Laser Doping Technique Investigation and Optimisation for High Efficiency Laser Doped Solar Cells Fabrication

Written by

Lei Zhang

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Supervisor: Martha Lenio, Stuart Wenham

Assessor: Prof. Stuart Wenham
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Abstract

Global warming is now a serious and imperative issue which requires addressing as it has a great impact on the environment. To reduce greenhouse gas emissions and simultaneously satisfy future electricity demand, solar energy comes into place as an alternative energy source. To necessitate a higher consumption percentage of solar energy on a worldwide level, high efficiency solar cells with simple fabrication and cost effective processes must be developed.

The use of lasers in junction fabrication has been studied for a long time. The use of laser doping to form the emitters has the major advantage of being able to fabricate heavily doped regions without the need for high temperature processes. This is particularly significant when using commercial wafers such as CZ or mc-Si whose lifetime degrades during high-temperature processes. Meanwhile, high efficiency cell structures such as PERL cell which incorporates a selective emitter design, and are not commercially viable due to high cost and complex fabrication sequence. However, laser doping has also been proven to be a good option compared with traditional thermal diffusion to form the heavily doped region of a selective emitter, and could simply fabricate PERL cells.

This thesis investigates the formation of n-type emitters on p-type wafers using a continuous wave laser, as part of an experimental investigation into DSLDSE (Double Sided Laser Doping Selective Emitter) cell design and the optimisation of the metallisation process via photoplatting. A study of the relevant surface passivation processing is presented and reasonable formation of ARC has been demonstrated. Promising development of standard light induced plating process developed by UNSW for laser doped solar cells with displaced aluminium reflector rears has been achieved. Characterization using Photoluminence, scanning electron microscope, focused ion beam and electron beam induced current etc. to fully record the cell’s performance during each stage of processing and sort out possible problems for further improvement.

The findings in this thesis show the viability of DSLDSE cell structure and provide greater insights into the application of LIMPID (Laser induced melt predeposited
impurity doping developed by Abbott et al.) technique. The need for further research is also indicated if high efficiency cell is to be made, especially the light induced plating process and rear surface passivation.
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Pursue your dream, be it what it will, steadily and indefatigably

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Chapter 1

Introduction

Over the last hundred years or so, the instrumental temperature record has shown a trend in climate of increased global mean temperature, i.e., global warming. What is meant by this is not merely a common recognition that the earth is heating up, evidence of observed climate change has brought us detrimental effects like a probable increase in frequency of some extreme weather events and changes in rainfall patterns. Moving from global to regional scales, there is increased uncertainty over how climate will change. The probability of warming having unforeseen consequences increases with the rate, magnitude, and duration of climate change. [1] What causes all of these? Green house gas emission is to bear the brunt of blame. Hence, cooperation between countries is urgently required to reduce greenhouse gas emission.

Australians are among the highest per-person greenhouse gas polluters in the developed world. Most of Australia’s greenhouse gas emissions come from the burning of fossil fuels for energy. According to statistics [2], the main sources of Australia’s greenhouse gas emissions are:

- 50% from stationary energy, primarily electricity generation;
- 16% from agriculture, mostly from cattle and fertilizers;
- 14% from transport;
- 6% from land use changes, and
- 5% from industrial processes such as cement and aluminum production

So a clear conclusion can be drawn that major contribution of greenhouse gas emissions is due to the reliance on fossil fuels burning for electricity generation. The type of energy distribution plays a vital role in alleviating carbon dioxide in the long run, as reported, one kWh of energy generated by coal will produce 0.6 kg of carbon dioxide. [3] An alternative energy is therefore required to be productively applicable in order to solve the
problems we are facing as well as feed future electricity usage. For the time being, 80.3% of energy generated in the world (Gas/Oil/Coal) emits greenhouse gasses [4] as shown in the figure 1.1

![Figure 1.1 2007 World Energy distributions [4]](image)

Renewable energy is gaining market share in global energy production, however, the portion of it is still overwhelmed by that of traditional fossil fuels. Moreover, solar energy accounts for even smaller percentage though this resource abundant on the earth wherever sunlight is. To make solar energy more accessible, one of the biggest barriers for photovoltaic energy usage compared to Gas/Oil/Coal energy production currently is the price. PV energy costs per watt. Several factors contribute to this:

- Raw materials cost, especially high quality Silicon wafers
- The conversion efficiency of Solar cell
- Solar cell fabrication processes
- Lifetime of Solar modules.

Hence, two clear technical trends in the silicon solar cell community to date can be observed: (i) the use of thinner substrates and (ii) the quest for higher conversion efficiencies. Both goals go hand in hand because a reduction of cell thickness will give
rise to a noticeable loss of cell performance when cell structures of only modest quality are used. [5] Up to now, high-efficiency cell structures which ensure a high cell performance on thin cells have been developed for quite a long time. Nevertheless, quite a few of the high-efficiency concepts cannot be transferred from laboratory into industrial production due to their complex and costly processing. Therefore, cell structures that have excellent optical and electrical properties while strongly simplified compared to laboratory precursors are well in need.

This thesis intends to combine light induced plating which is a simple and fast metallization process with laser doping technology and corresponding surface passivation methods for the production of high efficiency double sided laser doped selective emitter (DSLDSE) structure on CZ p-type wafers. This will allow high efficiency DSLDSE cell to be produced in-line.

1.1 High efficiency silicon solar cells

The theoretical maximum photovoltaic conversion efficiency for a single p-n junction solar cell is 31% at an optimal band gap of 1.3 eV. [6] For conventional silicon solar cells which have a band-gap of 1.12eV, this limit falls to 28.8%. Key features of high-efficiency monocrystalline silicon solar cells aim at reducing the loss mechanisms of junction losses, contact losses and recombination losses. Major improvements compared to standard industrial cells are found in different cell components [5]:

1. Anti-reflection coating and light trapping

Anisotropic texturing processes on single crystalline silicon can bring consistently good result in industrial scale production, there is no obvious difference between lab cells and those in production environment.

2. Front contacts and emitter

The quality of the emitter is closely related to the front contact type. Standard screen-printed contacts require high surface dopant concentration to allow for a sufficiently low contact resistance and good ohmic contacts out of high work function. This will
lead to high surface recombination (Auger recombination) and cannot be improved in a significant way by surface. Poor blue response and low open-circuit voltage is inevitably a big problem to tackle.

High efficiency cells, such as the PERL cell shown in figure 1.3, solve this problem using a two-step emitters or metallization schemes which allow contact of lowly doped emitter profiles. This structure is selective emitter and this issue will be in depth in the next chapter. [7-8]

![Figure 1.3: PERL cell (Passivated Emitter, Rear Locally Diffused) [7-8]](image)

The blue response of this emitter structure is very high and overall cell performance is good as well for its incorporation of selective emitter to reduce short wavelength generated minority carriers recombination. [7] The details of PERL cell will be discussed in the next chapter.

3. Substrate.

As widely noted in literature, CZ boron-doped silicon shows a severe degradation of minority carrier lifetime induced by illumination or carrier injection. [9] The main reason is the existence of boron and oxygen. This problem can be resolved by either using n-type substrate or using higher price float-zone silicon which has little oxygen incorporated due to its process method. The new low-cost rear-contact cell of
Chapter 1. Introduction

Sunpower, a structure extremely sensitive to material quality has been successfully made on n-type substrate, demonstrating efficiencies higher than 20%. [10]

4. Surface passivation

Surface passivation is a well-known technique used to achieve the high efficiency from the crystalline silicon solar cells. [11] PERL cell again, holding the highest conversion efficiency of Si so far, 25%, features delicate fabrication of front and rear surface passivation using silicon dioxide. [7-8]

1.2 Laser doping techniques and Double Sided Laser Doped Emitter Structure

Selective emitters (SE) are commonly incorporated into high efficiency silicon solar cell. Traditional fabrication steps via photolithography or scribing followed by thermal diffusion are used to define the lightly and heavily doped regions. However, selective emitters are rarely used in commercial manufacturing due to the high expense and long duration of processing, reducing final yield. Moreover, from an electrical point of view, two or more high temperature treatments are not suitable for many multicrystalline wafers. [12] A particularly effective and simple way of achieving SE is by laser doping to selectively remove the anti-reflection coating layer and simultaneously melt the underneath silicon and incorporate dopants into the melted region, creating a heavily doped layer. This is a self-aligned mechanism that allows for applying the plated melted contacts directly to the heavily doped regions. [12-13] This approach can be easily fed into current standard screen-printed production line and impressive efficiencies above 19% have been achieved in single sided laser doped solar cells (SSLD) with excellent spectral response to short wavelength [14].

1.3 Light induced plating

One of the key steps to achieving high efficiency silicon solar cells is forming low recombination, low resistance ohmic contacts. Currently, industrial screen printing, metal
ink-jet printing, electrolytic plating methods have been used for front side metallization. However, all of those ways have technical issues needed to be aware of which a new concept of plating will not address, that is, Light induced plating (LIP) or photoplating. LIP is a photo-oxidation-reduction process in which metal is reduced onto the front surface (the cathode) and oxidized at the rear (anode). This will result in the deposition of a metal piece, also its self-aligning property eliminates the need for a mask, making the process a lot simpler. In the industrial scale production, LIP has been applied inline due to its fast and low-temperature cell processing without being subjective to mechanical pressure so compatible with thinner substrates. More significantly, LIP can be developed well in conjunction with laser doping as laser doped emitter provides a self-aligned pattern for metallization.

Commercial inline plater has the configuration of Light induced model developed by Fraunhofer, Germany. [15]

![Figure 1.4: Principle of Light induced Plating.][16]

A sacrificial anode contacts every single cell during the plating process. However, this configuration will increase the overall cost of LIP metallization process by connecting the electrode with every single solar cell rear surface. [16] In this thesis, another Light induced plating approach developed by UNSW has been used. The new top contact scheme for proposed next generation P-type DSLDSE cell is:
1.4 Thesis Objective

The objective of this thesis is to explore the following possible fabricate techniques for the next generation Double Sided Laser Doped Selective Emitter silicon solar cell on P type substrates.

1. To investigate the emitter profiles of thermal and laser doped phosphorous diffusions.

2. To investigate the surface passivation of laser doped emitters using silicon oxynitride, especially for the rear surface.

3. To investigate the suitability of aluminum evaporations and light induced plating for use in fabrication of double sided laser doped solar cells.

1.5 Thesis Outline

This thesis begins with a brief introduction to several high efficiency solar cell and the key issues for consideration to achieve such high efficiency.

In chapter 2, a review of existing selective emitter solar cell structures is presented with the emphasis on laser doping technology and back surface passivation. A brief introduction of next generation laser doped selective emitter solar cell is given to illustrate the its potential in achieving high efficiency.
Chapter 3 presents a comparison between the thermal diffusion emitter and laser doped emitter. Junction profiling of both methods using Trilogy etch have been demonstrated. The optimization of laser-induced melting of predeposited impurity doping has also been demonstrated. Critical issues have been concluded for passivating both the n-type and p-type surfaces. Details of the experiment on SiON passivation developed by UNSW have been given. In the later section, an investigation into laser doped lines through SiON dielectric layer is performed and emitter sheet resistance for different laser doping speed conditions has also been summarized.

Chapter 4 focuses on the development of light induced plating on p-type double sided laser doped selective emitter cell, six groups of different experiment have been presented with discussion and explanations about the results. The results state that photoplatting can be combined with this next generation laser doped selective emitter structure, however, further study into better rear surface passivation, point contacts configuration and light induced plating need to be done before a decent performance can be achieved.

Chapter 5 presents the conclusions of the thesis.

1.6 References:


Chapter 2

Review of High Efficiency Selective Emitter Silicon Solar cells

This chapter presents an overview of selective emitter structure on high efficiency silicon solar cells and the incorporation of this structure into high-efficiency cell concepts such as world record holding passivated emitter with rear locally diffused cell (PERL) and the buried contact solar cell. Then selective emitter formation by laser doping technique and its performance is illustrated. An insight into the features of the aforementioned cell designs is presented. The latter section of this chapter describes a new cell concept of next generation doped selective emitter cell, which is, Double Sided Laser Doped Selective Emitter (DLDSE) cell, this structure makes use of the approach what PERL cell does in a cheaper cost manner.

2.1 Selective Emitter

The traditional and industrially widespread use of producing Solar cells is Screen-printing (SP). This is due to its simplicity and low cost. However, rather than these, SP has several disadvantages: Heavily doped emitter brings poor blue response hence low current, and High shading losses from wider metal lines for reducing the metal contact resistance.

Forming selective emitters confronts inherent limitations of the traditional homogeneous emitter and screen-printed metallization process: [1]

1. Front surface metallization, which “requires a heavily diffused emitter to achieve both a sufficiently low contact resistance and adequate lateral conductivity”. [2]
2. Top surface metal shading losses resulting from line width limitations (typically 120-150μm).
3. Poor surface passivation as a result of the large metal/silicon interface area and the lack of a selective emitter to more effectively isolate this high recombination velocity
interface from active region of the cell.

![Conventional Selective Emitter Structure](image)

**Figure 2.1 Conventional Selective Emitter Structure**

Theoretically, this structure provides the silicon solar cell a superior light absorption passivation, hence a better cell efficiency than SP structure in that:

1. By restricting the heavily doped material to the immediate regions beneath the metal contact, little light absorption takes place in such regions thereby allowing the rest of the surface region to be lightly doped and thus better blue response.
2. Metal contacts feature very large S0 values (~106 cm/s). As the metal contacts are opaque anyway, the formation of a ‘dead layer’ below the metal contact does not reduce Jsc but at the same time increases Voc. The reason for the Voc increase is that metal contact recombination requires an electron and a hole. By locally heavily doping (n++) the region below the metal contact (‘selective emitter’), the density of holes at the surface is greatly reduced, reducing Surface recombination rate. The heavy doping also improves the fill factor, as it reduces the metal-semiconductor contact resistance with closer spaced metal fingers configuration.

The most common selective emitter types are grouped into five categories:

1. Etch-back.
2. (Screen-printed) phosphorous-doped paste.
3. Buried contacts.
4. Diffusion masking.

5. (Single-step) laser doping.

The first two methods do not necessarily require any laser-based equipment, however, the other three are laser assisted:

1. Laser scribing for forming scribe grooves (Buried Contact Cell)
2. Laser dielectric ablation for ablate openings
3. Laser dopant diffusion.

2.2 Buried Contact Cell

![Figure 2.2 Buried Contact Solar Cell](image)

Buried Contact (BC) cell is called “the father” of selective emitter solar cells. This cell structure was invented by UNSW scholars Professor Stuart Wenham and Professor Martin Green in mid 1980s and commercialized by BP solar as the Saturn Buried Contact Cell. The demonstrated commercial efficiencies on CZ wafers can be achieved up to 18.3%. However, this cell structure can be never implemented commercially on multicrystalline Silicon substrate due to the two high temperature thermal diffusion process.

Contacts (Nickel/Copper) using the novel electroless plating method are buried into grooves which are machined with a laser and exhibit a strong phosphorus thermal diffusion formed. Electroless plating is self-aligned and Ni/Cu contact demonstrates a relatively low contact resistance and also a lower cost than traditional screen-printed
Silver paste. The rest of the surface is covered with a lowly doped emitter which is effectively passivated with SiNx.[3]

Due to the low shadowing losses and the good electrical properties of this emitter, the blue response and the overall performance of this cell structure is very high. The processing sequence has also shown itself capable of producing considerable gettering benefits during processing.[4] Evidence of laser damage during the grooving process appears to be beneficial in that this can be effective gettering site. During heavily diffusion, the phosphorus will diffuse preferentially in damaged areas and hence passivate the laser induced damage. [5]

Nevertheless, the front contact scheme of BC cell has been perfectly designed, the back contact still retain the form (or modified version, evaporation or sputtering Aluminum and alloy) of screen-printing, this puts the limit on the highest efficiency this cell structure can achieve. To further improve the cell’s performance, point contacts scheme on the rear should be developed like PERL cell structure.

**2.3 PERL Cell**

![PERL Cell Diagram]

Figure 2.3 Structure of the PERL (Passivated Emitter and Rear Locally-Diffused) Cell [6]

PERL was invented and demonstrated at UNSW by Jianhua Zhao and Aihua Wang in the early 1990s, the initial record efficiency is 24.7% on Float Zone wafers. This record is updated to 25.0% in 2008 due to change in spectrum standard, which is the world’s highest for silicon solar cell. [6]
Chapter 2 Review of Selective Emitter Silicon Solar cells

The cell structure is fabricated using many add-on technologies to increase efficiency but add the costs as well: [6]

1. Anti-reflection coating
2. Photolithography patterned etching of dielectrics
3. Good passivation
4. Photolithographically defined mask metal evaporation.

Among all the features PERL cell has, the very important one is passivation. To obtain high cell performance, recombination throughout the cell has to be kept to a minimum. It is obvious that there are many advantages in producing increased output current. In an operating solar cell, it makes no sense to waste photogenerated carriers by allowing them to recombine before being collected. [7]

PERL cell can reduce bulk recombination by simply using high quality float zone monocrystalline. However, the most challenging task is to reduce surface recombination and contact area recombination.

(1) Surface Passivation

Recombination in non-contacted areas of the surface can be minimized by the growth of a high-quality thermal oxide. The conditions for producing low interface state densities have been well documented for microelectronics. [8]. However, for p-type surfaces, as voltages across the cell builds up, a transition effect that hole recombination becomes rate-limiting process will occur and this effect can be exaggerated by work function differences between p-type silicon and metals such as aluminum and titanium at lower voltage. Hence, the design rule for non-diffused surfaces is to keep the hole concentration at the surface to a minimum. [7]

(2) Contact Area Recombination

The regions where metal contact to the cell are the regions of potentially high recombination. Two strategies are used in the PERL cell to reduce contact area recombination. The first one is to keep the contact area small. On PERL cell rear surface, the rear contact is made through 10μm x 10μm contact holes and spaced
250µm apart. [7] So the metal contact area is only 0.2% of the rear surface. The second strategy is adding a diffused layer underneath the metal contact area that can suppress the minority carrier rates and passivate the contact surface. Boron emitter thermal diffusion is done for the contact passivation.

Although PERL cell holds the world’s highest efficiency record, there is a major disadvantage when considering technology transfer, that is, the fabrication processes are way too complicated and there is still no standard inline equipment available in the market.

2.4 Single Sided Laser Doped Selective Emitter Cell

Pioneered by UNSW in the mid-1990s, the patented Laser Doped Selective Emitter technology achieves energy-conversion efficiency over 19% using standard monocrystalline p-type or n-type substrates. Over 17% cell performance has also been achieved on multicrystalline substrates. [9] This represents a 15 percent performance improvement compared to standard screen-printed solar cells using the same wafers and materials.

![Figure 2.4 Schematic cross section of a p-type LDSE cell [9]](image)

Single Sided Laser Doped cell structure is fabricated by using a laser to selectively remove dielectric and transiently melt the silicon lying beneath. At the same time dopants on the surface (Spun on) are incorporated into the melted region. The process flow chart can be seen from the figure 2.5:
Subsequent self-aligned metal contact formation to these exposed heavily doped regions is achieved with novel light-induced plating. This results in metal lines only 20µm wide, with perfect alignment to the localized heavily doped regions. The antireflection coating is retained in non-metalized regions and acts as a plating mask, providing excellent surface passivation and antireflection qualities. [9]

A very important feature of laser doped selective emitter technology is that it is compatible with production based on lower cost wafer types especially the multicrystalline because LDSE only applies the necessary heat for the formation of localized heavily doped regions locally, which leaves the rest of the wafer free of prolonged high temperature thermal treatment.

The only problem with Single Sided Laser Doped Selective Solar cell is that its poor rear surface when compared with its front surface. The rear surface uses conventional aluminum screen-printing and firing to form a rear p+ layer, this, as mentioned
previously, will have a high recombination in the silicon metal interface. In order to improve this, other techniques such as a passivated rear with localized contacts (PERL cell) rather than screen printing are to be used in a relatively low cost manner.

2.5 Next generation LDSE solar cell

By improving laser doping operation, damage to the silicon wafer can be reduced and the quality of the laser doping process is enhanced. This provides a chance to apply LDSE to front and back surface to replicate the rear of the PERL cell. Based on the PERL cell rear contacting scheme, extensive research into the next generation p-type LDSE cell is underway.

![Figure 2.6 Structure of Next generation P-type LDSE cell: Double Sided Laser Doped Selective Emitter Solar Cell [11]](image)

By applying LDSE to front and back surface of the wafer with suitable passivation, higher efficiency (over 21.5%) is expected to be achieved.
2.6 Chapter Summary

Selective emitter is a very effective design to overcome the poor blue response of screen printed solar cells. Many high efficiency solar cell structures have taken selective emitter as the base of front contacting scheme such as PERL cell, buried contact solar cell and the laser doped selective emitter solar cell.

The use of laser doping to form a selective emitter has been proven to be a suitable method for industrial scale production. However, the major limitation of doped solar cells to date is the high recombination in the large Silicon metal interface at the back. Inspired by the back surface contact of PERL cell, the next generation laser doped solar cell makes use of laser doping to create localized contact areas on the rear, combining with the use of high quality passivation of the remaining surface using aluminum oxide or silicon oxynitride.

Double Sided Laser Doped Selective Emitter Solar cell is a very promising cell structure and its process sequence is simply to be fixed into the production line. Before achieving a stable high efficiency of over 21% which can be commercialized, much work needs to be done.

2.7 References


[6] PERL cell, UNSW Innovation Poster
Chapter 2 Review of Selective Emitter Silicon Solar cells


[10] Laser Doing Selective Emitter, UNSW Innovation Poster

Chapter 3

Junction profiling and laser doped emitter surface passivation

In this chapter, a comprehensive investigation into the emitter formed by thermal diffusion and laser doping has been done. The prerequisite for fabricating a reliable and good level of double sided laser doped selective emitter is the back surface passivation. The optimization of laser operation has been done first and then study of newly developed SiON for passivating laser doped emitter is conducted.

3.1 Typical Junction Profiles

PERL cell uses a two step solid state phosphorus diffusion to form its front selective emitter. For thermally diffused emitters, the “dopant profile” depends on three main factors: (1) time, (2) temperature and (3) properties of dopant atoms in the host wafer, ie. solid solubility and diffusivity. There are a lot of papers talking about the mechanisms of phosphorus diffusion in silicon and due to the page limitation of this thesis, a not in-depth discussion about it will be presented. In order to fabricate good solar cells out of solid source diffusion, it is crucial to control the process to give the correct profile: (1) surface concentration of dopant atoms (2) the junction depth (3) the conductivity of the diffused region ie. sheet resistance.

![Figure 3.1 Two typical types of junction profiles](image-url)
Figure shown above describes the diffusion profile of laser doped emitter on the left and solid state diffused emitter on the right. The uniform laser doped emitter profile is largely due to the diffusion coefficient of phosphorus in molten silicon is orders of magnitude higher than in the solid phase. This fast diffusion, combined with additional dopant spreading due to convective fluxes within the melt, leads to rapid formation of a heavily doped region throughout the entire melt area. After the laser pulse finishes the silicon melt cools and rapidly recrystallizes through a process of epitaxial growth. [2] We can also see the final profile of solid state diffusion should be well approximately depicted in Gaussian function, the derivation using Fick’s first law and second law in finite source supply condition is saved here.

3.1.1 Junction depth and doping Level

Considering the actual generation rate of carriers in a silicon wafer when illuminated by sunlight, the highest rate of generation will occur right at the semiconductor surface. [3] For monochromatic light, the generation rate is:

\[
G = (1-R)\alpha Ne^{-\alpha x}
\]  

(3.1)

x is the distance below the surface and alpha the absorption coefficient.

Applied to sunlight,

\[
G(x) = \int_0^{\lambda_{\text{max}}} [1 - R(\lambda)]\alpha(\lambda)N(\lambda)e^{-\alpha(\lambda)x} d\lambda
\]

(3.2)

The generation rate has a very strong peak near the surface precisely where the probability of collection is low. Hence, typical one-step emitter design is to make junction as close to the surface as possible.
Chapter 3. Junction profiling and Laser doped Emitter surface passivation

![Figure 3.2 Collection probability, curve (2) has a better collection than (1) [1]](image)

However, in order to reduce resistance of the contact/silicon interface and the lateral resistance and series, doping level has to be sufficiently high. Heavy doping effects on the electrical and optical properties of silicon are severe: [4]

1. High doping has detrimental effects upon minority-carrier lifetimes due to Auger recombination mechanism.

2. Heavily doped regions will experience the effective narrowing of the forbidden band gap of silicon and hence alter the intrinsic concentration.

3. Carrier mobility is reduced due to the increased scattering of carriers.

4. Degeneracy occurs in free carrier absorption.

As has been discussed in the last chapter, selective emitter design has tackled this problem, and investigation into the heavy diffusion step of the two steps processing is worthwhile. By looking into the property of heavy laser doped line through the dielectric layer, further optimization of laser doped selective emitter can be achieved via transferring the idea and results gained in this chapter.

Many literatures have confirmed that to form ohmic contact to a solar cell device it is necessary to achieve a surface concentration of at least $1 \times 10^{19}$ atoms/cm$^2$. [2]
Table 3.1: Theoretical sheet resistance values for solid state thermal diffused and laser-induced melting of predeposited impurity doping junctions, calculated using PC1D with Gaussian junction and uniform profile.[2]

<table>
<thead>
<tr>
<th>Dopant Type</th>
<th>Junction Depth (µm)</th>
<th>Surface Conc. (atoms/cm²)</th>
<th>Solid State Diffusion Sheet Resistance (Ω/sq)</th>
<th>LIMPID Sheet Resistance (Ω/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1</td>
<td>$1 \times 10^{19}$</td>
<td>75.02</td>
<td>80.91</td>
</tr>
<tr>
<td>P</td>
<td>1.5</td>
<td>$1 \times 10^{19}$</td>
<td>50.01</td>
<td>53.94</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>$1 \times 10^{19}$</td>
<td>37.51</td>
<td>40.45</td>
</tr>
<tr>
<td>P</td>
<td>2.5</td>
<td>$1 \times 10^{19}$</td>
<td>30.01</td>
<td>32.36</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>$1 \times 10^{19}$</td>
<td>25.01</td>
<td>26.97</td>
</tr>
<tr>
<td>n</td>
<td>1</td>
<td>$1 \times 10^{19}$</td>
<td>46.76</td>
<td>52.23</td>
</tr>
<tr>
<td>n</td>
<td>1.5</td>
<td>$1 \times 10^{19}$</td>
<td>31.17</td>
<td>34.82</td>
</tr>
<tr>
<td>n</td>
<td>2</td>
<td>$1 \times 10^{19}$</td>
<td>23.38</td>
<td>26.11</td>
</tr>
<tr>
<td>n</td>
<td>2.5</td>
<td>$1 \times 10^{19}$</td>
<td>18.7</td>
<td>20.89</td>
</tr>
<tr>
<td>n</td>
<td>3</td>
<td>$1 \times 10^{19}$</td>
<td>18.7</td>
<td>17.41</td>
</tr>
</tbody>
</table>

Generally, laser doped emitter demonstrates a higher sheet resistivity than solid state diffusion for the same junction depth. This in the other way means that for the same sheet resistivity, laser doped junction will be deeper, this is not satisfied as what have been mentioned before, nevertheless, in the selective emitter design, the emitter junction depth is not important for the cell performance within normal ranges. It is only the emitter surface passivation steps that determine the final emitter profile. [2] Another observation is that Phosphorus atoms are much more easily doped on P-type wafers than boron and this is basically due to lower diffusion coefficient of Boron.

3.1.2 Thermal diffused emitter profiling

In commercial silicon solar cell manufacturing sequences today, it is a crucial part to acquire the information about the diffused junction profile. The reason for that is obvious, in the following stage of Silver firing should be controlled not to penetrate too deep into the junction. The worst result can be shunting but as the work function of Silver is high so normally acts as a Schottky barrier to prevent contact w/p-Si, therefore, this is less a problem. However, chances are that “Current crowding” effect as well as silver’s directly contacting lighter doped n-Si in Selective emitter structure that can result in high series resistance.
Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is a frequently used characterization technique for elemental analysis of the surface of a solid sample. The basis of the technique constitutes sputtering of a sample surface by energetic ions, causing ejection of neutral atoms/molecules as well as positive and negative ions out of the surface from the close vicinity of impact. Stemming from a very shallow depth of the sputtered surface, the liberated positive and/or negative ions can be mass analyzed by electric and magnetic separation, providing information on the chemical composition or the relative concentration distribution of selected elements. [5]

The problems for using this technique is it is not economically cost-effective, paying nearly US$350 per test is not sustainable and it loses the flexibility of measuring textured surfaces.

Electrochemical Capacitance Voltage

Electrochemical Capacitance Voltage (ECV) effectively each away the silicon surface by chemical reactions and measure the capacitance, which is a function of V. In this method, only the electrically-active dopants are detected.

The drawbacks of this approach are the whole process is time-consuming and it has some fundamental limitations on the maximum depth which can be profiled as well as on the depth resolution [6]

For the purpose of this thesis, the availability of accurate junction profiling techniques was limited for this work, making it necessary to rely primarily on sheet resistance measurements during the process optimization. Profiling of solid state diffusion used by PERL cell and continuous wavelength laser induced melting of predeposited impurity doping junctions is conducted is conducted by trilogy etch profile method.

Trilogy Etching profiling.

Isotropic silicon etchant “Trilogy Etch” is intended for isotropically etching silicon, both doped and undoped single-crystal. The solution is mixed from:
Chapter 3. Junction profiling and Laser doped Emitter surface passivation

126 parts Nitric acid HNO3: 60 Parts DI water H2O: 5 parts Ammonium Fluoride NH4F.

The fundamental reaction is:

\[ Si + 4HNO_3(aq) + 5HF(aq) \rightarrow H^+ + SiF_5^- + 4H_2O(l) + 4NO_2(gas) \]

The temperature for processing will be at 20°C. Before use, the solution should be mixed for several hours to yield a stable etch rate. Etching rates have been calculated [7]

<table>
<thead>
<tr>
<th>Etch</th>
<th>SI (100)</th>
<th>Float-Zone SI</th>
<th>Poly Si LPCVD</th>
<th>Poly Si LPCVD</th>
<th>Poly Ge LPCVD</th>
<th>Poly SiGe LPCVD</th>
<th>Graphite Ion-Milled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Iso Etch</td>
<td>150</td>
<td>W</td>
<td>100</td>
<td>310</td>
<td>890</td>
<td>550</td>
<td>60</td>
</tr>
<tr>
<td>KOH</td>
<td>1100</td>
<td>F</td>
<td>670</td>
<td>&gt;1000</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10:1 HF</td>
<td>S</td>
<td>S</td>
<td>0</td>
<td>0.7</td>
<td>0</td>
<td>0.42</td>
<td>-</td>
</tr>
</tbody>
</table>

However, the etch rate for heavily doped p-Si is not found in literatures, so test on this has been performed first.

Profiling theory:

The resistivity of phosphorus doped region is

\[ \rho = \frac{1}{q\mu_e n} = \rho_{\text{sheet}} \times \text{thickness} \]

(3.3)

Ionized dopants are very effective scatters because of their associated net charge, therefore, as silicon becomes heavily doped, the average time between collisions and hence the mobility will decrease. [8] Empirical expression relating the n-type carrier mobilities to the level of dopants N(in cm-3) is:

\[ \mu_e = 65 + \frac{1265}{1+(N/8.5 \times 10^{16})^{0.72}} \text{cm}^2/\text{Vs} \]

(3.4)

Sheet resistance is measured before an etch and after an etch. Here we assume the sheet resistivity of etched off layer is always the same as the thickness of it is negligibly small.
The figure shown above gives the philosophy of this profiling method,

\[
\frac{1}{\rho_{\text{sheet before}}} = \frac{1}{\rho_{\text{sheet after}}} + \frac{1}{\rho_{\text{sheet etched}}} \quad (3.5)
\]

Hence, we can get the sheet resistance of the etched off layer, thereafter use excel to iterate the steps until get a consistent surface concentration before that etch and the corresponding mobility.

**Thermal Diffusion Wafers Preparation:**

Three P type 1ohmcm CZ wafers are used, FE1-1, FE1-2 and FE1-4. Triology etch solution has been put away for 1.5 hours after mixed. Blue resist is used as a mask for this etchant.

**Table 3.3 Trilogy Etch Process Sequence**

<table>
<thead>
<tr>
<th>Process Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Saw damage etching to 240µm and RCA2</td>
</tr>
<tr>
<td>2. RCA Full Clean</td>
</tr>
<tr>
<td>3. Phosphorus pre deposition for 12 mins at 820°C</td>
</tr>
<tr>
<td>4. TCA oxidation drive-in for 3 hrs at 1100°C</td>
</tr>
<tr>
<td>5. Spin coating HMDX and then Blue Resist FSC-M, spinner speed 4500rmps for 30s</td>
</tr>
<tr>
<td>6. Bake at 140°C in the oven for 10 mins</td>
</tr>
<tr>
<td>7. HF dip till the front surfaces are hydrophobic</td>
</tr>
</tbody>
</table>
Chapter 3. Junction profiling and Laser doped Emitter surface passivation

8. Trilogy ech, FEI-1 for 15S, 30S, 45S, 1min,
FEI-2 for 45 secs, 1.5mins and 2.5mins, FEI-4
for 1min, 2min, 3min
9. Detak thickness measurement

Before etching, the three wafers are tested with four point probe for sheet resistance measurement. They are FEI-4:70Ohm/sq, FEI-2:65ohm/sq, FEI-1:63ohm/sq respectively.

![Etch rate comparison](image)

**Figure 3.4 Calculated Trilogy etch rates on heavily doped emitters**

One observation from this curve is that the higher doping level is, the faster the etching rate will be. The etching rate is approximately 250nm/min for the heavy doped silicon, etch error rate of 2.3% is calculated. This approximation is reasonable for laser doped emitters as the impurity concentration is almost the same across the n type layer. During use, the solution agitates and this will result in increasing uniformity. It is also said that the solution gets weaker with use. [7] So each solution will be used for 4 etches in the following experiments implemented.

The prediction of the sheet resistance measurement is during the course of etches after etches, the readings exhibit a trend of constant rise and once the n-type phosphorus diffused layer has been totally etched away, the reading bounces back. One way to detect the existence of n type layer is using Hot Probe. For this experiment, the heat source of
150 degreeC is placed on the positive lead of a voltmeter, hence, if there is no emitter any more, a negative voltage reading will be displayed.

![Doping Profile #1](image)

**Figure 3.5 Thermal diffused p-type emitter with sheet resistance of 70 ohm/sq**

<table>
<thead>
<tr>
<th>Wafer</th>
<th>FE1-1</th>
<th>±5.75E+17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Concentration(#/cm³)</td>
<td>1.88E+18</td>
<td>±5.75E+17</td>
</tr>
<tr>
<td>Junction depth(µm)</td>
<td>3.3</td>
<td>±0.14</td>
</tr>
</tbody>
</table>

Table 3.4 Excel calculated Surface concentration and junction depth for the emitter shown in figure 3.5

From the result we can see, Solid state diffusion is a process really hard to control the junction depth and surface concentration for desired emitter formation due to wafers being exposed to high temperature for a long duration. This will especially have thermal degradation impacts on the bulk life time of multicrystalline Silicon. In addition, not uniform of surface sheet resistance has been found and although the silicon wafers are placed back to back between two source planes for front side diffusion, evidence has shown that lightly diffused region on the back is inevitable.
3.1.3 Laser doped emitter profiling

Laser-induced melting of predeposited impurity doping

Laser tool selection requires combining lessons which include short wavelengths for localized absorption, sufficient average powers to activate the heat-generated dopant diffusion, fluency levels to ablate passivation layers while avoiding damage and short pulse widths to reduce heat-affected zones. [9]

The depth of a laser doped junction is determined by the melt depth. This is because of the fast liquid phase diffusion and convective mixing of dopant atoms. The depth of a laser melted region is strongly related to the absorption of the laser light. [2] This means high energy short wavelength light forms shallow junctions and longer wavelength light forms deeper junction. The actual situation is more complicated as the absorption coefficient is depending on temperature. Literatures state that small variations in incident laser intensity will result in large differences in peak temperatures of the melted zone: 10% variation in initial energy resulted in a 100°C difference in surface temperature for short-absorption length and 2000°C for long absorption lengths [10]. So when deciding the choice of laser wavelength, the second case is not appropriate which may result in very non-uniform melting and possibly cause ablation.

The choice of laser wavelength for this thesis is 532nm, which is the only option available for continuous wavelength laser equipment. Operating at 532nm is desirable due to its high absorption coefficient (8300 cm⁻¹), this means most of the energy will be absorbed within 1-2 μm from the silicon surface, which enables a small volume of silicon being melted and yields low stresses upon solidification, yet it allows sufficient time for the phosphorus to diffuse into the molten silicon to form good ohmic contact. [11]

The implementation of continuous wavelength laser rather than Q-switched Nd:YAG laser is due to less thermal cycling of the silicon as Q-switched laser emits energetic pulses in a high repetition rate. Furthermore, Q-switched laser will have a reported problem of blasting out hydrogen atoms when laser beam fires through the dielectric SiN layer. This problem can be solved by using continuous wavelength laser in that the silicon wafer can be heated up prior to laser beam actually reaching the melting spot and
hence the segregation coefficient along the path stays almost the same, which allows the hydrogen atoms to diffuse through the SiN for passivation function. Finally, continuous wavelength demonstrates a heavier diffusion capability. [17] The laser used in this work is a 15W stabilized continuous wave at 532 nm with the laser beam width of 10-20μm.

Beyond choosing appropriate laser wavelength and model, other factors to achieve heavy doping including: optimization of the dopant source, thermally treating the dopant film, changing laser speeds etc. have also taken into account during the development of a laser doping process.

**Laser doped wafers preparation:**

The same wafers for solid stated diffusion are used. The wafers were saw damage etched to 240μm. A film containing dopant atoms was applied in a conventional spinner at room temperature. The influence of laser settings and application of spun on dopants (SOD) on the sheet resistance will be investigated first.

**SOD application**

The doping process is strongly influenced by the application and type of SOD. Normally, thicker the SOD is the more laser energy it will absorb and thus resulting in no formation of doped region. Higher spin speeds can be one easy solution, or diluting the dopant film with isopropyl alcohol can be another option. The other critical issue is the curing temperature of the dopant film. If the temperature is too high, dopant film will be brittle and removed by the surface expansion of heated silicon. Consequently, dopants cannot be incorporated into the melt for subsequent laser passes and the surface doping concentration is low.

<table>
<thead>
<tr>
<th>Dopant Type</th>
<th>Product</th>
<th>Dilution (SOD:IPA)</th>
<th>Spin Speed (rpm)</th>
<th>Spin Time (seconds)</th>
<th>Cure Temp (°C)</th>
<th>Cure Time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>Phosphorus acid (20%)</td>
<td>none</td>
<td>3000</td>
<td>20</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Boron</td>
<td>PBF1</td>
<td>none</td>
<td>2000</td>
<td>30</td>
<td>130</td>
<td>10</td>
</tr>
</tbody>
</table>
The dopant settings shown in the table 3.5 above are used throughout the rest of this work, and down to 10 ohm/sq and 20 ohm/sq for p-type and n-type heavy doping is achieved respectively.

Profiling

Two p-type, 1ohmcm CZ wafers were used, 8 laser patches were formed by optically scanning the laser over an area of 10mmX10mm on each of the wafer using different speeds. After laser doping, sheet resistances are measured:

![Figure 3.6 Wafer #1 and #2 sheet resistance versus laser speed](image)

For comparison with the solid state diffusion, we use 70ohm/sq patch. 10 ohm/sq and 156ohm/sq patches are also used for comparing the junction depth of heavy and light diffusion.

Similar trilogy etches and sheet resistance measurements were repeated, etching rate is still 250nm/min in the profile plotted next page.
Chapter 3. Junction profiling and Laser doped Emitter surface passivation

Figure 3.7 Emitter profiles of laser doped emitters
Table 3.6 Calculated Surface concentration and Junction depth of the emitters shown in figure 3.7

<table>
<thead>
<tr>
<th>Sheet Resistance (Ω/sq)</th>
<th>156</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Concentration (#/cm³)</td>
<td>2.00E+18</td>
</tr>
<tr>
<td>Junction Depth (µm)</td>
<td>2.7</td>
</tr>
<tr>
<td>Sheet Resistance (Ω/sq)</td>
<td>70</td>
</tr>
<tr>
<td>Surface Concentration (#/cm³)</td>
<td>3.00E+18</td>
</tr>
<tr>
<td>Junction Depth (µm)</td>
<td>3.4</td>
</tr>
<tr>
<td>Sheet Resistance (Ω/sq)</td>
<td>10</td>
</tr>
<tr>
<td>Surface Concentration (#/cm³)</td>
<td>4.00E+19</td>
</tr>
<tr>
<td>Junction Depth (µm)</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Figure 3.8 EBIC picture of laser doped junction at the speed of 5m/s with a junction depth of 3 µm [18]

The EBIC picture shown above gives a look of the cross section look at the laser doped junction. 3 µm depth is consistent with trilogy etch results using the same laser speed.

**Discussion**

The surface concentration of Laser doped emitter at the same sheet resistance as solid diffusion one is higher. And the junction depth is also deeper, which proves the prediction made. The fact that the junction created by LD is deeper compared to the thermal diffused one, is due to the high diffusion coefficient of the dopant in the liquid phase. The fact that the dopant concentration is constant is due to the high segregation coefficient (almost 1), which means that dopant concentration is almost independent of the depth.

High surface concentrations with low junction depths may appear as a high sheet resistance while lower surface concentration with deeper junction depths may appear as
low sheet resistance. To fully optimize the laser doping process it is necessary to incorporate some form of doping profiling, such as SIMS, to verify both the junction depth and surface concentration. [2]

Another observation is the faster speed is, the higher sheet resistance and surface concentration of the emitter is, and correspondently deeper junction, however, when considering laser doped through the dielectric layer, the actual case should be more complex, this issue will be further addressed later in this thesis.

So herein we can come to conclusion that laser doping technique provides a comparatively easy way to control the sheet resistance of the emitter and junction depth. However, its application to industrial scale production is subject to limitation. Considering the laser beam used, 10μm width melt each pass. Standard wafer is 156mm x 156mm, so it will take at least around 8 minutes per sample to complete the diffusion step, 7.4 wafers in an hour. For a production tool, normal range of throughput should be around 30MW or 1200 wafers per hour. That is to say, the current type of laser used is not suitable for the inline whole emitter diffusion. However, wider laser beam such as excimer laser can be used to solve this problem.

3.2 Laser doped emitter passivation

Once an emitter of good quality is formed, it is crucial to passivate it. Key issues for passivating laser doped emitter include: [17]

1. Surface defects density

2. Capture cross-sections. (Low capture cross-sections is preferred as it has lower opportunities to become a minority carriers recombination site. The highest capture cross-section is located right in the middle of conduction band and valence band.)

3. Minority carrier concentration.

4. Hydrogenation and thermal treatment

5. Electrostatic effects
Plasma enhanced chemical vapor deposition (PECVD SiNx) films are the most commonly used ARC in the solar cell industry. In addition, as previously mentioned, silicon dioxide is used as the passivating layer for high efficiency solar cell (PERL cell). In this thesis, an alternative ARC film developed at UNSW is used for the full laser doped emitter passivation. Silicon oxynitride (SiON) could combine the benefits of SiNx and SiO2: [12]

1. SiON has a relatively high positive charge density like SiNx and it provides good field effect passivation.

2. SiON can minimize the defect density by passivating surface defects like SiO2.

Besides the strengths listed above, SiON is effective to replace the actual aluminum back surface field which is responsible for high constraint on thin solar cells, and acts as a good rear surface reflector.

Previous work done by Hallam et al. proves that SiON can provide excellent surface passivation properties on planar surfaces as well as on textured surfaces. [13]. SiON with a range of film compositions can be obtained by changing the deposition pressure and gas flow ratios, hence SiON has a high flexibility of being used as front and back surface passivation medium. The work here uses the recipe which demonstrates the best passivation result on P-type planar wafers.

3.2.1 Method

The objective is to apply SiON onto the laser doped rear surface design and to see what implied Voc can be extracted from this. 7 wafers with bulk resistivity of 2Ωcm CZ crystalline n-type planar wafer were used. Saw damaged etched to 165μm first. Dopant films PBF1 and Phosphorus Acid were applied to the surface of the wafer and according thermal treatment is executed as mentioned before. Then, laser doped 8cm² patches using different speeds. SiON with a thickness of 75nm was deposited using a Roth & Rau AK400 microwave remote PECVD system. The recipe was developed by Hallam et al to have outstanding passivation result on the front surface of n-type wafers. 5 minutes and 15 minutes 450 °C forming Gas Annealing steps were conducted. A Sinton contactless
Chapter 3. Junction profiling and Laser doped Emitter surface passivation

Photoconductance (PCD) lifetime tester is used after each step to measure the passivation properties.

Table 3.7 Brief process sequence

<table>
<thead>
<tr>
<th>Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
</tr>
<tr>
<td>2.</td>
</tr>
<tr>
<td>3.</td>
</tr>
<tr>
<td>4.</td>
</tr>
<tr>
<td>5.</td>
</tr>
</tbody>
</table>

3.2.2 Results and Discussion

Table 3.8 Life time before and after laser doped

<table>
<thead>
<tr>
<th>Wafer</th>
<th>iVoc (mV)</th>
<th>Dopants type</th>
<th>After laser doped iVoc (mV)</th>
<th>Sheet Resistance (ohm/sq)</th>
<th>After SiON deposition iVoc (mV)</th>
<th>After 5 mins annealing iVoc (mV)</th>
<th>After 15 mins annealing iVoc (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ-VM</td>
<td>678</td>
<td>p</td>
<td>516</td>
<td>130</td>
<td>589</td>
<td>610</td>
<td>615</td>
</tr>
<tr>
<td>NZ-VX</td>
<td>682</td>
<td>p</td>
<td>533</td>
<td>140</td>
<td>602</td>
<td>626</td>
<td>613</td>
</tr>
<tr>
<td>NZ-KA</td>
<td>692</td>
<td>p</td>
<td>528</td>
<td>135</td>
<td>628</td>
<td>645</td>
<td>642</td>
</tr>
<tr>
<td>NZ-NE</td>
<td>691</td>
<td>n</td>
<td>570</td>
<td>60</td>
<td>629</td>
<td>631</td>
<td>629</td>
</tr>
<tr>
<td>NZ-NT</td>
<td>706</td>
<td>n</td>
<td>571</td>
<td>70</td>
<td>633</td>
<td>640</td>
<td>629</td>
</tr>
<tr>
<td>NZ-MZ</td>
<td>698</td>
<td>n</td>
<td>549</td>
<td>90</td>
<td>617</td>
<td>629</td>
<td>629</td>
</tr>
<tr>
<td>NZ-NN</td>
<td>706</td>
<td>n</td>
<td>547</td>
<td>110</td>
<td>611</td>
<td>615</td>
<td>619</td>
</tr>
</tbody>
</table>

Up to the laser doped step, an average degradation of 160 mV and 140 mV for p type and n type doped patches in implied open-circuit voltage respectively. It seems that heavier doped patches will have slightly less damage or recombination loss from the table. This could be explained as when the speed is lower, laser beams have enough time to melt the silicon rather than ablate it. This issue will be furthered discussed later.

One interesting thing to notice is that as the laser speed is faster, the doping level for phosphorus dopants is decreasing while for boron dopants the sheet resistance stays the same. This is a very critical issue to tackle when fabricating DLDSE cell on n-type substrates in terms of heavily diffused localized p+ back surface field design.
As can be seen from table 3.8 implied Voc of all the samples demonstrates a rise after the deposition of 75nm SiON.

It is well known that annealing of the SiNx film can improve the bulk lifetime of mc-Si wafers by releasing hydrogen during the hydrogenation process. The same result has been obtained for SiON on c-Si, after a 5 min anneal samples show iVOC of up to 645 mV. The improvement in iVOC on p-type doped patches is substantially higher than n-type doped patches.

Schmidt et al. reported that the first 30 min of FGA (forming gas atmosphere) at 400°C improves the passivation, while degradation can be observed for a longer annealing. [14]. While for the SiON used in this work, after a cumulative 15 minutes thermal annealing, most of the samples experience degradation and the iVocs drop back a little. This behavior could be partly explained by the composition of SiON, the disappearance of Si-H bonds with anneal occurs.

The highest iVoc gained in this experiment is 645 mV on p-type doped patches after 5 mins annealing. This result is reasonable for the back surface design for DLDSE cell as doped lines or points are formed instead of large patches, thus less damage to the wafer and less recombination center on the surface, higher iVoc may be obtained.

A material that has recently regained interests for the passivation of crystalline silicon back surface is aluminum oxide (Al2O3). The surface passivation mechanism of Al2O3 is mainly based on field-effect passivation by a high fixed negative charge density Qf in
the Al₂O₃ film, the fixed charge density in Al₂O₃ is in orders of magnitude higher compared to commonly used a-SiNx:H, SiO₂ and a-SiCx.[15] This will relax the requirements on the interface defects density especially when laser doping technique is applied. Further optimization of passivation on the rear side of DLDSE cell can be realized by Al₂O₃ plasma-assisted atomic layer deposition.

3.3 Laser doped through dielectric layer.

As has been mentioned in chapter 2, laser doping selective emitter has shown great performance and already been incorporated into manufacturing lines. However, before going into the fabrication of double side laser doped emitter selective solar cell, the conditions of laser fire through dielectric layer especially SiON used in this work.

**Speed test**

Speed at around 2m/s displays the most uniform alignment of the doped pattern. [16] Speed too slow may create excessive melting of the silicon and expose lightly doped silicon under SiON layer, especially at the edge of the scribed line, which can result in shunting in the following stage of metallization. Speed too fast will have the problem of incorporating dopants into the melt silicon due to the laser beam doesn’t have the chance to punch through the dielectric layer in a short time, meanwhile, laser beam at this speed may ablate the silicon which can be clearly seen when the laser speed is at 10m/s.

For phosphorus acid doped lines, very similar results have been obtained.

**Sheet Resistance Summary**

According to the work of Western et al., sheet resistance of different dopants film applied on various condition of wafers’ surface in a range of speeds have been measured, this figure can be used as a guideline for choosing the proper speed for the purpose of forming laser doped selective emitter in a certain situation.

One ultimate conclusion of the results is that 2m/s laser beam used shows the heaviest doped performance through the dielectric layer, [16] with speed lower or higher than that will give higher sheet resistance, which is a little different from laser doping on a wafer without thermal diffused emitter formed beforehand.
3.4 Chapter Summary

By comparing the profile of laser doped emitter and solid diffused junction, we can see the quality of laser doped emitter is easy to control by simply changing the scanning speed of the continuous wavelength laser used throughout this work. Nevertheless, the application of laser doping technique to form emitter on the whole surface of the wafer is limited due to the duration of processing. In this thesis, laser doped selective emitter combined with photoplating for the contact scheme is implemented.

Laser doped selective emitter has shown excellent performance, while laser induced defects are to be eliminated for improving the performance. Silicon oxynitride has been used as an alternative antireflection coating for a-SiNx:H or SiO2, it demonstrates both good electrical passivation effects and thermal effects. This film is incorporated into the structure of double sided laser doped selective emitter cell, further improvement of the rear surface passivation can be achieved by adopting aluminum oxide, while intensive research has to be done.

The impacts of laser speed on sheet resistance has been summarized for different silicon surface conditions, the experimental work described in the next chapter makes use of this.

3.5 References


[3] Martin A. Green, Solar Cells, Chapter 8, section 2, major consideration, 1998


Chapter 3. Junction profiling and Laser doped Emitter surface passivation


[16] Ned Western, unpublished work, 2010

[17] Stuart R. Wenham, unpublished work, 2010

[18] Brett Hallam, unpublished work, 2010
Chapter 4

Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

The previous chapter investigated laser-induced melting of predeposited impurity doped emitters and surface passivation. To be useful in the production of solar cells, laser processes must be compatible with the other cell fabrication steps and must perform electrically well in finished devices. Combining laser doping with selectively plated metallization was first proposed by Wenham and Green [1]. Double Side Laser Doped Selective Emitter (DSLDSE) cell structure presented in this chapter incorporates laser doping without requiring any complicated processing metallization step to complete the device.

In this chapter, the aim is to investigate whether light induced plating is suitable for laser doped rear surface with aluminum evaporation. First, standard light induced plating (LIP) is performed on all samples to investigate the effect of laser doping scan speed on the LIP process on samples with screen printed rears. The remaining experiments then investigate evaporated aluminum rears with localized laser doping through a dielectric film.

4.1 Light Induced Plating Theory

LIP or photoplasting is a photo-oxidation-reduction process in which metal is reduced onto the front surface (the cathode) and oxidized at the rear (anode) [2]. This process make use of the electrical property of solar cell itself. When light is projected on the solar cell, the energy of the photon is absorbed and an electron-hole pair is generated. An electron in the valence band is elevated to the conduction band which result in the hole being left in the valance band, hence current can flow. For a p-type substrate, the negative potential electrons in the n-type front emitter surface attract the positive metal ions in the solution and these metal ions are reduced to deposit on the emitter surface, in the meantime, oxidation occurs at the rear surface.
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As the photovoltaic effect of the solar cell keeps the current flowing, the electrons of the emitter continue depositing metal on the cell front grid while the oxidation reaction continue to occur on the standard screen printed aluminum rear surface. The electrons generated during oxidation can recombine with the light generated holes.

In this thesis, the standard photoplating process developed by UNSW is adopted. A thin nickel layer is first deposited to form a low-contact resistance barrier layer for a subsequent thinner copper layer, copper has good conductivity and is relatively cheap, well suited for forming low-resistance fingers on a solar cell. Before the deposition of the copper, the nickel layer is sintered to form a layer of nickel silicide, which has a very low resistivity around 14μΩ [4], this further reduces the contact resistance of the final metal contact.

4.1.1 Ni photoplating

The standard nickel photoplatting uses nickel sulfamate [Ni(NH2SO3)2] and the nickel deposition from this solution has low internal stress high rates of deposition and is highly pure as well.

When nickel is plated onto the grid patterns with screen printed rear aluminum surface as the anode, the whole reactions are:
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

Cathode:

Reduction occurs on N-type emitter surface:

\[ \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}, E_0 = -0.25V \]
\[ 2H^+ + 2e^- \rightarrow H_2, E_0 = -0.00V \]

Anode:

Rear Aluminum surface is oxidized:

\[ A\ell \rightarrow A\ell^{3+} + 3e^-, E_0 = -1.66V \]
\[ 2H_2O + O_2 + 4e^- \rightarrow 4OH^- \]
\[ A\ell + 3H^+ \rightarrow A\ell^{3+} + \frac{3}{2}H_2, \text{or, } 4A\ell + 6H_2O \rightarrow 4A\ell(OH)_3 \]

As shown in the anode reaction above, an alkaline environment is created at the surface of the corrosion pit at the rear surface and an acidic environment is formed inside the pit.

4.1.2 Copper Photoplating

The plating solution used in UNSW standard LIP process is acid based copper sulphate \([\text{CuSO}_4 \cdot 6\text{H}_2\text{O}]\). This type of solution contains the simplest ingredients of all the solutions available in the market nowadays and it can also tolerate higher current densities with high efficiency at the anode and cathode.

During plating, the concentration of copper sulphate plays a vital role. Higher copper sulphate concentration will result in higher resistivity of the plated metal while in the other way around. A solution with lower copper sulphate concentration requires a higher current to activate the deposition of copper. Acid based solution contains sulphuric acid, which can ensure a high conductivity environment and also prevent the copper salts from precipitating. [2]

4.1.3 Trade-off

For the purpose of metallization on silicon, a good aspect ratio of the finger is to be established. However, there is a trade-off when deciding the thickness of plated metal. The greater the thickness of nickel layer is, the lower the resistivity is, while relationship between adhesion and deposition thickness of nickel and copper may be inversely proportional. [2] Hence, optimum thickness of deposited nickel and copper layer needs to be found.
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4.2 Development of the light induced plating process for DLDSE cell

4.2.1 Experiment Descriptions

This chapter focuses on LIP development for the DLDSE cell structure. Up to now, six groups of experiment have been done.

Table 4.1 Descriptions of six groups of experiment

<table>
<thead>
<tr>
<th>Exp. 1 Standard LIP on single sided laser doped selective emitter with standard screen printed rear cell with silver tabs</th>
<th>Exp. 2 Standard LIP on single sided laser doped selective emitter with standard screen printed rear cell without silver tabs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 3 Standard LIP on Single Side Laser doped Selective Emitter with aluminum evaporation without SiON passivated rear cell with silver busbars</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.2 Schematic diagram of P-type DLDSE cell
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

<table>
<thead>
<tr>
<th>Exp. 4 Standard LIP on Double Side Laser Doped Selective Emitters with aluminum evaporation and SiON passivated rear cell without silver busbars</th>
<th>Exp. 5 Standard LIP on Double Side Laser Doped Selective Emitters with aluminum evaporation and SiON passivated rear Cell with silver sprays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 6 Standard LIP on line laser doped front and point laser doped back selective emitters with aluminum evaporation and SiON passivated rear cell with silver sprays</td>
<td></td>
</tr>
</tbody>
</table>

The purpose of experiment 1 and 2 is to test the metallization quality of standard light induced plating on single sided laser doped front emitter using standard screen printed aluminum wafers with and without silver tabs on the rear. Experiment 3 tries to strip off screen-printed aluminum layer and replace it with aluminum evaporation to test the metallization quality of standard light induced plating on single sided laser doped front emitter. Experiment 4 incorporates the laser doped rear emitter and corresponding SiON passivation into the process sequence of experiment 3 to investigate whether the double sided laser doped structure with evaporated aluminum can work well using standard LIP. Experiment 5 extends experiment 4 process steps with adding a silver spray stage to further improve the plating. Experiment 6 makes use of the results from experiment 5 and develops into using point contacting scheme on the rear, the metallization is implanted in the same way as previous experiments to see how the plating will be.

**4.2.2 Experiment 1 and 2**

**Method**

These two experiments are aimed to investigate the impacts of different Laser doping speeds on the outcome of standard light induced plating on standard screen printed single crystalline cells

**Wafers preparations**

5 inch standard screen printed P-type CZ 1ohmcm wafer is cleaved into small 2 inch wafers with and without Silver tabs on the rear. The wafers were primarily processed in an industrial environment up to the end of the screen printing/firing step. The process sequence for experiments 1 and 2 is as follows

<table>
<thead>
<tr>
<th>Table 4.2 Process Sequence of Experiment 1 and 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Spin-on 20% phosphorus acid on the front.</td>
</tr>
</tbody>
</table>
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

2. Laser doped lines the front at different speeds

3. Rinse off the dopants

4. Standard nickel plating: 3 minutes at the temperature of 40°C and rinse in DI water for 2 minutes

5. Nickel Sintering and cool for 10 minutes.

6. Quick HF dip and rinsing

7. Standard copper plating (10 minutes at room temperature) then rinse in DI water

The laser doping pattern on the front is an 8 cm² box with 1 mm spacing between the fingers and 80 microns between adjacent busbars. Totally 2 mm in width with 25 busbars.

![Figure 4.3 PL image of contact pattern used, not to scale](image)

**Figure 4.3 PL image of contact pattern used, not to scale**

**Configuration of Nickel Plating:**

![Figure 4.4 Elevating the solar cell in nickel plating solution with Teflons](image)

**Figure 4.4 Elevating the solar cell in nickel plating solution with Teflons** [2]
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

Copper plating used the same configuration during the experiment

Nickel Plating Solution: [6]

MacDermid Barrett SN nickel sulphamate:

- Nickel Sulphamate 327 g/L
- Equivalent nickel metal 76.5 g/L
- Boric acid 30 g/L
- Barrett Additive B 3 g/L

Copper Plating Solution: [6]

MacDermid Copper Helios Solution:

- Copper sulphate (CuSO4.6H2O) 240 g/L
- Sulphuric acid, at 96% concentration (H2SO4) 220 mL/L

Normally, there should be a nickel strike step between nickel plating and copper plating, however, in this thesis, this step is neglected because the satisfactory condition of metal plated rather than the good adhesion between the copper and nickel is to achieve, in the meantime, comparison can be directly made between different silicon rear surface situations.

The formation of a Ni film on a Si substrate goes through a sequential phase transition of Ni2Si, NiSi and NiSi2 from 200°C to 700°C. [7] Each nickel silicide phase has different crystalline structure and electrical properties. A stoichiometric NiSi phase gives the lowest resistivity among many nickel silicide phases. 350°C nickel sintering for a period of 3 minutes is developed in UNSW, which is proved to be a uniform and repeatable NiSi formation process.

**Characterization tool**

**Optical and Scanning Electron Microscope**

Images of laser doped emitters in the silicon nitride ARC, plated nickel and plated copper lines were recorded with both optical and scanning electron microscope (SEM) techniques.
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**Photoluminescence:**

After each stage of process, photoluminescence images were recorded for fast determination of the implied open circuit voltage and therefore the predicted cell performance. PL imaging rather than photoconductance measurement is implemented, this is because once the Al rear is on the cell we cannot do lifetime measurements using the QSS-PC technique. PL over comes this problem by allowing us to look at the implied voltage of the cell, hence give a measure of the lifetime of the cell. This can be done both with and without metal on the device. Hallam et al [8] has established the relationship between the voltage ($V$) of a ideal cell and the average PL intensity ($I_{pl}$). $C$ is a calibration constant determined by the geometry of the sample:

$$eV = kT \ln I_{pl} + C$$

$$\frac{eV}{e^\frac{V}{kT}} = \frac{n_pe}{n_n^2}$$

For a specific surface, the equation (4.2) can be changed to:

$$iVoc = C_1 kT \ln I_{pl} + C_2$$

Where $C_1$ and $C_2$ are calibration constants which need to be determined experimentally.

**Focus Ion Beam:**

FIB pictures were also recorded for nickel plated fingers and copper plated fingers to observe the cross-section condition of the metallization.

**Results and Discussions**

**Table 4.3 Optical Microscope Pictures after Phosphorus Acid laser doping at different speed. Magnificence X50**

<table>
<thead>
<tr>
<th>Wafer/Laser speed</th>
<th>ST-6-5 1m/s</th>
<th>ST-4-6 2m/s</th>
<th>ST-5-6 3m/s</th>
<th>ST-4-4 4m/s</th>
<th>ST-4-6 5m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finger Discontinuities</td>
<td><img src="image1.png" alt="Image" /></td>
<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>
</tbody>
</table>
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

From the pictures shown in the table 4.3, lower laser doped speeds are the best ones in that the laser doped lines are quite uniform, even at where there are discontinuities, the line still looks good. For higher laser doping speeds, the lines become rougher at the sides and even break in the middle of the finger. This is consistent with what have been discussed before in chapter 3 section 3, 2m/s gives the heaviest and finest doping performance. However, as can be seen later, this does not ensure the best plating result out of the batch. Plating may compensate for breaks in the line and connect broken regions, but may still lead to higher series resistance.

Table 4.4 Magnificence X2k SEM pictures of Nickel Plating with Ag tabs on the rear [3]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Busbar</th>
<th>Finger</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-5-7</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>2m/s</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>ST-4-9</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>5m/s</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>

It is indicated from table 4.4 for the laser speed at 2m/s, the doping level at the edge of the finger line than in the middle because there is more nickel plated on the sides. While the laser speed at 5m/s demonstrates more uniform nickel plating.
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**Figure 4.6** Magnificence X 8.00k FIB picture of closer look at the faulted 2m/s nickel plated finger [3]

This can be explained by “Current Crowding Effect”,

![Diagram](image)

**Figure 4.7** Definition sketch of ideal contact for mathematical analysis. The y-axis is greatly expanded for clarity. [9]

Nickel plating is related to the current flow which is generated by surface reaction. When there is nonuniformity in the current across the laser doped opening area for plating, the amount of nickel being deposited in this area will be nonuniform. The value of current over an area, the current density, at a specific point is determined by how far the current can be transferred to from the opening edge in 1D direction, the transfer length is:

\[
L_T = \sqrt{\frac{\rho_c}{R_s}}
\]  

\(\rho_c\) is the contact resistivity and \(R_s\) is the sheet resistance of a specific point on the laser heavily doped emitter. We can assume \(\rho_c\) is a constant at every point of the laser doped opening area once the nickel plating starts. Hence transfer length is largely affected by...
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the sheet resistance, the heavier doped the region or point is, the shorter the transfer length is. [10]

Dimensionless Contact Half-width:

\[
\mu \equiv \frac{l}{L_t} = \frac{l}{\sqrt{\rho_c R_s}}
\]  

(4.5)

\(l\) equals to half of the laser line width, around 5\(\mu\)m.

\[
\frac{\text{Current, at, edge}}{\text{Current, at, Centerline}} = Cosh(\mu)
\]  

(4.6)

Hence the current density at the edge is higher than in the center of the laser line, which results in more nickel plated at the edge as we can clearly see from table 4.5 at the laser speed of 2m/s.

In addition, the reason why it is heavier doped at the sides than in the middle for the Gaussian beam laser used in this experiment is possibly due to the waveform of the laser, the power in the middle of the beam is stronger and this can cause a little ablation of silicon while the surrounding area enjoys suitable power hit to incorporate dopants into silicon. However, this is just a hypothesis which needs to be further proved.

Table 4.5 Magnificence X2k SEM pictures of Nickel Plating without Ag Tabs on the rear [3]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Busbar</th>
<th>Finger</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-5-4 5m/s</td>
<td><img src="image" alt="Busbar SEM picture" /></td>
<td><img src="image" alt="Finger SEM picture" /></td>
</tr>
</tbody>
</table>

By comparing the SEM pictures in table 4.4 and table 4.5, the difference between wafers with Ag tabs on the rear and without at the same speeds is not quite noticeable, suggesting that Ag tabs are not required to allow adequate plating to occur, this fact could be used to reduce fabrication costs by not needing Ag tabs on the rear, but this would
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then require the need for other contacting methods to the rear of the solar cell such epoxy glues etc. Theoretically, Ag helps oxidation on the rear which acts like the redox catalyst, and this can be further demonstrated in the following experiments.

Another conclusion drawn from this stage is the finest and heaviest doped line doesn’t turn out to be the most suitable for nickel plating. 5m/s laser speed is the best choice.

![Figure 4.8 Magnificence X2k SEM pictures of Copper Plating with Ag tabs on the rear left: laser speed at 2m/s, right: laser speed at 5m/s [3]](image)

No matter how the previous stage of Ni plating is, all of the wafers at different laser doped speed tend to have copper plating on it. However, if there is no Ni underneath this will lead to shunting in the long term. Otherwise Cu can penetrate into the solar cell and shunt the device. The copper plating result is not satisfactory, many balls are formed on the sides of the finger which are referred as the “treeing effect”. Ideally, a very smooth deposit of metal especially Ni is required. Cu layer could also be smooth, however not necessary. The shape of the finger cross section should be in an arc style. From the result of the experiment, 1μm of nickel (including nickel silicide) with around 4 microns of copper have been plated. For normal metallization purpose, only 0.2 microns of nickel is needed, hence less nickel plating time should be undertaken.
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Figure 4.9 Magnificence X 2.00K FIB NiSi on surface, but extra nickel peeling off from NiSi. Copper attached to the Ni above. [3]

In some of the plated fingers, Ni has lifted off surface. There also appears to be poor adhesion between Ni and Cu. Possible reasons could be with very thick Ni deposit, there are larger thermal stresses induced in the plated metal contact during the Ni sinter, which is not good for cell performance. An expectation can be made that with thinner Ni deposit this problem should be overcome.

Darkstar IV measurement has been done after making complete devices:

<table>
<thead>
<tr>
<th>Table 4.6 Measured Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>ST-3-6 no Ag Tabs</td>
</tr>
<tr>
<td>ST-3-5 no Ag Tabs</td>
</tr>
<tr>
<td>ST-5-3 with Ag Tabs</td>
</tr>
<tr>
<td>ST-5-9 with Ag Tabs</td>
</tr>
</tbody>
</table>

Compared with a standard screen printed Cell, much higher current and higher voltage has been achieved but these cells suffer from lower FF. This could be due to poor plating which brings high series resistance. With further optimization, it is possible to yield FF of 79% as has been achieved in Single Side Laser Doped Emitter Cell Structure. This would yield an efficiency of 19.5%.

The wafers with silver tabs seem to have better electrical performance than those without. The silver is aiding in the plating process, but no silver tabs gives much higher voltages therefore shows the potential to achieve higher efficiencies once the process is optimized.

The measurement above can be used as an indicator to extract implied Voc from the relevant PL images for our later use.
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Figure 4.10 5V-1s mode PL images after copper plating a) ST-3-6 with laser doped speed at 1m/s b) ST-3-5 with laser doped speed 2m/s c) ST-5-9 with laser doped speed at 1m/s d) ST-5-3 with laser doped speed at 2m/s.

Table 4.7 Photoluminescence measured parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>PL intensity (Ipl)</th>
<th>Time/s</th>
<th>Voc/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-3-5 No Ag tabs</td>
<td>29646</td>
<td>1</td>
<td>641.4</td>
</tr>
<tr>
<td>ST-3-6 No Ag tabs</td>
<td>28132</td>
<td>1</td>
<td>639.7</td>
</tr>
<tr>
<td>ST-5-3 With Ag tabs</td>
<td>16960</td>
<td>1</td>
<td>625.3</td>
</tr>
<tr>
<td>ST-5-9 With Ag tabs</td>
<td>18537</td>
<td>1</td>
<td>623.3</td>
</tr>
</tbody>
</table>

(A notice is that Laser doped speed at 2m/S is giving a slightly higher Voc than 1m/s both with and without silver tabs, this is inconsistent with what have been discussed before.)

Figure 4.11 Calculated Constants using Excel

So the constants for equation (4.3) can be calculated out as:

$$C_1kT=32.401, C_2=307.54$$ (4.7)
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

Till now, CW Laser doped front Selective emitter plus standard plating technique has proven to work on standard screen printed p-type solar cells, though further optimizations need to be done to optimize the plating process such that smoother Ni deposits are achieved which could reduce large series resistances losses and potential shunts in the devices fabricated.

4.2.3 Experiment 3:

Wafer preparations:

Same wafers as per Experiment 1 are used.

Table 4.8 Process Sequence for Experiment 3

| 1. Strip off screen printed aluminum Layer. (Using Grove Etch Solution for a period of 15 mins) |
| 2. Piranha cleanings then rinse in DI water |
| 3. Al evaporation on the rear (2.6 microns of Al evaporation layer) |
| 4. Al annealing (400 °c in forming gas for a period of 30 minutes) |
| 5. Spin-on 20% Phosphorus Acid on the front. |
| 6. Laser doped lines the front at different speeds |
| 7. Rinse off the dopants |
| 8. Standard Nickel Plating and rinse in DI water for 2 minutes. |

Only 20 seconds’ rinsing off dopants is done before Nickel plating to ensure the Aluminum evaporation layer will not be attacked too much.

Another notice is that although the screen printed aluminum layer has been stripped off, the embedded silver tab bits still stick to the silicon, which acts as the aluminum oxidation catalyst

Results and Discussions
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

Table 4.9 5V-1s mode Photoluminescence monitoring of degradation in iVoc at different stages:

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Original cell (including Silver Tabs) iVoc(mV)</th>
<th>iVoc After Al Evap. (mV)</th>
<th>iVoc after Al Annealing(mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-3-9</td>
<td>642</td>
<td>577</td>
<td>575</td>
</tr>
<tr>
<td>ST-3-7</td>
<td>640</td>
<td>574</td>
<td>574</td>
</tr>
<tr>
<td>ST-4-1</td>
<td>643</td>
<td>576</td>
<td>576</td>
</tr>
<tr>
<td>ST-4-2</td>
<td>640</td>
<td>574</td>
<td>575</td>
</tr>
<tr>
<td>ST-3-3</td>
<td>643</td>
<td>576</td>
<td>575</td>
</tr>
</tbody>
</table>

The iVoc of all the cells decrease in a large portion after aluminum evaporation, but the main damage to the cell is caused by the previous screen printed strip-off step. When the original screen-printed aluminum is stripped off, the back surface filed has been also taken off the rear surface hence the cell is losing a electric field opposing high recombination rate carriers. After Al annealing, nearly no change in iVoc is observed, which is reasonable as the annealing step is only to recrystallize the amorphous evaporated aluminum and it does not actually form a back surface field. However, the idea of Al evaporation instead of screen printed Al is applied because Al evaporation demonstrates denser Al epitaxial layer growth on the rear. Moreover, Al evaporation and the following annealing is a combined low temperature step, optimization of surface passivation can therefore be achieved (as can be seen in experiment 4&5), rather than being reliant on a screen printed firing step (at approximately 850 °c). This should yield higher efficiencies.

![Figure 4.12 Magnificence X 1k SEM Busbar cross section fault plating at laser speed of 5m/s [3]](image)

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Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

The laser doped speed at 5m/s still displays the best nickel plating result in this experiment. One interesting thing to mention is that at the cross area of busbars (Circled out in red), less amount of nickel is plated. This is due to the laser beam running through the cross area twice perpendicularly in order to connect those busbars, therefore more heavily doped region is formed, especially the overlapped edges of these two paths (More heavily doped at edge of the laser line as discussed before.).

![Microscope Image](image)

**Figure 4.13 Microscope Left: Magnificence X 5k Mess surface condition after plating with Al bits (White) Aluminum Oxide (Brown) and Exposed Silicon (Light Blue) Right: Magnificence X 20k Closer look at Aluminum Corrosion**

Excessive corrosion at the rear aluminum evaporation occurred, with even the exposure of Silicon at some places. Thicker deposition of aluminum can solve this problem.

From the above results, standard screen-printed cell with displaced aluminum reflector rear and silver tab bits also proves to be viable for the front contacting scheme via laser doped selective emitter plus standard photoplating.

Moreover, this structure allows for improvement such as adding a passivation layer between silicon rear surface and thick enough Al evaporation layer. Further improvement to reduce back surface recombination is to localized contacts, which can also be achieved with heavily laser doped selective emitters on the rear to confine the contacting area to only several lines.

**4.2.4 Experiment 4 & 5**

In these two experiments, standard photoplating on double side laser doped selective emitter cell structure is developed.
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

Wafer preparations

Wafers without silver tabs on the rear as per Experiment 2 are used.

<table>
<thead>
<tr>
<th>Process Sequences for Experiment 4 and 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment 4</strong></td>
</tr>
<tr>
<td>1. Strip off screen printed aluminum layer using grove etch solution</td>
</tr>
<tr>
<td>2. Piranha cleaning, then rinse in DI water</td>
</tr>
<tr>
<td>4. SiON deposition on the rear</td>
</tr>
<tr>
<td>5. Spin-on PBF1 on the rear and soft bake</td>
</tr>
<tr>
<td>6 Laser Doped lines on rear at 2m/s</td>
</tr>
<tr>
<td>7. Rinse off the dopants</td>
</tr>
<tr>
<td>8. Aluminum evaporation, thickness of around 3 μm</td>
</tr>
<tr>
<td>10 Spin-on 20% phosphorus acid</td>
</tr>
<tr>
<td>11 Laser doped lines the front at different speeds</td>
</tr>
<tr>
<td>12. Rinse off the dopants</td>
</tr>
<tr>
<td>15. Laser doped lines the front at different speeds</td>
</tr>
<tr>
<td>16. Rinse off the dopants</td>
</tr>
</tbody>
</table>

Rear Laser Doped Pattern:

Same pattern as per the front pattern used in Experiment 1. Alignment of the rear pattern should be parallel to the front laser doped pattern.

Result and Discussion

<table>
<thead>
<tr>
<th><strong>Table 4.11 5V-1s mode Photoluminescence monitoring of degradation in iVoc at different stages for experiment 4</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment 4</strong></td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Experiment 4</td>
</tr>
</tbody>
</table>

The average iVoc after laser doped rear through SiON layer still stays over 620mV, which indicates that SiON is doing a good job in mitigating the damage by LD process and also after Al evaporation annealing, the average iVoc rises up to over 630mV. This is a really encouraging result in that though a lot of damages have been done to the rear
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SiON can still passivate the surface to a relatively acceptable level. During annealing the Al evaporation layer, the SiON also undergoes an annealing effect which can release hydrogen atoms to combine with the dangling bonds at the rear surface. However, whether the major benefit is coming from annealing SiON or annealing Al with SiON underneath is yet to be determined.

Table 4.12 5V-1s mode Photoluminescence monitoring of degradation in iVoc at different stages for experiment 5

<table>
<thead>
<tr>
<th></th>
<th>Average iVoc after SiON annealing (mV)</th>
<th>Average iVoc After Al evap (mV)</th>
<th>Average iVoc After Al evap annealing (mV)</th>
<th>Average iVoc After Ag Sprays and Soft-baking(mV)</th>
<th>Average iVoc after LD rear(mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 5</td>
<td>640</td>
<td>630</td>
<td>641</td>
<td>639</td>
<td>615</td>
</tr>
</tbody>
</table>

From the PL analysis for experiment 5, a clear conclusion can be drawn that the best passivation is achieved by separately anneal SiON and Al evaporation layer. Up to adding oxidation catalyst (The silver spray and soft baking) stage, iVoc that can be extracted from the cell is around 640mV despite of damages, which predicts a pleasant plating result as surface reaction during the metallization course is related to the photo-potential of silicon under illumination.

Figure 4.14 Magnificence X 1.0K SEM Pictures of right: Experiment 4 5m/s laser speed Nickel plated bus bars, left: Experiment 5 5m/s laser speed Nickel plated bus bars [3]

The best nickel plated performance found in both Experiment 4 and Experiment 5 is again when the laser operates at 5m/s. However, a noticeable difference between the best results obtained from these two experiments can be seen. Silver has been used as an oxidation catalyst for many years [5], and for our purpose, adding silver sprays onto the
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aluminum facilitate the oxidation of aluminum and as the sprays are uniform deposited, the corrosion on the aluminum surface looks more uniform than what have been seen in experiment 3.

![Image of Al Surface Corrosion](image)

**Figure 4.16 Optical Microscope Picture of Al Surface Corrosion**

Although the nickel plating in Experiment 5 turns out to be good, one problem has come up: the finger ends tend to have better plating than the parts near the busbars. One reason for this is the bus bars are spaced closely together (80 micron), so there needs to be much more current through those areas than just a finger, where they are 1mm apart. These indicate that point contacts on the rear with low coverage area but closer located will allow for more uniform plating.

Up to experiment 5, a reliable standard photoplating process on Double Side Laser Doped Selective Emitter structure cell has been developed, although further optimization of the photoplating process is needed such as change plating solutions and corresponding processing time and temperatures. Also, a nickel strike may need to be added to the process sequence. The localized contacting pattern at the rear are lines, further study on points contacts is done in experiment 6.

### 4.2.5 Experiment 6

From previous experiments, key issues for optimizing the standard photoplating on DLDSE cell are summarized:

1. Photoplating on Doubled Side Laser Doped Selective Emitter cells work well.
2. 2m/s Laser doped speed results in heaviest doping on bare silicon or through dielectric layers.
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3. 5m/s laser doped speed on the front gives the best Nickel plating result.

4. Al evaporation facilitates the application of back surface passivation using SiON.

5. Ag sprays on Al evaporation layer helps nickel plating.

6. Good nickel plating does not ensure good Cu plating in the following stage.

7. PL image shows before Plating, iVoc as high as 630mV can be achieved. This may be higher if using wafers which were not initially screen printed.

8. Nickel Photoploating on DLDSE cells with points contacting scheme on the rear needs to be investigated.

**Wafers preparation**

Wafers as per Experiment 4&5 are used.

<table>
<thead>
<tr>
<th>Table 4.13 Process Sequences for Experiment 6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment 6</strong></td>
</tr>
<tr>
<td>1. Strip off screen printed aluminum layer.</td>
</tr>
<tr>
<td>2. Piranha Cleaning and then rinse in DI water.</td>
</tr>
<tr>
<td>3. Standard RCA full clean and HF dip</td>
</tr>
<tr>
<td>4. 75μm SiON (Developed by Hallam et al.) PECVD deposition on the rear</td>
</tr>
<tr>
<td>5. 5mins SiON annealing</td>
</tr>
<tr>
<td>6. Spin-on PBF1 on the rear then soft bake.</td>
</tr>
<tr>
<td>7. Laser doped points with different openings and spacings on rear at 2m/s using masks.</td>
</tr>
<tr>
<td>8. Rinse off the dopants</td>
</tr>
<tr>
<td>9. Aluminum evaporation, thickness of around 2.5μm</td>
</tr>
<tr>
<td>10 Al annealing</td>
</tr>
<tr>
<td>11. Quick HF dip and DI water rinse</td>
</tr>
<tr>
<td>12. 2 silver sprays on the rear</td>
</tr>
<tr>
<td>13. Soft bake silver sprays</td>
</tr>
<tr>
<td>14. Spin-on 20% Phosphorus Acid on the front</td>
</tr>
<tr>
<td>15. Laser doped lines at 5m/s on the front</td>
</tr>
<tr>
<td>16. Rinse off the dopants</td>
</tr>
<tr>
<td>17. Standard Nickel Plating and rinse in DI water</td>
</tr>
</tbody>
</table>
Chapter 4. Development of the light induced plating process for laser doped solar cells with displaced aluminum reflector rears

Table 4.1 Points Patterns

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Rear LD speed</th>
<th>Points spacing</th>
<th>Point opening width</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-11-6</td>
<td>2m/s</td>
<td>1mm</td>
<td>40μm</td>
</tr>
<tr>
<td>ST-8-4</td>
<td>2m/s</td>
<td>500μm</td>
<td>25μm</td>
</tr>
<tr>
<td>ST-10-6</td>
<td>2m/s</td>
<td>300μm</td>
<td>25μm</td>
</tr>
<tr>
<td>ST-10-4</td>
<td>2m/s</td>
<td>200μm</td>
<td>25μm</td>
</tr>
</tbody>
</table>

(Smallest value of the opening width achieved is 25μm due to the resolution scale of equipment used for making masks.)

**Results & Discussions**

Just like laser doped lines, ablation occurs in the center of the point if laser speed is too low. 2m/s laser speed portrays the finest point in the size of 25μm by 10μm.

Table 4.15 Optical Microscope Pictures of Nickel plating at different point spacings

<table>
<thead>
<tr>
<th>Point Spacing (μm)</th>
<th>Nickel plated Bubars</th>
<th>Nickel Plated Fingers (away from busbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results given above are straight forward. The closer the points on rear are, the contacting area is larger if the size of the points are the same and also allows for a more effective collection of current by the contacts, hence more reactions of oxidation on the rear are taking place, which drives more nickel to deposit on the laser doped lines on the front. For the standard LD cells, the metal contact on the back has full coverage so no
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Extra distance for carriers to travel to allow current through the device and get plating to occur, while having closely spaced point contacts should simulate this design more. In this sense, it seems closely located points pattern is preferred. 200μm spacing demonstrates pleasant nickel plating and this proves the point contacts structure is compatible with standard photoplatting process.

Considering the coverage of points, as a matter of fact, by reducing the area of laser doping on the back, the metal/Si interface is reduced and higher Voc can then be achieved. This is why the point contacts are used on the PERL cell as discussed in Chapter 2. There is an effect on the series resistance of the cells, with point contacts having an advantage.

Take the point contact size of 40μm by 10μm with a spacing of 1mm as an example, coverage of points:

\[
Coverage = 0.04\% 
\]  
(4.8)

While for the point contact size of 25μm by 10μm with a spacing of 200μm:

\[
Coverage = 0.63\% 
\]  
(4.9)

Compared to the line patterns:

\[
Coverage = 0.99\% 
\]  
(4.10)

Table 4.15 5V-1s mode Photoluminescence monitoring of degradation in iVoc at different stages:

<table>
<thead>
<tr>
<th>Spacing(μm)</th>
<th>1000</th>
<th>500</th>
<th>300</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>iVoc after SiON deposition (mV)</td>
<td>639</td>
<td>640</td>
<td>641</td>
<td>641</td>
</tr>
<tr>
<td>iVoc after LD rear (mV)</td>
<td>624</td>
<td>621</td>
<td>613</td>
<td>610</td>
</tr>
</tbody>
</table>

Although denser points configuration, which means more coverage of points, has better nickel plating but more chances of recombination at the rear and the iVoc is lower. It is not worthwhile to make a complete device in this situation. Therefore, a trade-off must be met to allow for a relative high iVoc and decent plating at the same time. One possible solution is combining the benefits of the two factors mentioned above: on the rear, setting closer laser doped points where the front pattern’s busbars are, and laser doping farther
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located points outside the front busbars area. A complex current collection modeling needs to be gone through to see which is the best configuration.

![Figure 4.18 Left: Magnificence X20 Optical Microscope Pictures of Brown rings outside the points (40μm X 10μm in size, 1mm in spacing) around 250μm in diameters (Edge corrosion effect). Right: Magnificence X 50 Closer look at the Edge Effect](image)

Brown rings indicate oxidation reaction occurs on the back surface, such as for samples with 500 microns and 1mm spacing the rings occurred. However for 200 and 300 microns spacing, the rings were not visible around each point contact, but on the edge of the active cell area, a brown ring occurred again 125 micron from the outermost point contact. This suggests that the oxidation of aluminum is more uniform if the point contacts are closer.

### 4.3 Chapter Summary

Experiment 1 and 2 proves that continuous wave laser doped front selective emitter plus standard plating technique works on standard screen p-type printed solar cells, though further optimizations need to be done to optimize the plating process such that smoother Ni deposits are achieved which could reduce large series resistances losses and potential shunts in the devices fabricated.

In experiment 3, standard screen-printed cell with displaced aluminum reflector rear and silver tab bits also proves to be viable for the front contacting scheme through laser doped selective emitter plus standard photoplasting.

Moreover, this structure allows for improvement such as adding a passivation layer between silicon rear surface and thick enough Al evaporation layer. Further improvement to reduce back surface recombination is to localized contacts, which can also be achieved
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with heavily laser doped selective emitters on the rear to confine the contacting area to only several lines

Up to experiment 5, a reliable standard photoplatinization process on Double Side Laser Doped Selective Emitter structure cell has been developed, although further optimization of the plating process is needed such as change plating solutions and corresponding processing time and temperatures. Also, nickel strike step needs to be added to the process sequence.

Experiment 6 investigates the point contacting scheme on the rear and tests the standard light induced nickel plating process with different point’s configuration. Results are encouraging, especially good plating using the point contact size of 25μm by 10μm with a spacing of 200μm. Double Sided Laser Doped Selective Emitter point contacts structure combined with photoplatinization technique has been developed. However, author does not have a chance to make a complete cell for efficiency measurement. Predictions can be made that the complete device’s Voc and Jsc using these fabrication steps will not be decent until further improvement such as rear surface passivation and finer points configuration have to be made.

4.4 References


[3] With the help of Yuk (Chris) Yeung,


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[9] Dennis Coyle, REDOX Basics & 1D model of Light-Induced Plating, UNSW group meeting presentation, 2010

Chapter 5

Conclusion

This thesis investigates heavily doped emitter formed by traditional solid source thermal diffusion and continuous wave laser doping. By comparing the profile of laser doped emitter and solid diffused junction, the quality of laser doped emitter is seen to be easy to control by simply changing the scanning speed of the Continuous wave laser used throughout this work. However, the application of laser doping technique to form emitter on the whole surface of the wafer is limited due to the duration of processing. In this thesis, laser doped selective emitter combined with photoplating for the contact scheme is implemented.

In chapter 3, Laser doped selective emitter has shown excellent performance, while laser induced defects are to be eliminated for improving the performance. Silicon oxynitride has been used as an alternative antireflection coating for a-SiNx:H or SiO2, it demonstrates both good electrical passivation effects and thermal effects. This film is incorporated into the structure of Double side laser doped selective emitter cell, further improvement of the rear surface passivation can be achieved by adopting Aluminum Oxide, before that, intensive research has to be done.

The impacts of laser speed on sheet resistance has been summarized for different silicon surface conditions, the experimental work described in the next chapter makes use of this.
Based on these investigations, in chapter 4, Double Sided Laser Doped Selective Emitter Solar Cell structure has shown to be a viable on CZ p-type wafers. A series of experiment has been gone through to develop reliable process sequence for DSLDSE cell. Inspired by the PERL cell back contact structure, using the laser doped point rear contacting scheme combined with Standard Light Induced Plating developed by UNSW has proved to give pleasant front contact metallization result, although further improvement is needed. Moreover, due to the perfect metallization not being achieved yet, no such efficiency measurements were obtained on completed devices.

In summary, the findings establish a relatively reliable fabrication process and provide greater insight into light induced plating metallization process and back contacting scheme. The need for further research is also indicated for the successful implementation of this structure.