the defect levels could vary across the samples such that no reliable trend could be observed from simulations performed on the non-hydrogenated samples. Using the parameters from Table 5.7, the measured ECV profiles of the hydrogenated samples [from Figure 5.4(b)] and the bulk lifetime as the fit parameter, the V_{oc} was modelled in both superstrate and substrate. However, since the V_{oc} measurements performed using the customized fixture were affected by sample damage [e.g. refer to V_{oc} measurements in Figure 5.10(a)], those V_{oc} measurements were discounted from this study because they were not representative of the actual V_{oc} shown by the samples. Instead, the V_{oc} simulations were performed only for the superstrate measurements without the customized jig [refer to V_{oc} measurements in Figure 5.6(a)]. Table 5.8 summarizes the experimental and simulated V_{oc} in superstrate. The expected V_{oc} values in the substrate configuration were also calculated from the simulation model.

| | | Supe | Substrate | |
|--------------------|--------------------|-----------------------------------|---|-----------------------------------|
| Sample | Bulk lifetime [ns] | Simulated V _{oc} [mV] | Experimental V _{oc} [mV] | Simulated V _{oc} [mV] |
| S2_(610_0.5hr)_hyd | 1.2 | 424 | 423 | 434 |
| S2_asdoped_hyd | 0.7 | 367 | 364 | 384 |
| S1_(700_0.5hr)_hyd | 2.0 | 445 | 446 | 451 |

Table 5.8: Experimental and simulated V_{oc} of the hydrogenated samples measured in superstrate. The expected V_{oc} values in the substrate configuration were also calculated from the simulation model.

The above results show that the bulk lifetime was the highest for the sample annealed at 700 °C for 30 min before hydrogenation. This is also in good agreement with the earlier findings that samples annealed at 700 °C for 30 min showed the highest V_{oc} and *pFF* due to improved defect annealing.

Comparing the simulated V_{oc} in superstrate to that of the theoretical V_{oc} in substrate, the data predicts a V_{oc} increase of ~10 mV in substrate arrangement. However, it is seen from Figure 5.11(a) that the V_{oc} in superstrate and substrate arrangements were relatively similar. This is because the standard error in the V_{oc} measurements was either comparable or larger than ~10 mV such that any difference in the V_{oc} was not perceptible. As explained earlier, the lower V_{oc} and large standard deviation in the measurements was attributed to sample damage due to probing. Lastly, the addition of a SiN_x layer on top of the n^+ layer is likely to boost the V_{oc} by a further 10 mV because the SiN_x couples more photons into the solar cell as well as passivates the n^+ layer.

5.6 Conclusion

In this Chapter, the first reported application of LCP in fabricating an *n*-type emitter for poly-Si thin film solar cells on glass was described. After dopant activation in a nitrogen-purged oven under different conditions, the measured sheet resistances of the annealed samples were about 2-5 k Ω/\Box and the dopant concentration was about 8 x 10^{18} to 1 x 10^{19} cm⁻³ at a doping depth of less than 350 nm (as measured by electrochemical capacitance-voltage). Selected LCP-doped samples were then subjected to a hydrogenation process in a LPCVD reactor tool with an inductively coupled remote plasma source.

ECV measurements revealed that carrier mobility was considerably improved after the hydrogenation process which resulted in lower sheet resistances. From the ECV profiles, it was also observed that the hydrogenation process shifted the p-njunction only slightly as compared to conventional poly-Si thin film solar cells on glass. This is promising for LCP-doped poly-Si thin film solar cells as it increases the collection efficiency of the devices.

Suns- V_{oc} measurements were then carried out before and after hydrogenation. A major improvement in V_{oc} (reaching values > 400 mV) and pseudo-fill factor (*pFF* > 65%) was realized by hydrogenation. It was discussed that the annealing step was the limiting factor for a higher V_{oc} and *pFF* as demonstrated by the samples annealed at 700 °C for 30 min. The best cell had an average V_{oc} of (446 ± 7) mV and a *pFF* of (68.3 ± 0.9) %.

To study the influence of the location of the *p*-*n* junction over the collection efficiency of the fabricated solar cells, the cells were measured in substrate and superstrate using a customized fixture. It was found that the V_{oc} and the *pFF* were

relatively similar. The lower average V_{oc} and the *pFF* were attributed to sample damage from repetitively probing the n^+ and p^+ layers.

PC1D modelling was used to simulate the LCP-doped solar cells in substrate and superstrate. The bulk lifetime of the solar cells was calculated and it was found the sample annealed at 700 °C for 30 min before hydrogenation showed the highest lifetime. The simulation model also showed that the addition of a SiN_x layer on top of the n^+ layer is likely to boost the V_{oc} by a further 10 mV.

Lastly, it was discussed that the V_{oc} and the *pFF* in the current work may be further improved by using a RTP process for dopant activation and optimizing the hydrogenation conditions to yield the best V_{oc} and *pFF*. Furthermore, LCP-doped profiles are characterized by a flat-top profile which makes LCP an attractive technique for doping poly-Si thin film solar cells on glass.

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CHAPTER 6 STRUCTURAL PROPERTIES OF LCP-DOPED POLY-SILICON THIN FILMS ON GLASS

6.1 Introduction

Structural defects (e.g. disorder, dislocations, grain boundaries etc.) are detrimental to the performance of a solar cell as they affect carrier mobility and lifetime. This chapter investigates the structural properties of LCP-doped poly-silicon thin film on glass. Ultra-violet (UV) reflectance measurement and transmission electron microscopy (TEM) were utilized to assess the crystalline quality of the LCP-doped layer. The structural properties of the LCP-doped poly-silicon thin films were further studied with Raman spectroscopy. The transverse-optical (TO) phonon mode and the full width half maximum (FWHM) were used to assess the stress and defect density in the LCP-doped films respectively. The structure disorder degree, *C* was determined from the Raman data and it was found that *C* decreased after post-LCP annealing. Lastly, grain size and plastic deformation were studied by electron backscattering diffraction (EBSD). It was found that LCP did not induce any significant change in the average grain size and plastic deformation within the poly-Si.

6.2 Structural defects in poly-silicon

Poly-silicon is made up of crystallites (grains) bounded by grain boundaries. Within each crystallite, the atoms are arranged in a lattice structure that can be considered as that of single crystal silicon [1]. However, these grain boundaries are defective transitional regions between differently orientated crystallites and contain a high density of dangling bonds (e.g. 10^{12} - 10^{13} cm⁻²) [1, 2]. Also, each grain includes a significant amount of structural defects such as dislocations, impurity atoms, vacancies, interstitials etc. [3, 4].

In poly-silicon thin film solar cells, both grain boundary and intra-grain defects act as recombination sites and subsequently lower the carrier lifetime [5]. The defects at grain boundaries are decreased either by hydrogenation (passivation of dangling bonds) or by reducing the grain boundary density. Hydrogenation not only reduces the density of trap states but also decreases the effective recombination velocity at grain boundaries [2, 6]. One way of lowering the grain boundary density is through high temperature deposition/ growth processes that increase the poly-Si grain size [4]. However, despite using these techniques, physical imperfections still exist within the grains in the form of dislocations, intra-grain boundaries (such as $\Sigma 3$ grain boundaries and twins) or point defects.

Line defects exist in the form of dislocations and are grouped into edge and screw dislocations. The former is the result of extra or missing partial plane in the lattice while screw dislocation arises from fault in the atomic stacking. Another category called misfit dislocations are generated from a mismatch in lattice constant of two different materials [3]. Charged dislocations are electrically-active and affect the minority carrier lifetime of the solar cell. Literature reports that metallic impurities such as copper, nickel and iron etc. enhance the electrical activity of these dislocations [7, 8].

Area defects exist at the crystal surface and in the form of grain boundaries. If the atoms on one side of a grain boundary are a mirror image to those on the other side, the grain boundary is called a twin boundary and if no dangling bonds are formed along the boundary, it is called a stacking fault [3]. Impurity gettering of metals such as aluminium and iron can render those electrically-active. Additionally, Σ 3 grain boundaries are a class of low energy intra-grain boundaries which form readily during poly-Si crystal growth [4]. Those can also be activated by high concentrations of impurity gettering [9].

Point defects encompass a multitude of atomic defects such as vacancies, interstitials and dopant impurity atoms, amongst others. Point defects are readily formed during the solar cell fabrication process and consist of native point defects (self-vacancies and self-interstitials in silicon) as well as foreign point defects introduced by dopant impurity atoms [2, 3, 4]. During the poly-Si thin film fabrication process, the RTP step anneals the point defects in the film. In the following Section, the structural quality of the LCP-doped layers is investigated to identify the optimum LCP conditions for device fabrication.

6.3 Study of structural properties by ultra-violet reflectance and transmission electron microscopy (TEM)

In the early stages of LCP research, it was speculated that the high sheet resistance after LCP could be due to amorphous silicon (amorphisation) being formed during LCP. The cooling effect induced by the impinging liquid jet may increase the solidification velocity of the melt during LCP [10]. Since the formation of amorphous silicon is dependent upon the solidification velocity of the melt (typically above 15 m/s) [10, 11], a higher solidification velocity could introduce an amorphous silicon phase in the poly-Si. In this study, UV reflectance was used to evaluate the crystalline quality of the LCP-doped poly-Si films. More details about the assessment of crystalline quality by UV reflectance can be found in Chapter 3.

6.3.1 Experimental procedure

UV reflectance measurements were conducted on selected LCP-doped samples (asdoped and annealed under different conditions) using a Perkin Elmer UV/VIS Lambda 950 spectrometer. The LCP doped lines were carefully aligned to the beam such that the full beam was incident onto the doped area. The spectrometer was covered with a black cloth during every measurement to ensure that stray light did not influence the measurements. A float-zone (FZ) (100) boron-doped double-sided polished Si wafer was used as reference to assess the crystal quality of the LCP-doped samples. Figure 6.1 displays the UV reflectance curves of two samples processed using a 60 ns pulse length and two different laser fluences [(sample Y5 processed with a laser fluence of 3.0 J/cm² (below the ablation threshold) and sample Y1 processed with a laser fluence of 3.5 J/cm² (close to the ablation threshold)] after annealing under different conditions. In the diagram, the solid black line corresponds to the reflectance of a float zone (FZ) Si reference while the dashed black line displays the reflectance of the undoped poly-silicon. The dashed blue line is the reflectance of the as-doped sample while the other colored lines denote the respective reflectance of each sample after each thermal anneal.



Figure 6.1: UV reflectance curves of two LCP samples processed using two different pulse energies and annealed under different conditions – (a) Y5, processed below the ablation threshold. The inset in Figure 6.1(a) is a magnified view between 360-370 nm. (b) Y1, processed close to the ablation threshold. The as-doped curve (dashed blue line) of Y1 is located further away from the undoped polysilicon (dashed black line) due to an increased defect density in the sample.

From Figure 6.1, it is observed that the two crystalline peaks (around 280 nm and 365 nm) corresponding to crystalline silicon are clearly visible implying that the LCP-

doped layer was crystalline silicon. However, the as-doped curve shows that the LCPdoped layer sustained some material damage and upon annealing, the sample recovered part of its original material quality. For sample Y5, the as-doped curve was closer to that of the undoped sample implying a better crystalline quality while Y1 had a large defect density and was located further away from the undoped sample. The annealing conditions at 610 °C for 30 min appeared to be the best for the LCPdoped samples. In contrast, annealing the samples for longer time (e.g. 610 °C for 2 hours) or at higher temperatures (e.g. 700 °C for 30 min) appear to yield a poorer crystal quality. A possible explanation might be related to the appearance of a surface oxide that reduces the reflectance of the film [12]. The formation of the surface oxide is likely due to oxygen precipitation and is explained in Section 6.5.

Even though UV reflectance provides a fast and contactless assessment of the crystalline quality, the measurement is sensitive to other imperfections in the near-surface region of the sample such as the presence of a silicon oxide layer and surface roughness amongst many others [12]. Therefore, it needs to be complemented by other techniques such as TEM and X-ray diffraction (XRD).

Cross-sectional TEM (XTEM) images and selected area diffraction (SAD) patterns were acquired on two selected samples; an as-doped and a corresponding oven-annealed sample (e.g. S5 as-doped and S5 annealed at 610 °C for 30 min from Table 6.1). Both samples were processed under identical LCP conditions - 1.5 J/cm², 20 ns and 90% pulse overlap.

Figure 6.2(a) and (c) show the XTEM of the as-doped and annealed sample (S5 from Table 6.1) indicating the LCP-doped and undoped area while Figure 6.2(b) and (d) display the SAD pattern gathered at the surface of S5 (as-doped) and at the

surface of S5 (annealed at 610°C for 30 min) illustrating the crystallinity of the LCPdoped regions.



Figure 6.2: (a) XTEM of an as-doped sample (S5 from Table 6.1) showing the LCP-doped and undoped area (b) SAD pattern gathered at the surface of S5 (as-doped) showing the crystallinity of the LCP-doped region (c) Corresponding LCP sample (S5) annealed at 610 °C for 30 min illustrating the LCP-doped and undoped area (d) SAD pattern at the surface of S5 (annealed at 610°C for 30 min) illustrating the crystallinity of the LCP-doped area.

From the SAD patterns of the samples shown in Figure 6.2(b) and (d), it is clear that the poly-silicon films were fully crystalline and did not contain any amorphous material. The interface between the LCP-doped and undoped region can also be distinguished in Figure 6.2(a) and (c) by the columnar grains formed within the LCPdoped area as a result of the melt-solidification process during LCP. The depth of the LCP-processed area was about 350 nm. Additionally, the XTEM pictures show that the LCP-doped regions were of reasonable material quality.

6.4 Structural properties by Raman spectroscopy

The threshold for laser-induced damage depends on the wavelength of the laser, the laser parameters (for e.g. pulse length, pulse shape, number of pulses etc.) as well as the initial structural and surface quality of the substrate [13]. In a laser doping process, the melt lifetime is also a critical factor that determines dopant/impurity diffusion. Additionally, the solidification velocity of the melt is equally important as fast solidification velocities can generate electrically-active structural defects [3, 14]. During LCP, a long melt lifetime enables melt expulsion by the liquid jet which results in poor structural quality [10]. The high thermal gradient during LCP may also induce thermal stress in the poly-Si [15]. Studies on thin films indicate that stress leads to nucleation and propagation of dislocations as well as the formation of voids, cracks and peeling of thin films [16]. Besides mechanical damage, stress also influences carrier mobility and carrier lifetime. Fell *et al.*[15] showed through a simulative approach that depending upon the LCP conditions, high thermal gradients were generated during LCP and that the thermal stress could result in sample damage.

There exist multiple ways to study stress in thin films- for instance, XRD, wafer curvature method, XTEM and Raman microscopy, amongst others [17]. For

example, XTEM and convergent beam diffraction can evaluate stress at nanoscale but is destructive and is subjective to sample preparation. In contrast, XRD is a nondestructive technique but the beam size is larger and only average values of the stress components can be determined from the data [16, 17]. Amongst these methods, Raman spectroscopy is a quick, non-destructive technique that is capable of evaluating structural quality and localised stress as a result of its low spatial resolution [18]. There are numerous studies in literature detailing stress and defects in polysilicon thin films studied by Raman spectroscopy – some of these focus on low pressure chemical vapor deposition (LPCVD) films [19] and laser-crystallised poly-Si [20] amongst others [21]. In the following section, the structural quality of the LCPdoped layers is assessed by Raman spectroscopy and the LCP parameters are correlated to these findings to identify the optimum LCP conditions.

6.4.1 Experimental details

In this Section, the LCP-doped samples are characterized by Raman spectroscopy. The sample fabrication process is described in Chapter 4. Raman measurements were conducted in backscattering geometry on a Bruker Senterra system equipped with a 532 nm argon-ion laser and a 50X objective. The laser power was kept low (less than 10 mW) to prevent any sample heating. The sample parameters are listed in Table 6.1. A few measurements were acquired at various locations on each sample. All measurements were carried out at room temperature. Each spectrum was then fitted with a Lorentz distribution to evaluate the FWHM and the TO peak. Raman measurements were also acquired on the non-laser doped poly-Si (i.e. p^- layer) to investigate any influence of the annealing conditions on the structural quality of the sample.

Stress in poly-Si films has been well studied by Raman spectroscopy. It is related to the shift in TO peak and is given by Equation (6.1) [22, 23].

$$\sigma = -250 \left(\frac{\text{MPa}}{\text{cm}}\right) \times \Delta\omega \tag{6.1}$$

where $\Delta \omega = x_{poly} - x_{Si}$ and refers to the peak shift (in cm⁻¹) between the measured TO peak of poly-Si and that of single crystal Si (~521 cm⁻¹). It is worthy to note that the TO peak of single crystal Si is dependent upon the setup, calibration of spectrometer and measurement conditions [16]. The exact value is not critical as mentioned in Ref. [16] but rather the relative peak change between the measured sample and the reference peak. In this thesis, the peak was defined at 521 cm⁻¹. If the TO peak is shifted to lower wavenumber, it is indicative of tensile stress and vice-versa. On the other hand, the FWHM reflects the structural quality of the sample and is related to doping, structural defects etc. [24]. More details about Raman backscattering spectroscopy are described in Chapter 3.

The Raman signal corresponds to a volume defined by the diameter (2-3 μ m) and wavelength of the laser beam [16]. This interaction is dependent upon the scattered light intensity, and the depth is determined by the absorption coefficient of silicon at the laser wavelength. This depth, d_p is given by [16]:

$$d_p = \frac{2.3}{2\alpha} \tag{6.2}$$

For a 532 nm laser, this is equivalent to a penetration depth of ~1 μ m in silicon. Therefore, in this investigation, the Raman signal is the result of the interaction from the *p*⁻ layer and the *n*⁺ LCP-doped layer.

| Pulse length | Parameter optimisation | | Experiment number | Fluence [J/cm ²] | Pulse |
|--------------|--|--------------|----------------------|---------------------------------|---------|
| | | Pulse energy | | | overlap |
| | | [µJ] | | | [%] |
| 20 ns _ | Influence of laser energy (repetition rate was kept at 100 kHz and pressure was set at 130 bars) | 10.5 | E5 | 1.5 | 80 |
| | | 12 | E3 | 1.7 | 80 |
| | | 14 | E1 | 2.0 | 80 |
| | | 21 | E7 | 3.0 | 80 |
| | Influence of pulse-to-pulse overlap (as compared to S3, S2 and S1) | 10.5 | E6 | 1.5 | 90 |
| | | 12 | E4 | 1.7 | 90 |
| | | 14 | E2 | 2.0 | 90 |
| 60 ns – | Influence of laser energy | 14 | S 7 | 2.0 | 80 |
| | | 17.5 | S4 | 2.5 | 80 |
| | | 21 | S5 | 3.0 | 80 |
| | | 24.5 | S6 | 3.5 | 80 |
| | Influence of pulse overlap (as compared to S4, S5 and S6) | 17.5 | S3 | 2.5 | 90 |
| | | 21 | S2 | 3.0 | 90 |
| | | 24.5 | S 1 | 3.5 | 90 |

Table 6.1: Parameters used for LCP processing. Unless otherwise mentioned, LCP parameters were kept at a pressure of 130 bar, a square-shaped pulse and a laser repetition rate of 100 kHz.

6.4.2 Results and Discussion

A) Effect of thermal anneal on undoped poly-silicon films

Raman measurements were first conducted on two non-LCP doped (i.e. p^{-1} layer) samples to investigate the influence of the annealing conditions on the stress and the structural quality of the poly-Si before LCP. Figure 6.3(a) and (b) show the effect of the annealing conditions on the TO peak and FWHM of two such poly-Si samples (denoted as untreated). The error bars reflect the standard deviation in the

measurements. Besides sample inhomogeneities, these arise from instability of the laser and spectrometer, as well as changes in the focusing of the laser onto the sample [16].



Figure 6.3: Influence of the annealing conditions on FWHM and TO peak of two non-LCP doped poly-Si samples. The error bars reflect the standard deviation in the measurements. It is observed that annealing at higher temperature (e.g. RTP at 1000 °C for 1 min) lead to better structural quality (i.e. lower FWHM) and compressive stress (i.e. Raman peak is closer to \sim 521 cm⁻¹.

From Figure 6.3(a) and (b), the TO peak of both non-LCP doped poly-Si samples showed indications of tensile stress before any thermal treatment. This was due to thermal stress generated during the sample fabrication and caused by the mismatch in coefficient of thermal expansion (CTE) between the borosilicate glass, the silicon nitride and poly-Si layers. The thermal annealing relieved the tensile stress and improved the structural quality of the poly-Si as evidenced by the lower FWHM and the TO peak moving towards higher wavenumber. The best structural quality was achieved after a RTP anneal. In Figure 6.3(b), the untreated sample already showed a lower tensile stress and a better crystalline quality. Therefore the trend in stress relaxation and improvement in structural quality was less obvious. Nevertheless, the data shows that the best results were achieved under RTP at 1000 °C for 1 min.

b) Influence of pulse energy on the structural quality of samples processed with a 20 ns pulse length

Since it was shown earlier that the p^- layer showed only a slight indication of tensile stress before LCP processing, it can be assumed that most of the stress originated from the thermal gradient during LCP processing. Figure 6.4 shows the influence of the laser fluence on the TO peak and FWHM of as-doped samples processed with a 20 ns pulse length, a 80% and 90% pulse overlap. The error bars reflect the standard deviation in the measurements and also represent the structural inhomogeneity in the samples after LCP.



Figure 6.4: Influence of laser fluence on (a) FWHM and (b) TO peak of as-doped samples processed with 80% and 90% pulse overlap. The samples were processed with a pulse length of 20 ns, a square-shaped pulse and a repetition rate of 100 kHz. The error bars reflect the standard deviation in the measurements.

From Figure 6.4(a), it is observed that as the fluence was increased from 1.5 J/cm^2 to 3.0 J/cm^2 , the FWHM decreased progressively. It was speculated that at high laser
fluences, a major portion of the doped layer was removed by laser ablation and expulsed by the pressurized liquid jet. The remaining layer was then mostly the p^{-} poly-Si with the heat affected zone. This possibly explains the low FWHM but relatively high tensile stress (i.e. low TO peak).

Another noticeable feature is that at low laser fluence (~1.5 J/cm²), the FWHM was higher for the sample processed with 80% pulse overlap as compared to a sample processed with the same laser fluence and 90% pulse overlap. It would be expected that at 90% pulse overlap, the FWHM would be larger due to increased dopant diffusion. A possible explanation could be that at relatively low laser fluence, the laser anneals a fraction of the laser-induced defects leading to better structural quality (recall that the number of melt cycles per unit area is increased at 90% pulse overlap).

As the laser fluence was increased to $\sim 1.7 \text{ J/cm}^2$, the melt lifetime was increased as a result of the higher pulse energy, which allowed more impurities and phosphorus at a deeper doping depth. In this case, the sample processed with 90% overlap showed a higher FWHM due to enhanced dopant/impurity diffusion. This finding also correlates well with the low sheet resistances and deeper doping depth achieved under such LCP conditions. Once the laser fluence was increased beyond a certain threshold (e.g. 2.0 J/cm²), the samples with 80% and 90% pulse overlap showed relatively similar structural quality.

From Figure 6.4(b), the TO peaks were shifted towards lower wavenumber (~517/518 cm⁻¹) as compared to ~520 cm⁻¹ for the untreated sample. This indicates the presence of tensile stress in the samples after LCP, most likely from the high thermal gradient during LCP. It is seen that, for samples processed with a 90% pulse overlap, increasing the laser fluence up to 2.0 J/cm² resulted in a TO peak that was less shifted,

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indicating that tensile stress decreased. A possible explanation could be that the increased number of melt cycles per unit area reduced the thermal stress in the poly-Si. At a laser fluence of 2.0 J/cm², the thermal stress was relatively similar for both samples most likely because the thermal gradient during LCP under those conditions was relatively similar. At high laser fluence (e.g. 3.0 J/cm²), the poly-Si showed relatively high tensile stress due to laser ablation and material expulsion by the liquid jet.

c) Influence of pressure and pulse length on the structural quality

In Chapter 2, it was discussed that the silicon melt is removed by the liquid jet if the melt lifetime exceeds a characteristic melt expulsion time. The latter is dependent upon the hydrodynamics of the liquid jet and is inversely proportional to the velocity of the liquid jet [15]. Therefore, the higher the jet velocity, the shorter is the characteristic melt expulsion time. The jet velocity is determined by the output pressure from the pump. On the other hand, the melt lifetime is dependent upon the LCP conditions for e.g. pulse energy and pulse length. Table 6.2 summarizes the measured TO and FWHM of selected as-doped poly-Si samples processed with different jet pressure and pulse length. The error bar represents the standard deviation in the measurements.

From Table 6.2, the average FWHM of samples E14 & E15 and that of samples E13 & E7 are almost similar for both laser fluences. Therefore the liquid jet pressure had a minor influence on the structural quality of the samples processed under these conditions. The TO peaks were also relatively similar at a laser fluence of 2.0 J/cm², most likely because there was no significant melt flow under those process

conditions. As explained in Chapter 2, a thin vapor layer exists above the silicon melt and acts as a thermal insulating layer against the liquid jet. In contrast, at higher laser fluence (e.g. 3.0 J/cm^2), the TO peak showed less stress for the sample processed with 130 bar. A possible explanation is that at low characteristic melt expulsion time (due to high jet pressure of 130 bar) and high laser fluence (e.g. 3.0 J/cm^2), melt expulsion by the liquid jet is increased significantly. Therefore, a larger fraction of the LCPdoped layer was removed and the Raman interaction resulted mostly from the *p*-type poly-Si layer.

An increase in pulse length lead to a higher FWHM (refer to samples E1 & S7). This is because a longer pulse length increased the melt lifetime and enhanced dopant diffusion in the poly-Si. On the other hand, the TO peak showed less tensile stress in the poly-Si. This is because a longer pulse length homogenized the temperature distribution within the melt and decreased the temperature gradient across the film. Hence, the thermal stress was lower in the LCP-doped layer [15].

d) Influence of pulse energy/pulse overlap on the structural quality of samples processed with a 60 ns pulse length

Figure 6.5 shows the influence of the laser fluence on the TO peak and FWHM of the as-doped samples processed with a 60 ns pulse length, for 80% and 90% pulse overlap respectively. The error bars reflect the standard deviation in the measurements.

| Parameter optimisation | Sample | Pulse energy [µJ] | Laser fluence [J/cm ²] | Pulse length [ns] | Jet pressure [bar] | TO peak [cm ⁻¹] | FWHM [cm ⁻¹] |
|---------------------------|------------|-------------------------|--|-------------------------|--------------------------|--------------------------------|-----------------------------|
| Influence of pressure | E14 | 14 | 2.0 | 20 | 60 | 518.3 ± 0.4 | 7.4 ± 0.6 |
| | E15 | 14 | 2.0 | 20 | 130 | $518.5\pm\!0.3$ | 7.3 ± 0.4 |
| | E13 | 21 | 3.0 | 20 | 60 | 517.4 ±0.6 | 6.3 ± 0.3 |
| | E7 | 21 | 3.0 | 20 | 130 | $518.2\pm\!0.5$ | 6.4 ± 0.3 |
| Influence of pulse length | E1 | 14 | 2.0 | 20 | 130 | 517.9 ±0.5 | 6.8 ± 0.4 |
| | S 7 | 14 | 2.0 | 60 | 130 | 518.7 ±0.4 | 7.1 ± 0.3 |

Table 6.2: LCP parameters used in this work. LCP parameters were kept at a pulse overlap of 80%, a repetition rate of 100 kHz and square-shaped pulse.



Figure 6.5: Influence of laser fluence on (a) FWHM and (b) TO peak of as-doped samples processed with 80% and 90% pulse overlap. The samples were processed with a pulse length of 60 ns, a square-shaped pulse and a repetition rate of 100 kHz. The error bars reflect the standard deviation in the measurements.

From Figure 6.5(a), the trend shows that the FWHM decreases with an increase in laser fluence using a 60 ns pulse regime. Using high laser fluences in conjunction with a 60 ns pulse length, the melt lifetime was significantly increased as compared to conditions under a 20 ns pulse regime. Hence, there was enhanced dopant/impurity diffusion inside the poly-Si resulting in a higher FWHM [for e.g. compare the sample processed with a laser fluence of 2.0 J/cm² and 80% pulse overlap in Figure 6.4(a) to the sample processed under similar laser fluence and pulse overlap in Figure 6.5(a)]. As the laser fluence increased, the melt lifetime became progressively longer and melt expulsion by the liquid jet removed the LCP-doped layer. Additionally, above a laser fluence of 2.5 J/cm², the defect density in the film was quite high and thus, the increased number of pulses per unit area (i.e. using a 90% pulse overlap) did not contribute significantly in annealing laser-induced defects, which explains the relative similarity between the FWHM of samples processed with 80% and 90% pulse overlap. At increasing laser fluence (e.g. > 3.5 J/cm²), most of the LCP-doped layer was ablated and the FWHM showed large standard deviation in the measurements.

From Figure 6.5(b), the frequency of the TO peaks decreases with an increase in laser fluence implying that thermal stress became more significant in the poly-Si. Additionally, the samples processed with 80% and 90% pulse overlap showed relatively similar TO peaks as compared to samples processed with 20 ns pulse length. This is because as the fluence was increased, the increasing melt lifetime allowed more melt expulsion by the liquid jet.

e) Influence of post-LCP annealing conditions on the structural quality of the LCP-doped samples

Earlier, it was established that post-LCP annealing activates the dopants in the LCPdoped poly-Si. Annealing the samples at high temperatures yields lower sheet resistances due to improved carrier mobility. In this Section, the effect of the post-LCP annealing conditions on the structural quality and tensile stress in the LCP-doped layers is investigated. Figure 6.6(a)-(d) displays the trend in TO peak and FWHM of two selected samples – sample E5 processed with a laser fluence of 1.5 J/cm^2 , a 20 ns pulse length and 80% pulse overlap and sample S3 processed with a laser fluence of 2.5 J/cm^2 , a 60 ns pulse length and 90% pulse overlap. The as-doped sample refers to the control LCP-doped sample that had not undergone any thermal anneal. The error bars represent the standard deviation in the measurements.

From Figure 6.6(a) and (b), it is evident that for both samples, post-LCP annealing had a considerable effect over the TO peak and FWHM. Upon annealing at higher temperature, the TO peak became progressively closer to ~521 cm⁻¹, i.e. the TO peak of single crystal silicon indicating that the tensile stress in the poly-Si was almost relieved. In the same way, the FWHM decreased significantly upon annealing at higher temperature. Interestingly, annealing at 450 °C for 2 hours and at 610 °C for 30 min yielded relatively similar structural quality but the films showed different levels of stress as seen from Figure 6.6(a) and (b).



Figure 6.6: Influence of thermal anneal on (a) TO peak and (b) FWHM of a LCP-doped sample processed with a laser fluence of 1.5 J/cm^2 , 80% pulse overlap and 20 ns pulse length (c) TO peak and (d) FWHM of a LCP-doped sample processed with a laser fluence of 2.5 J/cm^2 , 90% pulse overlap and 60 ns pulse length. The error bars represent the standard deviation in the measurements.

A possible reason was attributed to the formation of thermal donors or nonelectrically active precipitates [25-26]. The latter are identifiable by means of transmission electron microscopy (TEM) or high resolution TEM whereas the thermal donors can only be revealed by electrical measurements [25]. For example, Cazcarra *et al.* [26] investigated the curing and generation of oxygen thermal donors over a range of annealing temperatures. More details about this study are described in Chapter 7. From Ref. [26], it appears that annealing at a temperature of about 610 °C annihilated existing thermal donors in the poly-Si but also generated new thermal donors upon further thermal treatment. This hypothesis may also explain the rise in the FWHM upon annealing the poly-Si under the same temperature for 2 hours [refer to Figure 6.6(d)] whereby new oxygen donors were generated in the poly-Si. Another consideration is that the high carbon content in the film ($\sim 10^{20}$ cm⁻³) could have accelerated the donor annihilation process at a low temperature of about 450 °C. Literature mentions that below 950 °C, high carbon content precipitates oxygen in the form of C-O complexes [27]. More details about the oxygen donor generation and annihilation can be found in Chapter 7.

A similar trend was observed for the sample processed with 60 ns pulse length. An increase in annealing temperature and duration leads to improved stress relaxation and better structural quality. From Figure 6.6(c), the TO peak of the sample annealed at 700 °C for 30 min indicated slightly more tensile stress than the sample annealed at 610 °C for 2 hours. The reason was attributed to the generation of new oxygen donors within this temperature range that were harder to anneal and required much higher temperature (e.g. 1000 °C) for complete annihilation [26]. In both Figure 6.6(b) and (d), the best structural quality is obtained under RTP conditions - most likely because the donors are completely annihilated at this temperature [26].

6.5 Study of structure disorder in LCP-doped samples

Recently, Wang *et al.*[24] assessed the structure disorder in LPCVD poly-Si film by a figure of merit, *C*, known as the structure disorder degree. The latter was derived from the anharmonic vibrational potential energy in disordered structures as in Equation (6.3):

$$V(x) = dx^2 - gx^3 - fx^4$$
(6.3)

where d, g and f are positive terms. The cubic and quadratic terms refer to the asymmetry of the mutual repulsion of the atoms and the softening of the vibration at

large amplitudes respectively. The structure disorder is an inherent property of a material and is the ratio of f and g. C is given by Equation (6.4). The derivations can be found in Ref. [24]:

$$C = \frac{\Delta\omega}{\Gamma^2} \tag{6.4}$$

where $\Delta \omega$ is the peak shift between the measured TO peak and that of single crystal silicon taken as 521 cm⁻¹ and Γ is the FWHM of the TO peak.

In this study, the influence of the post-LCP anneal conditions on the structure disorder, C in the LCP-doped samples was studied in an attempt to understand the bond re-arrangement occurring during the thermal treatment. C was averaged over five measurements taken across different locations over the samples. Figure 6.7(a) and (b) show the influence of the annealing conditions on the structure disorder degree of some selected samples. The LCP conditions are listed in Table 6.1.

From Figure 6.7(a), the LCP-doped samples, except for sample S5 show a decreasing structure disorder upon annealing until they reach their lowest value (almost zero) under RTP conditions. It is also observed that the low temperature anneal (e.g. 450 °C for 2 hours) can significantly reduce *C*. As explained earlier, it is possible that the high carbon content in the film precipitated oxygen in the form of C-O complexes. As for sample S5 at 610 °C for 30 min, it is possible that the higher concentration of oxygen in the film (the increased melt lifetime under those LCP conditions result in enhanced impurity diffusion) created more oxygen thermal donors and therefore, the structure disorder increased. Literature reports that the depending upon the range of temperature, the oxygen donor generation process is also dependent upon the oxygen concentration in the film [25]. Upon annealing at RTP conditions, the thermal donors are almost completely annihilated.



Figure 6.7: Influence of post-LCP annealing conditions on the structure disorder degree of selected samples processed using a (a) 20 ns pulse length (b) 60 ns pulse length. The LCP conditions are listed in Table 6.1. The error bars reflect the standard deviation in the measurements. The lines are guides to the eye.

The trend in Figure 6.7(b) is slightly different than that in Figure 6.7(a). The structure disorder decreases upon annealing. Within the temperature range of 600 °C–825 °C, new oxygen thermal donors are created that are thermally more stable. At RTP conditions, the structure disorder again falls back to a very low value (almost zero).

Overall, it appears that the change in structure disorder upon annealing is related to bond re-arrangement. Thus, it is likely that the generation and annihilation of oxygen thermal donors is responsible for the structure disorder. Additionally, high impurity content such as carbon and nitrogen are likely to influence the kinetics of the oxygen donor generation/annihilation process.

6.6 Electron backscattered diffraction (EBSD)

The grain size may have a direct influence upon the open-circuit voltage (V_{oc}) of polysilicon thin film solar cells. For example, bigger grain sizes could lead to the V_{oc} being limited mostly by intra-grain defects. It is reported that the V_{oc} of poly-Si solar cells is also dependent upon intra-grain defects and dislocations in the solar cells [29]. In this Section, EBSD is used to assess the grain size of LCP-doped films after LCP. Dislocations can be further grouped into statistically stored dislocations (SSDs) and geometrically necessary dislocations (GNDs). SSDs are typically formed during crystal growth and are not associated with lattice curvature [4]. On the other hand, GNDs are related to lattice curvature. GNDs are formed when atoms become mobile at temperatures (> 0.3 times the melting temperature of silicon) and they rearrange into arrays forming a low angle grain boundary (LAGB) [28]. Typically, the misorientation between two regions of crystals across a LAGB is ~5°. These small lattice rotations represent lattice curvature and can be detected by electron backscattered diffraction (EBSD).

From EBSD measurements, the grains within the sample (e.g. poly-Si) are detected and indexed by the EBSD system based on their diffraction pattern. Once the grain distribution map is obtained, an orientation matrix is generated for every pixel in the map. Based on this map, the misorientation angle between two pixels can be calculated and used to generate the misorientation maps.

In this work, the grain average misorientation (GAM), texture and grain size of selected samples were quantified by electron backscattered diffraction (EBSD) measurements performed using a Quantax EBSD CrystAlign (Bruker, Germany). A large majority of samples suffered from drifting effect under SEM and therefore the EBSD measurements were non-conclusive. GAM measures the accumulated orientation changes relative to the average orientation within the grain and therefore is a reasonable representation of plastic deformation within a material. GAM maps were studied to identify the misorientation gradients within the LCP-doped layers. A colour map from blue (0°) to red (3°) was used to measure the misorientation between the reference pixel and every other pixel for a grain. Table 6.3 shows the average measured grain sizes of two selected as-doped samples, sample S3 processed with a 60 ns pulse length and sample E5 processed with 20 ns pulse length. To study the influence of the thermal anneal on the grain size and GAM, sample S3 annealed at 610 °C for 30 min and 610 °C for 2 hours are included.

Table 6.3: Average measured grain sizes of two as-doped samples, sample S3 processed with a 60 ns pulse length and sample E5 processed with 20 ns pulse length. Sample S3 annealed at 610 $^{\circ}$ C for 30 min and 610 $^{\circ}$ C for 2 hours are also included to study the effect of the thermal anneal on the grain size.





As shown in Table 6.3, the average grain size of the as-doped and annealed samples were relatively similar and the grains were randomly oriented. Therefore the LCP conditions used in our work did not influence the average grain size significantly. In comparison, the grain size of poly-Si fabricated by the solid phase crystallisation (SPC) process is also about 1 μ m.

From Table 6.3, the grain misorientation maps (GAM) show a misorientation angle of less than $1.0^{\circ}-1.5^{\circ}$. Since the misorientation noise in the measurement is about 1° [4], it can be concluded that the LCP-doped poly-Si showed little or no plastic deformation. This is also in good agreement with the work by Law *et al.*[28]

who reported that little or no plastic deformation was found in poly-silicon with grain sizes $< 3 \mu m$. The authors claimed that the dislocations were mostly SSDs.

6.7 Conclusion

The electrical activity of structural defects is linked to the performance of solar cells. Microstructural defects (e.g. dislocations, grain boundaries etc.) affect carrier mobility and lifetime. Therefore a detailed investigation of the structural quality is essential to assess the defect density in the solar cells. In this Chapter, the crystalline quality of LCP-doped poly-Si films was first evaluated by ultra-violet reflectance and crosssectional transmission electron microscopy (XTEM). It was found that the LCP-doped layers did not contain any amorphous material and possessed satisfactory structural quality.

A more in-depth structural investigation was carried out by Raman spectroscopy. It was found that depending upon the pulse regime, increasing the laser fluence improved dopant and impurity diffusion up to the ablation threshold. The results were in good agreement with the sheet resistance and electrochemical capacitance-voltage measurements. Enhanced impurity diffusion also increased the tensile stress in the film. Annealing the LCP-doped samples relieved the tensile stress and lowered the FWHM whereby the structural properties of the poly-Si improved upon annealing at high temperature and longer duration. The best structural properties were obtained for samples that were subjected to a RTP at 1000 °C for 1 min.

A more detailed study of the structure disorder degree, C revealed that bond re-arrangement occurred during annealing. It was hypothesized that oxygen thermal donors was responsible for the change in tensile stress and structural quality. Depending upon the impurity content and the thermal treatment imparted to the samples, the oxygen donors were either partially cured or completely annihilated. In contrast, prolonged annealing at the same temperature generated new oxygen donors.

Lastly, the grain size, texture and plastic deformation in the LCP-doped samples were studied by electron backscattering diffraction. The average grain size was comparable to that of non-LCP doped poly-silicon made by the solid phase crystallisation approach. The plastic deformation in the LCP-doped poly-Si was below the detection limit and therefore it was argued that LCP did not introduce appreciable plastic deformation in the poly-Si. This finding was also in agreement with earlier reported work about plastic deformation in poly-Si of grain sizes (< 3 μ m).

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CHAPTER 7 ELECTRICALLY-ACTIVE DEFECTS IN LCP-DOPED POLY-SILICON THIN FILMS ON GLASS

7.1 Introduction

Electrical and structural defects limit the performance of solar cells. They act as recombination sites and decrease the minority carrier lifetime. In this Chapter, laser-induced defects that limit the performance of LCP-doped solar cells are discussed. The effective ideality factor (n_{eff}) is introduced as a critical parameter for assessing the overall device quality of a poly-silicon thin film solar cell. From the n_{eff} , it is shown that the dominant recombination behavior in LCP-doped hydrogenated solar cells was confined within grain boundaries or the space-charge region. Further investigation by Raman spectroscopy revealed that electrically-active (Si-H₂)_n defects were introduced in the LCP-doped samples as a result of excessive hydrogenation. It is speculated that oxygen precipitation during thermal annealing is also responsible for the improvement in structural and device quality of the films.

7.2 Effective ideality factor

Several methods have been reported for fitting the ideality factor of poly-Si thin film diodes on glass [1, 4]. For instance, by fitting the light intensity against V_{oc} , Terry *et al.*[3] determined the 1-Sun V_{oc} across each diode as well as R_{sh} . Other techniques can

be found in literature [4]. Another way is to calculate an effective ideality factor which is determined from the slope of the Suns- V_{oc} curve. Basically, it is the ideality factor of a single diode that allows the best fit for the Suns- V_{oc} data [2]. Thus, a solar cell with an ideality factor close to 1 is dominated by recombination in the quasineutral bulk regions and at the surfaces whereas an ideality factor close to 2 reflects recombination within the space charge region or at grain boundaries. The effective ideality factor (n_{eff}) is calculated by [5, 6] as in Equation (7.3):

$$n_{eff} = \frac{V_{oc}(\text{MPP}) - V_{oc} (1 \text{ Sun})}{V_T \times \ln(\text{Suns}(\text{MPP}))}$$
(7.3)

where V_{oc} (MPP) and V_{oc} (1 Sun) denote the open-circuit voltage at maximum power point (MPP) and at 1 Sun respectively, V_T is the thermal voltage (0.0257 V at 25 °C) and *Suns*(MPP) is the illumination intensity in Suns at MPP of the pseudo-I-V curve.

7.3 Effective ideality factor of hydrogenated LCPdoped samples

In this Section, the effective ideality factor (n_{eff}) of the hydrogenated LCP-doped samples was extracted from the Suns- V_{oc} data. The n_{eff} was derived from the Suns- V_{oc} measurements conducted in superstrate. Figure 7.1 shows the extracted n_{eff} and the average measured V_{oc} of the LCP-doped samples after a hydrogenation process at 600 °C for 30 min in a low pressure chemical vapour deposition (LPCVD) tool with an inductively-coupled remote plasma. The LCP conditions are listed in Table 7.1. For comparison purposes, the open-circuit voltages (V_{oc}) of those cells are also included.



(a)



Figure 7.1: (a) Extracted n_{eff} (b) average V_{oc} of the samples after a hydrogenation process at 600 °C for 30 min in a LPCVD tool with an inductively-coupled remote plasma. The measurement uncertainty reflects the standard deviation in the measurements. The best V_{oc} (> 400 mV) and pFF (> 65%) were achieved for the samples that were annealed at 700 °C for 30 min prior to the hydrogenation process.

From Figure 7.1, the best V_{oc} (> 400 mV) were achieved for the samples that were annealed at 700 °C for 30 min prior to the hydrogenation process. It is observed that the effective ideality factor of the LCP-doped samples was close to 2, implying that the dominant recombination behaviour resulted from either the space-charge region or at grain boundaries. In contrast, the Suns- V_{oc} parameters of a reference hydrogenated poly-silicon thin film solar cell on glass (from Table 5.5 in Chapter 5) showed a V_{oc} and a n_{eff} of 413 mV and 1.4 respectively. The Suns- V_{oc} measurements of the reference solar cell were also conducted in superstrate.

To gain more insight into the recombination behaviour of those cells after LCP, the effective ideality factor was compared before and after the hydrogenation process. The n_{eff} were only compared for the measurements conducted in superstrate configuration. The n_{eff} of the as-doped samples could not be extracted before the hydrogenation process because Suns- V_{oc} measurements could not be conducted on the samples as a result of the non-activated dopants. Figure 7.2 shows the effective ideality factor of the hydrogenated and non-hydrogenated solar cells after LCP.

As seen in Figure 7.2, there is an increase in the effective ideality factor of most hydrogenated samples (in particular for the samples annealed at 610 °C for 2 hours and 700 °C for 30 min) as compared to before hydrogenation. It was expected that the n_{eff} would decrease upon hydrogenation due to passivation of grain boundary defects such as dangling bonds etc. Instead, the results suggest that relatively high ideality factor could arise from hydrogenation-induced defects. Sample S1 from the as-doped hydrogenated batch showed a much higher effective ideality factor and lower *pFF* (refer to Table 7.1). This could be due to processing inhomogeneities during LCP and hence, it was treated as an outlier in this experiment.



Figure 7.2: Effective ideality factor of the hydrogenated and non-hydrogenated solar cells after LCP. The effective ideality factor of the non-hydrogenated as-doped samples was not included because the dopants were not activated.

The effective ideality factor of a complete batch of hydrogenated as-doped (i.e. LCP + hydrogenation) samples was subsequently investigated to study the effect of the LCP conditions on the device performance. Table 7.1 summarizes the measured and extracted Suns- V_{oc} parameters from the batch "LCP + hydrogenation".

From Table 7.1, sample S5 has a lower effective ideality factor (~1.4) as compared to sample S1 and S3 processed with the same laser fluence. The n_{eff} of sample S5 is comparable to the reference hydrogenated poly-Si thin film solar cell (~1.3). A possible reason could be that for the same laser fluence, the longer pulse length used for sample S5 homogenized the temperature distribution within the melt and decreased the temperature gradient across the film. Hence, the thermal stress was lower in the LCP-doped layer. Additionally the dopant distribution inside the film was also more uniform. Even though S6 displayed a similar effective ideality factor, the high fluence during the LCP process introduced significant material damage to the cell.

| Sample number | Voc | pFF | n_{eff} |
|-----------------------------|--------------|--------------|---------------|
| Sumple number | [mV] | [%] | -37 |
| S1 | | | |
| [14 µJ, 100 kHz, 20 ns, 80% | 348 ± 14 | 59 ± 5 | 2.1 ± 0.4 |
| overlap] | | | |
| S2 | | | |
| [12 µJ, 100 kHz, 20 ns, 80% | 364 ± 7 | 65.7 ± 2 | 1.6 ± 0.2 |
| overlap] | | | |
| S3 | | | |
| [14 µJ, 100 kHz, 20 ns, 90% | 365 ± 8 | 65.4 ± 3 | 1.6 ± 0.2 |
| overlap] | | | |
| S4 | | | |
| [12 µJ, 100 kHz, 20 ns, 90% | 376 ± 5 | 66.5 ± 2 | 1.6 ± 0.2 |
| overlap] | | | |
| \$5 | | | |
| [14 µJ, 100 kHz, 40 ns, 80% | 353 ± 9 | 67.5 ± 0.9 | 1.4 ± 0.1 |
| overlap] | | | |
| S 6 | | | |
| [24 µJ, 100 kHz, 60 ns, 80% | 370 ± 20 | 68.2 ± 0.1 | 1.5 ± 0.1 |
| overlap] | | | |
| S8 | | | |
| [16 µJ, 150 kHz, 20 ns, 87% | 344 ± 12 | 63.4 ± 0.6 | 1.7 ± 0.1 |
| overlap] | | | |
| S 9 | | | |
| [12 µJ, 200 kHz, 20 ns, 90% | 369 ± 4 | 63.9 ± 1 | 1.7 ± 0.1 |
| overlap] | | | |
| | | | |

Table 7.1: Measured and extracted Suns- V_{oc} parameters from the batch "LCP + hydrogenation". The measurement uncertainty reflects the standard deviation in the measurements.

The increase in n_{eff} after hydrogenation suggests that hydrogenation may have generated electrical and structural defects in the poly-Si. Studies have shown that hydrogenation can also lead to detrimental effects such as de-activation of dopants, particularly *p*-type dopants [7], platelets [8] etc. For instance, a recent study by Qiu *et al.* [9] revealed that depending upon the hydrogenation temperature, platelets can be localized at different depths within the poly-Si thin film solar cells. Such hydrogeninduced defects have localized states within the band gap and can decrease V_{oc} and *pFF* significantly.

7.4 Investigation of the structural properties of LCPdoped solar cells

In order to assess the structural quality of the samples after hydrogenation, Raman backscattering spectroscopy was conducted on the samples. The critical parameters for assessing the structural quality are the transverse-optical (TO) phonon peak and full width half maximum (FWHM). More details about Raman spectroscopy can be found in Chapter 3 and 6.

7.4.1 Experimental procedure

Raman measurements (Renishaw inVia) were conducted in backscattering geometry using an argon-ion laser of wavelength 514 nm. The laser power incident on the samples was less than 10 mW to prevent any sample heating. Several measurements were taken across the samples and were performed at room temperature. The spectral range was between 400 cm⁻¹ to 600 cm⁻¹. The Raman spectrum was fitted with a

Lorentz distribution to determine the TO peak and the full width half maximum (FWHM).

7.4.2 Results and Discussion

Table 7.2 summarizes the average measured TO peak and FWHM of the hydrogenated samples. The error bars reflect the standard deviation in the measurements.

Table 7.2: Average TO peak and FWHM of the hydrogenated samples. The error bars reflect the standard deviation in the measurements.

| Sample number | Parameter | LCP + hydrogenation | LCP + oven anneal at 610 °C for 30 min+ hydrogenation | LCP + oven anneal at 610 °C for 2 hrs + hydrogenation | LCP + oven anneal at 700 °C for 30 min + hydrogenation |
|------------------|-----------|------------------------|---|--|--|
| S1 | TO peak | 520 ± 0.3 | 520 ± 0.3 | 520 ± 0.3 | 520 ± 0.1 |
| | FWHM | 5.8 ± 0.2 | 6.1 ± 0.2 | 6.1 ± 0.2 | 6.2 ±0.1 |
| S2 | TO peak | 520 ± 0.2 | 520 ± 0.3 | 520 ± 0.2 | 521 ± 0.2 |
| | FWHM | 6.0 ± 0.2 | 5.9 ± 0.2 | 6.0 ± 0.3 | 6.0 ± 0.2 |
| S9 | TO peak | 521 ± 0.3 | 520 ± 0.2 | 520 | 520 ± 0.2 |
| | FWHM | 5.7 ± 0.2 | 6.1 ± 0.2 | 6.2 ± 0.1 | 6.0 ± 0.3 |

From Table 7.2, it is observed that a clear comparison could not be drawn from the samples. The TO peaks and FWHM of the hydrogenated samples were relatively similar \sim 520 cm⁻¹ and \sim 6.0 cm⁻¹ respectively implying that the samples had almost identical structural quality after the hydrogenation process. A possible reason could be

that the samples sustained a similar level of structural damage during the hydrogenation process.

7.5 Investigation of electrically-active defects in LCPdoped poly-silicon thin film solar cells

Raman backscattering on silicon provides a wealth of information, ranging from structural quality and stress to chemical bonding and hydrogen defects [10]. Generally, non-hydrogenated poly-Si thin film solar cells contain a high density of dangling bonds at grain boundaries and other defective regions. These dangling bonds introduce states in the band gap and therefore increase the bulk recombination of the solar cells [7]. During hydrogenation, hydrogen atoms diffuse into the poly-Si and attach to these dangling bonds thereby removing the in-gap states. However, despite the significant benefits of hydrogenation in improving device performance, excessive hydrogenation generates new defects such as platelets in the solar cell [8, 10-12]. Those are micro-cracks between two adjacent planes of silicon atoms stabilised by hydrogen that trap molecular hydrogen in voids. The voids are the building blocks of platelets and arise from dangling bonds or intra-grain defects induced by the hydrogenation process. In Raman spectroscopy, the local vibration mode (LVMs) of Si-H, Si-H₂ or (Si-H₂)_n and Si-H₃ are used to detect dangling bonds and other hydride defects in platelets. Those are assigned the values of 2000 cm⁻¹, 2090 cm⁻¹ and 2140 cm⁻¹ respectively [13]. On the other hand, molecular hydrogen (H_2) is distinguished by its frequency at \sim 4157 cm⁻¹ and is attributed to hydrogen molecules trapped within the voids created by platelets [8, 12, 13].

7.5.1 Experimental procedure

In the following study, a few representative hydrogenated samples were investigated by Raman scattering spectroscopy (Renishaw inVia) to detect the presence of dangling bonds and molecular hydrogen. The measurements were conducted using an argon-ion laser of wavelength 514 nm. The LCP conditions are summarized in Table 7.1. The laser power was ~12.5 mW. All measurements were carried out at room temperature.

7.5.2 Results and Discussion

Figure 7.3 shows the Raman spectra of silicon-hydrogen bond for LCP-doped sample (S1) after a hydrogenation process at 600 °C for 30 min in a LPCVD reactor with an inductively-coupled remote plasma source. For comparison purposes, the Raman spectrum acquired on a reference poly-Si sample (Hyd. reference sample) hydrogenated at 450 °C for 15 min is also included.

From Figure 7.3, it is observed that all the hydrogenated LCP-doped samples (shown in red, green and cyan) displayed a clear $(Si-H_2)_n$ peak at ~2100 cm⁻¹. In contrast, sample S1_asdoped (shown in black) and its annealed counterpart S1[LCP+700(0.5hr)] (shown in blue) did not exhibit such peak. The reference hydrogenated sample (magenta) showed a faint peak at ~2100 cm⁻¹. The results can be explained by the fact that hydrogenation performed at lower temperature and shorter duration generated fewer defects in the films. Previously it was reported that temperatures below 300 °C can generate hydrogenation-induced defects in silicon [14]. Therefore, optimum hydrogenation conditions saturate the dangling bonds (Si-H) in the poly-Si but excessive hydrogenation simultaneously generates (Si-H₂)_n defects. Comparing the as-doped sample and its annealed counterpart S1[LCP +

700(0.5hr)], it would have been expected that, after annealing the sample at 700 °C for 30 min, sample S1[LCP + 700(0.5hr)] would have displayed a clear peak at ~2000 cm⁻¹ due to the dissociation of Si-H bond. Instead the results show that LCP does not create any dangling bonds in the poly-Si. As for the LCP-hydrogenated samples, it is evident that the hydrogenation conditions were excessive and created $(Si-H_2)_n$ defects in the poly-Si. As reported in Ref. [13], the origin of the $(Si-H_2)_n$ are rather complicated but are attributable to intra-grain defects. These results are also in reasonable agreement with the FWHM of the LCP-doped hydrogenated samples which are higher than that of a reference hydrogenated poly-Si sample (e.g. ~6.0 cm⁻¹ as compared to ~5.3 cm⁻¹) thus indicating the presence of structural defects. Lastly, molecular hydrogen peaks located at ~4157 cm⁻¹ could not be resolved clearly due to the high signal-to-noise ratio and are assumed to be under the detection limit.

To gain more insight into the hydrogenation-induced defects in the other samples, a complete batch of hydrogenated samples previously annealed at 700 °C for 30 min was investigated by Raman spectroscopy. The measurements were conducted under the same conditions as in Figure 7.3. Figure 7.4 displays the silicon-hydrogen Raman spectra of the LCP-doped samples annealed at 700 °C for 30 min and subsequently hydrogenated at 600 °C for 30 min in a LPCVD reactor with an inductively-coupled remote plasma source.

From Figure 7.4, it is clear that all the samples, irrespective of their LCP conditions showed a distinct peak at around 2100 cm^{-1} which is in agreement with the earlier findings that the hydrogenation conditions generated defects in the poly-Si.



Figure 7.3: Raman spectra of silicon-hydrogen bond for LCP-doped sample S1 after a hydrogenation process at 600 °C for 30 min in a LPCVD reactor with an inductively-coupled remote plasma source. For comparison purposes, the Raman spectrum acquired on a reference poly-Si sample (Hyd. reference sample) hydrogenated at 450 °C for 15 min is also included.

From the results described in this Section, it is evident that the performance of the hydrogenated LCP-doped samples was limited by the defects generated during the hydrogen process. Furthermore, literature reports that hydrogenation performed at higher temperature (e.g. 610 °C) creates deeper defects into the poly-Si (~1 μ m deep) whereas hydrogenation carried at lower temperature of 420 °C creates defects in the sub-surface region which can be removed by post-hydrogenation processes such as dry etching [9]. Therefore, it is imperative that the hydrogenation conditions are optimized to maximize the performance of the solar cells.



Figure 7.4: Silicon-hydrogen Raman spectra of LCP-doped samples S1 annealed at 700 °C for 30 min and subsequently hydrogenated at 600 °C for 30 min in a LPCVD reactor with an inductively-coupled remote plasma source.

7.6 Laser-induced defects in poly-silicon

The localised heating imparted by a laser beam is advantageous for processing because only a fraction of the material is melted without heating the bulk [17]. However, the fast melting and solidification cycles introduces thermal stress and significant amount of contaminations such as oxygen and nitrogen into the film. Those affect the electrical properties of the laser-doped layer [15-17]. There are many studies in literature detailing about laser-induced defects in silicon. Some of those are described below.

Studies on laser-crystallised silicon revealed that rapid cooling created electrically-active point defects within the molten layer as a result of the fast solidification (or recrystallization) velocity. Such defects were shown to be detrimental for the performance of silicon solar cells as they lower minority carrier lifetime and thus, the open-circuit voltage. For instance, some researchers reported a critical solidification velocity of about 1-1.5 m/s and considered this value to be the threshold for the formation of such defects [15]. In another study to further support the argument of a threshold solidification velocity during laser-assisted processes, Young *et al.*[18] used substrate heating during a laser annealing process to slow down the recrystallisation speed. They reported a decrease in the point defect density of the silicon film. In the same way, other studies claimed that there were two thresholds for laser power - one beyond which there was formation of bulk defects and one which corresponded to visible material damage [19].

There are also reports of traps being generated in silicon as a result of thermally-induced stress. Arora *et al.*[20] claimed that there exists a threshold energy beyond which laser damage and electrically-active defects are generated. This energy was found to depend mainly upon the pulse duration and the number of pulses per unit area incident on the silicon [20]. This argument is also in agreement with the fact that longer pulse length generates less thermal stress. Furthermore, stress also induces cracks in the poly-Si films. Thermal stress accounts for defect generation at depths that are larger than the doping depths in laser-crystallised films [17].

Besides the factors affecting solidification kinetics, impurities such as oxygen and nitrogen lower carrier lifetime in silicon. For instance, Karg *et al.*[21] showed that in the presence of oxygen and nitrogen, there were about 7 species of shallow thermal donors and up to 16 species of thermal donors that were formed within a temperature range of 300 °C to 600 °C in mono-crystalline silicon. Those donor-like complexes were electrically active and it was reported that nitrogen could either act as a catalyst for the formation of these donors or could be part of the complexes. The oxygen-related defect centers were annihilated by a heat treatment at temperatures above 600 °C.

Other research also focused on the effect of oxygen and carbon on Czochralski (CZ) silicon. A detailed study conducted by Kishino *et al.*[22] revealed that high interstitial oxygen levels $(10^{18}-10^{21} \text{ cm}^{-3})$ decreased upon annealing CZ wafers at high temperatures. Additionally they found that thermally-induced micro-defects appeared upon annealing and that the defect density was largely influenced by the thermal history of the substrates. It was demonstrated that high cooling rates lead to small micro-defects whereas slow cooling rates lead to bigger micro-defects. They speculated that the carbon and oxygen content in the wafers played a significant role in the defect density.

Cazcarra *et al.* [23] reported the annihilation and generation of oxygen thermal donors over a range of temperatures. They found that thermal treatments within the temperature range of 600 °C-900 °C rapidly eliminated thermal donors generated during a pre-annealing step at 450 °C. However, prolonged annealing also created new oxygen donors. These donors generally appeared after an incubation time related to the oxygen concentration in the silicon and once generated, were more difficult to annihilate than donors generated at a temperature of 450 °C. They postulated that donors created at low temperature (e.g. 450 °C) were attributed to aggregates of few oxygen atoms that were easily cured and hence did not introduce stress in the silicon. In contrast, donors generated at temperatures between 600 °C-900 °C were related to oxygen precipitation and induced stress in the silicon. They speculated that this

behaviour could be due to heavy clusters of Si_y-O_x atoms acting as nucleation centers for oxygen precipitation. They hypothesized that those electrically-active Si_y-O_x clusters were also quite thermally stable and thus, higher temperatures were required to annihilate them. In the same way, Borghesi *et al.* [24] described the precipitation of oxygen as the aggregation of oxygen atoms inside the silicon and that the process was driven over a wide temperature range subjective to the kinetics of the diffusion reaction. They further explained that based on the electrical activity, the agglomerates of oxygen can be further divided into thermal donors and non-electrically active precipitates. The latter are identifiably by means of transmission electron microscopy (TEM) or high resolution TEM whereas the thermal donors can only be revealed by electrical measurements. An excellent review about oxygen precipitation is given in Ref. [24].

Carbon is also known to affect the precipitation kinetics of oxygen in silicon. In literature, there are different views about the influence of carbon on the precipitation of oxygen in silicon. Some claim that carbon enhances precipitation while others have observed no profound effect on oxygen precipitation mechanisms. For instance, Londos *et al.*[25] studied the effects of oxygen in carbon-lean ($< 10^{16}$ cm⁻³) and carbon-rich (10^{16} cm⁻³) silicon and found that carbon had a significant role in the precipitation kinetics. They observed that in carbon-rich samples, the precipitation annealed out at lower temperature (\sim 720 °C) as compared to carbon-lean samples which occurred at 800 °C. From their findings, they claimed that below \sim 950 °C, carbon assisted the precipitation process by providing additional seeding sites for heterogeneous precipitation through the formation of C-O complexes and above 950 °C, carbon played a catalytic role in the precipitation by minimizing the interfacial energy.

7.7 Impurity concentration in LCP-doped films

Secondary ion mass spectrometry (SIMS) profiling was carried out to investigate the level of contamination in the LCP-doped samples. The carbon and oxygen concentration in an as-doped (sample E5 from Table 4.1) and a corresponding LCP sample annealed at 1000 °C for 1 min was assessed by SIMS measurements. The sample structure was n^+ (LCP-doped)/ p^- /SiN_x/glass. Both samples underwent a hydrofluoric acid (HF) etch to remove the native oxide layer before SIMS. The profiling was carried out from the LCP doped layer up to the silicon nitride layer. Figure 7.5 shows the measured SIMS profiles of carbon and oxygen in (a) an as-doped LCP sample and (b) a LCP sample processed under the same conditions and subsequently RTP annealed at 1000 °C for 1 min. Both samples were processed with a fluence of 1.5 J/cm², a pulse length of 20 ns and a pulse overlap of 80 %.



Figure 7.5: Measured SIMS profiles of carbon and oxygen in (a) an as-doped LCP sample and (b) a corresponding LCP sample subjected to RTP at 1000 °C for 1 min. The oxygen level was $\sim 8 \times 10^{20}$ cm⁻³ and $\sim 2 \times 10^{20}$ cm⁻³ in the as-doped and annealed sample respectively. The carbon content was $\sim 5 \times 10^{18}$ cm⁻³ and $\sim 4 \times 10^{18}$ cm⁻³ in the as-doped and annealed sample respectively.

From Figure 7.5, the oxygen level in the LCP-doped layers was $\sim 8 \times 10^{20}$ cm⁻³ in the as-doped sample and $\sim 2 \times 10^{20}$ cm⁻³ in the annealed sample. From the above data, it appears that a fraction of the oxygen was removed after the thermal anneal and the HF etch. As reported in literature [23-26], oxygen thermal donors or non-electrically active precipitates may have been formed at this temperature and was subsequently removed during the HF etch. This possibly explains the discrepancy in oxygen levels between the as-doped and annealed sample. Additionally, high carbon concentration of $\sim 10^{20}$ cm⁻³ was also measured in other LCP-doped samples (refer to Figure 7.7) which could have precipitated oxygen in the form of C-O complexes.

Figure 7.6 shows the measured SIMS profiles of carbon and oxygen in two as-doped LCP samples processed with a fluence of 1.5 J/cm^2 and (a) a pulse overlap of 94% and a pulse length of 60 ns (b) a pulse overlap of 96% and a pulse length of 80 ns. As seen, it is likely that the high carbon and oxygen concentration played a role in the oxygen precipitation kinetics upon annealing. Furthermore, LCP on bulk silicon wafers previously showed high levels of nitrogen ($\sim 10^{19}$ cm⁻³) [27]. Although the level of nitrogen impurity was not measured in the LCP-doped poly-Si samples, it is speculated that nitrogen may be present in relatively high concentration. This is because the same LCP setup utilizing a doping source coupled in compressed dry air (CDA) was used for the LCP experiments in this thesis. Additionally, SIMS profiling on hydrogenated poly-Si samples fabricated from the solid phase crystallisation (SPC) approach (i.e. baseline solar cell) previously showed nitrogen concentration of $\sim 6 \times 10^{18}$ cm⁻³. Overall, it would be tedious to isolate the performance-inhibiting mechanisms in LCP-doped poly-Si thin film solar cells because carrier recombination could arise from structural defects, electrically-active defects or the significant amount of impurities in the LCP-doped layers. Other advanced characterisation techniques such as X-ray absorption spectroscopy, deep level transient spectroscopy (DLTS) are mandatory and could not be performed within the timeframe of this work. However, some performance-limiting mechanisms can be identified from the findings in this thesis.



Figure 7.6: Measured SIMS profiles of carbon and oxygen in two as-doped LCP samples processed with a fluence of 1.5 J/cm^2 and (a) a pulse overlap of 94% and a pulse length of 60 ns (b) a pulse overlap of 96% and a pulse length of 80 ns.

Firstly, a detailed study of the effective ideality factor of the hydrogenated samples showed that carrier recombination originated mostly within grain boundary or space-charge region. A further investigation by Raman spectroscopy revealed that hydrogenation generated (Si-H₂)_n defects in the poly-Si. Although the origin of (Si-H₂)_n defects is not clearly understood, it is speculated that they originate from intragrain defects [13]. Thus, it appears that the V_{oc} and *pFF* were limited by
recombination within the space-charge region. Also, findings from literature state that depending upon the hydrogenation temperature, the platelets extend deeper (~1 μ m) in the poly-Si than the sub-surface platelet defects typically encountered after hydrogenation at lower temperature (e.g. 450 °C) [9].

Secondly, the results in Chapter 6 showed that after annealing the samples at temperatures below 700 °C, the transverse-optical (TO) peak as measured by Raman scattering showed some residual stress in the film. For example, the TO peak of the sample annealed at 700 °C was ~519 cm⁻¹ (indicating the presence of tensile stress) while the TO peak of a similar sample annealed under RTP at 1000 °C for 1 min was \geq 520 cm⁻¹ indicating that the tensile stress was almost completely relieved. These results can be explained by oxygen thermal donor generation and annihilation over the range of investigated temperatures. For instance, at a temperature of 700 °C, new oxygen thermal donors are generated while other species of oxygen donor are annihilated and thus, the poly-Si still shows residual stress. On the other hand, under RTP conditions, the donors are mostly annihilated and therefore the poly-Si showed no residual stress. In contrast, annealing carried out at lower temperatures (below 700 °C) showed increasing levels of stress in the poly-Si because the donors were not effectively removed. These findings are in reasonable agreement with the study by Cazcarra et al. [23] who observed that depending upon the thermal treatment, oxygen donors were mostly annihilated at 1000 °C. Additionally, the carbon and nitrogen content in the LCP-doped films possibly acted as catalyst or enhanced the precipitation reaction. A supporting argument may be the low temperature (below 500 °C) that is sufficient for dopant activation in the LCP-doped samples. In this case, the carbon in the film may have precipitated the oxygen in the form of C-O

complexes at such low temperatures [24]. Therefore, the electrical quality of the LCPdoped layer is influenced by the annealing conditions and the oxygen thermal donors.

7.8 Conclusion

In this Chapter, the electrically-active defects that limit the performance of LCPdoped poly-Si thin film solar cells was investigated by Suns- V_{oc} measurements as well as Raman spectroscopy. The effective ideality factor was introduced as a parameter to assess the recombination in the solar cells. From these measurements, it was found that the performance of the solar cells was mostly limited by recombination within the space-charge region or grain boundary defects. A more in-depth study of the hydrogenated LCP samples by Raman spectroscopy revealed that the hydrogenation process induced (Si-H₂)_n intra-grain defects in the poly-Si as a result of excessive hydrogenation. A further study of the FWHM and TO peaks indicated that the LCPdoped samples were of relatively similar structural quality after hydrogenation.

The carbon and oxygen impurities in the LCP-doped films were assessed by SIMS measurements. Significant levels of impurities were measured in the LCPdoped samples. A comparison of the SIMS profiles before and after annealing revealed that oxygen precipitation in the form of oxygen thermal donors may have been generated or annihilated upon annealing. It was further discussed that carbon and nitrogen influenced the generation/annihilation of oxygen thermal donors over a range of temperatures. The structural quality of the films as investigated by Raman spectroscopy in Chapter 6 indicated that the annealing conditions influenced the residual tensile stress in the poly-Si. This is because the thermal donor annihilation and generation process is a competitive reaction and is also in agreement with reports in the literature. Additionally, the high impurity levels such as carbon and nitrogen were likely to influence the kinetics of the oxygen precipitation reaction over a range of temperatures.

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CHAPTER 8

CONCLUSION AND FUTURE WORK

8.1 Summary

Lasers are promising for a multitude of thin film applications such as doping, crystallisation and defect annealing, amongst others. They are fast, versatile, capable of spatial patterning and can be tailored for various purposes. Generally, laser doping on poly-silicon thin film is carried out either using externally applied precursors (i.e. in the form of spin-on dopants or pre-doped layers such as silicates) or by gas immersion laser doping. Each of the aforementioned techniques is limited in terms of supply of dopants, high cost, specialised infrastructure, and increased number of pre-processing steps etc.

In this thesis, a novel laser doping process known as laser chemical processing (LCP) was proposed and applied for doping *p*-type poly-Si thin films. Initially, LCP was developed by Fraunhofer ISE for doping and micro-structuring applications on bulk crystalline silicon wafer solar cells. The technique consists of coupling a laser light (pulsed or continuous) inside a highly pressurized ultra-thin liquid jet carrying a doping precursor. Through total internal reflection, the laser is then wave-guided towards the substrate for doping applications. During the process, precursors are atomized *in situ* within the liquid jet and therefore a practically infinite supply of doping precursors exists at the reaction site. Using such favorable features from LCP, the current work demonstrated a laser doping technique that was both selective and featured a practically infinite supply of doping precursors during the doping process. Using a frequency-doubled (532 nm) tunable nanosecond Nd:YAG laser and

phosphoric acid (42.5%) as the doping source., LCP was applied solely for *n*-type doping of poly-Si. Additionally, the potential of LCP for poly-Si thin film was further shown by fabricating an active layer for poly-Si thin film solar cells on glass. To the best of the author's knowledge, such LCP work is being reported for the first time.

Chapter 2 detailed the laser-induced physical and chemical interactions occurring during LCP to provide the reader with a better understanding of LCP. The laser-material interactions were similar to those of dry laser doping on silicon and therefore a large number of mathematical models used in dry laser doping were relevant for LCP. The parameters within the models were changed accordingly to suit the LCP conditions applied in this thesis. These also served as input for the melt depth and melt lifetime simulations carried out in Chapter 4. It was explained that the simulation model was intended to provide a qualitative understanding of the LCP process and that it was limited by the lack of empirical parameters such as the intensity profile of the beam, path enlargement of the laser inside the beam and so forth.

Chapter 3 dealt with a comprehensive description of poly-Si thin film on glass solar cells and it was shown that poly-Si thin film on glass photovoltaics was promising as a robust and cost-effective technology. Furthermore the process flow for the fabrication of poly-Si on glass for LCP was described in detail. The chapter also gave an overview of the relevant characterisation techniques for assessing the structural and electrical properties of the LCP-doped layers.

Chapter 4 investigated the LCP conditions for *n*-type doping of poly-Si thin films on glass. Throughout the study, it was found that a thermal anneal was necessary for dopant activation. Additionally, it was demonstrated that the ambient conditions did not contribute to dopant activation as shown by the samples with a silicon oxide barrier layer during the thermal treatment. Different LCP and annealing conditions were investigated and the sheet resistances and active dopant profiles were measured by four point probe and electrochemical capacitance-voltage (ECV) measurements respectively.

Within a particular pulse regime, increasing the pulse energy and pulse overlap (below the ablation threshold) resulted in a deeper doping depth as a result of enhanced dopant diffusion inside the poly-Si. ECV profiling of the LCP-doped samples revealed a flat-top profile implying that the dopants were uniformly distributed across the doped layer. Comparison of the ECV and secondary ion mass spectrometry (SIMS) profiles showed that for samples processed with a 20 ns pulse regime, the peak doping concentration agreed to within 70%. The discrepancy was explained by artefacts affecting both ECV and SIMS profiling. On the other hand, the investigation of pulse length over the doping profiles showed that using longer pulse lengths at the same laser fluence resulted in higher peak doping concentration and deeper doping depth. However, it was explained that under conditions of high laser fluences and long pulse lengths, the melt lifetime may exceed the characteristic melt expulsion time and consequently the melt flow may be dominated by the pressurized liquid jet. Additionally, it was shown that for samples processed using a 60 ns and an 80 ns pulse length, there was a large disparity between the ECV and SIMS profiles. It speculated that doping segregation effects might have caused dopant was accumulation in the near-surface layer of the samples.

Melt depth and melt lifetime simulations were carried out using LCP conditions employed in this work. The simulations were performed using the SLIM (simulation of laser interaction with materials) software and provided a qualitative understanding of the LCP conditions on the doping profiles. The limitations of the

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simulation model were clearly described. Next the sheet resistances were calculated using a suitable model from literature. Good agreement was obtained between the calculated and measured sheet resistances. The discrepancy was attributed to the limitations of the mathematical model as well as experimental artifacts affecting the sheet resistance and ECV doping profiles. Finally, optical characterisation using a scanning electron microscope (SEM) revealed the influence of the LCP conditions on the surface quality of the LCP-doped layers. At high laser fluences and longer pulse lengths, the surface quality deteriorated from melt expulsion by the liquid jet. Overall, the findings from this chapter indicated that the peak doping concentration (~10¹⁹ cm⁻³), the doping depth (less than 350 nm) and sheet resistances (< 5 kΩ/□) were favorable for making an active layer (e.g. an emitter or a back surface field) for poly-Si thin film on glass solar cells.

Chapter 5 reported the first application of LCP in fabricating an active layer for poly-Si thin film solar cells on glass. The optimized LCP conditions from Chapter 4 were used to make an *n*-type emitter on a p^{-}/p^{+} poly-Si thin film on glass. After dopant activation, the samples were assessed by four point probe and ECV measurements. The sheet resistances of the annealed samples were about 2-5 k Ω/\Box and the dopant concentration was about 8 x 10¹⁸ cm⁻³ to 1 x 10¹⁹ cm⁻³ at a doping depth of less than 350 nm (as measured by electrochemical capacitance-voltage). Selected LCP-doped samples were subjected to a hydrogenation process in a low pressure chemical vapor deposition (LPCVD) reactor tool with an inductively coupled remote plasma source.

After hydrogenation, the samples were again subjected to sheet resistance and ECV measurements. ECV profiling revealed that the lower sheet resistances were due to improved carrier mobility rather than an increase in the peak active dopant

concentration. From the ECV profiles, it was also observed that the hydrogenation process shifted the p-n junction only slightly as compared to conventional poly-Si thin film solar cells on glass. The implication of this shift on the collection efficiency of the devices was discussed and was deemed to be promising for the performance of LCP-doped poly-Si thin film solar cells on glass.

Suns- V_{oc} measurements were carried out before and after hydrogenation. A major improvement in open-circuit voltage (V_{oc}) (> 400 mV) and pseudo-fill factor (*pFF*) (> 65%) was realized through hydrogenation due to passivation of dangling bonds. The best cell had an average V_{oc} of (446 ± 7) mV and a *pFF* of (68.3 ± 0.9) %. It was discussed that the annealing step was the limiting factor for a higher V_{oc} and *pFF* as demonstrated by the samples annealed at 700 °C for 30 min. To further study the influence of the location of the *p*-*n* junction over the collection efficiency of the devices, the cells were measured in substrate and superstrate using a customized fixture. It was found that the V_{oc} and the *pFF* were relatively similar. The lower average V_{oc} and *pFF* measured in substrate configuration were attributed to sample damage from repetitively probing the n^+ and p^+ layers.

The solar cell modeling software PC1D was utilized to calculate the V_{oc} of the LCP-doped solar cells (in substrate and superstrate). The simulated V_{oc} were in reasonable agreement with the experimental V_{oc} . Lastly it was discussed that the V_{oc} and the *pFF* could be further improved by using a RTP process for dopant activation and optimizing the hydrogenation conditions to yield higher V_{oc} and *pFF*.

Chapter 6 investigated the structural quality of the LCP-doped layers. It was mentioned that structural defects were critical towards device performance as they affect carrier mobility and lifetime. Evaluation of the LCP-doped layers through ultraviolet reflectance and cross-sectional transmission electron microscopy (XTEM) revealed that the high sheet resistances were not caused by amorphisation. The XTEM also demonstrated that the poly-Si possessed satisfactory material quality.

An in-depth structural investigation was carried out by Raman spectroscopy. It was found that depending upon the pulse regime, increasing the laser fluence increased structural defects (i.e. impurity diffusion and laser-induced defects) in the film. The results were in good agreement with the sheet resistance and electrochemical capacitance-voltage measurements. Enhanced impurity diffusion also increased the tensile stress in the film. Annealing the LCP-doped samples relieved the tensile stress and lowered the FWHM whereby the structural properties of the poly-Si improved upon annealing at higher temperature and longer duration. The best structural properties were obtained for samples that were subjected to a RTP at 1000 °C for 1 min.

To further understand the microstructural properties of the poly-Si, the structure disorder parameter *C* was determined from the Raman measurements. It was established that upon annealing the poly-Si, bond re-arrangement occurred in the poly-Si. It was hypothesized that the precipitation of oxygen in the form of oxygen thermal donors was responsible for the structure disorder. The generation and curing of oxygen thermal donors was discussed within the investigated temperature range. The high impurity levels in the LCP-doped layers likely played a role in the kinetics of the precipitation reaction.

Lastly, the grain size, texture and plastic deformation in the LCP-doped samples were studied by electron backscattered diffraction (EBSD). The average grain size was comparable to that of non-LCP doped poly-silicon made by the solid phase crystallisation approach. The measured plastic deformation in the poly-Si was below the detection limit of the EBSD system and it was argued that LCP did not introduce appreciable plastic deformation in the poly-Si. This finding was also in agreement with earlier reported work about plastic deformation in poly-Si of grain sizes (< $3 \mu m$).

Chapter 7 discussed the electrically-active defects that limited the performance of the LCP-doped solar cells. The device quality of the poly-Si was evaluated by the effective ideality factor (n_{eff}) determined from Suns- V_{oc} measurements. It was found that the hydrogenated LCP-doped solar cells displayed a n_{eff} close to 2 indicating that the performance of the devices was mostly limited by recombination within the spacecharge region or by grain boundary defects. An in-depth study of the hydrogenated LCP samples by Raman spectroscopy revealed that excessive hydrogenation introduced (Si-H₂)_n intra-grain defects in the poly-Si. Assessment of the structural quality through the FWHM and TO peaks indicated that the LCP-doped samples possessed relatively similar structural quality after hydrogenation.

The carbon and oxygen content in the LCP-doped films were measured by SIMS profiling. Significant levels of contaminants were observed in the LCP-doped samples. A comparison of the SIMS profiles before and after annealing revealed that oxygen precipitation may have occurred upon annealing. It was further discussed that carbon and nitrogen influenced the generation/annihilation of oxygen thermal donors over the range of annealing temperatures. Therefore, it was likely that the thermal treatment imparted to the samples controlled the oxygen thermal donor generation/annihilation process in the poly-Si.

8.2 Conclusion

The main contributions of this thesis towards LCP on poly-Si thin films are:

- A straightforward technique for doping poly-Si thin films was demonstrated using a frequency-doubled (532 nm) tunable nanosecond Nd:YAG laser and phosphoric acid as the doping medium. Doping technique is selective and can be extended to large area applications (e.g. 20 cm by 20 cm).
- A systematic investigation of optimum LCP parameters and post-LCP annealing conditions was carried out for *n*-type doping of poly-Si thin films on glass through the detailed study of structural and electrical properties of the LCP-doped layers.
- A qualitative understanding of the influence of LCP conditions over the peak doping concentration and doping depth of the LCP-doped layers through melt depth and melt lifetime simulations was presented.
- A modified analytical model was shown for calculating the sheet resistance of the LCP-doped layers.
- A thorough study of the structural properties of LCP-doped films was performed by Raman spectroscopy, cross-sectional transmission electron microscopy (XTEM) and electron backscattered diffraction (EBSD). Proposed that oxygen precipitation in the form of thermal donors was responsible for the observed structural disorder in the films upon thermal annealing.
- A poly-Si thin film solar cell on glass featuring an *n*-type active layer (e.g. emitter) made by LCP was successfully fabricated.
- The device performance [i.e. open-circuit voltage (V_{oc}) and pseudo-fill factor (pFF)] and diode quality [i.e. effective ideality factor (n_{eff})] of the fabricated solar cells was evaluated by Suns- V_{oc} measurements.

• The performance-limiting factors affecting the LCP-doped solar cells were identified. The post-LCP anneal step, excessive hydrogenation and oxygen thermal donors were discussed to be the underlying reasons.

8.3 Future work

Considering the early stages of LCP research on poly-Si thin film, the present study has shown that the V_{oc} and *pFF* of LCP-doped solar cells were reasonable and showed potential for further improvement. Given the timeframe of the current work and the fact that the author's laboratory was affected by a major fire during the course of his PhD candidature, some research areas were left unexplored. However, it is the author's belief that such work can further improve understanding of LCP on poly-Si thin films and ultimately increase device performance.

Firstly, an optimisation of the hydrogenation conditions is essential for the LCP-doped poly-Si thin film solar cells. It was shown that the performance of the cells was limited by $(Si-H_2)_n$ defects due to excessive hydrogenation. This study entails a careful investigation of the device performance (e.g. by Suns- V_{oc} measurements) and hydride defects with respect to the hydrogenation conditions. A trade-off is necessary between the optimum hydrogenation conditions, defects and device performance.

Secondly, another motivating study consists of metallising the solar cells and measuring light current-voltage (I-V) and external quantum-efficiency (EQE) for a complete assessment of the device performance. It is believed that the surface roughness imparted to the poly-Si during LCP is a welcome side-effect to minimise overall reflectance losses to the solar cells. Therefore, it will be interesting to compare the light-generated current in the LCP-doped devices to a baseline solar cell (i.e. nonLCP doped). Furthermore, from the reflectance, EQE and light I-V data, the diffusion length of the carriers can be calculated using PC1D. From the data, the LCP conditions can be optimized further to decrease carrier recombination within the LCPdoped layers.

Thirdly, a detailed study of the surface composition of the poly-Si by X-ray photoelectron spectroscopy (XPS) will be useful to identify the chemical states before and after annealing in order to have a better understanding of the dopant activation mechanisms occurring during the thermal treatment. Additionally, studies by X-ray absorption spectroscopy (XAS) can complement information about the local electronic structure of the elements in the poly-Si (e.g. silicon, oxygen or phosphorus).

Lastly, the present study dealt only with *n*-type doping on poly-Si thin films. It would be equally interesting to investigate *p*-type doping on poly-Si. Another area of study would be to extend LCP application towards crystallisation and doping of amorphous silicon.