Laser Technology in the Fabrication of High Efficiency Solar Cells

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Abstract 350 words maximum: (PLEASE TYPE)

This thesis focuses on the development of laser processes to be used for advancements in solar cell fabrication. Two different types of laser processing applications are investigated.

The first part of this thesis involved the development of a new concept of laser doping with grooving to form narrow grooves with heavily doped walls in a simultaneous step, with the self-aligned metal contact subsequently formed by plating. This process capitalizes on the benefits of both buried contact solar cells (BCSC) and laser doped selective (LDSE) solar cells. The unique feature significantly reduces the formation of laser-induced defects. The exposed walls allow for nucleation of the subsequent metal plating. This novel structure also benefits from greatly enhanced adhesion of the plated contact due to it being buried underneath the silicon surface in the same way as the BCSC. Cell efficiencies of over 19% are achieved by using this technology on p-type Czochralski (Cz) wafers with a full area aluminium (Al) back surface field (BSF) rear contact.

The second part of this project is focused on using laser illumination to control the charge state of hydrogen atoms within the silicon. A laser hydrogenation tool was developed together with a colleague. Laser hydrogenation has been shown to be able to potentially transform low quality UMG silicon wafers into ones similar in quality to monocrystalline Cz silicon wafers, and this approach has been shown to improve cell efficiency and eliminate light induced degradation (LID) in p-type monocrystalline solar cells. The development of two prototype commercial tools shows the technology is ready to be transferred to the industry.

Finally the laser doping and grooving technology is incorporated with the advanced laser hydrogenation. Over 1 % absolute efficiency improvement was achieved on cells with a relatively large amount of laser induced defects, resulting in the defected cells achieving similar performance to those with less laser damage introduced during fabrication. This suggests that the laser doping and grooving cell technology could be carried out with a wider processing window if advanced hydrogenation technology is incorporated.

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Abstract

This thesis focuses on the development of laser processes to be used for advancements in solar cell fabrication. Two different types of laser processing applications are investigated. The first is the development of an innovative laser doping with grooving technique. Both buried contact solar cells (BCSC) and laser doped selective emitter (LDSE) solar cells have achieved considerable success in large-scale manufacturing. Both of these technologies are based on plated contacts. The high metal aspect ratios achieved by BCSC allow for low shading loss while the buried metal contacts in the grooves provide good contact adhesion strength, which has in some cases been shown to exceed that of conventional screen-printed contacts. In comparison, although the LDSE cell achieves significantly higher efficiencies and is a much simpler approach for forming the selective emitter region and self-aligned metal plating, the metal adhesion strength falls well short of that achieved by the BCSC. The first part of this thesis involved the development of a new concept of laser doping with grooving to form narrow grooves with heavily doped walls in a simultaneous step, with the self-aligned metal contact subsequently formed by plating. This process capitalizes on the benefits of both BCSC and LDSE cells. The laser-doped grooves are only 3-5 μm wide and 10-15 μm deep; the very steep walls of these grooves remain exposed even after the subsequent deposition of the antireflection coating (ARC). This unique feature significantly reduces the formation of laser-induced defects since the stress due to the thermal expansion mismatch between the ARC and silicon is avoided. Furthermore, the exposed walls allow for nucleation of the subsequent metal plating. This novel structure also benefits from greatly enhanced adhesion of the plated contact due to it being buried underneath the silicon surface in the same way as the BCSC. Cell efficiencies of over 19% are achieved by using this technology on p-type Czochralski (Cz) wafers with a full area aluminium (Al) back surface field (BSF) rear contact. Test structures indicate that much higher voltages and consequently higher efficiencies could be achieved if this technology is combined with a passivated rear approach.

The second part of this project is focused on using laser illumination to control the charge state of hydrogen atoms within the silicon. The diffusivity of hydrogen in silicon can vary by up to a few orders of magnitude depending on the charge state of the interstitial atoms. Recent studies show that illumination or carrier injection plays an important role in controlling the charge state of hydrogen. A laser hydrogenation tool was developed together with a colleague to study this effect. By carefully controlling the charge state of hydrogen, defects and
recombination centres can be passivated within the silicon wafer. This has been shown to be able to potentially transform low quality UMG silicon wafers into ones similar in quality to monocristalline Cz silicon wafers, and this approach has been shown to improve cell efficiency and eliminate light induced degradation (LID) in p-type monocristalline solar cells. A prototype tool based on LEDs was developed to demonstrate this technology on 6-inch commercial solar cells. A laser equipment manufacturer has also developed a commercial tool based on this laser hydrogenation technology, showing that this technology not only works in the research lab but is ready to be transferred to the industry.

Finally the laser doping and grooving technology is incorporated with the advanced laser hydrogenation with the goal of passivating laser induced defects. Over 1 % absolute efficiency improvement was achieved on cells with a relatively large amount of laser induced defects, resulting in the defected cells achieving similar performance to those with less laser damage introduced during fabrication. This suggests that the laser doping and grooving cell technology could be carried out with a wider processing window if advanced hydrogenation technology is incorporated.
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Acronyms

AI-BSF = Aluminium Back Surface Field
ARC = Anti-Reflection Coating
BSF = Back Surface Field
BCSC = Buried Contact Solar Cell
c-Si = Crystalline Silicon
CW = Continuous Wave
Cz = Czochralski grown
EBIC = Electron Beam Induced Current
H = Hydrogen
LCP = Liquid Chemical Processing
LID = Light Induced Degradation
LIP = Light Induced Plating
LDSE = Laser Doped Selective Emitter
LTD = Low Temperature Diffusion
PECVD = Plasma Enhanced Chemical Vapour Deposition
PERL = Passivated Emitter Rear Locally diffused
PV = Photovoltaics
qCW = quasi-Continuous Wave
SEM = Scanning Electron Microscope
SPREE = School of Photovoltaics and Renewable Energy Engineering
SRH = Shockley Read Hall
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Chapter 1

1 Introduction

1.1 Motivation
The forms of energy and technologies available determine the way people live. The evolution of technology is facilitated by the evolution of energy. Widespread use of fossil fuels enabled the industrial revolution, which has pushed the development of technology enormously but also has brought some adverse consequences such as global warming. Greenhouse gas emissions have risen dramatically since the industrial revolution, resulting in reduced radiation emitted from the Earth to space and causing a rise in Earth’s surface temperature [1]. Continued surface temperature rise could lead to sea level rise, extreme weather, changing ecosystems, and large-scale abrupt impacts [2]. Alternative sustainable energy sources to fossil fuels need to be employed in order to prevent irreversible consequences that could result from global warming. Ultimately the energy of everything on Earth comes from the Sun. Photovoltaics (PV) is one of the best alternatives to fossil fuels, generating electricity directly from the sunlight. PV has already reached grid parity in many countries, including Australia [3]. However, many governments including current USA and Australian governments are supporting the fossil fuel industries. Continued improvements in solar cell efficiencies (and/or reductions in cost) for lower cost/watt are therefore required for PV to be the obvious choice over fossil fuels economically as well as environmentally. This thesis focuses on the use of laser technology in the fabrication of high efficiency solar cells.

Lasers are powerful and versatile tools that provide monochromatic photons through highly directional electromagnetic waves. They have been used in the solar industry for decades [4]. With appropriate optics, a laser beam profile can be manipulated to suit different process requirements. When it is focused, it delivers a large amount of energy quickly and locally, ensuring versatile and precise cell processing. It can also be expanded to illuminate a large area. In this case the laser is used as a light source providing mainly photons rather than focused energy.
Two solar cell structures using laser-based processes developed at the University of New South Wales (UNSW) have been successfully manufactured in large scale production: the buried contact solar cell (BCSC) and laser doped selective emitter (LDSE) solar cell.

The BCSC structure was developed at UNSW during the 1980s and 1990s [5-10]. Laser grooving of silicon (Si) to form buried contacts has previously been shown to have a range of benefits in terms of device performance, including the ability to use plated copper (Cu) contacts instead of silver, and suitability for a large scale manufacturing in the form of BP Solar’s Saturn Technology [11, 12]. Although the BCSC has been shown to have at least the same durability as screen printed solar cells [13], their manufacturing process is more complicated and thermally expensive with laser grooving followed by damage etching, groove diffusion and subsequent preparation for plating.

Another plating-based technology making extensive use of lasers is the LDSE solar cell. Similar to the BCSC, this structure has also been manufactured in large-scale [14-16]. In this method, a spin-on dopant source is applied on top of the dielectric layer that acts as an antireflection coating, surface passivation layer, and most importantly, as a mask for the subsequent metal plating process [17]. Laser scribing locally melts the regions where metal contact will be formed to remove the dielectric and incorporate the dopant source into the Si. In this way, selectively heavily doped emitters are formed together with a self-aligned plating mask [17]. Despite the success of the conventional LDSE structure, it has a few drawbacks. The main two have been identified to be laser-induced defects caused by thermal expansion mismatch between the Si and the overlying dielectric layer [18], and the relatively weak adhesion of the metal contacts, which may peel off during module production [18-20].

The first part of this thesis develops a new laser doping and grooving process that capitalizes on the major benefits of both BCSC and LDSE cells, without many of the drawbacks mentioned. However, laser-induced defects always remain of concern when using lasers to locally heat the silicon to above its melting temperature. This therefore leads to the second part of this thesis which involves the development and application of improved hydrogen passivation for the purpose of passivating the laser-induced defects and any other forms of recombination within the silicon. This part of the thesis employs lasers for another innovative new technology, to control the charge state of interstitial hydrogen to improve its diffusivity and reactivity and therefore its ability to passivate laser-induced defects and other forms of recombination in silicon solar cells.
Interstitial hydrogen can exist in three charge states, positive (H\(^+\)), negative (H\(^-\)), and neutral (H\(^0\)). H\(^0\) has much higher mobility in doped silicon as it is not affected by electric fields or electrostatic effects and can therefore diffuse rapidly compared to the dominant charge state H\(^+\) in p-type silicon. H\(^0\) has a single unpaired electron, which also makes it highly reactive [21]. Recent studies have shown that by manipulating the charge state of atomic hydrogen, interstitial hydrogen can interact and passivate a range of defects in silicon, such as B-O defects [22], interstitial iron [23], and laser induced defects [24]. Hamer et al. [25] used LED illuminated annealing to manipulate the charge state of hydrogen and achieved significant improvement in bulk passivation of p-type wafers. In this thesis the ability of controlling the charge state of interstitial hydrogen by laser illumination combined with temperature is investigated for passivation of p-type wafers and laser damage.

1.2 Thesis objectives
This aims in this thesis focus on the development and optimization of two applications of laser technology in the fabrication of solar cells and combines them together in one cell structure.

The primary aim in the first part is to develop an innovative laser doping and grooving technique that capitalizes on the benefits of the BCSC cells but with the simplicity of LDSE cells, while overcoming the drawbacks of both. The laser doping and grooving technique aims to simultaneously form narrow grooves and a heavily doped selective emitter along the groove walls. Laser parameters will be explored to study the geometry of grooves. The quality of the p-n junction along the groove walls will be investigated. Laser doped and grooved lifetime test structures will be fabricated to study the damage caused by the laser doping and grooving process. A cell structure is developed based on the laser doping and grooving technique to illustrate the potential of the concept.

The aim in the second part of the project is to develop a laser hydrogenation tool and employ lasers to control the charge state of interstitial hydrogen to passivate defects such as laser-induced defects and other crystallographic defects in silicon solar cells. The ability to manipulate the interstitial hydrogen charge state using laser illumination combined with thermal annealing will be studied. The laser hydrogenation passivation process will be applied to different kinds of defects such as those in low cost material upgraded metallurgic grade Si (UMG), boron-oxygen (B-O) complexes in commercial solar cells, as well as possible crystallographic defects caused by the new laser doping and grooving techniques.
Finally, after successful development of the laser doped grooves, and laser hydrogenation processes, the primary aim becomes the application of the laser hydrogenation technique to laser doped and grooved solar cells. A secondary aim of this work is the development and use of a commercial hydrogenation tool and the evaluation its performance. The effect on cell parameters and losses will also be investigated.

1.3 Thesis outline
After this introductory chapter, Chapter 2 reviews literature relevant to this project. First, the conventional screen-printed cell structure is compared with high efficiency cell structures based on laser technologies that benefit from selective emitters, and considers their advantages and drawbacks. The second part is a review of surface morphology modification by laser processing with an emphasis on processes that could be suitable for the purpose of the laser doping and grooving technique. The third part reviews the interstitial hydrogen charge states in Si, defects in Si and their hydrogenation passivation, and the use of illumination to control interstitial hydrogen’s charge state.

Chapter 3 presents the development of the innovative concept of selective emitter formation by simultaneous laser doping and grooving. The concept of laser doping and grooving is discussed. Laser parameters are explored to study the possible groove geometries, the process of groove formation, as well as the quality of the selective emitter along the groove walls.

Chapter 4 presents the development of another innovative technique, advanced laser hydrogenation. The manipulation of interstitial hydrogen’s charge state using a laser is presented, including the effect of temperature and illumination, effect of cooling rate and the effect of different wavelengths. The laser hydrogenation process is then applied onto low cost material, commercial solar cells, and laser doped and grooved lifetime test structures.

Chapter 5 covers the development of solar cells fabricated using the laser doping and grooving technique. Lifetime test structures are used to investigate the laser-induced damage caused by the process. Light induced plating is used to form metal contacts that nucleate inside the grooves. The metal contact adhesion strength is also tested. Cells with laser doping and grooving on the front side and full area aluminium back surface field (Al BSF) on the rear side are fabricated and analysed. Finally the laser hydrogenation technique is applied to finished laser doped and grooved solar cells, with the effects and implications discussed.

Chapter 6 presents the development of a prototype hydrogenation tool based on LEDs to process 6-inch cells, to demonstrate that the advanced hydrogenation technology is suitable
for full size commercial cells as well. Some encouraging results from commercial laser hydrogenation equipment are also presented, showing that the technology is ready to transfer to the photovoltaic industry.

Chapter 7 summarises the important results discussed in this thesis and the direction for future work.
Chapter 2

2 Literature Review

2.1 Conventional solar cells vs. high efficiency, selective emitter solar cells

Upon absorbing photons from sunlight, solar cells generate electron-hole pairs in the bulk. The hole excess positive side (p-type) and electron excess negative (n-type) side of the cell are separated by the carrier depleted p-n junction region. The electric field of the junction collects and separates minority carriers on either side, sweeping them into the region in which they become majority carriers. These carriers then enable a continuous current to flow through an external load circuit if ohmic contacts are made to the p-type and n-type regions of the solar cell. Currently, screen-printing is typically used to form these contacts; however, there is a push for more economical alternative metallisation techniques [26]. The structure of conventional screen-printed solar cell technology and the benefits of higher efficiency cell structures with selective emitter designs are reviewed here.

2.1.1 Screen-Printed Solar Cells

Screen-printed solar cells have dominated the PV market for the past three decades, due to their robustness, simplicity, and their relatively inexpensive and easily automated fabrication [27]. Figure 2-1 illustrates the schematic of a conventional p-type screen-printed solar cell. It consists of a p-type bulk substrate, an n-type homogenous emitter, a full area rear metal contact, and wide metallic front finger contacts. Due to the relatively big width of the fingers, they have to be placed 2.5 – 3 mm apart to reduce shading loss. This spacing requires carriers generated midway between fingers to travel a relatively large distance in order to be collected, which means that the emitter needs to have high lateral conductivity. Hence, a heavily doped emitter is needed. A high surface dopant concentration is also required to reduce the contact resistance at the Si–metal interface. Therefore, the sheet resistance of a conventional screen-printed solar cell is typically 60 – 80 Ω/sqr. [19].
Despite the fact that screen-printed metallization is the most widely used technique for commercial Si solar cells, the screen-print technology has some fundamental limitations. The heavily doped and relatively deep emitter required for good contacting is one of the main drawbacks. Because of the heavy doping, Auger recombination is high within the emitter. Short wavelength photons are absorbed within the first few nanometres of the silicon and the high recombination rate within this region reduces the cell’s short wavelength response dramatically. In effect, the carriers that are generated by the short wavelength light are lost and do not contribute to the light generated electrical current. Hence the heavily doped layer is often referred to as the dead layer. Another limitation of screen-printed solar cells is the high shading loss due to large finger widths, up to 50 – 60 μm [27], meaning that a not-insignificant percentage of the front surface will be shaded. Wider screen-printed contacts generally also involve larger Si-metal interfaces; this interface region also causes high recombination and a consequent reduction in cell voltage. For these reasons, as well as the high cost of the silver used in screen printed front contacts, there has been a trend towards thinner contact fingers. However, the industry is approaching the limits of practical printed line widths [29]. Additionally, the high contact resistance and low metal conductivity of screen-printed contacts can result in relatively low fill factors (FF) [19], which further emphasizes the need for alternative approaches if significant improvements are to be obtained.

The selective emitter approach is one of the best ways to overcome the limitations of screen-printing and it is a common technique used for high efficiency solar cells. Conventional industrial solar cells have a homogeneously doped emitter, which is normally balanced by the compromise between emitter performance and low contact resistance. The use of a selective
emitter can overcome this compromise. A selective emitter consists of a heavy diffusion directly underneath the metal contacts and a light diffusion for the rest of the emitter region. This enables a good short wavelength response (blue response) while also providing low contact resistance. The selectively heavily doped area can be much smaller than the typical screen-printed metal contact area, and can therefore enable narrower metal contacts to reduce interface recombination and shading losses when used in conjunction with alternative metallization techniques such as plating. There are several methods [30] which can be used to create a selective emitter, these include: etch-back emitter [31], inline selective emitter concept [32], add-on laser tailored selective emitter [33], laser doped selective emitter (LDSE) [34], doped Si inks [35], and ion implantation [36]. High efficiency cell structures usually employ a selective emitter. The following sections review such high efficiency cell structures with an emphasis on those fabricated using laser technology.

2.1.2 The PERL Solar Cell

The passivated emitter rear locally-diffused solar cell (PERL) is one of the highest efficiency cell structures [37]. When first developed, it achieved an efficiency record of 25%; the PERL structure then held the record for highest efficiency single junction solar cells for over 20 years [38]. Figure 2-2 shows the schematic of a PERL cell.

![Figure 2-2 PERL solar cell structure [39]](image)

There are several features of this design that enable high efficiencies to be achieved. Firstly, the passivation layers of SiO₂ on both sides of the cell keep the surface recombination losses low. Secondly, the small, localised contacting area at the rear ensures that the recombination in this area is kept to a minimum. Thirdly, immediately beneath the metal contacts, the silicon is heavily doped to suppress minority carrier concentrations, effectively shielding the high recombination interface. Together with a light background doping, these heavily doped
regions form selective emitters (and local back surface fields). The lightly doped emitter provides a good short wavelength response and the heavily doped regions directly beneath the front metal contacts also reduce the Si metal contact resistance. Other features include a rear reflector and inverted pyramids to reduce optical losses. The pyramids reduce reflection of external as well as internal incident light. By using thin metal fingers, inverted pyramids and a double layer antireflection coating the reflection losses are kept below 3.5% [39].

Table 2-1 lists the electrical parameters of PERL solar cells under the standard AM1.5 spectrum. The average efficiency of commercial screen printed solar cell is between 19% to 20%. The PERL cell has significantly higher efficiency than commercial screen-printed cell. However, the fabrication used for the PERL cell here involved many high temperature and photolithographic processing steps, which make it expensive and unsuitable for mass production.

Table 2-1 Electrical parameters PERL solar cells (AM1.5 spectrum, 100mW/cm², 25 °C) [19]

<table>
<thead>
<tr>
<th>Resistivity (Ωcm)</th>
<th>Area (cm²)</th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (mV)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PERL CZ</td>
<td>1.2</td>
<td>42.7</td>
<td>628</td>
<td>79.4</td>
<td>19.3</td>
</tr>
<tr>
<td>PERL FZ</td>
<td>1</td>
<td>38.7</td>
<td>706</td>
<td>82.8</td>
<td>25</td>
</tr>
</tbody>
</table>

The PERL cell highlights the importance of a selective emitter, well-designed front metal grid and well-passivated rear surface. The next two sections review two alternative high efficiency selective emitter solar cell structures that are fabricated using laser technology and have simpler processing sequences.

2.1.3 Buried Contact Solar Cells
One of the main advantages of the PERL cell is the selective emitter, with regions directly beneath metal contacts heavily diffused. This provides a good response to short wavelength light (blue response) and reduces the recombination and contact resistance at the Si and metal interface. The selective emitter of PERL cell is formed by photolithography, which is a complex and costly process. In late the 1980s, Wenham and Green introduced the Buried Contact Solar Cell (BCSC) [40, 41]. Figure 2-3 shows the schematic of BCSC cell structure.
The fabrication of the BCSC is much simpler compared to that of the PERL cell. It does not require photolithography, double layer antireflection coating, or expensive metallization. The basic fabrication sequence starts with selectively etching the surface to create a textured surface. The top surface is then lightly diffused and oxidised, followed by a laser scribing to form deep and narrow grooves in the top surface. The laser formed grooves are then chemically etched and doped much more heavily through a second diffusion process. The oxide layer formed earlier acts as an alignment mask during the second diffusion so that this heavy diffusion is restricted to the grooves only. Al is then deposited onto the back surface and sintered. Finally nickel (Ni) and copper (Cu) are electrolessly plated, deposited to the grooved areas and the rear of the cell. The oxide once again acts as a mask for the plating process such that only the grooved areas are plated with metal [5].

The BCSC approach has several advantages. One obvious advantage is the high aspect ratio and large cross section of the metal contact. The nature of the buried contacts allow the technology to be transferred onto large area cells without an increase in shading loss, which is a common problem for other high efficiency cells. The laser-scribed fingers have a narrow width, allowing them to be placed closer, reducing series resistance. This permits the emitter to be diffused very lightly so that an excellent blue response can be achieved. Another advantage is the simplified sequence, in which the oxide serves several purposes: an etch mask, a diffusion mask, a plating mask, a passivation layer and an antireflection coating. The heavily diffused regions beneath the metal contacts also protect the active region of the cell from the high recombination Si metal interface and laser damaged areas [6].
Because of its streamlined fabrication process and easy transfer to full size commercial cells, the BCSC technology attracted considerable attention worldwide from established manufacturers. Four of the world’s largest PV companies at that time licenced the technology, including BP solar, Solarex Corporation, Telefunken System, and Technik. BP solar produced 1 billion US dollars’ worth of BCSC’s by 2003, which they called the Saturn cell [12]. Commercial cells with 18.3% efficiency were demonstrated in 1991. In the World Solar Car Challenge in 1990, the winning team from Switzerland used BCSC panels, which produced 25% more power than those used by the second-placed Honda car [9]. The buried contact concept developed at UNSW was a big success in the industry in the 1980s to 1990s. The world’s first PV module reaching 20% efficiency was also based on this technology.

Despite this success, when compared with conventional commercial cells, BCSC’s fabrication sequence is still relatively complicated and thermally expensive as it requires chemical damage etching of the grooves after laser processing, a double diffusion to heavily dope the groove walls, and subsequent surface preparation for metal formation.

2.1.4 Laser Doped Selective Emitter Solar Cells
As discussed, screen-printing technology dominates the industry due to its simplicity and relatively low cost. However, it has some well-known limitations such as relatively low current due to a poor blue response and high shading loss due to the large width of the metal contact lines on the front. The selective emitter approach is one way to overcome some of these limitations and improve cell performance. In this case, the localised heavily doped region reduces contact resistance, provides easy collection of carriers generated in the heavily doped region, and enables the rest of the surface to be lightly diffused to provide much better response to short wavelength light [34]. Both the PERL and BCSC structures use selective emitters in order to achieve high efficiency. However, their fabrication processes require more than two high temperature steps, limiting their commercial viability. In the past decade or so, laser technology has been used to create selective emitters in solar cells, as it is a fast and energy efficient way to form the heavily doped regions.

The University of Stuttgart developed the line-beam system which is depicted in Figure 2-4. The laser beam is shaped into a line with a wide long axis focus and very narrow short axis focus. Together with sputtered phosphorus precursors, the line-beam laser doping process can be used to create homogeneous doping profiles. 18.9% efficient solar cells were fabricated on Float-zone (FZ) wafers with a large area emitter formed by the laser beam [42]. The line-beam laser can also be used to create a selective emitter to eliminate shunting directly underneath
the front contact and increase the fill factor [43]. Roder et al. used an additional laser processing step to form a selective emitter with a screen-printed Al-BSF rear, which resulted in 0.5% absolute higher efficiency than standard laser diffused cells. This fabrication process starts with texturing the surface with random pyramids, followed by a conventional furnace diffusion to create the n-type emitter. Then the laser melts the surface coated with phosphosilicate glass (PSG) to locally add and redistribute dopants before the silicon cools down and re-crystallizes epitaxially. The penultimate step is to etch away the PSG layer using hydrofluoric acid. The final step is to screen print the front and back contacts [33]. Although it achieved a 0.5% absolute increase in efficiency, the screen-printed lines were still wide and did not benefit from the potential for narrow metal contacts offered by laser doping.

UNSW has also developed a laser doping method to create selective emitters, known as laser doped selective emitter (LDSE) solar cells [17]. Figure 2-5 shows the structure of the UNSW LDSE solar cell. The fabrication sequence begins with texturing the front surface, then a light diffusion to create the light homogenous emitter, followed by plasma-enhanced chemical vapour deposition (PECVD) of SiNₓ. Al is screen printed on the rear surface and fired to form a BSF. Then phosphoric acid is spun on the top surface to act as a dopant source. The next step is to laser scribe the surface, during which the dielectric layer is patterned, the Si melts, and the dopant gets incorporated into the molten silicon to then form the selective emitter as the Si re-solidifies epitaxially. The final step is to form the front metal contacts, formed here (and commonly) by light induced Ni/Cu plating (LIP) [44].

Figure 2-4 Line-beam system [43]
The LDSE solar cell has a simple processing sequence and provides several advantages. It simultaneously patterns the SiN$_x$ ARC layer and incorporates dopants into the molten Si, creating a heavily doped region so that low contact resistance is achieved. The selective emitter allows for a lightly doped homogeneous emitter such that the cell response to short wavelength light is improved significantly. Laser doping also creates a self-aligned scheme for light induced plating, using SiN$_x$ as a plating mask. By combining the laser doping and light induced plating methods, minimum Si-metal interface is achieved with $<30$ μm wide metal fingers, whereas standard screen-printed metal fingers can have a width of over 50 μm. The small finger width of the LDSE cell allows more current to be generated as the shading loss is reduced. In 2011, efficiencies as high as 19.3% were achieved on large area $p$-type CZ commercial wafers using a modified commercial production line [44].

However, unlike BCSC, the aspect ratio of the metal contacts cannot be controlled and the metal contacts’ adhesion strength is relatively poor since the metal is deposited on the Si surface rather than buried underneath. Another key drawback of the LDSE cell is that laser-induced defects are formed due to the thermal expansion mismatch between Si and SiN$_x$ [20]. This mismatch places Si under tension during the laser doping process; this stress appears to induce large amounts of defects, since Si is known to be weak under tension [45].

This section has so far reviewed the conventional screen-printed cell structure, the advantages of the high efficiency PERL cell structure, and two laser based cell technologies, BCSC and LDSE solar cells, both of which feature a selective emitter. In the next section, the concept of a combined laser doping and grooving technique is proposed.

2.2 Potential of the laser doping and grooving process
Both of the BCSC and LDSE cell structures previously discussed feature a selective emitter and have some advantages and drawbacks. The first part of this project aims to develop a new...
selective emitter solar cell through simultaneous laser doping and grooving of silicon followed by self-aligned metal plating.

The BCSC has a high and controllable aspect ratio but lengthy and expensive process to form the selective emitter. LDSE creates the selective emitter by laser doping, which is fast and compatible for multi-crystalline and other low cost wafers, but the aspect ratio of metal contacts is not controllable and the adhesion of metal contacts is much poorer than that of the BCSC. LDSE cells also exhibit laser induced defects due to thermal expansion mismatch between the Si and SiNₓ. If the two fabrication processes could be incorporated together, it is believed that a new and commercially feasible fabrication sequence could be developed.

It is proposed that the formation of grooves, groove etch, and the lengthy groove diffusion involved in the BCSC approach could be substituted with a single laser process. The process would be similar to that of the LDSE, however rather than just melting the silicon, the laser simultaneously creates a groove and dopes the groove wall to create the selective emitter. There could be several benefits to this new approach: any molten Si that regrows by liquid phase epitaxy can be heavily doped to form the selective emitter; the grooves can be very narrow to enable narrow metal lines; the narrow width of the grooves could allow SiNₓ to be deposited after laser grooving and the grooves to still be plated subsequently; laser doping and grooving prior to SiNₓ deposition would avoid laser induced defects due to thermal mismatch; the laser doping and grooving process would also define the location for metal nucleation; plating into the grooves should greatly improve metal contacts’ adhesion strength.

If successful this technique could capitalize on the benefits of the BCSC structure but with the fabrication simplicity of LDSE cells. Therefore, the first part of this thesis aims to develop a reliable and repeatable laser doping and grooving process. The next section reviews further literature specific to the mechanisms involved in the laser doping and grooving process and experimental work.

2.3 Surface morphology modification by laser processing

Laser is an acronym for light amplification by stimulated emission of radiation. It is a powerful tool that is suitable for a wide range of applications, such as semiconductor processing, metal welding and some medical treatments. Laser processing often leads to changes in a material’s mechanical and/or chemical properties [46]. A focused laser beam can deliver a large amount of energy quickly and locally, ensuring versatile and precise processing with spatial resolution down to the nanometre scale. One of the most popular applications for this well-established
technology is laser micromachining. It is a complicated process that may involve a variety of mechanisms, including melting, vaporization, material expulsion by recoil pressure, explosive boiling, plasma formation, plasma shielding by ejected material, and hydrodynamic instabilities [47].

Laser micromachining can also be applied to solar cells and is capable of reliably forming grooves [5, 9] and heavily doped regions [17, 19, 34]. In BCSC laser ablation is used to create grooves with 40 μm depth and 20 μm width and the heavy doping along the groove wall is introduced in slow high temperature diffusion subsequent to the laser damage etching inside the groove [5]. The first aim of this project is to use laser micromachining techniques to form grooves while selectively doping material along the groove walls in a simultaneous step. This process aims to retain as much of the molten silicon inside the grooves as possible to create the heavy doping along the groove walls as oppose to the laser ablation and subsequent diffusion process in BCSC. Although both BCSC and laser doped and grooved cells have grooves created by laser scribing, the mechanism and resulted groove geometries are completely different. Therefore, the laser process mechanism as well as laser parameters required for the laser doping and grooving process is quite different from the BCSC. This section discusses the procedure used and the potential mechanisms that cause modification to the surface morphology, resulting in the possibility of forming a crater or groove using laser processing.

2.3.1 Surface melting and convection
A material surface becomes liquefied if its temperature reaches the material’s melting point which can be achieved through absorbing energy from incident laser irradiation. Upon removal of the radiation, re-solidification occurs and, depending on the laser condition, the surface will be modified to a certain extent. Several absorption mechanisms are involved in semiconductors absorbing laser irradiation [48]:

a. Lattice vibrations are excited by absorption of photons with energy well below the bandgap energy;

b. Free or nearly free carriers are excited by absorption of light with energy smaller than the bandgap energy, which are always present due to temperature or doping;

c. Electron – hole pairs are excited by photons with energy higher than the bandgap energy;

When the mean square root amplitude of the lattice vibration becomes equal to some critical fraction of the mean radius of the unit cell [49], melting starts as the lattice atom structure rearranges to change phase from solid into liquid.
Figure 2-6 illustrates the surface temperature behaviour when a material is heated by a single laser pulse with $\tau_l$ pulse duration [46]. The surface temperature increases gradually to the melting temperature $T_m$ during $\tau_m$. As the substrate continues to absorb energy from the laser beam, the surface temperature stays relatively unchanged, only increasing slowly as the absorbed energy is used to change the phase of the material from solid into liquid, i.e. melting the material. Subsequent absorption of energy continues to heat the material until the peak temperature is achieved at the end of the pulse $\tau_l$. The material then cools and resolidifies within $\tau_s$. For many applications the duration of the molten phase $\Delta t_m$ is important. It depends on $\tau_m$ and the melt depth required in the process.

Surface melting may result in the generation of convective flux in the liquid layer, which could also change the surface morphology and plays an important role in material transport such as laser doping. Convective flux may result from changes in material density due to temperature gradients and surface tension effects. With focused laser light, the latter is more pronounced. The direction of the convective flux depends on the sign of $\frac{d\sigma}{dT}$, where $\sigma$ is the surface tension. This effect may result in surface deformations as shown in Figure 2-7, a) describes the situation when surface tension decreases with increasing temperature, and b) shows the case where the surface tension increases with increasing temperature [46].
The surface tension of Si decreases with increasing temperature according to the Equation 2-1 [50]. Hence the direction of conductive flow would be similar to a) in Figure 2-7 where a crater may form in the middle of the melt. Depending on the temperature gradient of the melt and its interaction with the laser beam, the crater size and depth may vary. If the depth of molten Si could reach more than a few microns and Si re-solidifies before the laser induced flow refills the crater, a desired geometry for laser doping and grooving might be achievable.

\[
\sigma(T) = 765 - 0.016(T - T_m)
\]  \hspace{1cm} \text{Equation 2-1}

**2.3.2 Vaporization and liquid-phase expulsion by recoil pressure**

One of the most widely used laser application is local material removal via ablation. Ablation is a general term that describes material removal processes involving one to a few physical mechanisms. Among them is material vaporization accompanied by liquid-phase expulsion. High laser intensities generate significant material vaporization and a dense vapor plume is formed (Figure 2-8). A fraction of the vapor phase material becomes ionized as the intensity increases, resulting in a vapor/plasma plume consisting of electrons, atoms, ions, molecules and clusters. A recoil pressure is generated when species leave the molten surface, which causes and expulsion of liquid which happens mainly near the edges if the irradiated area as shown in Figure 2-8 [46, 51].
Recoil pressure during laser processing was studied as early as the 1960s, where Anisimov et al. [52] presented the following expression for recoil pressure $p_{rec}$ by solving the conservation equation of molecules across the Knudsen layer:

$$p_{rec} = 0.56 p_{sat}(T_s)$$  \hspace{1cm} \text{Equation 2-2}

where $p_{sat}$ is the saturation pressure of the vapor at surface temperature $T_s$.

More recently, Galasso et al. [53] presented an expression (Equation 2-3) for the recoil pressure to describe the velocity of mass flow. The recoil pressure pushes stationary molten material at the bottom of the crater towards the atmospheric pressure region, resulting in a movement of molten material towards the surface along the crater wall as shown in Figure 2-9.
\[ p_{rec} = \frac{1}{2} \rho v_m^2 + p_{atm} \rho gh_c + \frac{2\sigma(T)}{h_m} \]  

Equation 2-3

Where \( \bar{\rho} \) is the average density at between melting temperature and the surface temperature, \( v_m \) is the mass velocity, \( h_c \) is crater depth, \( h_m \) is melt thickness and \( \sigma \) is temperature dependent surface tension. The expression for mass velocity, neglecting the gravity component in the Bernoulli balance is as follows [53]:

\[
v_m = \sqrt{\frac{2(p_{KL}-p_{atm}) - \frac{\sigma(T)}{h_m}}{\rho}}
\]

Equation 2-4

where \( p_{KL} \) is the pressure at the outer side of the Knudsen layer.

Molten material expelled by liquid-phase expulsion can result in a dent or crater in the material’s surface. The resulting morphology depends on material properties, laser parameters, and the interaction between the cooling material and incident laser beam. For metals, if the surface temperature is not significantly higher than the melting temperature or the evaporation rate is low, there might not be a noticeable recoil pressure. For higher surface temperatures, which can be achieved using increased laser intensities, recoil pressure is the dominant factor removing melt from the irradiated interaction zone under hydrodynamic flow. At even higher surface temperatures, the evaporation effects dominate [54].

Lee et al. [55] measured the recoil momentum during laser ablation of Si under 532 nm Nd:YAG laser illumination by using a cantilever. The recoil pressure increased from below \( 40\times10^9 \) Pa to over \( 200\times10^9 \) Pa for laser irradiance from \( 70\times10^9 \) W/cm\(^2\) to close to \( 300\times10^9 \) W/cm\(^2\) in a linear relationship. The authors suggested that this large recoil pressure could result from a complicated ablation processes that involve plasma formation and phase explosion. They also photographed the shockwave and ablation plume, showing clearly the propagation of the shockwave and the lasting ablation plume continuing several microseconds after the irradiation had ceased.

The mechanism of liquid-phase expulsion has the potential to form selectively doped grooves if the crater resulting from the expulsion and/or after melt backflow only happens at the centre of the melt, retaining doped molten material along the crater wall, and if parameters could be controlled to form a series of connected craters to form a groove. Of key importance will be the length of time the silicon remains molten before resolidifying since this will determine whether dopants entering the molten silicon will have sufficient time to redistribute throughout the molten region before it solidifies.
2.3.3 Plasma filled keyhole
Lasers are a common tool for welding. At low to moderate laser intensities, the welding type is conduction limited as shown in Figure 2-10 a) where no significant vaporization occurs. With higher laser intensities that cause sufficient material vaporization, a vapor cavity is formed in the melt pool, as shown in Figure 2-10 b). This is known as deep-penetration laser welding, where laser illumination is strongly absorbed due to multiple reflections and plasma-enhanced coupling within the keyhole. With a scanning laser beam, the molten material ahead of the laser spot flows around the keyhole and solidifies behind it. For a continuous wave (CW) laser scribe, the maximum temperature point is located behind the laser beam centre instead of coinciding with the true centre of the beam [46]. High speed photography [56] has revealed that a rapid melt flow around the keyhole is induced by recoil pressure. This significantly affects the shape of the keyhole opening and the vapor jet emitting from it. Comparison between experimental data and calculations based on capillary surface wave and volumetric melt motion has shown that it is satisfactory to assume that there is significant volumetric melt motion during the laser-material interaction.

![Figure 2-10 Models for laser welding [46]](image)

If the void created via the keyhole could be retained during cooling, instead of having the melt flow around it and re-solidify behind it closing the void, a continuous groove might be formed by a scanning laser beam.

2.3.4 Explosive boiling
Explosive boiling or phase explosion during laser processing is another mechanism that may result in a dent or crater on material surfaces. Theoretical analysis in the 1970s [57] found that, for certain laser and material properties, the material subsurface temperature may be higher than the surface temperature resulting in explosive material removal and has predicted material removal proceeding after the laser pulse has ended. Rapid heating from laser pulses can result in a superheated molten layer, which is metastable when temperature reaching over $0.8 T_{rc}$ (thermodynamic critical temperature) [58, 59] and leads to fluctuations in density [60].
These can result in vapor bubbles being developed and trapped in the buried superheated liquid. Once the bubble size reaches a critical radius, they transform into a mixture of vapor and liquid droplets ejecting from the surface, described as explosive boiling [57-62]. The ejection of material has been observed to continue after the laser pulse has finished [57, 62-64]. Because of the cooling effect on the surface, the maximum temperature may lie underneath the surface of the molten pool [57, 63], and in some cases, this could lead to a second re-solidification front to develop at the surface [65, 66].

Craciun et al. [67] found that a 1064 nm Nd:YAG laser incident on single crystal silicon at low fluences was able to form a crater with a frozen wave morphology at the centre. It was found that trapped bubbles and big bubbles form from the merging of multiple smaller ones up to several microns deep at fluences higher than 3 J/cm², suggesting explosive boiling during nanosecond laser ablation of silicon. However, a similar effect was not observed when using a 266 nm wavelength laser with fluences up to 18 J/cm², which could be due to the small thickness of the molten layer resulting from the high absorption coefficient of the silicon at 266 nm.

Yoo et al. [64] pulsed a 266 nm Nd:YAG nanosecond laser beam on crystalline silicon at irradiances from 1×10⁹ to 1×10¹¹ W/cm². Time resolved shadowgraph images (Figure 2-11) showed that for energy intensities higher than 2.2×10¹⁰ W/cm², micrometer sized droplets leave the silicon surface after an approximate 300 ns delay and lasted up to 30 μs after the single laser pulse finished. The pulse duration was 3 ns. For a few nanoseconds following the pulse, a shockwave propagated from the silicon surface into the air. Then, after a few hundred nanoseconds delay, mass leaving the silicon surface begin to appear. The ejection of particles lasted about 30 μs. Lu et al. [68, 69] demonstrated that thermal diffusion and subsequent explosive boiling after the pulse may be the primary source of the delayed mass ejection observed around 2.2×10¹⁰ W/cm² for a 266 nm laser and at 4×10¹¹ W/cm² for a 532nm laser. They also showed that a plasma shielding effect can modify the threshold of such a phenomenon significantly. Delayed mass ejection following laser radiation has also been observed in other materials [70-72].
Explosive boiling is another mechanism that is potentially suitable for creating selectively doped grooves. This is possible only if a small and controlled amount of molten material is ejected, retaining most of the molten silicon (selectively doped while molten) and leaving a crater on the surface due to the ejection. A series of these craters could then be connected to form grooves.

2.3.5 Hydrodynamic Instability
Instabilities are observed in many types of laser processing. They are caused by small perturbations of the system, which grow with time. Their development can lead to the formation of periodic structures. Coherent or non-coherent structures can originate from mechanisms such as local thermal expansion, changes in optical or thermal properties, surface tension effects, surface acoustic waves, capillary waves, melting, vaporization, transformation energies, chemical reactions, and several other processes [46].

Hydrodynamic motion within the molten surface and/or liquid or gaseous ambient media are important in many types of laser processing. These motions and their interactions can lead to the development of instabilities. Such hydrodynamic instabilities can be grouped according to the Kelvin-Helholtz (KH) and Rayleigh-Taylor (RT) classifications [73]. KH instabilities are developed at liquid interfaces when different layers are in relative tangential motion, which could be related to the lateral expansion in vapor, the liquid layer motion due to recoil pressure, gas jets in liquid-phase expulsion, or surface tension effects. These tangential motions excite capillary waves in the molten surface. Once the velocity exceeds a critical value,
unstable perturbation occurs [46]. RT instabilities happen at interfaces between fluids of different densities that are superimposed and are under an external force. The force is from the high density fluid to the low density one. Further development of the instability may lead to turbulent mixing.

Hydrodynamic instabilities can result in surface corrugations and the formation of droplets (Figure 2-12). Depending on the laser processing condition, the size of the droplets can vary from 0.05 μm up to several hundred microns, with a formation time from a couple nanoseconds to milliseconds. Surface corrugations may be formed due to KH instabilities and/or the instabilities of the evaporation front causing solidification between successive pulses. With multiple pulse irradiation and low to medium laser influence, only a thin layer becomes molten during each pulse. The liquid moves out of the valley due to pressure or other factors, increasing the amplitude of the corrugation (Figure 2-12 b)). Near the peaks the motion results in a centrifugal acceleration, this may develop an RT instability and form droplets. If the amplitude becomes large, shear-flow KH instabilities may develop (Figure 2-12 c)). If the amplitude is large enough, the mechanism may cause necking and formation of particulates with diameter up to several microns [46].

Figure 2-12 Droplet formation due to hydrodynamic instability during laser induced melting and ablation a) tangential velocity excites surface capillary wave. b) with multiple pulse irradiation, motion of the liquid from the valley of the capillary waves increases the corrugation. c) shear-flow KH instability. d) Necking and formation of solid particulates [46]

Brailovsky et al. [74] suggested three types of instability leading to droplet formation and macro particle ejection from the melt surface. The droplets are believed to be formed due to breakaway of liquid at the peak of an aperiodically unstable capillary wave. The first
mechanism is associated with the instability of the plane of liquid evaporation, where surface structure is formed due to modification of pressure in the near surface layer followed by melt outflow and re-solidification, shown in Figure 2-13. The pressure near the concave region is higher than that above the convex part, forcing molten material to outflow to the humps, which increases local curvature and the depth of pressure modification.

Figure 2-13 Melt-droplet formation and breakaway [74]

The second mechanism works when multiple laser pulses are required instead of one to eject droplets. Melted material outflows from pits to humps. It experiences centrifugal force around the convex area, which may introduce Rayleigh-Taylor type instability at the liquid vapor interface, shown in Figure 2-14.

Figure 2-14 Droplets formation due to Rayleigh-Taylor instability at the convex area [74]

The third mechanism occurs when the humps develop into vertical columns. Because the vapor velocity is higher than the liquid layer, Kelvin-Helmholtz instability may develop at the column surface, Figure 2-15. Particles with radii up to 10 \( \mu \text{m} \) could result from multiple pulses. Other instabilities may introduce droplets formation as well. The specific mechanism is determined by the instability increment.
Brailovsky et al. [74] has specified the dispersion equation of the surface capillary wave and the condition for forming droplets due to the three types of hydrodynamic instabilities.

For the purpose of this project, the laser process needs to dope the molten material and retain the doped material as much as possible while forming a groove on the material surface. The hydrodynamic instability effects described in this section seem to be good candidates to fulfill these conditions if the amount of instability can be controlled such that few droplets form while the pit depth is maximized. This could be the case at the stage where droplets are just about to break away from the melt surface at the top of the humps.

### 2.3.6 Laser ablation

Laser ablation is a general term describing the process of material removal by laser. It is a complicated process which could involve material melting, vaporisation, sublimation, expulsion by recoil pressure, plasma formation, explosive boiling, hydrodynamic instability and the interaction of these phenomenon with the incident laser beam.

Laser ablation has been employed widely in the manufacturing of microelectronics devices, in processes such as drilling, cutting, and marking [75]. In these processes it is important to have little melt residues or molten material re-deposition upon cooling, in order to increase micromachining accuracy and resolution. Substantial research has been carried out towards improving laser ablation efficiency and effectiveness, often with a particular focus on the reduction of melt re-deposition or debris formation. Comparisons between nanosecond laser ablation and ultrashort (picosecond or femtosecond) pulse ablation of silicon using the same laser irradiance have revealed that ultrashort pulses remove silicon mainly by sublimation due to large amounts of energy being deposited in an extremely short time, whereas nanosecond laser ablation creates a super-heated melt which is removed by expulsion leaving behind a thick layer of cooled molten silicon upon removal of the radiation [76-81]. In terms of
wavelength, it is reported that short wavelengths such as those in the ultraviolet range (UV) are more energy efficient for ablation as they are absorbed strongly by silicon and less by the laser induced plasma [77]. Conversely, infrared (IR) laser beams provides the benefit of being able to penetrate deep into the silicon bulk, making it suitable for cutting or hard marking [75]. There are relatively more studies on silicon ablation by UV lasers [77-80, 82, 83] and IR lasers [76, 81, 84-88] than mid-range visible lasers [77, 89-91].

Nanosecond laser silicon ablation thresholds using different laser wavelengths have been reported in the literature and are summarized in Table 2-2. There are limited reports on the 532 ns laser ablation threshold for silicon. However, the ablation thresholds for wavelengths from UV light to IR light range from $4 \times 10^7$ W/cm² to $5 \times 10^8$ W/cm².

This section has reviewed several potential mechanisms that are suitable for the formation of grooves on the surface of silicon by laser processing and also retain the molten layer along the groove walls in a simultaneous step. The rest of this chapter reviews the potential for hydrogen to be used to passivate residual laser-induced defects and unwanted impurities in Si before entering Chapter 3 which presents the development of simultaneous laser doping and grooving emitter formation.
<table>
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<th>Ablation threshold (W/cm²)</th>
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<td>$4 \times 10^8$</td>
<td>[84]</td>
</tr>
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<td>$4.8 \times 10^8$</td>
<td>[92]</td>
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<td>[86]</td>
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<tr>
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<td>30 ns</td>
<td>$5 \times 10^7$</td>
<td>[82]</td>
</tr>
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<td>[79]</td>
</tr>
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<td>20 ns, 5 ns</td>
<td>$1 \times 10^8$, $3.5 \times 10^8$</td>
<td>[93]</td>
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<td></td>
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<td>Nd:YAG, 10 ns</td>
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<td>[90] (Chinese)</td>
</tr>
</tbody>
</table>
2.4 Hydrogen in silicon

The second part of this thesis follows naturally if the aims of the first part involving the development of a laser doping and grooving process are successfully achieved. Inevitably, such a localised laser-based process that involves melting and potentially ablating the silicon, will lead to some level of laser-induced defects. Even with optimised laser processes, it would be expected that enhanced hydrogen passivation of the remaining defects (and potentially other forms of recombination) could potentially significantly reduce the impact of such defects and enhance device performance. The second part of the thesis will therefore aim to utilize lasers to enhance the hydrogen passivation of defects (hydrogenation) by controlling the charge state of the hydrogen atoms within the silicon to enhance their diffusivity and reactivity. This section reviews the impact of the charge state of interstitial hydrogen in Si, manipulation of the hydrogen charge state by illumination, and hydrogenation of defects in silicon.

Hydrogen is one of the fundamental elements of the universe. It is believed that over 90% of the universe was made up of just hydrogen and helium after the big bang. Hydrogen has an atomic number of 1 and has the simplest atomic structure with one proton and one electron. An electrically neutral hydrogen atom has one proton and one electron bound to the nucleus by Coulombic force. The atomic radius of hydrogen is 53 picometres and the Zemach radius of the proton is just 1.08 femtometers \[94\]. Because of its small size, light weight and simple atomic structure, hydrogen moves and combines easily with other elements, making it an ideal candidate for passivating defects in solar cells.

2.4.1 Charge state of interstitial hydrogen

Interstitial hydrogen within silicon can exist in any one of three charge states; it could have no electron to form H\(^+\), one electron to form neutral H\(^0\), or two electrons to form H\(^-\). In thermal equilibrium in \(p\)-type silicon most atomic hydrogen is H\(^+\) due to the shortage of electrons, and in \(n\)-type silicon most of hydrogen is H\(^-\) due to an abundance of electrons. Figure 2-16 shows that H\(^0\) cannot reach a large concentration in equilibrium. However, the relative concentration of each of the various hydrogen charge states in silicon is influenced by the Fermi level \(E_f\). Changing its position relative to the middle of the band-gap \(E_g\) would change the amount of electrons available to bond and hence the concentration of charged hydrogen atoms \[21\].
2.4.2 Hydrogenation of defects in silicon

Hydrogen passivation of defects (hydrogenation) in solar cells has been widely studied. This section reviews defects in silicon solar cells and the application of hydrogenation to passivate them.

B-O defects

Commercially produced monocrystalline silicon solar cells are most commonly made with $p$-type Cz wafers, which are known to degrade when subjected to illumination. This light induced...
degradation (LID) effect is due to the formation of boron-oxygen (B-O) defects [98, 99]. Reducing the formation of B-O defects by using lightly diffused wafers or replacing B with gallium can avoid such degradation. However, it is difficult to form good screen printed contacts on lightly diffused emitters and large resistivity variations are observed in gallium doped wafers due to gallium’s low segregation coefficient [100]. The majority of commercial cells are therefore still made from B doped Cz wafers and still suffer from LID to some extent.

It has been shown that B-O can be permanently deactivated by heat treatment under illumination [22, 101-103]. The presence of hydrogen and the charge state of the interstitial hydrogen have been proven to be critical for the permanent deactivation of B-O defects [104, 105]. Hallam et al. [103] showed that by controlling the charge state of hydrogen, B-O can be permanently deactivated [96].

**Metal impurities**

For PV to become dominant over fossil fuels, continuing improvement of solar cell efficiency and reduction of the cost per watt is required. To reduce the cost, alternative purifying and wafering methods for creating Si substrates have attracted interest. One example of this is the use of upgraded metallurgical-grade silicon (UMG) material. The tradeoff in this case is that the wafers can be produced at a lower cost, but more defects and impurities would result in the substrate, including metal impurities. Figure 2-17 shows the transition energy levels for some of the metallic impurities as well as that of the hydrogen [25]. It is shown that most of the metallic impurities in p-type silicon would prefer the positive state. As discussed earlier, the dominant charge state of hydrogen in p-type Si at room temperature is H⁺, which is not the preferred state for passivating these metallic impurities as coulombic repulsion will inhibit interaction. Therefore it is important to be able to control the charge state of hydrogen in order to effectively passivate metallic impurities.
Hamer et al. [25] reported that by controlling the charge state of hydrogen via illumination, the lifetime of UMG samples was significantly improved. Liu et al. [23] found that the reduction of interstitial iron concentration in multicrystalline Si was not caused by gettering or enhanced diffusivity, but conjectured to be the bonding of positively charged iron with negatively charge H⁻.

**Structural defects**

Structural defects such as localized dislocations and other crystal defects are detrimental to minority carrier lifetime [106-109]. The ability to passivate crystallographic defects is important if a solar cell is to achieve a high open circuit voltage ($V_{oc}$), FF and efficiency. Hydrogen has been found to be able to passivate dislocations in Si up to 250 μm deep [110]. Sopori et al. [111] showed that vacancies in the Si structure could increase the diffusivity and solubility of hydrogen in Si.

Localized laser processing introduces plastic deformation and other crystallographic defects into Si [19, 112], which are structural defects that would decrease minority carrier lifetime and diminish the electrical properties of a finished solar cell [113]. Benton et al. [114] and Hallam et al. [24] have previously demonstrated that laser induced defects can be passivated by hydrogen.

Many types of defects and impurities that could reduce minority carrier lifetime can exist in Si. Hydrogen has been widely reported to be able to passivate these defects, and is particularly effective when the charge state of hydrogen is controlled to encourage bonding with charged defects. The next section reviews the control of hydrogen’s charge state by illumination.
2.4.3 Manipulation of hydrogen charge state by illumination

As discussed earlier, the charge state of hydrogen in Si could be manipulated by changing the Fermi level relative to the mid band gap. Carrier injection via illumination is one simple and effective method to achieve this.

The 1st generation of UNSW’s hydrogenation process [22, 103, 115] can be easily implemented in a belt furnace where only the top lamps are used to maintain the temperature. This forces the top lamps to increase power output and therefore light intensity, which enables better control of the hydrogen charge state. In this technology the hydrogen source is the SiN$_x$ layer, which is also the ARC and plating mask. Therefore it is very simple to implement and is compatible with current commercial production technology. In fact, it is already used by many companies commercially.

There are some limitations of using a belt furnace to implement the hydrogenation process, especially for carrying out systematic experiments and research. Hamer et al. [25] implemented the technology using illumination from a 660 nm LED and a hotplate, achieving significantly enhanced hydrogenation of defects by controlling the charge state.

The second part of this thesis details the progression of this approach of using illumination and temperature to control hydrogen charge state. A new laser hydrogenation tool is developed to significantly enhance the ability to control the charge state of hydrogen. This setup does not require high temperature processing as with the furnace implementation, it therefore requires a much lower thermal budget and is compatible with cell structures that are sensitive to high temperature processes.
2.5 Conclusion
This chapter reviewed conventional screen-print cell technology vs. high efficiency cell structures with selective emitters. It was proposed that a laser doping and grooving technique could capitalize on the advantages of the BCSC approach but with the simplicity of LDSE solar cell fabrication. The potential for hydrogen to be used to passivate residual laser-induced defects and unwanted impurities in Si was also reviewed with an emphasis on the charge state control of interstitial hydrogen. A laser hydrogenation system was identified to be a useful tool to further enhance the ability to control the charge state of hydrogen. Chapter 3 presents the development of the simultaneous laser doping and grooving emitter formation; Chapter 4 presents the development of the advanced laser hydrogenation; and in Chapter 5 solar cells processed using the laser doping and grooving are fabricated and incarnated with the advanced laser hydrogenation process. Chapter 6 presents two prototype industrial tools based on the advanced hydrogenation, demonstrating the feasibility of using LED based light sources as replacement for lasers in commercial production tool to implement the advanced hydrogenation technology.
Chapter 3

3 Selective emitter formation through simultaneous laser doping and grooving

The first part of this thesis develops a new laser doping and grooving process which capitalizes on the major benefits of both BCSC and LDSE cells. This chapter presents the development of simultaneous laser doping and grooving process by introducing the concept of laser doping and grooving following the details of the laser equipment, followed by the optimization of the groove geometry, a proposed groove formation process, and the junction quality of laser doped grooves. This process is further developed into a cell structure and presented in Chapter 5.

3.1 Q-switched laser

3.1.1 Suitability
As discussed in Section 2.3, most laser processes which modify material morphology are based on pulsed laser beams, such as Q-switched lasers. Dauer et al. [116] deposited gold film on silicon substrate to create resistors by direct writing using a 532 nm Q-switched laser, with a small amount of droplets found on the surface and little damage to the substrate. Most of the melted material formed a 3 to 6 μm wide bulge with 2 to 3 μm height (Figure 3-1) [116].

![Figure 3-1 Cutting kerf from different focal distance [49]](image)

During the investigation of the influence of laser power from a 532 nm Q-switched laser on the properties of laser doped solar cells [20], Hameiri found that a p-n junction could still be
formed when using a laser diode current high enough to cause ablation. However, most of these junctions were not continuous (Figure 3-2), possibly due to cracks or defect formation.

Figure 3-2 EBIC cross-sectional scan highlighting p-n junctions formed by laser doped lines with high laser diode current [20]

The geometry of the structures in Figure 3-1 and Figure 3-2 achieved using 532 nm Q-switch lasers could potentially be suitable for forming grooves with selectively doped walls, provided that the grooves can be made clean and continuous and that the doping along the groove walls is uniform and also continuous.

A pulsed nanosecond 532 nm green laser is much cheaper than a UV laser and is suitable for the laser doping and grooving project. A nanosecond pulse ensures there is a molten pool of silicon formed at the surface, which is doped to form the selective emitter. The optical penetration depth of 532 nm light into silicon is about 0.5 μm, which ensures the molten pool extends far enough for form a deep p-n junction. The pulsed nature of the laser beam is also important. The energy of the electromagnetic wave is delivered onto the silicon surface in timed small packages. This pulsed characteristic allows the molten pool to cool between pulses and it produces a shockwave which helps the formation of grooves.

Therefore, a 532 nm Q-switched laser (Figure 3-3) has been selected for this work. The specification of the laser from the manufacturer is summarized in Table 3-1. Appendix C includes details of achieving laser power stability. The system has a scribing stage that moves in the X and Y directions while the laser beam stays stationary.

Laser parameters such as average laser power, scribing speed and pulse frequencies were tested to optimize groove geometry in Section 3.3. Throughout this chapter measured average laser power in watt (W) is used to indicate the different intensities of the laser beam. The unit of scribing speed is mm/s and the unit of pulse frequency is kHz, both of which are the set parameters of the laser system.
Table 3-1 Yuemao laser specification

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser medium</td>
<td>Nd³⁺:YVO₄</td>
</tr>
<tr>
<td>Wavelength</td>
<td>532 nm</td>
</tr>
<tr>
<td>Beam expanded angle</td>
<td>≤ 2.0 mrad</td>
</tr>
<tr>
<td>Beam power</td>
<td>0 – 5 W</td>
</tr>
<tr>
<td>Modulated frequency</td>
<td>0 – 100 kHz</td>
</tr>
<tr>
<td>Scribing speed</td>
<td>0 – 300 mm/s</td>
</tr>
<tr>
<td>Pulse full width at half maximum (FWHM measured by Dr. Hameiri)</td>
<td>35 – 45 nm [15]</td>
</tr>
</tbody>
</table>

3.2 Concept of laser doping with grooving

Once a method to maintain an adequately controllable operating condition was established, the laser parameter space was explored to form narrow grooves on Cz p-type Si wafers while simultaneously heavily doping the groove walls to form selective emitter regions in preparation for metal contact formation. After exploring the laser parameter space and studying the geometry of the grooves, optimal groove geometry was achieved using a range of laser parameters, as shown in the next section.

Figure 3-4 is a scanning electron microscope (SEM) image of a typical groove cross-section. All
the SEM images in this chapter are taken after the laser doping and grooving process to examine the geometry of the grooves. The groove width and depth are estimated from these images according to the scale on the bottom right of the image as indicated by the two arrow bars in Figure 3-4. At this point there is no coating layer on top of the Si surface and the samples are textured wafers with laser doped grooves on them. Unless stated otherwise, the SEM images are taken cross-sectional to the grooves by snapping through it perpendicularly from the rear surface of the sample. It can be seen in Figure 3-4 that the melted Si is pushed up to the sides and leaves only a small gap during epitaxial re-solidification throughout the cool down process. The pyramids next to the melted region are clearly visible, which suggests that the level of laser induced stress and defects are not enough to destroy the texturing at the close vicinity of the groove. The laser beam diameter used is 10 to 15 μm. One of the innovative features of this process is that by using the epitaxial regrowth of heavily doped silicon in the groove walls, the groove formed is only 3 to 5 μm wide and 10 to 15 μm deep, despite using a laser-beam diameter of 10 to 15 μm. This optimal geometry ensures that the grooves are deep enough to provide good metal contact adhesion strength for subsequently plated contacts [50] but not too deep to introduce excess laser damage that generates high dark saturation current. Additionally, the narrow width of the grooves ensures that during the dielectric layer deposition after groove formation there is only minimal deposition inside the grooves, leaving the groove walls exposed to allow nucleation during the subsequent plating process. The key to enabling this innovative approach to work effectively by creating these narrow, heavily doped grooves with deep junctions, is to use the right laser pulse duration, frequency and power, with each parameter needing to be carefully controlled. This is so that the energy delivered to the molten silicon is sufficient to create a level of expansion or turbulence within the molten region that literally pushes about 10% of the molten silicon out of the groove region and to a location above the original wafer surface. This characteristic can be clearly seen in the grooves shown in Figure 3-4 where it is observed that the silicon at the mouth of the grooves extends several microns above the original silicon surface. This importantly reduces the molten silicon available within the groove during the epitaxial regrowth process, leaving an insufficient amount to return the silicon to its original state whereby the groove would be completely filled in and the groove width shrinks to zero. Importantly, this penetration of the silicon above the wafer surface at the mouth of the grooves and the associated volume of silicon, ultimately determines the groove width and therefore the effectiveness of this technology. As will also be appreciated, the width of these grooves relative to the laser beam diameter (which determines the width of the molten
region) is what then determines the distance between the resolidified surface and the silicon surface from which the epitaxial growth nucleates. In other words, if the epitaxially regrown region is heavily doped and of opposite polarity to the silicon wafer, then the width of the new groove relative to the laser-beam diameter then determines the depth of the junction formed by the epitaxially grown heavily doped silicon. As explained, this is also an important parameter.

![Cross-section SEM images of two representative examples of a groove](image)

Figure 3-4 Cross-section SEM images of two representative examples of a groove

A large range of laser settings could be used to reliably form grooves with desired geometry of 10-15 μm depth and 3-5 μm width. Such a groove geometry has numerous benefits as it ensures that the grooves are: 1) Sufficiently deep to provide good metal contact adhesion without causing significant damage to the Si; 2) narrow enough to prevent the dielectric layer from being significantly deposited inside the groove; and 3) wide enough to allow easy nucleation during plating. It is also important to produce continuous grooves with uniform and smooth surfaces along the groove wall and Si top surface, which will ensure uniform dielectric layer deposition and metal nucleation. The next section discusses how this geometry is achieved in further detail.

3.3 Groove geometry optimization

As discussed in Section 2.3 there are several potential mechanisms that are suitable for the formation of grooves on the surface of silicon by laser processing and also retain the molten layer along the groove walls in a simultaneous step. This molten layer would be incorporated with dopants while in the molten state and thus forms a p-n junction after epitaxial re-growth. The first aim of this project is to find laser conditions that can create selectively doped grooves and to then look at the possibilities of developing such technology towards solar cell fabrication.
3.3.1 General trends
To test the laser parameter space, textured Cz p-type wafers with a resistivity of 1.6 $\Omega \text{cm}$ and thickness of 180 $\mu\text{m}$ were scribed under different laser settings. A group of 10 lines were scribed for each parameter setting. The spacing between each line was 50 $\mu\text{m}$. The varied parameters were measured: average laser power, scribing speed, and pulse repetition rate. The cross sections of scribed lines were studied under SEM.

Figure 3-5 plots the depths of grooves vs. scribing speed at six different power levels, all at a frequency of 100 kHz. There is no groove formation when the average laser power is below 0.63 W. The depth of groove increases with increasing power and decreases as scribing speed increases. The three images on the left are SEM images of three data points on the graph. It is observed that when the scribing speed and frequency are constant, the depth of the groove increases with power.

Figure 3-6 plots the width of the groove opening vs. scribing speed at six laser power levels and a frequency of 100 kHz. The three SEM images on the left illustrate that under constant laser power and frequency, groove width increases with increasing scribing speed. When the speed is increased, the overlapping ratio of successive pulses is reduced. Therefore a smaller amount of silicon has the chance to be re-melted and fill up the groove cavity by epitaxial growth along the groove wall.
The effect of the repetition rate of laser pulse was also studied. Table 3-2 shows SEM images of grooves that were scribed at different laser frequencies with a 100 mm/s scribing speed and 0.66 W average laser power. When the laser frequency is high, the pulse-overlapping ratio is high, allowing more silicon to be re-melted and re-doped. Therefore the higher the laser frequency the more uniform the resulting groove is.

Table 3-2 Effect of frequency on groove geometry at 0.66 W and 100 mm/s

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Groove Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 kHz</td>
<td><img src="image1" alt="SEM image of groove at 100 kHz" /></td>
</tr>
<tr>
<td>90 kHz</td>
<td><img src="image2" alt="SEM image of groove at 90 kHz" /></td>
</tr>
<tr>
<td>80 kHz</td>
<td><img src="image3" alt="SEM image of groove at 80 kHz" /></td>
</tr>
<tr>
<td>70 kHz</td>
<td><img src="image4" alt="SEM image of groove at 70 kHz" /></td>
</tr>
</tbody>
</table>

Exploration of the laser parameter space showed that, as expected, the depth of laser doped groove increases with laser power. However, it was also found that the groove width increases with scribing speed, and the uniformity improves with increasing pulse frequency. Grooves with a depth of 0 – 40 μm and width of 0 – 20 μm can be produced by varying the laser...
parameters. The aim of this work is to have laser doped grooves deep enough to provide excellent metal adhesion strength, but not so deep as to cause excess damage introduced by high laser power which can result in a detrimental increase in dark saturation current caused by the heavily doped selective emitter region along the groove walls. The width of the groove needs to be narrow enough so that during dielectric layer deposition there is minimal penetration to within the grooves, leaving the heavily doped groove walls mostly exposed to allow nucleation during subsequent plating. The grooves also need to be wide enough to allow plating solution to easily get into the groove and replenish during metal contact plating. In the next section the parameter space is further narrowed down in order to form grooves with optimal geometry.

3.3.2 Clarification of the parameter space

The adhesion strength of plated contacts has been demonstrated to be greatly improved by forming anchor points or grooves on Suntech’s Pluto production line [117, 118]. Wenham et al. [117] found that grooves need to be deeper than 10.5 μm in order to sufficiently improve metal contacts’ adhesion strength. For the purpose of this project, groove depths are desired to be deep enough to provide good adhesion strength with minimal excess damage introduced by these deep grooves. This requires a process that forms grooves around 10 μm with minimum laser energy put into the silicon. Data from Figure 3-5 indicated that 0.63 W average laser power was not enough to produce any groove while an average power of 0.80 W could produce grooves more than 15 μm deep. The laser power range from below 0.63 W up to 0.80 W was therefore explored further.

At a 100 kHz repetition rate, scribing speed was varied from 10 mm/s to 150 mm/s, and the measured average laser power was varied from 0.46 W to 0.77 W. The wafer used was a textured Cz p-type wafer with resistivity of 1.6 Ωcm and thickness of 180 μm. A group of 10 lines were scribed for each setting. The spacing between each line was 50 μm. The cross-sections of grooves were examined under SEM and summarized in Figure 3-7. Figure 3-7 (a) with 20 μm scale bar shows the typical groove geometry of each laser condition and Figure 3-7 (b) with 100 μm scale bar shows the consistency and repeatability of each condition with 5 adjacent grooves. For each laser condition, a typical groove/line from the group was imaged as well as the adjacent five grooves/lines to show the consistency and repeatability of each condition.

The groove depth was again observed to be increase with laser power and the opening width of grooves increased with scribing speed. In the lowest laser power group only surface melting
was observed for the four scribing speeds, which resulted in reflective smooth laser scribed lines after solidification. The 0.55 W group resulted in surface roughing for the higher two scribing speeds, 100 mm/s and 150 mm/s. This group and the next laser power group at 0.61 W, showed the edge conditions when grooves were just starting to form. In the 0.61 W group, a speed of 10 mm/s produced bulges of melted and re-solidified silicon, which appeared to be squeezed along the scribed line by surface capillary waves and pushed up to form bulges higher than the textured pyramids. As the speed was increased to 50 mm/s, the amount of surface disruption was just right to form a narrow and continuous groove. However, across the 10 lines in the group, not all of them resulted in a continuous groove. With the final two faster speeds, continuous and consistent grooves were formed but with wider openings and shallower depths. The 0.66 W and 0.73 W group produced clean and continuous grooves at all speeds except 10 mm/s. The 0.77 W group indicated that this power level could be too high as the grooves from the slowest two speeds closed up near the surface and the faster two speeds resulted in grooves with wide openings.

Similar laser power and scribing speed parameter mapping was carried out at 90 kHz, 80 kHz, 70 kHz, 60 kHz, 40 kHz and 20 kHz. As the pulse frequency decreased, the pulse overlapping rate was reduced, therefore resulting in less uniform surfaces. Tables of SEM images for each condition are summarized in Appendix A. These images show the same trend as the 100 kHz group whereby the groove depth increases with laser power, groove width increases with scribing speed and the surface uniformity increases with pulse frequency. The images of the 100 kHz group is presented here as this is the most relevant group because both the lifetime test samples and cell structures presented in Chapters 4 and 5 are developed from conditions within this group.

In summary, the average laser power range from 0.61 W to 0.73 W at 100 kHz with speeds of 50 mm/s and 100 mm/s appeared to be a good parameter space for producing consistent narrow grooves which were 10 – 15 um deep and 3 – 5 um wide. This range of parameters was used later on to test the damage caused by the laser doping and grooving process to carrier lifetimes.
<table>
<thead>
<tr>
<th>Laser Power Range (W)</th>
<th>0.73-0.81</th>
<th>0.70-0.75</th>
<th>0.65-0.67</th>
<th>0.58-0.64</th>
<th>0.52-0.57</th>
<th>0.44-0.51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scribing Speed (mm/s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mm/s</td>
<td>0.77</td>
<td>0.73</td>
<td>0.66</td>
<td>0.61</td>
<td>0.55</td>
<td>0.46</td>
</tr>
<tr>
<td>50 mm/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 mm/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150 mm/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3-7 (a)** Groove geometries at 100 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels with 20 μm scale bar

**Figure 3-7 (b)** Groove geometries at 100 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels with 100 μm scale bar showing 5 grooves in each group
3.4 Groove formation
As mentioned the laser diameter is 10 – 15 μm, however the formed grooves are only 3 – 5 μm wide. It is not clear exactly how the grooves are formed during the laser process. There could be a few possible mechanisms involved such as recoil pressure due to plume formed by vaporization (section 2.3.2s), explosive boiling that happened after laser pulse finishes (section 2.3.4), or hydrodynamics instability in the silicon melt (section 2.3.5). These three mechanisms are often associated with laser ablation. This section discusses the mechanisms involved and proposes a possible groove forming process.

3.4.1 Irradiance requirements
Laser ablation is a general term describing the process of material removal by laser. It is a complicated process which could involve material melting, vaporisation, sublimation, expulsion by recoil pressure, plasma formation, explosive boiling, hydrodynamic instability and the interaction of these phenomenon with the incident laser beam.

A pulsed nanosecond 532 nm green laser is much cheaper than a UV laser and is suitable for the laser doping and grooving project. A nanosecond pulse ensures there is a molten pool of silicon formed at the surface, which is doped to form the selective emitter. The optical penetration depth of 532 nm light into silicon is about 0.5 μm, which ensures the molten pool extends far enough for form a deep p-n junction. The pulsed nature of the laser beam is also important. The energy of the electromagnetic wave is delivered onto the silicon surface in timed small packages. This pulsed characteristic allows the molten pool to cool between pulses and it produces a shockwave which helps the formation of grooves.

Nanosecond laser silicon ablation thresholds using different laser wavelengths have been reported in the literature and are summarized in Table 2-2. There are limited reports on the 532 ns laser ablation threshold for silicon. However, the ablation thresholds for wavelengths from UV light to IR light range from 4×10⁷ W/cm² to 5×10⁸ W/cm².

The measured average laser powers with groove formation at f = 100 kHz in Figure 3-7 are listed in Table 3-3. Assuming that variations between pulses are negligible and a laser beam diameter of d = 15 μm with a τ = 40 ns pulse width (FWHM), the peak power and peak irradiance (Table 3-3) are calculated using Equation 3-1 and Equation 3-2. Figure 3-7 illustrated that grooves start to form at 0.61 W average laser power and can be formed consistently at an average power 0.66 W or higher. These correspond to peak irradiances of 8.6×10⁷ W/cm² and 9.3×10⁷ W/cm² respectively, which are in the range of reported ablation irradiance in the literature. This means that the formation of grooves requires laser irradiance in the vicinity of
laser ablation.

\[ P_{\text{peak}} = \frac{P_{\text{measured}} \times 1s}{t \times f} \]  
\[ I_{\text{peak}} = \frac{P_{\text{peak}}}{A} = \frac{P_{\text{peak}}}{\pi \left( \frac{D}{2} \right)^2} \]  

Table 3-3 Measured average laser grooving power and calculated irradiance and energy density

<table>
<thead>
<tr>
<th>Measured average power (W)</th>
<th>Peak power (W)</th>
<th>Peak irradiance (W/cm²)</th>
<th>Energy density (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.61</td>
<td>153</td>
<td>8.6E+07</td>
<td>3.5</td>
</tr>
<tr>
<td>0.66</td>
<td>165</td>
<td>9.3E+07</td>
<td>3.7</td>
</tr>
<tr>
<td>0.73</td>
<td>183</td>
<td>1.0E+08</td>
<td>4.1</td>
</tr>
<tr>
<td>0.77</td>
<td>193</td>
<td>1.1E+08</td>
<td>4.4</td>
</tr>
</tbody>
</table>

3.4.2 Multi-pulse effects

The laser pulse irradiance required to form grooves is in the vicinity of the laser ablation threshold for silicon. At the threshold energy level, the ablation depth of each pulse is of the order of one micrometre. Figure 3-8 shows a top view and cross sectional view of the results from a series of such pulses with little overlap. The effects of each of the pulses can be clearly seen and the cross section image shows that these pulses can create a small dent. Having pulses with the right energy level is not enough to create grooves. They also need to be pulsed in a specific sequence onto the silicon in order to form a groove. Studies on the effects of multiple moving pulses and the effect of different pulse frequencies on the ablation of silicon have seldom been reported. The laser grooving process is essentially laser scribing by using a string of moving pulses at the threshold level, and is capable of forming 3 – 5 \( \mu \text{m} \) wide and 10 – 15 \( \mu \text{m} \) deep grooves. This section discusses how the moving pulses could create grooves deeper than 10 \( \mu \text{m} \) and much narrower than the beam diameter, when each individual pulse could only result in a wide dent of no more than a couple of microns deep.
Pulse laser frequency determines the time interval between successive pulses. Together with scribing speed, they define the pulse overlapping rate for a given pulse width and duration. Change of scribing speed at fixed frequency changes the pulse overlapping rate; the slower the scribing speed the higher the overlapping rate. Figure 3-7 shows that at 100 kHz, for a given laser power, different scribing speeds would result in different groove geometry. The scribing speed and the overlapping rate are summarized in Table 3-4. The SEM images of grooves scribed at 0.66 W from Figure 3-7 are also included in the table. Assuming that the laser spot diameter is 15 μm, the overlapping rate changes from 99.3% to 90% for scribing speeds 10 mm/s to 150 mm/s. For example, when scribing speed is 10 mm/s at 100 kHz, the distance each pulse travels is 0.1 μm. Hence, with 15 μm beam diameter, the overlap between consecutive pulse is calculated to be (15 – 0.1) / 15 ≈ 99.3%. It is clear that groove geometry at these conditions is different. When the pulse overlap is more than 95%, the groove is narrow and deep, while the other two overlapping rates produce wider and shallower grooves.
Table 3-4 Pulse speed and overlapping rate at 100 kHz

<table>
<thead>
<tr>
<th>Scribing speed (mm/s)</th>
<th>Pulse speed (μm/pulse)</th>
<th>Pulse overlapping rate in % (assuming 15 μm beam diameter)</th>
<th>Groove geometry at 0.66 W average laser power</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1</td>
<td>99.3</td>
<td><img src="image1.jpg" alt="Image" /></td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>96.7</td>
<td><img src="image2.jpg" alt="Image" /></td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>93.3</td>
<td><img src="image3.jpg" alt="Image" /></td>
</tr>
<tr>
<td>150</td>
<td>1.5</td>
<td>90.0</td>
<td><img src="image4.jpg" alt="Image" /></td>
</tr>
</tbody>
</table>

An experiment was performed to confirm whether the pulse overlapping rate was the cause for groove formation. The approach used was to generate the same pulse overlap at different pulse frequencies, which involves changing the time interval between pulses but fixing the distance each pulse moves and the intensity of each pulse. It was assumed that any change in pulse shape was negligible. This was achieved by changing the pulse frequency and scribing
speed to alter the distance each pulse moved relative to the previous pulse, and adjusting the laser diode current accordingly so that the irradiance was kept at approximately $9.2 \times 10^7$ W/cm$^2$. Because of the available speed and frequency settings, only 1 $\mu$m/pulse and 5 $\mu$m/pulse could be generated at two different frequencies, with the results shown in Table 3-5. A more comprehensive table for constant pulse energy at varied pulse moving speed is in Appendix B. Very distinct groove geometries were produced for both 1 $\mu$m/pulse and 5 $\mu$m/pulse at two different pulse frequency settings. For example, in the 1 $\mu$m/pulse case: when the pulse cycle was 100 $\mu$s, a wide and shallow trench was produced, with redeposited debris and droplets covering the trench wall making it rough and messy; when the pulse cycle was 10 $\mu$s, a much narrower and deeper groove was formed, with smooth walls with the appearance of a frozen liquid layer. A similar trend was observed for the 5 $\mu$m/pulse case, shorter pulse cycles created a narrower, deeper and smoother groove.

Table 3-5 Constant pulse overlap under different pulse frequencies for pulse intensity approximately $9.2 \times 10^7$ W/cm$^2$

<table>
<thead>
<tr>
<th>Pulse Cycle</th>
<th>10kHz (100 $\mu$s cycle)</th>
<th>100kHz (10 $\mu$s cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\mu$m/pulse</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>20kHz (50 $\mu$s cycle)</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>60kHz (16.7 $\mu$s cycle)</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>5 $\mu$m/pulse</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

There could be two possibilities causing this groove geometry and morphology difference. One is that the change in pulse shape and energy distribution caused by altering the pulse frequency and diode current is significant enough to cause the geometry change. Another
possibility is that the effect of a change in the pulse shape on groove geometry is negligible, and the groove geometry difference is caused primarily by the difference in pulse cycle. Appropriate equipment for testing pulse shape and energy distribution is not available. The second possibility is considered here.

If pulse frequency plays an important role in the formation of grooves, it means that the time interval between pulses is crucial. This suggests there could be thermal residual effect after each pulse finishes. Thermal residuals introduced by pulse lasers have been previously reported in the literature. Tao et al. found that after a 200 ns pulse at a 1064 nm wavelength and irradiance of $5 \times 10^8$ W/cm$^2$, silicon surface melting continued up to 160 μs and lasted 1000 μs after 10 pulses [86]. Other groups have reported thermal residual effects after pulsing ended at higher laser intensities where explosive boiling was involved [57, 58, 62-64, 69]. Yoo et al. reported silicon droplet ejection started 300 ns after a 3 ns pulse with $2 \times 10^{10}$ W/cm$^2$ irradiance and lasted up to 30 μs. Even though in the latter case the laser intensity is much higher, it is still evident that energy from the electromagnetic wave of the laser beam is absorbed and transformed into thermal energy, and more importantly that this thermal energy remains locally and continues to change silicon property over a period of time of more than several hundred times the pulse length after the pulsing has completed.

### 3.4.3 Thermal effect modelling

It is rather hard to believe that there could be thermal effect left at the end of a 10 μs pulse cycle after a 40 ns pulse (100 kHz in Table 3-5). To further investigate the possibility of such a thermal residual effect, a MatLab silicon laser processing simulation model developed by Fell et al. [119, 120] was used to simulate the laser scribing process. This model simulates laser heating, melting and evaporation of silicon. Even though this model neglects melt fluid dynamics such as melt convection flow and the liquid expulsion effect, it provides a good thermal dynamics simulation, which could provide some insight towards the possibility of thermal residual effects. The two sets of laser parameters for the two 1 μm/pulse cases in Table 3-5 were simulated using a Gaussian pulse, the simulated parameters are listed in Table 3-6. Both conditions resulted in 1 μm/pulse pulse speed and intensity of approximately $9.2 \times 10^7$ W/cm$^2$. There were 700 successive laser pulses in each simulation. In the simulation, the pulse energy distribution, laser irradiance and distance each pulse travels are the same between the two sets. The only difference is the time interval between pulses, the pulse cycle of Set 1 is 100 μs and for Set 2 is 10 μs. Note that a 2D model based on a flat surface was used in this case.
Table 3-6 Simulation parameter sets for 1 μm/pulse for laser intensity approximately 9.2×10^7 W/cm²

<table>
<thead>
<tr>
<th>Set number</th>
<th>Pulse frequency (kHz)</th>
<th>Scribing speed (mm/s)</th>
<th>Average laser power (W)</th>
<th>Pulse length at FWHM (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>0.065</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>100</td>
<td>0.65</td>
<td>40</td>
</tr>
</tbody>
</table>

During each pulse the temperature of every heat affected point is calculated and the maximum temperature is recorded and plotted. Figure 3-9 plots the maximum temperature over the 1st and 200th pulses for parameter Set 1 where the pulse cycle is 100 μs. During the first pulse, the irradiated silicon quickly heats up to 1,938 °C and starts to cool once the 40 ns pulse finishes. The temperature continues to decrease for the rest of the pulse cycle and reduces to 30 °C by the end of the cycle. After 200 pulses, the maximum temperature reaches 1950 °C during the pulse and the temperature at the end of pulse cycle reaches 94 °C. This suggests that even though silicon melts during each pulse and cools after solidification, it does not cool completely, instead there is some amount of thermal residual introduced by each pulse. This thermal residual effectively adds up over time and results in a maximum temperature of 94 °C after 200 cycles.

A similar trend is observed for parameter Set 2 (Figure 3-10) where the 10 μs pulse cycle used is 10 times shorter than Set 1. During the first pulse, the maximum temperature reached is also 1,938 °C. Then the maximum temperature drops once the pulse is finished. There is a stationary stage which occurs at the silicon melting temperature and is more evident in these plots because the pulse cycle is much shorter. This stage represents the solidification process. At the end of the 1st pulse cycle, the maximum temperature is 44 °C instead of 30 °C as in the previous simulation. After 200 pulses, the maximum temperature reaches 1,996 °C, 16 °C degrees higher than the previous one. At the end of the 200th pulse, the maximum temperature is 231 °C, more than double that of the previous setting.
Figure 3-10 Maximum temperature for the 1st and 200th pulses of parameter Set 2 (100 kHz, 10 μs pulse cycle)

Figure 3-11 plots the maximum temperature at the end of each pulse cycle for 700 successive pulses for parameter Set 1 (10 kHz) and 2 (100 kHz). In both cases the post-pulse temperature increases with the number of pulses, with the 100 kHz case increasing more rapidly than the 10 kHz case and is in general more than twice hotter than the 10 kHz case. The temperature at the end of the 700th pulse is still rising for both frequencies. This suggests that after 700 pulses the accumulation of thermal residual has not yet reached steady-state.

Figure 3-12 illustrates the melt duration during each pulse cycle for both parameter sets. Both of them start at 0.21 μs during the first pulse cycle. Since the starting temperature of each pulse is increasing (Figure 3-12), as expected, the duration of silicon staying molten increases with the number of pulses. The melt duration of Set 1 reaches 0.29 μs after 700 pulses, an increase of 38% compared to the first pulse. The melt duration of Set 2 reaches 0.43 μs during the 700th pulse cycle, which is double the melt duration of the first pulse. There is an interesting wave-like pattern in the two curves which has a period of about 150 pulses. Further
investigation is required to see whether this has physical meaning or is caused by the computing of the simulation.

Figure 3-12 Melt duration of each pulse cycle for 700 pulses for parameter Set 1 and 2

The simulation of the 1 μm/pulse pulse speed at both 100 μs and 10 μs pulse cycles indicates that firstly, at the end of each pulse cycle silicon might not be completely cooled to its starting temperature and this thermal residual accumulates as the number of pulse increases; secondly, this thermal residual accumulation could be affected by the length of the pulse cycle, the shorter the pulse cycle the quicker the build-up of thermal residual; thirdly, the accumulated thermal residual could increase the duration that silicon stays in a molten state.

It is worth noting that the simulation model has some assumptions, which means the simulation may not be a true representation of reality. In the simulation, a flat surface was used instead of a textured surface. This could underestimate the amount of absorption of incident light by more than 15% [121]. This model also neglects flow motion in the silicon melt, which could be induced by liquid expansion, convective flow, surface tension, recoil pressure, and hydrodynamics instabilities. The author believes that the motion of the liquid state is crucial for the groove formation, which is why this model is unable to simulate the formation of grooves. Moreover, once a groove starts to form, the incident laser light would be reflected multiple times inside the groove, leading to more energy absorption. Therefore, even though after 700 pulses the simulation shows the starting temperature of the next pulse is 386 °C and still rising, in reality, the textured surface and multi-reflection effect may result in much higher temperatures achieved in fewer pulses and grooves formed due to the flow motion of the melt. The groove walls might even stay relatively soft due to high temperature when the next pulse comes in. Nevertheless, it is believed that this simulation model provides a good
estimation of the overall thermodynamics, excluding the effect of melt flow, and has suggested the possibility of a strong thermal residual effect between laser pulses. One implication could be that with appropriate laser equipment that allows proper studies of the effect of laser frequencies, the thermal residual effect between pulses could be further investigated and possibly used to improve the doping profile along the groove walls.

3.4.4 Proposed possible groove formation process
Laser processing is a complicated process involving many physical phenomena and their interactions. More study is required to fully understand the laser grooving process, in which multiple laser pulses with intensity close to silicon’s ablation threshold form a narrow groove with a width much smaller than the laser beam diameter and form a selective emitter at the same time. Here, a possible groove formation process is proposed based on the study of influence of laser parameters on groove geometry, thermal modelling and literature reviewing.

**Stage One – thermal energy build up**
The first stage is the build-up of thermal energy. The first pulse would only result in a shallow dent on the silicon surface and leave a small amount of thermal residual when the second pulse hit the surface with a 93.3% pulse overlap. The second pulse would deepen the dent and add to the thermal residual, increasing the surface temperature and making the molten period slightly longer compared to the previous one. As subsequent pulses hit the surface with the same overlap, the thermal residual effect gradually builds up, increasing the molten pool lifetime and depth during the coming pulse cycle. At some point, the volume and duration of the molten silicon would become significant enough such that the liquid motion of the molten silicon would alter the surface morphology significantly.

**Stage two – void formation**
Once the melt duration is long enough and the depth is deep enough, there could be several mechanisms to form a small gap at the melt surface, which would remain void upon cooling.

a. The first possible mechanism is the thermal expansion of liquid silicon. The density of solid silicon is 2,320 kg/m$^3$ while that of the liquid silicon is 2,520 kg/m$^3$ [88]. Changing from solid state into liquid state silicon’s volume would increase by 8.5%. As the temperature of the molten silicon increases, its volume would increase further due to a further decrease in density. The volume expansion over 1,077 to 1,577 °C is expressed in the Equation 3-3 [50], where $T_m$ is the melting temperature. At 1,577 °C the liquid volume would increase by 13% compared to at melting temperature, let alone the volume increase due to phase change. Hence the volume of silicon would increase by more than 20% when changing from solid into liquid and heating up to 1,577 °C.
As the liquid silicon continues to expand, part of it would inevitably extend to above the original surface of the silicon wafer and therefore penetrate out of the groove. This coupled with convection flow due to surface tension changes (Section 3.1.1) or recoil pressure (section 3.1.2) induced melt flow, could cause the liquid over the silicon surface to flow sideways forming a bulge and leaving behind insufficient molten silicon within the groove to fully fill it as the silicon contracts during solidification, therefore leaving a small void in the centre. In other words, once cooled and re-solidified, this void remains because some of the displaced silicon is now on top of the surface.

b. Molten silicon is a low viscosity liquid with viscosity in the order of 1 mPa s [50], making it susceptible to any perturbation, such as hydrodynamic instability (Section 3.1.5). The dynamics between the evaporated matter and laser plume may introduce a special modulation of pressure, leading to capillary wave instability in the field of plume pressure [74]. Pressure near the concave region is higher than the convex region, making melt flow out from the pit to a relief hump and increasing the local curvature of the surface, which in turn increases the pressure gradient further. As the amplitude of the capillary wave grows to a certain value, droplets would break away from the liquid at the peak. Under multi-pulse irradiation, Rayleigh-Taylor instabilities at the liquid-vapor interface may develop at the convex area due to centrifugal force. The generation of capillary waves and droplets breakaways due to hydrodynamic instabilities would also alter the surface morphology of the silicon melt leaving behind a crater or small void. Figure 3-13 shows examples of droplets in the process of breaking away from the melted region. This confirms the involvement of hydrodynamics instabilities in the formation of grooves.
c. Another possibility is due to explosive boiling (Section 3.1.4). The intensity at the centre of laser beam is likely to be significantly higher than the average intensity. As the thermal residual builds up over time, if the energy at the centre is high enough to cause explosive boiling, silicon droplets or particles would be ejected from the melt. This ejection might also leave behind small voids.

d. The laser system uses a moving XY stage to control scribing speed. Because of the low viscosity and surface tension of liquid silicon, the motion of the stage could also contribute to the generation of capillary instability and voids.

There could be several mechanisms or a combination of a few that would generate the first small gap or void on the molten surface. Figure 3-14 shows an SEM image of the cross section of six laser-scribed lines, illustrating the start of void generation. The laser-scribed areas are not flat but wavy, with intermittent voids observable on the waves. In this case, the laser condition has not generated enough thermal energy or capillary wave amplitude to connect the voids into a gap, which could have then further developed into a groove.
Stage three – deepen connected voids into a groove
When the first generated void or gap is big enough, a large portion of the coming pulse would hit into the void and be multi-reflected and absorbed. This would generate a molten silicon layer along the inside wall of the void. Recoil pressure and other mechanisms discussed in the previous section would then induce the molten silicon to flow out of the void. Some of the molten silicon would flow out of the void and pile up on edge creating a bulge; other parts would be re-deposited onto the wall. In the meantime the void would be enlarged in the direction of beam travel and deepened since the silicon at the bottom of the void has been molten and re-deposited onto the wall or on top of the surface. This melting and re-deposition process continues as more pulses come in, making a void into a groove that gets slightly deeper with each incoming pulse until a steady state is reached. This melt re-deposition process could be the key in explaining the fact that the groove width is much smaller than the laser beam diameter. It is also crucial for the formation of a selective emitter along the groove walls. If grooves get too deep or the pulses move too slowly, the redistributed or re-deposited silicon would close up the groove.

In this section the process of groove formation has been discussed in detail. Such formations require laser irradiance levels close to the silicon ablation threshold. It has been proposed that a thermal residual effect is generated and built up overtime by multi-pulses. This build-up eventually leads to the melt flow of molten silicon to be significant enough to alter the surface morphology and result in the formation of grooves. Further laser pulses continue to melt the silicon and redistribute the molten layer, which results in grooves with widths much smaller than the laser beam diameter.
3.5 Junction quality of laser doped groove

The success in forming a suitable groove leads to the potential to improve metal contacts’ adhesion strength if metal is plated into the groove. However, a groove alone is not enough to develop high efficiency solar cells. The quality and continuity of the heavily doped region along the groove walls is critical to protect the active region of the cell and to minimize shunting losses. Electron Beam Induced Current (EBIC) imaging was used as a non-destructive method to examine the grooves and to spatially resolve the p-n junction at the groove walls. The EBIC signal highlights the junction location as well as its continuity, and by comparing or superimposing this on the corresponding SEM image, a clear indication of the junction depth in each region can be ascertained.

Table 3-7 shows SEM and EBIC images of four typical grooves. The junction depth of each groove has been extracted from these images. For each groove, the junction depth is extracted at six points along the groove walls and the averaged junction depths are included in Table 3-7. Figure 3-15 is an example of the junction depth extraction position at one of the six points. A straight line is drawn from the groove wall surface perpendicularly across the junction. The grey value of this line is plotted vs distance pixels. The peak of the grey value curve denotes where the junction is and the distance in pixels of the peak from the groove wall is converted into microns using the scale bar (in this case the 10 \( \mu \)m scale bar is 120 pixels). Using this method the junction depth at the point indicated in Figure 3-15 is extracted to be approximately 1.7 \( \mu \)m. Using the same method the junction depth at another five locations are exacted as well. The average of the junction depths of six positions is calculated to be 1.89 \( \mu \)m and is included in Table 3-7. The same junction depth extraction is done for the other three images and the results are included in Table 3-7. The average junction depth of the four grooves are 1.39 \( \mu \)m, 1.96 \( \mu \)m, 1.89 \( \mu \)m, and 1.32 \( \mu \)m, respectively. The second and third groove profiles are the preferred ones as their junction is 40% deeper than the other two profiles. The groove walls need to be sufficiently heavily doped to prevent groove wall surfaces from contributing significantly to the device total dark saturation current. However, increased volume of heavily laser-doped silicon in the groove could also reduce device voltages. The damage introduced by the laser doping and grooving process should also be minimized. Figure 5-2 and Figure 5-3 present results of damages induced by different scribing speeds and hence different laser geometries as shown in Table 3-8, from which laser conditions resulting in high \( iV_{oc} \) are chosen to fabricate laser doped and grooved solar cells.
When the groove is very deep (first groove profile in Table 3-7), although the heavy doping along the groove wall is continuous, there is not enough junction depth to electrically isolate the high recombination velocity surfaces within the grooves from the active regions of the cell. This will decrease cell voltage due to an increase in dark saturation current. The second and third groove profiles are the preferred structures, as can be clearly seen, the widths of the grooves are very narrow and yet the EBIC scans reveal that the junctions are quite deep within the groove walls. These deeper junctions have been shown to achieve significantly higher voltages by reducing the dark-saturation current. If too much silicon is lost from the molten region, the groove opening becomes too wide and again, the junction will be too shallow. The grooves with wide opening will also have additional SiNx deposited into the groove therefore necessitating some etching back of the SiNx to expose the silicon surface and allow nucleation for subsequent plating in the groove.
Table 3-7 Typical laser doped grooves

<table>
<thead>
<tr>
<th>SEM</th>
<th>EBIC</th>
<th>SEM &amp; EBIC COMBINED &amp; average junction depth</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="SEM Image" /></td>
<td><img src="image2" alt="EBIC Image" /></td>
<td><img src="image3" alt="Combination Image" /></td>
</tr>
<tr>
<td>Junction depth ≈ 1.39 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image4" alt="SEM Image" /></td>
<td><img src="image5" alt="EBIC Image" /></td>
<td><img src="image6" alt="Combination Image" /></td>
</tr>
<tr>
<td>Junction depth ≈ 1.96 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image7" alt="SEM Image" /></td>
<td><img src="image8" alt="EBIC Image" /></td>
<td><img src="image9" alt="Combination Image" /></td>
</tr>
<tr>
<td>Junction depth ≈ 1.89 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image10" alt="SEM Image" /></td>
<td><img src="image11" alt="EBIC Image" /></td>
<td><img src="image12" alt="Combination Image" /></td>
</tr>
<tr>
<td>Junction depth ≈ 1.32 μm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
An experiment was carried out in order to investigate the quality of the p-n junction before and after emitter diffusion. The process sequence began with spinning dopant onto the textured wafer surface, followed by scribing at four different speeds using both single and double passes. Twenty lines were scribed for each scribing condition. After rinsing off the dopant, the wafer was cut into two pieces: one was studied using EBIC immediately, and the other was studied after a 100 $\Omega$/sqr emitter diffusion. The EBIC and SEM images were overlayed on top of each other and are summarized in Table 3-8. Note that there were twenty lines in each group and the image before and after emitter diffusion might not come from the same line. In general, double scribes created a deeper groove; the p-n junctions in all cases were continues; there was no obvious change of junction depth after emitter diffusion; the depth of the junction was mainly affected by the scribing speed. It is interesting to observe that some EBIC images of grooves before emitter diffusion indicated that the junction might have extended to both sides of the groove on the silicon surface. This effect needs to be verified and ideally further studied.

Table 3-8 Combined EBIC and SEM image with only laser grooving and with laser grooving and emitter diffusion

<table>
<thead>
<tr>
<th>Speed and number of passes</th>
<th>After laser grooving</th>
<th>After laser grooving and emitter diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mm / s Single pass</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>10 mm / s Double pass</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>50 mm / s Single pass</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>
The study of the junction quality suggests that the laser doping and grooving process is capable of forming a groove with continuous and deep $p$-$n$ junctions. This implies that there is good potential for developing this process into a cell structure.
3.6 Conclusion
This chapter has presented an innovative approach for forming heavily doped, narrow grooves in the surface of a silicon wafer for subsequent metal plating nucleation and the theoretical basis for such laser groove formation has been discussed in detail. The concept of laser doping and grooving in a simultaneous step to form a selective emitter was presented and the influence of various laser parameters on groove geometry was studied experimentally. Given that groove formation is a complicated process, a possible theoretical explanation of the groove formation process has been proposed. Finally, EBIC imaging has demonstrated that the $p$-$n$ junction along the groove wall is continuous and could be deep enough to form good contact with limited dark saturation current. The next step for this work is to study the damage caused by this process (second part of Chapter 4) and explore the potential of developing it into a complete cell structure (Chapter 5).
Chapter 4

4 Laser hydrogenation

The previous chapter presents the concept of laser doping and grooving using focused laser beam. This chapter explores the abilities of expanded laser beam as the light source for Advanced Hydrogenation and demonstrates its ability to passivate a range of defects including laser induced defects in the laser doped and grooved lifetime samples. The charge-state of hydrogen atoms in silicon can have a large impact on their diffusivity and reactivity [96]. It has been shown that such charge states can be controlled by varying illumination levels to alter the injection levels and corresponding charge-state fractions [21], and that this can significantly enhance hydrogen passivation of defects, particularly when using infra-red photons with energy sufficient to generate electron-hole pairs in the silicon [122]. This is being referred to as Advanced Hydrogenation. Lasers appear to be ideal for adaptation for the implementation of Advanced Hydrogenation. They are powerful and versatile tools which provide monochromatic photons of almost any desired wavelength through highly directional electromagnetic waves. When the beam is focused it can deliver large amount of energy to a local area for precise processing, such as the laser doping and grooving technique discussed in the previous chapter. Beams can also be expanded to deliver photons to a larger area. This chapter presents the development of a laser hydrogenation tool for defect passivation, which was developed together with a colleague (Alison Ciesla [123]). The application of this tool towards the advanced hydrogenation of low cost upgraded metallurgical-grade (UMG) material, light induced degradation in Cz material and laser induced defects in laser doped and grooved Cz samples are also discussed.

4.1 The laser hydrogenation tool
Hydrogen is one of the fundamental elements of the universe. It is believed that over 90% of the universe was made up of just hydrogen and helium after the big bang. Hydrogen atoms have the simplest atomic structure with one photon and one electron, allowing it to easily combine or react with other elements, including silicon. The reactivity and diffusivity of interstitial hydrogen in silicon depends on its charge state, with the former reported to vary up to 5 orders of magnitude [21]. Recent study have shown that the charge state of hydrogen can be manipulated by illumination at elevated temperature via changing the electron quasi—
Lasers produce single wavelength light, of which the intensity and waveform can be easily controlled, allowing versatile and precise experiment designs. A laser hydrogenation tool was developed together with a colleague (Alison Ciesla [123]) to study the effect of controlling the charge state of hydrogen atoms within the silicon with an aim towards enhancing their mobility and reactivity. Figure 4-1 is a photo of the laser hydrogenation tool that has been developed with the schematics of the system shown in Figure 4-2.

The laser hydrogenation tool consists of a diode laser, which is fed into a beam homogenizer via an optical fibre and then expanded onto a hotplate using a plano-convex lens. There are six different plano-convex lenses at the bottom of the beam homogenizer which can be selected using a rotating wheel enabling changes in the illumination area according to processing area and intensity requirements. By using the hotplate together with laser, the charge state of hydrogen can be manipulated via the combination of temperature and illumination.
4.2 Laser illumination for manipulating charge state of hydrogen

4.2.1 Effect of temperature and illumination

Interstitial hydrogen can exist in one of three charge states: H⁺, H⁰, and H⁻, which have large differences in diffusivity and reactivity as discussed in Section 2.4 [21, 124]. As shown in Figure 2-17, the H⁺ level is located close to the conduction band, which means a small amount of thermal energy is necessary to convert H⁰ to H⁺. The fact that H⁺ sits above H⁻ level in the band gap, makes hydrogen a ‘negative-U impurity’ [21], which means H⁰ will never be a stable state as it will always lower its energy by losing or gaining an electron to form H⁺ or H⁻ respectively. The position of the Fermi level determines the charge state of hydrogen. If it is significantly away from mid-gap, hydrogen will be almost entirely in one charge state or the other with minimal amounts in H⁰. In p-type silicon it will be primarily H⁺ while in n-type silicon it will be primarily H⁻ depending on the absence or presence of electrons respectively.

In p-type silicon the dominant charge state is H⁺ at room temperature and in the dark. The positive charge will prevent it diffusing due to Coulombic attraction to the ionized dopant atoms with have negative charge [124]. H⁺ has no electron for bonding to positively charged defects or dangling bonds [25]. H⁰ state is highly reactive and diffusive because it has a single unpaired electron and is not affected by any fixed charges or electric field. Converting hydrogen to minority charge state should therefore be beneficial. The minority charge states of hydrogen can be increased by generating a large amount of excess minority carriers, shifting the Fermi level closer to the middle of band-gap and therefore making the silicon act more like intrinsic silicon [106]. There are two methods of shifting the Fermi level towards the mid band-gap: an increase in temperature and the use of high intensity illumination [21] [25]. Increasing the temperature can increase the concentration of minority hydrogen charge species, the reactivity, and the diffusivity of hydrogen [125]. However, increasing the temperature will also increase the dissociation of hydrogen-defect complexes [126]. Hamer et al. demonstrated that changing the relative concentration of atomic hydrogen had a significant impact on the minority carrier lifetime in p-type upgraded metallurgic grade (UMG) silicon [25]. It was shown that illuminated annealing resulted in higher effective lifetime.

The newly developed laser hydrogenation tool was used to investigate the effect of different illumination intensities and temperature [122]. Fourteen 4 cm × 4 cm UMG silicon wafers from an experimental ingot fabricated with a modified version of the PHOTOSIL process [127]
produced by Apollon Solar were used for these experiments. The wafers were chemically etched and cleaned. A layer of hydrogenated silicon oxynitride (SiO$_{x}$Ny:H) [128] was deposited on both sides by using remote microwave plasma-enhanced chemical vapor deposition (PECVD) in a laboratory type Roth and Rau AK400 tool.

The samples were then annealed on a hotplate under illumination from an 808 nm laser with adjustable intensity, at temperatures between 127 °C and 477 °C for 3 minutes before being quenched. Three illumination intensities were used in this work, with photon fluxes of $1.2 \times 10^{17}$, $9 \times 10^{17}$ and $1.7 \times 10^{17}$ photons/cm$^2$/s, as measured using a reference photodiode under illumination. The reflectivity of the samples at this wavelength was measured to be 12.4%. The actual sample temperature was monitored in-situ using an infrared detector. To reduce any possible impact of the thermal history and to demonstrate the reversibility of the results, anneals were performed in a random order.

The samples were characterized immediately after each thermal treatment in order to minimize degradation of the wafers. The effective lifetime as a function of minority carrier density was measured using a Sinton WCT-120 tool and the generalized technique [129]. Additionally photoluminescence (PL) imaging [130] with an illumination intensity of 1 Sun was performed to identify any spatial effects.

Figure 4-3 summarizes the $iV_{oc}$ data obtained after illuminated annealing with the 808 nm laser. The temperature is actual sample temperature measured by an infrared detector. An error bar is included in the figure to account for the difference between the infrared temperature measurement and thermal couple measurement, which can only be used when the laser is off and the enclosure open. There is a clear trend of increased $iV_{oc}$ for the temperature range 177 °C to 327 °C and a sharp decline for temperatures below 177 °C. For temperatures above 327 °C there is a small initial decline and slight increase with increasing temperature. The response of minority carrier lifetime with different light intensities provides evidence as to whether it is the photons, minority carrier concentration, or the charge state of hydrogen that is responsible for the improved defect passivation. The charge state of hydrogen depends on the quasi-Fermi level, which is influenced by the injection of carriers. Depending on the position of the quasi-Fermi level relative to the mid-band gap, if there is an excess amount of electrons the majority of atomic hydrogen is H$^-$ with two electrons, if there is a shortage of electrons the majority of atomic hydrogen is H$^+$ with no electron. If it is due to the direct involvement of photons or the minority carrier concentration, then high illumination would result in higher minority carrier lifetimes for all temperatures. Such a trend is not observed.
Instead, the data is in broad agreement with the hypothesis that it is the charge state of hydrogen that has the greatest influence. The modelling of hydrogen charge state was done by Hamer et al. [131] [25] based on the hydrogen model of Herring et al [21]. Increasing the temperature can increase the concentration of minority hydrogen charge species, the reactivity, and the diffusivity of hydrogen [125]. However, increasing the temperature will also increase the dissociation of hydrogen-defect complexes [126]. Figure 4-3 also presents the simulated fractional $\mathcal{g}$ concentration for the excess carrier densities involved in this experiment. There is a definite peak in each. However, simulations predicts an increase in $\mathcal{g}$ concentration with increasing excess carrier density, which is not observed in the experimental data.

The laser hydrogenation tool was used to control the H charge state locally. The image in Figure 4-4 shows its large impact on the diffusivity and reactivity of H in silicon. The UMG sample was fired in a belt furnace with peak temperature of 700 °C to release hydrogen from the dielectric layer into the silicon. It was maintained at 250 °C with only the centre area illuminated by the laser for 60 seconds to control the H charge state locally. The interstitial H under the illuminated area was controlled to be $\mathcal{g}$ while $H_0$ in the rest of the area was in the H+ state. As the mobility and reactivity of H atoms in the illuminated area was significantly improved, they were able to passivate defects much more effectively and transform the low quality UMG material into high quality silicon.
4.2.2 Effect of cooling rate

Not only does temperature and illumination affect the hydrogenation process, the cooling rate after processing is essential as well. Once again, p-type UMG wafers purified using the PHOTOSIL process [127] were used for the experiment. These wafers were cleaned and then coated on both sides with oxynitride (SiOxNy:H) [128]. Half of samples were pre-fired at 700 °C in a belt furnace to release hydrogen from the dielectric layer into the silicon. The other half of the samples had no pre-firing treatment. All wafers were then annealed on a 250 °C hotplate with the left half on the hotplate and the right half off the hotplate for 3 minutes. The samples were illuminated with 808 nm wavelength illuminations, with photon fluxes of $9 \times 10^{17}$ photons/cm$^2$/s and $1.7 \times 10^{18}$ photons/cm$^2$/s. The samples were then quenched on a wet filter paper after processing to minimize changes that may occur during cooling without illumination.

Figure 4-5 shows the PL response of the UMG samples after the laser hydrogenation process. The top two wafers, a) and c), did not have the pre-firing process whilst the bottom two, b) and d), were pre-fired in the belt furnace. Wafers a) and b) were illuminated with $9 \times 10^{17}$ photons/cm$^2$/s intensity and wafer c) and d) were illuminated with $1.7 \times 10^{18}$ photons/cm$^2$/s intensity. All the wafers had the left half on the hotplate during the process. It is observed that the half of the sample off the hotplate performed much better than the half on the hotplate. Since the half on the hotplate was at a higher temperature, it is possible that the higher temperature was not suitable for hydrogen passivation. However, it is more likely that the 250 °C of the hotplate is high enough for the passivation to be undone quickly after processing. Limitations in the system mean that interlocks on the laser enclosure prevent access to the sample until the laser is off, and then there is a small delay in opening the enclosure and removing the sample to quench it. The part of the sample off the hotplate may have cooled quite quickly to room temperature and therefore received reduced thermal energy that could...
undo the passivation. The pre-fired wafers responded much better than the non-fired ones as hydrogen was already distributed across the wafer during firing. In the non-fired samples, regions closer to the hotplate responded better since these regions had higher temperature to release more hydrogen and faster cooling rate to lock-in the passivation. These results potentially indicate the importance of effective cooling, and no further processing at temperatures higher than 250 °C to maintain the achieved passivation.

Figure 4-5 PL images of samples after illuminated annealing. Top wafers (a and c) were as deposited with no pre-firing process. Bottom wafers (b and d) were pre-fired at 700 °C in belt furnace to activate hydrogen and distribute it throughout the bulk. First column wafers (a and b) were illuminated with the photon flux with $9 \times 10^{17}$ photons/cm²/s. And second column wafers (c and d) were illuminated with $1.7 \times 10^{18}$ photons/cm²/s. For each sample, the left half of the sample was heated on the hot plate, while the right half was off the hot plate.

The illuminated firing in the belt furnace was used to demonstrate the effect of cooling. The bottom lamps in the last two firing zones were turned off to force the top lamps to operate at maximum capacity in order to reach the set temperature and therefore generate maximum top illumination in the furnace. This was an attempt to control illumination and temperature in the belt furnace for hydrogenation. Furnace zones one to four were set to 400 °C, 450 °C, 550 °C, and 700 °C respectively. The temperature of the last zone was varied from 700 °C to 850 °C and the belt speed was varied from 50 to 200 inches per minute (IPM) to modulate the cooling rate. Figure 4-6 plots the sample temperature profile when Zone 5 is set to 700 °C for 100 IPM and 200 IPM. It shows that changing the belt speed modulates the cooling rate as well.
as the sample peak temperature. The results in Figure 4-7 could be the combination of both effects.

Lightly diffused industrial Cz wafers with double sided SiN\textsubscript{x} passivated surfaces were used in the experiment. Two layers of standard 75nm SiN\textsubscript{x} layers were deposited on each side to provide extra H source. Figure 4-7 plots the \( iV_{oc} \) vs belt speed after firing together with the \( iV_{oc} \) directly after SiN\textsubscript{x} deposition. Under the effect of different cooling rate and peak temperature, the \( iV_{oc} \) of samples ranged from 670 mV to over 700 mV. 850 °C was too high such that the dielectric surface passivation for all the tested belt speeds was destroyed resulting in an \( iV_{oc} \) lower than the deposited state. In the 800 °C and 750 °C cases, the higher the belt speed (faster cooling rate) the better the sample lifetime achieved, while in the 700 °C case the belt speed did not introduce much variation in sample lifetime. This result implies that cooling rate after hydrogenation could have a significant impact on the resulting sample lifetime.
4.2.3 Effect of laser wavelength

It has been shown that illumination and temperature control is crucial for effective hydrogenation. The laser hydrogenation tool was therefore upgraded to use a 120 W 938 nm laser in place of the original 75 W 808 nm laser. The maximum photon flux that the 808 nm laser could generate over a 4 cm by 4 cm sample was $1.7 \times 10^{18}$ photons/cm$^2$/s. The use of a longer wavelength and more powerful laser together with a more uniform hotplate leads to improved precision and control and broader parameter space exploration. Defects need to be formed before they can be passivated by hydrogenation. It is believed that for photons with energy above the Si band gap, the defect formation rate and effectiveness of hydrogenation is correlated to the total number of photons injected into the sample. Figure 4-8 plots the hydrogenation rate of UMG samples under the two different laser illumination wavelengths. Samples were from the same batch as those detailed in sections 4.2.1 and 4.2.2. They were fired at 700 °C in the belt furnace and laser hydrogenated at 250 °C – 270 °C under the two different laser sources. The x-axis of Figure 4-8 is the accumulated laser hydrogenation time where zero represents the belt furnace firing; the y-axis is the $iV_{oc}$ value throughout the various stages of the hydrogenation process. It is observed that at a photon flux of about four times that of the 808 nm laser, the 938 nm laser could passivate the UMG sample much faster, resulting in over 710 mV $iV_{oc}$ in 2 minutes instead of over 8 minutes when using the 808 nm laser. The longer wavelength laser is able to generate more photons for the same input power and enables faster defect formation and hydrogenation passivation. The 938 nm wavelength photons can penetrate three times deeper than 808 nm photons up to over 50 μm deep, which could be more effective in passivation defects in the Si bulk.
In this section the control of the hydrogen charge state via laser illumination and temperature control for defect passivation has been presented. The cooling rate after high temperature processing was shown to be important for maintaining the hydrogen passivation of defects. Furthermore, the use of a longer wavelength laser was shown to enable faster defect formation and passivation as it is able to generate a higher photon flux. The next section discusses in detail the laser hydrogenation and stability of UMG materials.
4.3 Laser hydrogenation of low cost material and resulting stability

UMG Cz silicon materials are fabricated at a significantly lower cost compared to the semiconductor grade Cz silicon produced by the Siemens Process. Due to the specific purification process used, UMG materials typically contain increased B-O defects, metallic impurities and crystallographic defects in comparison to semiconductor grade material. Standard Cz materials typically have sufficiently low metal impurities that their lifetime is limited by the metastable B-O defects [102, 132]. In comparison, UMG materials may have other impurities and/or defects limiting their lifetime, but still have the potential to be used to fabricate high efficiency solar cells if such recombination mechanisms can be deactivated, such as by advanced passivation techniques.

It is shown that the hydrogen charge state can be manipulated using laser illumination and that longer wavelengths, with energy levels approaching but still above that of that bandgap, are superior in terms of enhancing hydrogen passivation [122]. A 938 nm laser was therefore set up in the laser hydrogenation tool and an experiment was performed to investigate the ability to hydrogen passivate UMG silicon and its corresponding stability, with implied $iV_{oc}$ values of over 710 mV achieved [133]. Evidence was provided as to whether the instability due to degradation under light illumination is due to generation of new defects or instability in the passivated defects.

UMG silicon wafers from an experimental ingot with a modified version of the PHOTOSIL process [127] produced by Apollon Solar were used in these experiments. The wafers were chemically etched and cleaned. A layer of hydrogenated silicon oxynitride (SiOxNy:H) [128] was deposited on both sides by using remote microwave plasma-enhanced chemical vapour deposition in a laboratory type Roth and Rau AK400 tool. For comparison, standard Cz wafers were processed in parallel.

The UMG wafers were put through a high temperature belt furnace anneal to release hydrogen from the dielectric layer and allow it to diffuse into- and throughout the bulk of the silicon. The samples were then light soaked under illumination of 0.6 Suns and at approximately 50 °C for stability testing. Subsequently, the samples were processed using the laser hydrogenation technique, where they were annealed on a hotplate together with illumination from a 938 nm laser to control the charge state of the interstitial hydrogen within the silicon. The wafers were processed at 250 °C – 270 °C with a photon flux of $6.9 \times 10^{18}$
photons/cm²/s for one minute. Light soaking followed each laser hydrogenation process in order to assess resulting stability. The laser hydrogenation was repeatedly performed.

The recombination in the samples was characterized after each treatment, by measuring the effective lifetime as a function of minority carrier density using a Sinton WCT-120 tool and analysing the photoconductance data using the generalized technique. PL imaging was also used to identify spatial effects. In addition, curve fitting was used to identify the different components of the lifetime. It was assumed that the bulk lifetime was limited by Shockley-Read-Hall recombination.

4.3.1 Over 710 mV \( iV_{oc} \) on UMG material after laser hydrogenation

Table 4-1 shows that the \( iV_{oc} \) of Cz material can be improved to be over 700 mV, appearing to indicate the ability to hydrogen passivate B – O defects. It is also shown that, starting from between 600 mV to 610 mV, the \( iV_{oc} \) of UMG wafers can also be improved to be over 710 mV. This is approximately the same as the standard \( p \)-type Cz wafer produced from semiconductor grade silicon purified via the Siemens process. This appears to suggest that the hydrogen passivation process not only passivates the B – O defects as with the normal Cz material, but also the additional contaminants present due to the use of much lower purity silicon which led to the low initial material minority carrier lifetimes.

<table>
<thead>
<tr>
<th>Wafer type</th>
<th>As deposited ( V )</th>
<th>After hydrogenation ( V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cz</td>
<td>0.654</td>
<td>0.705</td>
</tr>
<tr>
<td>Cz</td>
<td>0.649</td>
<td>0.708</td>
</tr>
<tr>
<td>UMG</td>
<td>0.603</td>
<td>0.704</td>
</tr>
<tr>
<td>UMG</td>
<td>0.609</td>
<td>0.715</td>
</tr>
</tbody>
</table>

Figure 4-9 presents the PL image of a UMG wafer before and after the laser hydrogenation process. It can be seen that the PL signal which correlated to the minority carrier lifetime is significantly improved. By applying the laser hydrogenation process, the UMG material has reached a similar \( iV_{oc} \) value to the Cz material and equivalent uniformity across the wafer.
4.3.2 Evaluation of passivation stability via light-soaking

The treated wafers have been observed to degrade under illumination. Figure 4-10 shows that both the UMG and Cz material degrade quickly in the first 15 hours and start to stabilize after 20 hours. Cz wafers are known to have light induced degradation caused by B – O defects. UMG wafers have a range of other impurities in addition to the B – O defects, such as metal impurities. The fact that the degradation curve of the UMG wafers is similar as the Cz wafers may imply that the main cause of the light induced degradation in the UMG could be B-O defects. However the increased level of degradation for the UMG could lead to some variations in this interpretation such as there being additional instabilities within the UMG material in addition to the B-O defects that cause the increased level of degradation. Another interpretation could be that the originally hydrogen passivated defects remain stable and that the degradation is caused by the progressive formation of new B-O defects, with more new defects therefore arising in the UMG material due to the boron concentration being double that of the normal 2 ohm-cm Cz wafer.

To give additional insight into the behaviour of the UMG material in comparison to the normal Cz material, the hydrogen passivation process was repeated followed by additional stability testing.
4.3.3 Repeated hydrogenation and stability testing

The UMG wafers were treated with the laser-based hydrogen passivation process after each light degradation process. It is observed that the stabilized $iV_{oc}$ after each treatment is higher than the previous stabilized value, continuously approaching that of the Cz wafer formed from semiconductor grade silicon on each successive occasion (Figure 4-11).

Figure 4-11 shows that repeated hydrogenation and light-soaking of the UMG material leads to the material becoming progressively more stable with higher and higher $iV_{oc}$'s. This would suggest that the degradation is unlikely to be caused directly by the breaking of the hydrogen bonds responsible for the passivation, or else similar stability outcomes would be expected to result following repeated hydrogenation. Instead, the improved stability suggests that the degradation is being significantly contributed to by the formation of new recombination sites (mechanisms) which can then be subsequently hydrogen passivated, with the overall stability improving with time simply because light-soaking progressively leads to less new defects (B–O or otherwise) being formed.
Lifetime curve fitting was performed after each stability test to analyze the asymmetry between the hole and electron components of the SRH recombination. It was assumed that the bulk lifetime was limited by Shockley-Read-Hall recombination and fitted by the equation:

$$\frac{1}{\tau_{SRH}} = \frac{N_A + \Delta n}{\tau_p n_0 (N_A + p_1 + \Delta n) + \tau_n n_0 (p_1 + \Delta n)}$$

Equation 4-1

From the fitting, the electron and hole components of lifetime $\tau_n$ and $\tau_p$ were extracted. The ratios of extracted electron and hole capture cross sections are summarized in Table 4-2. It has been reported that in a B – O limited, standard Cz wafer, the ratio of electron and hole capture cross section is approximately 10 [134]. It is observed that the asymmetry of electron and hole capture cross sections for the UMG material before laser hydrogenation was much higher than that of the Cz material. This appears to suggest that, at the start, the lifetime limiting recombination sites in the UMG material is not B – O. One explanation could be that there are alternative defects that have higher electron/hole asymmetry than B – O. The fact that successive laser hydrogenation reduced the asymmetry of the UMG material to be closer to that of the Cz wafer may indicate that the influence of these defects were reduced each time, such that the UMG material was becoming more B – O defect limited and hence more comparable to standard Cz silicon.
Table 4-2 Ratio of the capture cross sections for electrons and holes after each stability testing

<table>
<thead>
<tr>
<th></th>
<th>Electrons and holes capture cross sections ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZ after hydrogenation</td>
<td>9.76</td>
</tr>
<tr>
<td>UMG before laser hydrogenation</td>
<td>17.93</td>
</tr>
<tr>
<td>UMG after laser hydrogenation</td>
<td>15.03</td>
</tr>
<tr>
<td>UMG after 2nd laser hydrogenation</td>
<td>10.47</td>
</tr>
</tbody>
</table>

Figure 4-12 PL image of one UMG wafer showing regions with improved stability (Process 1: Localised hydrogenation; Process 2: Localised hydrogenation followed by full area hydrogenation; Process 3: 16 hour light soak after 2nd hydrogenation)

Figure 4-12 shows another example of improved stability after repeated hydrogenation treatments. In this case a UMG wafer was first hydrogenated locally, then full area hydrogenation was applied. After 16 hours of light soaking, it can be seen that the region that has been processed twice is the most stable.

It is observed that repeatedly activating defects through light-soaking and then using hydrogenation on UMG material leads to improved UMG which has long term parameters close to that of standard Cz material. It importantly indicated that, although the advanced
hydrogenation appears capable of passivating almost all forms of recombination within these UMG wafers, it can only passivate defects that have already formed. Instabilities within the material that lead to the future generation of recombination within such wafers during operation in the field, cannot be hydrogen passivated before they have been formed. In parallel work to this project, new techniques for rapidly forming such defects to rapidly subsequently remove any instabilities in a matter of seconds, have been developed and demonstrated [135, 136]. It is expected that the optimisation of laser hydrogenation from this project will then lead to more stable passivation of such UMG wafers to $iV_{oc}$ values in excess of 700mV.
4.4 Laser hydrogenation of B – O defects and LID in commercial solar cells

The same laser hydrogenation setup was used to investigate the formation and passivation of the metastable B – O defects [136]. Hamer et al. found that the formation rate of B – O defects is highly dependent on the illumination intensity [135]. A hydrogenation process that could passivate B – O defects in a few second was developed.

This technology has been extensively demonstrated on commercial solar cells from multiple industry partners. Figure 4-13 shows PL images comparing samples with and without laser hydrogenation treatment. These are mono crystalline PERC solar cells from an industry partner. They were cut into small cells to be processed using the advanced hydrogenation treatment. The cell on the left had the hydrogenation treatment, whereas the cell on the right did not. Both of them were subsequently exposed to light soaking for 48 hours to test stability and gauge the level of any light induced degradation (LID). As can be seen in the images, the hydrogenated cell showed improvement right after the treatment and the improvement was relatively stable after 48 hours of light soaking. The control cell which had no hydrogenation treatment degraded significantly after light soaking. Figure 4-14 plots the efficiency change of the cells: without hydrogenation treatment the efficiency decreased by 0.67 % absolute compared to the as-received state, whereas with hydrogenation there was an efficiency increase of 0.37 % absolute.

![Figure 4-13 PL image of hydrogenation on commercial solar cell](image-url)
It has been shown that the advanced hydrogenation technique can passivate different defects effectively. The next section discusses its effect on laser induced defects in laser doped and grooved lifetime test structures.

### 4.1 Advanced hydrogenation of laser induced defects in laser doped and grooved lifetime test structures

#### 4.4.1 Laser doping and grooving minimizes laser induced defects

Chapter 3 presented the innovative concept of selective emitter formation through simultaneous laser doping and grooving. This section and the following section discuss the laser induced damage caused by the laser doping and grooving process as well as the possibility to hydrogenate laser damage using the laser hydrogenation tool.

The groove geometry SEM images shown in Figure 3-7 show that 50 mm/s and 100 mm/s scribing speeds can reliably form grooves with the desired geometry of 10-15 um depth and 3-5 um width. This geometry ensures that the grooves are deep enough to provide good adhesion without too much damage into the Si and narrow enough to prevent excessive amounts of dielectric getting inside the groove during subsequent depositions, yet still wide enough to allow easy nucleation during plating.

Based on results from the study of groove geometry, two scribing speeds (50 mm/s and 100 mm/s) that could produce the desired geometry were chosen to be used for the fabrication of lifetime test-structures to investigate laser-induced damage. Since the laser-doping and grooving process can be completed before the deposition of a dielectric layer, it can also be completed before or after the emitter diffusion. To test the optimum sequence the 50 mm/s
samples were scribed before and after the emitter diffusion, while the 100 mm/s samples were scribed only before the diffusion process to compare with the 50 mm/s group.

To investigate laser induced damage as a function of laser power, three groups of 6 lifetime samples with 3 cm×3 cm cell pattern were fabricated, each processed at four laser power levels ranging from 610 – 770 mW. Control samples (i.e. no laser processing) were included in each group. Industrial grade 1.6 Ω.cm p-type Cz wafers were used for this experiment. All samples underwent standard alkaline texturing at the same time. After spinning phosphorus acid onto one side of each sample in group I and II, samples in group I were then laser scribed at 50 mm/s, and those of group II scribed at 100 mm/s to form the grooved selective emitter, a light emitter diffusion was then performed (130 – 150 Ω/sq). The emitter diffusion was conducted at 795 °C for 25 minutes followed by 30 minutes drive-in at 885 °C. Group III was diffused at the same time as the other two groups, but had the laser doping and grooving process completed at 50 mm/s after the emitter diffusion. All wafers then had a SiNx layer deposited on both sides. The SiNx was deposited using an industrial scale MAiA tool optimized to create a 75 nm thick layer with a refractive index of 2.08 (at 633 nm).

Figure 4-15 plots the implied open-circuit voltage under one-sun illumination for the different wafer groups, as a function of the laser power, juxtaposed with control samples with no laser processing. The measurements were carried out at room-temperature using an intrinsic carrier concentration determined from the model developed by Nagel et al. [129]. Comparison of the two 50 mm/s groups reveals that the group diffused after laser-doping and grooving has 15 to 20 mV higher $iV_{oc}$ than the group that received the diffusion prior to the laser processing. This suggests that during the emitter diffusion, at least some of the crystallographic defects introduced by the laser-doping and grooving process were gettered or passivated. Analysis of EBIC images showed no obvious change in junction depth along the groove walls before and after emitter diffusion, however, it is possible that the emitter diffusion process helped to reduce dopant surface concentration and distribute dopants more uniformly. A standard RCA clean was performed before emitter diffusion and SiNx deposition, this is not expected to have a significant contribution in terms of laser damage removal. Passivating/gettering defects during emitter diffusion is one of the benefits of the laser-doping and grooving process, which not only avoids defects caused by thermal mismatch between the Si and dielectric layer, but also allows laser-induced defects to be passivated without requiring additional processes. In comparison to the Buried Contact Solar Cell (BCSC), which requires chemical etching back of the laser damaged area in the grooves and a second heavy diffusion to form the selective
emitter, the proposed technology of this work forms the selective emitter by laser doping and grooving simultaneously. In this case the laser induced defects can be passivated by the subsequent emitter diffusion or potentially by laser hydrogenation at a later stage.

Figure 4-15 also indicates that the 100 mm/s group has higher $iV_{oc}$ value than the 50 mm/s group, which can be explained by reduced laser-induced damage due to the lower laser power introduced into the Si. It is interesting to note that there is only 5 to 8 mV degradation in $iV_{oc}$ when using the lowest laser power compared to the non-scribed samples (the 100 mm/s group). This degradation is much smaller than that caused by the LDSE process [19]. This is further strong evidence that the laser doping with grooving process has the potential to greatly reduce laser induced defects compared to the standard Laser Dosed Selective Emitter (LDSE) approach. As the average laser power increases, both the laser-induced damage and the depth of the grooves (unpassivated Si) increases, resulting in a reduced $iV_{oc}$. Another explanation could be that the increased volume of heavily laser-doped Si (due to deeper grooves) could cause a reduction in $iV_{oc}$ due to Auger recombination [137].

As discussed previously, in conventional LDSE solar cells, the laser doping process is performed after the deposition of the dielectric layer so that only the laser-doped Si is exposed in preparation for the plating of the metal contacts. Despite the success of LDSE solar cells in achieving numerous performance records on p-type Cz Si [14, 16, 138], one of the technology’s key drawbacks, is laser-induced defects caused by thermal expansion mismatch between the Si substrate and the SiNx layer on top [20]. This mismatch places the Si under tension during the laser doping process; this stress appears to induce large amounts of defects, since Si is known
to be weak under tension [45]. Laser doping with grooving makes it possible to avoid this laser induced thermal mismatch. This is because the innovative process developed in this work allows very narrow grooves to be formed on bare Si, prior to dielectric layer deposition. By applying the dielectric layer after the laser grooving step, thermal mismatch between Si and SiNₓ can be avoided, which means laser induced defects are also minimised. The very narrow groove geometry allows the dielectric layer to be deposited mainly on the exposed top surface of the Si while minimal deposition gets down inside the groove to coat the steep narrow groove walls. This allows nucleation of subsequent metal plating.

Figure 4-16 presents photoluminescence (PL) images [130] of different regions of the same wafer. These PL images have been de-convolved to minimise the effects of photon smearing and improve clarity by the method of Teal and Juhl [139, 140]. A screen-printed aluminum (Al) back surface field (BSF) was formed on the rear side, while the laser processes was done on the front. Figure 4-16(a) presents a standard LDSE cell where the laser doping process was applied after the SiNₓ deposition; in comparison, Figure 4-16(b) shows a solar cell processed using the proposed laser doping with grooving method, where the laser process is carried out before the SiNₓ deposition. The figure clearly shows that the laser-doping process after SiNₓ deposition significantly degrades the PL response, probably due to the formation of significant recombination through laser-induced defects, caused by thermal mismatch. In comparison, significantly reduced damage can clearly be seen in Figure 4-16(b) due to the absence of the dielectric layer during the laser doping process. This result is surprisingly good considering that the vertical groove walls are exposed and unpassivated (even after the deposition of the dielectric layer). This suggests that the groove walls are sufficiently heavily doped to prevent these regions from significantly contributing to the device total dark saturation current. This is an important result given that these exposed surfaces will be metallized and therefore maintain a very high surface recombination velocity.

![PL image of a wafer with laser doping and grooving](image)

Figure 4-16 PL image of a wafer where a) the laser doping process was done after SiNₓ deposition; and b) the laser grooving was done before the deposition.
Implied Voc measurements were also conducted on lifetime test structures that were processed using the new laser doping with grooving technology compared to those that were processed using the conventional LDSE laser-doping techniques. Figure 4-17 plots the iVoc values obtained on representative samples of test structures processed using the two different types of laser processes.

The graph on the left clearly shows that, for LDSE solar cells, there is a significant drop in lifetime or iVoc values after laser processing (red dots) compared to before laser processing (black dots) at all points across the wafer surface. In fact there is approximately on average a 20 mV loss from about 680 mV to 660 mV. Even though most of this loss could be recovered by high temperature belt furnace firing, it requires an additional step to passivate these defects.

In contrast, the graph on the right shows that, for a laser-grooved solar cell using the new process, there is only a small drop in lifetimes and iVoc values after laser processing (red dots) compared to samples without the laser processing (black dots) with the loss being in the vicinity of only about 5mV.

Lifetime test structure studies show that the laser doping with grooving technology produces much less laser induced damage in comparison to the conventional LDSE process, resulting in only 5 to 8 mV degradation in iVoc compared to non-scribed samples. The laser doping and grooving process minimizes laser induced defects. The next section presents an investigation into the use of laser hydrogenation to mitigate the remaining defects.

4.4.2 Laser hydrogenation of laser doped and grooved lifetime test structures
The laser hydrogenation process has been shown to work well in passivating UMG material and B – O defects in p – type screen printed cells. In this section it is applied to laser doped and
grooved lifetime test structures with the aim of passivating the laser induced damage caused by the fabrication process.

The laser hydrogenation process was applied to the laser doped and grooved lifetime test structure. The process sequence was texturing, followed by simultaneous laser doping and grooving, emitter diffusion, double side SiNx deposition, firing, and finally laser hydrogenation. To optimize the hydrogenation processing conditions, sample temperatures were varied from 250 °C to 350 °C and at each temperature a range of laser illumination intensities was applied by changing the laser input current. Figure 4-18 plots the changes in effective lifetime after the laser hydrogenation process at each condition. The figure implies that processing temperature is more important than the illumination intensity. In fact, it seems the laser intensity did not have much effect. The 250 °C process improved sample lifetime by 12 % to 15 %, the 300 °C process improved sample lifetime by 17% to 21%, and the 350 °C process improved sample lifetime between 11% to 14%. It is interesting that the middle temperature 300 °C performed best rather than the higher 350 °C.

The laser hydrogenation condition of $1.3 \times 10^{19}$ photons/cm$^2$/s (40 A laser current) photon flux and 300 °C sample temperature was applied to laser doped and grooved samples created using various grooving conditions. Figure 4-19 shows the $iV_{oc}$ values for a range of laser doping and grooving powers together with the non-scribed group. It is observed that the hydrogenation process improved sample lifetime. The higher the laser grooving power, the more improvement was achieved by hydrogenation. This suggests that the low values of $iV_{oc}$ of the high laser power group may be caused primarily by laser-induced defects, which were then passivated by the hydrogenation process. The PL images shown in Figure 4-20 compare a laser...
doped and grooved wafer before and after laser hydrogenation. It is clear that the grooved regions were quite uniformly improved. The mechanism of laser hydrogenation on the laser doped and a grooved sample is not yet clear. Further thorough study is required to fully understand and optimize this process.

Figure 4-19 Laser hydrogenation of laser doped and grooved lifetime test structure

Figure 4-20 PL image of lifetime sample before and after laser hydrogenation
4.5 Conclusion

This chapter presents the development of a laser hydrogenation tool and its ability to manipulate the charge state of hydrogen via changing sample fermi level by illumination and temperature. Low cost UMG material quality was improved to have $iV_{oc}$ over 710 mV. Commercial PERC cell efficiency was improved by 0.37 % absolute and shown to be stable via work in conjunction with a colleague. Lifetime test structure of laser doped and grooved samples were also improved. The next chapter details the continued development of laser doped and grooved cell structure and the incorporation of laser hydrogenation with the cell structure along with the resulting changes in solar cell output characteristics.
Chapter 5

5 Solar cells fabricated using the laser doping and grooving technique and the incorporation of hydrogenation

The concept of simultaneous laser doping and grooving to form selective emitter was introduced in Chapter 3, where it was shown that a range of groove geometries can be formed with continuous heavy doping along the groove walls. This chapter further investigates the laser induced damage caused by this process as well as the effects of gettering/passivation during emitter diffusion, plating into the grooves to form metal contacts, development of cell structures and finally the incorporation of laser hydrogenation for laser doped and grooved solar cells.

5.1 Minimizing laser induced damage

Laser processing generates dislocation and crystallographic defects and residue stresses in the Si crystal structure [112]. Some of these damages are electrically active, which would reduce minority carrier lifetime and hence cell voltages [113, 114]. In this section, the laser induced damage caused by the laser doping and grooving process is studied using lifetime test structures.

5.1.1 Effect of laser irradiance and scribing speed

Laser doping and grooving parameters were explored using lifetime test structures in order to study the laser induced damage. The $iV_{oc}$ values were compared with non-scribed samples and samples scribed with the conventional LDSE process. Industrial $p$-type 1.6 $\Omega$cm Cz wafers were processed in the sequence shown in Figure 5-1. Eleven 6-inch wafers were first alkaline textured and then diluted Phosphoric (P) acid was spun onto the wafer surface to act as dopant source for the subsequent laser doping and grooving process. Nine laser irradiances (Table 5-1) were used to laser dope and groove cell patterns on nine of the wafers, and the other two wafers were not scribed and therefore used as control samples. Note that due to the instability of the laser power (discussed in Section 3.2), a range of laser power levels were
recorded for each input setting. The average of the recorded minimum and maximum power was used to calculate the irradiance. Each of the nine wafers was laser doped and grooved with 9 cell patterns (3 cm × 3 cm) at 4 different speeds (Table 5-2). Three patterns were scribed at 100 mm/s and two patterns were scribed for each of the other speeds (10, 50 and 150 mm/s). After laser doping and grooving, all wafers were lightly diffused and a SiN<sub>x</sub> passivation layer was deposited on both sides for lifetime measurements. Figure 5-2 is the PL image of one wafer after SiN<sub>x</sub> deposition. After SiN<sub>x</sub> deposition the control samples were scribed with LDSE cell patterns to compare with laser doped and grooved patterns.

![Flowchart](image.png)

**Figure 5-1 Laser damage lifetime test structure process sequence**

<table>
<thead>
<tr>
<th>Measured laser power range (W)</th>
<th>Measured average laser power (W)</th>
<th>Calculated irradiance based on Equation 3-2 (W/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36 – 0.40</td>
<td>0.38</td>
<td>5.3×10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.44 – 0.52</td>
<td>0.48</td>
<td>6.8×10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.49 – 0.54</td>
<td>0.52</td>
<td>7.3×10&lt;sup&gt;7&lt;/sup&gt;</td>
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<tr>
<td>0.53 – 0.62</td>
<td>0.58</td>
<td>8.2×10&lt;sup&gt;7&lt;/sup&gt;</td>
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<td>0.58 – 0.62</td>
<td>0.60</td>
<td>8.5×10&lt;sup&gt;7&lt;/sup&gt;</td>
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<tr>
<td>0.75 – 0.82</td>
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<td>1.1×10&lt;sup&gt;8&lt;/sup&gt;</td>
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<td>0.83 – 0.91</td>
<td>0.87</td>
<td>1.2×10&lt;sup&gt;8&lt;/sup&gt;</td>
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<tr>
<td>1.05 – 1.06</td>
<td>1.06</td>
<td>1.5×10&lt;sup&gt;8&lt;/sup&gt;</td>
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<tr>
<td>1.15 – 1.24</td>
<td>1.20</td>
<td>1.7×10&lt;sup&gt;8&lt;/sup&gt;</td>
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</table>
Table 5-2 Laser doping and grooving speeds

<table>
<thead>
<tr>
<th>Set speed (mm/s)</th>
<th>Pulse speed (at 100 kHz) (μm/pulse)</th>
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<tbody>
<tr>
<td>10</td>
<td>0.1</td>
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<tr>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>150</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 5-2 PL image of laser doped and grooved sample under different speeds at 1.2×10⁸ W/cm²

Figure 5-3 plots the $iV_{oc}$ values vs. scribing speed at different laser power irradiances. In general, the lower the laser grooving irradiance the higher $iV_{oc}$ was achieved as less energy was put into the silicon to cause stress and damage. Higher scribing speeds also resulted in better sample lifetimes. This could also be due to the lower power experienced at each part of the surface, however, another explanation could be that higher scribing speeds would result in shallower and wider grooves (Section 3.3). This would lead to less exposed surface area due to the shallow groove depth and potentially more SiNₓ deposition inside the grooves due to the wider groove opening. It is interesting to observe that the 10 mm/s speed sometimes resulted in better $iV_{oc}$ than the 50 mm/s speed at the same irradiance level. The geometry of grooves created at 10 mm/s and 50 mm/s speed is similar, with extremely narrow widths obtained for both cases (Figure 3-). Grooves created at 10 mm/s are more likely to close up due to their narrow width, especially in the bottom half of the grooves. This could lead to less exposed Si
area and consequently a higher $i_{Voc}$ in comparison to the 50 mm/s case which has similar geometry.

In Figure 5-3 the $i_{Voc}$ values of non-scribed sample and LDSE sample are indicated by the black and orange dashed lines respectively. There were two laser doping and grooving conditions which were found to achieve a higher $i_{Voc}$ than the LDSE process, proving that the laser doping and grooving process could be superior to the conventional LDSE process in terms of minimizing laser induced defects.

![Figure 5-3 $i_{Voc}$ vs pulse speed after SiNx deposition for a range of laser doping and grooving irradiance settings](image)

In fact it is clear from the results that the laser doping and grooving process is capable of achieving higher $i_{Voc}$ values than the conventional LDSE process, with only 5 – 8 mV difference between the best laser doped and grooved sample and the non-laser scribed sample, indicating minimal laser induced damage. To further verify this, an experiment was performed to gauge the repeatability of these high levels of post-processing sample lifetime.

5.1.2 Repeatability of high sample lifetime

In the previous experiment, there were two data points for each laser doping and grooving condition. The two fastest pulse speeds at low laser irradiances resulted in $i_{Voc}$ values within 10 mV of the samples which were not exposed to any laser scribing. A second experiment was performed to confirm the repeatability of this promising result which implies minimal defect generation.

Industrial p-type 1.6 $\Omega$ cm Cz wafers were processed using the same sequence shown in Figure 5-1 except from the last step for comparison with the LDSE process. Samples were scribed at
four laser irradiances from $8.6 \times 10^7$ W/cm$^2$ to $1.1 \times 10^8$ W/cm$^2$ at both 100 mm/s and 150 mm/s. Four samples were processed for each testing condition in order to test repeatability. Note that the measured irradiance levels were slightly different from those in the previous experiment. This was due to the instability in the output power of the laser tool. The reported irradiance was calculated from the average of measured minimum and maximum of power fluctuating range (refer to Table 5-1). The laser doped and grooved samples were then diffused using an 80 – 100 Ω/sqr emitter diffusion and a 75 nm SiNx layer was then deposited onto both sides.

Figure 5-4 plots the $iV_{oc}$ values for each testing condition together with that of the non-laser scribed samples. The two different pulse speeds result in similar sample lifetimes at the two lowest irradiance levels. And at both of these irradiances the result of 5 – 8 mV degradation in comparison to the non-scribed group is achieved again. At the two highest irradiances the slower 100 mm/s performs slightly worse, possibly because at higher irradiances the extra damage caused by introducing more laser energy and thermal cycling is more significant.

![Figure 5-4](image)

Figure 5-4 Repeatedly achieved minimal $iV_{oc}$ degradation compared to non-scribed samples at low laser irradiance and high scribing speed

It is shown that high sample lifetimes with minimal $iV_{oc}$ degradation compared to non-scribed sample can be produced repeatedly and reliably. Whether these laser doped and grooved samples could then be developed into a full solar cell structure would depend on the ability to form good metal contacts along the groove walls, which will be discussed in Section 5.2. Before that, the effect of double laser passes and the effect of the diffusion sequence will be discussed.
5.1.3 Effect of double laser scribing

In conventional LDSE processing, double laser scribing passes have been shown to smooth the laser processed surface, increase active dopant concentration and the uniformity of doping, but this technique can also induce excess laser damage [34]. The potential advantages mean that it is worth studying the effect of double scribing on laser doped and grooved samples. The geometry of laser doped grooves by double laser passes is presented in Section 3.5. It is shown that double scribing results in an increased groove depth with no obvious change of p-n junction quality in terms of depth and continuity. An experiment was therefore carried out to study the effect of double scribing on sample lifetime.

Industrial p-type 1.6 Ωcm Cz wafers were processed using the same sequence as shown in Figure 5-1 except from the last step for comparison with LDSE process. To create the laser doped grooves, one group of samples were scribed at 50 mm/s for one pass only, and a second group was scribed with two passes at the same pulse speed. This pulse speed was chosen since it is known to generate more defects than the faster alternatives. More laser induced defects would help highlight the effect of double passing. Both the single pass and double pass group were scribed at three irradiance levels. Six samples were processed for each testing condition. The laser doped and grooved samples were then diffused with a 100 – 120 Ω/sqr emitter diffusion before a 75 nm SiNx layer was deposited onto both sides.

Figure 5-5 plots the $iV_{oc}$ values for single pass and double passes at three laser irradiances. There is not much difference between the single pass and double pass approaches at the lowest laser irradiance. However, at the higher irradiance levels the double scribed group has higher sample lifetime than the single scribed group. Section 3.5 shows that double scribing produces deeper grooves. The fact that deeper grooves does not lead to lower sample lifetime suggests that the mostly unpassivated groove walls are doped heavily enough so that they do not contribute much to the device’s dark saturation current. In the cases where double passing resulted in higher sample lifetime than a single scribe, the second laser scribe may have driven the dopants further into the bulk consequently distributed them more evenly, resulting in a reduced dopant surface concentration and increased sample lifetime.
In the experiments above the laser doping and grooving processes was performed before the emitter diffusion. The nature of the laser doping and grooving technology allows the laser process to be employed before or after diffusion. The effect of the timing of emitter diffusion step is discussed in the next section.

5.1.4 Effect of diffusion sequence and subsequent low temperature diffusion

POCl₃ diffusion is conventionally used to diffuse P into p-type Si to form the n-type emitter. It starts with a deposition of phosphosilicate glass (PSG) followed by a drive-in step to move phosphorous deeper into Si. Conventional emitter formation is one of the first steps in cell processing. Normally the emitter diffusion is carried out after alkaline texturing and cleaning and before SiNx deposition. The ARC and surface passivation layer then needs to cover the whole cell surface except the areas where metal contacts are to be formed. Metal contacts are formed by firing screen-printed silver paste through the dielectric layer for screen printed cells, or by plating after Si is exposed during the laser selective emitter doping process for LDSE cells. In LDSE cell processing the emitter diffusion has to be done before SiNx deposition followed by laser doping prior to metal plating, during which the SiNx layer acts as a mask. However, for the laser doping and grooving technology developed in this work, because of the narrow width of the grooves, they can be formed before SiNx deposition and remain exposed and ready for metal nucleation during plating. This means that the laser doping and grooving process can be applied at any stage before the dielectric deposition, and can therefore be before or after the emitter diffusion step. An experiment was performed to study the effect of emitter diffusion on sample lifetimes where one group was laser doped and grooved before emitter diffusion and another group was laser doped and grooved after emitter diffusion.
Industrial $p$-type 1.6 $\Omega\text{cm}$ Cz wafers were processed using the sequence shown in Figure 5-6. Three groups of lifetime samples were prepared. Each group consists of six 3 cm× 3 cm cell pattern as shown in Figure 5-2. A slow scan speed of 50 mm/s which has been shown to generate more defects was chosen in order to highlight the effect of the emitter diffusion, and a speed of 100 mm/s which produced high lifetime samples was also included to confirm the preferred condition for laser doping and grooving. In addition, both of these scribing speeds are able to produce the desirable groove geometry where the groove is 3 – 5 $\mu$m wide and 10 – 15 $\mu$m deep, as discussed in Section 3.3 After texturing, Group 1 samples were then laser doped and grooved at three irradiances using a scan speed of 50 mm/s and Group 2 samples were scribed at a scan speed of 100 mm/s. All samples were then diffused with a 100 – 120 $\Omega$/sqr emitter including control samples where no laser processing was to be performed. After emitter diffusion, the samples in Group 3 were laser doped and grooved using the same conditions as Group 1 at 50 mm/s. Finally all samples were deposited with a 75 nm SiN$_x$ layer on both sides.
Figure 5-7 plots the $iV_{oc}$ values of all three groups after SiN$_x$ deposition. It is clear that the group which was subjected to laser doping and grooving before the emitter diffusion have 15 to 20 mV higher $iV_{oc}$ than the group that received the emitter diffusion prior to the laser process. This suggests that during the emitter diffusion, at least some of the crystallographic defects introduced by the laser-doping and grooving process were gettered or passivated. Analysis of EBIC images showed no obvious change in junction depth along the groove walls before and after emitter diffusion, however, it is possible that the emitter diffusion process helped to reduce dopant surface concentration and distribute dopants more uniformly. A standard RCA clean was performed before emitter diffusion and SiNx deposition, this is not expected to have a significant contribution in terms of laser damage removal.

![Figure 5-7](image)

Figure 5-7 Comparison of grooving completed before emitter diffusion and after emitter diffusion at 50 mm/s

Figure 5-8 compares the $iV_{oc}$ of the 50 mm/s group and the 100 mm/s, both of which received the laser process before emitter diffusion. The 100 mm/s group has much higher $iV_{oc}$ likely due to fewer thermal cycle induced defects. One of the reasons these two pulse speeds were chosen to explore further was that both of them could produce grooves with the preferred geometry. Whether they could be successfully developed into solar cell devices would depend on the ability to initiate metal nucleation along the groove walls, which is explored in the next section.
Passivating/gettering defects during emitter diffusion is one of the benefits of the laser-doping and grooving process, which not only avoids defects caused by the thermal mismatch between the Si and dielectric layer, but also allows laser-induced defects to be passivated without requiring an additional process. In comparison to the BCSC, which requires chemical etching back of the laser damaged area in the grooves and a second heavy diffusion to form the selective emitter, the proposed technology developed in this work forms the selective emitter by laser doping and grooving simultaneously, with the laser induced defects passivated by the subsequent emitter diffusion or potentially through laser hydrogenation at a later stage.

The phosphorous diffusion process is known to be capable of passivating crystallographic defects [141]. Several groups have reported that a subsequent low temperature diffusion process can also be beneficial in defect gettering metallic impurities [142-144]. Song et al. [145] found that such a low temperature diffusion (LTD) process following emitter diffusion can significantly enhance resulting cast mono solar cell efficiencies. It is therefore worth investigating the effect of such an LTD process on laser doped and grooved lifetime samples.

Laser doped and grooved industrial p-type 1.6 Ωcm Cz wafers were processed with and without an LTD process in order to study it’s effect. Three groups of wafers were processed in the sequence shown in Figure 5-9. Group 1 received laser doping and grooving before emitter diffusion and no LTD process was received. Group 2 received the identical process as Group 1 plus a 3 hour LTD process at 700 °C after emitter diffusion. Group 3 had no laser process before receiving emitter diffusion at the same time as the other two groups. Laser doping and grooving for Group 3 was then performed after emitter diffusion and followed by the 3 hour LTD process. These three groups were laser doped and grooved at 100 mm/s with two laser
irradiances: $9.1 \times 10^7$ W/cm$^2$ and $1.1 \times 10^8$ W/cm$^2$. All wafers were deposited with 75 nm SiN$_x$ on both sides then fired at 700 °C in the belt furnace with illumination. The illuminated firing was the hydrogenation process where the bottom lamps were turned off and the top lamps were set to operate at maximum capacity to maximise the illumination intensity for the hydrogenation process.

Figure 5-9 Process sequence for testing LTD on lifetime samples

Figure 5-10 and Figure 5-11 plots the $iV_{oc}$ of the two irradiance groups. In the low irradiance group, after SiN$_x$ deposition, there was not much difference between the three groups, which all had average $iV_{oc}$ around 660 mV. After 700 °C illuminated firing for enhanced hydrogenation, Group 2, which received laser doping and grooving before emitter diffusion and a subsequent LTD process, had the highest improvement of 14 mV on average, whereas Group 1 improved by 10 mV and Group 3 improved 7 mV on average. This suggested that the hydrogenation processes are more effective when combined with a LTD process subsequent to emitter diffusion. One explanation could be that the LTD process allows a reduction in the peak phosphorus doping concentrations in the emitter that therefore allows increased flow of hydrogen into the deeper regions of the silicon where the defect passivation could be more effective. Another explanation could be that the LTD process enhances the diffusion of P.
atoms into crystallographic defects along the groove walls and grain boundaries that penetrate through to the $p$-type side of the junction, providing a source of electrons in such regions that allow more effective passivation of defects by the hydrogen. This is equivalent to saying that such P diffusion along such crystallographic defects can transform $p$-type regions into $n$-type regions that therefore convert the $H^+$ into $H^-$ that can more effectively passivate any positively charged defects. In the high irradiance case that is expected to correspond to the high crystallographic defect density case, a similar trend was observed, whereby a LTD subsequent to emitter diffusion resulted in 10 mV higher $iV_{oc}$ than the other two groups. It is clear that the LTD process enhances passivation of crystallographic defect passivation.

In this section the effect of various processing conditions on the sample lifetime of test structures has been presented, where the implied open circuit voltage is taken as an indication
of the lifetime of minority carriers. Tested parameters include laser irradiance, laser scribing speed, number of laser scribe passes, timing of emitter diffusion, and a low temperature diffusion following the emitter diffusion. There is only a 5 – 8 mV difference in $iV_{oc}$ between the best laser doped and grooved samples and non-laser processed samples, indicating that it is possible to achieve minimal laser induced defects. The potential for developing the laser doping and grooving selective emitter formation technology into complete solar cell structures would depend on the ability to form metal contact inside the grooves and on the quality of the metal silicon interface. The next section discusses the development of light induced plating onto the simultaneously laser doped and grooved selective emitter inside the grooves.
5.2  Self-aligned plating and improved metal contact adhesion strength

Plating is a technique in which metal is deposited via an electrochemical process from a solution containing metal ions. A source of electron at the Si surface is needed for the reduction process. This source of electron could come from a reduction agent in the solution, an applied bias potential, or from the current generated by a solar cell under illumination [146].

Light induced plating (LIP) provides electrons from the current generated by the solar cell upon illumination. The LIP process of forming metal contact for LDSE cells following laser doping was developed at UNSW in early 2000s [17]. There are two ways to complete the electrical current circuit in order to initiate LIP for cells with an Al rear contact. Under illumination, electrons and holes are generated inside the solar cell. The electrons and holes are separated into the n-type and p-type region respectively by the electrical field of the p-n junction. In non-contact LIP the cell is immersed in the solution so that metal is deposited onto exposed Si at the front of the cell upon receiving electrons from the n-type region, while at the rear the Al gives up electrons due to oxidation. The circuit is complete and the metal plating on the front surface is sustained when the electrons from the Al oxidation recombine with holes from the p-type region. The solar cell typically operates close to open circuit voltage in non-contacted LIP. Bias-assisted LIP uses an external bias potential to make the cell to be plated operate close to short circuit condition. In this case, only the front surface is in contact with the plating solution and the rear Al is electrically connected to an external potential source. The potential source is in series with a sacrificial anode immersed in the solution in order to sustain the plating process.

5.2.1  Plating of different groove geometry

Despite the success of LDSE solar cells in achieving numerous performance records on p-type Cz Si, one of the technology’s key drawbacks, is laser-induced defects caused by thermal expansion mismatch between the Si substrate and the SiNx layer on top. This mismatch places the Si under tension during the laser doping process; this stress appears to induce large amounts of defects, since Si is known to be weak under tension. Laser doping with grooving makes it possible to avoid this laser induced thermal mismatch. This is because the innovative process developed in this work allows very narrow grooves to be formed on bare Si, prior to the dielectric layer deposition. By applying the dielectric layer after the laser grooving step, thermal mismatch between Si and SiNx can be avoided during laser processing, which means laser induced defects are also minimised. The very narrow groove geometry allows the dielectric layer to be deposited mainly on the exposed top surface of the Si while minimal deposition gets down inside the groove to coat the steep narrow groove walls. This allows
nucleation of subsequent metal plating. Not only does the laser doping and grooving process minimize laser induced defects, it also defines the location of subsequent metal contact plating.

The non-contact LIP technique was used to test the laser doped grooves’ ability to form metal contacts. The processing sequence is shown in Figure 5-12. Industrial p-type 1.6 Ωcm Cz wafers were laser doped and grooved with 1 mm spaced lines at four scribing speeds (10 mm/s, 50 mm/s, 100 mm/s, and 150 mm/s) using two laser irradiances, $9.3 \times 10^7$ W/cm$^2$ and $1.1 \times 10^8$ W/cm$^2$. This created a range of groove geometries in order to test their ability to form good metal contacts. The laser doped and grooved samples were diffused with a 100 – 120 Ω/sqr emitter followed by 75 nm SiN$_x$ deposition on the front surface. Al was evaporated onto the rear side and fired at 400 °C in a belt furnace. Finally the samples were plated with copper (Cu) using the non-contact LIP process.

Figure 5-13 is a schematic showing the non-contact LIP plating setup. Fluorescent lights were used as the light source. During plating, the sample was supported by Teflon blocks and was immersed in the Cu plating solution (from MacDermid). The depth of solution above the sample surface was maintained below 5 mm. Nickel (Ni) is widely used as a diffusion barrier for Cu, but cannot be as easily plated and observed using microscope or SEM imaging as Cu. In this early experiment, Cu plating directly onto n-type Si was performed to study the grooves’ ability to form metal contacts. Samples were deglazed in 1% HF solution for 60s to account for
the fact that laser doped walls inside the grooves might need a longer HF dip to expose the silicon surface in the event that some deposition took place within the grooves during the PECVD deposition. However, this was later proven to be unnecessary. After the HF dip, the samples were rinsed and dried before being plated for 12 minutes.

Table 5-3 shows the cross-sectional SEM images of the eight groove geometries. The 10 mm/s speed at both irradiances created very deep but closed up grooves. This was consistent with earlier results that demonstrated that at this high pulse overlapping rate it was difficult to obtain clean and continuous grooves due to their extremely narrow width. The slightest hydrodynamic movement in Si while molten would cause the narrow groove to close up. Even though the grooves were closed up and little plating inside the groove was observed, Cu was plated on top of the sample surface along the laser scribed line as on a typical LDSE cell. One explanation for this could be that some of the laser scribed areas were not fully covered during the SiNx deposition, and Cu nucleation then happened during plating. As plating continued these areas were connected and formed a Cu finger. This would reduce cell fill factor (FF) significantly since little area of Si was being contacted.

50 mm/s scribed grooves also had a narrow width as in the 10 mm/s case, but in this case the grooves were not as deep and they were more likely to be clean and continuous. In the lower irradiance case the groove was over 25 μm deep but Cu did not fill the groove completely, leaving the bottom 5-6 μm exposed. There could be several explanations for this. The first is that plating solution could not get so deep into the narrow groove due to surface tension or other effects and hence no plating happened at the deeper part of the groove. A second explanation could be that, due to non-uniform doping, uneven surface roughness or localized crystallographic defects along the groove walls, metal nucleation could not start uniformly along the whole surface of the groove wall and instead started from the shallower parts where the conditions might be more favorable. Electrons generated by photons would flow laterally in the emitter region to the heavily doped region where they could be collected at the metal-Si interface. The electron current would be highest at the regions where the emitter meets the
heavily doped region, the upper part of the grooves near the Si surface. The metal reduction rate and hence the plating rate would be higher at this region. It could be that fast plating at the upper part of the groove closed up the groove before the bottom part could be plated. Cu may continue to grow towards the groove bottom to fill up the groove but the regions where actual contact was made were only the areas where nucleation started.

In the 100 mm/s case, the grooves were wider and shallower, approximately 3-5 μm wide and 10-15 μm deep and in this case Cu filled the groove completely, except for a small void at the bottom of the groove for the higher irradiance process. A bulge on the Si surface along the two sides of the groove can be clearly seen. These bulges are a couple microns higher than the textured pyramids. This indicates that minimal molten Si was lost and there was a relatively thick layer of heavily doped region along the groove walls, protecting the active region from Cu. These wider and shallower grooves were easier to plate having the entire groove cavity filled with Cu. Because of the wide groove opening, even though there could be a non-uniform plating rate along the groove walls, the groove cavity was not closed up prior to being filled completely, as in the narrower groove case. However, there was a small void at the bottom of the groove for the higher irradiance process. This could be caused by the groove geometry. In this case, the groove had a bottle neck shape which Cu could have filled and closed up due to faster plating rate near the surface. This small void at the groove bottom phenomenon was observed in several groove fingers where there was a narrow section between the top and bottom part of groove. This could increase the series resistance in the metal finger and could be particularly bad in production since these voids could trap liquid inside and jeopardize the stability and reliability of a module. If the formation of voids inside plated fingers could be avoid, the geometry of grooves produced at 100 mm/s seem to be a good candidate for reliably forming metal contacts. This is promising because samples with laser doped grooves produced at this condition have the highest $iV_{oc}$ as shown in the previous section, which of course could also be the reason why they are easier to form metal nucleation and contacts with.

The grooves produced at 150 mm/s had similar geometry as those at 100 mm/s, but were slightly wider and shallower. The bulges on the two sides of groove were less obvious for these processing conditions, which could mean that the increased groove width may have resulted from losing more molten Si. Hence the junction depth would be shallower, as shown in Figure 3-7, providing less protection and more susceptibility towards shunting. The wide and shallow
grooves from 150 mm/s could be well plated, however, the reduced junction depth may lead to a reduced $V_{oc}$ and $FF$.

Note that in some of the cross-sectional SEM images, it appears that pieces of Si were broken away from the bulk, especially in cases where grooves were relatively well plated. This could be caused by the improved metal contact adhesion strength, meaning that chunks of Si could be pulled away when the sample was snapped for cross section imaging. The metal contact adhesion strength is discussed in the next section.

Table 5-3 SEM images of Cu plating of different groove geometries

<table>
<thead>
<tr>
<th>Scribing speed (mm/s)</th>
<th>$9.3 \times 10^7$ W/cm² laser grooving irradiance</th>
<th>$1.1 \times 10^8$ W/cm² laser grooving irradiance</th>
</tr>
</thead>
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<tr>
<td>10</td>
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</tr>
<tr>
<td>150</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
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</tbody>
</table>
Non-contact Cu LIP was performed to test the ability of different groove geometries’ to form metal contacts. Narrow and deep grooves were unable to form metal contacts that completely filled the cavity of the groove, probably due to variations in local nucleation and plating rates along the groove walls. Wider and shallower grooves may be more forgiving to the plating rate variations along the groove and could therefore be filled completed with Cu. However, if there is a narrow bottle neck shape between the top and bottom part of the groove, plated metal could close the groove up at the narrow point before the wider bottom part can be completed filled. It is therefore concluded that, in terms of being able to be reliably plated, V-shape cross-section geometry is more preferable than a vase-like geometry.

5.2.2 Plating process
To understand the process of metal deposition, a sample with laser doped grooves produced at 100 mm/s was cleaved into 2 cm strips and each strip was taken out of the plating process progressively at 20 s, 40 s, 60 s, 80 s, and 180 s and then studied under SEM. The process sequence of this sample was the same as that shown in Figure 5-12 and Figure 5-13 except that the Al rear contact was formed by screen printing and firing in a belt furnace instead of Al evaporation.

Table 5-4 shows the cross-section SEM images at each stage. It can be seen that the grooves were plated quickly, with small Cu balls accumulated near the opening at 20 s and almost complete filling after 60 s. The SEM images show that plating started near the groove opening region, where the Cu ion concentration and electrons from n-type region were highest. After 20 s, small Cu balls of 1-2 μm in diameter covered the groove’s top part, instead of uniformly coating the groove wall. This indicates that the actual contacting areas could be small and limited to the points where the Cu balls started nucleating. Figure 5-14 illustrates that if nucleation does not start uniformly and the plating rate is too fast then only the nucleation points are the actual contact areas. As these deposition points quickly build up into small balls, other areas in between these early nucleation points would be blocked out and restricted from forming contact points. Even though the plating rate is high and the groove is filled as the metal deposition continues, the quality of the contact between Si and metal could be poor, which would result in high series resistance and low FF in the final cell structure. It should also be noted that on the Si surface where Si bulges slope down towards the textured pyramids, there was also an accumulation of Cu balls. The reason for this could be that, during SiN₄ deposition, due to the height and slope of the bulge, Si was not completed covered by SiN₄, leaving some pin-holes where metal nucleation could begin. As metal deposition continues, the Cu balls on the sample surface grow into lines and connect with the Cu forming inside the
groove, and eventually form into a metal finger with a mushroom cross-sectional shape, as in the 180 s case. The mushroom shape provides a high aspect ratio metal contact, however, its width can only be as narrow as the distance between the initial Cu balls on either of the groove sides on the top wafer surface. If SiN$_x$ deposition is denser and covers the Si more completely, then the final finger width could be as narrow as the groove opening width of 3-5 $\mu$m.

The plating rate illustrated in Table 5-4 was relatively fast with Cu plating starting from the grooves’ top section before growing downwards to fill the groove cavity and upwards to form the semi-spherical ‘mushroom cap’ by connecting with plating started on the top surface. Although a fast plating rate is desirable in production, the contacts formed using this process could be poor, with limited actual contacting area between the Si and metal. The effect of fast plating on laser doped and grooved cell structures are further investigated and discussed in Section 5.3.1

<table>
<thead>
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<th>Cu plating time (s)</th>
<th>Cross-section SEM image</th>
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<td>60</td>
<td><img src="image3.png" alt="Image" /></td>
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</table>
5.2.3 Improved metal contact adhesion strength
Light induced plating was performed to test the laser doped grooves’ ability to form metal contacts. Figure 5-15 illustrates that metal completely fills the groove as well as having a good aspect ratio. One advantage of this process is that it could be possible to control the width and aspect ratio of the metal contacts. Since only the groove walls are unpassivated after dielectric layer deposition and therefore available for plating nucleation, the width of the metal contacts could be controlled to be as narrow as the groove width (typically 3 – 5 microns) or much
wider by changing the metal plating duration. Figure 5-16 is a top-view microscope image, showing that the width of metal contact could be as narrow as the groove opening. Having narrow metal contacts would reduce shading loss significantly, but of course would also increase resistive losses within the Cu unless the approach was combined with another metallisation scheme such as the smart – wire technology from Meyer Berger [147].

![Cross section SEM image of a plated finger](image1)

**Figure 5-15 Cross section SEM image of a plated finger**

![Metal fingers could be as narrow as the groove opening](image2)

**Figure 5-16 Metal fingers could be as narrow as the groove opening**

Cu is considered one of the best alternatives to Silver due to the much lower price and simple implementation. One of the concerns for plated contacts to really take off is their relatively poor metal contact adhesion strength compared to screen printed contacts. Another advantage of the laser-doping with grooving method is improved adhesion of the metal contacts. Since the metal contacts are buried under the Si surface instead of on top of it, it is much harder for the contacts to peel off from the Si. Figure 5-15 shows that with this approach, the metal can be buried up to 15 μm deep beneath Si top surface. Figure 5-17 illustrates the bottom of a peeled metal finger. It is clear that chunks of Si were removed together with plated metal. This indicates that the Si is forming good and strong mechanical contact with the metal and the adhesion of the overall contact is excellent.
The adhesion strength of the metal contacts was tested using a stylus-based adhesion tester developed by Young et al [148]. A weighted stylus scans across the cell while the horizontal force required to cut off or dislodge the contacts was measured. The adhesion strengths of laser doped and grooved cells, commercial screen-printed cells and LDSE cells were compared. The adhesion strength of each metal finger was normalized to that of the average screen-printed contact for comparison. Figure 5-18 plots the normalized data. It is observed that the adhesion strength of laser doped and grooved contacts is more than twice that of the laser doped cell and is slightly superior to the screen printed metal contact. Perhaps this explains the reported superior durability of the BCSC in the field compared to screen-printed solar cells [13]. Figure 5-19 is an SEM image of a grooved metal finger after the stylus-based adhesion test. It is observed that the metal finger is snapped off from the top maintaining the metal contact inside the groove. This indicates that the measured adhesion strength of the plated grooves is the mechanical strength of the plated metal itself instead of the actual adhesion strength of the contact. One could argue that the primary concern for plated contact is the thermal expansion issue during module making and the plated contacts have a different type of adhesion strength to screen printed contacts. Although the author has not done other adhesion tests on the plated contact of the laser doped and grooved cells other than the stylus testing presented, a colleague (Alison Ciesla [123]) has shown plated contacts on a similar structure can pass industrial standard adhesion testing as well as thermal cycling up to 400 °C, where she improved the adhesion strength of Pluto cells by introducing anchor points and grooves.
In this section the metal plating of samples with selective emitter formed by simultaneous laser doping and grooving on the front side and full area Al alloy contact on the rear side has been presented. Non-contact LIP was used to study different groove geometries’ ability to plate, including an analysis of the nucleation starting positions, and the adhesion strength of the plated metal contacts. It is shown that some groove geometries are able to form good metal contacts filling the groove cavity completely and the adhesion strength of the plated groove contacts is superior to that of industrial screen printed contacts and conventional LDSE contacts. The electrical properties of solar cell devices made by using the laser doping and grooving process with plated contacts is presented in the following section.
5.3 Selective emitter solar cell through simultaneous laser doping and grooving followed by self-aligned metal plating

As discussed there are many benefits of the laser doping and grooving technology. The laser doping and grooving on textured Si surface incorporates dopant into the molten Si and forms a selective emitter by liquid phase epitaxy, forming grooves with heavily doped walls in one simultaneous step. The grooves can be very narrow and therefore produce narrow metal contact lines. If the PECVD of SiNx happens after groove formation, the groove can still be plated, allowing laser doping to be performed prior to SiNx deposition which helps to avoid most laser induced defects. The laser doping and grooving process also defines the location for self-aligned metal plating, and plating into the grooves greatly enhances metal adhesion strength. In this section, solar cell devices made by using the laser doping and grooving technology are presented and analysed.

5.3.1 Cells with conventional Cu plating

The ability to form good metal-Si contact ultimately determines the efficiency of a finished solar cell. There is no point optimising the Si cell bulk structure if little current generated inside the cell can be channelled to the external circuit via the metal-Si interface. Cu has long been recognised for its potential to replace silver as a significantly cheaper alternative. Cu can be easily deposited by plating, but it is also active at room temperature and capable of diffusing into Si over time which can cause shunting and thus diminished device efficiency. Ni is widely used as a Cu diffusion barrier. However, it is harder to initialise Ni nucleation and difficult to control the plating uniformity. As a first test to study the electrical performance of cells made by the laser doping and grooving technology, non-contact LIP Cu plating was used without the Ni barrier.

A batch of laser doped and grooved cells were processed according to the sequence shown in Figure 5-20. Textured industrial p-type 1.6 Ωcm Cz wafers were coated with 85% phosphorous (P) acid and subsequently laser doped and grooved using four laser irradiances (8.6×10^7, 9.3×10^8, 1.0×10^8, 1.2×10^8 W/cm²). Two groups were processed, one at a scan speed of 50 mm/s and the other at 100 mm/s. The laser doped and grooved samples were then diffused with a 100 - 120 Ω/sqr emitter, together with a group of samples to be laser doped and grooved after emitter diffusion at the 50 mm/s condition and a group of non-scribed samples to be processed using the conventional LDSE technique after SiNx deposition to act as control samples for plating. The standard production sequence of PLUTO cells [14] is followed for the LDSE comparison group. The laser doping and grooving process is a proof of concept with little optimisation hence the standard industrial process is used for comparison. All samples were
subsequently coated with a 75 nm ARC of PECVD SiNx and then screen printed with full-area Al on the rear and finally fired in a belt furnace to form a full area Al alloy back contact. LDSE laser doping was performed on the control samples and then all samples were plated using the non-contact Cu LIP technique. The plating set up was the same as that previously shown in Figure 5-13. All samples were first deglazed in 1% HF for 30s and then plated for 12 minutes by LIP. After laser edge isolation all the cells, their electrical properties were characterized by measurement of I-V characteristics and Suns-Vsc.

Unfortunately this first batch of laser doped and grooved cells had almost no measurable efficiency at all with a typical FF of lower than 30% and Jsc lower than 10 mA/cm², while the LDSE cells had efficiencies over 16% and FF higher than 70%. Even though the results of LDSE cells indicated that the plating was not ideal, since the efficiencies were relatively low in comparison to standard LDSE cells, the substantial difference between the laser doped and grooved cells and the LDSE cells showed that the plated Cu was not making good contact with
the Si in the laser doped and grooved cells, meaning that little current could flow out to an external circuit.

Suns-Voc measurements further confirmed the fact that the plated Cu was not contacting the Si. The difference between pseudo fill factor (pFF) and actual FF is caused by a cells’ series resistance. The pFF values of the laser doped and grooved cells were over 82%, approaching the highest achievable by laser doped solar cells. The large difference between FF (< 30%) and pFF (>82%) of these cells clearly indicated there was a huge series and contact resistance. It was suspected that non-uniform Cu nucleation and fast plating was the reason for the poor metal contact formation, where sparse isolated points only were the actual contact areas, as discussed in Section 5.2.2. Another possibility could be that, due to the fast plating rate, metal quickly plates on the top part of groove towards the exposed wafer surface, closing the groove and prohibiting contact formation at the bottom part. Figure 5-21 shows an example of when the metal plating rate is too high and the groove opening has been blocked, preventing contact to be formed inside the groove.

![Figure 5-21 Cross section SEM image showing metal block groove opening, no contact inside groove](image)

Although the laser doped and grooved cells were not contacted properly to conduct current to external circuit, their measured Voc can still provide some useful insights into device performance. Figure 5-22 plots the Voc measured using Suns- Voc. The trend between the three groups was similar to that of the lifetime test samples (Section 4.1). Laser doping and grooving completed after emitter diffusion at 50 mm/s did not have the opportunity to getter or passivate laser induced defects during a diffusion, and this group therefore had the lowest Voc at less than 550 mV. The other 50 mm/s group with the laser process carried out using exactly the same laser conditions, but completed before the emitter diffusion to therefore benefit from defect passivation during diffusion, had 50 mV higher Voc of around 600 mV. The last group also had laser doping and grooving completed before emitter diffusion, but at a faster scribing speed of 100 mm/s. This group had the highest Voc at around 635 mV, possibly due to the reduced laser energy put into Si to generate defects. The Voc of all the LDSE cells were
between 620 mV and 630 mV, slightly lower than the best laser doped and grooved group. This confirmed that at a cell level, the laser doping and grooving technology could be superior to the standard LDSE approach. It is possible that once metal contact is made, the recombination under the metal finger might change the $V_{oc}$. However, the author believes that this will not reduce $V_{oc}$ dramatically, as shown in Table 5-5, where laser doped and grooved cells with over 19 % efficiency have similar $V_{oc}$ values over 630 mV.

It is worth noting that different laser irradiances did not lead to much variation in $V_{oc}$ at cell level within each group. Whereas on lifetime test samples it was shown that, in each laser speed group, the lower the laser doping and grooving irradiance the higher the $iV_{oc}$ was achieved (Section 4.1). Theoretically, a lower laser irradiance would induce less damage and hence result in higher sample lifetime as less energy is put into the Si. The fact that this effect is apparent in lifetime samples with SiN$_x$ passivation on the rear but not in cells with a full area Al back contact, indicates that the cells’ voltage levels are limited by the metal contact. It is expected that by improving the rear passivation such as by using a PERC cell structure, the voltages would be greatly enhanced and the difference caused by laser irradiance in each speed group would become more apparent.

![Figure 5-22 $V_{oc}$ measured by Suns-$V_{oc}$ measurement](image)

It was suspected that the poor contacting between the metal and silicon was at least partially due to non-uniform nucleation and too fast a plating rate. The next section presents cell results after attempting to slow down the nucleation and plating rate by diluting the Cu plating solution.
5.3.2 Slow Cu plating

It was suspected that the Cu nucleation and plating rate was too fast to form good and reliable metal-Si contact inside the grooves. This section presents the effect of reducing the Cu plating rate by diluting the plating solution.

The metal plating rate depends on the availability of metal ions and electrons at the Si surface to be plated. There are several methods to reduce the plating rate: the metal ion concentration could be reduced by diluting the plating solution or changing the pH value of the solution, or the number of electrons could be reduced by reducing the cell current via decreasing light intensity or the depth of solution above the cell surface. For this work, diluting the plating solution was chosen to slow down the plating rate since it allows cells to operate near their $V_{oc}$ condition, which enhances the uniformity of metal nucleation by causing resistivity to be the limiting factor [118].

A Cu plating solution from MacDermid was diluted by adding deionized (DI) water to reduce it to 50%, 33%, 25%, 20%, 4% and 1% of its original concentration. Samples were deglazed in 1% HF for 40s before being submerged in the diluted solutions. They were then taken out and observed under microscope at 10 minute intervals. No significant reduction in plating rate was observed in the 50% solution compared to the original solution and plating could be completed in 20 minutes; an obvious reduction was observed for the 33%, 25%, and 20% solutions and in these cases a plating duration of 40-50 minutes was required; the 4% and 1% concentration seemed too low to form metal contact, in this case Cu did not grow along the Si surface but Cu crystals seemed to form at isolated locations with a snowflake like appearance. Based on these results, the 20% concentration and a 40 minutes plating time was chosen to be uses for full cell fabrication in order to investigate if contact formation and $FF$ could be improved by slowing down the plating rate.

Laser doped and grooved samples with a full area Al back surface field (BSF) were prepared according to the first group’s sequence in Figure 5-20. Two laser irradiances (1.0×10⁸ W/cm² and 9.3×10⁷ W/cm²) were used with two samples made at each condition, scribing speed of 50 mm/s was used in all cases. After a 40 s deglaze in 1% HF, cells were then plated using the standard Cu and slow Cu method. In the standard Cu plating method cells were plated by using a full strength MacDermid Cu solution for 12 minutes, while in sthe low Cu method cells were plated by using 20% MacDermid Cu solution for 40 minutes.

Figure 5-23 plots the electrical parameters of plated cells, comparing the standard Cu plating approach and the slow Cu plating. It can be seen that standard Cu plating resulted in very low
FFs of below 40%. While slow Cu plating significantly increased cells FF to over 70%, which led to a substantial increase in $J_{sc}$ and cell efficiency. There was also some unexpected variation in $V_{oc}$ which needed more data to further investigate. However, it appears that the slow Cu plating method significantly improved metal-Si contact formation, resulting in FFs of over 70% and efficiencies of over 17%. This is clear evidence that selective emitters formed by simultaneous laser doping and grooving can potentially form good metal-Si contacts.

In this section, the approach of slow Cu plating by diluting plating solution has been shown to improve Si-metal contact formation and consequently cell FF significantly, proving the laser doping and grooving technology’s potential to form good metal contacts. The challenge with slow plating however is that it reduces throughput and the attractiveness of the technology for large-scale manufacturing. The next section presents cell results by using Ni plating along with slow Cu plating.

5.3.3 Ni plating plus slow Cu plating

In this part of the work, complete solar cell devices with an area of 9 – 10 cm² were fabricated using the laser doping and grooving process along with a screen printed full Al rear contact and plated front contact via non-contact Ni LIP and slow Cu LIP. The cell processing sequence is summarized in Figure 5-24. Textured Cz p-type wafers with a resistivity of 1.6 Ωcm and thickness of 180 μm were simultaneously laser doped and grooved to form selective regions of
grooves with heavily doped walls prior to a 100-120 Ω/sqr emitter diffusion. The laser condition used was a 100 mm/s scribing speed at 1.0×10⁸ W/cm² and 9.3×10⁷ W/cm² irradiances. A 75 nm PECVD silicon nitride was deposited on the front surface after diffusion, leaving the heavily doped groove walls relatively exposed. Non-contact light induced plating was used to nucleate and plate front metal contact in the grooves after the full area screen-printed Al back surface field was formed by screen printing and fast firing at 825 °C set peak temperature. Samples were deglazed in 1% HF for 40s before plated with Ni using standard MacDermid solution for 2 min followed by 20% diluted MacDermid Cu solution for 40 minutes. Cells were then laser edge isolated from the rear before characterization by PL imaging, Darkstar IV measurement, Suns-Voc measurement, spectral response and reflectance. All cell processing was done using industrial-scale tools.

Table 5-5 shows the IV parameters of three cells, with the highest efficiency being 19.2%. The result shows that the laser doping and grooving concept works well and that high current density is achievable. The three cells were processed at two different laser power levels for the laser-doping and grooving step. Cell 1 was processed at an irradiance of 1.0×10⁸ W/cm², while cells 2 and 3 were processed at 9.3×10⁷ W/cm². The higher laser irradiance resulted in deeper
grooves for the metal contacts. However, the IQE curves (Figure 5-25) indicate that all three cells have similar spectral response and hence current density. Figure 5-26 shows an SEM image of the top-view of a plated finger. The reasonably narrow finger reduces cell shading loss. The reflectance curve shows that the shading loss from the metal is at most 1.5%. The $V_{oc}$ is relatively low as it is primarily limited by the full area Al back surface field, which makes the cell voltage appear low compared to screen-printed PERC cells. The non-optimized firing conditions and non-optimal hydrogen passivation of defects for these cells could also reduce cell voltage. The results of lifetime samples (Section 4.1) indicated that laser doped and grooved cells are capable of much higher voltages if the full area Al rear contact is replaced by a passivated rear contact. Some variation in the series resistance between the cells is also apparent. This may be due to non-uniform doping and uneven surface roughness along the groove walls leading to variations during plating. Alternatively, SiNx could have partially deposited into the grooves which would also affect series and contact resistance. Further analysis and optimization is needed to fully understand and reduce this effect.

Table 5-5 Current-voltage parameters of initial laser doped and grooved solar cells and reference LDSE cells.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Average laser irradiance (W/cm²)</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>$I_{01}$ (A/cm²)</th>
<th>$J_{02}$ (A/cm²)</th>
<th>Rs (Ωcm²)</th>
<th>m @ 0.1 sun (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0×10⁸</td>
<td>630</td>
<td>39</td>
<td>76.1</td>
<td>5.8×10⁻¹³</td>
<td>4.5×10⁻⁸</td>
<td>0.57</td>
<td>1.4</td>
<td>18.7</td>
</tr>
<tr>
<td>(18-4-5a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.3×10⁷</td>
<td>633</td>
<td>39.1</td>
<td>77.4</td>
<td>4.7×10⁻¹³</td>
<td>3.7×10⁻⁸</td>
<td>0.39</td>
<td>1.5</td>
<td>19.2</td>
</tr>
<tr>
<td>(18-9-3b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9.3×10⁷</td>
<td>637</td>
<td>38.6</td>
<td>77.7</td>
<td>4.4×10⁻¹³</td>
<td>2.9×10⁻⁸</td>
<td>0.53</td>
<td>1.3</td>
<td>19.1</td>
</tr>
<tr>
<td>(18-12-3b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It seems that some defects were introduced to the junction region of the laser doped and grooved cells, despite the advanced process. These defects seem to be penetrating into the junction region, leading to a reduced $FF$ and $V_{oc}$. The higher laser-grooving irradiance of cell 1 naturally introduced more defects to the Si. This resulted in lower $V_{oc}$ and $FF$ in comparison to cells 2 and 3. The two-diode model was used to fit the IV curves of the cells. As shown in Figure 5-27, the two-diode model fits the curves very well. From the curve fitting, dark saturation current $J_{01}$ and $J_{02}$ values were extracted and are summarized in Table 5-5. The dark saturation current values of cell 1 are higher than those of cell 2 and 3. This could be caused by the increased defects due to the extra laser energy during the laser-doping and grooving process, resulting in crystallographic defects formed by intense rapid heating and cooling. This could introduce damage near the junction region which results in a high local ideality factor and low $FF$. Even though during emitter diffusion these crystallographic defects are partially gettered and/or passivated, the gettering is not sufficient to passivate all of the defects. Subsequent laser hydrogenation could potentially be used to passivate the remaining defects.
The high ideality factors of around 1.4 could be caused by a combination of crystallographic defects creating junction recombination along with the edge effect due to the small cell area. After plating, the cells are edge isolated by laser cleaving from the rear. Snapping through the emitter would expose the junction region and increase edge recombination. For small cells the increase in dark saturation current is more severe. In each case, the shunt resistance of the cells measured by Suns-Voc was in excess of 150,000 $\Omega \text{cm}^2$ and is therefore not believed to be significantly contributing to the high ideality factor or fill factor loss.

![Graphs of Suns-Voc measurement and Two-diode fit for cells 1, 2 and 3.](image)

Figure 5-27 Suns-Voc measurement and Two-diode fit for cells 1, 2 and 3.

The losses in current and FF for Cell 2 were analysed [19, 149]. Different components of current loss were separated out based on EQE measurement (Figure 5-25). Figure 5-28 shows a pie chart illustrating the percentage loss from each component, including metal shading, front reflectance, front escape, blue loss (which includes absorption in the front dielectric layer), rear absorption and rear collection. It is not surprising that the biggest current loss comes from light absorption in the full area Al-BSF back, which accounts for more than 50% of the total current loss. This means that a considerable portion of the light that enters the cell is parasitically absorbed by the metal instead of generating carriers to be collected. The second biggest current loss is from the front surface reflection. This suggests that the anti-reflection coating and texturing on the front side of the cell could be further optimized to increase...
overall absorption. To reduce current losses, our future work will focus on replacing the full-area-BSF rear contact with local contacts, such as those utilized by the PERC structure, which would also improve cell voltage significantly.

Figure 5-28 Current losses of cell 2

Figure 5-29 shows the breakdown of FF losses of Cell 2 based on Suns-Voc measurement (Figure 5-27) and the two-diode model [19, 149]. There is minimal loss due to shunt resistance. The biggest FF loss is due to the dark saturation current from the second diode $J_{02}$ which accounts for 52% of the total FF loss. We assume this loss is due to crystallographic defects introduced during the laser-doping and grooving process. Although some of these defects are passivated during diffusion, some of them may still increase the dark saturation current. Hydrogenation by controlling the charge state of hydrogen could be used to passivate the laser-induced defects [24]. The loss due to series resistance is also more than 48%. Further analysis of the series resistance and contact resistance is therefore needed and the plating process and/or subsequent sintering needs to be further optimized to reduce this effect. There is considerable room for process optimization and improvement.
Initial results indicate that a lower laser irradiance results in better cell parameters in terms of higher voltage and FF whilst maintaining similar current values to the cells with deeper grooves. The main loss in current comes from the absorption from the full area Al-BSF rear contact while the series/contact resistance and J02 components are causing the main losses of FF. The next step is to incorporate rear passivated contacts, to further optimize the plating/sintering process, and to incorporate hydrogenation technology to passivate defects introduced during cell fabrication. Figure 5-30 are a few examples of plated metal fingers by using standard Ni plating plus slow Cu plating. It can be seen that the grooves are completed fill with metal providing good metal-Si contact as well as good mechanical adhesion strength. It shows that even though the groove geometries are not exactly identical due to variations in laser conditions, the plating process is able to nucleate inside the grooves and deposit continuous metal contacts inside the groove.
In this section the development of cell devices with full area Al-BSF has been presented. It was shown that the laser doping and grooving technology has the potential to form good metal contacts with significantly improved metal contact adhesion strength. The process has been integrated into device fabrication, achieving over 19% efficiency with a full area Al-BSF rear contact. However further optimization is required to reduce the resistive losses to facilitate high fill factors and improved efficiencies. In Section 4.1 it is shown that laser hydrogenation could improve the lifetime of laser doped and grooved test structures. In the next section the effect of laser hydrogenation on finished laser doped and grooved cells is discussed.
5.4 Laser hydrogenation of laser doped and grooved cells

It has been shown that during emitter diffusion, some laser induced defects can be gettered or passivated. However, the diffusion alone may not be able to completely fix up all the defects, since cell results in the previous section show that remaining FF losses due to dark saturation current are significant. The application of laser hydrogenation to enhance laser doped and grooved lifetime samples has been previously discussed in Section. In this section, the effect of applying the same laser hydrogenation process on finished laser doped and grooved solar cell devices will be presented.

Two cells were processed in accordance with the sequence shown in Figure 5-24 with a 100 mm/s scribing speed and $1.1 \times 10^8$ W/cm$^2$ irradiance used for the laser doping and grooving process. All the other processing conditions were identical to the cells in previous section. The high laser irradiance was purposely chosen in order to generate more laser induced defects and thus highlight the effect of any effect passivation through hydrogenation. Hydrogenation was performed on the finished cells using the laser hydrogenation tool detailed in Figure 4-1. The laser hydrogenation processing was carried out at a photon flux of $1.3 \times 10^{19}$ photons/cm$^2$/s (40 A laser current) and sample temperature of 300 °C for 1 minute, matching the conditions that were previously shown to improve $iV_{oc}$ in lifetime test structures.

Cells parameters are summarized in Table 5-6. After plating, over 18% efficiency was achieved in both cells. However the local ideality factor was high, probably due to defects penetrating into the junction region, therefore leading to low FF and $V_{oc}$. One possible cause could be that during the laser doping and grooving process, crystallographic defects are introduced due to intense fast heating and cooling from the laser treatment. These could introduce damage near the junction region which results in a high local ideality factor and low FF.

Table 5-6 also summarizes the electrical parameters of the cells after hydrogenation. By using the laser hydrogenation process to control the charge state of hydrogen, laser induced defects near the junction region were passivated. This could explain the big improvement in FF and ideality factor in Cell 1. The FF and ideality factor improvement in Cell 2 was not as good, in fact its ideality factor at 0.1 Sun increased after laser hydrogenation. This indicates that there could be a shunting problem in Cell 2. Unfortunately no DLIT imaging was available to verify. However, the ideality factor increased after hydrogenation, which suggests there could be a shunting problem as well as residual crystallographic defects induced by the laser doping and grooving process. With the defects passivated, carrier lifetimes were increased and hence there was a 4% increase in Voc in both cells. Overall the cell efficiency was improved by 1.2% absolute in Cell 1 and 0.6% absolute in Cell 2.
Figure 5-31 shows the associated PL images and Figure 5-32 plots the IV curves of Cell 1 before and after the hydrogenation process. The PL images were deconvolved to minimise the effects of photon smearing and to improve clarity and accuracy [150]. PL images show that the cell was uniformly improved.

Table 5-6 Cells parameters before and after laser hydrogenation

<table>
<thead>
<tr>
<th>Cell</th>
<th>Average laser irradiance (W/cm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>m @ 0.1 Sun</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (18-4-4b)</td>
<td>After plating</td>
<td>1.1×10⁸</td>
<td>610</td>
<td>39.3</td>
<td>75.3</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>After laser hydrogenation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 (18-9-4b)</td>
<td>After plating</td>
<td>1.1×10⁸</td>
<td>611</td>
<td>39.5</td>
<td>75.6</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>After laser hydrogenation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-31 PL image of cell 1 before and after laser hydrogenation process

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The current losses and $FF$ losses of Cell 1 before and after laser hydrogenation were analysed. The pie charts in Figure 5-33 show the percentage of different loss components. Comparison of the cell losses before and after the hydrogenation process shows that there was not much change in the current loss, but the $J_{02}$ component in $FF$ loss was significantly reduced. This indicates that hydrogenation process has passivated some of the laser induced defects near the junction region and hence resulted in the increased $FF$ and reduced local ideality factor shown in Table 5-6.

Figure 5-33 IV curve of laser doped and grooved cell before and after hydrogenation

Figure 5-33 Current and FF loss analysis before and after laser hydrogenation
After laser hydrogenation the cells produced using high laser doping and grooving irradiance had efficiency values close to those processed using the lower laser irradiance. This indicates that the laser hydrogenation process could potentially fix up damage or non-uniformities which have occurred during cell processing, allowing for a bigger processing window for the laser doped and grooved cells.

In this section the laser hydrogenation process was applied to finished laser doped and grooved cells. Significant improvement in $FF$ and cell efficiency were achieved, possibly attributed to hydrogen passivating laser induced crystallographic defect near the junction region. An overall cell efficiency improvement of over 0.6% absolute was achieved.

### 5.5 Conclusion

This chapter presents the development of solar cell devices using the laser doping and grooving technology with full area Al BSF rear contact. Lifetime test structure showed that there is only a 5-8 mV difference between the best laser doped and grooved samples and non-laser scribed samples. Plating into the grooves greatly enhances the adhesion strength of a plated metal contact, resulting in adhesion that is slightly superior to screen printed contacts. With relatively little optimization, over 19% cell efficiency was achieved on cells with full area Al BSF. Laser hydrogenation has been shown to be able to improve cells which have relatively more laser induced defects to perform at a similar level to good cells with less laser induced damage. Over 1% absolute improvement in efficiency was achieved. It is therefore clear that laser hydrogenation is a powerful process capable of improving cell efficiency through passivation of different defects in the cell structure. However, it is not yet clear if the laser hydrogenation technique could be scaled up for commercial cell fabrication. In the next Chapter the development and progress towards commercialization of this advanced hydrogenation technique is presented.
Chapter 6

6 Commercialization development of advanced hydrogenation

The advanced hydrogenation technology has been extensively demonstrated in the laboratory through the use of a laser illumination system on small cells. As this new technology appears to have significant potential to benefit manufacturing, a prototype tool was developed to demonstrate the commercial significance of the technology and to be able to process commercial size cells. In particular, one aim of the new tool design was to move away from laser-based processes in favour of much lower cost LED based processes. A new LED-based prototype tool was therefore developed and evaluated together with A.Prof. Jingjia Ji and Dr. Ly Mai. In parallel, a laser equipment manufacturer has also developed a laser based commercial tool that duplicates the lab-based processes and therefore has a high probability of successfully implementing the advanced laser hydrogenation technology. One of the aims of this latter tool is also to make it available for the photovoltaics industry for large-scale manufacturing based on the advanced laser hydrogenation. The other aim for this laser-based tool is for it to act as a control when developing, demonstrating and evaluating alternative tool designs such as this LED-based tool in this work that have greater economic value and potential but have greater uncertainty technically as to their effectiveness at implementing the advanced hydrogenation technology.

6.1 Development of a prototype industrial LED based hydrogenation tool

A new prototype production tool was developed to demonstrate the compatibility of the advanced hydrogenation technology to large area production solar cells, using LEDs as a low cost non-laser-based light source for controlling the charge state of the hydrogen atoms.

6.1.1 LED hydrogenation – single LED

As a first step, the suitability of a 100 W white LED array for hydrogenation was tested. The LED was mounted onto a copper plate for effective cooling (Figure 6-1). The highest illumination level was found to be 4.5 cm away from the LED with an intensity of \(1.8 \times 10^{18}\) photons/cm\(^2\)/s, equivalent to 8 Suns assuming \(2.1 \times 10^{17}\) photons/cm\(^2\)/s for 1 Sun illumination.
Lightly diffused (150-200 Ω/sqr) Cz lifetime samples with double sided SiNx deposition and 700 °C belt furnace firing were used to test the ability to hydrogenate B – O defects using a single LED array. Samples were put through 48 hour light soak at below 40°C using 0.6 Suns illumination before the experiment to fully form the B – O defects [135]. They were then illuminated annealed at 250 °C on a hotplate at 4.5 cm beneath the LED for 2 minutes before being quenched on wet filter paper, this process was carried out at several different light intensity levels. Samples were then light soaked for 48 hours together with control samples that were not treated and samples that were heat treated in the dark as well as samples treated by the laser hydrogenation tool.

Figure 6-2 summarizes the $iV_{oc}$ values after each process step. Without any hydrogenation, the high lifetime achieved via 700 C firing was not stable and drops significantly after light soaking. The dark annealing could restore the lifetime but again it is unstable and re-degrades after further light soaking. This is because dark annealing dissociates B – O defects temporarily, but these defects then reform again over time when under illumination. Laser hydrogenated samples were relatively stable after light soaking, indicating that B – O defects are passivated effectively. Samples treated by the single LED were not as stable as the laser treated ones, but better than the dark annealed or non – processed samples, with higher intensity showing more stability. This indicates that the single LED process had passivated some of the B – O defects but not all. This could be caused by too low an illumination from a single LED or too short a process time for this given light intensity. Although passivation from the single LED was not as good as the laser hydrogenation process, the fact that it was superior to the control samples.
suggests that these LEDs have the potential to be developed into a hydrogenation tool upon optimizing illumination intensity and process parameters.

**Figure 6-2** $I_{Voc}$ results from single LED in comparison with laser hydrogenated, dark annealed and non-processed samples

One of the issues that was observed during the single LED test was that the light intensity of the LED was affected significantly by the LED temperature. Figure 6-3 plots the photon flux versus the LED temperature. As temperature increases, the LED is less efficient and hence gave out a lower light intensity.

The single LED testing showed that there was potential to develop a hydrogenation tool based on these LEDs but more effective cooling had to be designed to protect the lamps and optimise the system.
6.1.2 LED hydrogenation – 20 LED array
After confirming the potential of white LEDs for hydrogenation, 20 LED arrays were mounted onto a water cooled aluminium plate, shown in Figure 6-4. The array was positioned over a hotplate next to a sink through which the cooling recycled water was run. The light intensity of each LED was tested and plotted in Figure 6-5. The illumination was not uniform across the 20 LEDs. The brightest part of the array was used for testing as indicated by the 4 numbers in Figure 6-4, which represent the illumination in equivalent suns.
Commercial p-type PERC cells were processed at 250 °C for 2 minutes under different LED intensities set by the LED voltage. Figure 6-6 shows that cells processed at 30 V obtained a similar improvement in efficiency to the laser hydrogenation processed cells, where 0 on the y-axis refers to the starting cell efficiency before hydrogenation processing. For voltages below 30 V, there is a general trend of increased improvement with increased LED voltage. This could be explained by the increase in light intensity with increasing voltage setting. However, for voltages over 30 V there is a sharp drop in the stabilized efficiency. This suggests that cells processed over 30 V could be over heated by the LED illumination, resulting in a much higher cell processing temperature that is not favourable for hydrogenation of B – O defects.
The effect of processing time was also investigated. Figure 6-7 shows the PL images of cells after 48 hours of light soaking. These cells were processed for different durations under the LEDs and are shown alongside cells processed by the laser hydrogenation process and a cell that did not receive any hydrogenation process. It is clear that the cell that had no hydrogenation treatment degraded a lot compared to the hydrogenated cells. The cells processed by the LED setup resulted in similar stability as the ones processed by the laser. It appears that the variation in processing time did not have much effect on the effectiveness of the hydrogenation passivation in this case.

![PL image of LED hydrogenated cells and laser hydrogenated cells](image)

The development and initial testing of the water cooled 20 LED array revealed that the LED setup could achieve similar results on small samples as the laser hydrogenation tool in terms of deactivating B – O defects in PERC mono cells. However, the illumination intensity was not uniform, this issue must be resolved in order for the system to work for 6 inch full-size commercial cells.

### 6.1.3 LED hydrogenation – 40 LED array
The final phase of the LED prototype is an extension to a 40 LED array mounted on a custom built water cooled plate, as shown in Figure 6-8 and Figure 6-9. The intensity and uniformity of the illumination was improved by the inclusion of focusing lenses together with reflectors which are also shown in Figure 6-8. The LED array is mounted on a rack hanging over a hotplate equipped with a vacuum chuck.
This LED prototype makes it possible to apply the advanced hydrogenation technology on full-size industrial 6-inch cells. The processing parameters for passivating B–O defects in mono p-type cells were optimized to be 4 minutes at 250 °C. Mono crystalline PERC cells from an industry partner were processed using the LED prototype.

Figure 6-10 plots the efficiencies of the hydrogenated group and non-hydrogenated group. The PL images are summarized in Figure 6-11. The PL images and IV characteristics of the hydrogenated cells after hydrogenation treatment showed an increase in performance. This indicates that the hydrogenation treatment using the prototype production tool has passivated recombination centres in these solar cells which may have formed due to contamination and/or crystallographic imperfections. The PL images and IV characteristics of these cells showed no significant drop in performance following the light soaking step. This
shows that the hydrogenation treatment has solved LID in these solar cells and they will likely no longer suffer from LID during operation in the field.

![Figure 6-10 Efficiency of commercial 6 inch PERC cells processed by the LED prototype tool](image)

![Figure 6-11 PL images of hydrogenated and non-hydrogenated cells](image)
The development and testing of the LED based prototype has successfully demonstrated the industrial suitability and relevance of the advanced hydrogenation technology developed in the laboratory, with the conclusion that it is ready for commercialization and can be transferred to industry.

### 6.2 Laser based commercial hydrogenation tool for large scale production

A few production equipment manufacturers are interested in working with UNSW to design and build production tools for the mass production of the advanced hydrogenation technology. One of them is Wuhan DR Laser Technology corp Ltd (DR Laser), who is a high-tech laser equipment manufacturer. Figure 6-12 is a photo of the laser hydrogenation equipment being developed at DR Laser.

![Commercial laser hydrogenation tool](image)

Full-size 6-inch PERC cells from an industry partner were brought to DR Laser and processed by this commercial laser hydrogenation tool, with promising results achieved. Figure 6-13 shows the resulting cell parameters. Due to time limitations, the PERC cells were only light soaked for 6 hours before taking to DR Laser. Even with such a short light soaking duration, clear degradation in cell performance were observed. After being processed by the commercial laser hydrogenation tool, cells were taken back to UNSW for light soaking and testing. It can be seen that cell efficiencies were improved by 0.4% absolute and were stable after light soaking, indicating the successful passivation of B-O defects. The improvement mainly came from a $V_{oc}$ increase, which was around 10 mV. These results are very encouraging and demonstrate that commercial tools are now well-developed and available for the industry. These results also confirm that the LED-based prototype tool developed and used above is able to also
implement the advanced hydrogenation technology in a similar way to a laser-based process, with similar performance enhancements and improvements in stability.

![Figure 6-13 Commercial PERC cells processed by commercial laser hydrogenation tool](image)

### 6.3 Conclusion
In this chapter the development and initial testing of an LED-based prototype advanced hydrogenation tool for processing 6-inch commercial cells has been presented. 0.4% absolute improvement in PERC cells efficiency was achieved and this improvement was proven to be stable throughout light soaking, showing that the advanced hydrogenation technology can not only benefit lab size small cells but can also be beneficially applied to full size commercial cells. One of UNSW’s industry partners has developed a laser hydrogenation tool for implementation of the advanced hydrogenation into large-scale production and initial testing shown here has revealed promising results, demonstrating that the advanced hydrogenation technology is ready to be transferred to the photovoltaic industry. The two prototype industrial tools developed in conjunction with this work have also demonstrated the feasibility and success of using LED-based light sources as replacements for Lasers in commercial tools that implement the advanced hydrogenation technology.
Chapter 7

7 Conclusions and future work

The primary aim of this thesis was to develop laser technologies for the advancement of fabrication of solar cells. This involved the development of two techniques and corresponding processes. The first one is for the fabrication of a selective emitter solar cell through simultaneous laser doping and grooving followed by self-aligned metal plating. It has been clearly demonstrated that the concept of laser doping and grooving can work, with cell efficiencies of over 19% achieved by using this technology on p-type Cz wafers with a full area Al BSF rear contact. The second technology is that of laser hydrogenation in which the charge state of hydrogen is controlled by illumination and temperature. Through the work on this thesis, several outcomes were achieved:

In Chapter 3, the study of groove formation, the influence of laser parameters on groove geometry and the quality of the p-n junction along the groove walls showed that:

1. Laser processing can be used to form narrow grooves on Cz p-type Si wafers while simultaneously heavily doping the groove walls to form selective emitter regions in preparation for the metal contacts. Optimal groove geometry of 3 – 5 μm in width and 10 – 15 μm in depth can be achieved, despite using a laser-beam diameter of 10 to 15 μm. This geometry ensures that the grooves are deep enough to provide good metal contact adhesion strength for subsequently plated contacts [50] but not too deep to introduce excess laser damage that generates high dark saturation current. Additionally, the narrow width of the grooves ensures that during the dielectric layer deposition after groove formation there is only minimal deposition inside the grooves, leaving the groove walls exposed to allow nucleation during the subsequent plating process. The narrow grooves also give rise to narrow fingers which minimises shading losses.

2. The depth of grooves increases with increasing power and decreases as scribing speed increases. The opening width of groove increases as scribing speed increases. And the higher the laser frequency the more uniform the groove is.
3. To achieve groove formation, laser irradiances in the vicinity of laser ablation are required. Pulse repetition rate also plays an important role which suggests thermal effects between pulses could be involved.

4. An average laser power range from 0.61 W to 0.73 W at 100 kHz with speeds of 50 mm/s and 100 mm/s was found to be a good parameter space for producing consistent, narrow grooves that were 10 – 15 μm deep and 3 – 5 μm wide.

5. Deep grooves tend to have a shallow junction depth. Grooves with wide openings would have shallow junction depth as well due to the loss of excessive molten Si. Grooves with medium depth and narrow opening width have a relatively deep junction depth within the groove walls, which is 40% deeper than the other two profiles, and are shown to produce higher voltages due to a reduced dark saturation current (see Chapter 4 and 5).

6. The laser doping and grooving process is capable of forming grooves with continuous and deep p-n junctions. No obvious changes in the junction depth before and after emitter diffusion were observed under EBIC.

In Chapter 4, another technology was developed which employs lasers to control the charge state of interstitial hydrogen to passivate defects in silicon solar cells, it was shown that:

1. The charge state of hydrogen could be controlled by the combination of illumination and temperature, with the data being in broad agreement with the hypothesis that it is the charge state of hydrogen that has the greatest influence. These correlations might not be easily observed at high temperatures due to the dissociation of hydrogen defect bond at these high temperatures.

2. It seems there is correlation between the cooling rate after hydrogenation and the resulting sample lifetime, likely because fast cooling can prevent the dissociation of the hydrogen-defect complexes and in effect lock-in the hydrogen passivation of the defects.

3. $iV_{oc}$ values of UMG lifetime samples were improved from 610 mV to 710 mV. Defects need to be formed before they could be passivated. Repeatedly activating defects
through light-soaking and then using hydrogenation on UMG material lead to improved UMG having long term parameters close to that of Cz material.

4. B-O defects in commercial PERC cells can be effectively passivated by the advanced hydrogenation process. Over 1% absolute difference in efficiency after 48 hours of light soaking was demonstrated between samples which received the advanced hydrogenation process and samples which received no such process.

5. The advanced hydrogenation process was applied to lifetime samples prepared using the laser doping and grooving technique. It was observed that the hydrogenation process improved sample lifetime. The higher the laser grooving power, the more improvement achieved by hydrogenation. This suggests that the low values of $iV_{oc}$ determined for the high laser power group may be caused primarily by laser-induced defects, which were then passivated by the hydrogenation process.

In Chapter 5, the simultaneous laser doping and grooving technique was further developed to create full cell structures and the incorporation of advanced laser hydrogenation was also investigated for this new type of solar cell. The investigation showed that:

1. The laser doping and grooving process is capable of achieving higher $iV_{oc}$ values than the conventional LDSE process, with only 5 – 8 mV difference between the best laser doped and grooved sample and the non-laser scribed sample, indicating minimal laser induced damage. High sample lifetimes with minimal $iV_{oc}$ degradation in comparison to non-scribed samples can be produced repeatedly and reliably.

2. There is not much difference between the single pass and double pass approaches at the lower laser irradiance levels investigated. However, at the higher irradiance levels the double scribed group showed a higher sample lifetime than the single scribed group. The second laser scribe may have driven the dopants further into the bulk and consequently distributed them more evenly, resulting in a reduced dopant surface concentration and increased sample lifetime.

3. The laser doping and grooving process can be applied at any stage before the SiNx deposition. The optimal sequence is to perform the laser doping and grooving process
before emitter diffusion, during which the laser induced damage can then be passivated/gettered.

4. Deposition of SiNₓ can be processed after the groove formation and the groove can still be plated. This avoids the laser induced mismatch that exists due to the different thermal expansion coefficients between Si and SiNₓ.

5. Narrow and deep grooves tend to get closed up during plating, leaving the bottom part of groove with incomplete plating. It is easier to achieve complete metal filling with wider and shallower groove geometries. V-shaped cross-sectional geometry is preferred in terms plating reliability.

6. Plating into the grooves greatly enhances metal contacts’ adhesion strength. It is shown to be more than twice that of the conventional laser doped cell and is slightly superior to typical screen printed metal contacts, as determined using a stylus-based adhesion tester.

7. Solar cells with laser doping and grooving processed on the front and full area Al BSF rear contacts were fabricated. Use of a slow plating rate by diluting the plating solution was found to improve the metal-Si contact and hence cell $FF$. Over 19% cell efficiency was achieved with little process optimization.

8. An advanced laser hydrogenation process was applied onto finished cells with a relatively large amount of laser induced defects caused by the use of a higher laser doping and grooving irradiance. Over 1% absolute increase in cell efficiency was achieved, resulting in cell performance at a similar level to the cells which had fewer laser defects introduced during fabrication. This suggests that with process optimization and incorporation of advanced hydrogenation, the laser doping and grooving technology could have a larger processing window.

In Chapter 6, the development of an LED based prototype hydrogenation tool was discussed and the following conclusions were made:

1. The advanced hydrogenation technology could be realized using cheaper light sources such as LEDs instead of lasers.
2. The advanced hydrogenation technology was proven to work not only on lab-size small samples but also on commercial 6-inch cells.

3. An industry partner of UNSW who manufactures production tools for the photovoltaic industry has developed a laser based commercial hydrogenation tool for large scale production with over 90% illumination uniformity and a patented technology for cooling sample to room temperature in seconds. Promising test results suggest that the advanced hydrogenation technology is ready to be transferred to the photovoltaic industry.

7.1 Original contributions

1. A new laser grooving process that simultaneously dopes the groove walls has been developed and has demonstrated the ability to form narrow grooves of only 3 – 5 microns width in preparation for metal contact formation. The narrow width and steep walls of the grooves make it possible to deposit an ARC coating after the laser grooving process, in a manner whereby the groove walls remain uncoated to allow nucleation of subsequent metal plating. This process has been shown to significantly reduce laser-induced defects compared to when the laser process is applied after the ARC deposition.

2. Light-induced plating processes have been developed and implemented to suit direct plating of metal into these grooves whereby the plated contacts achieve significantly increased adhesion strength compared to conventional plated contacts.

3. A new silicon solar cell technology has been developed by combining the achievements from the above original contributions with wafer texturing, surface diffusion, SiNx PECVD deposition, screen printing of metal contacts and firing.

4. Through the evaluation and optimisation of the various processing parameters, over 19% efficiency has been achieved by using the laser doping and grooving process on p-type Cz wafers in conjunction with a full area Al-BSF rear contact.
5. A new advanced laser hydrogenation tool was developed together with a colleague, Alison Ciesla (formerly Wenham) [123].

6. An LED prototype hydrogenation tool was developed together with A/Prof Jingjia Ji and Dr Ly Mai.

7. Application of the advanced laser hydrogenation process for UMG and laser doped and grooved lifetime samples was optimized.

8. The laser doping and grooving technique was incorporated with the advanced hydrogenation process. Over 1% absolute efficiency increase was achieved on laser doped and grooved cell with full area Al BSF.

### 7.2 Future work

#### 7.2.1 Optimization of laser doping and grooving cell fabrication

The work of this thesis demonstrated that the concept of laser doping and grooving can work and solar cell devices have been made with good electrical properties. However, the cell fabrication process has not been fully optimized. The result of this work indicates that, due to its simple process sequence, the laser doping and grooving technology can potentially be developed to be used for large-scale production of high efficiency solar cells, and it has the potential to provide a solution for the major concern for plated contacts, metal contact adhesion strength. It is therefore recommended to further optimize the cell fabrication process.

#### 7.2.2 Optimization of advanced hydrogenation for laser doped and grooved cells

The results show that laser doped and grooved solar cells responds well to the advanced hydrogenation process, which passivates the remaining laser induced defects that are not gettered or otherwise passivated during emitter diffusion. However, the advanced hydrogenation was only applied onto finished cells. Optimization in conjunction with the cell fabrication process is recommended so that the best defect passivation and stability can be achieved.

#### 7.2.3 Development of cell structures with improved rear passivation

Lifetime test structure results show that there can be only a 5 – 8 mV degradation in $iV_{oc}$ between laser doped and grooved samples and non-scribed samples. It is expected that much
higher voltages and consequently higher efficiencies could be achieved if this technology is combined with a passivated rear approach, such as a PERC structure.

Initial results showed that it is possible to form laser doped grooves on a rear surface with an aluminum oxide and SiNx stack layer. However, there was not sufficient time during this thesis to further investigate the quality of the $n$-type doping along the groove walls, damage caused by the process, and the ability to form contacts on the rear. It is recommended to further investigate and possibly develop a double sided laser doped and grooved cell structure.

7.3 Conclusion

In this thesis, a simultaneous laser doping and grooving selective emitter solar cell has been developed. This process benefits from the advantages of BCSC but with the simplicity of the LDSE approach. An efficiency of over 19% was achieved on cells with full area Al BSF rear contacts. An advanced laser hydrogenation tool was developed and shown to be able to passivate a range of different defects. The advanced hydrogenation process was shown to be commercially scalable and was also incorporated with the laser doped and grooved cells, achieving over 1% absolute improvement in cell efficiency.
List of publications

Journal papers
Revision to be submitted to SOLMAT:


Published:


Conference papers


Appendix A

Groove geometry at 90 kHz, 80 kHz, 70 kHz, 60 kHz, 40 kHz and 20 kHz

**Figure A-1:** Groove geometries at 90 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels
Figure A-2: Groove geometries at 80 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels
Figure A-3: Groove geometries at 70 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels.
Figure A-4: Groove geometries at 60 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels

<table>
<thead>
<tr>
<th>60 kHz</th>
<th>1130 to 1170 mW</th>
<th>1070 to 1130 mW</th>
<th>1010 to 1030 mW</th>
<th>933 to 1040 mW</th>
<th>841 to 874 mW</th>
<th>756 to 806 mW</th>
</tr>
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<tr>
<td>10 mm/s</td>
<td><img src="image1.png" alt="Images" /></td>
<td><img src="image2.png" alt="Images" /></td>
<td><img src="image3.png" alt="Images" /></td>
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<td><img src="image5.png" alt="Images" /></td>
<td><img src="image6.png" alt="Images" /></td>
</tr>
<tr>
<td>50 mm/s</td>
<td><img src="image7.png" alt="Images" /></td>
<td><img src="image8.png" alt="Images" /></td>
<td><img src="image9.png" alt="Images" /></td>
<td><img src="image10.png" alt="Images" /></td>
<td><img src="image11.png" alt="Images" /></td>
<td><img src="image12.png" alt="Images" /></td>
</tr>
<tr>
<td>100 mm/s</td>
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<td><img src="image14.png" alt="Images" /></td>
<td><img src="image15.png" alt="Images" /></td>
<td><img src="image16.png" alt="Images" /></td>
<td><img src="image17.png" alt="Images" /></td>
<td><img src="image18.png" alt="Images" /></td>
</tr>
<tr>
<td>150 mm/s</td>
<td><img src="image19.png" alt="Images" /></td>
<td><img src="image20.png" alt="Images" /></td>
<td><img src="image21.png" alt="Images" /></td>
<td><img src="image22.png" alt="Images" /></td>
<td><img src="image23.png" alt="Images" /></td>
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Figure A-5: Groove geometries at 40 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels.
<table>
<thead>
<tr>
<th>20 kHz</th>
<th>1380 to 1420mW</th>
<th>1340 to 1360mW</th>
<th>1300 to 1340mW</th>
<th>1310 to 1330mW</th>
<th>1230 to 1240mW</th>
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<tbody>
<tr>
<td>10 mm/s</td>
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<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>50 mm/s</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>100 mm/s</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
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<tr>
<td>150 mm/s</td>
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<td><img src="image18.png" alt="Image" /></td>
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Figure A-6: Groove geometries at 20 kHz laser-pulse frequency using 10 mm/s, 50 mm/s, 100 mm/s and 150 mm/s at six laser power levels
Appendix B

Constant pulse energy at varied pulse moving speed

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Power</th>
<th>Pulse Distance</th>
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<tr>
<td>1kHz</td>
<td>6.5mW</td>
<td>10 um/pulse</td>
</tr>
<tr>
<td>2kHz</td>
<td>13mW</td>
<td>50 um/pulse</td>
</tr>
<tr>
<td>3kHz</td>
<td>22mW</td>
<td>33 um/pulse</td>
</tr>
<tr>
<td>10kHz</td>
<td>63mW</td>
<td>10 um/pulse</td>
</tr>
<tr>
<td>Frequency (kHz)</td>
<td>Power (mW)</td>
<td>Move (um/pulse)</td>
</tr>
<tr>
<td>----------------</td>
<td>------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>20kHz</td>
<td>131mW</td>
<td>Move 0.5 um/pulse</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Move 5 um/pulse</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Move 15 um/pulse</td>
</tr>
<tr>
<td>40kHz</td>
<td>273mW</td>
<td>Move 0.25 um/pulse</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Move 2.5 um/pulse</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Move 7.5 um/pulse</td>
</tr>
<tr>
<td>60kHz</td>
<td>392mW</td>
<td>Move 0.17 um/pulse</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Move 1.7 um/pulse</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Move 5 um/pulse</td>
</tr>
<tr>
<td>80kHz</td>
<td>520mW</td>
<td></td>
</tr>
<tr>
<td>Move</td>
<td>Move</td>
<td>Move</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>0.125 um/pulse</td>
<td>1.25 um/pulse</td>
<td>3.75 um/pulse</td>
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<table>
<thead>
<tr>
<th>Move</th>
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</tr>
</thead>
<tbody>
<tr>
<td>0.1 um/pulse</td>
<td>1 um/pulse</td>
<td>3 um/pulse</td>
</tr>
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</table>

100kHz
642mW
Appendix C

Testing laser power and stability

The first optimisation step was to broadly explore the laser parameter space to find suitable conditions for forming clean and continues grooves before examining the quality of doping. However, data from initial experiments did not lead to useful conclusions since using the same set laser diode current and scribing speed resulted in quite different surface morphologies, as shown in Figure C-1. The figure shows three sets of laser scribed lines on the same day using 28.5 A set current at a pulse frequency of 100 kHz and a 10 mm/s scribing speed. Even though the set laser scribing parameters were identical, the resulting surfaces were very different. Some had intermittent grooves while others only exhibited surface melting. It was suspected that the power output from the laser was not consistent and thus required further investigation.

![Figure C-1 Three sets of laser scribed lines at 28.5A set current using 10 mm/s at 100 kHz on the same day](image)

Given that the laser was manufactured close to 10 years ago, the manufacturer suggested to improve stability by setting the diode current at its nominal current range of 30 – 32 A and to modulate the laser power by using attenuators. The power fluctuation at 28.5 A was 13.3 % of the average power while at 32 A it was 5.3 %.

Therefore a 70/30 beam splitter was used to reflect 70% of incident light to a beam dump and transmit only 30% of the light, such that the
laser diode current could be set in the nominal range with reduced power fluctuation.

However, using the beam splitter alone was not sufficient to reduce the power fluctuation to within a workable range. The average power from the laser beam was measured at different set currents on several days and plotted in Figure C-2. For a given set diode current, there was a range of possible output laser powers. For instance, for a current setting of 31 A, the average laser power could range from just above 0.6 W to over 0.9 W, which covers the laser processing range from just melting the silicon surface to forming grooves, making it difficult to control groove formation with consistency.

![Figure C-2 Measured average laser power at different current setting with a 70/30 beam splitter](image)

Further investigation revealed that this fluctuation was closely related to the actual temperature of the laser module monitored by a built-in sensor. Figure C-3 shows that the average laser power increases significantly with laser temperature when the temperature was below 30°C and it was relatively stable for temperatures between 33°C and 36°C.
Figure C-3  Measured average laser power vs laser temperature at 32 A set current

Given that the laser power was only relatively stable for a small temperature range, an air conditioner was used together with the beam splitter to successfully reduce power fluctuations. The laser temperature and output power were closely monitored during experiments to ensure the power fluctuation was kept within an acceptable range. This approach was successful in restricting the power fluctuations to within an acceptable range of ±0.05 W.
References


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