

Improved carrier selectivity of diffused silicon wafer solar cells

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IMPROVED CARRIER SELECTIVITY OF DIFFUSED SILICON WAFER SOLAR CELLS

Alexander To

A thesis in fulfilment of the requirements for the degree of
Doctor of Philosophy



School of Photovoltaic and Renewable Energy Engineering
Faculty of Engineering

December 2017

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Abstract:

The majority of commercial solar cells are fabricated on crystalline silicon wafers with diffused homojunctions. This is forecast to continue into the near future. This thesis explores how improving the carrier selectivity of homojunction solar cells can achieve higher conversion efficiencies, by reducing the losses at the contacts and non-contacted surfaces.

The majority carrier conductivity at the metal-silicon contact was investigated for both heavily doped n^+ and p^+ silicon. For diffused n^+ electron collectors, it was shown that thin layers (<5 nm) of aluminium oxide (AlO_x) deposited between the silicon nitride (SiN_x) and screen-printed silver paste can improve contact resistivity, whereas thicker layers increased the contact resistivity. Through simulation and cell fabrication, this effect was shown to be beneficial for solar cells limited by contact resistance, whereas the adverse effects of thicker layers were mitigated by changing the paste formulation. For diffused p^+ hole collectors, a method of electroless plating nickel seed layers to boron diffused silicon was developed which demonstrated contact resistivity's $< 1 \text{ m}\Omega\cdot\text{cm}^2$ for lightly diffused p^+ silicon. However, it was found that the contact recombination and contact resistivity was higher for the electroless nickel plated contacts in comparison to aluminium evaporated references.

Regarding the non-metallised, heavily doped silicon surfaces, improved understanding of the recombination rate at diffused inverted surfaces was achieved through modelling of the injection level dependent lifetime behaviour with technology computer-aided-design (TCAD) simulations. This resulted in the development of a novel contactless method of extracting the interface charge (Q) and surface recombination velocity parameters from passivated and diffused silicon surfaces. This addresses a current limitation of existing interface characterisation techniques, and allows the study of the electronic properties of these highly relevant surfaces. This method was demonstrated on a range of dielectric passivated n^+ and p^+ surfaces, and the extracted Q values were comparable to results obtained using conventional techniques.

Finally, the findings were implemented in TCAD simulations of state-of-the-art homojunction interdigitated back contact (IBC) solar cells, demonstrating the technology potential. This work highlights novel technologies and methods to be used to improve the next generation of diffused silicon wafer solar cells.

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“No. No out. No back. Only in. Stay in. On in. Still...
Ever tried. Ever failed. No matter. Try again. Fail again. Fail better.”

- Samuel Beckett, *Worstword Ho*

ABSTRACT

The majority of commercial solar cells are fabricated on crystalline silicon wafers with diffused homojunctions. This is forecast to continue into the near future. This thesis explores how improving the carrier selectivity of homojunction solar cells can achieve higher conversion efficiencies, by reducing the losses at the contacted and non-contacted surfaces.

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LIST OF SYMBOLS

Al	Aluminium
Ag	Silver
Δn	Excess carrier density
D_{it}	Interface defect density
E_i	Intrinsic Fermi energy
E_F	Fermi level
E_{fn}	quasi-Fermi level of electrons
E_{fp}	quasi-Fermi level of holes
η	Efficiency
HF	Hydrofluoric acid
σ_n	Electron capture cross section
σ_p	Electron capture cross section
J_{sc}	Short circuit current density
J_{0c}	Contact saturation current density
J_{0e}	Emitter dark saturation current density
J_{0s}	Surface saturation current density
k	Boltzmann's constant
N_A	Acceptor concentration
$N_{A,s}$	Surface concentration of acceptors
NaH_2PO_2	Sodium hypophosphite
n_d	Electron concentration at distance d from the surface
n_0	Electron concentration at equilibrium
NH_4OH	Ammonium hydroxide
n_i	Intrinsic carrier concentration
$n_{i,eff}$	Effective intrinsic carrier concentration

Ni	Nickel
NiSi	Nickel silicide
NiSO ₄	Nickel (II) Sulphate
N_D	Donor concentration
N_c	Density of states in the conduction band
n_s	Surface concentration of electrons
N_v	Density of states in the valence band
p_d	Hole concentration at distance d from the surface
PdCl ₂	Palladium (II) chloride
p_0	Hole concentration at equilibrium
p_s	Surface concentration of holes
ρ_c	Specific contact resistivity
q	Elementary charge
Q	Interface charge density
Q_f	Fixed interface charge density
R_c	Contact resistance
R_{total}	Total resistance
Si	Silicon
S	Surface recombination velocity
S_{eff}	Effective surface recombination velocity
SnCl ₂	Tin (II) chloride
ψ_s	Electrostatic potential at the surface
S_{n0}	Surface recombination velocity parameters for holes
S_{p0}	Surface recombination velocity parameter for electrons
T	Temperature
V_{oc}	Open-circuit voltage

LIST OF ABBREVIATIONS

Ag-Si	Silver-silicon
ALD	Atomic layer deposition
Al-BSF	Aluminium back surface field
AlO _x	Aluminium oxide
ARC	Anti-reflection coating
a-Si:H	Hydrogenated amorphous silicon
BSF	Back surface field
BSG	boron-silicate glass
BGN	band gap narrowing
BRL	Boron rich layer
CO ₂	Carbon dioxide
COCOS	Corona oxide characterisation of semiconductor
CTLM	Circular transmission line method
CV	Capacitance-voltage
c-Si	Crystalline silicon
ECV	Electrochemical capacitance-voltage
EDX	Energy-dispersive X-ray
FEM	Finite-element model
FZ	Float zone
GHG	Greenhouse gasses
HfO _x	Hafnium oxide
IBC	Interdigitated back contact
LCOE	Levelised cost of electricity
LHS	Left hand side
LTLM	Ladder transmission line method

PC	Photoconductance
PECVD	Plasma enhanced chemical vapour deposition
PERC	Passivated emitter and rear contact
PERL	Passivated emitter with rear locally diffused
PERT	Passivated emitter with rear totally diffused
PESC	Passivated emitter solar cell
PL	Photoluminescence
PSG	Phosphorus silicate glass
PV	Photovoltaics
QSSPC	Quasi-steady-state photoconductance
QSSPL	Quasi-steady-state photoluminescence
RCA	Radio Corporation of America
RHS	Right hand side
SEM	Scanning electron microscope
SiN _x	Silicon nitride
SiO _x	Silicon oxide
SiO ₂	Silicon dioxide
SRH	Shockley-Read-Hall
SRV	Surface recombination velocity
TEM	Transmission electron microscopy
TCAD	Technology computer-aided-design
TLM	Transmission line method

1 INTRODUCTION

The recent and rapid increase in the concentration of greenhouse gases (GHG), such as carbon dioxide (CO₂), in the atmosphere and its associated climate altering effects, incentivise mankind to reduce human-activity related GHG emissions. Rising GHG emissions are increasing global average surface air temperatures, acidifying the ocean, shrinking glacial systems, and altering weather patterns across the globe [1, 2]. Without curtailment, rising GHG emissions may cause an increase in average global temperatures of 4 °C, which would see widespread climate change across the globe, significantly impacting natural biodiversity and landscapes, established weather patterns, access to fresh water, and rising sea levels [3].

The energy sector, which is responsible for electricity generation, is a significant emitter of GHG from the burning of fossil fuels such as thermal coal and natural gas for electricity generation. In 2016, 86.3 % of electricity generation in Australia was produced using fossil fuels [4], and this accounted for 35 % of all GHG emissions in the country—the single largest contribution of any sector [5]. This trend is mirrored globally, with electricity and heat production contributing 25 % of global GHG emissions, again the single largest contributor by sector [6]. Therefore, there is a strong imperative to transition the total electricity generation mix towards renewable and low-emissions electricity generation technologies, such as solar photovoltaics and wind energy converters.

Globally there are signs that this shift towards ‘cleaner’ electricity generation technologies is gaining momentum—in 2016 the majority (55.3 %) of new generating capacity installed worldwide was renewable [7]. This is supported by the increases in the

number of people employed in the renewable energy sector worldwide—which grew by 1.1 % over 2015 to employ 9.8 million globally—with solar photovoltaics (PV) the single largest employer in this sector, growing 12 % in 2015 [8]. The PV industry has grown exponentially over the past decade, with approximately 75 GW of capacity added in 2016, and with the cumulative global installed capacity at the end of 2016 surpassing the 300 GWp milestone [9]. In addition, the cost of photovoltaics has also reduced dramatically over the past decade, and the PV module price is expected to reach a value as low as US\$0.37/W in 2017 [9], driven by the long term learning rate of 22.5 %. The rapid pace at which cost reductions are being realised in the industry will put downward pressure on the levelised cost of electricity (LCOE) from PV generators which, during 2016, was estimated to have dropped to US\$101/MWh [7]. Accordingly, some forecasts predict solar PV to become cheaper than most, if not all fossil fuel sources of electricity generation in the near future [10].

Driving these cost reductions is substantial investment in PV material production (such as silicon feedstock) and PV module production, coupled with consistent PV research and development efforts at PV manufacturers, universities and research institutes across the globe. Current research and development activities in the PV industry can be broadly categorised as focused towards 1) realising incremental improvements in the maximum conversion efficiency of solar PV, and to 2) reduce the manufacturing cost of commercial solar photovoltaics. Central to the former aim is improving the ability of solar cells to successfully extract the maximal amount of power from terrestrial solar irradiance. Once the electrons and hole pairs are separated via the photovoltaic effect, a solar cell must perform the task of separating the electrons and holes such that they are extracted at separate electrodes, in a process known as charge separation. This process of separating, sustaining and extracting the carriers within the device, is known as carrier selectivity, and is the useful means by which solar cells extract energy and, in addition to the photoelectric effect, is the fundamental physical phenomena driving their operation.

Carrier selectivity is about manipulating the electron and hole conductivity of certain regions in the solar cell to promote or negate carrier concentrations spatially within the device. Carrier selectivity is engineered to reduce recombination, which is quantified by the pre-factor to the recombination current density J_0 , and/or to facilitate the extraction of charge carriers at the metal electrodes, which is measured by the contact resistivity ρ_c . To successfully transfer the high efficiency solar cell concepts demonstrated in the

laboratory, the industry must reduce recombination losses to realise the performance potential of these advanced structures. As such, the latest technology roadmap for the PV industry forecasts a significant reduction in the various J_0 components of the bulk and surface regions of the solar cell, as shown in Figure 1.1. Improving carrier selectivity within the device, at the near-surface and surface regions of the solar cell and at the metal electrodes where power is extracted, will be required to realise this forecast and is a key focus of this work.

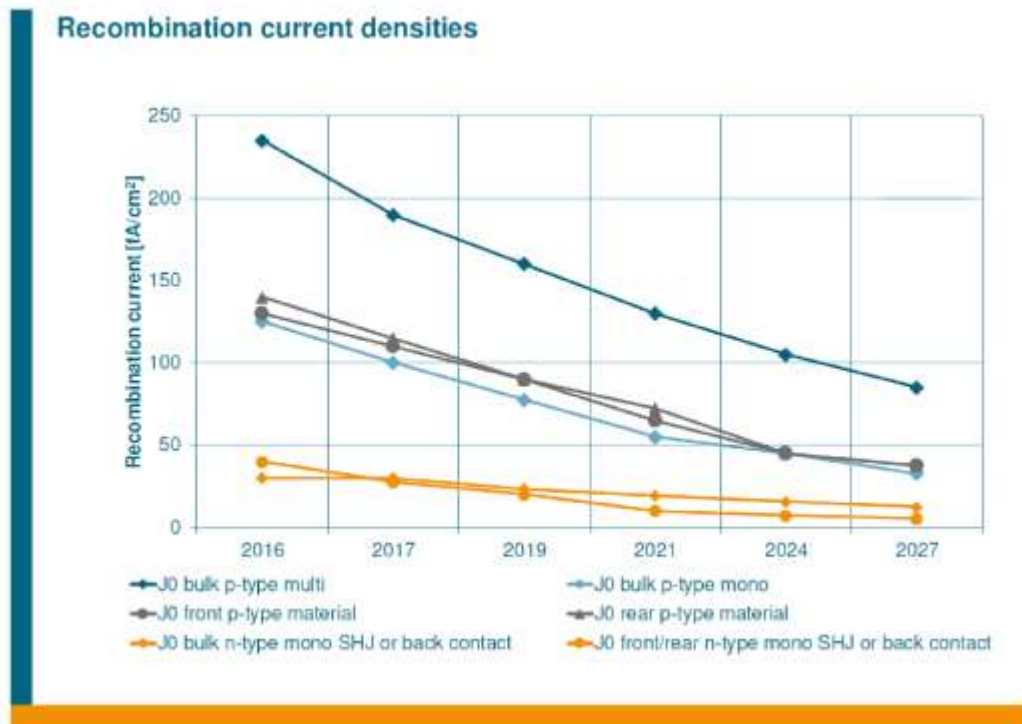


Figure 1.1 Predicted trend for recombination current density factors J_{0bulk} , J_{0front} , J_{0rear} for p-type and n-type solar cell concepts, sourced from the ITRPV [9]

Similarly, the development of high performance carrier selective contacts which minimise parasitic resistance losses during power extraction is essential to the efficient operation of solar cells. Technologies which enable low-cost, high performance contacts—defined to have low contact recombination density J_{0c} and low ρ_c —are currently the focus of much research and development within the PV field. The latest technology roadmap predicts, on the one hand, the continued use of the dominant screen printing technology and over time ceding a growing (albeit small) percentage of market share to the plated metallisation approaches which, through avoiding the use of expensive silver (Ag) screen-printing pastes, have greater potential for future cost reduction [9]. The forecasted market share growth of plated technologies at the expense of screen-printed

approaches is depicted in Figure 1.2. Consequently, the carrier selectivity of screen-printed contacts needs to be improved in line with the forecasted J_0 reductions. Simultaneously, lower cost approaches—such as nickel plated contacts—need to be developed and their carrier selectivity optimised to fulfil their role as an alternate, lower cost technology approach to the use of silver pastes, without sacrificing solar cell performance, process reliability and manufacturability.

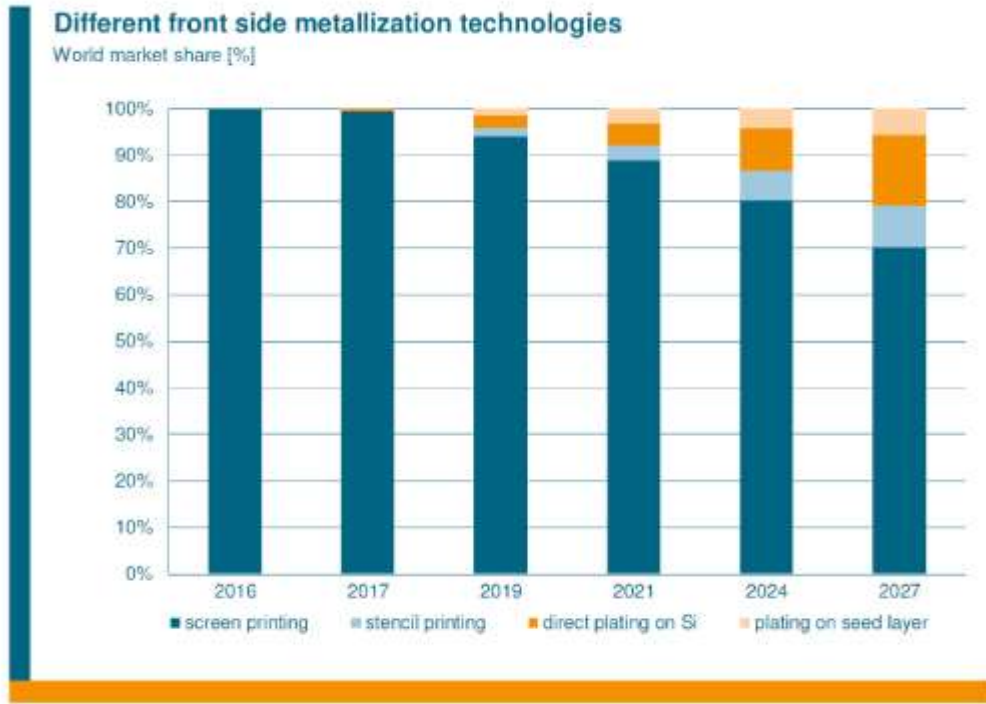


Figure 1.2 Predicted trend for different front side metallisation technologies, sourced from ITRPV [9]

1.1 Thesis objectives

The aim of this thesis was to investigate how the carrier selectivity of the current generation of diffused silicon wafer based solar cell technologies can be improved. Specific focus was directed towards the contacted surfaces and the diffused regions underneath them collectively as a carrier selective contact, in accordance with the definition given by Brendel *et al.* and outlined further in Section 2.1 [11]. These improvements were achieved by a combination of improved device design, analysis and test structure fabrication, which demonstrate the potential for improvements in carrier selectivity on existing and next generation solar cell architectures.

As depicted in Figure 1.2, currently the dominant screen printing technology is applied to ~90 % of all commercial cells [9] and this thesis assessed some of the complications with screen-printed solar cells as it applies to the passivated emitter and rear cell (PERC) architecture—which is increasingly being fabricated in commercial production lines [9]. Specifically, the effect of parasitic deposition of aluminium oxide (AlO_x) onto the front-side silicon nitride (SiN_x) prior to metallisation was assessed and optimised to show how this effect can be manipulated to improve the majority carrier conduction.

As previously mentioned, there is also a competing aim to replace the expensive silver front contact with cheaper metals such as nickel and copper, as these present opportunities for further cost reductions in line with the second broad aim of the industry at present (to reduce the cost of solar PV). The development of nickel plated contacts to diffused p -type hole collectors, and their resulting carrier selective properties as assessed by J_{0c} and ρ_c , is required to enable the next generation of high performance n -type solar cell structures, and therefore this thesis also assessed the carrier selectivity of such contacting structures.

Surface passivation is a key element of solar cell design to achieve high efficiency, as it maximises the amount of electron hole pairs available for extraction. Surface passivation is typically achieved by establishing chemical bonds at the surface to reduce the number of recombination sites at the silicon surface. It may also involve the use of charge to selectively repel minority carriers within the vicinity of the surface. Practically, this is achieved via the deposition or growth of thin-film dielectrics such as silicon dioxide (SiO_2), AlO_x , SiN_x or hydrogenated amorphous silicon (a-Si:H) [12]. The engineering of the interface properties of such films—including the interface charge density, and fundamental surface recombination parameters—has been the focus of much research and development over the course of solar cell development. This work developed a novel metrology for assessing the carrier selectivity at the surface induced by dielectric thin-films deposited on diffused surfaces.

This thesis is structured as a collection of separate studies of how principles of charge separation can be further understood, and applied to various technologies. These include screen-printed contacts on PERC cells, and aluminium evaporated and electroless nickel plated contacts formed on boron diffused surfaces. Furthermore, by understanding the recombination rate at inverted surfaces, a unique relationship between the non-linear injection level dependent lifetime behaviour and the interface parameters of passivated

diffused surfaces was studied, which lead to the development of a method of assessing the interface parameters of passivating dielectrics. Finally, these findings were input into an interdigitated back contact (IBC) solar cell to simulate how these effects can improve solar cell performance in state-of-the-art diffused IBC solar cells.

The specific aims of this thesis can be summarised as follows. Firstly, the carrier selectivity of screen-printed and nickel plated contacts on heavily diffused n^+ and p^+ silicon surfaces respectively was explored, seeking to:

- 1) Determine the effect of unintended AlO_x deposition onto the SiN_x anti-reflection coating (ARC) on the electron conduction at the silver fired contacts.
- 2) Model the above-mentioned effect for varying AlO_x thicknesses and extents using Griddler simulations and demonstrate any benefits/detriments to the carrier selectivity of the silver contact experimentally in fabricated devices.
- 3) Develop an electroless nickel process for the plating of nickel contacts to boron diffused p^+ hole collectors. Subsequently determine the carrier selective properties of electroless nickel plated contacts after sintering, assessing the minority carrier recombination and majority carrier conduction for these contacts, in comparison to aluminium evaporated contacts.

Next, diffused inverted surfaces was studied. The aims of the work in this section was to:

- 4) Simulate and explain the non-linear injection level dependent lifetime behaviour of inverted diffused surfaces as they relate to, for instance, IBC solar cells.
- 5) Develop a method of extracting the interface charge and surface recombination velocity parameters of diffused passivated surfaces from contactless photoconductance (PC) measurements, assessing any limitations of this approach.
- 6) Demonstrate the above method on a range of diffused surfaces with varying passivating dielectrics, doping concentrations and polarities, exploring and simulating the underlying physics which governs these effects.

Finally, the results of the previous chapters are brought together and applied in the final chapter. The purpose of the work was to:

- 7) Develop an all IBC solar cell baseline to study the effect of the previous chapters—specifically the effect of the various rear passivation schemes and contacting technologies—on the simulated and actual IBC solar cell performance.

1.2 Thesis outline

This thesis covers multiple technologies linked by the broader aim of achieving improved solar cell carrier selectivity. The specific contexts and development imperatives of each area of work are outlined separately within the context of their respective chapters. The exception to this is Chapter 2 which begins with an overview of the concept of carrier selectivity as it is engineered in diffused homojunction solar cells and the fundamental physical principles of surface recombination and semiconductor-metal contact transport which underpin the body chapters. To frame the specific context of each section of work, a brief review of the research imperative and its relation to the broader thesis of improved carrier selectivity is outlined in the introduction section of each chapter, before delving into the details of the research and experimental work conducted.

Chapter 2 outlines the fundamental physical processes related to this work, and how these are measured and applied in the measurement and simulation of the various physical constants which are used to assess both carrier selectivity and the overall solar cell device performance in the experimental chapters of this work. A brief overview of the operating principles of solar cells, outlining the fundamental role of carrier selectivity in achieving charge separation within solar cells is presented. The physics relating to surface recombination, as they are modelled and measured within this work are then discussed, outlining the measurement apparatus and techniques used and their corresponding assumptions and corrections. The means of assessing metal-silicon contact performance—by measuring contact resistance—is then outlined, presenting an overview of the theory behind the test structures used to extract the contact resistivity.

Chapter 3 begins by outlining the issue of unintended AlO_x deposition on the front-side of PERC solar cells and explores the error in the ladder transmission line method (LTLM) measurement method used to measure the ρ_c . The effect of varying thicknesses of AlO_x “wrap-around” on the ρ_c for various firing settings and silver paste formulations is then explored. These results were input into finite-element model (FEM) simulations to determine the effect of varying extents and thicknesses of AlO_x wrap-around on PERC solar cell performance. To verify these results, solar cells with various AlO_x thicknesses deposited on the sunward SiN_x ARC were fabricated and the resulting effect on performance measured and presented.

Chapter 4 presents a study of the contact recombination and contact resistivity of electroless nickel plated contacts to boron diffused p^+ hole collectors. Two methods of electroless nickel plating were assessed—with and without prior activation—and the process without activation was characterised. The contact recombination properties were extracted via a technique which calibrates the photoluminescence (PL) signal to PC lifetime measurements using 3D computer simulations, which accounts for the spatial geometric effects on the contact recombination of the metal contacts. The ρ_c was extracted from circular and linear transfer length method patterns on the wafers. The carrier selectivity of these nickel plated structures was assessed for a range of boron diffusion profiles of varying dopant depth, and surface concentration of dopants. Aluminium evaporated contacts on otherwise identical structures were fabricated and presented alongside these results as a control.

Chapter 5 begins by reviewing the injection level dependent lifetime behaviour of diffused and inverted surfaces, highlighting a non-linear trend which although acknowledged by numerous previous researchers, was not fully explained to date. The experimental work in this chapter verified this effect as distinct from a measurement artefact and using Sentaurus TCAD simulations, was able to reproduce this lifetime behaviour.

Chapter 6 takes the main findings of Chapter 5 and explores in more detail the underlying surface physics relating to the carrier populations as they are affected by interface charge, doping level and carrier injection. This is achieved by developing a Matlab based model for simulating the carrier populations at a diffused surface with fixed charge present at the interface. This model takes into account Fermi-Dirac statistics, degeneracy and band gap narrowing effects. From this understanding, a method of extracting the interface properties of fixed charge, and the surface recombination parameters S_{n0} and S_{p0} from the corrected injection level dependent lifetime curves was developed. This method was then demonstrated on AlO_x , SiN_x and HfO_x passivated surfaces, demonstrating how key parameters relating to the carrier selectivity of surfaces can be measured using this technique.

Chapter 7 combines the findings of Chapters 4-6, by demonstrating how the contacts developed in Chapter 4, and the surface recombination behaviour identified in Chapters 5 and 6 affect the performance of a diffused IBC solar cell. With reference to separate work contained in Appendix A, a brief overview of the development of a baseline planar

IBC solar cell, outlining key processing considerations which can affect their performance is discussed. The results from the previous chapters are then simulated in a Sentaurus TCAD model of the baseline device, highlighting the effect of varying contact and surface passivation characteristics on the solar cell performance.

Chapter 8 summarises the main conclusions and novel contributions of this work. Areas for future work and research relating to address the limitations of this thesis are also presented.

2 LITERATURE REVIEW

CARRIER SELECTIVITY, SEMICONDUCTOR SURFACES AND CONTACTS

2.1 Introduction: solar cell carrier separation and selectivity

The operation of crystalline silicon (c-Si) based solar cells is based on the absorption of solar irradiation in the form of photons within the device. If the absorbed incident photons have sufficient energy to overcome the c-Si band gap E_g , electron-hole pairs are created. These generated carrier pairs must then avoid parasitic losses as they move towards the metallic electrodes where, upon successful extraction into the metal contacts, they are used to power an external load.

The above basic description of a solar cell identifies the three key functions of a solar cell:

- 1) the generation of the maximum amount of electron and hole pairs generated via the photoelectric effect,
- 2) the avoidance of carrier recombination during carrier transport from the point of generation within the device to the metal electrodes, and
- 3) the extraction of the carriers at the metal electrodes.

In this way, the ideal solar cell can be visually depicted as a device with three regions; 1) an absorber region where electron and hole pairs are generated, 2) an electron selective region with high electron conductivity and low hole conductivity, and 3) a hole selective region with high hole conductivity and low electron conductivity [13]. This is depicted schematically in Figure 2.1.

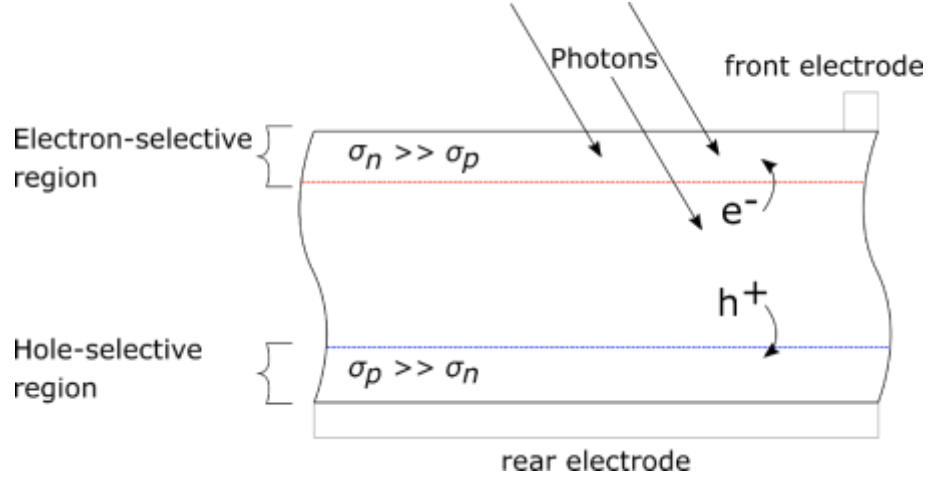


Figure 2.1 Schematic representation of a basic solar cell, depicting the basic processes occurring in the device which facilitate power conversion and extraction, adapted from [14]

This thesis mainly focuses on processes 2 and 3 above, with specific focus on how recombination and resistive losses can be suppressed by manipulating the carrier concentrations to both shield minority carriers from highly recombinative sites, and promote majority carrier conduction within the carrier selective regions and at the contacts. Achieving carrier selectivity requires an understanding of the basic forces present on electrons and holes in solar cell devices, which can then be manipulated to affect the carrier concentrations throughout the device. Electrons and holes in a solar cell are subject to forces which affect their movement; namely an electric force from an electric field E , and more importantly a generalised force related to the gradient of their spatial concentration throughout the device [15]. The associated charge currents for electrons j_e and holes j_h as a result of these forces are expressed as

$$j_e = \frac{\sigma_e}{q} \text{grad} \epsilon_{FC}, \quad \text{Eq. (2.1)}$$

$$j_h = \frac{\sigma_h}{q} \text{grad} \epsilon_{FV}. \quad \text{Eq. (2.2)}$$

Where q is the elementary charge; $\text{grad} \epsilon_{FC}$ and $\text{grad} \epsilon_{FV}$ is the gradient of the (quasi-) Fermi energy of electron in the conduction and holes in the valence bands respectively; and σ_e and σ_h are the electron and hole conductivities, defined as

$$\sigma_h = qn\mu_h, \quad \text{Eq. (2.3)}$$

$$\sigma_h = qn\mu_h, \quad \text{Eq. (2.4)}$$

where n and p are the electron and hole concentrations respectively and μ_e and μ_h are the electron and hole mobilities respectively. Two important conclusions can be drawn from Eq. 2.1 and Eq. 2.2; that the carrier transport is driven by the gradient of the Fermi energies and that the overall charge carrier current is a function of its conductivity. Given the dependence of the carrier flows on the conductivity, by affecting the values of σ_h and σ_e within the device, carriers flow in some regions are facilitated, whereas in other regions, these flows are negated. This latter notion is the underlying principle behind charge separation in solar cells.

A quantitative definition for carrier selectivity was recently proposed by Brendel *et al.*, which assigns the ratio of the majority carrier resistance to the minority carrier resistance as the selectivity S , is outlined briefly herein [11]. The minority and majority carrier recombination current density J_m and J_M respectively are defined as

$$J_M = J_c \left(\exp \left(\frac{V}{V_{th}} \right) - 1 \right), \quad \text{Eq. (2.5)}$$

$$J_m = J_c \left(\exp \left(\frac{V}{V_{th}} \right) - 1 \right). \quad \text{Eq. (2.6)}$$

Where J_c is a recombination parameter related to the flow of carriers into the contact at some voltage V , and V_{th} is the thermal voltage. The carrier resistance is voltage dependent, and so the inverse slope is used to define the minority and majority carrier resistance V/J as,

$$\rho_m = \left(\frac{dJ_m}{dV} \Big|_{V=0} \right)^{-1} = \frac{V_{th}}{f_c J_c}, \quad \text{Eq. (2.7)}$$

$$\rho_M = \left(\frac{dJ_M}{dV} \Big|_{V=0} \right)^{-1} = \frac{R_c}{f_c}. \quad \text{Eq. (2.8)}$$

Where R_c denotes the contact resistance and f_c is the contact fraction. The selectivity S is then defined as the ratio between the minority carrier and majority carrier resistance,

$$S = \frac{\rho_m}{\rho_M} = \frac{V_{th}}{J_c R_c} \quad \text{Eq. (2.9)}$$

Which is typically expressed on a logarithmic scale $S_{10} = \log_{10}(S)$. This definition can be shows that the carrier selectivity is affected by the contact resistance (which in turn is affected by the contact resistivity) and the contact recombination. As such, the study of these parameters forms a major part of this thesis. It is also worth noting that although metal-silicon interfaces are in themselves not selective, in combination with diffused

regions, the combination of the diffused region underlying the metal contact is considered in this work as a carrier selective contact.

There are currently two broad approaches to achieving carrier selectivity to facilitate charge separation within a solar cell device—via doping the semiconductor in the near-surface regions to form a homojunction, and/or via the formation of a heterojunction. The use of diffused homojunctions is the dominant solar cell architecture in commercial production, and this architecture demonstrated impressive results in the 1990's, with record conversion efficiencies of up to ~25 % achieved for c-Si based devices [16]. Heterojunction architectures have only recently overtaken their homojunction counterparts in terms of efficiency, and at the time of writing, lead the efficiency tables for single band gap, silicon based solar cells [17]. Despite these recent gains, the overwhelming majority of commercial solar cells are currently manufactured with homojunctions, and the recent technology roadmap for commercial solar cells predicts that this trend is likely to continue into the near future [9]. This is despite the recent world record results demonstrated with amorphous-silicon based heterojunction structures [18], and the emergence of dopant free solar cells with alkali metal salts and transitional metal oxides to enhance carrier selectivity [19]. As a result, this thesis focuses on the specific issues which relate to solar cells with diffused homojunctions to achieve carrier separation within the device and improve conversion efficiency.

2.1.1 Carrier selectivity for diffused solar cells

Engineering of carrier selectivity within diffused solar cells to improve device performance is evident throughout the history of solar cell development. The first *p-n* junction photoelectric device was demonstrated somewhat ‘unexpectedly’ by Russel Ohl, who upon solidifying a silicon melt in a crucible, found that the upper regions of the crystallised silicon had a different granular structure (likely from the introduction of impurities which segregated out of the bottom silicon melt during solidification) which had positive polarity when light was incident upon the device, and negative polarity at the bottom of the device [20]. Later, Kingsbury and Ohl improved on these devices by using purer silicon to avoid the grown-in junction, and helium ion bombardment to form the rectifying junction [21, 22]. Around this time, Shockley developed the theory of *p-n* junctions, leading to the invention of the *n-p-n* transistor outlining the underlying mechanisms of charge separation in such devices and their characteristic rectifying

behaviour [23, 24]. The development of silicon p - n junctions was referenced in the paper by Chapin *et al.*, which demonstrated the first ‘efficient’ silicon solar cells in the early 1950’s [25]. This early structure had p -type and n -type contacts on the rear, and these devices achieved efficiencies up to ~6 %.

Although these early cells were too expensive at the time for large scale terrestrial electricity generation, these devices found applications in powering extra-terrestrial satellites. This drove much of the further development of these devices at Bell Laboratories over the next decade, where the efficiencies improved to ~11 % by the early 1960’s, achieved through improvements in the device architecture to have front and rear contacts, and reducing the series resistance losses in the front diffused layer [26]. Subsequent technological developments focussed on improving the generation of photons within the device, whilst also optimising the properties of the carrier selective surface diffused region. In addition to assisting in charge separation, this effectively passivated the surfaces by reducing the conductivity of the minority carrier species. This is evidenced in the ‘Violet cell’ by Lindmayer and Alison in the early 1970’s, which demonstrated an efficiency of ~13.5 % by; 1) removing the heavily diffused ‘dead layer’, which improved the blue response and reduced Auger recombination; and 2) improving the front contact design to reduce series resistance and shading losses [27]. Other improvements, such as the implementation of front surface texturing to improve light absorption was demonstrated in a structure known as the ‘black cell’ [28], and accompanied by appropriate optimisation of the front grid contact geometry to reduce shading losses. During this period in the early 1970’s, Mandelkorn and Lamneck developed the back surface field (BSF) solar cell, where a rear aluminium-doped p^+ region was formed by alloying an evaporated aluminium contact layer directly onto silicon at 800°C in an argon ambient for 4 hours [29]. The authors explain that this was done to create localised barriers to minority carrier flow in the device. This work is an early example of carrier selectivity being engineered to improve the conduction of holes at the rear into the metal contact, and selectively reduce the concentration of minority carriers at the rear. The culmination of all these technological improvements resulted in AM1.5 conversion efficiencies of 16.7 % by the mid-1970s [26, 30].

The first attempt at surface passivation of the front diffused region was demonstrated by Fossum and Burgess, who developed solar cells with a single SiN_x layer deposited onto a boron diffused p^+ silicon surface, achieving conversion efficiencies of up to 15.9 %

[31]. In their early work, it was found that thermally growing a thin SiO_x layer underneath the SiN_x layer was able to reduce the front surface recombination velocity to further boost the efficiency up to 16.8% [31]. The invention of the metal-insulator-NP junction (MINP) solar cell in 1983 evolved from the earlier metal-insulator-semiconductor (MIS) solar cell structure, which omitted a diffused p-n junction [32]. MIS structures however, were later abandoned since this structure was abandoned due to the poor electron conduction at the electron collector- SiO_2 -metal interface. The MINP structure was a later example of thin film based surface passivation to complement the use of doping for surface passivation, by growing a thin thermal SiO_2 layer across the front surface of the solar cell, including underneath the contacts [33]. To improve majority carrier conduction, the passivated emitter solar cell (PESC) was developed, which featured localised openings in the SiO_2 passivation to improve carrier conduction at the front contact. This structure also had a metal-silicon interface smaller than the actual metal area to limit metallised contact recombination and reached a record 19.1 % in 1984 [34]. In a further optimisation of this structure, light trapping in the form of grooves were implemented which pushed silicon solar cell efficiencies beyond 20 % for the first time.

Further gains were achieved by improving the passivation of the surfaces and modifying the solar cell architecture to feature localised carrier selective regions. The passivated emitter and rear (PERC) solar cell featured limited area localised contacts to an undiffused p -type rear passivated with thermally grown SiO_2 , to improve the rear surface recombination velocity and achieved a conversion efficiency of 22.8 % [35]. The rear back surface field was re-introduced to improve majority carrier conduction and reduce minority carrier recombination in the passivated emitter, rear totally-diffused (PERT) solar cell [16]. Finally, the development of the passivated emitter, rear-locally diffused (PERL) solar cell featured localised heavily diffused n^{++} and p^+ regions underneath the solar cell contacts to again improve majority carrier conduction and inhibit the conduction of minority carriers into the high recombination metallised regions [16]. The development of these structures throughout the 1990's set world leading solar cell conversion efficiencies and demonstrate continued engineering of carrier selectivity—via doping and modifying the cell architecture—to improve device performance. Recently, the MINP solar cell structure was revisited by Zilke *et al.* and Bullock *et al.* as a means of implementing passivated contacts on diffused homojunction solar cells [36-38]. Zielke *et al.* studied the effect of 1-2 cycles of ALD AlO_x deposited between an n^+ diffused layer

and evaporated metal contacts, demonstrating that a 0.24 nm AlO_x layer helped improve the cell V_{oc} relative to an un-passivated reference [36]. Similarly, Bullock *et al.* was able to demonstrate improved contact recombination and resistivity using intermediate a-Si interlayers between evaporated aluminium and n^+ silicon, whilst p^+ surfaces passivated with amorphous silicon interlayers did realise these same improvements [38].

The development of charged dielectrics has enabled improved passivation at the non-contacted surfaces within diffused silicon solar cells. To avoid the high thermal budget of processing with SiO_x, thin film deposition of dielectrics such as SiN_x and AlO_x are specifically engineered to maximise the fixed charge when passivating n -type and p -type surfaces respectively [39]. In doing so, the charge-effect reduces the minority carrier concentration whilst enhancing the majority carrier concentrations, leading to a lower recombination rate—an effect which will be discussed in more detail in the forthcoming sections of this chapter. Both SiN_x and AlO_x passivation stacks have achieved S_{eff} values $< 2 \text{ cm.s}^{-1}$ on undiffused silicon substrates [12].

In this work, the technological issues which affect the current state-of-the-art diffused silicon wafer solar cell technologies are studied. The remaining content of this chapter seeks to outline the underlying physical principles which relate to the operation of these devices, as they are applied to the optimisation work of this thesis. This involves a review of the physical principles which underlie surface passivation and charge transport at metal-semiconductor interfaces, focusing on how enhanced carrier selectivity in these regions boost solar cell performance.

2.2 Semiconductor surfaces

The surfaces of solar cells are an important multifunctional interface, critical to solar device operation. As depicted in Figure 2.1, energy is absorbed and transmitted into the solar cell at the surface, and the generated electron and hole pairs are contained within the insulating surface regions until they reach the conductive surface regions, which allow for power extraction. Thus, surfaces have a role in transmitting, collecting and extracting power in any solar cell, and the design of optimised surfaces which perform each of these functions with minimal losses has been the focus of intense research over many decades.

At the surface of a semiconductor, the periodicity of the atomic lattice ends, and atoms at the surface lack sufficient neighbours to bond with. This creates localised sites where the atomic outer shell consists of vacant ‘dangling’ bonds, which are highly recombination

active. Dangling bonds introduce discrete energy levels across the forbidden energy gap, which electrons and holes use as sites to facilitate a transition from the conduction to the valence band in recombination processes.

Any process which seeks to reduce the surface recombination rate is known as surface passivation. Recombination is a complementary process which requires both an electron and hole to be present, and at the surface additional interface states are also participant in the process as sites which facilitate capture. Surface passivation methods can be categorised into two broad strategies:

1. Reduce the number of interface sites at the surface.
2. Reduce the population of either electrons or holes at the surface.

In high performance solar cells, surface passivation techniques are applied to the conductive and non-conductive regions of the surface, with each region deploying different methods to suppress recombination. Point two above is referred to as charge-effect passivation, and can be achieved by the introduction of an external electric field, and/or by manipulating the carrier concentrations at the surface by doping. The former can be achieved by the introduction of an electrostatic potential at the surface, which serves to affect a large asymmetry in the majority carrier and minority carrier population at the surface. Since the recombination rate is limited by the minority carrier concentration, an overall reduction in the minority carrier population will reduce the overall recombination rate. Two ways in which this can be achieved is, via an external electric field induced from a gate dielectric, or more commonly, by depositing insulating dielectric thin-films such as SiN_x and AlO_x onto the surface which are typically engineered to have a high density of fixed positive and negative charge respectively. The other way that carrier concentration asymmetry is achieved is through doping: as the concentration of holes (electrons) is increased through doping, the concentration of electrons (holes) reduces to ensure a constant product equal to the square of the intrinsic carrier concentration at equilibrium. This is a consequence of the law of mass action, $pn = n_i^2$. As previously outlined, this has traditionally been utilised at metalised point contact regions to improve majority carrier conductivity and selectively reduce the minority carrier conductivity, which affects the recombination rate at the highly recombination active metal-silicon interface.

The second broad strategy to achieve surface passivation is commonly referred to as chemical passivation. It is commonly achieved by growing thin-film dielectrics onto the

surface such as silicon dioxide or amorphous silicon which—among other benefits—have good lattice matching with the underlying silicon and therefore passivate the dangling bonds effectively. Chemical passivation can also be achieved by a technique known as hydrogenation, where hydrogen atoms are introduced to permanently bond with the empty lattice sites, and hence suppress the recombination rate via defect assisted mechanisms.

In practice, both charge-effect and chemical passivation mechanisms are used to suppress surface recombination and assist in charge conduction to the contacts. Thin film dielectrics such as SiN_x are often engineered to have a high density of fixed positive charge, to attract majority carriers and repel minority carriers in an underlying n -type doped region. This is in addition to being hydrogen rich such that during subsequent thermal processing, hydrogen is released from the film and into the substrate to chemically passivate the interface. Careful trade-offs need to be met between the polarity and magnitude of fixed charge in a dielectric film, and the underlying substrate doping. This is particularly the case when both polarities of dopants exist at the surface, such is the case for interdigitated back contact solar cells. Furthermore, where charge-effect passivation is achieved through doping, careful trade-offs between the electrical conductivity and the recombination rate need to be met since increasing doping levels leads to effects such as band gap narrowing (BGN) and increased Auger recombination [40]. In some processes, inactive dopant precipitates can also enhance recombination processes in the device. Consequently, it is important that the means of achieving charge-effect passivation and its by-products are traded off to ensure optimal device performance. This thesis seeks to enhance our understanding of the interplay between doping, surface passivation and properties.

2.2.1 Energy and potentials in semiconductors

The population of electron and holes in a semiconductor is defined by their Fermi energy level in the band gap. For an intrinsic semiconductor, $n = p = n_i$ where n_i is the intrinsic carrier concentration. In this case, the Fermi level is equal to the intrinsic Fermi-energy, E_i . With the introduction of dopants, the quasi-Fermi levels of electrons (E_{fn}) and holes (E_{fp}) deviate away from the intrinsic level towards the conduction (E_c) and valence (E_v) bands, depending on the magnitude and polarity of the active dopants. At thermal

equilibrium (denoted by subscript 0), the concentration of holes and electrons are solved by the law of mass action and conservation of charge,

$$p_0 n_0 = N_c N_v \exp\left(\frac{E_v - E_c}{kT}\right) = n_i^2, \quad \text{Eq. (2.10)}$$

where N_c and N_v are the density of states in the conduction and valence bands respectively, k is Boltzmann's constant and T is the temperature in Kelvin. For doped semiconductors, $n_0 \cong N_D^+ = N_D$ and $p_0 \cong N_A^+ = N_A$ where N_D is the concentration of donors and N_A is the concentration of ionised acceptors. For non-equilibrium conditions in a non-degenerate semiconductor, (i.e. $E_c - E_F$ and $E_F - E_v \gtrsim 3kT$), the concentration of electron and holes can be written using Boltzmann approximations as

$$n = N_c \exp\left(\frac{E_{Fn} - E_v}{kT}\right) = n_i \exp\left(\frac{E_{Fn} - E_{Fi}}{kT}\right), \quad \text{Eq. (2.11)}$$

$$p = N_v \exp\left(-\frac{E_{Fp} - E_v}{kT}\right) = n_i \exp\left(-\frac{E_{Fp} - E_{Fi}}{kT}\right). \quad \text{Eq. (2.12)}$$

For a degenerate semiconductor, Boltzmann statistics are no longer a valid approximation, and Fermi-Dirac statistics should be used instead. In this case, the exponential functions in Eq. 2.11 and Eq. 2.12 are replaced by the half-order Fermi-Dirac integral, defined as:

$$F_{1/2}(\eta) = \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{\epsilon^{1/2}}{1 + \exp(\epsilon - \eta)} d\epsilon, \quad \text{Eq. (2.13)}$$

which can be evaluated by analytical approximations.

2.2.2 Band bending at semiconductor surfaces

Electrical charge is often present at the surface of the semiconductor from an overlying dielectric layer Q_f , trapped interface states Q_{it} or from a gate contact Q_g . This charge induces a balancing net charge in the semiconductor, which extends from the surface into the device and is represented as a bending of the energy bands towards the surface of the semiconductor in the energy band diagram shown in Figure 2.2. The region at the surface affected by charge is known as the 'space-charge region', and its magnitude away from the surface will depend on the total concentration of charge at the interface Q_{tot} , the concentration of uncompensated ionised dopants, and the number of free holes and electrons as they vary in concentration near the affected surface. Mathematically the surface space-charge region extends infinitely into the device, however, there is some

distance d , whereby the effects of the surface charge is negligible, and beyond this point, the region is known as the quasi-neutral region.

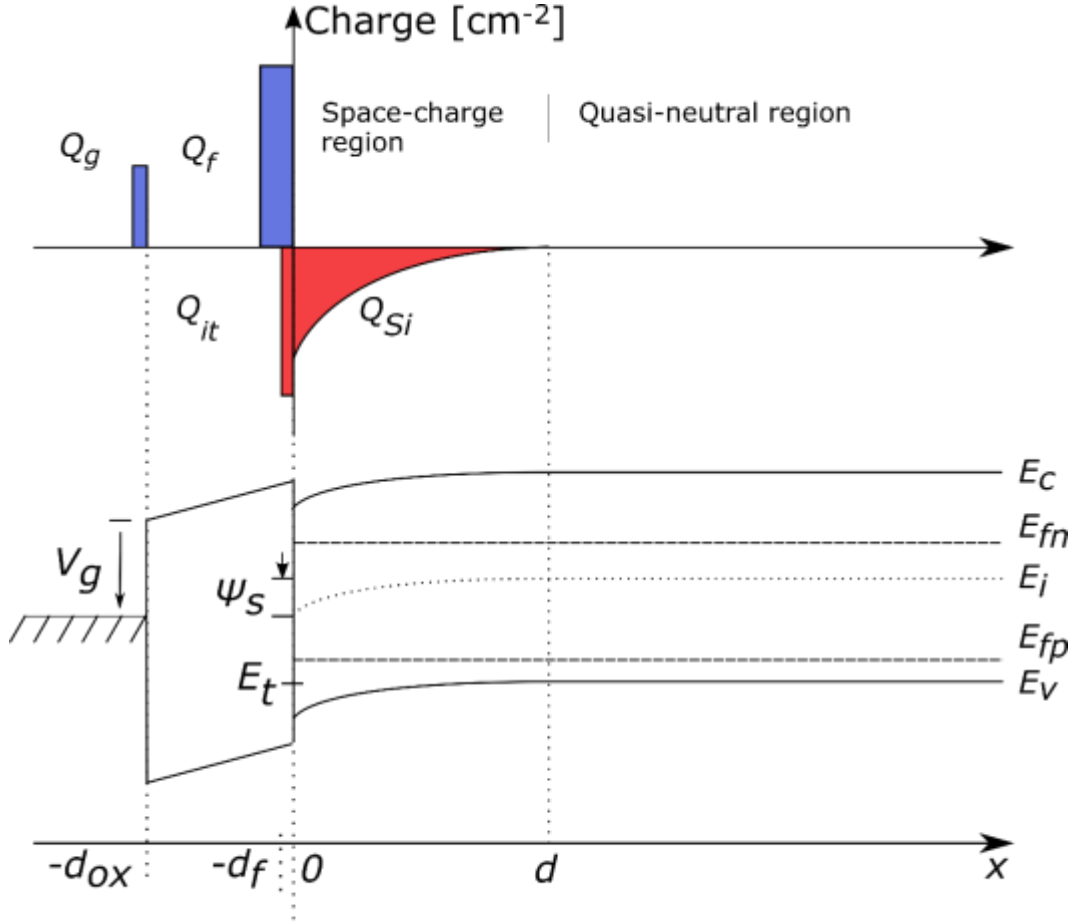


Figure 2.2 Charge distribution (top) and band diagram (bottom) at a p -Si/dielectric/gate interface showing the definitions of the potentials and electron energies as a function of depth into the surface. The individual contributions of charge from Q_g , Q_{it} and Q_f are shown to balance the charge in the semiconductor (in this instance silicon), Q_{Si} .

Positive (negative) surface charge will attract electrons (holes) within the semiconductor to the surface whilst repelling holes (electrons). Depending on the polarity of the underlying semiconductor, this will create either accumulation, depletion or inversion conditions at the surface. These conditions, as outlined by Grove and Fitzgerald are outlined in Table 2.1.

Table 2.1 Sign of the quantities involved in the analysis of semiconductor surface state

	p-type			n-type		
	Accumulation	Depletion	Inversion	Accumulation	Depletion	Inversion
ψ_s^1	< 0	> 0	> 0	> 0	< 0	< 0
Q_{si}	> 0	< 0	< 0	< 0	> 0	> 0
Q_n	-	-	< 0	-	-	-
Q_p	-	-	-	-	-	> 0

¹ ψ_s is defined as the electrostatic potential at the surface relative to the Fermi level in the bulk, Q_{si} is the total net charge in the semiconductor, and Q_p and Q_n are the charge contributions from holes and electrons at the surface respectively. Sourced from [41].

Charge neutrality requires that the total charge at the interface is balanced by the net charge in the semiconductor Q_s , such that $Q_s + Q_{tot} = 0$. In Figure 2.1, the charge contributions of Q_{tot} are such that $Q_g + Q_f + Q_{it} = Q_{tot} = Q_{si}$. In addition to these contributions, additional charge can be deposited externally by corona charging, for instance [42, 43]. In this work, the gate terminal is not present, and for most well passivated surfaces—such as the Si-SiO_x interface— Q_{it} is deemed negligible [44]. Nevertheless, there are many published formulae for calculating the contributions of Q_g and Q_{it} [41, 44-46]. Q_f is commonly measured via capacitance-voltage (CV) measurements, or through non-invasive techniques such as electric-field induced second harmonic generation (EFISH) [47]. The main contribution to Q_{tot} is most often dominated by dielectric fixed charge, Q_f for dielectrics AlO_x and SiN_x.

To determine the surface concentration of holes (p_s) and electrons (n_s) – which is required in the calculation of surface recombination – the extent of band bending at the surface, ψ_s , needs to be known. An exact solution requires solving Poisson’s equation with the charge carrier continuity equations, as outlined by Otaredian [48], or by using advanced TCAD software packages such as Sentaurus [49] in one dimension for the electric field in the space-charge region of the semiconductor. Alternatively, the carrier concentrations can be solved numerically in a sequence outlined by Girisch [46]. This technique is applied and outlined in greater detail in the work comprising Chapter 6 of this thesis and therefore only briefly outlined herein. In this method, the carrier concentrations at the edge of the quasi-neutral region (denoted by subscript d), n_d and p_d are calculated noting that,

$$n_d = n_{0d} + \Delta n_d, \quad \text{Eq. (2.14)}$$

$$p_d = p_{0d} + \Delta n_d, \quad \text{Eq. (2.15)}$$

where n_0 and p_0 are the equilibrium concentrations of electrons and holes respectively and calculated taking into account the concentration of ionised acceptors, and donors. The Δn term is the excess carrier concentration assuming $\Delta n = \Delta p$, which holds true in the quasi-neutral region. The excess carrier concentration at d and in the bulk are equal, however in the case that the region is not homogeneously doped an alternate approach which takes into account varying generation, recombination, BGN and carrier mobility over this diffused region, as outlined by [48, 50-52] needs to be used. The total net charge in the semiconductor is given by

$$Q_s \equiv \int_0^\infty \rho \, dx, \quad \text{Eq. (2.16)}$$

where $\rho = q[p - n + N_D - N_A]$. Poisson's equation can be written:

$$\frac{d^2 \xi_s}{dx^2} = -\frac{q}{kT\epsilon\epsilon_0} \rho, \quad \text{Eq. (2.17)}$$

Assuming flat quasi-Fermi levels in the space charge region, by substituting the individual charge contributions above into the one-dimensional Poisson equation above, a relation between the electric field strength ξ and the potential ψ from d to the surface is obtained. From Gauss's law, the total charge induced in the silicon is then found as a function of ψ_s as [41, 53, 54]

$$Q_s = (2n_i kT \epsilon \epsilon_0)^{1/2} \left\{ N_c \left[\exp\left(\frac{E_{Fn} - E_c + q\psi_s}{kT}\right) - \exp\left(\frac{E_{Fn} - E_c}{kT}\right) \right] + N_v \left[\exp\left(\frac{E_v - E_{Fp} - q\psi_s}{kT}\right) - \exp\left(\frac{E_v - E_{Fp}}{kT}\right) \right] + \frac{(N_A - N_D)}{n_i} \left(\frac{q}{kT} \psi_s\right) \right\}^{1/2}. \quad \text{Eq. (2.18)}$$

Equation 2.13 has a corresponding form when degeneracy is taken into account, which replaces the exponents with Fermi-Dirac operators [55, 56]. It can also be written in more relatable terms, such that

$$Q_s = (2kT \epsilon \epsilon_0)^{1/2} \left\{ n_s - n_d + p_s - p_d + (N_A - N_D) \left(\frac{q}{kT} \psi_s\right) \right\}^{1/2}. \quad \text{Eq. (2.19)}$$

When applying the Girish method, the above equation is solved iteratively for ψ_s until $Q_{si} + Q_f + Q_{it} + Q_g < \delta$, where δ is some small limiting value. The surface concentration of electrons and holes can then be calculated as

$$n_s = n_d \exp(-\beta \psi_s), \quad \text{Eq. (2.20)}$$

$$p_s = p_d \exp(\beta \psi_s). \quad \text{Eq. (2.21)}$$

When the quasi-Fermi levels are not flat, deviations in the exponential relations for the electron and hole concentrations at the surface are taken into account by the RHS of the equations [48]:

$$n_d - n_s \exp(-\psi_s) = \frac{R(n_s, p_s)}{D_n} \int_0^d \exp(-\psi_s) dE, \quad \text{Eq. (2.22)}$$

$$p_d - p_s \exp(\psi_s) = \frac{R(n_s, p_s)}{D_p} \int_0^d \exp(\psi_s) dE, \quad \text{Eq. (2.23)}$$

where R is the total surface recombination rate and D_p and D_n is the diffusion coefficient of holes and electrons respectively. In this instance, the Girisch method is not applicable. These equations are applied throughout this work to model the carrier concentrations in diffused surface regions passivated with charged dielectrics to develop a method of assessing the carrier selectivity of a surface by measuring interface properties of passivated diffused surfaces. The following section outlines the basic recombination processes as they are modelled in subsequent chapters of this work.

2.2.3 Recombination processes

2.2.3.1 Radiative Recombination

Radiative recombination is the reverse process of electron hole pair generation via absorption of a photon. In this process, an electron in the conduction band relaxes to the valence band, recombining with an empty state, emitting all or some of its excess energy as a photon. For indirect band gap semiconductors, where the minimum energy state in the conduction band and the maximum energy state in the valence band have the same momentum k -vector, this process involves conservation of momentum via phonon emission, whereas transitions in direct band gap semiconductors do not. Due to the involvement of a phonon, radiative recombination is suppressed in indirect semiconductors such as silicon. The net recombination rate for radiative recombination is given by [57]:

$$U_{rad} = Bnp \quad \text{Eq. (2.24)}$$

where B is the spectral radiance of a body, or radiative recombination coefficient for the material, n and p are the electron and hole concentrations respectively. Values for B have been evaluated experimentally and in this work a value of $B = 4.73 \times 10^{-15} \text{ cm}^3 \cdot \text{s}^{-1}$ at 300 K is used [58]. The corresponding lifetime component for radiative recombination is given by the expression [57]:

$$\tau_{rad} = \frac{\Delta n}{U_{rad}} = \frac{1}{B(n_0 + p_0 + \Delta n)}. \quad \text{Eq. (2.25)}$$

At present, radiative recombination is not the dominating loss mechanism in silicon based photovoltaic devices and is included here for completeness.

2.2.3.2 Auger Recombination

Band-to-band Auger recombination involves an electron in the conduction band transmitting excess energy to a third charge carrier (either a hole in the valence band or an electron in the conduction band) and relaxes to the valence band. This process does not involve the emission of a photon since the energy is transferred to a third carrier which absorbs both the energy and momentum and returns to its original state, for instance, by the emission of phonons [59-62]. Auger recombination models two processes; when the excess energy of the Auger recombination process is transferred to another electron (“ eeh ” process) or another hole (“ ehh ” process) [63]. These transitions are modelled to be interactions between noninteracting quasi-free particles so that the rate of recombination is proportional to the product of the concentration of each participating particle [59, 60, 63, 64]. The corresponding recombination rates of “ ehh ” and “ eeh ” processes are given by the formulae $U_{eeh} = C_n n^2 p$ and $U_{ehh} = C_p n p^2$, where C_n and C_p are the Auger coefficients of electrons and holes respectively. Commonly used values of C_n and C_p were found by Dzierwior and Schmid to be $C_n = 2.8 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ and $C_p = 9.9 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$ at 300 K [65]. The net recombination rate from Auger processes is the sum of U_{eeh} and U_{ehh} given by:

$$U_{Aug} = U_{eeh} + U_{ehh} = C_n n^2 p + C_p n p^2. \quad \text{Eq. (2.26)}$$

$$U_{Aug} = U_{eeh} + U_{ehh} = C_n n^2 p + C_p n p^2. \quad \text{Eq. (2.27)}$$

In reality, the particles involved are not non-interacting quasi-free particles and the Auger recombination is enhanced by attractive coulombic interactions of holes and electrons. To account for these effects, the coulomb-enhanced Auger recombination rate enhancement factors g_{eeh} and g_{ehh} are multiplied by C_n and C_p respectively, giving enhanced Auger coefficients, $C_n^* = C_n \cdot g_{eeh}$ and $C_p^* = C_p \cdot g_{ehh}$ [66]. Altermatt *et al.* derived an empirical expression for the temperature and dopant concentration dependence of the low injection Auger lifetime between 70 and 400 K in line with Coulomb-enhanced Auger theory [67]. More recently, Kerr and Cuevas devised an empirical parameterisation for the intrinsic lifetime at 300 K taking into account Auger processes, radiative recombination according to Schlagenotto *et al.* [68], the dopant level and the excess carrier density. In that work the Auger recombination rate is given as [69]

$$U_{Aug} = np(1.8 \times 10^{-24} n_0^{0.65} + 6 \times 10^{-25} p_0^{0.65} + 3 \times 10^{-27} \Delta n^{0.8})$$

Eq. (2.28)

with the intrinsic lifetime (taking into account radiative and Auger processes) given as

$$\tau_{intrinsic,Kerr} = \frac{\Delta n}{np(1.8 \times 10^{-24} n_0^{0.65} + 6 \times 10^{-25} p_0^{0.65} + 3 \times 10^{-27} \Delta n^{0.8} + 9.5 \times 10^{-15})},$$

Eq. (2.29)

As surface passivation techniques improved, measurements exceeding the intrinsic limit proposed by Kerr and Cuevas were observed, consequently Richter *et al.* further refined the parameterisation based off new measurements. In their work, the intrinsic lifetime is given as

$$\tau_{intrinsic,Richter} = \frac{\Delta n}{(np - n_i^2) (2.5 \times 10^{-31} g_{eeh} n_0 + 8.5 \times 10^{-32} g_{ehh} p_0 + 3 \times 10^{-20} \Delta n^{0.92} + B_{rel} B_{low})}.$$

Eq. (2.30)

The enhancement factors are given by

$$g_{eeh}(n_0) = 1 + 13 \left\{ 1 - \tanh \left[\left(\frac{n_0}{N_{0,eeh}} \right)^{0.66} \right] \right\}, \quad \text{Eq. (2.31)}$$

$$g_{ehh}(p_0) = 1 + 7.5 \left\{ 1 - \tanh \left[\left(\frac{p_0}{N_{0,ehh}} \right)^{0.63} \right] \right\}, \quad \text{Eq. (2.32)}$$

where $N_{0,eeh} = 3.3 \times 10^{17} \text{ cm}^{-3}$ and $N_{0,ehh} = 7.0 \times 10^{17} \text{ cm}^{-3}$, B_{low} is the relative radiative recombination coefficient $= 4.73 \times 10^{-15} \text{ cm}^3 \cdot \text{s}^{-1}$ at 300 K [58], and B_{rel} is the relative radiative recombination coefficient according to Ref. [70]. In this work, the intrinsic model according to Richter *et al.* is mostly used, otherwise, the coefficients according to Dziewior and Schmid are used in combination with the model according to Altermatt *et al.* and radiative recombination modelled using the value of B given in Ref. [58], as stated in the appropriate sections of this thesis.

Auger recombination is an intrinsic property of materials like silicon, and together with radiative recombination determines the upper limit of photovoltaic device performance. Auger recombination processes is the dominant intrinsic recombination mechanism for a wide range of doping and injection levels—particularly in the high injection and highly doped case [71].

2.2.3.3 Recombination via Defects

Defects and impurities in the crystal lattice form discrete energy levels within the forbidden energy gap. These levels allow for electrons in the conduction band to be captured by these states before relaxing into the conduction band via recombination with a hole. The model for this process, known as Shockley-Read-Hall (SRH) theory [72, 73], statistically models the transitions of four processes, shown in Figure 2.3:

- 1) An electron in the conduction band is captured by an empty defect level.
- 2) A hole in the conduction band is captured by a filled defect level.
- 3) Electron emission by a filled defect level towards the valence band.
- 4) Hole emission by an empty defect level.

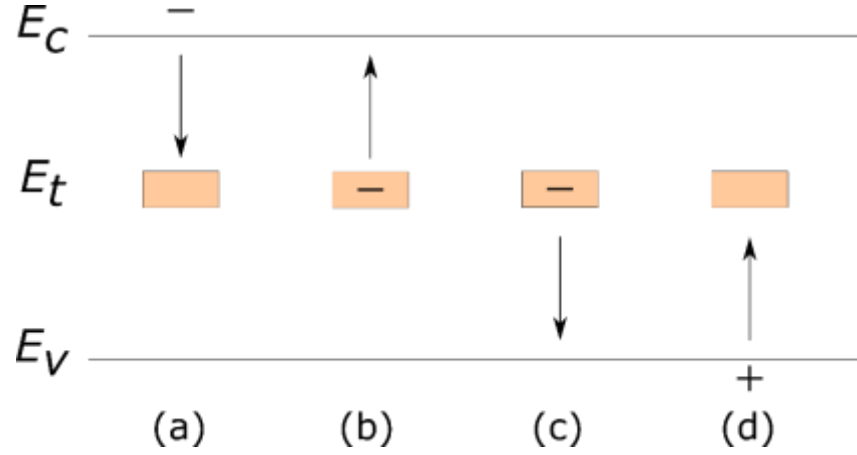


Figure 2.3 Capture processes involved in defect assisted recombination; a) electron capture, b) electron emission, c) hole capture and d) hole emission. Adapted from [72].

It is assumed that the states are non-interacting and the capture and relaxation time of carriers by the defect is non-limiting. For a single state located at some energy E_t , the recombination rate U_{SRH} is given by

$$U_{SRH} = \frac{pn - n_i^2}{\tau_{p0}(n + n_1) + \tau_{n0}(p + p_1)}, \quad \text{Eq. (2.33)}$$

where the numerator term represents the deviation from thermal equilibrium, which drives the net recombination rate. The terms n_1 and p_1 are the electron and hole concentrations for at the defect energy level, E_t (i.e. $E_{Fn} = E_{Fp} = E_t$), given by

$$n_1 \equiv N_c \exp\left(\frac{E_t - E_c}{kT}\right), \quad \text{Eq. (2.34)}$$

$$p_1 \equiv N_v \exp\left(\frac{E_v - E_t}{kT}\right). \quad \text{Eq. (2.35)}$$

These latter terms may be approximated by their non-degenerate forms, by replacing the exponent by the Fermi-Dirac operator, $F_{1/2}$, when located away from the band edges. The terms τ_{p0} and τ_{n0} are the capture time constants of holes and electrons respectively are defined as

$$\tau_{p0} \equiv \sigma_p v_{th,p} N_t, \quad \text{Eq. (2.36)}$$

$$\tau_{n0} \equiv \sigma_n v_{th,n} N_t. \quad \text{Eq. (2.37)}$$

Where v_{th} is the thermal velocity, N_t is density of defect sites and σ_n and σ_p are the capture cross section of electron and holes respectively. The capture cross sections represent the cross section for capture, such that the multiple of the capture cross section and the

thermal velocity represents the probability per unit time that an electron or hole in the energy range is captured at a site. The thermal velocity of electrons and holes and its temperature dependence can be modelled independently according to Green [74], however more commonly, this value is considered equal for electrons and holes and is approximated as 10^7 cm/s at 300 K in silicon.

2.3 Surface recombination

As previously mentioned, the surface of the semiconductor is an abrupt interruption to the ordered atomic lattice, with a high concentration of defect sites. The recombination processes at the surface is a specific case of defect-assisted recombination, and Eq. 2.32 can be appropriated to describe the recombination at the surface for a single defect level as

$$U_s = \frac{p_s n_s - n_i^2}{S_{p0}(n_s + n_1) + S_{n0}(p_s + p_1)}. \quad \text{Eq. (2.38)}$$

In this case, the subscript s denotes a property located at the surface, and S_{n0} and S_{p0} are the surface recombination velocity parameters, given by

$$S_{p0} \equiv \sigma_p v_{th,p} D_{it}, \quad \text{Eq. (2.39)}$$

$$S_{n0} \equiv \sigma_n v_{th,n} D_{it}, \quad \text{Eq. (2.40)}$$

where D_{it} the number of states, at a singular energy level, per unit area, which is distinct from N_t , which has units in cm^{-3} . Consequently, S_{n0} and S_{p0} have units in cm.s^{-1} and has the dimension of velocity, whereas U_s has units of $\text{cm}^{-2}\text{s}^{-1}$. The total recombination rate is found by adding the individual contributions from each defect energy level across the band gap. This involves an integration of Eq. 2.37 over all energy levels, E , written as

$$U_s = \int_{E_v}^{E_c} \frac{p_s n_s - n_i^2}{S_{p0}(n_s + n_1) + S_{n0}(p_s + p_1)} dE. \quad \text{Eq. (2.41)}$$

It is worth noting that simplifications to this equation exist. For instance, n_1 and p_1 can be omitted where the recombination is not dominated by interface states very close to the band edges [75, 76]. This occurs when either the surface is in strong inversion or accumulation, such that n_s or p_s is largely independent of the excess carrier concentration Δn , or when the Δn is large.

At very high injection, as the carrier concentrations at the surface increase, the bands will flatten eliminating the space-charge region. As a result, the surface recombination velocity will no longer be dependent on the surface charge and doping of the sample, and instead will be dependent on the concentration of interface defect states and their relaxation time [77].

2.3.1 Surface recombination parameters

When n_s and p_s are known, for instance by solving numerically in the procedure outlined previously, the surface recombination velocity S , can be calculated as

$$U_s \equiv S \cdot \Delta n_s, \quad \text{Eq. (2.42)}$$

where Δn_s is the excess carrier concentration at the surface. In the instance that n_s and p_s are unknown, it is common to describe the S in terms of an effective surface recombination velocity S_{eff} . This parameter is defined as the recombination rate at a virtual plane parallel to the surface located at distance d , which marks the edge of the surface space charge region

$$U_s \equiv S_{eff} \cdot \Delta n_d, \quad \text{Eq. (2.43)}$$

where Δn_d is the excess carrier concentration at the edge of the space-charge region. The nature of S_{eff} , as it is affected by interface charge and dependent on the underlying substrate properties and injection level, has been the focus of numerous studies. Early work commonly presented S_{eff} as a constant parameter [78-81], however numerous subsequent studies have since revealed a non-constant S_{eff} depending on the sample properties and surface condition [48, 82-90]. Aberle *et al.*, applying the Girisch formulation, was able to calculate the dependence of S_{eff} for varying fixed interface charge levels and substrate doping levels [83], whereas Otaredian was able to show the variances of S_{eff} with illumination level, surface charge and substrate doping in the absence of a gate contact, and where the surface potentials are resolved internally—as is the case with most passivated regions in solar cells [48].

Observing the growing evidence of varying S_{eff} , (such as in Ref. [83]), researchers began to attempt to categorise and explain the variances in S_{eff} with injection level and substrate conditions. Kuhlmann derived an equation of S_{eff} describing the low injection behaviour of S_{eff} in the presence of fixed charge, revealing a dependence on Q_f and substrate doping

in this regime [86]. Brody and Rohatgi extended this analysis to derive analytical expressions for S_{eff} in four specific cases (including the condition covered by Kulhmann), covering the effect of substrate doping and fixed charge at low and high injection [87]. Most recently, McIntosh and Black took the cases derived by Brody and Rohatgi and derived analytical expressions for S_{eff} , demonstrating the conditions for which S_{eff} increases with increasing doping level, thus highlighting how the use of S_{eff} to compare passivation between samples with varying doping is problematic [76]. This was presented alongside an alternate parameter, introduced as the surface saturation current density, J_{0s} defined as

$$J_{0s} = qU_s \left(\frac{p_s n_s - n_i^2}{n_i^2} \right)^{-1}. \quad \text{Eq. (2.44)}$$

In their study, McIntosh and Black compare analytical approximations for both S_{eff} and J_{0s} for four cases, revealing the dependence on these parameters on the underlying substrate and condition. These conditions and their analytical approximations are reproduced in Table 2.2 for an n -type silicon substrate. Upon comparison, for Cases 3 and 4, J_{0s} is the preferred parameter since S_{eff} in these regimes is dependent on the substrate doping, n_d , which varies with both doping level and injection level (since $n_d = N_D + \Delta n$). However, for Case 2, J_{0s} is dependent on n_d and hence S_{eff} is the parameter suited for comparison between samples with different background doping levels. In this thesis, most of the surface passivation studies were performed on samples in Case 3 and 4.

Table 2.2 Solutions for J_{0s} and S_{eff} for n -type silicon under various conditions.

Case	Approximation	S_{eff}	J_{0s}
1	Negligible Q (flat-band conditions)	S_{p0}	$q \frac{S_{p0}}{n_d} n_{ie}^2$
2	Low Q , Low injection	$S_{p0} \exp\left(\frac{-Q}{\sqrt{kT\epsilon_{Si}N_D}}\right)$	$q \frac{S_{p0}}{n_d} \exp\left(\frac{-Q}{\sqrt{kT\epsilon_{Si}N_D}}\right) n_{ie}^2$
3	Large positive Q (strong accumulation)	$\frac{S_{p0} n_d 2kT\epsilon_{Si}}{Q^2}$	$q \frac{2kT\epsilon_{Si} S_{p0}}{Q^2} n_{ie}^2$
4	Large negative Q (strong inversion)	$\frac{S_{n0} n_d 2kT\epsilon_{Si}}{Q^2}$	$q \frac{2kT\epsilon_{Si} S_{n0}}{Q^2} n_{ie}^2$

Sourced from [76]

2.3.1.1 Recombination in doped regions and the parameter J_{0e}

Diffused regions in semiconductors increase intrinsic recombination processes through increased Auger recombination. The presence of dopants, depending on how they are diffused, can also increase the concentration of defect sites within the lattice and at the semiconductor surface, which increases SRH recombination potential. As such, recombination in the diffused region is a combination of intrinsic and SRH recombination processes. Separation of each component requires sophisticated characterisation and modelling of the diffused region [91]. However in most practical cases the total recombination in the diffused region is commonly measured by the emitter dark saturation current, J_{0e} (the term emitter, whilst not technically applicable to solar cells, is commonly used to describe diffused regions in solar cells and is a legacy from the integrated-circuits industry—for more information, see for instance [92]). The emitter dark saturation current lumps together contributions from the heavily diffused surface and the bulk region of the diffused region, which is typically less heavily diffused in the surface (exceptions to this being, for example, in epitaxially grown diffused regions or in cases of severe dopant depletion from oxidation in a heavily boron diffused surface). The general definition of J_{0e} is the recombination current at the edge of the space charge region, divided by the normalised pn -product, given by the formula [93, 94]

$$J_{0e} \equiv \frac{J_n(x_e)}{n(x_e)p(x_e) - n_{i,eff}^2(x_e)} n_{i,eff}^2(x_e), \quad \text{Eq. (2.45)}$$

where J_n is the electron recombination current across the point x_e , defined as the edge of the space charge region (i.e. the junction) and $n_{i,eff}$ is the effective intrinsic carrier concentration, which takes into account the effect of band gap narrowing, degeneracy and non-equilibrium conditions. The equation for J_{0e} takes many forms during extraction with contactless PC measurements, and the various equations will be discussed in greater detail in the following section.

2.3.2 Effective lifetime

The effective lifetime is a general term given to the lifetime measured which takes into account all the recombination mechanisms present in a sample. The effective lifetime component due to the combined impact of intrinsic and SRH mechanisms in the bulk regions of the sample (i.e. the regions excluding surfaces and diffused regions) is referred to as the *bulk lifetime* given by:

$$\frac{1}{\tau_{bulk}} = \frac{1}{\tau_{intrinsic}} + \frac{1}{\tau_{SRH}} = \frac{1}{\tau_{Aug}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}}. \quad \text{Eq. (2.46)}$$

When the surfaces and diffused regions (if any) are taken into account, additional components are added to Eq. 2.45 to give the *effective minority carrier lifetime*, producing the equation:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surfaces}} + \frac{1}{\tau_{diffused}} = \left(\frac{1}{\tau_{Aug}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}} \right) + \frac{1}{\tau_{surfaces}} + \frac{1}{\tau_{diffused}}.$$

$$\text{Eq. (2.47)}$$

2.4 Characterising surface recombination

In this work, we will study both metallised and non-metallised surfaces and the following section outlines the theory behind the techniques used in this work to characterise the surface recombination rate on these two surface types.

2.4.1 Contactless photoconductance measurement technique

2.4.1.1 Measurement principle

Contactless PC measurements were first proposed in 1955 and are a simple and common means of extracting the effective lifetime from semiconductor samples[95]. In this work, PC measurements were used to characterise the effective lifetime and extract surface recombination parameters from test devices. In this measurement, the sample conductivity is measured in a contactless configuration, inductively coupled via a coil connected to a radio-frequency bridge. The sample conductivity is given by

$$\tau_{n0} \equiv \sigma_n v_{th,n} N_t. \quad \text{Eq. (2.48)}$$

where the electron and hole mobilities are calculated with a carrier density dependent mobility model [96, 97]. A reference solar cell and oscilloscope measure the time dependence of excess photoconductance $\Delta\sigma(t)$ and illumination $I(t)$. The average excess carrier density assuming $\Delta n_{av} = \Delta p_{av}$ can be determined iteratively from

$$\Delta n_{av}(t) = \frac{\Delta\sigma(t)}{q(\mu_n + \mu_p)W}, \quad \text{Eq. (2.49)}$$

where W is the sample width and noting that the mobilities are concentration dependent. Given this relation of the conductivity to the excess carrier density, the lifetime can be

inferred from three general measurement and analysis types which are all based on the continuity equation for excess minority carriers [98, 99]

$$\frac{\partial \Delta n}{\partial t} = G_{bulk}(t, x) - U_{bulk}(t, x) + \frac{1}{q} \frac{dJ_n}{dx}, \quad \text{Eq. (2.50)}$$

where U_{bulk} and G_{bulk} is the recombination and photogeneration rate in the bulk respectively and J_n is the electron current density. The transport term represents the surface recombination rate and is omitted assuming surface recombination is zero [100]. From Eq. 2.49, the effective lifetime may be derived for the three measurement types performed in this work: generalized, transient and quasi-steady-state. Nagel *et al.* proposed the generalised analysis method [100], where the effective lifetime is given by

$$\tau_{eff} = \frac{\Delta n}{G_{av}(t) - \frac{\partial \Delta n_{av}(t)}{\partial t}}, \quad \text{Eq. (2.51)}$$

where Δn_{av} is the average excess carrier density and G_{av} the average generation rate over the whole wafer thickness W . The generation rate as measured by the reference solar cell is given by [101]

$$G_{av} = \frac{G_0 \times EOT \times J_{sc}}{qW}, \quad \text{Eq. (2.52)}$$

where G_0 is the measured illumination in suns, EOT is the effective optical transmission (EOT, hereafter referred to as the optical constant) and J_{sc} is the short-circuit current density of the reference cell at one sun illumination. For transient measurements, the measurement occurs after illumination is extinguished and hence $G \equiv 0$, simplifying Eq. 2.50 to become,

$$\tau_{eff} = \frac{\Delta n}{\frac{\partial \Delta n_{av}(t)}{\partial t}} \quad \text{Eq. (2.53)}$$

Finally, in the quasi-steady-state case, the light pulse varies very slowly compared to the effective lifetime, and therefore $\partial \Delta n / \partial t \equiv 0$, producing [102]

$$\tau_{eff} = \frac{\Delta n}{G_{av}(t)}, \quad \text{Eq. (2.54)}$$

which is valid when the carrier lifetime is significantly lower than the decay time of the illumination source. For both generalised and quasi-steady-state measurements, both Δn and G need to be known to determine the effective lifetime, whereas only the former is required in the transient measurement case.

A Sinton Instruments WCT-120 PC stage was used in this work, allowing for both transient, quasi-steady-state and generalised measurements. The transient mode has the advantage that the optical constant does not need to be known. However, for a strict transient measurement, an abrupt termination of the light source relative to the carrier decay is required. As a result, transient decay measurements with the apparatus used in this work are only recommended for relatively high lifetime samples ($\tau_{eff} > 100 \mu s$) [103]. In quasi-steady-state measurements, this limitation is overcome by the relatively slow illumination decay time, allowing for samples with much lower lifetimes to be measured without the need for fast switching sensors. Consequently, transient and quasi-steady-state measurements have different measurement signals. An example trace curve from transient and quasi-steady-state measurements is shown in Figure 2.4. However, in generalised analysis mode, the optical constant needs to be accurately known. There are numerous ways the optical constant can be calculated including; fitting transient and generalised measurements (preferably over a range of injection levels) by varying the optical constant until the measured lifetimes match; estimating the optical constant from reflectance measurements, which can be used to predict the J_{sc} using tools such as OPAL 2 [104].

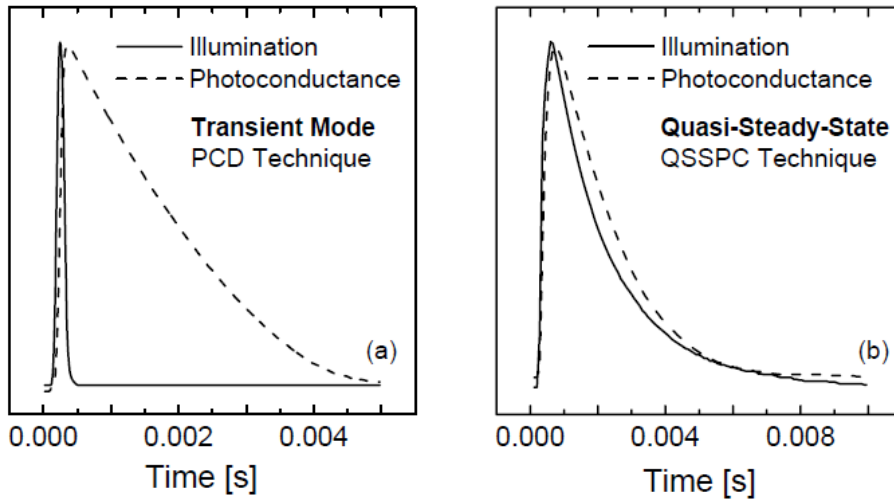


Figure 2.4 Typical time dependent illumination and photoconductance measured in a QSSPC system, during transient (left) and the quasi-steady-state mode (right). Note the sharp cut off in illumination in transient mode, in contrast to the closely followed illumination and photoconductance traces in quasi steady state mode. Sourced from [98].

2.4.1.2 Extraction of surface recombination parameters

One of the main advantages of the PC measurement technique is that it allows for the separation of surface and bulk recombination parameters from the sample. In a homogeneously doped sample without any additionally diffused regions, the effective lifetime is a combination of bulk and surface recombination, given by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surfaces}}, \quad \text{Eq. (2.55)}$$

where τ_{bulk} incorporates SRH and intrinsic recombination processes, and $\tau_{surfaces}$ consists of the surface recombination velocities at the front S_{front} and rear S_{rear} . The surface lifetime is given by [48, 105-107]

$$\frac{1}{\tau_{surface}} = \alpha_0^2 D, \quad \text{Eq. (2.56)}$$

where α_0 is the smallest eigen value solution of the relation

$$\tan(\alpha_0 W) = (S_{front} + S_{rear}) / (\alpha_0 D - \frac{S_{front} S_{rear}}{\alpha_0 D}). \quad \text{Eq. (2.57)}$$

Where W is the sample width and D is the injection level dependent diffusion constant of excess carriers, equal to the diffusion constant of minority carriers in low injection and the ambipolar diffusion constant in high injection [107]. Assuming S_{front} and S_{rear} are identical—as is often assumed for symmetrically passivated lifetime samples—taking limiting scenarios of high and low surface recombination rates, analytical expressions can be derived from Eq. 2.56 which allow for the calculation of S_{eff} .

1. For very high S values, the surface recombination rate is limited by the supply of carriers to the surface, since all carriers immediately recombine. In that case, $\tau_{surface}$ is given by the equation [98, 107]

$$\frac{1}{\tau_{surface}} = 12 D_n \left(\frac{1}{W} \right)^2, \quad \text{Eq. (2.58)}$$

for $SW/D_n > 100$.

2. For samples with low S values and high bulk lifetime, the surface recombination rate depends on the surface and bulk properties, and not carrier diffusion to the surfaces. Sproul has shown that for sufficiently low S values [98, 107],

$$\frac{1}{\tau_{surface}} = \frac{2 S_{eff}}{W}, \quad \text{Eq. (2.59)}$$

for $SW/D_n < 1/4$.

The above expressions are accurate to within 4 % [107]. The sum of Eq. 2.57 and Eq. 2.58 can be used as an approximation of the intermediate case to an accuracy within 5 % [108]. Equation 2.58 is frequently used to extract S_{eff} from undiffused symmetrically passivated lifetime samples. These structures are widely used in the characterisation of surface passivating dielectrics, and consist of an undiffused wafer with identical surface passivation on both surfaces. Edge recombination is assumed to be negligible since the edges are often passivated during the surface passivation process, most carriers cannot diffuse to the edge regions, and the proportion of edge surface area relative to the total surface area for thin wafers is negligible. A schematic of such a sample is shown in Figure 2.5, and the ideal characteristics for these samples include:

- 1) High purity material with few lattice defects, such that the sample is limited by intrinsic recombination mechanisms. This is best achieved with float-zone (FZ) wafers.
- 2) The surface should be easily passivated and uniform, with the surface finish as uniform as possible. Wafers which are mechanically polished to mirror finish are therefore best suited in this case.
- 3) High resistivity wafers are used to minimise Auger recombination processes and maximise τ_{bulk} .

In summary, double-side polished, high resistivity FZ silicon is an ideal substrate type for studying isolating the surface recombination effects and studying surface recombination parameters and are used throughout this work as both substrates for surface recombination studies, and emitter and surface recombination monitors during cell processing.

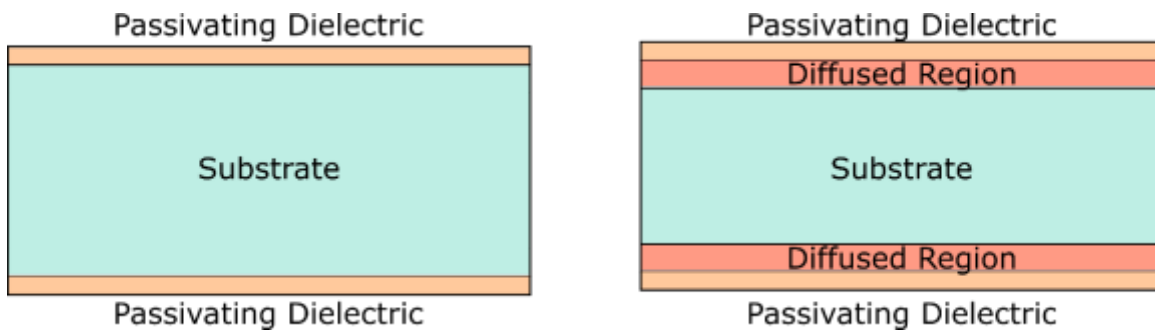


Figure 2.5 Schematic view of a typical symmetrical lifetime structure for the extraction of J_{0s} (left) and J_{0e} (right) used in this work.

In undiffused, well-passivated surface limited lifetime structures with minimal SRH recombination in the bulk, such as that depicted in Figure 2.5, assuming uniform Δn in the sample, the effective lifetime can be written as

$$\frac{1}{\tau_{eff}} = \left(\frac{1}{\tau_{intrinsic}} + \frac{1}{\tau_{SRH}} \right) + \frac{1}{\tau_{surfaces}} \cong \frac{1}{\tau_{intrinsic}} + 2 \frac{S_{eff}}{W}, \quad \text{Eq. (2.60)}$$

which can be rearranged for S_{eff} ,

$$S_{eff} = \frac{W}{2} \left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{intrinsic}} \right). \quad \text{Eq. (2.61)}$$

The parameterisation by Richter *et al.* [71], for instance, can be used to solve for $\tau_{intrinsic}$. This method gives a simple and quick method for extracting the surface recombination velocity from a symmetrically passivated sample. Note that, as discussed previously, for most samples not in flat-band conditions since in this regime, S_{eff} scales with the substrate doping and charge [76].

In the instance where the surfaces are diffused, the above method would consider the edge of the space charge region on the diffused region side as the effective surface, thus lumping together diffused region recombination and the surface recombination rate. As previously outlined, this is problematic since S_{eff} , under non-flat band conditions, is a function of Q and substrate doping. An alternative approach is to describe the recombination in terms of a saturation current density J_0 , which is defined at the edge of the diffused region, and includes all intrinsic and defect-assisted recombination mechanisms in the diffused region and at the surface. Assuming that the sample is in high injection, the effective lifetime is written as [109]:

$$\frac{1}{\tau_{eff}} = \left(\frac{1}{\tau_{intrinsic}} + \frac{1}{\tau_{SRH}} \right) + J_0 \frac{2(N_b + \Delta n)}{qWn_i^2}, \quad \text{Eq. (2.62)}$$

where N_b is the dopant concentration in the bulk. Assuming that τ_{SRH} is independent of Δn , differentiating with respect to Δn yields the form,

$$J_0 = \frac{1}{2} q n_i^2 W \frac{d}{d\Delta n} \left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{intrinsic}} - \frac{1}{\tau_{SRH}} \right), \quad \text{Eq. (2.63)}$$

which enables the extraction of J_0 from the linear portion of the slope of $1/\tau_{eff} - 1/\tau_{intrinsic}$ vs. Δn . The bracketed term in the RHS of Eq. 2.62 is often referred to as the corrected lifetime, τ_{corr} . This method is commonly referred to as the ‘‘Kane-Swanson method’’, and is a simple, quick and powerful method for the extraction of J_0 . For symmetrically

diffused and/or passivated samples, J_0 is analogous to J_{0e} or J_{0s} respectively, provided that in the latter case the sample is under strong inversion or accumulation (if not, S_{eff} is the more appropriate parameter). In the original 1985 paper, Kane and Swanson outlined key assumptions affecting the accuracy of this method;

- 1) Assumed uniform excess carrier density in the bulk, which allows the average generation rate in the bulk to be approximated as a uniform generation rate in the sample. This is not strictly correct due to finite carrier mobility within the sample. Kane and Swanson recommend reducing the sample width and minimising the surface recombination velocity to minimise this effect.
- 2) n_i is constant, and therefore not taking into account BGN effects with increasing injection.
- 3) The sample must be in high injection, as in this region the bulk region has a linear dependence on injection level, whereas the surface has a quadratic dependence. As a rule of thumb, $\Delta n_{min} > 10N_b$ was suggested.
- 4) The sample must not be limited by Auger or SRH recombination in the bulk in high injection; the bulk lifetime is constant.
- 5) The diffused region is electrically “invisible” and contributes negligibly to the conductance measurement.

Mäckel *et al.* extensively studied the effect of each of these approximations and demonstrated that J_0 should be determined from the analytical solution as a function of Δn (see approximation 6 in Ref. [94]), arguing the effect of SRH processes cannot be ignored (even in FZ wafers) [94]. In practice, these assumptions introduce an error and as a result, numerous authors have proposed corrections to the original Kane-Swanson method. Firstly, King *et al.* proposed a bulk auger correction factor, $C_A \Delta n^2$ be added to the RHS of Eq. 2.61, where $C_A = 1.66 \times 10^{-30} \text{ cm}^6/\text{s}$ [110] is the ambipolar bulk Auger coefficient to improve the linear fitting in high injection [111]. The differentiation to produce Eq. 2.62 assumes n_i is independent of Δn , which is not correct when band gap narrowing effects are taken into account, and so to correct for band gap narrowing effects, Blum *et al.* [112] implemented a correction to the intrinsic carrier concentration, to instead use a $n_{i,eff}$. This accounts for band gap narrowing effects according to Shenck [113], with an original value of $n_{i,0}$ taken from Sproul and Green [114]. The corrections by Blum *et al.* and King *et al.* are automatically implemented in the standard Sinton Instruments WCT-120 PC software package and used in this work unless stated

otherwise. Thomson *et al.* proposed a method of correcting for the non-uniform carrier generation rate in the sample, by numerically solving the one-dimensional excess carrier density profile as a function of depth into the sample, so that the simulated average excess carrier density $\Delta\bar{n}$ agrees with the measured Δn [115]. This method when compared to the Kane-Swanson method (and therefore not incorporating any of the previously mentioned corrections), significantly under-estimated J_0 by 2-8 % for lightly boron-doped samples ($N_A = 1.3 \times 10^{14} \text{ cm}^{-3}$) and 10-80 % for moderately phosphorus-doped samples ($N_D = 1.5 \times 10^{15} \text{ cm}^{-3}$) with an uncertainty of 6 %. Kimmerle *et al.* proposed a correction to take into account the SRH lifetime and the finite diffusion length of carriers adopted from the results of Sproul [107] to produce the relation [116]

$$\frac{1}{\tau_{SRH}} = \frac{1}{\tau_{corr}(\Delta n_{av})} - \frac{1}{\frac{W q n_{i,eff}^2 (\Delta n_{av})}{2 J_0 (N_b + \Delta n_{av})} + \frac{1}{12} \frac{W^2}{D}}. \quad \text{Eq. (2.64)}$$

In Eq. 2.63, τ_{SRH} is calculated via an iterative procedure which converges τ_{SRH} and J_0 and was shown to reduce the underestimation of J_0 over a broad range of sample bulk lifetimes, in particular, low bulk lifetime samples where SRH recombination in the bulk is non-negligible. Min *et al.* developed a method which uses numerical device simulations to show that J_{0e} can be underestimated in certain ranges, and recommended extracting J_0 over a finite Δn range and taking the maximum [117]. Recently, Juhl *et al.* developed an analysis package which applies the aforementioned corrections of King, Blum and Kimmerle, over a range of injection levels according to Min *et al.*, to the output measurement files from a Sinton Instruments WCT-120 PC PC lifetime tester [118]. This package is used in this thesis to minimise error associated with J_0 extraction. As a final note on S_{eff} and J_0 , the two terms are related by the equation

$$S_{eff} = J_0 \frac{N_b + \Delta n}{q n_{i,eff}^2}, \quad \text{Eq. (2.65)}$$

where N_b is the doping level in the bulk.

2.4.2 Photoluminescence measurement

In a photoluminescence (PL) measurement, excess carriers are generated from a short pulse of incident photons with energy greater than the material band gap such that $E_{photon} > E_g$, generating electron and hole pairs. The photons emitted, as the generated electron and hole pairs recombine, are captured by a sensor which creates a spatially resolved

‘image’ of the recombination across the sample. PL measurements performed in this thesis were taken using a BT Imaging LIS-R1 system which uses the quasi-steady-state technique to measure excess carrier density. In this type of measurement, the PL signal is given by [119]

$$I_{PL} = A_i B(T) np = A_i B(T) \Delta n (\Delta n + N_b), \quad \text{Eq. (2.66)}$$

where A_i is a scaling factor, and $B(T)$ is the temperature dependent radiative recombination coefficient. In this work, PL measurements are used in combination with PCD measurements to create spatially resolved calibrated PL images which map J_0 of both metallised and passivated regions of solar cell test structures. This technique is based on the work of Fell *et al.* [120, 121] and is discussed in greater detail in Chapter 6.

2.5 Contact resistance and carrier transport

For most solar cell architectures, a metal-silicon contact is used to extract the generated charge carriers from the solar cell device, where they are used to power an external load. At the contacts, the aim is to extract the majority carrier type, whilst avoiding significant recombination and this requires enhanced carrier selectivity within the vicinity of the contacted regions to reduce the concentration of minority carriers available to recombine. In the following chapters of this thesis, the properties of metal-silicon contacts formed by a range of metallisation technologies is assessed. The key metric for carrier extraction in these cases is the specific contact resistivity ρ_c , which is a measure of the ease at which charge carriers are extracted without significant parasitic losses and is independent of the contact area. The contact resistance R_c , in ohms, takes into account the contact area and hence reflects the properties of the actual contact in question, but is not useful for comparing contacts with different contact geometries. In the remainder of this chapter, a brief review of the physics underlying charge carrier extraction across metal-semiconductor interfaces and the metrologies used in this work to characterise the carrier selectivity of these contacts is reviewed.

2.5.1 Metal-semiconductor contacts

When a metal comes into direct contact with a semiconductor, assuming there is no interfacial layer present, there will be a balancing of the electrochemical potentials within the materials such that there is a continuous, flat electrochemical potential across the interface [99]. Depending on the position of the metal work function Φ_m relative to the

semiconductor Fermi level, an accumulated, depleted or neutral band structure will form in the semiconductor, since the majority of potential balancing occurs in the semiconductor [122]. The different types of interface conditions before and after metal-semiconductor contact are shown in Figure 2.6 below.

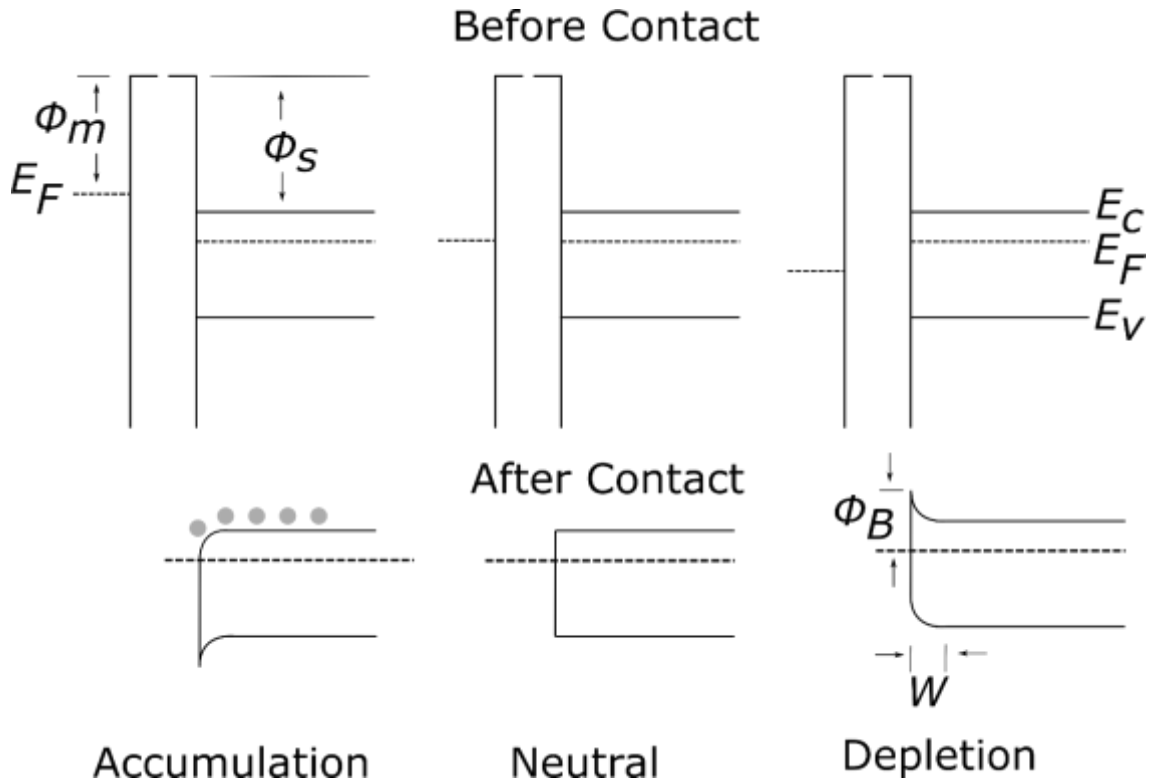


Figure 2.6 Ideal metal-semiconductor contacts according to Schottky-Mott theory, depicting the metal-semiconductor system before (upper) and after (lower) contact. The formation of accumulated, neutral or depleted surfaces at the semiconductor-metal interface is a result of the relative position of the metal and semiconductor Fermi-levels [99, 123].

The accumulated contact is the ideal structure, since this energy band configuration poses the least resistance for electron flow across the interface. According to ideal theory, this should be easily realised by selecting metals with high work functions such that $\Phi_m > \Phi_s$, however in practice it has been observed that a depletion type contact with rectifying behaviour is formed for silicon, and that the barrier height is relatively constant and independent of metal work function. This type of contact is known as a Schottky barrier and refers to a metal-semiconductor contact with large barrier height, and a doping concentration less than the density of states in the conduction or valence bands [99]. The relative constancy of the barrier height is attributed to Fermi-level pinning, where the Fermi-level in the semiconductor is ‘pinned’ to create a depletion-type contact. The

precise cause of Fermi-level pinning is still unclear and competing theories exist in the literature [124-126], however, Fermi-level pinning rules out tailoring the metal barrier height to achieve an accumulation type contact. Furthermore, a high concentration of defect states within the silicon band gap at the metal-semiconductor interface results in the interface being a potential site of extremely high SRH recombination—the recombination rate at such interfaces has been shown to be limited by the diffusivity limit (the rate at which carriers can diffuse from the bulk to the contact region), corresponding to a contact saturation current density J_{0c} of $\sim 1 \text{ nA/cm}^2$ [127].

A solution to this issue is to improve the carrier selectivity of the contacts via doping the near surface regions within the area of the contacts. Typically, phosphorus and boron dopants for n -type and p -type doping respectively are diffused at concentrations above $\sim 10^{18} \text{ cm}^{-3}$ to improve carrier selectivity. Doping of the surface has two effects. Firstly, the conductivity of the majority carrier is improved within the contact region—which outweighs a corresponding decrease in carrier mobility—and reduces the minority carrier concentration in the region, suppressing the maximum recombination rate. Secondly, the barrier width at the interface is reduced. As the surface concentration of dopants increases, current transport across the barrier transitions from thermionic emission processes (for low doped semiconductors), to thermionic field emission processes (for moderate doping levels), until quantum mechanical tunnelling is dominant via field emission processes (for heavily doped semiconductors). This transition is depicted in Figure 2.7, which shows the change in barrier width and transport processes with increasing dopant concentration. This enables the transition from Schottky behaviour to ohmic contact behaviour, which is characterised by linear or quasi-linear current-voltage characteristic, and requisite for high performance solar cell devices.

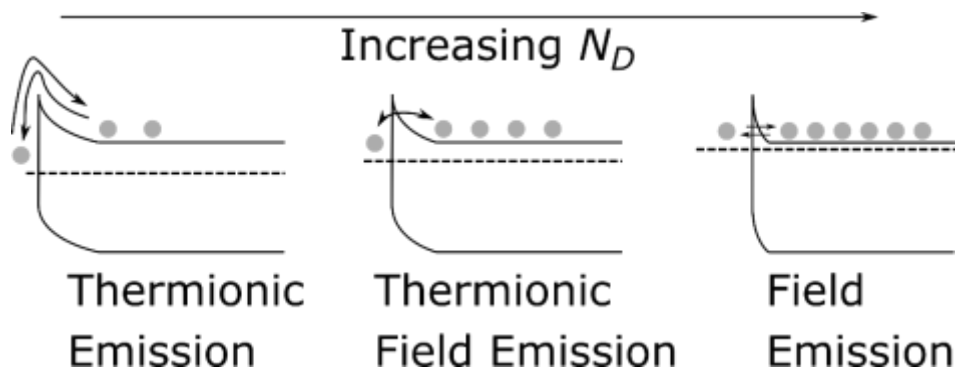


Figure 2.7 Interface band structure of depleted contacts showing the effect of increasing doping concentration on the barrier width and transport mechanism across.

2.5.2 Assessing specific contact resistivity

The contact resistance is a measure of the resistance to majority carrier flow between a metal-semiconductor interface and includes the resistance inherent in the metal-semiconductor contact, known as the specific interfacial resistivity ρ_i , and also any other associated effects from current crowding and interfacial oxides that may be present [105]. Contact resistance is also a function of the direction of current flow, since this will alter the effective contact area. Therefore, test structures to extract the contact resistance need to replicate the current transport direction within the device to accurately model the resistance characteristic. In the instance of the metal-silicon contacts for diffused electron and hole collectors studied in this work, the majority of generated carriers will have to diffuse laterally towards the contacts as the contacts are not full area contacts. Therefore, the methods which measure the resistance associated with lateral current flow into a metal contact are most applicable and presented herein.

The transmission line model technique is a two-terminal measurement technique initially proposed to take into account current crowding and extract ρ_c , however, the original model proposed by Murrmann and Widmann assumed zero sheet thickness of the diffused semiconductor layer [128]. Consequently, Berger extended the TLM model to take into account the semiconductor sheet thickness, restricting current flow to be one-dimensional [129]. For a lateral current flow into the contact, carriers transfer from the semiconductor into the metal via the path of least resistance, encountering resistance from the semiconductor sheet underneath the contact, and as contact resistance flowing into the contact. This is depicted in Figure 2.8, and the potential distribution under the contact is given by the expression [129]

$$V(x) = \frac{I\sqrt{R_{sheet}\rho_c}}{W} \frac{\cosh[(L-x/L_T)]}{\sinh(L/L_T)} \quad \text{Eq. (2.67)}$$

Where W is the contact width, I is the current flowing into the contact, L is the contact length, x is the distance across the contact, R_{sheet} is the sheet resistance underneath the contact—in this case assuming R_{sheet} is unaffected by the contacting process, and L_T is the transfer length or inverse of attenuation constant. The transfer length is the distance over which most of the current transfers from the metal into the semiconductor or vice-versa, defined as

$$L_T = \sqrt{\frac{\rho_c}{R_{sheet}}}. \quad \text{Eq. (2.68)}$$

For a two-terminal contact probed at $x = 0$, the contact front resistance is given by the equation

$$R_{cf} = \frac{V}{I} = \frac{\sqrt{R_{sheet}\rho_c}}{W} = \frac{\rho_c}{L_T W} \coth\left(\frac{L}{L_T}\right). \quad \text{Eq. (2.69)}$$

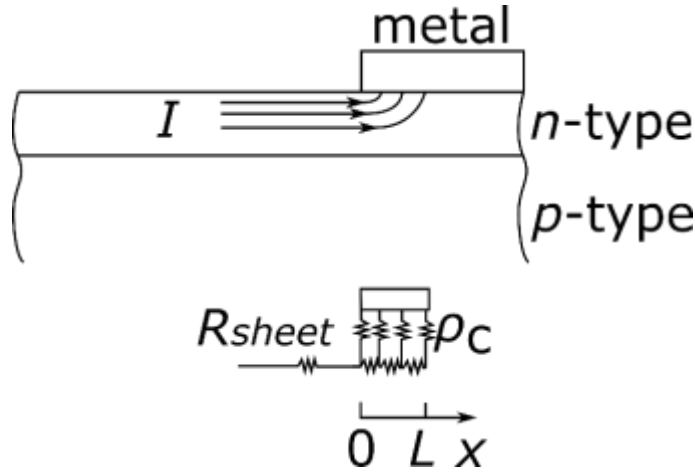


Figure 2.8 Current transfer from semiconductor to metal showing the equivalent resistance network. The sheet resistance and contact resistance components the charge carriers encounter over a length L before entering the electrode is also depicted.

This relationship is the basis of the two-terminal methods used in this work. The transfer length method (TLM) was originally proposed by Shockley in Ref. [130], and consists of a sequence of linearly spaced contacts which are probed sequentially in a ladder structure, depicted in Figure 2.9a. The metal pads in this case are contacted sequentially along the ladder—and across interjacent fingers, which affects the voltage and resistance measurement and therefore the overall extraction of contact resistivity. These effects are discussed in more detail in Chapter 3, where this technique is applied to assess the effect of parasitic AlO_x deposition intervening the front side SiN_x and screen-printed silver, prior to firing. The need to compensate for the effect of interjacent contacts is overcome by having a non-equidistant spacing between the contact pads, depicted in Figure 2.9b.

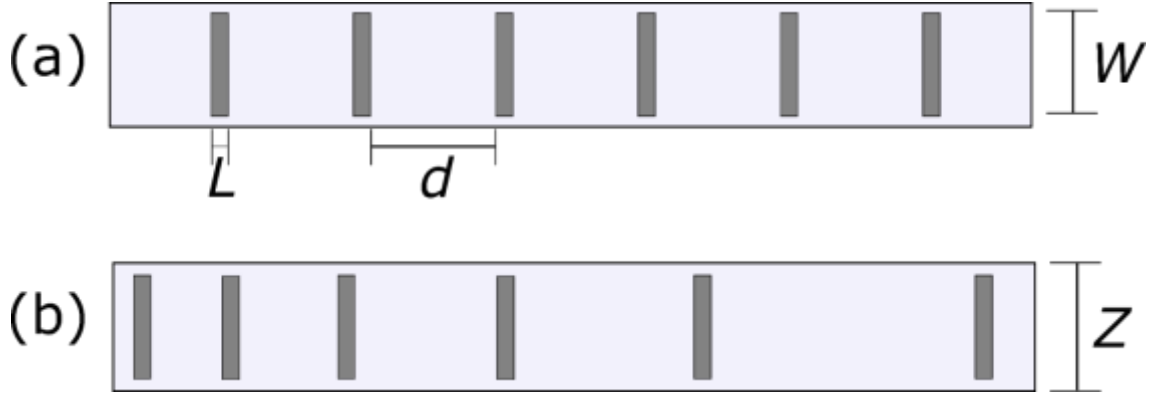


Figure 2.9 Ladder (a) and Linear (b) TLM patterns with metallic contact pads shaded in dark grey.

In this instance, the total resistance between contacts R_{total} is plotted as a function of distance, and a linear relation between increasing R_{total} and contact spacing d is achieved. Assuming that the contact length $L < L_T$, a simple expression can be written for the total resistance between two pads [131]:

$$R_{total} = \frac{R_{sh}d}{L} + 2R_c \approx \frac{R_{sh}}{L}(d + 2L_T). \quad \text{Eq. (2.70)}$$

From this plot, the following parameters may be extracted;

- 1) The sheet resistance, R_{sh} is extracted from the slope,
- 2) The contact resistance R_c is extracted from the y-intercept, and
- 3) The transfer length is calculated from the x-intercept, from which the specific contact resistivity may be calculated using Eq. 2.67.

However, Eq. 2.69 assumes that the sheet resistance underneath the metal contact is identical to the sheet resistance in-between the contacts, which is not the case for some metallisation techniques which involve alloying at the metal-silicon interface only. In this instance, the contact resistance is expressed as [132]

$$R_c = \frac{R_{sk}L_T}{L} \coth\left(\frac{d}{L_T}\right). \quad \text{Eq. (2.71)}$$

with

$$L_T = \sqrt{\frac{\rho_c}{R_{sk}}}. \quad \text{Eq. (2.72)}$$

Where R_{sk} is the sheet resistance underneath the metal contact. In this instance, Eq. 2.69 is modified to the form,

$$R_{total} = \frac{R_{sh}d}{L} + \frac{2R_{sk}L_T}{L} = \frac{R_{sh}}{L} \left(d + \frac{R_{sk}}{R_{sh}} L_T \right). \quad \text{Eq. (2.73)}$$

Reeves and Harrison proposed a method of separately extracting R_{sk} , using an end resistance measurement [133]. This involves probing the voltage and current separately between three terminals in a configuration depicted in Figure 2.10. The end resistance R_e is calculated as:

$$R_e = \sqrt{\frac{\rho_{sk} R_{sk}}{L} \frac{1}{\sinh\left(\frac{d}{L_T}\right)}}, \quad \text{Eq. (2.74)}$$

which, upon dividing Eq. 2.72 by Eq. 2.73 produces,

$$\frac{R_c}{R_e} = \cosh\left(\frac{d}{L_T}\right). \quad \text{Eq. (2.75)}$$

In this way, the L_T and can be determined accurately, by using Eq. 2.74. Taking the y-intercept to extract the value of R_c , R_{sk} is then calculated from Eq. 2.80. This does not make the assumption that $R_{sk} = R_{sheet}$. More accurate values of ρ_c can then be obtained by inputting the values of L_T and R_{sk} into Eq. 2.71.

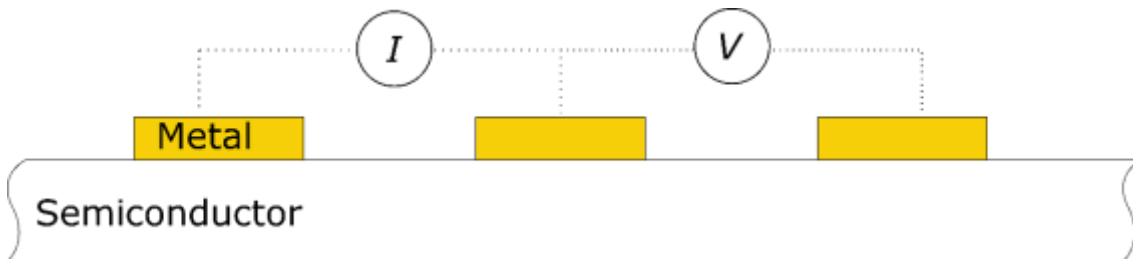


Figure 2.10 End resistance structure as proposed by Reeves and Harrison. The current and voltage are probed across three metal contacts in the configuration above. The end resistance is calculated $R_e = V/I$.

The transfer length method, in addition to transmission line measurement methods, assumes one dimensional current flow. This may not be the case if the width of the contact pad (W) is less than the emitter width (Z). In this work, this is overcome by cleaving the widths of the samples such that $W = Z$ and minimising the overall contact width. However, in some instances, this is not practical without destroying samples which may be required for other testing. To overcome this issue, Reeves proposed the circular transmission line method (CTLTM) structure, whereby the current-voltage characteristic is probed between an inner contact pad surrounded by a series of isolated concentric metallic rings [134].

This structure is depicted schematically in Figure 2.11a, where the increase in pad spacing is achieved by increasing the outer ring radius. To avoid the issue of interjacent metallic contacts affecting the measurement, Marlow and Das proposed a series of circular contacts of varying radius [135], depicted in Figure 2.11b.

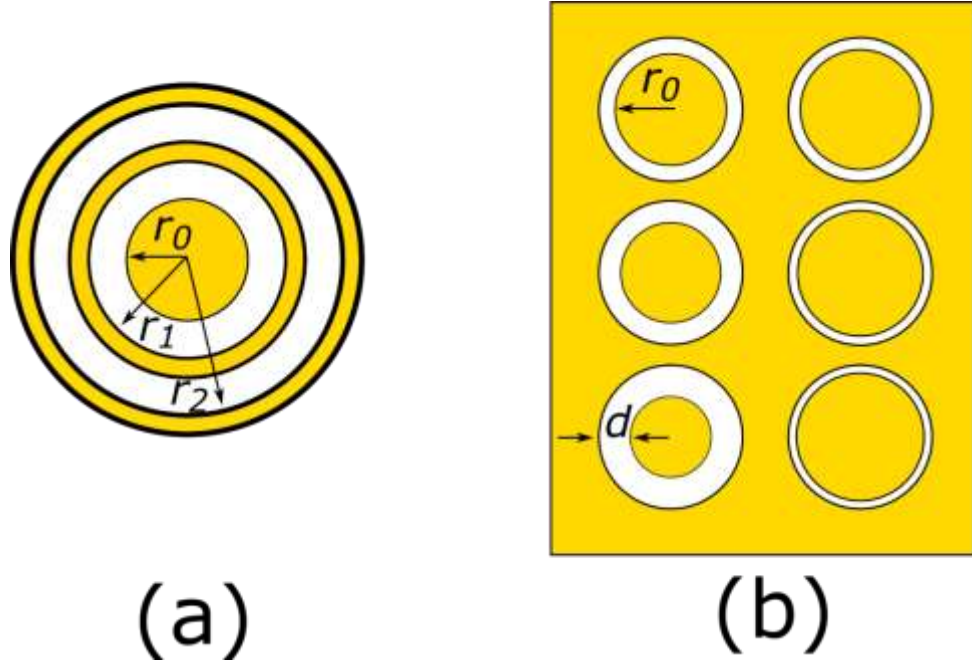


Figure 2.11 Circular TLM patterns as proposed by Berger (a) and Marlow and Das (b). The metal contact pads are coloured in gold.

For a circular TLM pattern, when r_0 and $r_1 \gg 4L_T$ (assumption 1) the resistance between the inner and outer pads is given by the equation [134, 136]

$$R_{total} = \frac{R_{sheet}}{2\pi} \left[\ln \left(\frac{r_1}{r_1 - d} \right) + L_T \left(\frac{1}{r_1} + \frac{1}{r_1 - d} \right) \right], \quad \text{Eq. (2.76)}$$

If $r_1 \gg d$, (assumption 2) then the above expression simplifies to:

$$R_{total} = \left(\frac{R_{sheet}d}{2\pi r_0} + \frac{2R_{sk}L_T}{2\pi r_0} \right) C. \quad \text{Eq. (2.77)}$$

Where C is the correction factor given by

$$C = \frac{r_0}{d} \ln \left(1 + \frac{d}{r_0} \right). \quad \text{Eq. (2.78)}$$

Finally, if the inner radius r_0 , is much greater than the ring spacing, d (i.e. $r_0 \gg d$ or $d/r_0 \ll 1$, assumption 3), then this simplifies to

$$R_{total} = \frac{R_{sheet}d}{2\pi r_0} + \frac{2R_{sk}L_T}{2\pi r_0}. \quad \text{Eq. (2.79)}$$

In this work, a circular TLM pattern consisting of six circular contacts of radius r_0 surrounded by a metal contact ring of inner radius r_1 is used in Chapter 4 and Chapter 7, where it is ideal to not destroy the sample by removing the circular TLM structures. The validity of the contact geometry used in this work, as determined by their consistency with the three assumptions, can be assessed by calculating the quantities and relations which underpin the assumptions. These quantities and relations for the contact geometry used in this work is listed in

Table 2.3. The maximum transfer lengths calculated as $r_0/4$ for each geometry, are much larger than would be achieved for an ideal ohmic contact, and therefore simplification based on Assumption 1 is valid. Similarly, the calculated correction factors related to assumption 2 are close to unity, signifying a slight deviation from a linear approximation, and therefore in this work, the correction factor is applied to all measurements regardless that the deviations are only small. Finally, Assumption 3 is also verified, with the calculated values $d/r_0 \ll 1$.

Table 2.3 Circular TLM geometry and calculated quantities used in the validation of the test pattern design

Pattern	Dimension			Assumption			Correction Factor
	r_0	r_1	d	$r_1 \gg 4L_T$	$r_1 \gg d$	$d/r_0 \ll 1$	
	$[\mu\text{m}]$	$[\mu\text{m}]$	$[\mu\text{m}]$	$L_T \text{ max } [\mu\text{m}]$	$r_1 - d$	d/r_0	
1	850	1000	150	212.5	700	0.176	0.921
2	875	1000	125	218.75	750	0.143	0.935
3	900	1000	100	225	800	0.111	0.948
4	925	1000	75	231.25	850	0.081	0.962
5	950	1000	50	237.5	900	0.053	0.975
6	975	1000	25	243.75	950	0.026	0.987

2.6 Chapter summary

The fundamental physical principles related to carrier selective, diffused silicon wafer solar cells has been presented in this chapter. A brief overview of how carrier selectivity is fundamental to charge separation and the underlying physics was presented. This was followed by a brief review of the development of diffused homojunction solar cells, highlighting how engineering carrier selectivity in these devices was fundamental to achieving sustained improvements in conversion efficiency. Specific focus on outlining the strengths and drawbacks of the parameters which measure surface recombination— J_{0s} , J_{0e} and S_{eff} —were outlined, in addition to the issues related to their extraction via PC techniques. PC measurements, as performed in this work, was also reviewed highlighting the considerations taken into account during measurement and analysis. Finally, the metrics and methods used to assess carrier selectivity at metal silicon interfaces was outlined, presenting the theory behind the test structures used and validating the test pattern geometries used in the experimental sections of this work.

3 IMPROVED MAJORITY CARRIER TRANSPORT FOR SCREEN-PRINTED SOLAR CELL CONTACTS

INTRODUCTION

Of all the current technologies available to create metal-silicon contacts, screen-printed metal contacts dominate as the main type of technology used in the production of silicon based photovoltaic cells. Taking note of the dominance of screen-print technology, this chapter responds to two prevailing trends in the industry [9]:

- 1) The industry transition from *p*-type aluminium back surface field (Al-BSF) to *p*-PERC solar cell structures [9, 137, 138].
- 2) The push to doped regions with lower surface concentrations without sacrificing majority carrier transport properties (contact resistance) and minority carrier recombination (contact recombination) when forming screen-printed silver contacts to a phosphorus doped electron collector.

This chapter seeks to improve the majority carrier transport characteristics of screen-printed silver contacts to phosphorus doped electron collectors by exploiting a production non-ideality. The PERC solar cell structure is distinguished from the Al-BSF solar cell by a passivated and localised point contact scheme on the rear of the device. For *p*-type solar cells, this is commonly achieved by the deposition of an AlO_x rear dielectric, which is subsequently capped with PECVD SiN_x and locally patterned (via for instance laser ablation), before screen printing the rear aluminium contact [139-141]. The passivating AlO_x dielectric is typically deposited by either plasma enhanced chemical vapour deposition (PECVD) or atomic layer deposition (ALD), with PECVD being the dominant technology used in production today [9]. In industrial PERC manufacturing processes, 5-10 nm of AlO_x is typically grown in an $\text{AlO}_x/\text{SiN}_x$ stack to provide negative fixed

interface charge at the rear[141-144]. An early study demonstrated slightly superior solar cell performance of PECVD grown AlO_x layers over ALD grown layers in p -PERC solar cells [145], however ALD deposited layers have the advantage of; 1) excellent surface passivation [146-148], 2) monolayer growth control, 3) excellent micro-feature conformality [149], 4) pinhole free growth and 4) low deposition temperatures [150]. It is for these reasons, coupled with the advent of high-throughput spatial ALD deposition systems [151], that the use of ALD deposition in PERC cell production continues to attract research attention for industrial applications [138, 141]—the latest technology roadmap for the PV industry predicts an increase in the use of ALD deposition during PERC solar cell production in the future [9].

The single sided deposition of thin films is critical for ideal cell processing, since the properties of each dielectric film are carefully matched to the characteristics of the underling silicon. However, in practice it can be difficult to achieve a truly single-sided deposition in both ALD and PECVD reactors. Single-sided deposition is particularly difficult when both sides of the sample are coated in the same process run, as is enabled by dual deposition sources above and below the wafer—which is the set-up in some commercially available inline production tools [152]. So-called ‘wrap-around’—where unintended material deposition encroaches around the target surface onto the opposing surface from the edges—of AlO_x or SiN_x deposition of up to 10 mm has been reported for ALD deposition systems [153] and up to 20 mm for PECVD systems [154]. This wrap-around is likely to affect the metallurgical alloying process during screen-print firing, and the optical properties of the dielectric stack in the case that AlO_x is unintentionally deposited on top of, or underneath, the front SiN_x film.

Despite concerns about the effect of wrap-around deposition, only limited studies have been published which discuss its impact on solar cell performance. Kohler *et al.* showed that when AlO_x is deposited before the front side SiN_x (i.e. the AlO_x underlies the SiN_x at the edges), a reduction in cell efficiency was observed [155]. The authors attributed this effect to the negative fixed charge present in the AlO_x which results in a poor passivation of the n^+ layer, as was reported in detail by Hoex *et al.* [156] However, in some PERC solar cell processing sequences, the front SiN_x is deposited before the rear $\text{AlO}_x/\text{SiN}_x$ stack; therefore, the wrap-around will occur on top of the sunward SiN_x layer. A p -PERC solar cell structure schematically showing this case is depicted in Figure 3.1 and was studied exclusively in this chapter. In this case, the primary concerns would be the impact

on the contact formation during cofiring and the optics of the front side ARC. Dual sided deposition without adverse effects on solar cell performance would allow for greater flexibility in high throughput ALD tool design and a potential reduction of total cost of ownership, since considerable development cost and effort are currently expended to ensure mono-facial deposition, at the expense of throughput and manufacturing cost.

The effect of unintended AlO_x deposition onto the SiN_x ARC on the performance of p -type PERC solar cells was studied in this chapter. This work is separated into three separate studies; the first study focussed on the effect of AlO_x wrap-around on the resistivity of the screen-printed silver contact. This is followed by simulation results of the effect of varying wrap-around extents on solar cell performance. This was performed by taking the values for ρ_c from the first study and using them as input parameters for FEM simulations using Griddler v2.5 [157]. Finally, p -type Al-BSF solar cells were fabricated with varying thicknesses of AlO_x on the front side to assess the overall effect of full area wrap-around on solar cell performance.

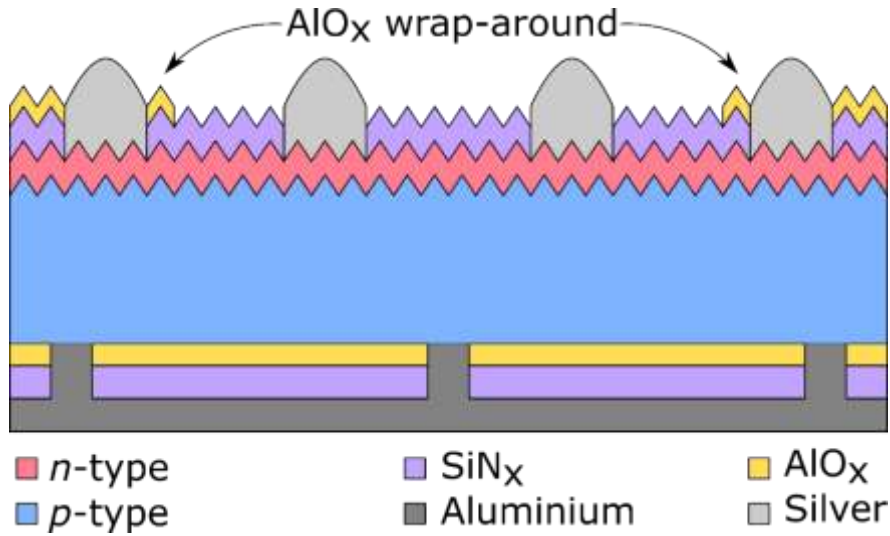


Figure 3.1 Schematic of a p -PERC solar cell with AlO_x wrap-around on the front surface edges studied in this work. The AlO_x is deposited unintentionally on the front side in a fabrication sequence where the SiN_x ARC is deposited followed by the rear $\text{AlO}_x/\text{SiN}_x$ stack.

3.1 The effect of AlO_x wrap-around on silver contact resistance

An analysis of the effect of AlO_x wrap-around on the majority carrier transport of electrons, for the case where the rear AlO_x film was deposited prior to the front SiN_x , is discussed in this section. Two separate precursor structures for screen print solar cells were tested. The first was a typical PERC structure featuring local Al-BSFs and the second was an ion-implanted PERT structure. This was done to assess the impact of the wrap-around effect on different electron collectors that are of interest in PV manufacturing.

3.1.1 Methodology

Industrial *p*-type Al-BSF/PERC and PERT solar cell precursors fabricated on monocrystalline Czochralski (Cz) silicon wafers were obtained from an industrial solar cell line and used as substrates in this experiment. The PERC cell precursors samples were fabricated with a PECVD SiN_x ARC dielectric deposited on an *n*-type electron collector (POCl_3 diffusion) on a *p*-type wafer. The PERT samples were fabricated with a diffused rear p^+ hole collector, and a front ion-implanted n^+ electron collector, which were subsequently annealed to drive-in the dopants. This drive-in process formed a residual SiO_2 layer approximately 1-2 nm thick, which was not removed and remained underneath the SiN_x ARC. A range of samples were ALD deposited with AlO_x layers on top of the SiN_x ARC with thicknesses of 3, 5, and 10 nm to simulate the effect of AlO_x wrap-around during a typical industrial deposition process. AlO_x layers 7 nm thick were also fabricated on the PERT precursors only. Samples without a layer of AlO_x on the SiN_x were used as control samples. After AlO_x deposition, samples from each group were screen-printed with commercial silver screen-print paste and subsequently fired in a commercial firing furnace (Schmid SierraTherm, 7K9) using different peak temperatures and belt speeds to modulate the firing duration. The Al-BSF samples were fired at a single speed of 5.54 cm.s^{-1} (denoted as S1) and the PERT samples were fired at varying belt speeds, 5.54 cm.s^{-1} , 5 cm.s^{-1} and 4.43 cm.s^{-1} (S1, S2 and S3 respectively). The Al-BSF samples were screen-printed with DuPont (PV19-B) paste, whereas the PERT samples were printed with the DuPont paste and Heraeus (9641B Ag front side paste). These were the state-of-the-art pastes offered by two leading manufacturers at the time of the study. The samples were screen-printed using a typical H-busbar front metallisation grid with finger

spacing of 2.33 mm and are depicted in Figure 3.2 as received (left) and after processing (right).

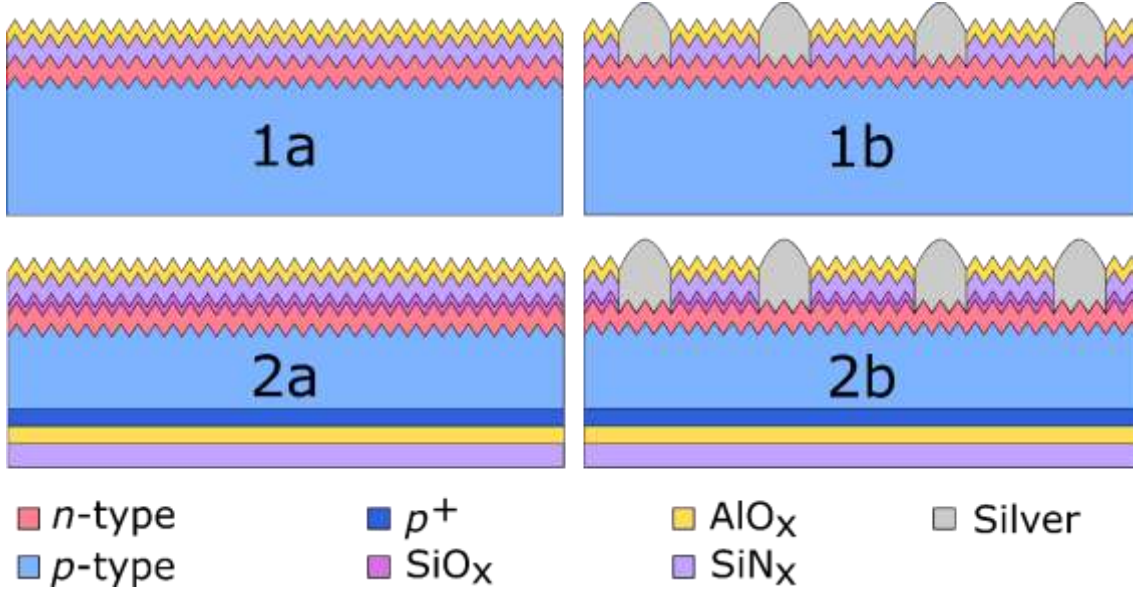


Figure 3.2 Schematic diagram of the *p*-type PERC (top) and PERT (bottom) test structures used in this experiment, showing the samples as received from the industrial supplier (1a and 2a) and after processing performed by the author (1b and 2b).

After firing, the samples were laser cleaved from the rear side (to avoid shunting the edges) and ρ_c measured via transfer length method (TLM) measurements. The details of the test structure used and an analysis of the error inherent to this measurement are discussed in Section 3.1.2.

To characterise the samples, the electrically active dopant profile depth and surface phosphorus concentration of both sample types were determined by electrochemical capacitance-voltage (ECV) profiling using a WEP-CVP21 tool. The sheet resistance was extracted by four-point-probe measurements to be $85 \, \Omega/\square$ with a standard deviation of $4.8 \, \Omega/\square$ (averaged over 16 equally spaced points on the as-diffused 6" wafer) for the PERC precursors, and $60 \, \Omega/\square$ for the ion-implanted samples with a standard deviation of $3.6 \, \Omega/\square$. The ECV profiles are displayed in Figure 3.3, with Profile A corresponding to the PERC precursor cells, and Profile B corresponding to the ion-implanted samples. In subsequent experiments outlined in Section 3.3, Al-BSF solar cells were fabricated with a phosphorous diffusion profile of reduced surface concentration. The phosphorous diffusion profile for those cells is shown in Profile C of Figure 3.3. Although the samples were obtained from industrial solar cell lines, of principal interest in this study is the relationship between the sample surface concentration of donors ($N_{D,s}$) and the obtained

Ag-Si contact resistivity as a result of varying firing conditions, wrap-around thicknesses and paste formulations. Therefore, hereafter the solar cell structures shall be referred by their surface dopant concentration, as opposed to the cell architecture type that they are precursor to. Hence, the PERC structures are referred to as the samples with $N_{D,s} = 1.8 \times 10^{20} \text{ cm}^{-3}$ and the PERT structures are the samples with $N_{D,s} = 6.6 \times 10^{19} \text{ cm}^{-3}$.

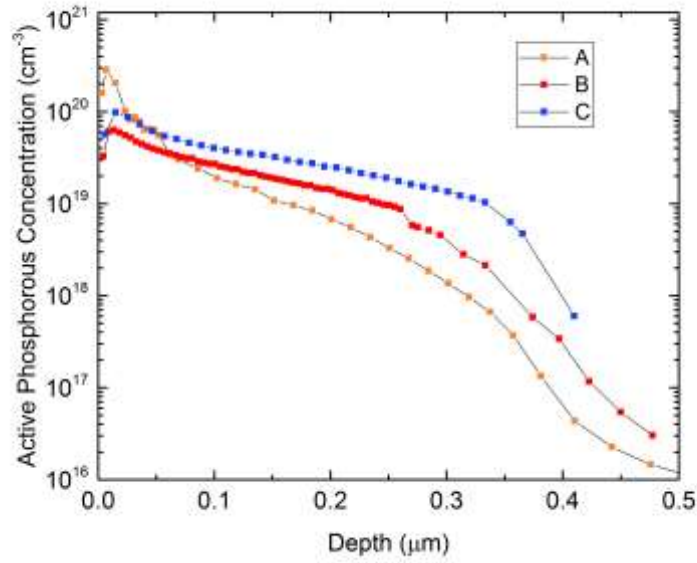


Figure 3.3 Measured electrically active phosphorus concentration as a function of depth for the three diffusion profiles used in the work described in this chapter. The lines serve as a guide for the eye.

To accurately determine the firing temperatures of the sample, the furnace was profiled at the same time as wafer processing. The temperatures were measured on an identical dummy wafer, using a thermocouple in contact with the sample and attached to a data logger (Q18, Datapaq) to an accuracy of $\pm 1 \text{ }^{\circ}\text{C}$. The temperature profiles recorded are shown in Figure 3.4, and depict a pre-heating zone, followed by the peak firing zone, followed by an intermediate ramp down zone, followed by cooling zones. The full processing and characterisation sequence is depicted in Figure 3.5.

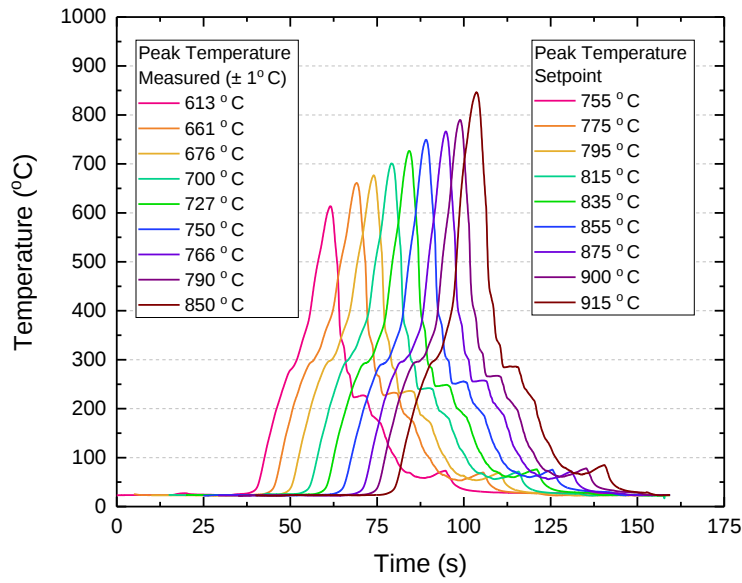


Figure 3.4 Measured temperature profiles of samples moving through the firing furnace as a function of time for a fixed firing furnace belt speed, S1. The plot compares the measured and set point temperatures for each firing temperature tested in this work. The time scale of the measurements has been intentionally staggered to appear sequential for greater clarity.

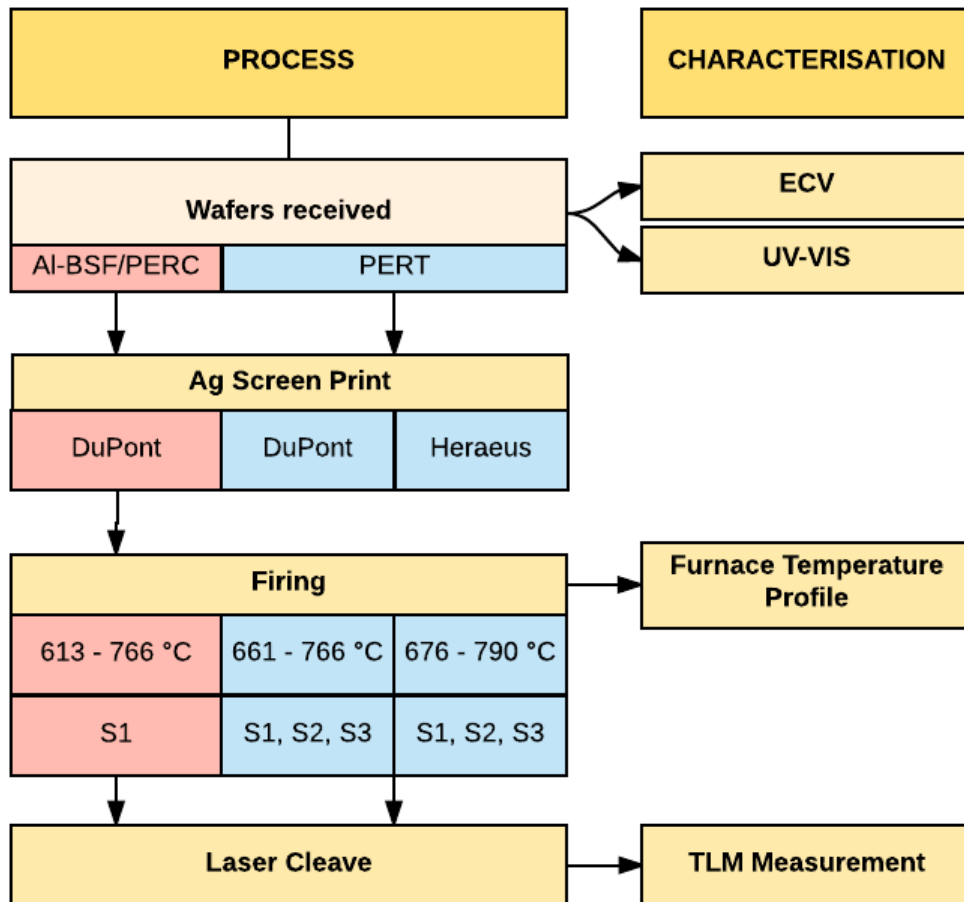


Figure 3.5 Processing sequence of the higher doped $N_{D,s} = 1.8 \times 10^{20} \text{ cm}^{-3}$ (PERC) and lower doped, $N_{D,s} = 6.6 \times 10^{19} \text{ cm}^{-3}$ (PERT) precursor structures.

3.1.1.1 Transfer length model methodology analysis

To extract the contact resistance from the samples, the sample fingers were cleaved into strips to create an equidistant-spaced ladder TLM pattern. This structure consisted of 8 fingers cleaved into a 5 mm wide rectangular sample and is depicted in Figure 3.6.

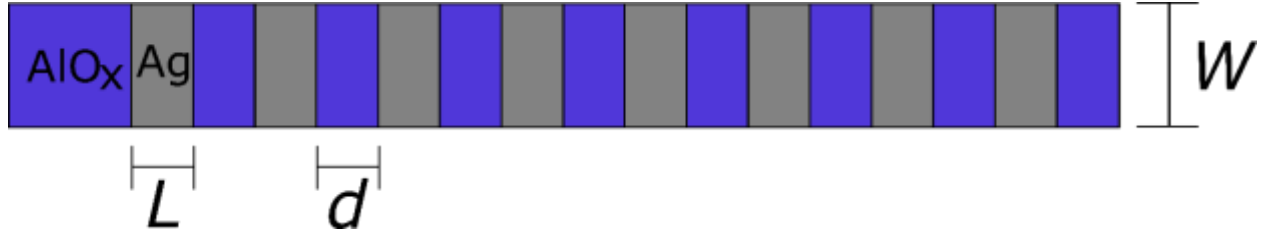


Figure 3.6 Top view of the equidistant linear TLM structure fabricated by laser cleaving the metallised finger region of the cells into strips consisting of eight consecutive finger segments. In these test structures, $W = 5 \text{ mm}$, $d = 2.3 \text{ mm}$ and $L = 100 \text{ }\mu\text{m}$.

The current and voltage characteristic was probed in the dark, sequentially between fingers. The resistance was probed across a maximum of eight fingers, including distances with interjacent fingers, resulting in a total of n measurements per sample, given by the expression;

$$n = \sum_{k=0}^{j-1} k \quad \text{Eq. (3.1)}$$

where n is the total number of measurements, and j is the total number of fingers probed, in this case a maximum value of eight. From this value, the resistance was calculated from the slope of the I - V curve since $R = V/I$, and the contact resistance extracted by the commonly applied slope-intercept method. Under this method, the ρ_c and contact resistance is extracted from a plot of the measured resistance, R_{total} , vs. contact spacing, d , [105]. Any variation in sheet resistance underneath the contact was taken into account with end resistance measurements, as outlined in Chapter 2.

The ladder TLM in this case has the advantage that the resistance of the fingers in the cell in question can be measured directly. Therefore, no assumption of equivalence between the samples and a dedicated test structure, as would be required for other TLM structures, was made. However, it has been shown that for this technique, an additional resistance network in the interjacent fingers needs to be added to Eq. 2.72 [158]. In this instance, current moving between fingers will preferentially flow into the interjacent finger,

depending on the contact resistance and transfer length of the contact. These additional resistance paths are added in parallel. The effective resistance of the resistance network, depicted in Figure 3.7, was calculated as [158]:

$$R_{eq} = \left(\frac{1}{r_{sk}} + \frac{1}{2R_c + R_{metal}} \right)^{-1} . \quad \text{Eq. (3.2)}$$

Where r_{sk} is the emitter resistance underneath the metal, given by the equation:

$$r_{sk} = \frac{R_{sk}L}{W}, \quad \text{Eq. (3.3)}$$

and R_{metal} is the resistance component as the current flows through the finger, defined as

$$R_{metal} = \frac{\rho_m l}{A}. \quad \text{Eq. (3.4)}$$

Where ρ_m is the resistivity of the metal, A is the cross-sectional area of the finger in the direction of current flow, and l is the length of the current path, which in this analysis was the width of the printed finger. For typical screen-printed silver contacts, R_{metal} is assumed to be negligibly small relative to the other resistance components and neglected in the following analysis. For a test structure with any number of n interjacent fingers, R_{total} becomes:

$$R_{total} = (n + 1) \frac{R_{sheet}d}{W} + 2R_c + nR_{eq}. \quad \text{Eq. (3.5)}$$

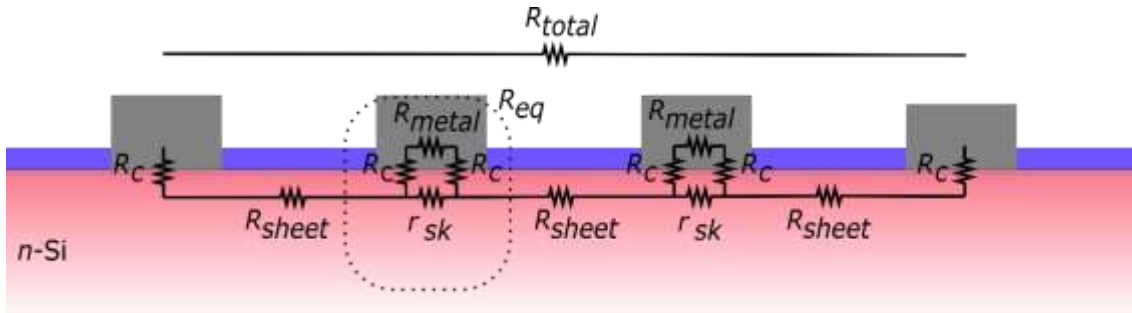


Figure 3.7 Equivalent resistance network for a system of with two interjacent fingers. In this diagram, R_{total} is probed between the outer fingers, with the equivalent resistance network depicted schematically and overlaid on a cross-section of the TLM test structure.

When Eq. 3.5 is plotted as a function of d , the resulting plot is non-linear with increasing d and, hence, in certain scenarios this will introduce significant error in the calculation. To estimate the error in this method, the following three cases were considered:

- **Scenario 1:** Negligible current flows in the interjacent finger. This occurs when R_c is high, and/or $L_T \gg L$, as is the case for a poor contact or a very thin finger. The absolute error in R_{total} (Eq. 3.5 subtracted from Eq. 2.69) becomes $\Delta R_{total} = nr_{sk}$. In this instance, a linear parameterisation is applicable provided R_{sk} is calculated accurately.
- **Scenario 2:** Negligible current flows through the doped region under the metal, and the majority of current flows in the interjacent finger. This alternative extreme case occurs when $L_T \ll L$ and R_c is low. This is the likely case for a low resistance contact such that $R_c \ll r_{sk}$. In this case, $\Delta R_{total} = n2R_c$ and the values used to plot R_{total} vs. d have a non-linear scaling, due to the n multiple of $2R_c$. For very low values of R_c relative to R_{total} , as for instance when R_c is less than the measurement error in R_{total} , negligible error to the linearisation of R_{total} vs. d is introduced.
- **Scenario 3:** Non-negligible current flows through both the interjacent finger and the underlying doped region. In this instance, $\Delta R_{total} = nR_{eq}$ which will introduce non-negligible error for high R_c , and r_{sk} .

The relative error in ρ_c and R_c values extracted is the important parameter of interest when assessing the validity of this technique. However, due to the linear fitting and extrapolation of ρ_c and R_c from R_{total} measurements, the relative error in the extracted values are difficult to quantify as the error was not simply added or multiplied through to the final calculation—rather it is input into a linear regression. Each R_{total} measurement has its own relative error, ΔR_{total} , and these errors are factored into a value which is ultimately used in the linear fitting of a parameter, making an absolute value for the relative error extraction complicated. A possible method to overcome this issue is to compare the different values of ΔR_{total} for each scenario above against the absolute measured values of R_{total} . A comparison of the magnitude of ΔR_{total} relative in R_{total} can then be used to qualitatively infer whether the linear fitting is appropriate. In this work, although a total number of 8 interjacent fingers is allowed by the structures, all extracted values were fitted with no more than 6 interjacent fingers (and therefore 5 distance intervals), and in the cases where high contact resistance was formed, a maximum of 4 distance intervals was used.

3.1.2 Results

3.1.2.1 Effect of wrap-around on optical properties

Reflectance measurements were taken on representative samples for each AlO_x thickness and are shown in Figure 3.8.

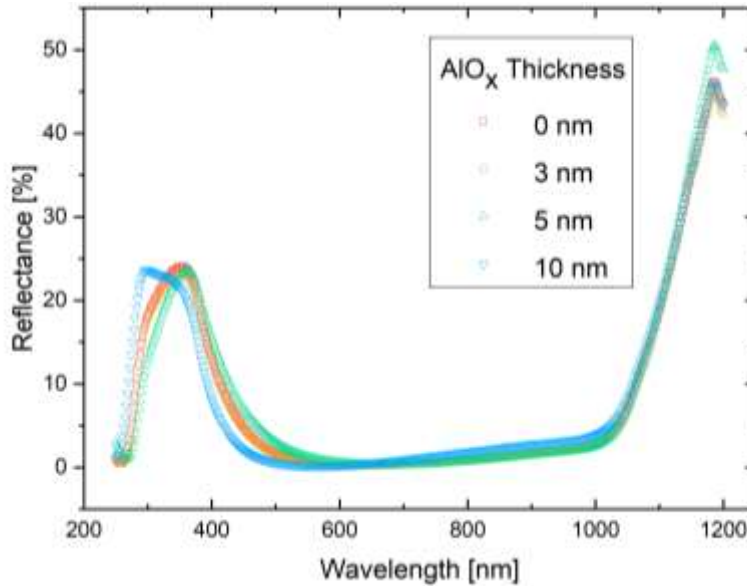


Figure 3.8 Reflectance as a function of wavelength for $\text{SiN}_x/\text{AlO}_x$ coated samples with various AlO_x thicknesses. The SiN_x thickness was ~ 75 nm for each sample.

The weighted average reflection (WAR) under air was found to be 4.26 % (0 nm AlO_x), 4.18 % (3 nm AlO_x), 4.08 % (5 nm AlO_x), and 4.74 % (10 nm AlO_x), respectively. The WAR was calculated using the AM1.5G spectrum from 280–1200 nm. To estimate the potential effect of wrap-around layers on the cell J_{sc} , the reflectance was modelled in OPAL 2 for a random pyramid textured surface, which found the J_{sc} to be 43.1 mA/cm², 43.1 mA/cm², 43.2 mA/cm² and 42.9 mA/cm² for the 0, 3, 5 and 10 nm cases respectively [104]. This suggests that a thin layer (3 and 5 nm) of AlO_x wrap-around is likely to have a very minimal effect, if any, on the overall optical performance of the solar cell.

3.1.2.2 Effect of paste formulation and firing duration for samples with $N_{D,s} = 6.6 \times 10^{19} \text{ cm}^{-3}$

The measured ρ_c for silver contacts formed on the lower $N_{D,s}$ precursor wafers ($N_{D,s} = 6.6 \times 10^{19} \text{ cm}^{-3}$) using the DuPont paste is shown in Figure 3.9, and the results for samples printed with Heraeus paste is shown in Figure 3.10. Upon inspection of Figure 3.9, a ‘U-shaped’ trend is evident for the control case, with optimum contact resistivity achieved for a firing temperature of 750 °C. In most cases, the measured ρ_c is higher for all AlO_x thicknesses, and the only exception was the samples fired at 676 °C, which had

slightly lower average ρ_c for the 3 nm AlO_x capping. The 3 nm samples approached acceptable ρ_c values, averaging $1.28 \text{ m}\Omega\cdot\text{cm}^2$ and $1.72 \text{ m}\Omega\cdot\text{cm}^2$ for the 726°C and 750°C groups, respectively. However, all other thicknesses and temperatures formed poor ohmic contact.

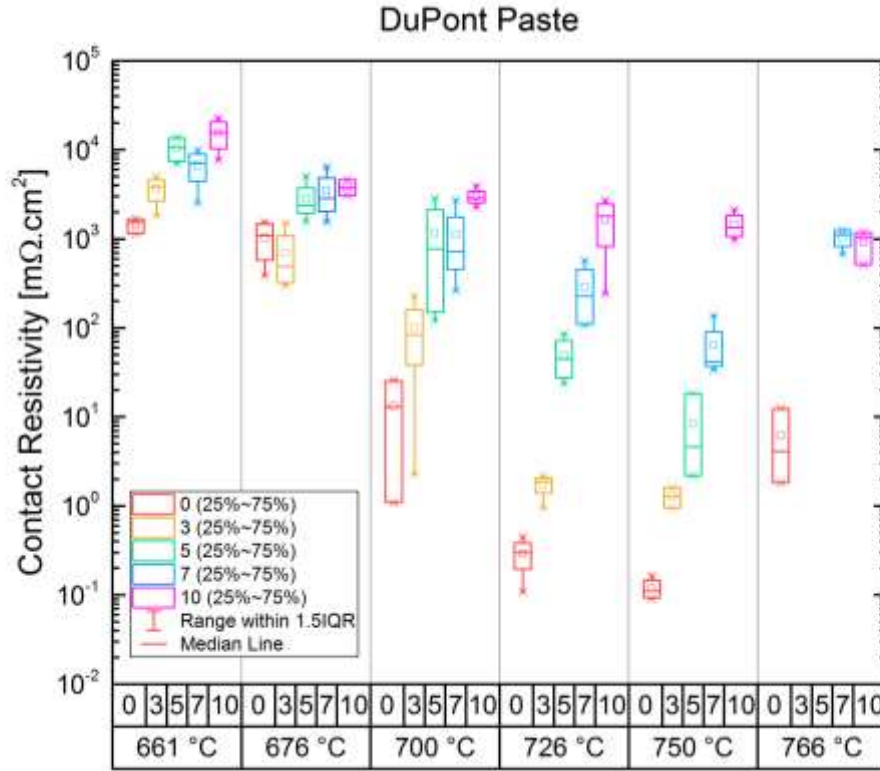


Figure 3.9 Contact resistivity vs. firing temperature for DuPont paste contacts formed on precursor wafers with $N_{D,s} = 6.6 \times 10^{19} \text{ cm}^{-3}$, for various AlO_x thicknesses.

Similar trends were observed for the Heraeus paste, with the uncapped control recording lower average ρ_c values for all temperatures. Comparing Figure 3.9 and Figure 3.10, the AlO_x samples printed with Heraeus paste recorded lower ρ_c values for all thicknesses (at given firing temperatures) with average ρ_c values $< 10 \text{ m}\Omega\cdot\text{cm}^2$ for 0, 3, 5 and 7 nm of AlO_x wrap-around. This suggests that to an extent, the adverse effects of wrap-around can be mitigated by simply changing paste formulation. However, the control samples recorded lower average values with DuPont paste for the optimum firing temperature range of $726\text{--}750^\circ\text{C}$.

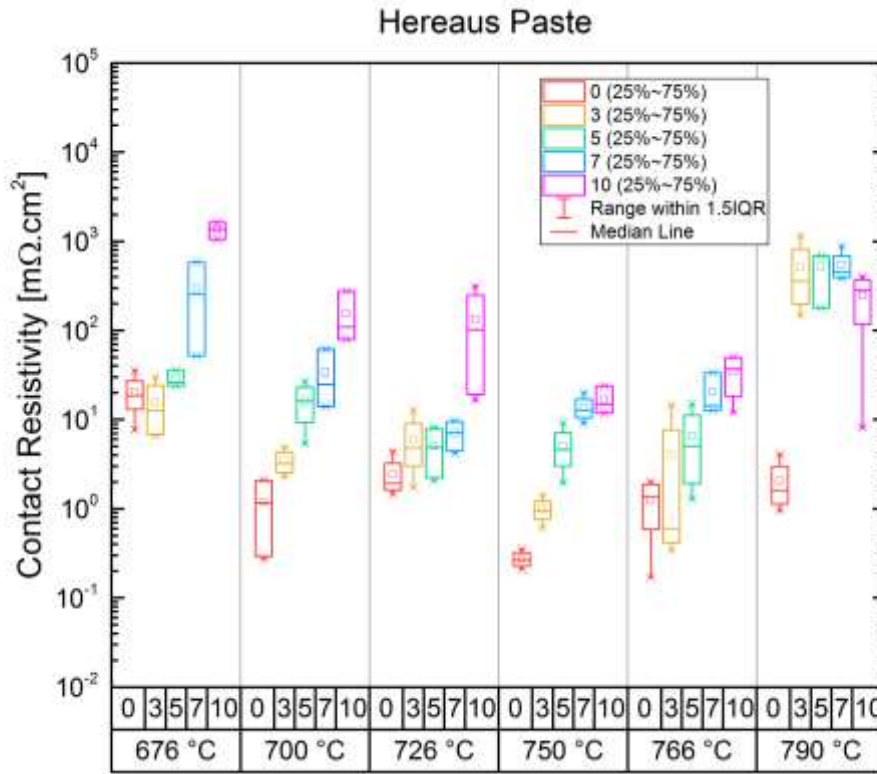


Figure 3.10 Contact resistivity vs. temperature for Heraeus paste contacts formed on precursor wafers with $N_{D,S} = 6.6 \times 10^{19} \text{ cm}^{-3}$, for various AlO_x thicknesses.

3.1.2.3 Effect of varying belt speed

The firing of screen-printed silver contacts is a time dependent processes with an optimum process duration; too short and the silver paste does not penetrate the SiN_x to the underlying silicon; too long and the silver penetrates deep into the diffused surface and, if severe enough, potentially shunts the cell by contacting the pn junction. Although this latter effect is quite unlikely for the current generation of commercial pastes. To assess if the high ρ_c values observed for the thicker AlO_x layers was a result of under firing, the belt speed was slowed to settings S1 (180 inches/min), S2 (160 inches/min) and S3 (140 inches/min), with S1 representing the control case. The corresponding ρ_c of the contacts formed at these speeds for two temperatures—726 °C and 750 °C, as they correspond to the minima in Figure 3.9 and Figure 3.10—is shown in Figure 3.11. The results do not indicate that increases in the firing duration will improve ρ_c for AlO_x wrap-around thicknesses above 7 nm, since high ρ_c values were measured for all speeds and thicknesses. However, the general trend of the Heraeus paste producing lower resistivity contacts for wrap-around AlO_x samples in comparison to the DuPont paste was consistent, particularly in the 750 °C range.

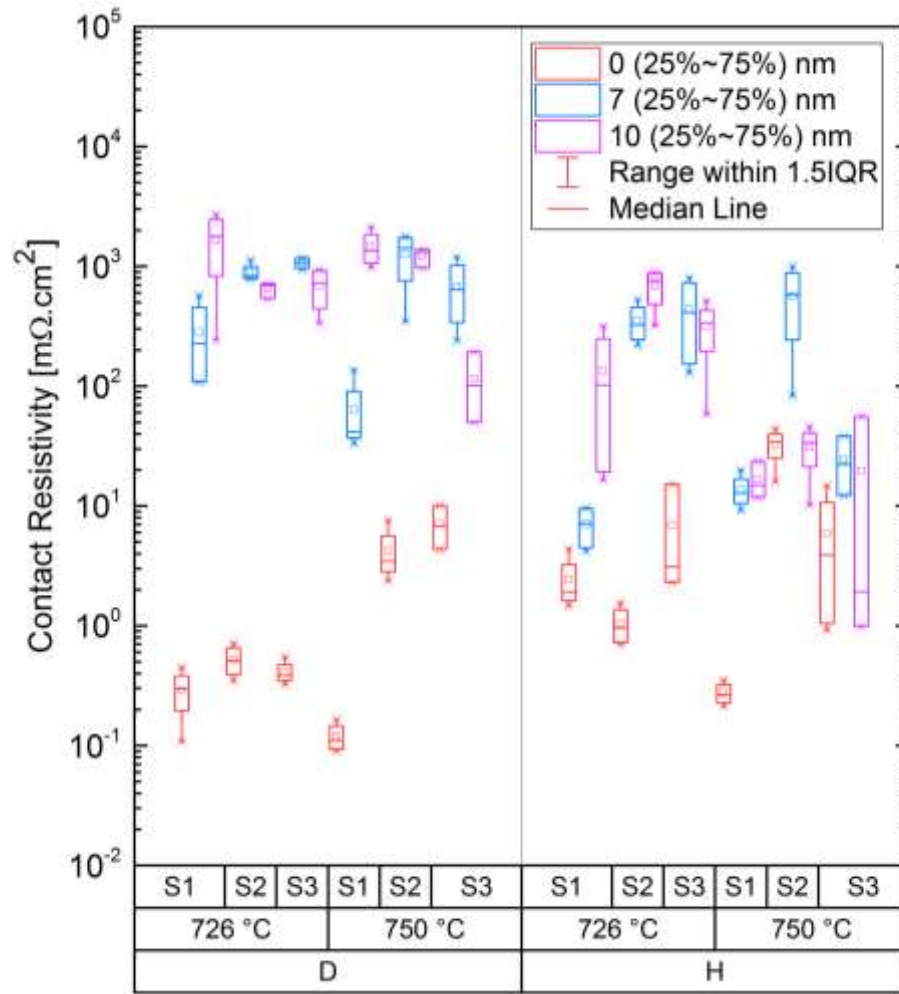


Figure 3.11 Contact resistivity for precursor samples with $N_{D,s} = 6.6 \times 10^{19} \text{ cm}^{-3}$ fired at belt speeds S1, S2 and S3 using both Heraeus and DuPont silver pastes, with AlO_x capping thicknesses ranging between 0–10 nm.

3.1.2.4 Effect of firing temperature on samples with $N_{D,s} = 1.8 \times 10^{20} \text{ cm}^{-3}$

The measured ρ_c values of the TLM structures fired over a temperature range of 613–766 °C is shown in Figure 3.12. The measured ρ_c as a function of temperature for the uncapped case follows a roughly parabolic ‘U-shaped’ trend, corresponding to the intermediate 727 °C setting. This was consistent for the 3 nm and 5 nm AlO_x thicknesses, where the ρ_c minimum has shifted to 700 °C and 676 °C, respectively. For the 10 nm AlO_x thickness, ρ_c was consistently high across the full temperature range and there was no clear trend towards an optimum firing value. Increasing the firing temperature to 750 °C and 766 °C (set points of 875 °C and 900 °C, respectively) did not result in lower values of ρ_c for all samples. In this higher range, it was likely that the contacts were ‘over-fired’—whereby the metal penetrates into the silicon and forms contact with lower

phosphorus doped silicon—especially in the control case. It is noted that the 3 and 5 nm contacts seem to be more resistant to this effect, as was evident in the low ρ_c values at 750 °C in comparison to the control. However, the 10 nm AlO_x samples do not appear to form low resistance ohmic contact at these increased temperatures, as ρ_c remains high at elevated temperatures. The low end of the firing range (i.e., 613–661 °C) resulted in a sharp increase in ρ_c , suggesting that the contacts were underfired at these temperatures for all thicknesses.

The results presented in Figure 3.12 suggest an optimum firing temperature range of 676–727 °C for the 3 nm, 5 nm and control samples. Samples with 3 and 5 nm thicknesses formed lower resistivity contacts in comparison to the control case across all temperatures in this range. In comparison to published values of ρ_c , the average values for the 3 nm and 5 nm cases at 0.06 $\text{m}\Omega\cdot\text{cm}^2$ and 0.11 $\text{m}\Omega\cdot\text{cm}^2$ were roughly an order of magnitude lower than previously published best-in-class results at equivalent surface doping concentrations [159, 160], although in making this comparison it should be noted that a ladder TLM pattern was not used in the cited comparative works, as it was used herein. Furthermore, the lowest ρ_c values for both 3 and 5 nm samples were achieved at temperatures lower than the optimum firing temperature of the control case. This suggests that 3 and 5 nm of AlO_x aids the formation of ohmic contact between the silver and the underlying silicon. In this AlO_x thickness range, the ρ_c was minimised for all firing conditions.

Furthermore, the optimum firing temperature appears to be lower for these samples, with the lowest ρ_c values for all thicknesses and the control case being 750 °C, in comparison to 700–727 °C the higher $N_{D,s}$ samples. In addition, the measured ρ_c values for the higher $N_{D,s}$ samples are lower for equivalent samples with lower $N_{D,s}$. These two effects are likely due to the combined effect of a residual SiO_x layer formed during the post-implantation annealing process, which presents an additional barrier to the silver paste contacting the silicon in these samples, which is absent in the higher $N_{D,s}$ samples. The difference in surface concentration between the samples, may also account for some of the observed differences between the two pastes, if one paste formulation was able to form better contact to lower surface concentrations. The 3 nm samples approached acceptable ρ_c values, averaging 1.28 $\text{m}\Omega\cdot\text{cm}^2$ and 1.72 $\text{m}\Omega\cdot\text{cm}^2$ for the 726 °C and 750 °C groups, respectively. However, all other thicknesses and temperatures formed poor ohmic contact.

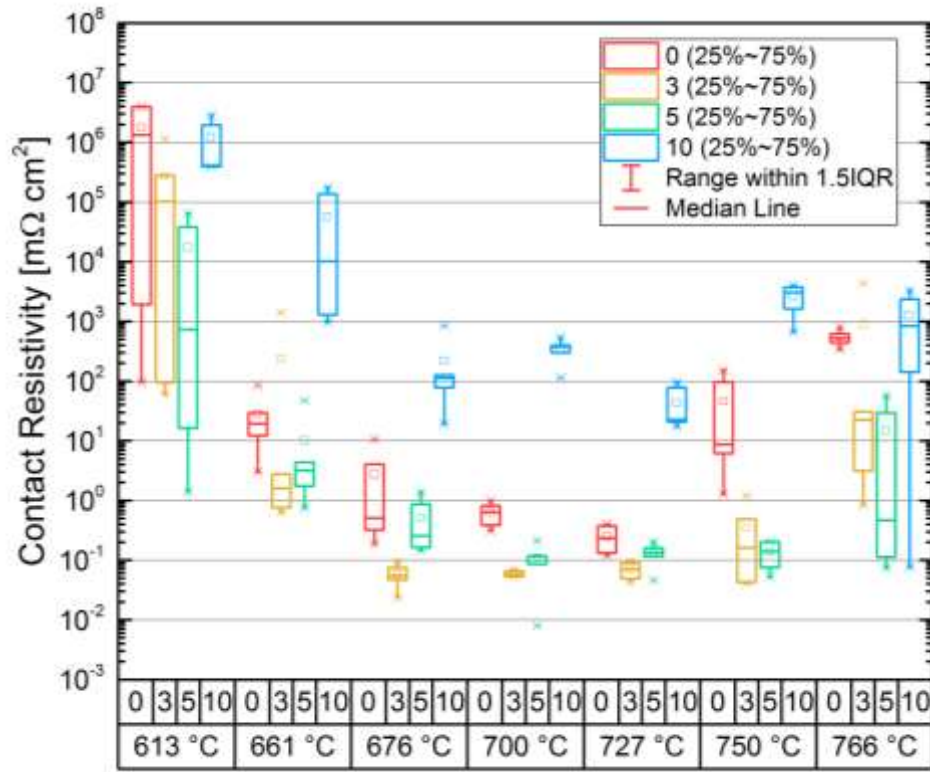


Figure 3.12 Contact resistivity vs. temperature for screen-printed silver fingers fired through an $\text{AlO}_x/\text{SiN}_x$ stack with $N_{D,s} = 1.8 \times 10^{20} \text{ cm}^{-3}$ (profile A, Figure 3.3). The AlO_x film thicknesses values are 3, 5, and 10 nm, with 0 nm representing the uncapped control scenario. These values were extracted from equidistant TLM test structures, as shown in Figure 3.6.

3.1.2.5 Discussion

The samples with 10 nm AlO_x resulted in high ρ_c values suggesting further optimisation was required. Figure 3.12 depicts a variance in the ρ_c which is reduced around the minimum firing temperature. This is partly a result of the systematic error in the TLM method used, which has higher inherent error for high resistance contacts, and less error for low resistance contacts—as is outlined in Ref. [161]. This inherent error was calculated to not significantly affect the results for ρ_c values below $10 \text{ m}\Omega\cdot\text{cm}^{-2}$; however this cannot account for the variances observed for samples with low ρ_c values, which was likely due to non-uniformities in the samples as they affect the metalisation process.

A thorough investigation of the silver-silicon (Ag-Si) interface during firing is required to explain the observed trend in contact resistance and temperature in Figure 3.12. This investigation is beyond the scope of this work and is made more difficult since the composition of the pastes used in this work are confidential. However, Al_2O_3 has been included previously in paste formulations studied by various researchers as part of the

composition of glass ceramics used to facilitate the wetting and etching of the SiN_x layer during firing [162-165]. Although the role of Al_2O_3 in these formulations is not singularly studied or acknowledged, it is known that glass frits are used to facilitate access of the silver ions to the interface where they may form precipitates, and that the thickness of the formed liquid glass interfacial layer affects the transport of silver particles to the silicon surface [162, 166]. Therefore, it is possible that a 3 and 5 nm layer facilitates in an optimal wetting and formation of a liquid-phase glass layer which is conducive to the formation of low ohmic contact at lower temperature through the improved transport of silver particles and etching at the interface via the frit process. However, when thicker AlO_x layers are applied, this optimal liquid-phase glass layer thickness and/or composition is surpassed, and hinders the flow of silver particles, and increases the contact resistance. Further investigation is required to fully understand the exact mechanism which underlies the observed results.

3.1.2.6 Contact resistivity error analysis

Figure 3.13 plots the various ΔR_{total} component values of R_{total} for each of the three scenarios listed in Section 3.1.1.1. The absolute error ΔR_{total} for the Scenarios 1, 2 and 3 is represented in Plots (a), (b) and (c), respectively, relating to the samples fired with DuPont paste only. By comparing the values in Figure 3.13 (a), (b) and (c) against Figure 3.13 (d), a qualitative impression of the relative error inherent in R_{total} —used in the linear extraction of R_c and ρ_c —was obtained. As ΔR_{total} increases relative to R_{total} , as a result of increasing n , R_c or R_{sheet} , the extracted values of R_c and ρ_c incur higher inherent error.

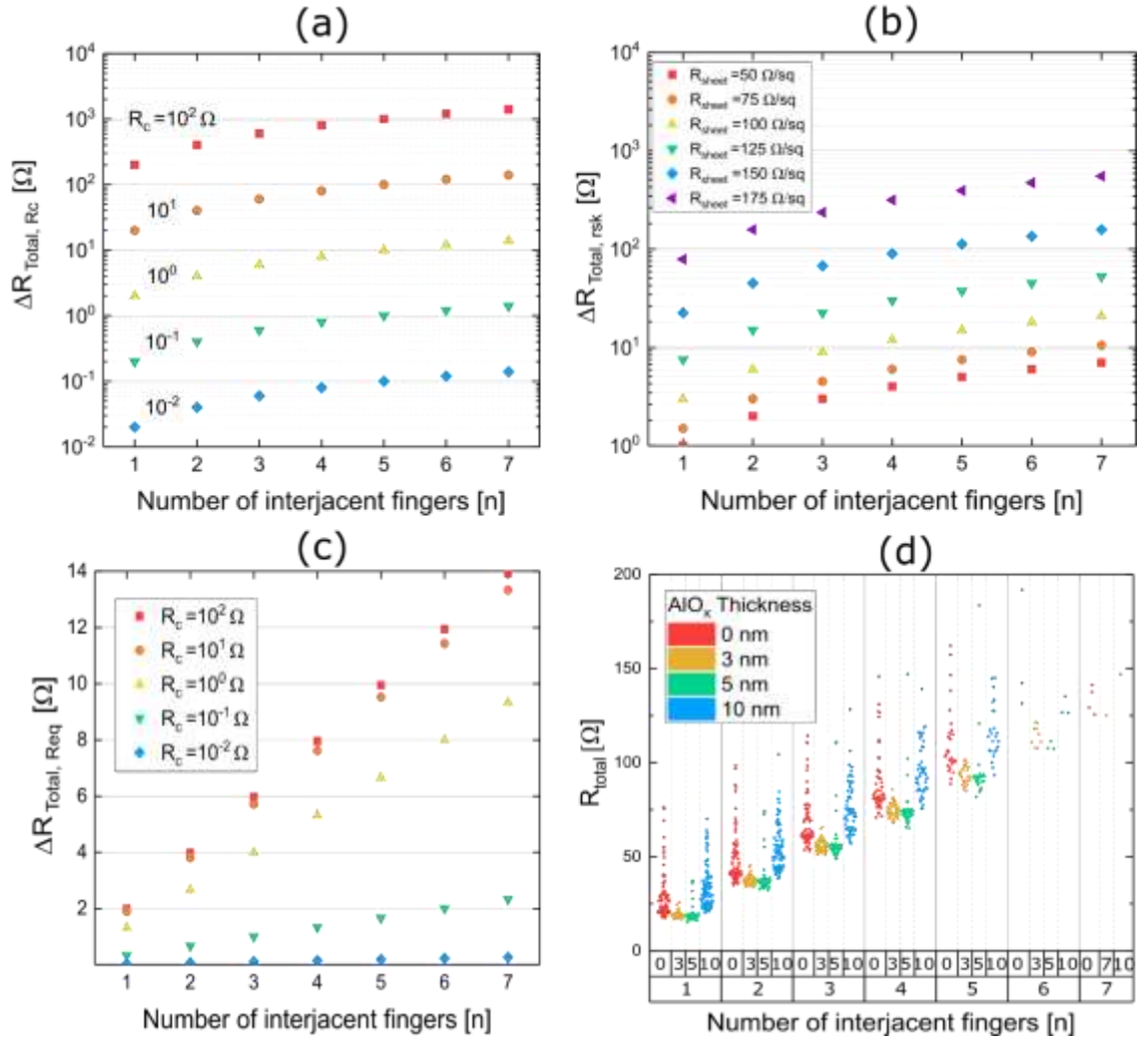


Figure 3.13 Absolute error ΔR_{total} for the Scenarios 1, 2 and 3, is represented in (a), (b) and (c), respectively, with (d) showing the measured R_{total} as a function of n for all samples and AlO_x thicknesses.

In all plots, it was evident that ΔR_{total} for all scenarios increases with n , which suggests that for this method, the addition of extra distances in the measurement does not necessarily result in a more consistent or accurate linear fit used to extract ρ_c and R_c . In Plot (a), a low R_c contact contributes less absolute error to R_{total} measurements, suggesting that this method is more accurate for low resistivity contacts. The same is true when R_{sheet} is low, as this will reduce the error component r_{sk} , plotted in Plot (b) of Figure 3.13. It follows that a low resistance contact which also has low r_{sk} (i.e., due to low R_{sheet} or a high W relative to L) will in turn result in a lower ΔR_{eq} , and that the converse is true for R_c and r_{sk} values resulting in high ΔR_{eq} and therefore higher error. In Scenario 3 (shown in Plot (c)), if $2R_c < r_{sk}$, because r_{sk} and R_c are in a parallel resistance network despite high values of $\Delta R_{total, rsk}$, the values of $\Delta R_{total, Req}$ are much smaller than $\Delta R_{total, rsk}$. In this sense,

the relative values of R_c and r_{sk} when added in a parallel network results in a lower value of ΔR_{total} relative to Scenarios 1 and 2 (which remain without the option of parallel current flow) as the current is split between the higher and lower resistance paths.

As ΔR_{total} increases relative to R_{total} , due to increasing n , R_c or R_{sheet} , the extracted values of R_c and ρ_c are fitted with values of higher error. Therefore, measurements across a larger number of fingers is not advised unless R_c and r_{sk} are known to be very low relative to R_{total} (hence, kept to a maximum of 6 interjacent fingers in the results presented). In summary, this technique has less inherent error for lower resistance contacts.

3.1.3 Summary

AlO_x wrap-around onto the front SiN_x ARC has a significant impact on the firing properties of silver screen-printed paste. It was found that a wrap-around thickness of 3–5 nm layers on precursor wafers with $N_{D,s} = 1.8 \times 10^{20} \text{ cm}^{-3}$ produced lower ρ_c values at a lower firing temperature than the uncapped control case. However, a 10 nm layer severely increased the ρ_c of the contact formed on these precursors. When comparing the results on PERT precursor samples with $N_{D,s} = 6.6 \times 10^{20} \text{ cm}^{-3}$, the benefits of a 3–5 nm layer were not observed. This was likely due to the combined effect of reduced surface concentration and the residual SiO_x layer affecting the metallisation process. Furthermore, increasing the firing duration did not affect a reduction in ρ_c within an acceptable range. However, it was found that samples printed with Heraeus paste produced lower resistivity contacts in comparison to DuPont paste samples of the same thickness and fired at the same temperature. This suggests that the adverse effects of thick AlO_x wrap-around can be mitigated by changing paste formulations.

For a typical H-pattern grid, the total series resistance scales linearly with the contact resistance, until below some threshold value, whereby other components of series resistance dominate and ρ_c becomes irrelevant. Therefore, given the ρ_c values achieved in Figure 3.12, a corresponding increase in efficiency from an improved fill factor (FF) when local AlO_x wrap-around is 3–5 nm thick may occur if the contact resistivity is limiting. Similarly, a decrease in performance for the 7–10 nm layers, would be expected. This effect was explored in detail through FEM simulations in Section 3.2.

3.2 Modelling the effect of AlO_x wrap-around

In this section, the results of the previous experiments were used as input parameters for Griddler (v2.5 Pro) simulation of a typical p -PERC solar cell to investigate the potential impact of wrap-around on the current, voltage and series resistance characteristics, to simulate the effect on FF and efficiency.

3.2.1 Methodology

A full area 156 mm square industrial p -PERC solar cell was simulated in Griddler using published performance parameters of a typical industrial p -PERC cell, with parameters taken from Refs [144, 167] and the measured ρ_c values from Section 3.1. The full list of simulation inputs, their values and corresponding references is listed in Table 3.1, as well as the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), FF and efficiency of the simulated baseline cell without wrap-around, which uses ρ_c values for the front silver contact from Section 3.1.

A standard front grid pattern was used in the simulation with 100 fingers of 60 μm width and 5 busbars of 1.33 mm width. Griddler uses well-known approximations to obtain effective recombination parameters of rear point contact schemes [168-170]. The rear p^+ diffused region consisted of localised line contacts of width 60 μm and pitch 1.29 mm. J_0 values for the passivated and metallised regions were set based on values from Ref. [144].

To study the effect of unintended front side AlO_x deposition, varying extents of wrap-around at the cell edge were simulated by imposing border regions of higher and lower contact resistance on the front side of the wafer. These border regions were scaled to simulate wrap-around thicknesses varying between 2–25 mm from the edge for 3, 5 and 10 nm AlO_x thicknesses, on the front side of the wafer. These border regions were enabled through Griddler's non-uniformity tool, in which an image of the non-uniformity was superimposed on the cell schematic to specify regions of variance of a given cell parameter. In this work, the ρ_c of the contact formed in the region with wrap-around, ρ_{c,AlO_x} , and the ρ_c in the region without wrap-around, ρ_{c,SiN_x} , were defined across the wafer through a normalised value given by

$$\rho_{c, \text{normalised}} = \frac{A_{\text{AlO}_x} \rho_{c,\text{AlO}_x} + A_{\text{SiN}_x} \rho_{c,\text{SiN}_x}}{A_{\text{AlO}_x} + A_{\text{SiN}_x}}, \quad \text{Eq. (3.6)}$$

where A_{AlO_x} and A_{SiNx} are the areas affected and unaffected by AlO_x wrap-around respectively. Griddler does not allow for the specification of A_{AlO_x} , A_{SiNx} , $\rho_{c,SiNx}$ and ρ_{c,AlO_x} directly, and instead derives these values from the non-uniformity image. The areas A_{AlO_x} and A_{SiNx} were extracted from the geometry of the non-uniformity image, whereas ρ_{c,AlO_x} and $\rho_{c,SiNx}$ were extracted according to their RGB colour value. A single average value of ρ_c for each thickness was used in the simulations, to obtain a representative value for each firing group taken from Section 3.1 for the firing temperature 727 °C and AlO_x thicknesses 0, 3 5 and 10 nm. With the non-uniformity specified locally, the solar cell efficiency and fill factor were calculated for each group to demonstrate the effect of non-uniform ρ_c .

Table 3.1 Input parameters for the Griddler simulation of a *p*-PERC solar cell

Symbol	Parameter	Value
T	Temperature	298.15 K
G	Illumination (Front)	AM 1.5 G
W	Thickness	180 μm [167]
	Wafer dimensions	156 mm x 156 mm, full square
	Number of fingers, front	100 [144] (H-grid,5 busbars)
	Rear BSF width	60 μm
	Rear contact pitch	1.29 mm
N_A	Bulk doping (<i>p</i> -type)	$1.05 \times 10^{16} \text{ cm}^{-3}$ [144]
τ_{bulk}	Bulk minority carrier lifetime	600 μs [144]
$R_{sheet, front}$	Front n^+ sheet resistance	90 $\Omega/\square$ [167]
$R_{sheet, rear}$	Rear p^+ sheet resistance	61 $\Omega/\square$ [167]
$\rho_{c, front}$	Front contact resistivity ¹	0.241 $\text{m}\Omega.\text{cm}^2$
$\rho_{c, rear}$	Rear contact resistivity	5 $\text{m}\Omega.\text{cm}^2$ [167]
$J_{01, front}$	Front passivation J_{01}	168 fA/cm^2 [167]
$J_{02, front}$	Front passivation J_{02}	3 nA/cm^2 [144]
$J_{01, metal front}$	Front metal recombination	595 fA/cm^2 [167]
$J_{01, rear passivatedl}$	Rear metallised recombination	13.1 fA/cm^2 [167]
$J_{01, rear metal}$	Rear passivated recombination	795 fA/cm^2 [144]
$J_{02 rear}$	Rear recombination	3 pA cm^{-2} [144]

¹This value corresponds to the average ρ_c of the control case measured fired at 727 °C in Section 3.1. This parameter was varied as input to the simulations in this section.

3.2.2 Results

The Griddler simulated solar cell performance parameters of the non-wrap-around control case are shown in Table 3.2. The values for efficiency (η), V_{oc} , J_{sc} and FF matched well to current state of the art p -type PERC solar cells [140, 144, 167]. The simulated efficiency and FF of p -PERC solar cells with varying extents of wrap-around and AlO_x thickness is plotted in Figure 3.14(a) and Figure 3.14(b), respectively. This temperature setting was chosen to replicate the firing conditions in a manufacturing environment, as this temperature was the optimum temperature for the uncapped case and therefore any wrap-around would subsequently be fired at the same temperature. From the simulation results, it was evident that the effect of wrap-around on cell performance was highly dependent on the thickness of AlO_x deposited. For the 3 and 5 nm thicknesses—which for this temperature formed lower resistance contacts to the underlying silicon—the efficiency and FF were equivalent to the control case. Furthermore, as the wrap-around extent increased, the efficiency and FF remained effectively constant. This indicates that the cells were not limited by contact resistance at the Ag-Si contact; therefore, reductions in series resistance are masked by some other limiting component of series resistance—such as metal resistance, bulk resistance or sheet resistance.

Table 3.2 Griddler simulated performance characteristics of a p -PERC solar cell without AlO_x wrap-around.

Symbol	Parameter	Value
η	Efficiency	21.31 %
V_{oc}	Open circuit voltage	662 mV
J_{sc}	Short circuit current density	39.87 mA.cm ⁻²
FF	Fill factor	80.77 %

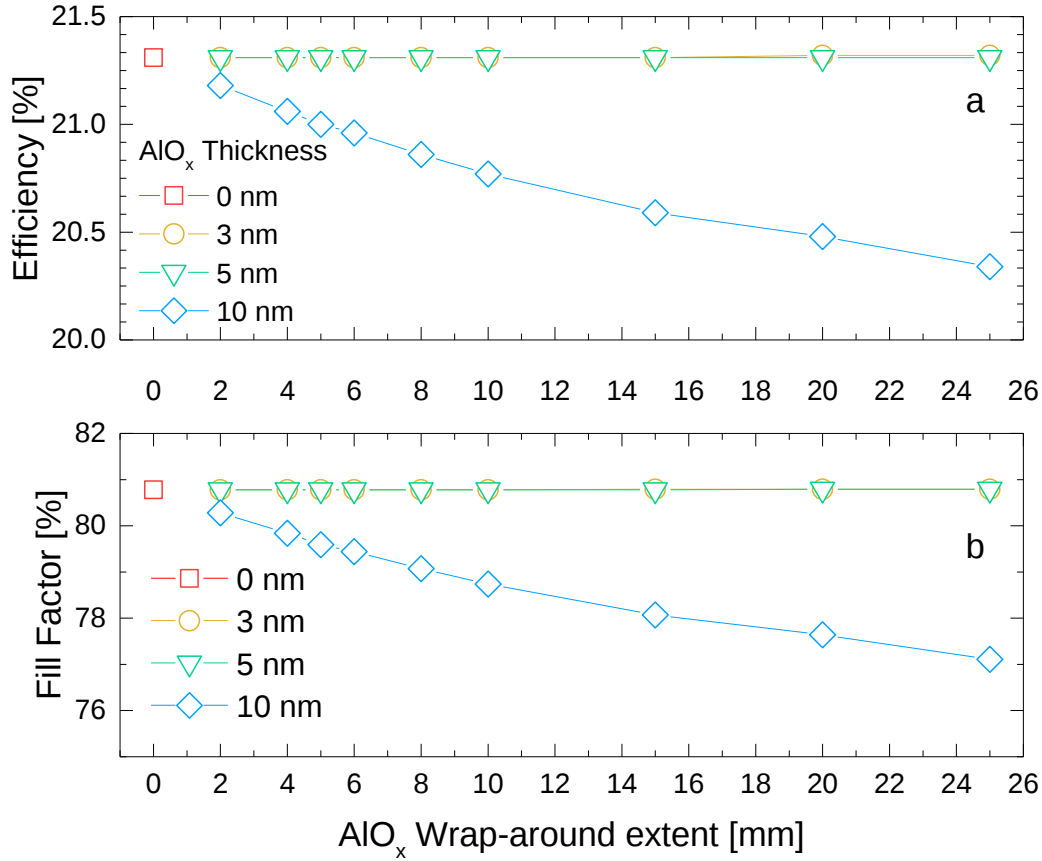


Figure 3.14 Simulated effect of parasitic front side AlO_x deposition on: (a) efficiency; and (b) *FF*, of a *p*-PERC solar cell. The simulation uses the input parameters listed in Table 3.1 and varies the front contact resistivity values, taking average values for each AlO_x thickness fired at 727 °C.

In contrast, the efficiency and *FF* of samples with a 10 nm AlO_x showed a strong response to increasing the extent of wrap-around. Both the efficiency and *FF* reduced with increased wrap-around extent, with only 25 mm of wrap-around causing a 0.84 % and 3.17 % absolute decrease in efficiency and *FF*, respectively. This was due to the increase in series resistance from collecting carriers from the outer affected regions of the cell. This effect was also evident in simulated photoluminescence (PL) images of the control and 10 nm wrap-around samples, taken at maximum power point voltage (V_{mpp}) with current extraction, shown in Figure 3.15, where areas of higher series resistance have higher luminescence counts. Carriers in areas of higher series resistance were not as effectively collected at V_{mpp} compared to carriers in areas with a lower series resistance, resulting in a higher carrier concentration and consequently higher PL intensity at these high resistance areas [171].

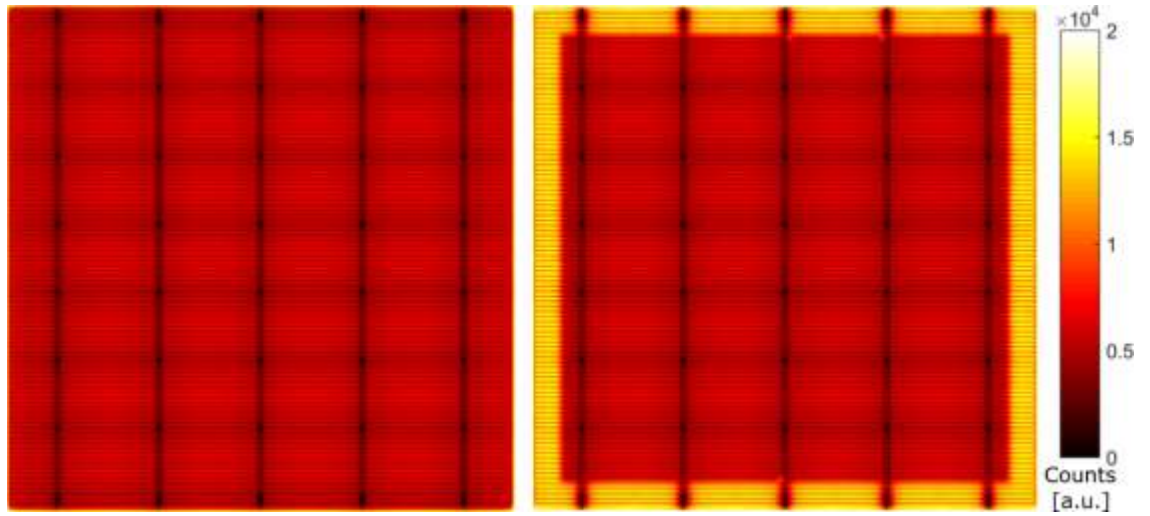


Figure 3.15 Simulated PL images (at V_{mpp} with current extraction) of a p -PERC solar cell with (left) 0 and (right) 10 mm of 10 nm thick AlO_x wrap-around deposition. The effect of increased ρ_c is resolved spatially across the wafer surface, as indicated by the brighter border on the right-hand image.

From the simulations, it is evident that a 10 nm wrap-around has an adverse impact on the cell performance. However, a 3 and 5 nm wrap-around extent is unlikely to have an adverse effect, when fired at an optimal firing temperature, and practically no appreciable difference was observed between the 3 and 5 nm scenarios, in fact, they are more likely to have higher efficiencies as the contact resistance is lower. The simulation results suggest that thin layers of 3 or 5 nm AlO_x on top of SiN_x have a negligible effect on industrial p -PERC cell efficiency for wrap-around of up to 25 mm in from the cell edge. However, in the event of thicker layers of AlO_x which increase the ρ_c , the cell performance will decrease with increasing wrap-around extent.

3.2.3 Summary

A p -PERC solar cell model was developed in Griddler Pro and the performance of a characteristic, industrial p -PERC solar cell successfully reproduced. The ρ_c results from Section 3.1.2 were input into the simulation to predict the effect of various wrap-around extents on a complete solar cell, as would be the case in a production environment. It was found that a 3 and 5 nm AlO_x wrap-around thickness does not reduce cell FF nor efficiency in the simulations, and was constant for all wrap-around extents simulated, as far as 25 mm in from the cell edge. This confirms the previous inference in the summary of the previous section, as the cells were likely limited by some other series resistance component. Furthermore, the 10 nm thick AlO_x wrap-around layers had an adverse effect

on the overall solar cell performance, with a 25 mm wrap-around extent producing a significant drop in FF and efficiency, again confirming the relationship between contact resistance and FF .

3.3 Effect on solar cell performance

A summary and analysis of cell results is presented in this section for full rear Al-BSF devices which were fabricated with varying thicknesses of ALD deposited AlO_x over the full area of the front SiN_x ARC. These results are a demonstration of the results presented in Sections 3.1 and 3.2.

3.3.1 Methodology

Full rear Al-BSF cells were fabricated using p -type Cz monocrystalline silicon wafers. The starting wafers were 180 μm thick, 156 mm pseudo-square in size and had measured average bulk resistivity of 1.6 $\Omega \cdot cm$. The wafers were saw damage etched in a standard NaOH solution (25 % w/v) to remove $\sim 10 \mu m$ from each side. The wafers were then alkaline textured (NaOH:IPA:H₂O, 75 °C for 25 minutes) before a full Radio Corporation of America (RCA) clean [172] and HF dip. They were subsequently diffused to form the n^+ emitter in an industrial POCl₃ tube furnace (TS8603, Tempress System). The results in Section 3.2 indicate that a ρ_c limited cell is required to distinguish the 3 and 5 nm layers, and so the cells described in this section were deliberately fabricated with a very low n^+ surface concentration. This was done to ensure that ρ_c was the limiting factor in the device, and to give greater relative insight into the differences between 0, 3, 5 7 and 10 nm thick AlO_x layers on top of the SiN_x ARC. The active phosphorus profile for these cells is shown in Figure 3.3, Profile C. The diffused region had a sheet resistance of 100 $\Omega/\square$ ($\pm 2.5 \Omega/\square$), as measured using a four-point probe, and an active phosphorus surface concentration of $\sim 5.7 \times 10^{19} \text{ cm}^{-3}$ atoms. Following a phosphorus glass removal in dilute HF, an 80 nm PECVD SiN_x ARC was deposited on the front side of the wafer (MAiA system, Roth & Rau). A single side deposition of ALD AlO_x at thicknesses of 3, 5, 7 and 10 nm was then applied on top of the ARC to simulate full AlO_x wrap-around (KF1000 Advanced ALD System, Leadmicro), with additional samples omitted from ALD AlO_x deposition to serve as control samples. The samples were then screen-printed with an industrial rear surface aluminium paste and dried, before being cleaved into smaller 39×39 mm token wafers. Each reduced area sample was then printed with an H-

grid front contact pattern with a single busbar and finger spacing of 2.33 mm, using one of two commercial silver screen printing pastes: a) DuPont PV-19B; or b) Heraeus 9641B. The samples were co-fired at varying speeds and temperatures to assess the resulting effect on front Ag-Si contact formation. Corresponding to the optimum firing temperatures of the 0, 3 and 5 nm layers in **Error! Reference source not found.**, temperatures of 676, 700 and 726 °C respectively, were chosen for the DuPont samples. To allow for a direct comparison, samples printed with Heraeus paste were also fired at the optimum temperature of 726 °C. Following co-firing, the samples were edge isolated by laser scribing the cell outline on the rear side and mechanically cleaving off the excess edges, resulting in final solar cell dimensions of 29 mm × 29 mm. The cleaving was performed in such a way that at least 5 mm of the original 156 mm wafer edge was removed, ensuring the possible effect of rear side AlO_x wrap-around during the rear firing process is minimised. This processing sequence is summarised in Figure 3.16.

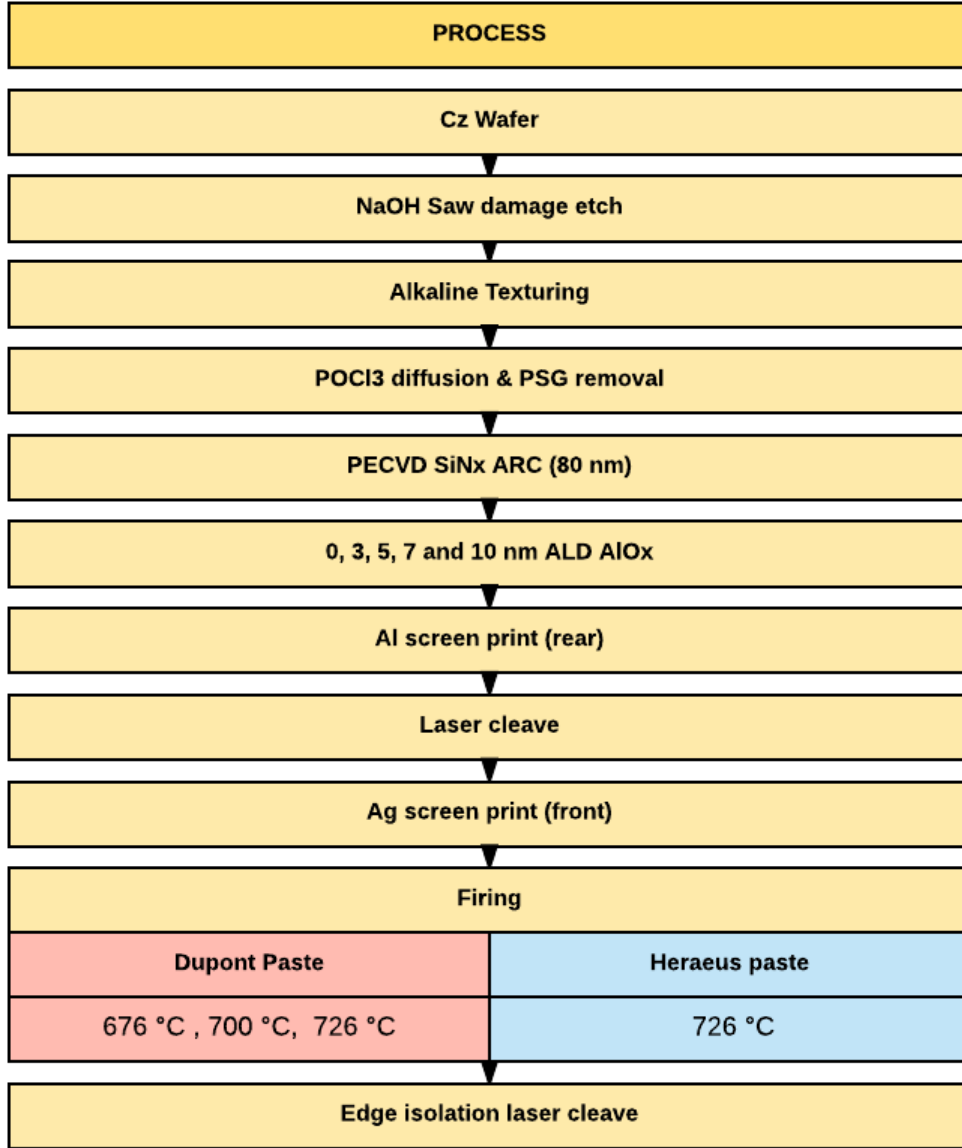


Figure 3.16 Processing sequence for the *p*-type Al-BSF cells fabricated in this work.

The cells were characterised using light and dark *I-V* measurements, as well as Suns- V_{oc} measurements using a Sinton Instruments WCT120 Suns- V_{oc} stage. The J_{02} and J_{01} parameters and shunt resistance were extracted from the Suns- V_{oc} measurement, and the series resistance was calculated according to the formula [173],

$$R_{series} = \frac{V_{mp,SunsVoc} - V_{mp,LIV}}{J_{mp,light}}, \quad \text{Eq. (3.7)}$$

where $V_{mp,SunsVoc}$ is the maximum power point voltage (V_{mp}) in the series-resistance free J_{sc} - V_{oc} curve, and $V_{mp,LIV}$ is the V_{mp} in the series-resistance affected light *I-V* curve, taking care to ensure that the cell resistivity, thickness and J_{sc} was accurately inputted, to reduce error in this method [174].

3.3.2 Cell results and discussion

The measured cell characteristics are shown in Figure 3.17 and Figure 3.18. Figure 3.17 (a) shows that the cells with 3 nm thick AlO_x layers were consistently the highest efficiency group for all firing temperatures. The cells with 5 nm thick AlO_x layers had similar average and median efficiency as the control case, although the variance of values was higher for the 5 nm samples. In Section 3.1, the lowest ρ_c values were achieved for a peak firing temperature of 676 °C and 700 °C for the 5 and 3 nm thicknesses, respectively. However, the best cell results were achieved for all thicknesses when fired at 726 °C. This was possibly due to non-optimal co-firing of the rear aluminium paste, since the results in Section 3.1 indicate that the front silver ρ_c was minimised at lower firing temperatures. Poorer n^+ passivation from a lower firing temperature may have played a minor role since the average V_{oc} values of the control case were marginally lower at 676 °C and 700 °C. However, this effect was not found to be statistically significant using a two-tailed t-test of significance level 0.05, and is at most 1 mV of difference on average between the control and 3 nm group. The cells with 7 and 10 nm AlO_x layers were less efficient for all temperature groups, which was consistent with the simulations and measurements presented in Sections 3.1 and 3.2.

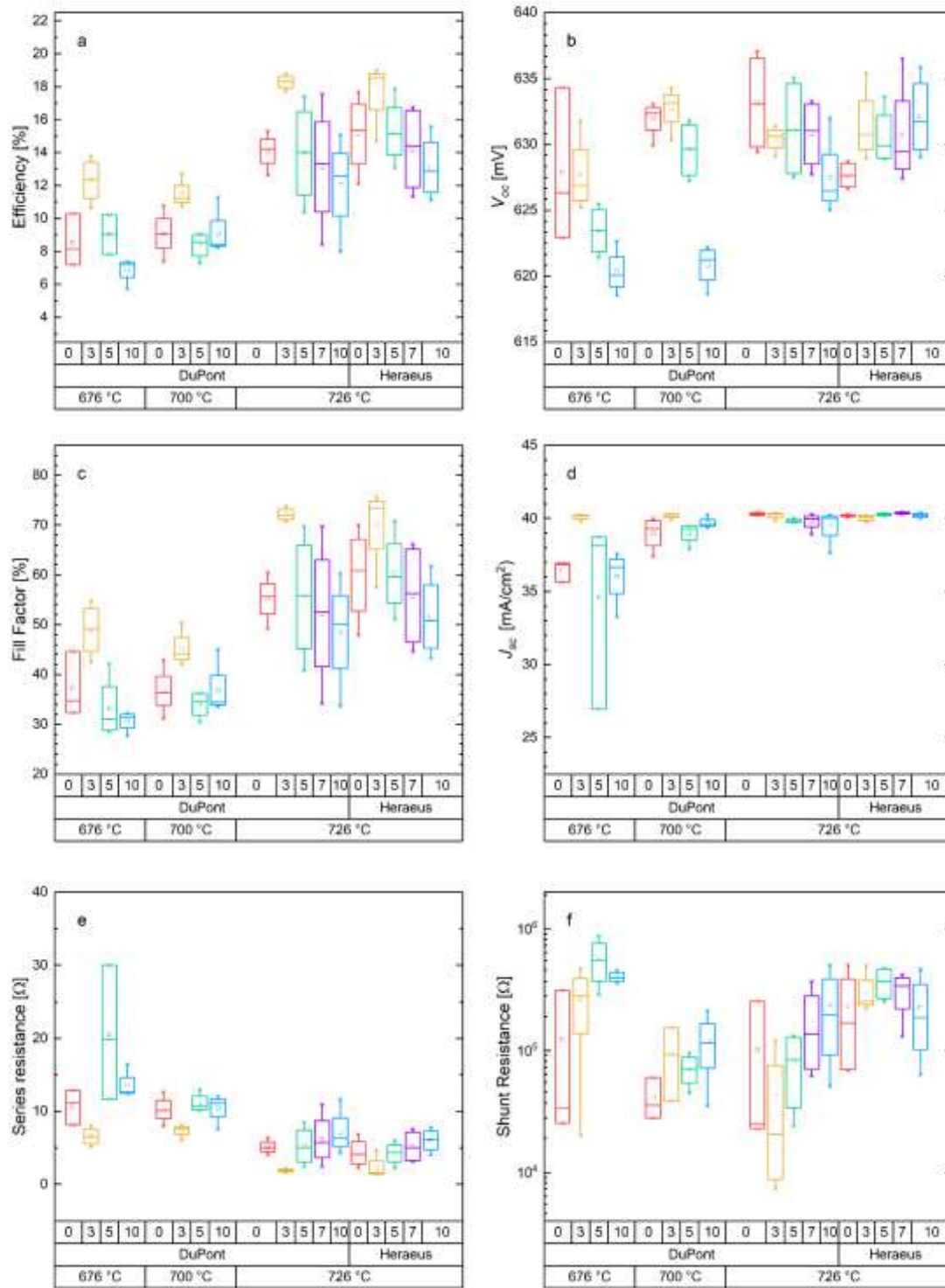


Figure 3.17 Cell characteristics extracted from light-IV, dark-IV and Suns- V_{OC} measurements for Al-BSF solar cells screen-printed with DuPont and Heraeus paste at varying peak temperatures.

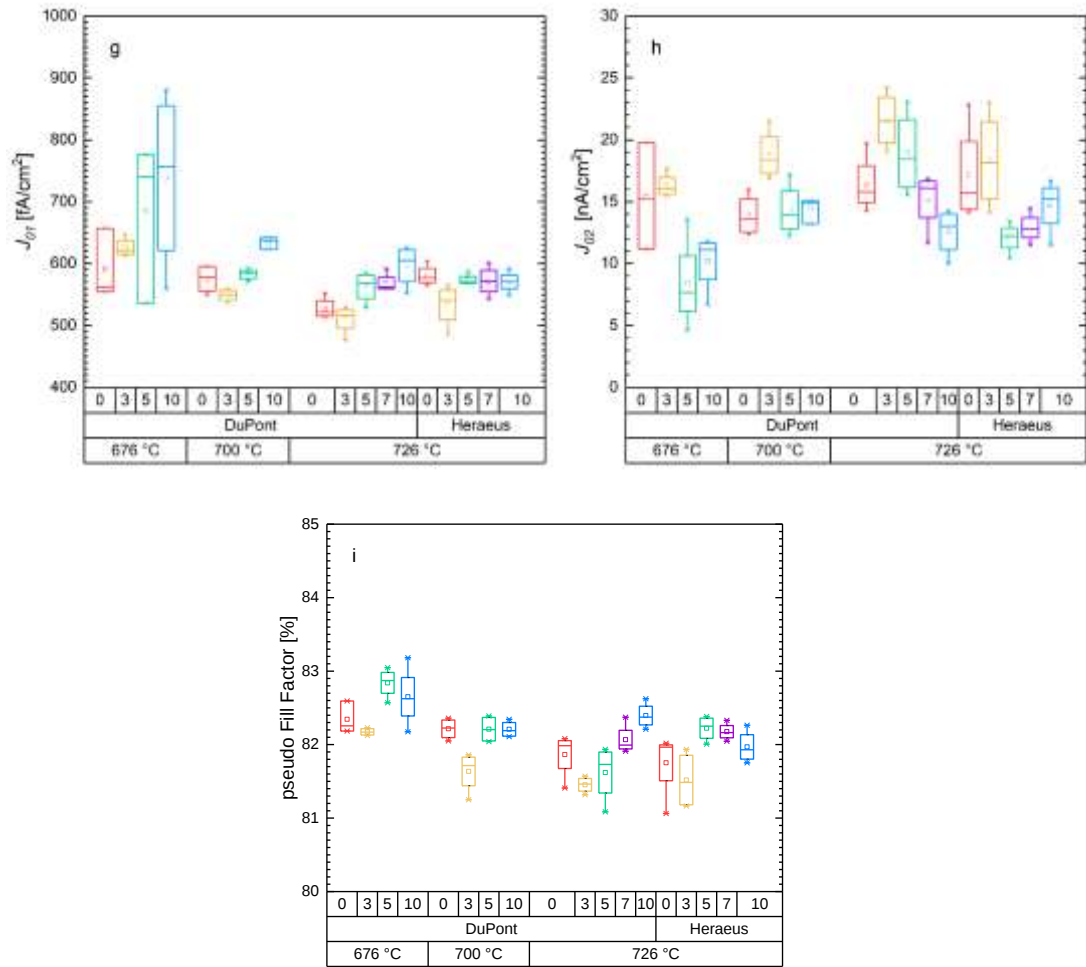


Figure 3.18 J_{01} , J_{02} and pseudo- FF values for Al-BSF solar cells screen-printed with DuPont and Heraeus paste at varying peak temperatures.

A comparison of the trend in efficiency, FF , and series resistance in Figure 3.17 shows that these factors are closely related. The extracted J_{01} , J_{02} and pseudo-efficiency curves, shown in Figure 3.18 showed no consistent trend with efficiency indicating that these cells were not significantly affected by non-ideal recombination. The plots of V_{oc} and J_{sc} are relatively constant across all experimental conditions, with the exception of considerably lower values for the 5 and 10 nm thick AlO_x cells fired at lower temperatures. This trend in V_{oc} appears to be correlated with the trend in extracted J_{01} values, and was potentially a result of non-ideal recombination at the metallised front silver contact. An assessment of the correlation between V_{oc} and J_{01} found a statistically significant mild correlation coefficient of -0.67 between these factors, using a two-tailed Pearson correlation test.

To further investigate these observed trends, a plot of the correlation between FF , V_{oc} , J_{sc} and efficiency is shown in Figure 3.19 (plots (a), (b) and (c) respectively). To assess the

correlation between these parameters, the sample Pearson correlation coefficient r value is depicted in each plot. In this case, a value closer to 1 indicates a strong positive correlation, with a value of zero indicating no correlation, whereas a value of -1 indicates a strong negative correlation. Red ellipses in Figure 3.19 represent a 95 % two-tailed confidence interval for the data. The strongest correlation was evident in Figure 3.19a, between FF and efficiency, suggesting that the observed trend in efficiency was correlated with changes in FF .

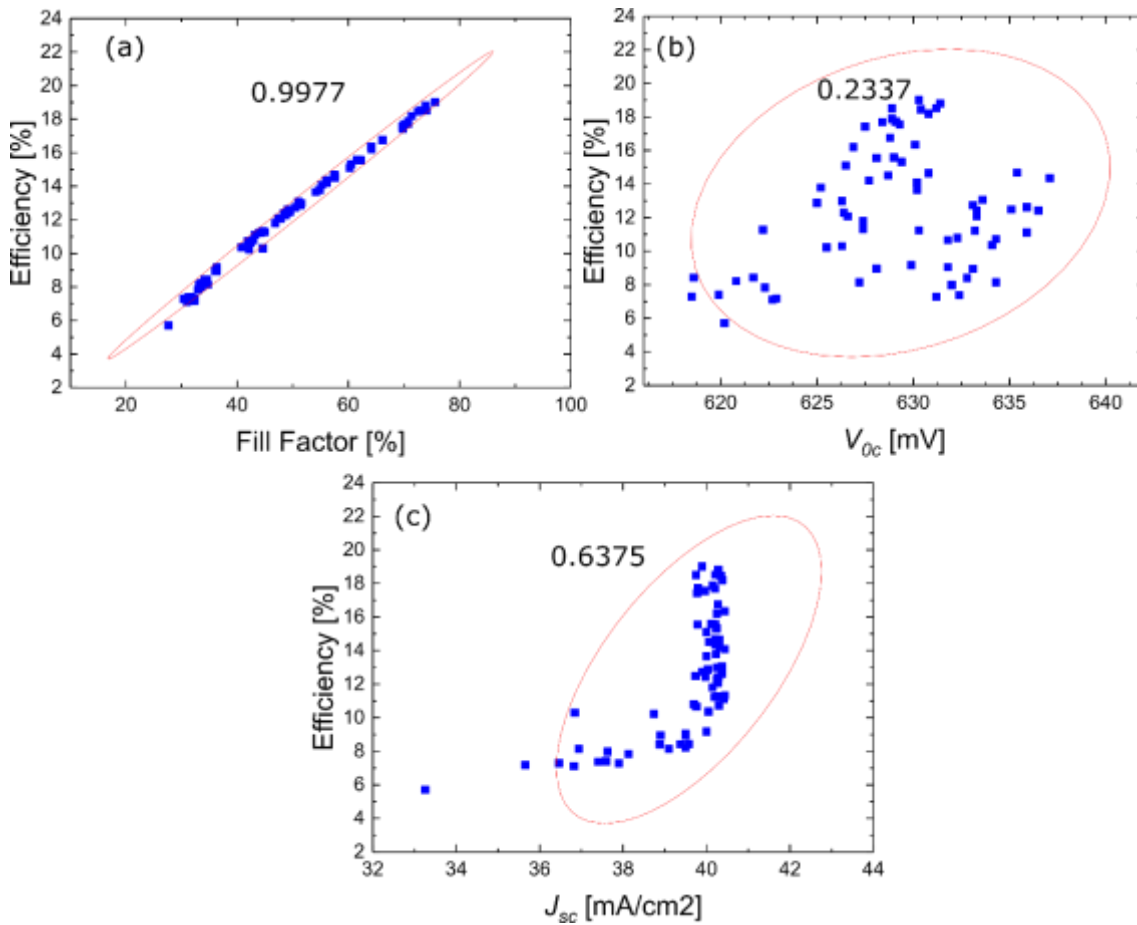


Figure 3.19 Plots of correlations between FF (a), V_{oc} (b) and J_{sc} (c) vs. efficiency. The Pearson correlation coefficient r value is depicted for each plot, and a 95 % two-tailed confidence interval is depicted by the red ellipse. FF shows the strongest correlation with efficiency.

To assess the factors affecting the change in FF , the correlation between J_{01} , J_{02} , series resistance and shunt resistance were assessed using the same Pearson's correlation test, with a two-tailed significance level of 0.95, $n = 84$. Scatter plots of J_{01} , J_{02} , series resistance and shunt resistance are depicted in Figure 3.20 (a, b, c and d respectively), which also depicts the r value and a 95 % two-tailed confidence interval for the data. A mild negative correlation between J_{01} and FF , and a weak correlation between shunt

resistance and FF was observed in Figure 3.20a and Figure 3.20d respectively. A mild positive correlation between J_{02} and FF does not make physical sense, and is possibly a result of insufficient sample numbers. The strongest negative correlation was observed between series resistance and FF in Figure 3.20c, which suggests that the series resistance was the factor with the strongest correlation to the measured efficiency, such that as the series resistance increases, the cell efficiency decreases, which was indicated by a reduction in FF .

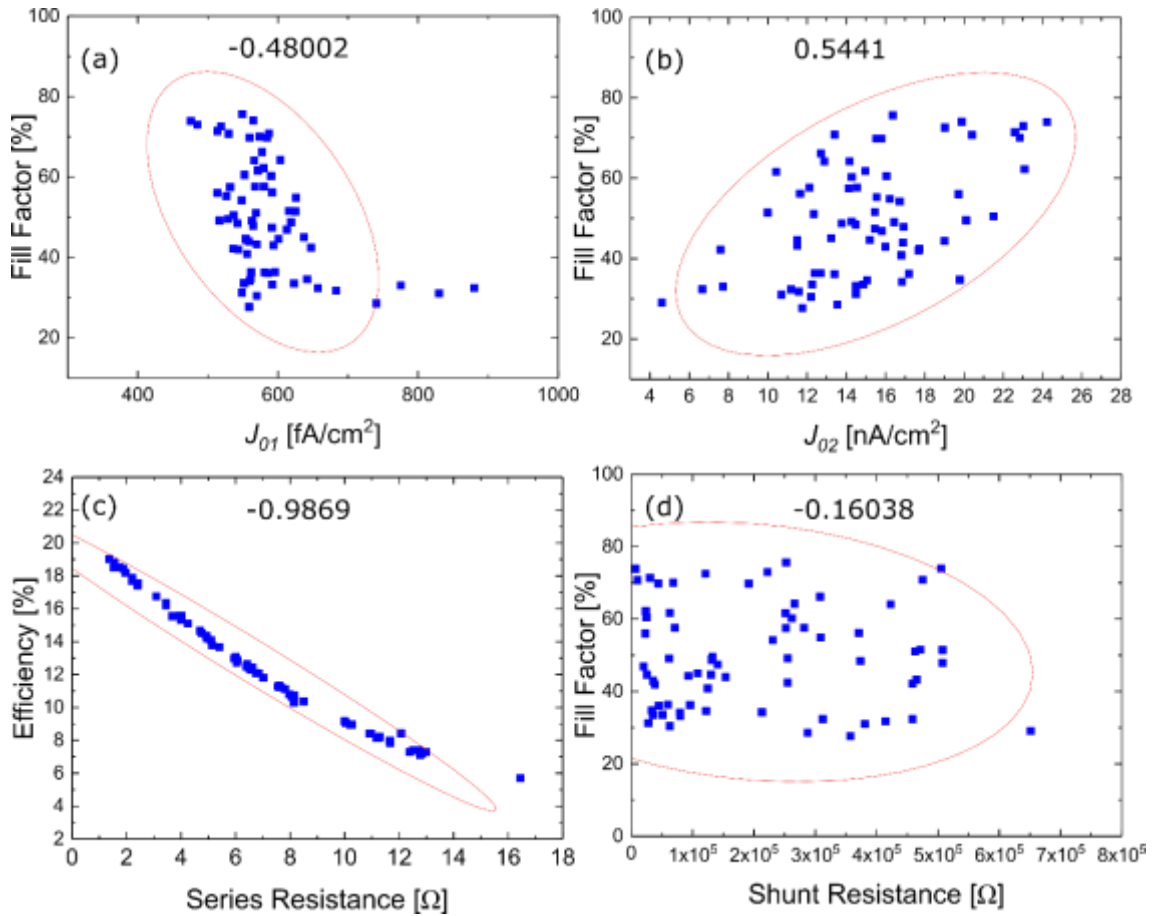


Figure 3.20 Plots of correlations between J_{01} (a), J_{02} (b) and series resistance(c) and shunt resistance (d) vs. efficiency. The Pearson correlation coefficient r value is depicted for each plot, and a 95 % two-tailed confidence ellipse is depicted by the red box, $n = 84$. Series shows the strongest negative correlation with FF , which in turn is likely the cause of the reduced efficiency.

The general trend whereby 3 nm thick AlO_x layers have the lowest series resistance and highest efficiency (followed by the control case) then decrease with increasing AlO_x thickness was found to be consistent for both pastes, reflecting the experimental data presented in Section 3.1. This suggests that wrap-around AlO_x of thicknesses up to 3 nm likely boost solar cell efficiency. Similarly, samples with 5 nm were found to produce

similar average cell efficiency's as the uncapped case when fired at 726 °C, although with larger variance. However, the transition to detrimental effects is rapid as devices with more than 5 nm AlO_x thicknesses generally performed worse than the control wafers.

The results of Section 3.1 showed that change in the AlO_x thickness and firing temperature will affect the ρ_c values, which is a component of the series resistance. Therefore, based on the results of the correlation analysis conducted and assuming all other series resistance components are unchanged among the samples, it was concluded that the changes in ρ_c due to AlO_x wrap-around was the most likely cause of the variance in efficiency observed. This was a demonstration on the cell-level that the contact resistance is affected as AlO_x wrap-around thickness, silver paste formulation and screen print firing conditions are varied, and is in agreement with the experimental work and simulations presented in Sections 3.1 and 3.2.

3.4 Conclusion

The effect of thin AlO_x layers, deposited on the front SiN_x ARC prior to silver screen printing, on the majority carrier transport and solar cell IV characteristics were studied in this chapter. A method of TLM analysis which allows for the direct measurement of contact resistance on completed solar cells was presented with specific focus on the error inherent in the method. It was shown that this method had less inherent error as the contact resistance decreases, which was the case for the 3 and 5 nm AlO_x wrap-around samples studied in this chapter. Subsequent measurement of dedicated TLM test structures found that a 3 and 5 nm AlO_x layer can enhance majority carrier transport in silver contacts, whilst broadening the acceptable temperature range for firing and allowing for lower peak firing temperatures on PERC cell structures. When applied to ion-implanted PERT precursor wafers, it was found that the advantages of enhanced majority transport were not applicable, likely due to the presence of an interfacial oxide layer produced during ion-implant drive in and annealing. However, the negative effects of increased contact resistance can be mitigated to a limited extent by simply changing paste formulations.

To simulate the effect of varying extents of wrap-around on PERC solar cell performance, Griddler simulations of a state-of-the-art industrial PERC solar cell was performed, with varying extents of AlO_x wrap-around. The ρ_c data from Section 3.1 was input into the model and spatial non-uniformity was superimposed onto the edges of the wafer. It was found that a 3 and 5 nm layer could boost cell efficiency slightly, until the improvements in series resistance are masked by some other limiting series resistance component.

Full rear Al-BSF p -type solar cell structures were then fabricated with low n^+ surface concentrations (to ensure ρ_c was the limiting series resistance factor in the cell) in order to provide greater insight into the effect of AlO_x wrap-around on measured device series resistance, FF and efficiency. Correlation analysis found that the cell efficiency was most strongly correlated with changes in FF , which in turn was most strongly correlated with the series resistance. This lead to the conclusion that the series resistance was the most significant factor affecting cell efficiency in the experiment. It was concluded that the experiment gave clear insight into the effect of wrap-around AlO_x as this was shown to affect the Ag-Si ρ_c , which was a component of the series resistance.

It was found that samples treated with a 3 nm thick AlO_x layer outperformed the uncapped control case, with a 5 nm AlO_x layer having similar cell characteristics to the

control. However, samples covered with AlO_x layers thicker than 7 nm resulted in higher series resistance for both the Heraeus and DuPont pastes tested.

As the industry moves towards *p*-PERC solar cells, this work suggests that thick layers (> 5 nm) of AlO_x wrap-around can have an adverse effect on cell performance, whereas thinner layers are likely to have a negligible effect. For cell manufacturers already using thinner layers of AlO_x (5 nm), this is not likely to have an adverse effect. However, the negative effects of thick layers of AlO_x wrap-around can be mitigated by changing paste formulations in the case that thicker passivation layers are grown, as was clear from the difference observed for the DuPont and Heraeus paste in Section 3.1.2. In particular cases, like the 3 nm layers outlined in this chapter, thin AlO_x wrap-around can in fact improve contact resistance at cell edges and boost cell efficiency relative to the uncapped case, for contact resistance limited solar cells. These results are of significance to industry, as significant effort and cost is currently being invested into developing tools that reduce unintentional wrap-around. Therefore, these findings may allow for greater flexibility in tool design, wider operating windows and, consequently, reductions in production costs. Future work could study in more detail the underlying cause of enhanced contact resistance when thin AlO_x layers are deposited, and/or the demonstration of this work on an industrial scale production line.

4 THE PROPERTIES OF ELECTROLESS NICKEL PLATED CONTACTS ON DIFFUSED p^+ SURFACES

INTRODUCTION

Screen print metallisation has been widely adopted for its process robustness, high throughput and relative simplicity. Furthermore, screen-printed p -PERC solar cells have achieved impressive efficiencies of 21.63 % and 22.61 % on multi-crystalline and monocrystalline silicon substrates, respectively [175]. However, there remains a strong imperative to develop alternative metallisation technologies for the following reasons:

- 1) Screen-printed silver paste represent a significant cost component of the overall solar cell (~13 % of the cell cost [9]), presenting an attractive option for cost reduction if the process can be substituted for an alternative, lower cost metal. Furthermore, silver is a precious metal and traded for investment purposes, which subjects the price of silver to volatility due to investor activity. This presents a risk for PV manufacturers as small changes in the silver price can have a large impact on their cost competitiveness, in an industry where margins are already very slim.
- 2) Although techniques such as double printing and stencil printing have been developed to improve printed finger aspect ratios [175-178], there remains a fundamental limit on the technology to produce very fine contacts with high uniformity and reliability. Thin finger widths with high aspect ratios are required to reduce front side optical reflection losses and maintain low series resistance.
- 3) By virtue of the metal-silicon alloying which occurs during the firing process, screen-printed contacts are not compatible with very high efficiency structures, such as heterojunction solar cells which employ passivated contact regions. Low

cost and high-throughput manufacturing compatible alternatives are required for these advanced structures.

Consequently, plating continues to be researched as an alternative metallisation technology. Plated contacts require a lower thermal budget, can contact silicon with low dopant concentrations and have the potential for higher aspect ratios. These features make them attractive for photovoltaic applications. Electroless plating of nickel (Ni) layers onto silicon for the formation of ohmic contacts was first demonstrated in the early 1950's by Sullivan and Eigler as a means of forming contact onto *n/p*-type silicon based semiconductor devices [179]. This study was followed up by Iwasa *et al.*, who attempted to explain the overall plating mechanism in alkaline solutions, observing a difference in the plating rate on *p*- and *n*-type surfaces [180]. These early investigations found applications for nickel-silicon plating in the integrated circuits (IC) industry [181-184], where it was identified that the formation of nickel silicide (NiSi) during subsequent annealing of plated nickel-silicon stacks can produce excellent ohmic contacts [184-188]. NiSi layers can also serve as barrier layers for copper diffusion—when nickel-copper (NiCu) metal stacks are formed—as copper diffusion into the bulk silicon has been shown to reduce solar cell device performance [189-193].

The application of Ni/Si plating for photovoltaic applications has received considerable research and commercial attention [189, 194-199], with notable early commercial demonstrations of plated contacts in solar cells including SunPower Corporation's solar cells [200], BP Solar's Saturn cell [201] and Suntech's Pluto cell architectures [202]. Due to the cost imperative to replace the silver front grid and the prevalence of *p*-type material as a base for silicon cells, the focus of most of the development of nickel plated contacts has been on the sunward diffused *n*-type electron collector (a notable exception is a laser doped bifacial cell architecture which required plating to both *p*- and *n*-type surfaces [203, 204]). However, there is an imperative to investigate the properties of nickel plated contacts on heavily diffused *p*⁺ silicon due to; 1) the forecasted growth in the use of *n*-type solar cell technologies [9]—which require the formation of contact to heavily doped *p*⁺ regions; 2) the difficulty in controlling Al spiking through the metallurgical junction when Ag/Al pastes are used, which is known to cause shunting [205]; and 3) findings that nickel and nickel silicides (NiSi_x) form a lower barrier height on *p*-type silicon in comparison to *n*-type silicon, suggesting high performance contacts on *p*-type material

are possible [206]. Nickel plated contacts to boron diffused silicon surfaces was investigated in response to these issues.

The latter finding suggests nickel and NiSi layers are ideal candidates as low resistivity p^+ contacts. To date, there are limited studies of the performance of nickel plated contacts on heavily doped p^+ silicon. An early study of plated nickel-phosphorus (Ni-P) contacts on heavily doped n -type and p -type silicon annealed at elevated temperatures (500, 600 and 700 °C) in an $N_2 + H_2$ ambient found that rectifying contacts formed on heavily doped p -type silicon [207]. Seren *et al.*, presented early work on the contact resistance of electroless nickel contacts made to three different boron diffused hole collector profiles, measuring ρ_c values between 0.6 and 81.1 $m\Omega.cm^2$ in a limited range of active dopant surface concentrations between $2-4 \times 10^{19} cm^{-3}$ [208]. A similar study using field-induced plating measured ρ_c of 0.57 and 1.01 $m\Omega.cm^2$ on boron diffused p^+ layers with surface concentration $2.8 \times 10^{19} cm^{-3}$ and $8.5 \times 10^{19} cm^{-3}$ respectively [209]. In both studies, a linear transfer length method (TLM) was used to extract the majority carrier conduction characteristics. Forward bias plating [210, 211] was demonstrated on laser processed p^+ hole collectors on n -type PERT cells with a conversion efficiency of 21.8 % [206]. Recently, n -PERT solar cells with nickel-copper plated p^+ contacts have achieved a record efficiency of 22.8 % with plated busbars and 23.1 % with wire-based metallisation [212], demonstrating the compatibility of this process with high performance cell structures. Interest in using electroless nickel has recently been renewed due to the interest in plating bifacial cells using a contacted plating system [212]. For example, if a seed layer of nickel can be plated on both the n -type and p -type silicon surfaces, then a copper plated grid can be plated in one step by simply contacting the plated nickel seed layer. Despite these promising plated cell results and the potential benefits of electroless plating processes, the carrier recombination rate at the nickel-silicon interface has not been reported. Consequently, this chapter focuses on the ρ_c and contact recombination properties of nickel plated contacts on p^+ surfaces. Comparative values are determined for a range of boron diffusion profiles relative to identical structures fabricated with evaporated aluminium contacts. Both the carrier transport properties and the recombination rate at the nickel-silicon interface were evaluated.

Having explored a technique to enhance the majority carrier transport properties of screen-printed silver contacts, an in-depth study of the majority carrier transport and minority carrier lifetime properties at the metal-silicon interface of solar cell contacts was

conducted. Two types of electroless plating solutions were used in this study; the first process required prior sensitisation and activation, whereas the second process used direct electroless plating of nickel to p^+ silicon. In both instances, samples metallised with thermally evaporated aluminium were used as control wafers, to compare an alternative direct metal-silicon interface with the electroless nickel plated samples. Following an outline of these two processes and their development, a discussion of the techniques used to extract the ρ_c and the saturation current density at the contact, J_{0c} , is then outlined. A methodology outlining the fabrication and analysis is then described, followed by the presentation of the experimental results.

4.1 Development of an electroless nickel plating process.

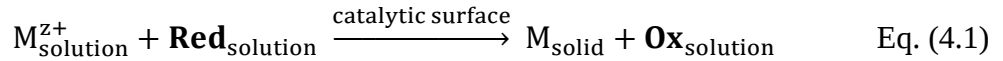
There are numerous approaches to metal plating contacts on silicon solar cells. These include conventional electroplating, bias-assisted light-induced plating (LIP) and field-induced plating (FIP), the latter also being referred to as forward-bias plating [189, 213]. The main disadvantage of these approaches compared to an electroless process is the requirement to control the potential at the plating surface using an external electrode in contact with the surface of the cell. Additionally, metal deposited by an electroless methods may be less porous than electrode deposition techniques [214]. For these reasons, and because the application of an external electrode could potentially hinder the characterisation methods used for this study, an electroless plating solution was studied. It was assumed that the carrier transport and recombination properties that were measured would be indicative of values that would be obtained from plating processes which use an external electrode to control the surface potential, and so would be relevant to metal contacts formed on boron hole collectors using FIP or forward-bias plating. In this section, the development of two different approaches to electroless nickel plating (ENP) process is outlined; the first process involves a series of surface activation steps prior to immersion in the nickel plating solution, the second does not require prior silicon surface activation.

4.1.1 Electroless nickel plating with surface activation

4.1.1.1 Technology background

Sensitisation and activation of the substrate prior to electroless plating can improve the deposition of metals on a wide variety of metallic and non-metallic substrates, and is

considered standard procedure when plating metals to materials such as plastics [214]. Prior exposure of the substrate to palladium (II) chloride (PdCl_2) and tin (II) chloride (SnCl_2) as electroless plating catalysts was initially demonstrated by Bergstrom [215], and subsequently has been used extensively to plate metals to silicon substrates [203, 207, 216-220]. The general form of the reaction for electroless metal deposition (with and without activation) is expressed as follows [214]:



where M is the metal to be deposited of valency z , **Red** is the reducing agent which reacts to form the oxidation product, **Ox**. In this reaction, the substrate is catalysed by immersion in a catalysing solution and the catalytic surface may be the substrate itself, or nuclei of deposited metal dispersed on the surface (and hence how growth sustains beyond the initial monolayer). A typical process involves the following steps [214]:

- 1) surface pre-treatment. This involves pre-requisite cleaning steps, and either an oxidation or oxide removal process depending on the desired surface condition, followed by either:

Sequence 1,

- 2) sensitisation in dilute SnCl_2 ,
- 3) catalysing in dilute PdCl_2 ,
- 4) immersion in the electroless bath containing a source of metal ions (to be reduced in the electroless plating reaction).

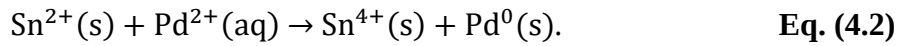
Or Sequence 2,

- 2) catalysing in a mixed colloidal SnCl_2 PdCl_2 ,
- 3) activation or acceleration in a working solution (typically a chloride based solution such as hydrochloric acid (HCl),
- 5) immersion in the electroless bath containing a source of metal ions (to be reduced in the electroless plating reaction).

Historically, the immersion exposure to SnCl_2 and PdCl_2 was performed in succession, in two separate solutions (Sequence 1). However this was eventually substituted for a single immersion in a colloidal $\text{SnCl}_2/\text{PdCl}_2$ solution (Sequence 2), at some point in the late 1970's [218]. The procedure outlined in Sequence 2 is used in this work and a brief

explanation of this process is outlined below. A more comprehensive explanation can be found in Refs [218, 219, 221-223].

The purpose of the catalytic step is to promote the nucleation of metal on the substrate surface. This is achieved via the adsorption of the colloidal Pd Sn on the substrate surface to promote initial metal deposition. The mixing of PdCl₂ with SnCl₂ in the catalysing step creates a solution containing palladium particles surrounded by a tin shell through the reduction of Pd²⁺ ions, according to the equation [222]: [224]



The Pd-Sn colloidal particles are stabilized by Sn(II) ions, and Sn(IV) precipitates form in the presence of oxygen [222]. During the activation step, the removal of excess Sn(IV) ions and Sn(IV) hydroxide surrounding the Sn-Pd alloy occurs [219, 222]. This leaves a surface state whereby Pd-Sn complexes serve as nucleation sites for the electroless deposition of the metal, in this case, nickel [222]. When immersed in the electroless bath, the nickel metal ions are reduced on the surface at the nucleation sites [223]:

Eq. (4.3)

In photovoltaic applications, PdCl₂ has been used to address the non-uniform plating rate of the *n*-type and *p*-type surfaces for nickel plated, laser doped bi-facial silicon solar cells [203]. PdCl₂ processes have been demonstrated in cell processing where, in addition to the previously mentioned laser-doped bifacial solar cell [203], Kim *et al.* demonstrated plating on phosphorus doped emitters using a PdCl₂ + HNO₃ solution, demonstrating a champion cell efficiency of 18.21 % [225, 226]. The use of Pd activation is preferably avoided due to the relatively high cost of Pd, and solar cells which do not use prior activation have been demonstrated in the works of Ref [224, 227, 228]. However its use was included in this study for comparison. In this study, a commercially available electroless plating solution was used, including Pd/Sn activator (D34C Activator, Macdermid) with a Ni(II) chloride based plating bath (MACuPlex Ni J60, Macdermid).

4.1.2 Electroless nickel plating without prior surface activation

4.1.2.1 Process overview

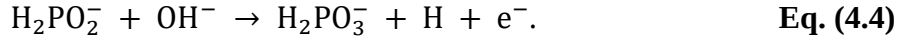
A typical ENP electrolyte consists of the following components:

- *Nickel source*: A source of elemental nickel for the growth reaction, typically nickel sulphate (NiSO_4) [183, 195, 196, 217, 220, 225, 229-237] and nickel chloride (NiCl_2) [179, 190, 208, 228, 238-242].
- *Reducing agent*: Chemical(s) to directly reduce the nickel ions to metal on the surface. The most common reducing agent used for nickel plating to silicon is sodium hypophosphite (NaH_2PO_2) [179, 190, 196, 217, 220, 225, 228, 230, 231, 233-235, 237-242].
- *Complexing agent*: Chemical(s) to stabilise the free Ni^{2+} ion concentration through complexation equilibrium, thereby allowing higher total Ni^{2+} bath concentrations without precipitation of nickel salts. In addition, complexing agents can have a buffering effect and prevent rapid changes in the pH [214].
- *Buffering agent*: Chemical(s) to maintain electrolyte pH and therefore the reaction rate. For acidic ENP solutions, ammonium fluoride is often used, whereas for alkaline solutions, ammonium hydroxide is a common buffering agent.

There are two competing theories that have been used to explain the nucleation and growth processes of nickel on silicon surfaces, with disputed claims of the roles of the various electrolyte reagents since ENP has been demonstrated on silicon surfaces with and without the presence of a reducing agent, in both alkaline and acidic solutions. As a result, it is likely that the surface chemistry of the nucleation and growth process is a complex process of numerous competing reactions which will vary based on the substrate properties and chemical composition of the solution. The first theory purports an identical nucleation and growth reaction, whilst the second theory proposes a self-limiting nucleation reaction followed by an autocatalytic growth phase. The point of difference lies in whether the supply of electrons to the nickel ions is solely from the reducing agent, or if there is an additional surface oxidation reaction which also supplies electrons to the nickel ions.

The first theory is based on the transfer of electrons from the reducing agent to the nickel ions at the silicon surface [182, 197, 234, 239, 243]. In this reaction, NaH_2PO_2 is oxidised

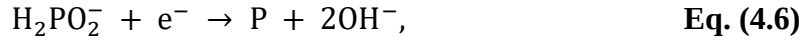
on the catalytic substrate (e.g., silicon), with the generated electrons being transferred to the silicon.



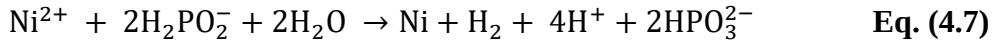
Nickel ions in the electrolyte are then attracted to the electron-rich surface regions, adsorb to the surface where they are reduced to metal (by accepting two electrons from the surface) on the surface according to:



Some hypophosphite ions can also be reduced to elemental phosphorus (by accepting one electron from the surface), and this phosphorus is incorporated into the growing nickel layer according to:



The overall reaction therefore becomes:



In the above reactions, nickel and phosphorus are deposited simultaneously. However, studies of the initial Nickel growth layers at the Si-Ni interface have found that phosphorus atoms were not present in the initial silicon layer [217, 220, 233]. Another study has reported ENP on silicon in the absence of a reducing agent for both alkaline and acidic solutions [217]. Furthermore, Abrantes and Correia showed that the surface potentials measured on the substrate in an ENP solution are not consistent with galvanic displacement theory [238]. However, the latter study was performed on a copper foil substrate, and therefore the surface conditions cannot be assumed to be identical on the silicon surface.

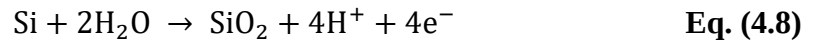
The alternative theory is that there is an initial surface activation reaction—corresponding to a nucleation phase—followed by an autocatalytic growth mechanism outlined previously involving the reducing agent. Takano *et al.* investigated three distinct possibilities for the mechanism of the initial nucleation growth [220]:

- 1) Nickel displacement takes place through the displacement of surface hydrogen atoms;
- 2) A photo-chemical reaction, whereby nickel is deposited cathodically by electrons photo-generated at the surface; and

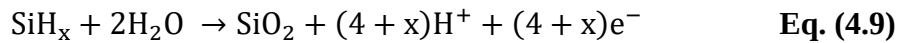
- 3) Galvanic displacement of silicon in the alkaline solution allows for the reduction of Ni^{2+} .

The first mechanism was calculated to be thermodynamically feasible. However this reaction would produce monolayer nickel growth, which was not observed. Further, this requires the sample to be in a H-terminated state (for example, due to a short HF acid dip), which contradicts observations of ENP on oxide terminated surfaces using solutions without reducing agent [231]. Regarding the second mechanism, no variation was observed in the plating rate for ENP solutions without reducing agents performed in the dark or under illumination, suggesting that the process is at least not entirely dependent on illumination [220].

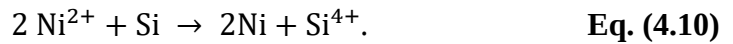
The third theory investigated by Takano *et al.*; that the initial surface activation reaction is a galvanic displacement process, in which silicon is galvanically displaced by nickel atoms as the silicon surface is oxidised has been investigated by numerous subsequent researchers [217, 229, 231, 233, 236]. The galvanic displacement reaction can be described by the following equations, [217, 220, 233] whereby the silicon surface is oxidised:



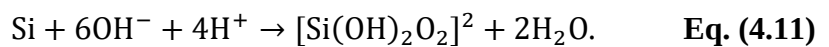
and for a H-terminated surface:



with the Ni^{2+} being reduced according to Eq. 4.5. The essence of the galvanic displacement reaction can therefore be expressed as [244]



Takano *et al.* concluded that the nickel deposition in highly alkaline solutions without prior catalysis was accompanied by the formation of SiO_x . This was verified by Tous *et al.* who also reported silicate formation through this process; the silicate creating a surface roughness that was visible under SEM imaging. The silicate forms according to [235]:



Takano *et al.*'s study was limited in that it did not attempt to verify if a galvanic displacement reaction occurred when the reducing agent was present or explain how these two reactions may compete during a deposition process. Therefore, it is still unclear what

the dominant mechanism at the surface is during the initial nucleation phase. Current knowledge is consistent with both galvanic displacement and reduction at the surface from the hypophosphite being feasible reactions.

Chow *et al.* reported that electroless nickel, deposited in highly alkaline solutions, has a face-centred-cubic structure [245], with other studies suggesting that the nickel-deposits are columnar in structure, growing out of a pure nickel nuclei [246, 247]. Zhang *et al.* reported that the addition of NH_4F to the plating electrolyte greatly assisted nucleation in baths without reducing agent, with prior catalysation [217], whereas others have observed galvanic displacement mechanisms in acidic ENP solutions which use NH_4F to moderate the pH levels [248, 249]. Figure 4.1 depicts the two-stage ENP process with an initial galvanic displacement surface reaction (Steps 1 and 2), followed by an autocatalytic reaction with reducing agent (Steps 3 and 4). In the figure, the oxidation at the surface occurs in the presence of hydroxide ions, and also due to the galvanic reaction— NaH_2PO_2 oxidation is assumed to not occur during this step.

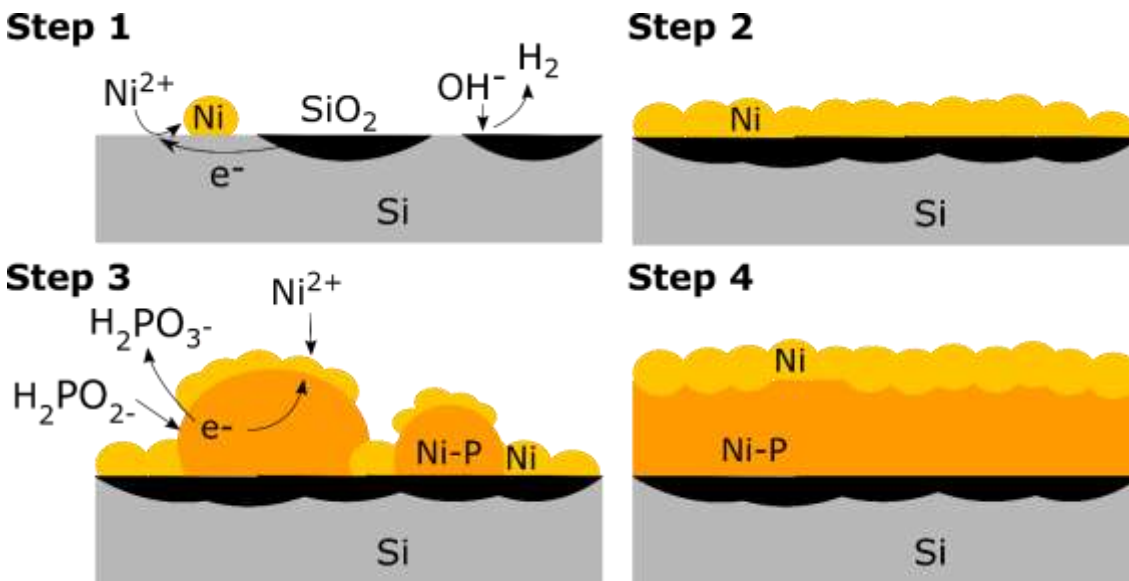


Figure 4.1 The nucleation and growth of electroless nickel plated layers in electrolytes with a hypophosphite reducing agent. Steps 1 and 2 depict the galvanic nucleation of the nickel-seed layer, which oxidises the surface due to the action of the hydroxide ions in the electrolyte. Steps 3 and 4 depict the autocatalytic growth phase, in which phosphorus is incorporated into the nickel deposit on account of the reducing agent.

It should be clear from the preceding discussion that there is no general consensus as to the growth and nucleation mechanisms underlying the ENP process. Although nucleation can occur in the absence of a reducing agent, it is not clear whether, in the presence of a

reducing agent, the nucleation process involves both galvanic displacement of silicon and the reduction of nickel ions by the reducing agent at the surface. Furthermore, it is not clear how the plating electrolyte, operating conditions and the sample properties (e.g., doping polarity and concentration) influence the nucleation process in terms of contributing reaction mechanisms. The presence of SiO₂ at the silicon interface suggests a galvanic displacement reaction, however it is also possible that silicon oxidation can occur simultaneously with the nucleation mediated by the reducing action of NaH₂PO₂.

4.1.2.2 Process development

In this study, alkaline solutions were selected to avoid the significant silicon etching observed when acidic solutions are used [236, 249]. High concentrations of boron ($N_a > 10^{19} \text{ cm}^{-3}$) can effectively limit or block etching of silicon by hydroxide solutions [234, 249, 250] and so it was hypothesised that silicon etching could be minimised using alkaline electrolytes. A commercially-available ENP solution (Niklad 1000, Macdermid) was used for the nickel plating experiments. This plating electrolyte, consists of NiSO₄ as the nickel source, NaH₂PO₂ as the reducing agent, malic acid (C₄H₆O₅) as the complexing agent, and sulfuric acid (H₂SO₄/HSO₄⁻) as the buffering agent. Semiconductor grade 29 % (w/v) ammonium hydroxide (NH₄OH) was added to the plating solution to achieve a basic (as opposed to acidic) solution at the required pH.

As outlined in the previous section, the ENP process involves multiple simultaneous reactions, and the plating electrolyte temperature and pH significantly affect the properties of the deposited nickel layers and consequently must be carefully controlled. Lower alkaline pH values have been linked to reduced phosphorus content in the deposit [251]; lower onset of deposition time, from increased surface oxidation rate due to increased OH⁻ concentration [233]; smaller nucleation grain sizes [195, 216, 231], which in turn has been linked to greater coverage and deposition uniformity [242] and lower activation energy of the Ni-P deposition on the silicon [252]. Increases in process temperature have been reported to increase the plating rate [242, 252] and increase grain size of the initial deposit [196, 231] which has also been linked to poorer coverage and homogeneity [195]. With a boiling temperature of 36 °C, the evaporation rate of NH₄OH increases with increased temperature. Therefore, it becomes increasingly difficult to maintain stable bath pH levels at elevated process temperatures, affecting process stability and repeatability.

Ideally, an ENP process should result in uniform coverage of nickel, high plated deposit adhesion and produce repeatable results. Initial experiments were performed with the objective of developing an optimised ENP process. A range of solution pH and temperatures was trailed in an optimisation experiment. In this study, 1×1 cm sample tokens were laser cleaved from 100 mm boron doped, *p*-type silicon wafers, with bulk resistivity 1 $\Omega\cdot\text{cm}$ and a double-sided mirror polished surface. After a standard RCA cleaning procedure, a 75 nm SiN_x layer was deposited in a remote PECVD reactor (AK400, Roth & Rau) on a single surface. Two exposed silicon surface states were investigated: 1) H-terminated surfaces were created by immersing the sample in 7:1 $\text{HF}:\text{NH}_4\text{F}$ buffered oxide etch (BOE) solution for 30 s prior to plating, and 2) oxide terminated surfaces were formed by immersing samples in a standard RCA2 clean for 6 min at 75 °C following the aforementioned BOE etching. The samples with H-terminated surfaces were not rinsed in DI water following BOE etch and prior to immersion in ENP solution. The nickel layer uniformity, coverage and adhesion over a relatively large area could be assessed on the exposed silicon surface; whilst the presence of parasitic plating on the SiN_x —commonly referred to as “ghost plating” [253]—was evaluated using the other SiN_x —coated surface of the sample.

All samples were immersed in 500 mL of ENP electrolyte which comprised 3.9-5.2 % NiSO_4 , 2.25-3.0 % NaH_2PO_2 , 0.75-1.5 % $\text{C}_4\text{H}_6\text{O}_5$ and ~0.1 % (v/v) H_2SO_4 , with DI water comprising the remainder of the solution (precise concentrations are not revealed by the manufacturer). The pH level of the solution was measured with a pH meter to be 5.2, and this level was varied within the ranges outlined in Table 4.1. The ENP electrolyte was contained within a glass beaker, which was immersed in a heated water bath via commercial immersion heater (Anova Precision Cooker, ANOVA) to control the temperature. During plating, mild agitation was provided for the duration of the process. A schematic of the plating apparatus is shown in Figure 4.2.

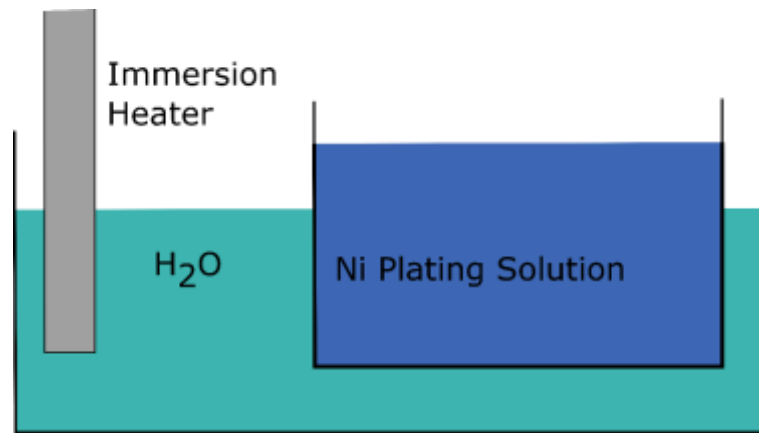


Figure 4.2 A schematic of the experimental apparatus used for the ENP performed in this study.

A qualitative description of the nickel growth is recorded in Table 4.1, which notes the presence of nickel, uniformity of coverage and the adhesion of the layer post-processing. Peeling/flaking of the deposited nickel layer was observed for some samples. This tended to increase as the deposited layer became thicker. For samples processed in Electrolyte B with pH 10.5 at 47 °C (see Table 4.1), peeling was not observed when rinsing in a heated rinse bath, provided the process duration was less than 300 s. No plating was observed for samples with an SiO_x layer on the surface. Ghost plating was observed on all samples (except those with RCA2 pre-treatment), likely due to pinholes in the SiN_x layers, as has been reported by numerous studies [253-257]. The presence of ghost plating suggests that this particular SiN_x recipe was not ideal for ENP plating. The temperature range was capped at 60 °C, since at higher temperatures, the pH was difficult to maintain constant over an extended period due to the evaporation of the NH₄OH.

Process C was selected due to the following factors.

- 1) The lower-temperature process had a lower rate of NH₄OH evaporation and therefore the pH was more consistent during an extended plating process. Although the higher-temperature processes also resulted in uniform plating, it was more difficult to ensure a stable pH.
- 2) The coverage of the plated layer had good uniformity across the entire wafer surface.
- 3) The layers demonstrated good adhesion for a range of rinse bath temperatures and durations.

To gain further insight into the process, focused-ion-beam milling and scanning electron microscope (SEM) imaging was performed for all samples processed using Condition C.

Cross-sectional images of the Si-Ni interface and EDX analysis (see Figure 4.3) showed that uniform layers of nickel were formed for plating durations > 60 s. The extent of surface etching was not investigated in detail, however the interface imaged for all plating durations appears smooth and uniform in appearance at the magnification used.

Non-uniform coverage of nickel was observed on the 30 s and 60 s samples, with small islands of growth observed randomly on the nickel surface. The thickness of these deposits was measured to be up to 70 nm thick, suggesting that the growth was in a nucleation phase. All samples inspected with ≥ 90 s process duration achieved uniform coverage. The deposited nickel thickness measured at five different points in the same cross-section for each sample of varying plating duration is graphed in Figure 4.4. The error bars in the graph represent the maximum and minimum values measured, with the dot representing the average thickness of the five measurements. The measured thicknesses in the growth phase fit a trend in growth rate of 1.76 nm/s, which was slightly lower than the manufacturer's quoted rate (2.43 nm/s). This growth rate appears to be distinct from the nucleation period, and supports a two-step growth theory of galvanic displacement driven nucleation, followed by an autocatalytic growth phase facilitated by the reducing agent NaH_2PO_2 .

Table 4.1 Qualitative results of nickel plating on silicon for the different ENP process conditions investigated.

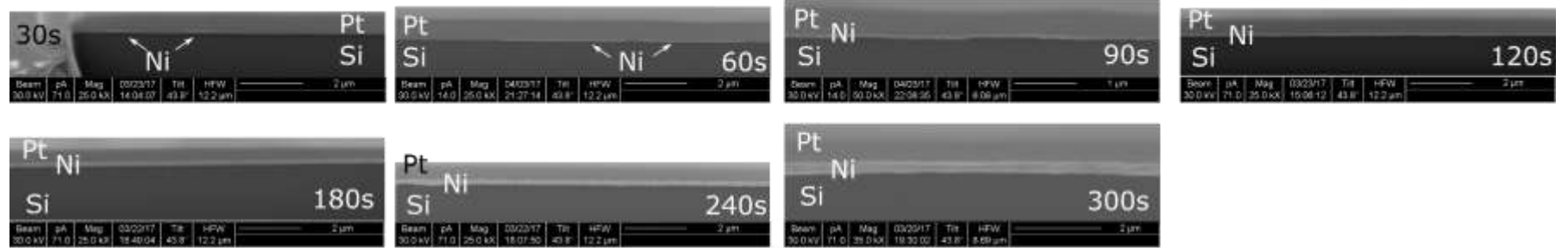
Process Condition	Temperature [°C]	pH	Process duration (s)						
			30	60	90	120	180	240	300
A ¹	50	9.5	[N]	[Y/NU/A]	[Y/NU/A]	[Y/NU/A]	[Y/U/A]	[Y/U/NA]	[Y/U/NA]
A ²	50	9.5	[N]	[N]	[N]	[N]	[N]	[N]	[Y/U/A]
B	47	10.5	[Y/NU/A]	[Y/NU/A]	[Y/NU/A]	[Y/U/A]	[Y/U/A]	[Y/U/A]	[Y/U/NA]
C	55	10.2	[Y/NU/A]	[Y/U/A]	[Y/U/A]	[Y/U/A]	[Y/U/A]	[Y/U/A]	[Y/U/A]
D	60	10	[Y/NU/A]	[Y/NU/A]	[Y/NU/A]	[Y/NU/A]	[Y/NU/A]	[Y/U/A]	[Y/U/A]

Results are displayed in format [X1/ X2/ X3] where X1 = Y (plating visible under optical microscope) or N (Plating not visible). X2 = U (Uniform 100 % coverage) or NU (Non-uniform coverage). X3 = A (film present after DI water rinsing at room temperature) or NA (Film partially or fully removed after DI rinse).

¹H-terminated samples.

²SiO_x surface condition.

(a) Interface Images



(b) Surface Images

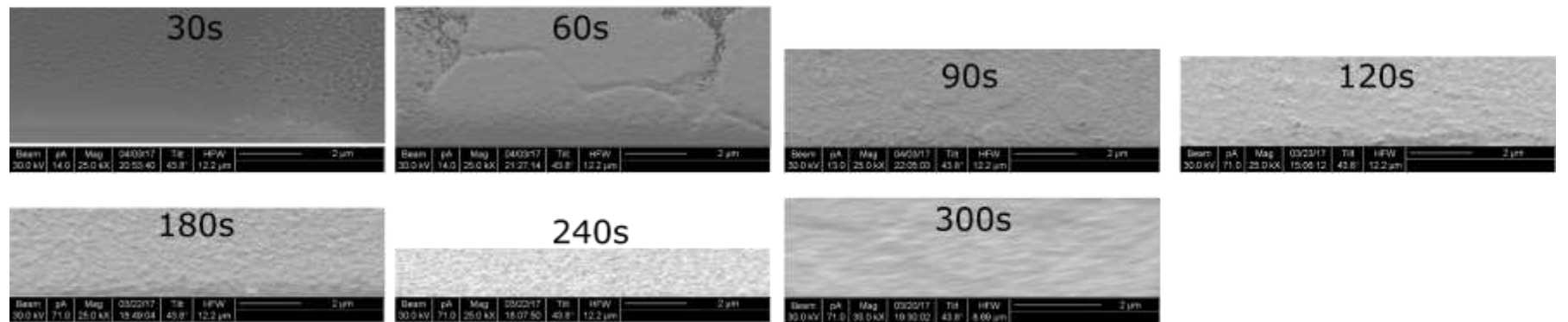


Figure 4.3 SEM images of the focused-ion-beam milled cross-sectional interface (a) and surface morphology (b) of the ENP layer for samples of varying plating duration.

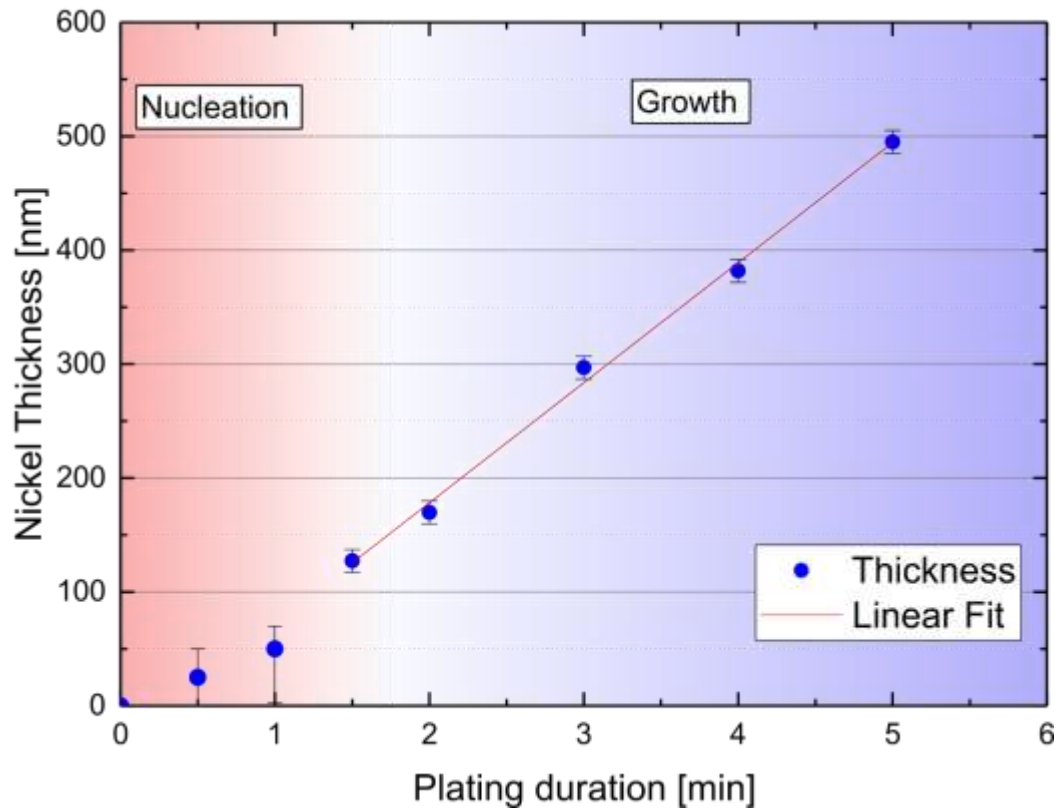


Figure 4.4 Measured average nickel thickness vs. immersion duration in an alkaline ENP electrolyte with a pH = 10.2 and $T = 52\text{ }^{\circ}\text{C}$. The error bars represent the maximum and minimum thicknesses measured. Non-uniform growth was observed for immersion durations of < 1 min (hence the large error bars for the 30 and 60 s plating duration samples). The growth rate for samples immersed for ≥ 1 min varied roughly linearly with time, and the extracted growth rate for this second phase was estimated to be 1.76 nm/s.

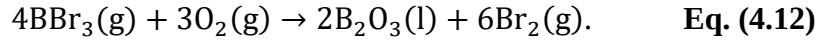
4.2 Development of a boron diffusion process

The recombination and the transport properties of metallised silicon contacts is influenced by the concentration and distribution of dopants at the silicon surface and underlying the metal-silicon interface. As discussed in Chapter 2, the active surface concentration of dopants is of particular importance, due to the trade-off between SRH and Auger recombination mechanisms, and its effect on the current transport mechanism at the metal-silicon interface. The metal-silicon interface is a site of high recombination activity due to the high concentration of surface defects, which serve as sites for SRH recombination activity [57, 258], and recombination enhancing phenomena such as Fermi-level pinning [259]. As the surface concentration of dopants increases, the minority carrier conductivity in the regions surrounding the contacts decreases and therefore the population of minority carriers decreases, which limits the maximum SRH recombination

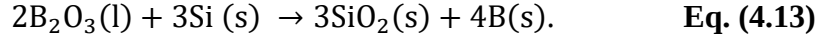
rate at the metal-silicon interface. Similarly, as the surface concentration of dopants increases, the probability of thermionic emission increases due to the lower potential barrier to current flow, and tunnelling through the potential barrier becomes more probable and dominates the current flow across the interface. This results in reduced resistance to current flow from the silicon to the metal. The consequence of the above discussion is that higher surface dopant concentrations result in ohmic contacts with lower resistance to current flow, however, there are other factors which also need to be considered.

Firstly, the Auger recombination rate is proportional to square of the majority carrier (dopant) concentration, and therefore increases with the dopant concentration at the surface region results in increased Auger recombination. As such, there is a trade-off between SRH and Auger recombination when designing optimised diffused hole collectors. Furthermore, band gap narrowing effects increase with increased dopant concentration, which is especially problematic when the diffused region also serves as an absorber layer of incident solar irradiation—which is the case for most full area diffused solar cells with front and rear metallisation. One approach employed by high efficiency solar cell designs is to fabricate localised, small area contacts with deep ($>1\text{ }\mu\text{m}$) diffused regions with relatively low surface concentration ($N_A \sim 10^{19}\text{ cm}^{-3}$) [260]. In this way, due to the depth of the diffused region, the probability of a minority carrier diffusing to the highly recombination active surface is greatly reduced. This approach also reduces detrimental BGN and enhanced Auger recombination effects to fractionally small contributions.

Furthermore, there are processing considerations which also affect the overall device performance, which cannot be overlooked when integrating heavily doped p^+ regions into solar cell devices. Heavily diffused p^+ regions formed in tube furnaces with liquid boron tribromide (BBr_3) source—as is used in this work, require the balancing of oxygen supply to the interface to, in one instance, prevent the formation of a boron rich layer, whilst also avoiding the significant depletion of the surface due to boron dopant atoms preferentially segregating into any SiO_2 layers formed at the interface. A brief outline of the boron diffusion process clarifies the intricate trade-offs when attempting to tune the surface concentration of p^+ doped regions. In a typical BBr_3 tube diffusion, BBr_3 gas is introduced into the furnace in an oxidising environment, which promotes the formation of boron glass B_2O_3 , via the reaction [261-263]:



The liquid B_2O_3 reacts with silicon, to enable elemental boron to diffuse into the bulk silicon [264, 265].



In the absence of sufficient oxygen supply, a boron rich layer is created at the surface as elemental boron ‘piles-up’, via the reaction [266-268]:



This layer can be ‘dissolved’ in an oxidation step via the reaction [269]



An increase in the surface concentration of diffused atoms is achieved by either increasing the process temperature, and/or reducing the oxygen supply to the interface, however, with consideration of Eq. 4.14 and Eq. 4.15, an increase in the process temperature or reduction in oxygen supply is problematic if this facilitates the formation of boron rich layer, which can reduce the silicon bulk lifetime from the introduction of dislocations [269-271], however the formation of a BRL layer has also been shown to have a gettering effect if removed after the diffusion process via wet chemical etching [261]. Furthermore, prolonged exposure to high temperatures in the range of 800-1000 °C has been shown to create vacancy rich defects in *n*-type FZ silicon [272, 273], and ring defects in *n*-type Cz material [274-277].

Thus, the formation of optimised p^+ hole collectors is a delicate trade-off between process conditions to create a diffusion profile which balances SRH recombination, with Auger recombination and BGN effects, whilst also ensuring a sufficient surface boron concentration for low resistance ohmic metal contacts. A process needs to be developed which limits the exposure to high temperature, bulk lifetime degrading processes, whilst also ensuring that any BRL layer created is subsequently dissolved. For the purposes of this study, a range of dopant concentrations was investigated. Specifically, the surface concentration and depth of active dopants was varied in order to get a broader understanding of the recombination and transport properties at the heavily diffused p^+ -metal-silicon interface. The boron diffusion processes that were investigated, used a three-step process comprising of:

- 1) *Deposition*: The dopant source was introduced into the furnace and deposited onto the silicon surface.
- 2) *Drive in*: A higher temperature step was performed, which served to promote the diffusion of dopants from the surface into the silicon bulk. In this work, the drive-in process was differentiated from the post-oxidation step in that this sequence was performed in an inert ambient (i.e. no oxygen present).
- 3) *Post oxidation*: A high-temperature step in which a saturated oxygen ambient was attempted, by maximising oxygen flow into the furnace. This step was designed to promote the oxidation of the silicon interface and dissolve any boron rich layer which may have formed in the preceding steps.

The full processing parameters of the diffusions in this work are listed in Table 4.2, and the corresponding ECV profiles of the recipes are shown in Figure 4.5. These recipes were specifically tuned so that a range of surface concentrations and depths were obtained in order to distinguish the effect of junction depth and surface concentration on the overall recombination rate. The main process parameters altered to achieve these variations in profile shown in Figure 4.5 and listed in Table 4.2, were the process temperature, gas flow (i.e. whether oxygen was introduced into the process tube during an in-situ post-oxidation step following the drive-in) and process duration. For instance, Recipes 1 and 2 had very different depths (~1000 nm and 310 nm for Recipes 1 and 2 respectively) due to the difference in process temperature. However, by changing the duration of the post-oxidation step, similar surface concentrations were achieved for both recipes. Similarly, to achieve similar depths, Recipes 3 and 4 had similar process durations and identical process temperatures, however the higher oxygen flow in Recipe 4 ensured vastly different surface concentrations between the two profiles. Similar variation of process temperature was used to modulate the profile depth, whilst variations in oxygen flow was used to alter the surface concentration, to achieve the characteristics of Recipes 5-8. In this work, it was found that for all recipes, there was no BRL present (the wafers were visibly hydrophobic after HF etch for < 5 min duration). However, a post oxidation was still performed in some instances in order to control the surface concentration and depth of the profile. This is because boron diffuses interstitially via boron-interstitial pairs in silicon [278, 279], and since oxidation injects interstitials into the silicon bulk [280], increases in the oxidation rate can enhance the diffusion of boron into the silicon bulk. In

this study, all boron diffusions were performed in a tube diffusion furnace (TS8063, Tempres), using a liquid BBr_3 as the dopant source.

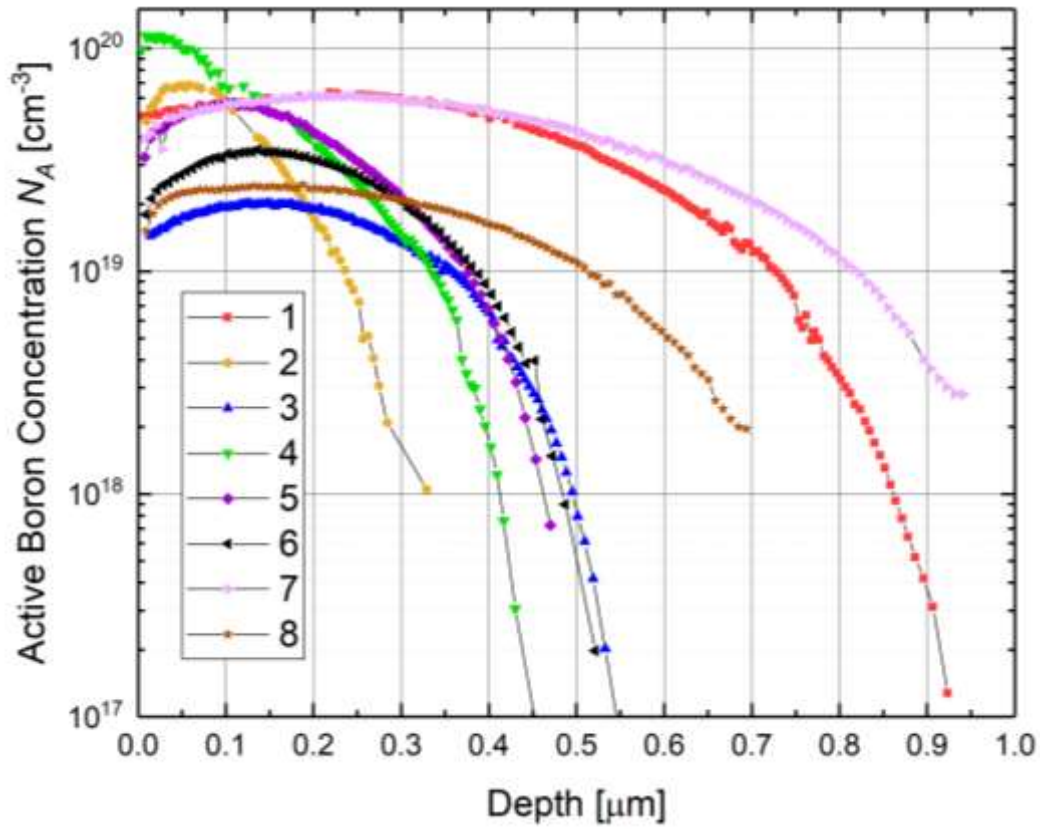


Figure 4.5 ECV profiles of the electrically-active boron concentration as a function of depth from the surface for the different boron diffusion recipes used in this study.

Table 4.2 Process parameters and measured characteristics of the boron diffusion recipes used in this study.

Recipe ID	Deposition				Drive-in				Post-oxidation				Average Sheet Resistance ^a	Surface conc. ^b	Peak conc. ^b	Junction depth ^b
	T [°C]	t [s]	O_2 [sccm]	BBr_3 [sccm]	T [°C]	t [min]	O_2 [slm]	N_2 [slm]	T [°C]	t [min]	O_2 [slm]	N_2 [slm]	R_{sheet} [$\Omega/\square$]	$N_{A,s}$ [cm ⁻³]	N_p [cm ⁻³]	x_j [μm]
1	850	15	400	400	970	60	0	7.5	970	15	15	5	41	4.95×10 ¹⁹	6.10×10 ¹⁹	1.0
2	850	15	400	400	870	70	0	7.5	870	5	15	5	110	4.70×10 ¹⁹	6.85×10 ¹⁹	0.31
3	850	15	400	400	920	60	0	7.5	920	45	15	5	140	1.40×10 ¹⁹	2.12×10 ¹⁹	0.59
4	850	15	400	400	920	90	0	7.5	N/A	0	0	7.5	63	9.90×10 ¹⁹	1.14×10 ²⁰	0.51
5	850	10	400	400	920	115	0	7.5	920	10	15	5	76	3.25×10 ¹⁹	5.67×10 ¹⁹	0.48
6	850	10	400	400	920	90	0	7.5	920	30	15	5	100	1.8×10 ¹⁹	3.51×10 ¹⁹	0.52
7	850	10	400	400	960	115	0	7.5	960	10	15	5	31	3.94×10 ¹⁹	6.14×10 ¹⁹	0.95
8	850	10	400	400	960	90	0	7.5	960	30	15	5	89.2	1.51×10 ¹⁹	2.45×10 ¹⁹	0.69

^aMeasured with four-point probe^bExtracted parameters from the 4-point-probe calibrated ECV profiles of active boron dopant concentration.

4.3 Experimental

Having outlined the process development of the boron diffusion process and the nickel plating processes used, the fabrication and characterisation flow of the test structures, and their design is outlined in this section. In this study, the contact recombination and ρ_c was measured for both nickel plated samples without prior activation and the comparative aluminium evaporated samples. For samples plated using the ENP process which utilised Pd activation, only the ρ_c values were measured. The plated samples without Pd activation were fabricated in a separate processing sequence with slight variations to the method used for the Pd activated samples. As a result, there are slight differences in the processing methodology which will become clear by first outlining the process for the samples without activation and their corresponding evaporated reference samples, and then highlighting the differences where applicable for the samples plated with activation and their corresponding evaporated references.

4.3.1 Processing sequence for samples plated without prior activation.

The processing sequence is depicted in Figure 4.7 as a numbered sequence and each step depicted is described in the following section. In this work, phosphorus diffused *n*-type FZ silicon wafers of bulk resistivity 4.5 $\Omega\cdot\text{cm}$ with double sided polished surface texture and $\sim 280\ \mu\text{m}$ thickness were used. The samples underwent a standard RCA clean, before being subject to a bulk stabilising anneal process [281], designed to prevent the degradation of the bulk lifetime via thermal processing, related to the growth of oxygen and nitrogen related vacancy defects. This process consisted of subjecting the wafers to a dry oxidising environment, at 1050 °C for 30 min in a Tempress systems furnace (Step 1). The grown oxide was subsequently removed by etching in 10:1 HF, and a standard RCA1 and RCA2 cleaning procedure was performed, followed by a short immersion in 2 % (w/v) HF solution to leave a H-terminated surface (Step 2). The samples were then boron diffused using the recipes 1-4 as outlined in Table 4.2 where two samples were diffused per unique boron diffusion recipe, such that one wafer could be metallised with nickel, the other with aluminium. Following the boron diffusion, the samples underwent BSG removal in 10 % HF for 5 min, leaving a hydrophobic surface (Step 3). All wafers were hydrophobic after 5 min of immersion in the HF, indicating that there was no BRL present on the surface of the wafers.

After BSG removal, the samples underwent another RCA cleaning cycle, however without the final HF step, leaving the surfaces covered with a thin chemically grown SiO_x layer. A 10 nm AlO_x layer was then deposited onto both surfaces of the wafer in a thermal ALD system (Savannah, Cambridge Nanotech) at 200 °C (Step 4). This AlO_x layer was then capped with a PECVD SiN_x in a remote, inline PECVD system (MAiA, Roth & Rau), deposited at 400 °C (Step 5). With a duration of ~5 min, this process can be considered as an in-situ anneal. Nevertheless, the samples were subjected to a further 10 min of annealing at 400 °C in a nitrogen rich environment, as previous trials of this sequence were found to slightly improve the extracted J_{0e} of identically fabricated samples. A test sample, hereafter referred to as M1, used to refine the process sequence and find an optimal annealing temperature for the nickel plated contacts was also fabricated with diffusion recipe 3. A key difference in this sample was that the SiN_x capping layer was deposited in a small scale PECVD reactor (AK400, Roth & Rau), which was found to be rich in pinholes and subsequent ‘ghost’ or ‘parasitic’ plating was observed, hence the use of the MAiA system as previously mentioned in subsequent experimentation. The results from this annealing experiment will also be presented.

An etch mask was patterned using photolithography to define the contact pattern (Step 6) and remove the insulating $\text{AlO}_x/\text{SiN}_x$ dielectric stack. This pattern is shown in Figure 4.6 and comprised three distinct regions: 1) four circular TLM patterns located in each quadrant of the wafer; 2) a series of 15 arrays of contact openings designed to replicate localised contact openings on an actual solar cell device; and 3) a central unprocessed region of dimension 45 mm×45 mm, which was used for the PC lifetime measurement. A fourth region, with linear TLM patterns were not used in this experiment. Full details of the dimensions of the TLM and contact array patterns are outlined in Sections 4.3.3 and 4.3.4 respectively. Photolithography was performed using positive photoresist (Az 6632, Microchemicals GmbH) which was spun onto both surfaces of the sample (4000 RPM, 45 seconds) and soft baked for 1 min at 110 °C on a hotplate. Following UV exposure (5 mW/cm²) the non-cross-linked resist was removed in Tetramethylammonium hydroxide (TMAH) developer with surfactant (MIF 826) and then rinsed. The samples were then hard-baked at 125 °C for 2 min on a hotplate. With the pattern defined, the unmasked $\text{AlO}_x/\text{SiN}_x$ was etched in BOE solution for 15 min to expose the underlying silicon. The etch mask was then removed in an acetone isopropanol clean (Step 7).

A second mask was then deposited to assist to facilitate metal lift off (Step 8). In this process, wafers were first cleaned with acetone and isopropanol, and then exposed to hexamethyldisilazane (HMDS) adhesion promoter in a reduced pressure environment for 10 min. Negative photoresist (nLOF 2035, Sicrochemicals) was spin-coated onto both surfaces of the wafer (4000 RPM for 45 s), followed by a soft bake at 110 °C on a hot plate. The pattern was precisely aligned to the prior etched contact openings, and following exposure, a short 1 min post exposure bake was performed for 2 min at 125 °C. The photoresist non-cross-linked was then removed in MIF 826, and rinsed. To improve alkaline resistance, the samples to be electroless plated underwent a further hard bake at 150 °C for 5 min. This step was not required or performed on the evaporated samples.

Prior to evaporation, the samples underwent a short 30 s immersion in BOE to remove any native SiO_x, before being loaded into the evaporator chamber. The time between drying and initiation of the pump down procedure was no more than 5 min for all evaporated samples. The chamber was pumped down to a pressure of 10⁻⁷ Torr, before current flow was initiated to the tungsten boats containing the aluminium evaporation sources (aluminium pellets of 99.99 % purity). Care was taken to ensure full outgassing of the metal before opening the chamber shutter, and thin layer of thermally evaporated aluminium was deposited (Step 9b), measured to be ~ 500 nm thick, as measured by an in-situ crystal thickness monitor.

Electroless nickel plating without prior activation was performed using the process outlined in Section 4.1.2.1, with pH 10.2 and a temperature of 52 °C for a duration of 8 min (Step 9a). The solution pH was measured and adjusted at the beginning of each process to minimise differences between the electrolyte conditions between samples. It was observed that the plating rate was much lower on the diffused samples than the undiffused monitor tokens used in the process characterisation experiment outlined in Section 4.1.2. This is likely due to the reduced electron concentration at the surface on account of the heavy p^+ doping, since electron supply is critical to the process. This is discussed in more detail in the discussion section of this chapter.

Finally, a lift-off procedure in acetone with ultrasonic agitation was performed to remove the metallisation mask (Step 10a and 10b). Both the evaporated aluminium samples and the ENP samples underwent a 5 min anneal at 350 °C in a nitrogen rich ambient. The evaporated nickel samples underwent an anneal for 5 min at 350 °C in nitrogen ambient.

At this point, the samples were then fully characterised in the procedure outlined in the following sections.

The majority carrier ρ_c was extracted using a circular TLM pattern, the dimensions of which are outlined in a proceeding section. Similarly, the characterisation process to extract the minority carrier recombination at the metal interface will be described in a forthcoming section.

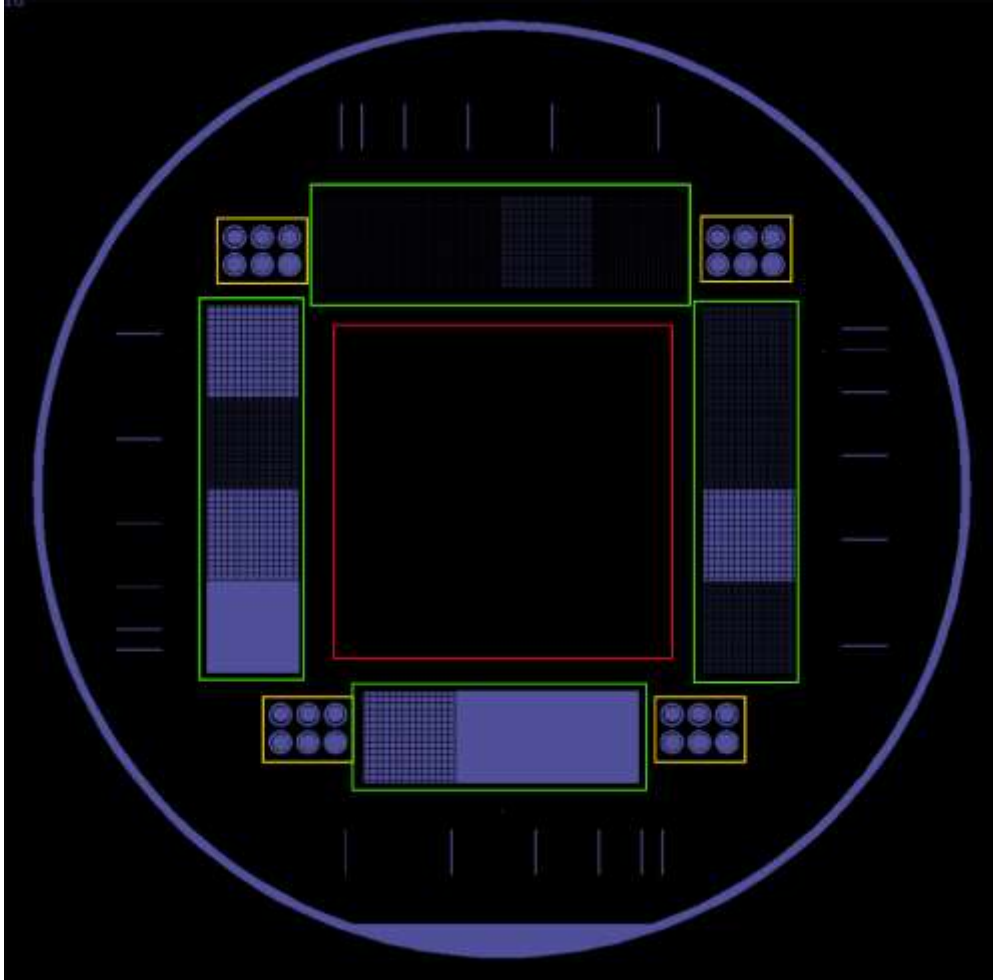


Figure 4.6 Schematic drawing of the 100 mm mask used to define the circular TLM patterns (yellow boxes), a series of 15 contact recombination arrays (green boxes), and a central region for PC lifetime measurement (red box). This mask was used for the samples plated with the ENP solution without prior activation. Note, some of the features of the contact array patterns were too small to be resolved accurately at this resolution and magnification, and therefore appear as either faint black areas, or poorly spaced solid blocks.

4.3.2 Processing sequence for samples plated with prior activation

As previously mentioned, there were some minor differences in the processing sequence for the samples fabricated. These differences are outlined below.

- 1) The samples used were 156×156 mm, phosphorus doped *n*-type Cz wafers with a bulk resistivity of 2 Ω .cm.
- 2) A different set of process conditions were used during the boron diffusion process, specifically Recipe 5-8 as outlined in Table 4.2.
- 3) A linear TLM test structure used to extract ρ_c was used, distinct to the mask depicted in Figure 4.6.
- 4) The nickel plating process included prior activation using palladium/tin activator (D34C Activator, Macdermid) and a Ni(II) chloride based plating bath (MACuPlex Ni J60, Macdermid).
- 5) The samples were laser cleaved to restrict flow around the edges (Step 11).

All other processing parameters were shared between both sample structures. Table 4.3 summarises the processing condition and applied characterisation methods of each sample used in this work.

Table 4.3 Processing conditions and characterisation methods for each sample of this study.

Metallisation	Diffusion recipe ^a							
	1	2	3	4	5	6	7	8
ENP, with activation					P5	P6	P7	P8
ENP without activation	P1, M1 ^b	P2	P3	P4				
Al evaporation	E1	E2	E3	E4	E5	E6	E7	E8
	Characterisation							
	Circular TLM & J_{oc} estimation				Linear TLM only			

^a Recipe number corresponds to the recipes listed in column 1 of Table 4.2

^b M1 was used in an anneal temperature split.

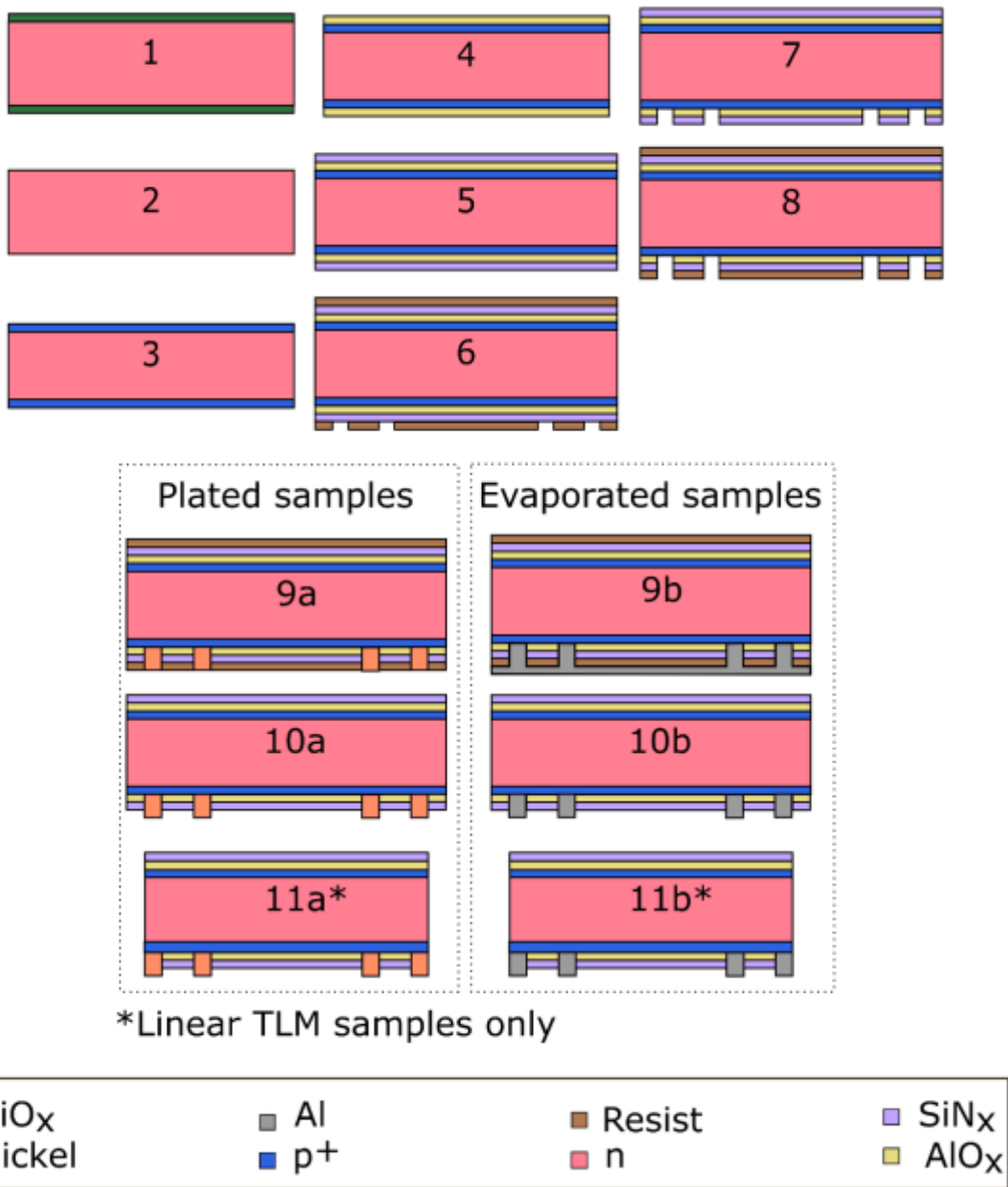


Figure 4.7 Processing sequence for all wafers used in this work.

4.3.3 Contact resistance measurements

The ρ_c was calculated using the linear and circular TLM patterns which were patterned using photolithography on the wafer (see Figure 4.8 and Figure 4.9 for linear and circular TLM patterns, respectively). A potentiostat (Ivium-n-stat, Ivium Technologies) was used to sweep the current-voltage (I - V) response of the contact pads using four probes, to enable separate sensing of the current and voltage characteristic.

The linear TLM pattern used for plated samples without activation and their corresponding aluminium references (samples E5-8 and P5-8, see Table 4.3), is shown in

Figure 4.8. The structures were laser cleaved out of the wafer, and the I - V response probed between contact pads. As mentioned in Chapter 2, a linear slope of the I - V response indicates formation of an ohmic contact, with the resistance being calculated as $R=V/I$. This resistance was then graphed as a function of distance, and the slope of the fitted line of the measured data is used to estimate ρ_c using a procedure which uses an end resistance measurement to correct for variances in the sheet resistance underneath the contact. The ρ_c was extracted by solving for the transfer length, according to the Eq. 2.68 and correcting for R_{sk} with an end resistance measurement.

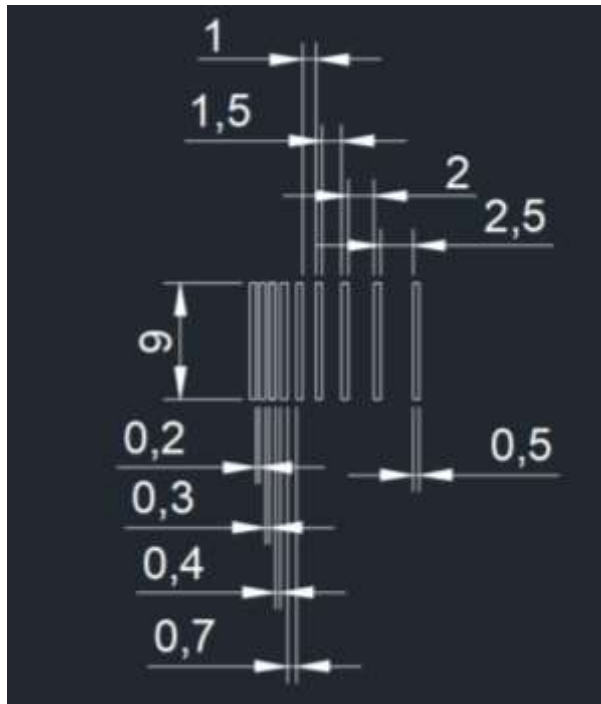


Figure 4.8 Linear TLM pattern used to estimate the specific contact resistivity for the samples plated with prior Pd/Sn activation before immersion in the ENP solution. The dimensions are depicted in units of mm. The cleaved width of the structure was 10 mm wide.

A circular TLM pattern was used for the samples plated without prior activation (samples E1-4 and P1-4, see Table 4.3). In this pattern, the radius of the inner circle, r_1 , was varied whilst keeping the radius of the outer circle r_2 constant, effectively varying the distance d for the majority carrier flow. The dimensions of the circular TLM pattern used is shown in Figure 4.9. The ρ_c was extracted according to Eq. 2.72.

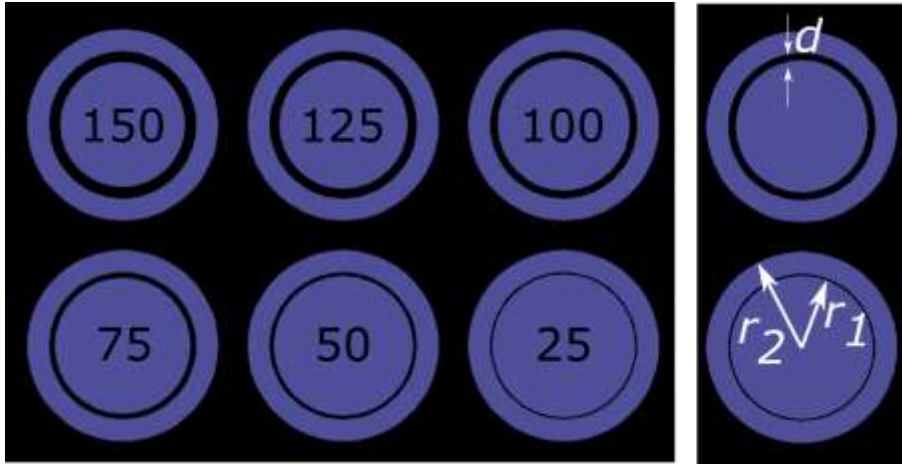


Figure 4.9 Circular TLM pattern (left 6 structures) used for the samples plated without prior Pd/Sn activation. The spacing (in units of microns) between the inner circle and outer ring d is written in the centre of the structure. The two structures on the right are depicted to define dimensional constants only.

4.3.4 Contact recombination measurements

In previous studies of contact recombination, the recombination rate at the metal-silicon interface has typically been estimated by graphing the recombination currents J_{01} and J_{02} of completed solar cells as a function of metalised fraction [282-284]. More recently, Fell *et al.* reported a method which uses Quokka [285] to extract the injection level dependent recombination current density of a sample with locally processed regions of interest from the area averaged PL signal, calibrated using PC measurements [120]. The advantage of this method is that local contact regions can be spatially resolved and the local J_0 values extracted. A full description of the technique to extract J_{0c} is outlined in Refs [120, 285], however a brief description of the method as it was applied to the samples plated without prior activation is outlined in the following sequence steps. Note that the ‘unprocessed regions’, where the PC measurement was taken, is depicted by the red central box in Figure 4.6.

- 1) *Characterisation of the test sample.* This involved a direct measurement of all the relevant samples parameters including:
 - a. Wafer thickness, measured using a micrometer
 - b. Active dopant concentration, including peak dopant concentration, the active dopant profile as a function of depth and sheet resistance. The sheet resistance was measured with a four-point probe, mapping 64 points across the wafer. This was used to calibrate the profile measured via ECV

- (CVP21, WEP) and was performed after all characterisation was complete, given the destructive nature of the test.
- c. Surface reflectance measured with UV-VIS spectroscopy (Lambda 750, Perkin Elmer).
 - d. The bulk resistivity, measured via dark conductance measurements.
 - e. Photoluminescence images of the patterned and un-patterned regions (LIS-R, BTImaging) using a 1025 nm short pass filter. These measurements were deconvolved using the PL Pro software package [286].
 - f. The J_{0e} , in the unprocessed regions measured via PC lifetime measurements (WCT-120, Sinton Instruments). Transient measurements were performed on all samples. The high injection behaviour was measured in generalised mode and the optical constant calibrated to the transient measurement.
 - g. The fixed bulk lifetime. This fixed parameter is required for Quokka simulations. It was extracted using Quokka's Suns- V_{oc} fitting tool, which effectively simulates a steady-state PC measurement, by calculating the carrier density during the Suns- V_{oc} measurement. In these situations, the bulk lifetime was used as a free parameter.
- 2) *Simulation of the photoluminescence of the unprocessed region.* This requires the measurement of the photon flux during PL imaging of the sample, and simulation of the generation rate under illumination during photoluminescence measurement. This can be simulated in software packages such as OPAL 2 [104]. The PL signal of the fully characterised symmetrical structure was then simulated in Quokka, yielding the simulated average PL counts for the unprocessed region.
- 3) *Calculation of the factor A.* This factor relates the simulated PL signal to the measured PL signal of the unprocessed region according to the equation:

$$A = \frac{\text{measured PL counts}}{\text{simulated PL counts}} \quad \text{Eq. (4.16)}$$

- 4) *Measurement of the average PL counts in the processed regions.* This involves measuring the average PL signal in the metallised processed region (green boxes, Figure 4.6).

- 5) *Calculation of the simulation target PL counts of each processed region*, by dividing the measured PL counts in each processed region by the calibration factor A . The target PL counts is the average PL counts that the Quokka simulation aims to replicate via changing the J_{0c} in the unit cell processed region and simulating the resulting average PL signal until the simulated and target PL counts match.
- 6) *Simulation of the PL counts to fit the simulated PL to the target PL values* by varying the free parameter J_{0c} .

As previously mentioned, a series of 15 arrays featuring contact openings of various dimensions and spacings was used to measure J_{0c} , taking into account any effects associated with the transport and geometry of the contacts. Each pattern had a total area of 10×10 mm with the unit cell mirrored throughout. Rectangular openings were fabricated to reduce the complexity of the simulations (fewer mesh points are required to accurately simulate a rectangle, in comparison to a circular edge, enabling faster simulations) although minor rounding of the corners of the squares was observed under microscope inspection. To reduce the effect of carriers in one patterned array diffusing into an adjacent array, arrays with similar contact fraction were located adjacent to each other. Two characteristic dimensions were varied in each array, the side length of the square contact opening s , and the spacing of the contact openings, d . This geometry is shown in Figure 4.10, which also shows the layout of the patterns on the wafer, as they appear during PL imaging (i.e. metallised side towards stage). The geometry of each pattern is listed in Table 4.3.

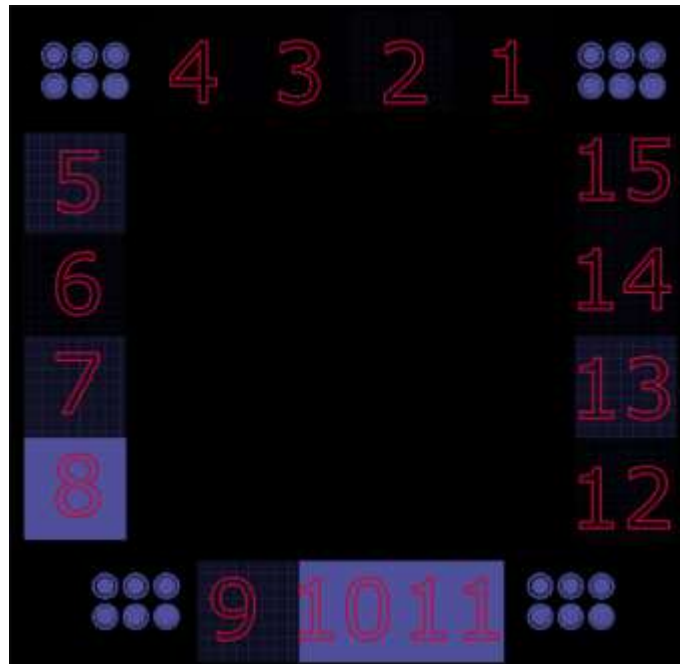


Figure 4.10 Spatial layout of the array patterns on the test structure. Due to the fine feature size some arrays are not fully resolved in this image. Details of the individual pattern geometry is listed in Table 4.4.

Table 4.4 Contact array geometry used in this work for J_{oc} extraction.

Pattern number	Side length, s [μm]	Array spacing, d [μm]	Contacted area fraction [%]
P1	20	500	0.16 %
P2	30	500	0.36 %
P3	30	250	1.44 %
P4	40	500	0.64 %
P5	20	250	0.64 %
P6	30	250	1.44 %
P7	15	125	1.44 %
P8	60	250	5.76 %
P9	30	62.5	23.04 %
P10	20	62.5	10.24 %
P11	40	125	10.24 %
P12	15	62.5	5.76 %
P13	30	125	5.76 %
P14	40	250	2.56 %
P15	20	125	2.56 %

4.4 Results and discussion

In the following analysis, samples are referred to as either EX or PX with reference to Table 4.3, where E signifies an evaporated sample, and P signifies a plated sample, X corresponds to the diffusion recipe number outlined in Table 4.2.

4.4.1 Contact resistivity

The ρ_c extracted from the linear TLM patterns, comparing the nickel plated samples (with the Pd/Sn activation) against evaporated aluminium contacts after sintering is shown in Figure 4.11. In comparison to the nickel plated samples, the evaporated samples recorded lower ρ_c values for all test structures, regardless of the surface concentration of dopants. The ρ_c values for the nickel samples showed a large variance around the mean, and there was no consistent trend between ρ_c and surface dopant concentration for these samples. Similarly, no statistically significant trend towards lower ρ_c values with increased surface concentration was observed for the aluminium samples.

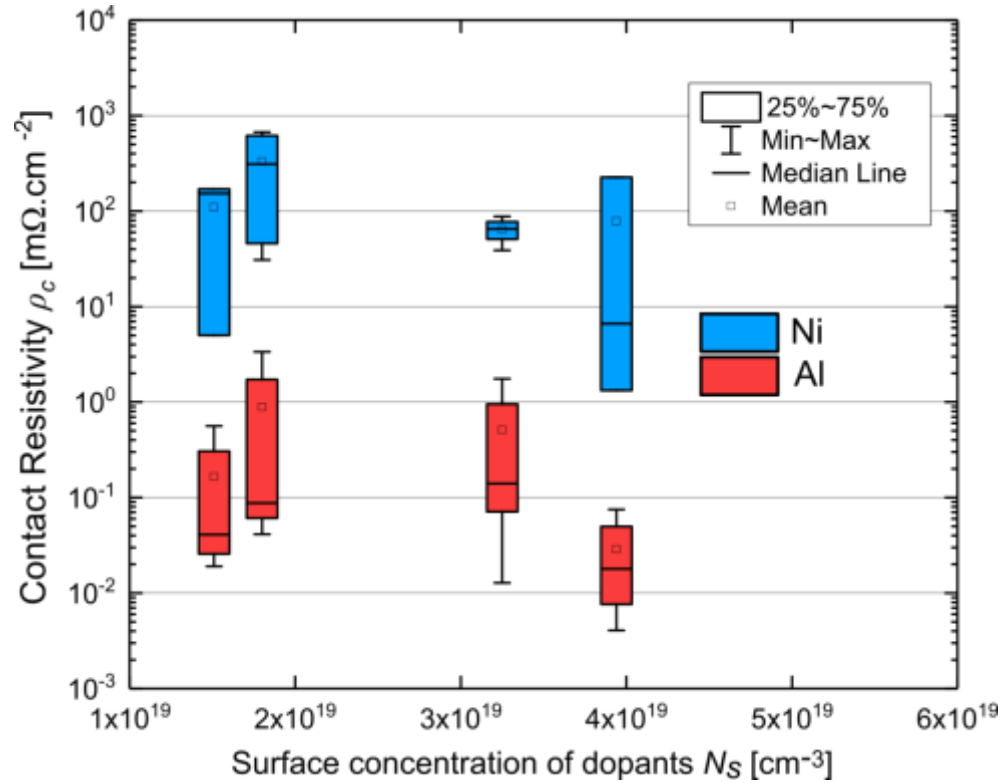


Figure 4.11 Contact resistivity vs. surface dopant concentration after annealing treatment, for nickel plated samples with prior Pd/Sn activation (blue), and aluminium evaporated samples (red).

The four circular TLM patterns on the test sample M1 (which was plated without Pd/Sn activation) were laser cleaved out of the main wafer, and each piece received a separate sintering treatment at a range of temperatures (350-425 °C at 25 °C intervals). The ρ_c of the four test pieces from sample M1 before and after annealing is shown in Figure 4.12. A low range of ρ_c values is achieved for all samples after annealing, with the minimum value of 0.22 mΩ.cm² achieved when annealed for 5 minutes at 425 °C. Since a low value of ρ_c was achieved at the 350 °C set point, the samples P1-4 were also sintered at this temperature—which also enables direct comparison with the aluminium evaporated samples and avoids affecting the passivation of the AlO_x/SiN_x stack.

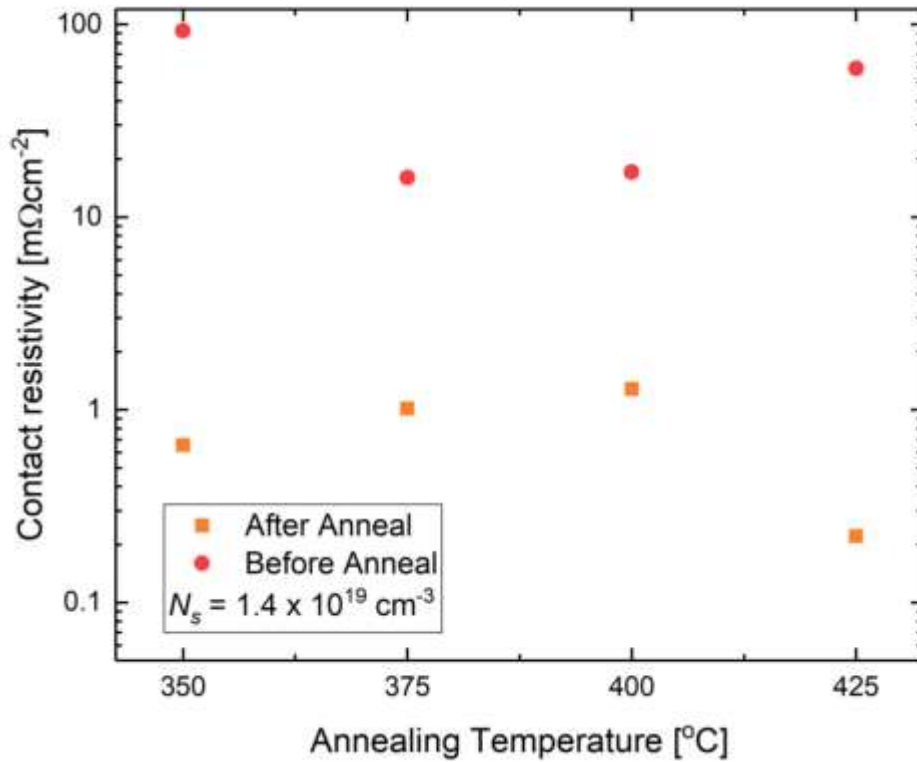


Figure 4.12 Effect of annealing temperature on ρ_c for the nickel plated monitor sample M1. The sample was plated in an alkaline based plating solution without prior activation and the anneal treatment for all temperatures was 5 min in duration.

The ρ_c of the wafers after annealing at 350 °C is shown in Figure 4.13. Again, the nickel plated contacts have higher ρ_c values for all samples in comparison to the aluminium evaporated samples. The evaporated samples do not trend with increasing surface concentration. Similarly, whilst the average ρ_c of the nickel plated samples P1-4 (blue boxes, Figure 4.13) tends to decrease with increased surface concentration, when the results of sample M1 (green boxes, Figure 4.13) was included in the comparison, this otherwise statistically significant trend disappears. Despite ‘identical’ processing conditions, the sample M1 recorded much lower ρ_c values for all anneal temperatures and duration. The reason for the large discrepancy between M1 and the ρ_c values of P1-4 is not clear and will be discussed in further detail in the following discussion section. Overall, the ρ_c values of the nickel plated samples remains relatively large in comparison to the evaporated samples.

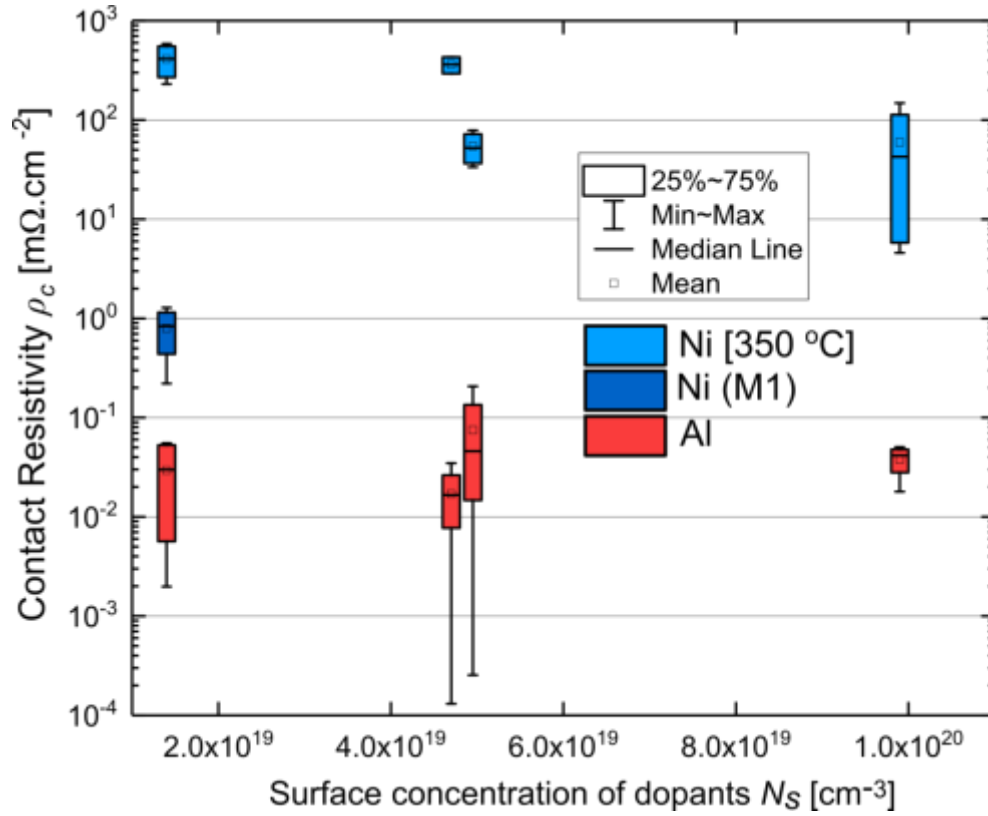


Figure 4.13 Contact resistivity of aluminium evaporated (red) and nickel plated (without prior activation, blue) boron diffused samples after annealing, as a function of surface boron concentration.

The results show that the nickel plated contacts have higher ρ_c than the evaporated reference samples of the same surface doping concentration, despite the published barrier height formed on *p*-Si being lower for nickel-silicon interfaces (0.51 eV [287]) than Al-Si (0.72 eV [99]). Furthermore, the overall nickel plated ρ_c results are notably inconsistent; sample M1 achieved the lowest ρ_c for all plated samples despite the low surface doping concentration. The results of M1 were not repeated for samples P1-4 despite efforts to perform an identical processing sequence between the M1 and wafers P1-4. Similarly, the ρ_c of samples P5-8 were high, with values of $\sim 100 \text{ m}\Omega\cdot\text{cm}^{-2}$, despite ρ_c being $< 10 \text{ m}\Omega\cdot\text{cm}^{-2}$ for P7 and P8. Thus, it was concluded that the ENP process used for this study was not consistent and resulted in highly variable ρ_c values. This suggests that further work is required to improve the process reproducibility and understand the causes for the variances, and mitigate them.

SEM imaging of the nickel plated surface of sample P2 after annealing was performed to assess the morphology of the plated layer, and is shown in Figure 4.14a and b. The images show a surface roughness dissimilar to that depicted in Figure 4.3 for a similar time interval, due to the presence of a number of round, globular features of various sizes

(Figure 4.14b). Further analysis, via for instance EDX analysis, is required to determine the exact nature of these deposits. The transition between galvanic displacement to autocatalytic growth is not fully understood and the electrochemistry at the surface is difficult to characterise. Therefore, to infer the cause of the thinner layer with the presence of large globules measured on these samples is not currently possible. Understanding the initial growth reactions, and its relation to the surface doping, is a key area of further study to improve the reproducibility of this process. However, the presence of the globules and difference in surface morphology suggests that a different growth mechanism may have occurred between the samples imaged in Figure 4.3 and Figure 4.14, possibly due to contamination of the solution or variations in the processing sequence. Alternatively, the globules may be plated contaminants in the solution which have deposited on the surface. Further imaging of the nickel-silicon interface of sample M1 could be performed to compare the interface of this sample with that of sample P2 and the samples imaged in Figure 4.3, to determine any visual indicators of a different plating mechanism occurring.

The presence of a thin interfacial layer is likely to affect the ρ_c results. Other studies have reported the presence of a thin interfacial SiO_x layer present at galvanic nickel plated interfaces [233, 235, 249] which increases the contact resistance. Given the reduced magnification of the images in Figure 4.3 and Figure 4.14, the presence of an interfacial oxide cannot be confirmed. The thickness of the interfacial oxide is related to the initial growth mechanism, which is related to the operating condition and composition of the electrolyte. Minute variations in the processing condition may produce a varying thickness of oxide, which account for the differences in ρ_c values between samples, and more drastically between sample M1 and P1-4, if an oxide layer is evident in either of these samples after annealing. Further high resolution TEM imaging of the interface can confirm this. The presence of an oxide at the nickel silicon interface before annealing is an indicator that the galvanic displacement reaction occurred, and was more dominant than a hypophosphite reduction reaction, which should not produce an oxide layer. This hypothesis can be tested via further interface imaging. Since the mobility of ions in silicon is higher than the mobility of ions in the solution, it is feasible that the galvanic displacement reaction was supplied predominantly by electrons in the boron diffused layer. This could potentially account for the clear difference in plating rate between the boron diffused product samples and the undiffused *p*-type samples used in the process

characterisation in Section 4.1.2; as heavily boron diffused silicon has significantly lower electron conduction and concentration.

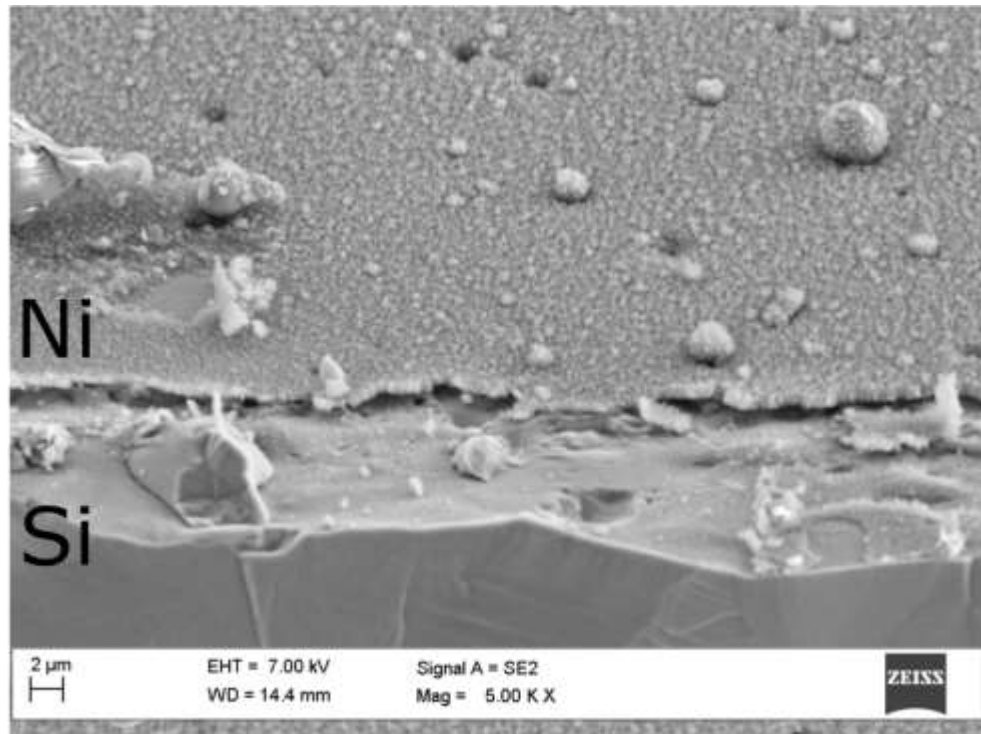
Therefore, the most likely cause for the increased ρ_c for nickel plated samples is due to the growth mechanism of the nickel at the interface and any potential interfacial oxide. Further high-resolution imaging and elemental analysis of each sample is required, as follows:

- 1) Plated test samples of Figure 4.3.
 - a. Inspect the interface for the possible presence of an interfacial SiO_x layer after deposition.
- 2) Sample(s) P1-4
 - a. Inspect the interface for an interfacial SiO_x layer, present before and after annealing.
 - b. Measure the deposit thickness.
 - c. Elemental analysis of the globules and nickel layer composition.
- 3) Sample M1
 - a. Inspect the interface for an interfacial SiO_x layer after annealing.
 - b. Elemental analysis to determine the elemental composition of the metal layer, assessing for NiSi_x formation.

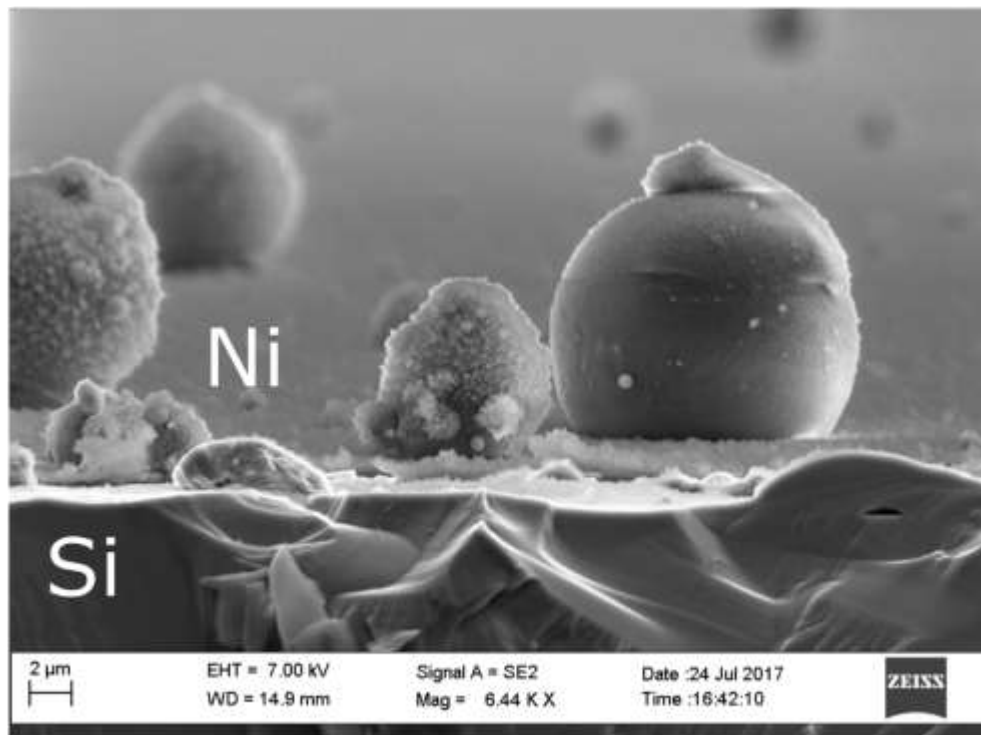
Comparison of the surface morphology and thickness of the deposited layers in the proposed images above may confirm potential variances in the surface reactions, indicating whether process variability can account for the difference in the observed results. Importantly, the presence of an interfacial oxide in samples P1-4 may account for the difference in ρ_c values between these samples and M1, if an interfacial oxide is not present, or as thick, on that sample. Finally, the elemental composition of the layers may give further insight into the initial growth mechanisms, and further explain the variances in ρ_c , if the presence of NiSi in M1 is confirmed, and absent in P1-4. Future plating experiments can improve the process reliability by having more precise measurement and control of the PH of the solution. Although fresh plating electrolyte was used for each plating experiment, by assessing the concentration of the active elements of the electrolyte, to ensure against electrolyte ageing and depletion effects.

As a final comment on the plated contact resistance results, published ρ_c values for aluminium evaporated and nickel plated contact are graphed against the results of this

work, and modelled ρ_c from a theoretical thermionic field emission process in Figure 4.15. The works of Seren *et al.* [208] and Fung [209] are shown as a reference for nickel plated contacts to *p*-type, and the results of Ref. [288] are shown as a comparison for the aluminium evaporated contacts. The ρ_c is modelled as a function of surface doping concentration and barrier height, according to Ref. [289]. For the nickel plated samples, the results of sample M1 show much promise, with an average $\rho_c = 0.74 \text{ m}\Omega\cdot\text{cm}^{-2}$ and lower than all other reported nickel plated contacts on diffused *p*-Si. Although these results were measured with a CTLM pattern, and the published values utilised LTLM patterns. This suggests that the ENP process has significant potential to achieve low contact resistivity values. The values for nickel plated contacts are much higher than the theoretical FTE modelled ρ_c , and higher than the aluminium evaporated samples. This suggests that future work effort is required to realise the potential of electroless plated nickel contacts.



(a)



(b)

Figure 4.14 SEM images of the nickel plated silicon surface (a) after annealing at 350 °C, and with close up view of the large deposits (b) which are non-uniformly distributed across the entire surface.

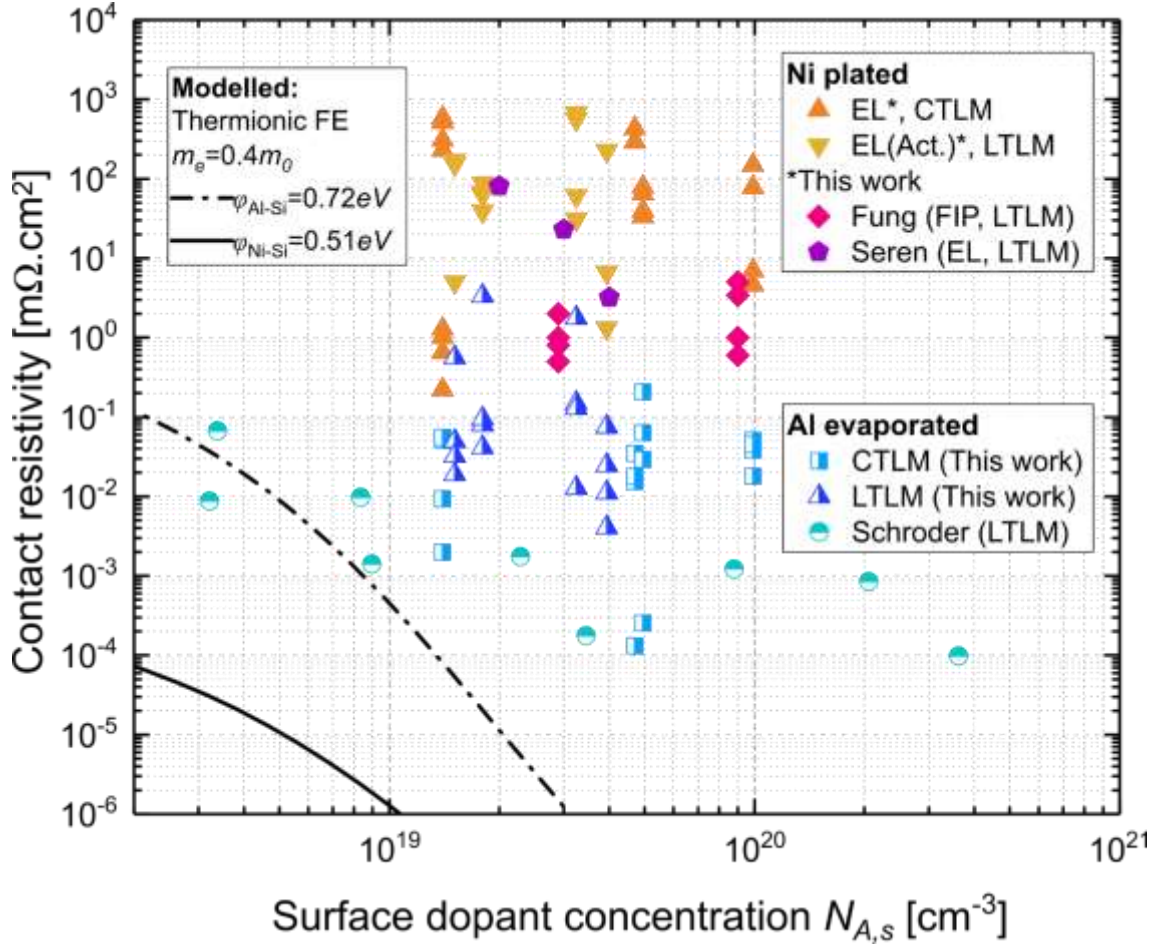


Figure 4.15 Compilation of measured ρ_c values resulting from aluminium evaporated and nickel plated contacts formed on heavily diffused p -type silicon. Solid and dashed lines indicate modelled thermionic field emission ρ_c values.

4.4.2 Contact recombination of nickel plated p^+ surfaces

Photoconductance measurements of each sample were taken to measure the injection level dependent lifetime in the unprocessed centre regions. Each wafer was measured separately to take into account any non-uniformity in sister wafers. With the bulk resistivity and thickness input into the PC analysis spreadsheet, the optical constant of the generalised QSSPC measurements was estimated via fitting the generalised data to the measured data over an injection level range of $\Delta n = 1.5\text{--}7 \times 10^{15} \text{ cm}^{-3}$. The Auger-corrected, inverse lifetime as a function of excess carrier density is shown for all samples in Figure 4.16, revealing a linear trend with injection level. As discussed in Chapter 2, there have been various corrections to the slope fitting method originally outlined by Kane and Swanson. To obtain a more accurate extraction of J_{0e} , the lifetime curves were processed in a Python-based software package [118] and J_{0e} values were corrected using King's Auger model [290], Blum's BGN correction [112] and Kimmerle *et al.*'s SRH

correction [116]. The J_{0e} value used was the maximum value extracted over the injection level range $\Delta n = 1\text{--}2 \times 10^{16} \text{ cm}^{-3}$, in line with the work of Min *et al*, who suggested extracting J_{0e} over a range of values and taking the maximum [117]. To demonstrate this procedure, the corrected J_{0e} values at a range of injection levels for sample P4 is shown in Figure 4.17a with the various corrections applied. Also depicted in Figure 4.17b is a box plot of the corrected J_{0e} at each injection level in the range previously specified, for all samples. Since samples EX and PX underwent the same diffusion, the estimated J_{0e} in Figure 4.17b should be similar. However, some sample pairs displayed a difference in estimated J_{0e} which was related to handling induced damage and process non-uniformity, and is discussed in more detail in the discussion section of this chapter.

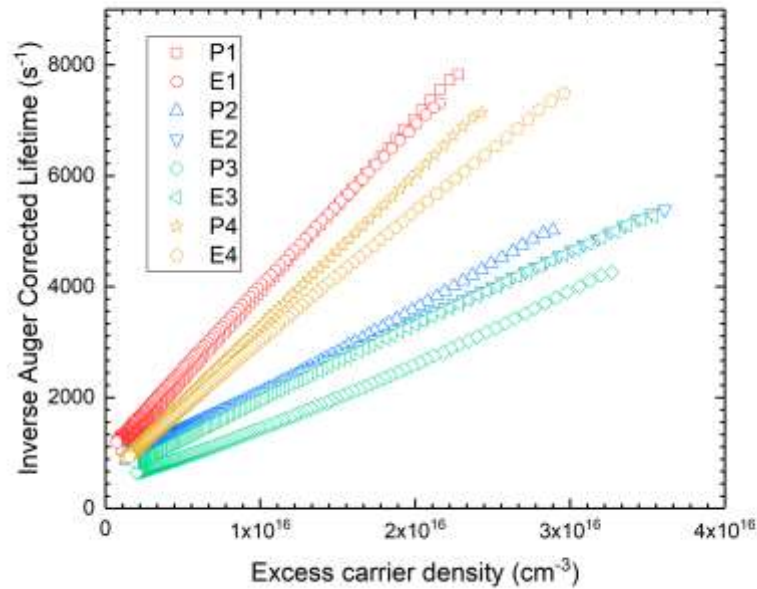


Figure 4.16 Auger-corrected inverse lifetime vs. excess carrier density for all evaporated and plated samples, correction for BGN effects on $n_{i,eff}$. The wafers were measured in the unprocessed centre regions of the wafer, and the optical constant was calibrated to transient measurements of the same samples.

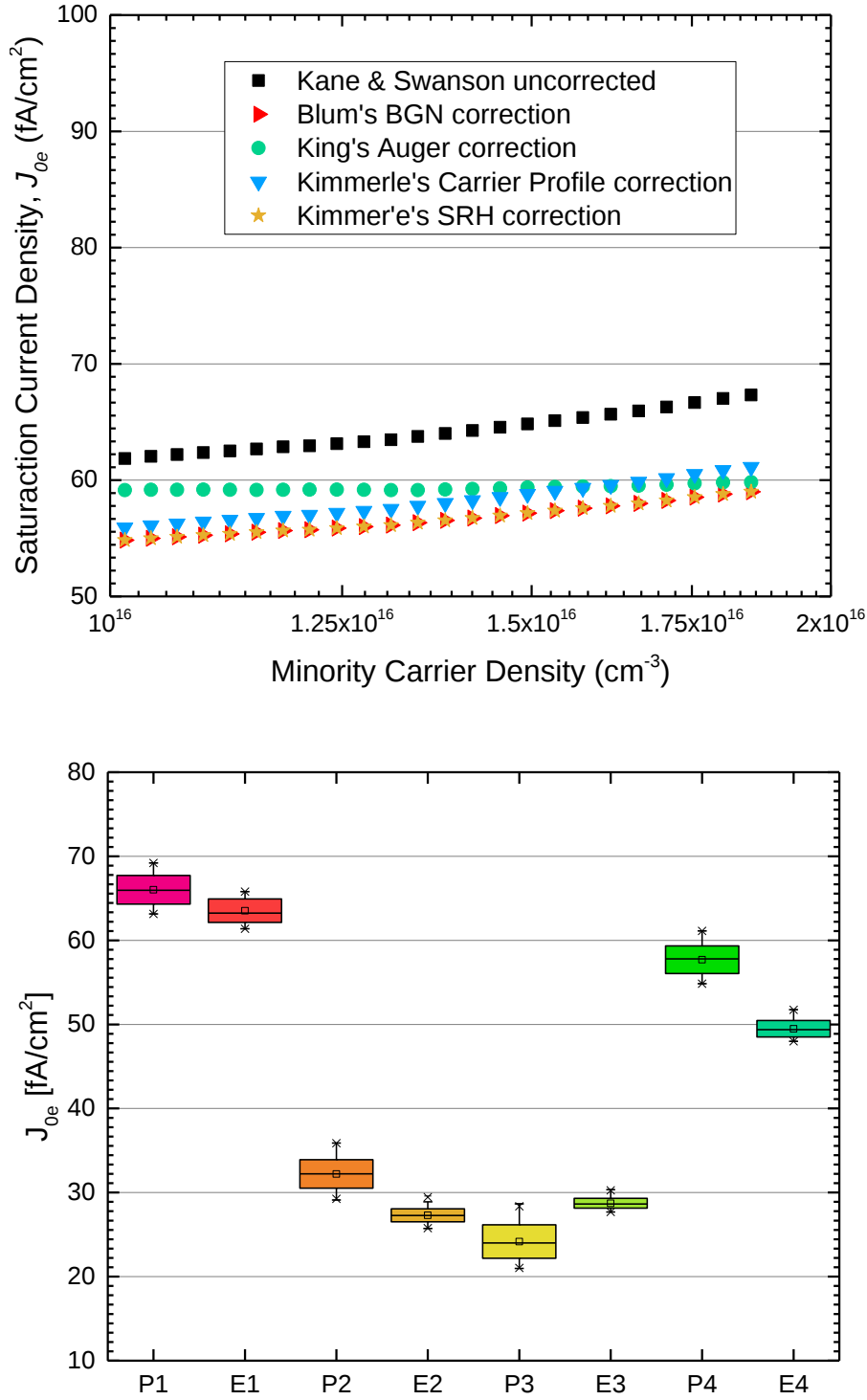


Figure 4.17 (a) Estimated J_{0e} values as a function of injection level for sample P4, showing the effect of correction. (b) Boxplot of J_{0e} for all samples, corrected for BGN, Auger recombination and SRH recombination. The boxes bound the 25-75th percentile data, and the mean and median represented by the square and line respectively. The maximum value is taken for each sample and used in the simulations to extract J_{0c} .

A fixed bulk lifetime $\tau_{bulk, fixed}$, was extracted using Quokka's Suns- V_{oc} curve fitting tool, which simulates the effective lifetime during a typical PC measurement. In this procedure,

the measured effective lifetime of each sample was fitted to the simulated effective lifetime of a symmetrically diffused and passivated lifetime structure (ensuring the same corrections to the PC lifetime measurement are applied in the Quokka simulation), using inputs of thickness, optical generation profile, and J_{0e} of the sample. An example of the fitted and simulated effective lifetimes is shown in Figure. 4.18, and the extracted values and corresponding R^2 values are listed in Table 4.5.

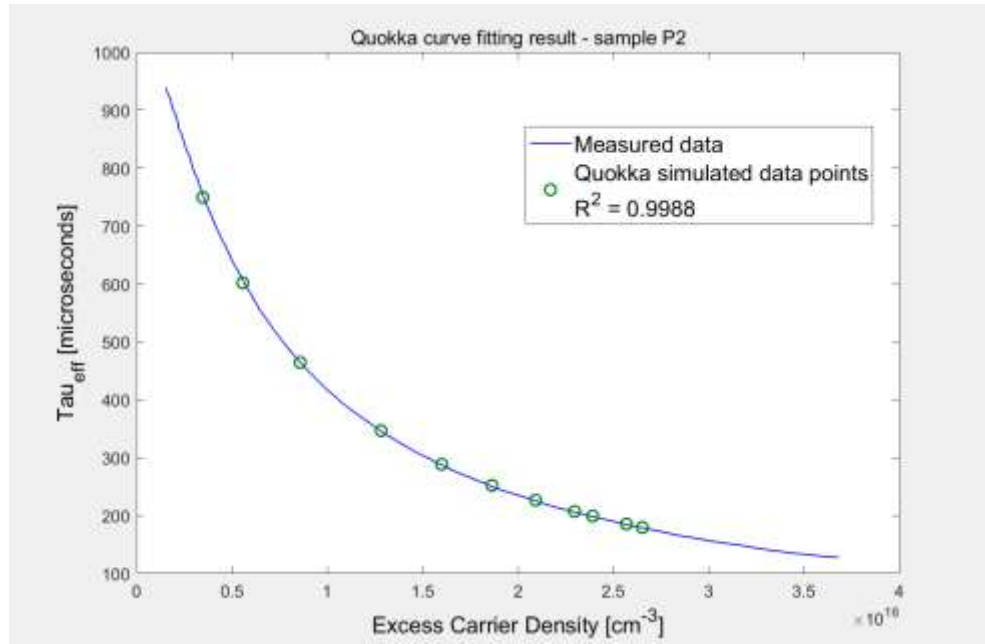


Figure. 4.18 Simulated effective lifetime (symbols) compared to the measured effective lifetime (line) for sample P2, demonstrating the fitting procedure used to extract $\tau_{\text{bulk, fixed}}$.

With the passivated regions of the samples fully characterised, the PL counts of the unprocessed areas were reproduced in Quokka, which takes into account the measured transmission of the 1025 nm short pass filter used in this work. The average PL signal of each array and PC calibration area was measured, and the calibration factor A was calculated for each sample. Figure 4.19 plots the average measured PL counts for each region of the metallised samples.

Table 4.5 Extracted bulk lifetime and boron diffused region performance parameters

	$\tau_{bulk, fixed}$	Bulk Fitting	$J_{\theta e_max}$	$J_{\theta e_average}$	$J_{\theta e_Auger}^1$	IQE ¹
	[μs]	R ²	[fA/cm ⁻²]	[fA/cm ⁻²]	[fA/cm ⁻²]	
E1	1453	0.9862	65.8	63.5	48.1	0.954
E2	1785	0.9989	29.6	27.3	18.9	0.993
E3	2554	0.9974	30.3	28.7	11.9	0.992
E4	3264	0.9910	51.8	49.5	9.8	0.983
P1	3232	0.9931	69.2	66.0	48.1	0.950
P2	3661	0.9988	35.9	32.2	18.9	0.991
P3	3603	0.9917	28.7	24.2	11.9	0.993
P4	5624	0.9947	61.1	57.8	9.8	0.980

¹ Extracted using EDNA2, with input of the ECV diffusion profile, assuming 100 % dopant ionization, and simulated using Fermi-Dirac statistics, Schenck's Band gap narrowing model [113] and Richter's [71] parameterisation for the intrinsic lifetime.

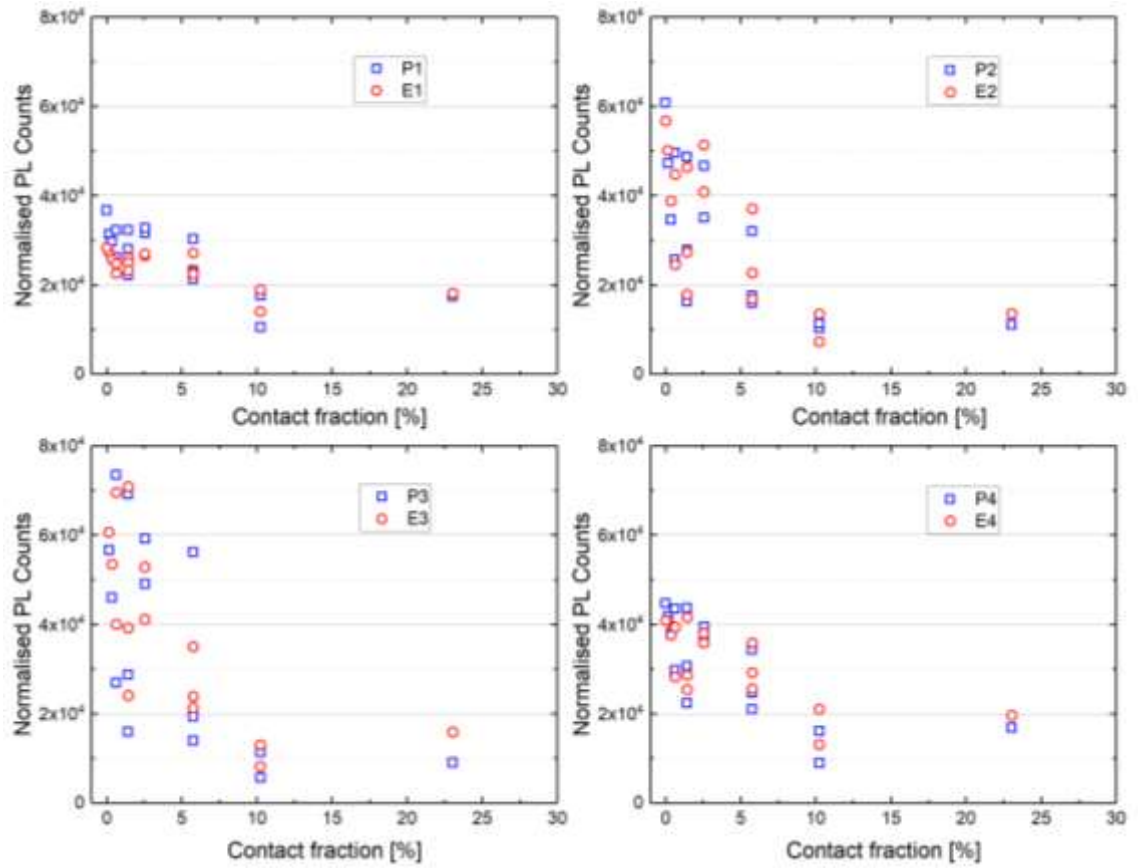


Figure 4.19 Average normalised PL counts as a function of the contact fraction of the individual arrays for plated and evaporated samples.

Finally, the target PL intensity was calculated by multiplying the measured PL intensity by the calibration factor A for each sample. The recombination at the contacts was then extracted for each array by fitting the simulated average PL to the calculated target values. A range of J_{oc} values was extracted for each contact fraction, for a given surface concentration and metallisation method (i.e., plated without activation or evaporated). Not all contact fractions converged successfully in the simulations and so data from these samples were omitted in the following results. Figure 4.20 graphs the estimated J_{oc} values as a function of contact fraction for each surface concentration, from which the following key trends are identified:

- 1) There are a range of J_{oc} values extracted for the same contact are fraction This suggests that the overall contact recombination may be affected by the contact geometry.
- 2) For samples E/P1 and E/P4, the J_{oc} values tended to decrease as the contact fraction increased. However, this trend is not evident for samples P/E2 and P/E3

where there was no strong correlation between contact fraction and the extracted J_{oc} values.

- 3) The J_{oc} values are higher for the plated samples in comparison to the aluminium evaporated samples.

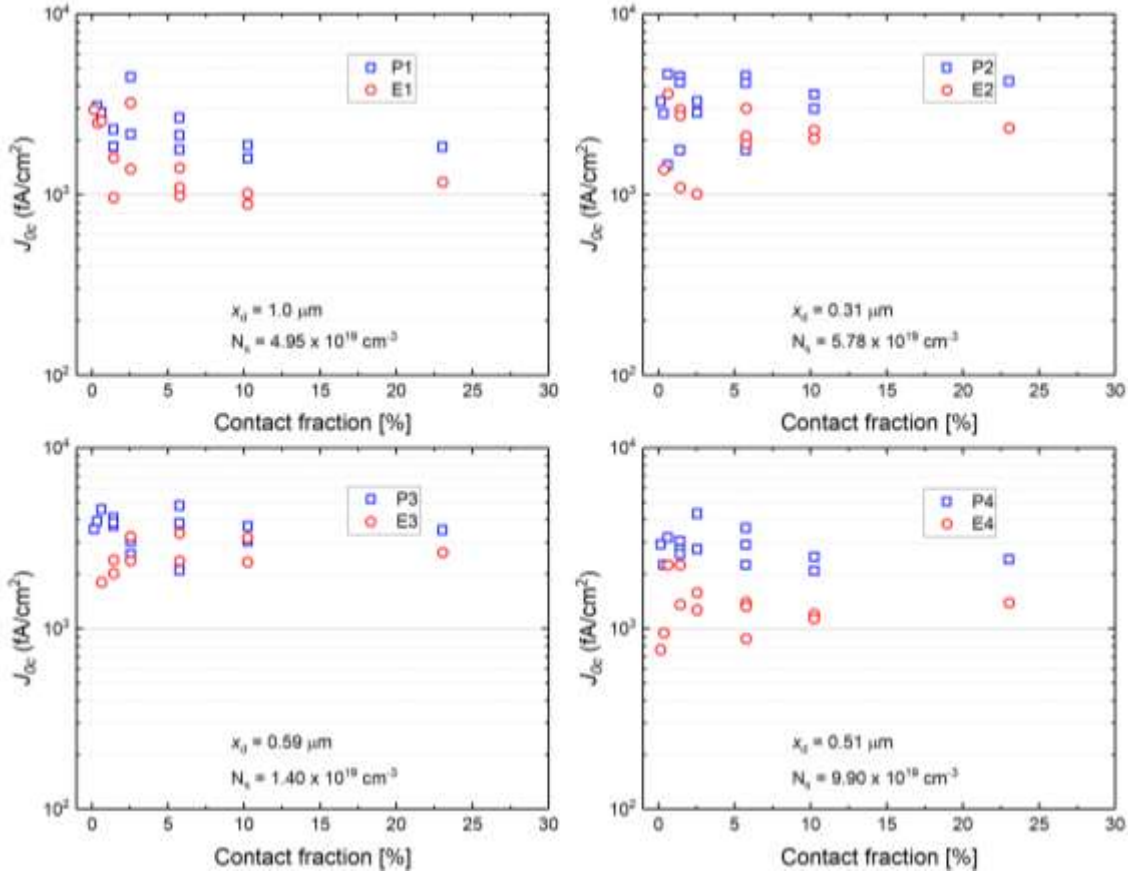


Figure 4.20 Estimated J_{oc} graphed as a function of contact fraction for each diffusion recipe.

To assess the effect of the diffusion profile on contact recombination, a boxplot of all the extracted J_{oc} values as a function of active dopant concentration at the surface for each sample is shown in Figure 4.21. This plot highlights the trend between J_{oc} , surface concentration of active dopants and metallisation method. It shows that:

- 1) As the surface concentration increases, the J_{oc} decreases, suggesting that reducing the minority carrier concentration at the contacts is highly important for both metallisation methods. This was evident upon comparison of E3(P3) and E4(P4), which have similar diffusion depths, yet a large difference in surface concentration of dopants. However, this observed difference in average J_{oc} between these samples was not found to be statistically significant using a two-tailed t-test with a significance level of 0.05. This suggests that more

measurements are required to confirm that the apparent trend is a result of the varying surface concentration.

- 2) A comparison of samples E(P)1 and E(P)2 in Figure 4.21b and d, which have similar surface concentrations but much larger junction depths, appears to show a trend in decreased J_{oc} with increased junction depth. Using a two-tailed t-test, the observed difference in mean between samples E(P)1 and E(P)2 was found to be statistically significant for the plated samples P1 and P2, but not for samples E1 and E2, at a significance level of 0.05. This suggests that increasing the junction depth can reduce the likelihood of recombination at the metal-silicon interface, although more measurements are required to confirm this trend is consistent with the evaporated samples.

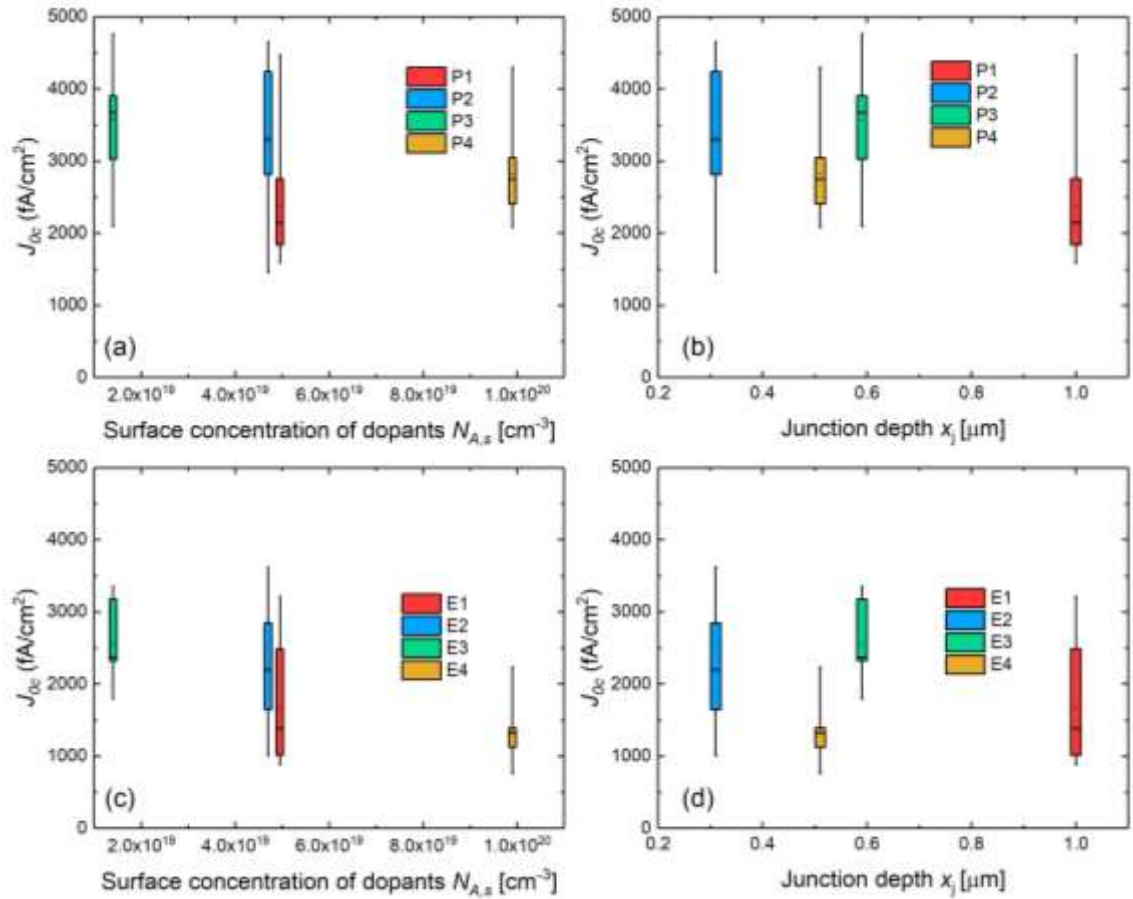


Figure 4.21 Estimated J_{oc} as a function of active surface dopant concentration and junction depth for plated (Plots A and B) and evaporated samples (Plots C and D). The box plot depicts the maximum, minimum and average values for each sample, with the box bounding the 25-75 percentiles.

During the process of J_{oc} estimation, all reasonable efforts were taken to minimise error in the simulations, however, not all simulations converged to a J_{oc} value. Overall, 13 out

of the total 120 simulations failed to converge, and the possible reasons for non-convergence are discussed below.

1) Sample non-uniformity

Sample non-uniformity can originate from a wide variety of sources, with the main causes being handling induced contamination and damage, and process non-uniformity introducing variances across the wafer. The PL intensity and lifetime characteristics in this technique are spatially aggregated measurements, and therefore the effects of any spatial non-uniformity are aggregated with the unaffected regions. This has implications for the extraction of the surface recombination properties, since only the contacted and non-contacted regions are simulated. If a third damaged /contaminated region was present in the sample (from, for instance, processing non-uniformities, or damaged regions) and incorporated into the area averaged region in the vicinity of the contact arrays, then in the event that this region has a lower J_{0e} than the un-affected areas, then the overall effect will be an underestimation of the extracted J_{0c} values. Similarly, if a damaged region—with lower J_{0e} /PL counts than the unaffected region between the localised contact openings—was present in the area averaged during the lifetime measurement (the red square in Figure 4.10), this effectively overestimates the J_{0e} of the passivated region in between the metal contacts, and will therefore underestimate the J_{0c} . This is because the PL counts contribution from the passivated region will be lower, and so a higher contribution of PL counts needs to be fitted in the contact region, resulting in a lower J_{0c} . As a result, all efforts to avoid surface contamination, and the measurement of areas with obvious surface contamination and damage were undertaken. Furthermore, as large an area as possible was measured in order to diminish the relative contribution of minor non-uniformities. The effect of non-uniformities can be assessed by inspection of the PL images of the samples after anneal, (see Figure 4.22). From the PL images, the counts are relatively uniform across all wafers, with the exception of samples E2 and E3, which have some spot contamination (E2) and general non-uniformities in the passivation (E3), which corresponds to a large variance in the estimated J_{0e} and J_{0c} values for these samples. It is interesting to note that these variances are not unique to those particular samples, and other samples with much more uniform PL signal also had similarly large variances in the extracted J_{0c} values (for instance, P1-4, which had large variances but relatively more uniform PL). Therefore non-uniformity in the PL signal from contamination or process non-uniformity cannot fully account for the variances observed in J_{0c} .

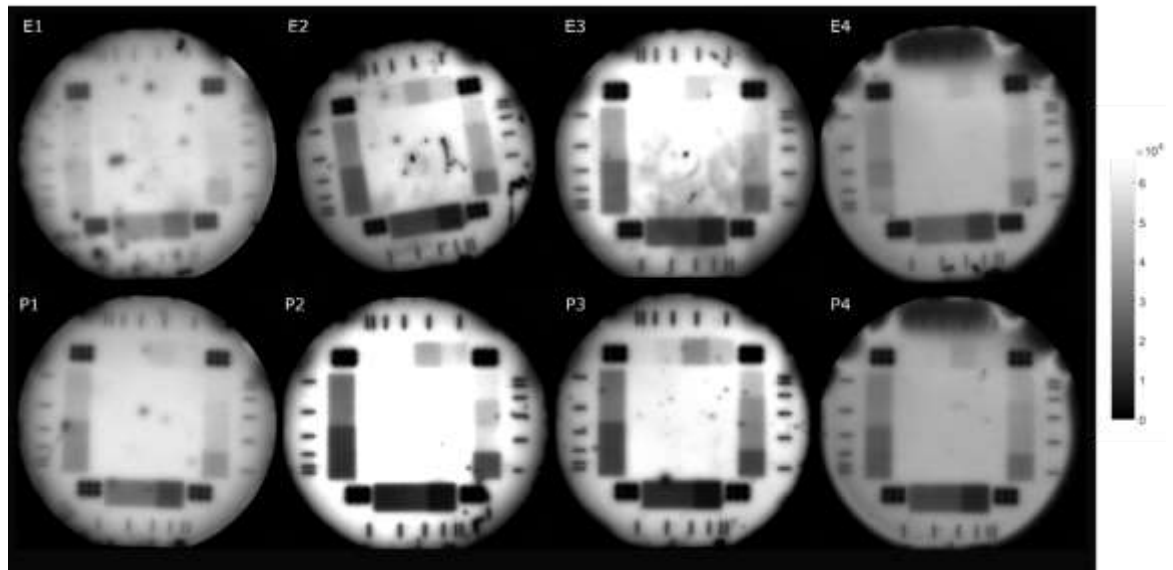


Figure 4.22 PL images of all samples after anneal and normalised to exposure time, depicting good uniformity for all samples except E2 and E3. The samples were imaged at 1 sun illumination for 0.1 s and were processed using PL Pro for point spread function correction [291]. Some images (P2, P3 and E3) appear saturated, however, this is an artefact of the image processing software, and all extracted values were measured on unsaturated images and scaled accordingly.

2) Pixel resolution of the PL images

The PL camera used in this work aggregates the PL signal of a $\sim 120 \times 120 \mu\text{m}$ area into a single pixel in the PL camera sensor. Therefore, there is a limit to the feature size which can be resolved in the image. Since in this instance the parameter of interest is the counts per pixel, provided that the camera is sensitive to the small variations in PL intensity due to the underlying features, the effect of limited resolution should be negligible, since the aggregated signal will scale with the constituent PL signal and the simulation fits the averaged simulated PL signal over the unit cell. Provided that the area averaged in the measured PL area is larger than the unit cell (which is true for all cases) then the finite resolution of the camera is unlikely to have had a significant impact.

This is a limitation of this method, since these feature sizes, although small, are within the geometry of similar features deployed in actual solar cells. Larger features could be fabricated, however in this case the simulation unit cell is much larger, which then sacrifices accuracy for solving time. These larger feature sizes may not replicate meaningful geometries in actual solar cells. This limitation could potentially be overcome by reimaging the samples with microscopic PL systems, which magnify a small area to achieve smaller coverage per pixel. However this would not overcome the limitations of

carrier smearing, and require recalibration of the flat field correction, point-spread function correction and the effect of the filters in the zoom lens on the filters.

3) Dependence on the bulk lifetime and J_{0e}

With higher bulk lifetime, the proportional amount of recombination occurring in the bulk is less and therefore the measured PL intensity is more sensitive to the surface recombination, which is ideal for this study. In this work, care was exercised to maximise the bulk lifetime and thereby reduce the dependence of the measurement on the bulk lifetime. High resistivity *n*-type FZ wafers were used and a bulk lifetime stabilisation pre-oxidation process was performed on all wafers to minimise bulk lifetime degradation during subsequent thermal processing. However due to the nature of this J_{0c} estimation technique, there remains a sensitivity to uncertainty in the extracted bulk lifetime. If the bulk lifetime is underestimated in the simulations, then the surface recombination will be underestimated, resulting in the extraction of J_{0c} values which are too low. If the bulk lifetime is overestimated, then the surface recombination at the contacts will be overestimated. This is because the PL contribution from the bulk is overestimated, which must then be compensated by increased surface recombination at the contacts. It is also important to consider the mutual dependence on J_{0e} since underestimation of J_{0e} will result in an overestimation of the J_{0c} , as a disproportionate amount of PL counts is simulated in the un-metallised regions, and so less PL counts is required from the contact regions, and hence the J_{0c} is overestimated. It was for this reason that significant effort was taken to estimate J_{0e} in the passivated regions accurately and the maximum J_{0e} over the full range of injection levels analysed was used in the simulations. To estimate the effect of variances in bulk lifetime and J_{0e} on the simulation, the PL signal of the unprocessed regions for a range of J_{0e} and $\tau_{bulk, fixed}$ values was simulated. Figure 4.23 overlays the extracted bulk lifetime and J_{0e} values of each sample (see Table 4.5) with the simulated dependence of the PL counts on J_{0e} and $\tau_{bulk, fixed}$. For $\tau_{bulk, fixed} < 2$ ms, there was a large variance in the PL signal, which plateaus for larger $\tau_{bulk, fixed}$ values. This suggests that any uncertainty in the $\tau_{bulk, fixed}$ value extracted has a larger impact on the extracted J_{0c} during Quokka simulation. Furthermore, this effect was more pronounced for lower J_{0e} values, as for lower J_{0e} values the bulk recombination makes up a larger portion of the overall recombination, and therefore the PL counts. There was likely to be higher uncertainty in samples E2 and E3 due their relatively low J_{0e} and low bulk lifetime.

For samples E1, P1 and P4, less of the variance observed in the extracted J_{0c} was likely to be due to uncertainty in the estimated $\tau_{bulk, fixed}$ value.

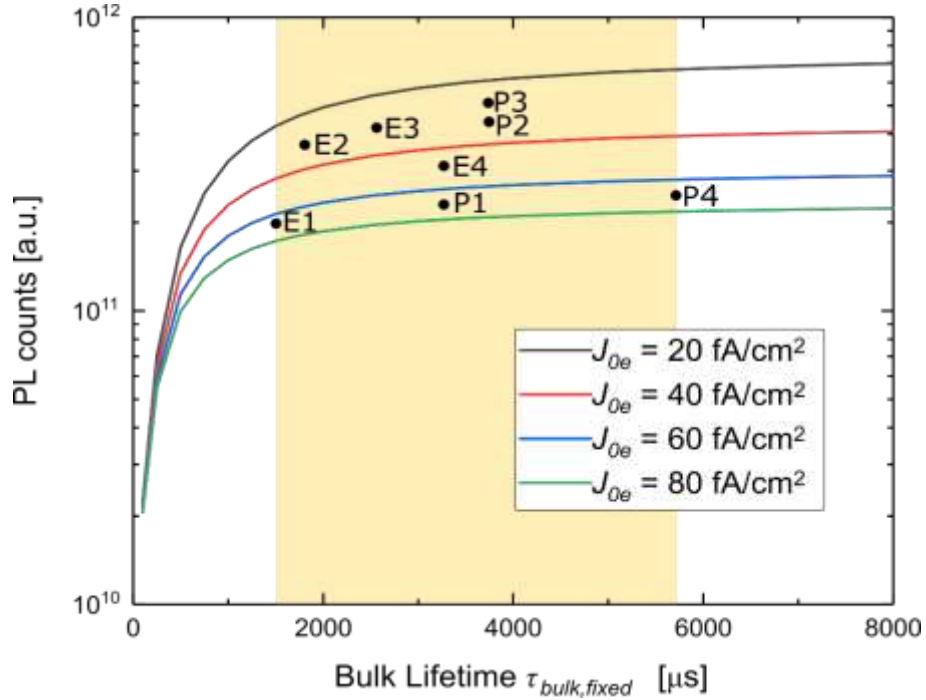


Figure 4.23 Quokka simulated PL counts for the unprocessed regions as a function of bulk lifetime, for varying J_{0e} (front and rear J_{0e} is set to equal). The bulk extracted bulk lifetime for each sample is indicated on the plot. The PL signal was particularly sensitive for lower bulk lifetime, and for higher J_{0e} values.

A large variance in the extracted $\tau_{bulk, fixed}$ between samples can be seen in Table 4.5. A variance in bulk lifetime, was not expected between similarly diffused sample pairs (for instance, E1 and P1 should have similar J_{0e} and τ_{bulk} , etc.) since these samples underwent identical processing. The difference in J_{0e} and $\tau_{bulk, fixed}$ comparing sample pairs can likely be attributed to variances in the diffusion process conditions. However, samples E1, E2 and E3 all recorded low bulk lifetimes which were lower than their respective P_x pair wafers. To determine the cause of the observed variance between sample pairs, the injection dependent corrected effective lifetime curves of the samples before (filled markers) and after metallisation (unfilled markers) is graphed for each sample pair in Figure 4.24. This corresponds to Steps 5 and 11a/b of the processing sequence depicted in Figure 4.7. Figure 4.24 shows that all sample pairs had almost identical lifetimes after passivation anneal, except for P1 and E1, which had different lifetime trends before metallisation. Therefore, the observed variance between samples E1 and P1 was likely due to process non-uniformity and handling differences incurred before metallisation. Samples pairs which underwent diffusion 2 and 3 display very similar injection dependent

effective lifetimes before metallisation, however the curves diverge after metallisation, which suggests that the difference in extracted bulk lifetimes was due to the differences in handling for the plated and evaporated samples during the metallisation procedure, which induces varying degrees of damage. Sample P4 and E4, had similar effective lifetime characteristics before and after metallisation, however the Quokka extracted $\tau_{bulk, fixed}$ values suggests that the bulk lifetime of sample P4 is ~ 2 ms larger than E4. This is likely due to the difference in J_{0e} extracted. Since P4 and E4 have similar effective lifetimes, the lower (higher) J_{0e} is ‘compensated’ by a higher (lower) bulk lifetime for P4(E4). In all cases above, the differences in $\tau_{bulk, fixed}$ observed between pairs of wafers extracted with Quokka was consistent with the variances in effective lifetime and J_{0e} extracted via the PC measurements. This is perhaps not surprising, since the extracted PC values were used as input into the Quokka bulk lifetime fitting procedure, and so the values are interdependent. Uncertainty in the $\tau_{bulk, fixed}$ values is therefore more likely due to the accuracy of Quokka to simulate an effective lifetime curve via the Suns- V_{oc} fitting procedure. This was minimised by fitting a large number of measured effective lifetime points and extracting high R^2 fitting values. Ideally, a separate independent measurement of the bulk lifetime is the most effective way of verifying the bulk lifetimes extracted using Quokka. To this end, an alternate method of determining the bulk lifetime could be trialled in future work (e.g. etching back the diffused layers and passivating the wafers in a superacid solution [292], to estimate the bulk lifetime from PC measurements).

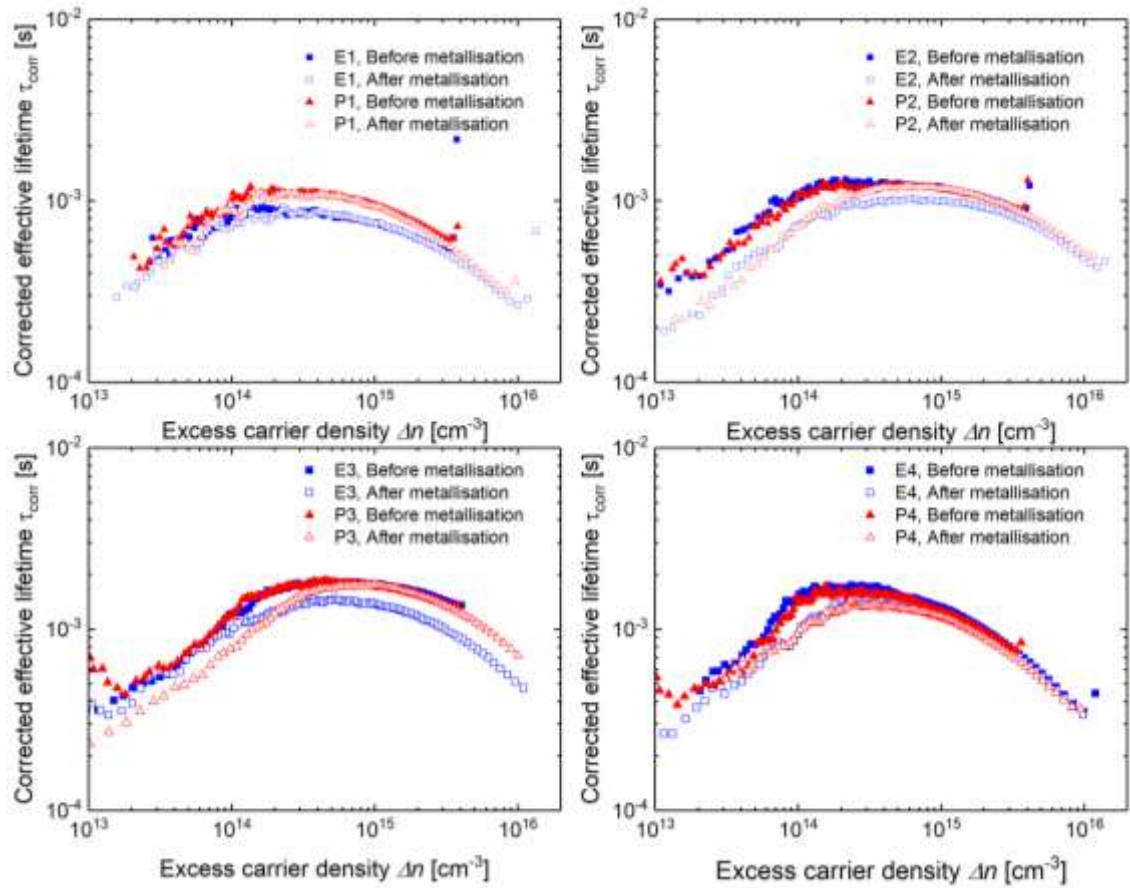


Figure 4.24. Measured injection level dependent, Auger-corrected effective lifetime curves before and after metallisation for each sample, grouped in pairs by diffusion recipe ID, measured by PC decay measurements.

4) Optical absorption at the rear

The PL system used an excitation a wavelength of 808 nm and therefore some incident photons will reach the rear of the wafer, where they can be absorbed within the metal contact regions. This effectively reduces the generation rate within the device, and the resulting reduced PL signal due to this effect was not accounted for in the analysis. Therefore, a difference in the rear optical properties of the metals will affect the measured PL counts and subsequent J_{oc} estimation. This is a general limitation of this J_{oc} estimation technique. The absorption in the metal is affected by the metal thickness, and the extinction coefficient of the material. Since the extinction coefficient for nickel at 808 nm is lower than aluminium [293], it was expected that the aluminium would absorb more of the incident radiation resulting in an overestimation of the recombination in the aluminium samples relative to the nickel plated samples. This will be mitigated somewhat by the fact that the generation rate at the rear is significantly reduced compared to the surfaces. However, it was observed in Figure 4.19 that the aluminium contacts had on

average higher PL counts than the nickel plated samples for a given contact fraction, and particularly at higher contact fractions where this effect is likely have a greater impact. Therefore, this effect is not likely to have significantly affected the results, although it does suggest the possibility that the J_{0c} for both aluminium evaporated and nickel plated contacts was overestimated, and that aluminium contacts were overestimated to a larger extent than the nickel plated samples. This effect could be accounted for by simulating the metal absorption in each layer, and then scaling the generation rate used in the simulation accordingly. However, this would need to be performed for each individual contact array and depending on the sensitivity of the sample thickness, is likely to be time-consuming.

Some variance in the results is expected from the varying contact geometry, which affects the carrier transport to the contacts as well as current crowding effects. Figure 4.19 shows that a range of PL counts was measured for the same contact fraction. In the event that this variation resulted from accurately resolved PL data, and was not affected by the area averaging of each pixel as previously discussed, then the variance observed can also be attributed to varying contact fractions affecting the charge carrier's ability to diffuse to the contact. Therefore, some spread in the J_{0c} data of Figure 4.20 and Figure 4.21 may arise due to this effect. This suggests that careful consideration of the contact geometry is required when optimising the geometry of rear point contact structures. Further analysis of the effect of contact geometry could be considered in future studies.

The key finding relating to J_{0c} is that for each sample pair, the average nickel plated contacts have higher J_{0c} than evaporated contacts on equivalent p^+ diffused surfaces. The difference in average J_{0c} between sample pairs was found to be statistically significant using a two-tailed t-test with a significance level of 0.05. To the extent that this difference in mean is due to variances in J_{0e} or the extracted bulk lifetimes, the previous discussion has shown that these effects are consistent with the measured effective lifetime of the samples and the observed non-uniformity from handling and processing induced damage. In other words, the factors which introduce variance cannot be related entirely to the J_{0c} extraction method. The results could be further verified by quantifying the optical losses due to metal absorption, to confirm that this effect was in fact insignificant, and to gauge the extent to which the J_{0c} values for both metallisation technologies were overestimated. Secondly, external measurement of the bulk lifetime, via for instance super acid passivation, could confirm the Quokka extracted $\tau_{bulk, fixed}$ values. In which case, the

systematic error inherent in the Quokka method is applied to all samples and therefore it can be assumed that the relative trends between samples were accurately resolved.

To investigate the underlying cause of the high J_{oc} values, the nickel plated interface of the samples could be imaged with high resolution Transmission Electron Microscopy (TEM). The interface could be inspected for features which would enhance surface recombination such as:

- i) *Surface roughening*. This increases the effective surface area of the metal-silicon interface, increasing the total surface recombination rate.
- ii) *Lattice distortion* of the silicon. This could introduce defect sites within the lattice and increase recombination in the silicon.
- iii) *Surface contamination*. Energy-dispersive X-ray spectroscopy (EDX) analysis could confirm the contamination of the underlying bulk silicon with, for instance metallic impurities from the nickel plated process.
- iv) *Etching of the silicon surface*. As previously mentioned, silicon etching has been observed in highly alkaline solutions [294], however in this work, etching of the silicon was hypothesised to be mitigated by the high boron concentration. In the event of significant surface etching, this may account for an increase in J_{oc} if a) the surface concentration underneath the contact is reduced such that the minority carrier conduction around the metal is increased and b) the effective surface area of metal-silicon interface is enhanced.

Comparison of the aluminium evaporated and nickel plated samples at the interface could reveal differences which support the observed results of higher J_{oc} on nickel plated samples.

4.5 Chapter conclusions

The J_{0c} and ρ_c characteristics of contacts formed by electroless nickel plating was explored in this chapter. A process to deposit nickel plated layers via electroless plating without prior activation on polished silicon substrates with good adhesion and uniformity was developed and characterised. Measurements of the plated metal thickness after various time intervals in the plating electrolyte are evidence to support a two-step growth mechanisms characterised by a nucleation phase, followed by an autocatalytic growth phase. This latter growth phase had an estimated growth rate of 1.76 nm/s.

A boron diffusion process was then developed and a range of samples with varying diffusion profiles which simulate the effect of varying surface concentration and depth on J_{0c} was fabricated. Dedicated ρ_c and J_{0c} structures were fabricated on a single wafer for each diffusion profile. The J_{0c} was extracted via a method which used Quokka simulations to extract the localised contact recombination from PC calibrated PL measurements, whereas ρ_c was extracted using a combination of CTLM and LTLM patterns.

The average J_{0c} values extracted were higher for nickel plated samples compared to the aluminium evaporated samples of the same surface dopant concentration. This trend was found to be statistically significant. Furthermore, although there was the appearance of a decrease in J_{0c} with increasing junction depth and increasing surface concentration, in most cases these trends were found to be statistically insignificant, suggesting more measurements are required to confirm if these trends are in fact a result of the characteristics of the underlying diffusion. Whilst most of the observed variances in J_{0c} could be accounted for due to variations in the samples induced from processing, there remains potential for further verifications of the results by; 1) quantifying the effect of pixel aggregation, 2) determining the extent of underestimation due to optical absorption at the rear and 3) external measurements of the bulk lifetime. The effects of contact geometry in causing a variance in J_{0c} values is an additional area of future work. Importantly, further analysis of the interface via EDX analysis and high resolution TEM imaging may assist in identifying the cause of the difference between nickel-silicon and aluminium-silicon contact recombination.

Similarly, the nickel plated ρ_c was measured to be higher than the aluminium evaporated ρ_c on silicon. This difference was found to be statistically significant. No statistically

significant trend of decreasing ρ_c with surface concentration was observed for nickel plated or aluminium evaporated contacts. Further elemental analysis and high resolution imaging of the interface may confirm the presence of an interfacial SiO_x layer formed during the plating process, which could account for the difference in ρ_c between the two metallisation technologies.

Cell efficiencies exceeding 23% have been achieved using nickel plating to boron-doped emitters of *n*-PERT cells [212]. However, unlike this study these results have been obtained using forward-bias plating, which is a form of electroplating that does not require an electroless process. In forward-bias plating the silicon surface is cathodically biased and consequently is less likely to be oxidised thereby ensuring no resistive barriers between the silicon and nickel. Recently, due to interest in plating bifacial cells, interest in using electroless nickel to deposit a Ni-seed layer has been renewed. This is because electroless plating would enable plating on both the *n*-type and *p*-type surfaces, which can subsequently be contacted and a copper plated grid deposited in one step, by contacting the nickel seed layer, simplifying the metallisation process [212].

However, the results from this study have highlighted the challenges faced by an ENP for boron-diffused surfaces. Further process development and understanding of the surface reactions is required to improve the reproducibility of the ENP process. With a reliable process, future studies could focus on the performance and adhesion of such contacts when integrated into a metal layer stack on an actual solar cell. That the plated layer is different in thickness and appearance for the product samples and the samples used in process development, suggests that the plating reactions are sensitive to the substrate doping. Deeper understanding of the initial nickel plating process during the nucleation phase, as it may produce a thick interfacial oxide or roughen/etch the surface needs to be understood to prevent the adverse effects which result in higher ρ_c and J_{0c} .

5 THE RECOMBINATION RATE AT DIFFUSED INVERTED SURFACES

INTRODUCTION

N-type crystalline silicon as a substrate material for the next generation of solar cells has seen growing commercial and research interest, and the most recent PV technology roadmap forecasts growing market share of *n*-type silicon in the near future [9]. This trend is also evident in the demonstration of high efficiency *n*-type solar cell designs such as the Panasonic HIT (Heterojunction with Intinsic Thin film) cell [295], the Sunpower Maxeon Cell [296], the PANDA [297] and BiSoN [298] cell structures. This growing interest is largely because *n*-type silicon has a higher tolerance to common metallic impurities, such as interstitial iron [299], and is less prone to reductions in carrier lifetime from carrier induced degradation due to boron-oxygen defects [300].

For most *n*-type solar cell structures, the formation and passivation of a carrier selective p^+ diffused hole collector is required for the collection of holes from the device. Due to the strong research and commercial use of SiN_x in passivating n^+ doped surfaces to date, there have been numerous studies which assessed the potential for SiN_x to passivate boron doped hole collectors. However, these early studies all reveal relatively high J_{0e} values, which are notably non-constant as a function of the bulk injection level in high injection, and understanding this non-ideal behaviour as it relates to the surface passivation of heavily diffused silicon is the focus of this chapter.

This chapter first reviews the non-linear trend in the injection level dependent Auger-corrected inverse lifetime curves at high injection, presented by other groups studying SiN_x passivation of p^+ hole collectors, highlighting that this behaviour was largely unexplained by researchers at the time. Symmetrical SiN_x passivated p^+np^+ structures were fabricated and characterised, which demonstrated the non-linear lifetime trend in

high injection experimentally. The PC lifetime measurements were reproduced in Sentarus TCAD [49] using the latest semiconductor models and the extended Shockley-Read-Hall formalism. It was shown that the non-linear lifetime behaviour at high injection was a result of the minority carrier species changing from electrons to holes at the surface, due to the positive fixed charge in the SiN_x film. Finally, analytical expressions for J_{0s} describing the behaviour are presented.

5.1 Review: SiN_x passivation of P^+ surfaces

The non-linear Auger-corrected inverse lifetime behaviour in high injection as a function of injection level was first reported by Kerr when comparing the passivation of PECVD SiN_x films on p -type and n -type diffused silicon samples. This phenomena is identified by a sharp increase in the corrected inverse lifetime, followed by a change in the gradient, which then assumes a roughly constant gradient; typical curves from this work are shown in Figure 5.1 (open triangles) below [301]. This non-linear scaling at high injection contradicts the linear relationship presented in early work by Kane and Swanson and discussed in Chapter 2, in which a linear scaling of lifetime with injection level at high injection is used to extract J_{0e} [109]. Kerr noted the unusual injection level dependence of p^+ surfaces passivated with SiN_x , and for this reason used the implied open-circuit voltage (iV_{oc}) at an illumination of 1 Sun to characterise the samples, since the Kane-Swanson method produces negative values from the non-linear trend. At the time, Kerr noted the trend in iV_{oc} and hypothesised that positive charge in the SiN_x layer may be impacting the carrier concentrations at the surface, as the doping and interface charge compete to determine the minority carrier concentration at the surface—in turn affecting the recombination. However this hypothesis was not directly related to the observed non-linear inverse lifetime behaviour at high injection and no quantitative model was given to confirm the original hypothesis.

In a similar study of SiN_x passivated boron diffused samples, Libal *et al.*'s proposition that the high fixed positive charge in the SiN_x layer increases the surface recombination velocity (SRV) by attracting electrons to the heavily diffused surface, although not further investigated, was an early attempt to explain the high injection behaviour with implicit reference to the SRH recombination rate [302].

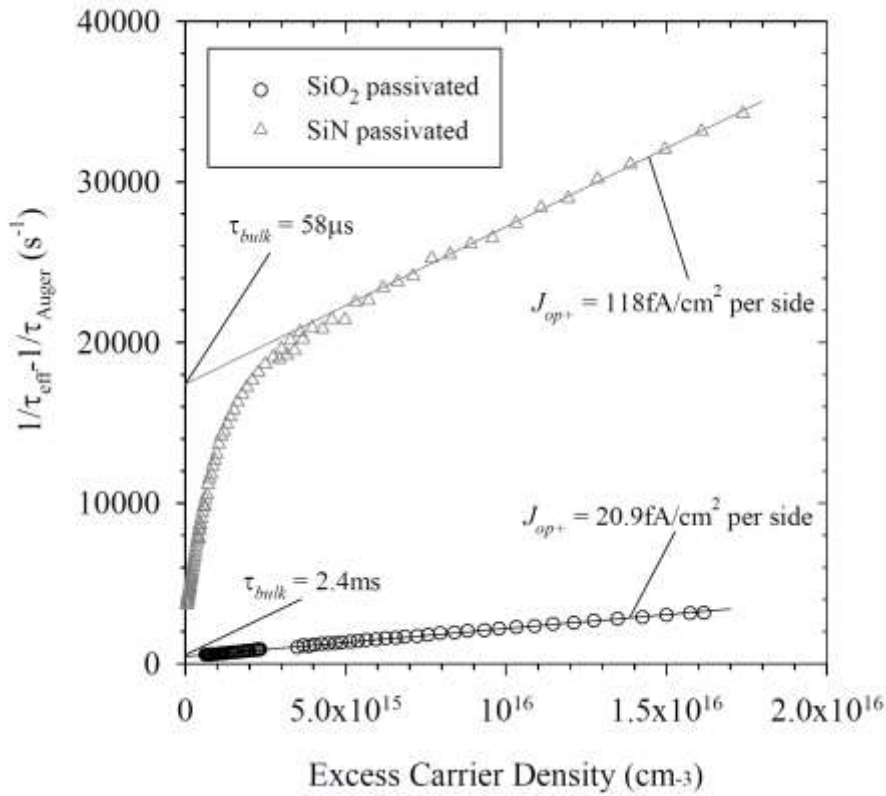


Figure 5.1 Injection level dependence of Auger-corrected inverse lifetime curves of a SiN_x passivated p^+np^+ passivated sample with $150 \Omega/\square$ diffusion measured via photoconductance measurements, sourced from [301].

Chen *et al.* observed similar lifetime trends when studying SiN_x passivated p^+ surfaces and noted that prolonged annealing ‘restored’ a linear trend to the lifetime curves, thereby enabling extraction of J_{0e} using the Kane-Swanson method [303]. Such prolonged thermal annealing has been shown to reduce the fixed positive charge density within SiN_x films [304], which suggests that the injection dependent lifetime behaviour was related to the fixed interface charge inherent in the SiN_x films deposited. In the same work, corona charging the samples with negative charge caused an improvement in the iV_{oc} of the samples, which also suggests that the fixed positive charge within the dielectric affects the recombination rate of the samples.

In another study, Nursam *et al.* were able to modulate the shape of the inverse lifetime curves of SiN_x passivated, boron diffused p^+np^+ lifetime samples to reproduce the characteristic ‘plateau’ in the curve at high injection. This was achieved by applying positive and negative corona charge to samples and subsequently measuring the inverse lifetime of the samples. The underlying mechanism was not discussed in this work [305].

Recent observations of the non-linear lifetime by Richter *et al.* highlighted the non-linear injection level dependence when studying AlO_x passivated phosphorous diffused n^+pn^+ samples [306]. In this instance, J_{0e} was analytically extracted, whilst modelling of the surface carrier concentrations in PC1D was performed to highlight the influence of the surface doping and interface charge on the iV_{oc} . However, the modelling did not account for BGN effects, nor was the non-linear lifetime at high injection quantitatively modelled.

The combined results from these previous studies indicate that the non-linear lifetime behaviour at high injection effect is related to the surface recombination parameters of the samples and the presence of fixed positive charges in the SiN_x films. However, this behaviour had not been comprehensively modelled in previous studies to date. The following sections of this chapter outlines work which addresses this knowledge gap. To this end, the injection level dependent corrected lifetime behaviour of actual photoconductance and photoluminescence measurements of identical test structures was first reproduced. The measured curves were then simulated in Sentaurus TCAD [49], by samples during PC measurement. By matching simulated with measured curves, insight into the sample properties and recombination mechanisms was gained. The following section outlines the experimental and simulation methods used in this work.

5.2 Experimental and simulation methodology

Symmetrical p^+np^+ structures were fabricated from 660 μm thick, 4.5 $\Omega\cdot\text{cm}$ phosphorus doped n -type float zone (FZ) $\langle 100 \rangle$ silicon wafers. A planarised surface condition was achieved from an alkaline etch process, consisting of immersion in a solution of 30 % w/v NaOH solution for 30 minutes at 80 ± 5 °C. Prior to deposition, the samples were cleaned in a standard RCA cleaning procedure followed by a short immersion in 5 % w/v HF acid to leave a hydrophobic, H-terminated surface. Subsequently, the samples were diffused in a commercial tube furnace (TS8603, Tempres Systems) using a boron tribromide (BBr_3) source, resulting in a p^+ diffusion on both sides of the wafer. The diffusion process consisted of three distinct steps; a BBr_3 deposition where liquid source BBr_3 was injected into the tube at 850 °C; a drive in at 920 °C in a nitrogen ambient; and finally, an in-situ oxidation at the same temperature. After the BSG layer was removed (10 % w/v HF for 5 minutes) the samples underwent SiN_x deposition in a Roth & Rau MAiA remote PECVD deposition tool, resulting in an 85 nm thick SiN_x layer with

refractive index $n=2.03$ on both sides. The process flow and resulting test structure schematic is shown in Figure 5.2 below:

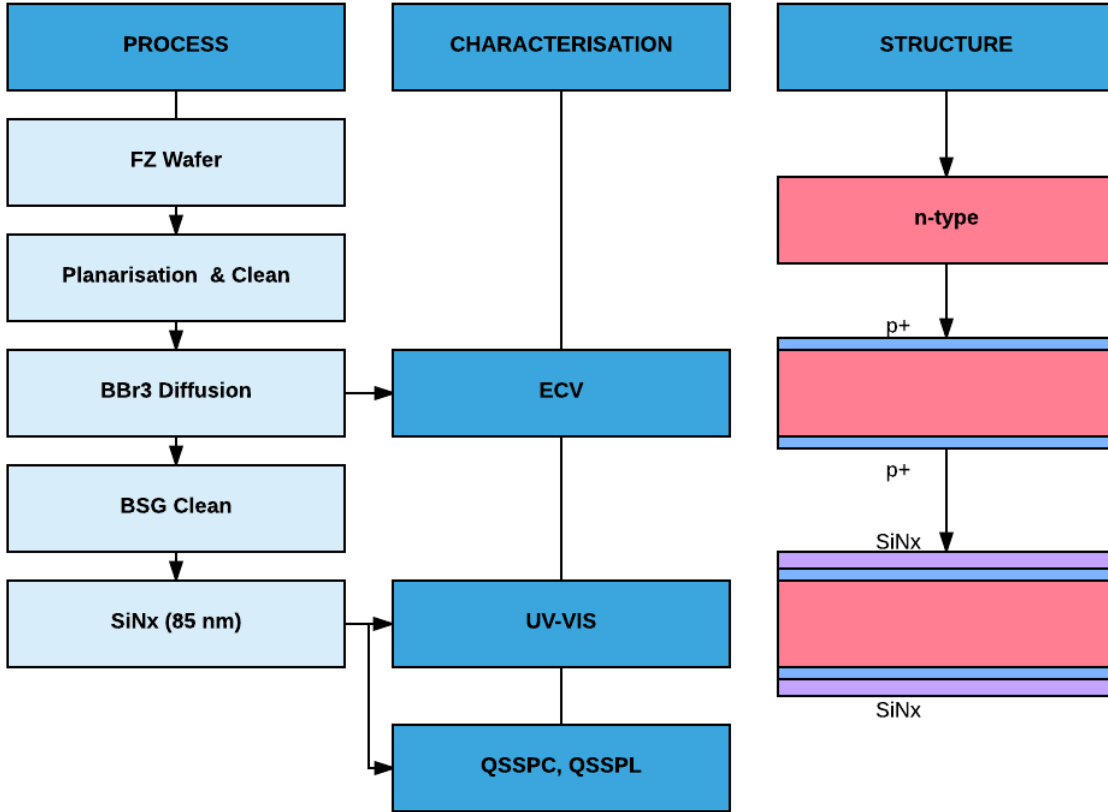


Figure 5.2 Experimental processing flow for the symmetrical p^+np^+ test structures used in this work; showing the processing sequence, characterisation processes and test structure schematic throughout the processing stages.

Once fabricated, the samples were characterised using a Sinton Instruments WCT-120 PC decay lifetime tester, and quasi-steady-state photoluminescence (QSSPL) measurements on a custom-built system were taken to confirm that the observed trend was not a measurement artefact of the PC measurements. The resulting p^+ profile had a sheet resistance of $115 \Omega/\square$ (as measured by four-point probe), a surface concentration of active dopants, $N_{A,s} = 1.9 \times 10^{19} \text{ atoms/cm}^3$ and a junction depth of approximately 450 nm (both determined by ECV (WEP, CVP21) measurements). This profile is shown in Figure 5.3. The active dopant profile of the p^+ diffusion on the diffused test structures was used as an input to the simulated structure. The optical generation profile was simulated in OPAL2 [104] for a planar surface with a 85 nm SiN_x by matching the UV-VIS measured reflectance curves with simulated passivation stacks and importing the calculated generation profile into Sentaurus. The bulk resistivity of the wafer was measured using a

combination of four-point probe sheet resistance measurements and dark conductance measurements, and the thickness of the wafers measured with a micrometer.

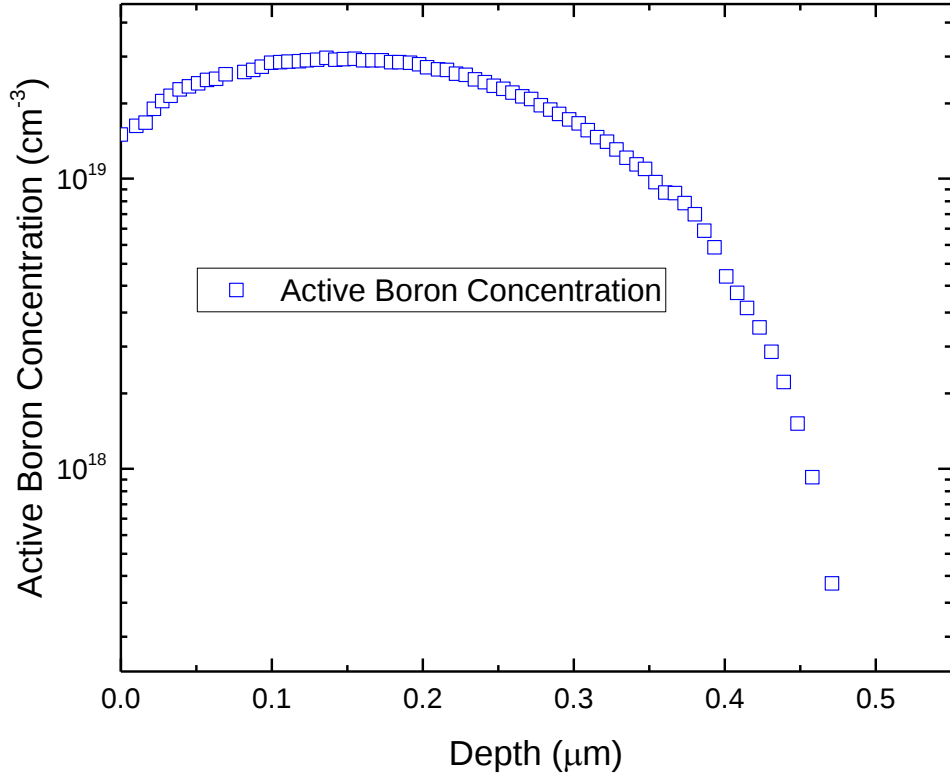


Figure 5.3 Active boron concentration vs. depth measured via ECV profiling and used as input in the Sentaurus lifetime simulations.

Using the extracted sample parameters as input, identical, symmetrical structures were constructed in Sentaurus. A QSSPC measurement was simulated by solving the structure at varying light intensities, and then extracting the corresponding carrier concentrations to enable calculations of the individual lifetime components within the device. The corrected inverse effective lifetime was calculated as the inverse sum of all recombination processes in the device, minus the contribution from Auger recombination in the substrate bulk, according to the equation:

$$\frac{1}{\tau_{eff,corrected}} = \frac{1}{\tau_{SRH, surfaces}} + \frac{1}{\tau_{SRH,Bulk}} + \frac{1}{\tau_{intrinsic}} - \frac{1}{\tau_{Auger,Bulk}} \quad \text{Eq. (5.1)}$$

Where $\tau_{SRH,surfaces}$ is the lifetime component due to SRH recombination in the front and rear surfaces; $\tau_{SRH,surfaces}$ models the SRH recombination processes in the substrate; $\tau_{intrinsic}$ is the lifetime component due to Auger recombination processes—including the

diffused regions and the bulk silicon—and radiative processes modelled with $B = 4.73 \times 10^{-15} \text{ cm}^3 \cdot \text{s}^{-1}$ [58], modelled using the parametrisation by Richter *et al.* [71]; and $\tau_{Auger,Bulk}$ models Auger recombination processes in the bulk. Table 5.1 outlines the physical models and constants used in this work. Of particular relevance to this work is the modelling of SRH recombination at the surfaces, which was solved numerically for a single mid-gap state for acceptors and donors respectively. In this work a value of 10^7 cm/s was used for $v_{th,e}$ and $v_{th,h}$, at 300 K and its temperature dependence modelled by the equation

$$v_{th}(T) = v_{th,300K} \sqrt{T/300}. \quad \text{Eq. (5.2)}$$

For the simulations, the interface charge Q and the density of interface defects D_{it} was used as free parameters in the simulations to reproduce the injection level dependence of the inverse corrected lifetime curves.

Table 5.1 Physical models and constants used in the Sentaurus simulations of this work.

Parameter	Value or model used
Temperature	298.15 K
Background doping	$N_D = 10^{15} \text{ cm}^{-3}$
Free carrier statistics	Fermi-Dirac
Intrinsic carrier density	$n_i = 8.26 \times 10^9 \text{ cm}^{-3}$. [307]
Band gap narrowing	Schenk [113]
Mobility	Klaassen [308, 309]
Auger recombination	Richter [71]
Radiative recombination	$B = 4.73 \times 10^{-15} \text{ cm}^3 \cdot \text{s}^{-1}$. [58]
Incident spectrum	Q-flash with IR pass filter. [310]
Optical properties of Silicon	Green [311], Schinke [312]

5.3 Results

The measured PC and QSSPL injection dependent Auger-corrected inverse lifetime curves for the fabricated p^+ doped structures are shown in Figure 5.4. The PC and QSSPL measurement show excellent agreement indicating that the measurement trend in lifetime was accurate and not a PC measurement artefact. In Figure 5.4, the inverse lifetime curve of an identically fabricated p^+np^+ sample passivated with Al_2O_3 -passivated is shown for reference, displaying the characteristic linear trend. This suggests that the observed trend was affected by the interface electrostatics.

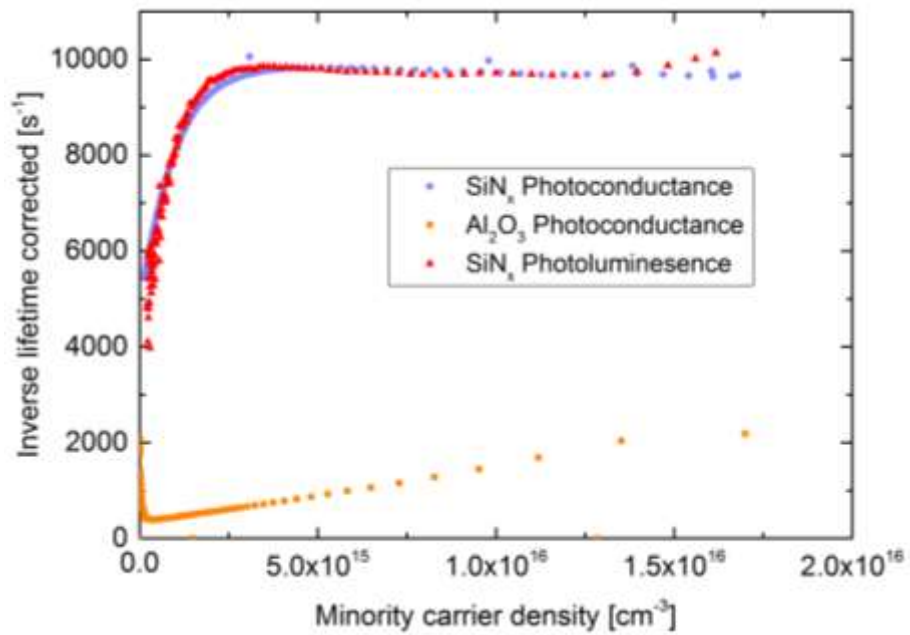


Figure 5.4 Measured Auger-corrected inverse lifetime of a lifetime sample featuring a symmetrical SiN_x -passivated p^+ surface. The effective minority carrier lifetime was measured by PC and PL to ensure that the observed behaviour was not a measurement artefact of the PC measurement. A measurement taken of a symmetrically diffused, Al_2O_3 -passivated p^+ sample is shown for reference as well.

Simulated and measured inverse lifetime curves of a SiN_x passivated p^+np^+ structure are shown in Figure 5.5, demonstrating that a good fit was achieved with input parameters $D_{it} = 7.5 \times 10^{11} \text{ cm}^{-2}$, $Q_f = 3.0 \times 10^{12} \text{ cm}^{-2}$ and $\sigma_n = \sigma_p = 10^{-17} \text{ cm}^2$ which was in good agreement with reported values for SiN_x passivation layers on lightly doped c-Si substrates [254, 313]. A clear transition in the gradient of the lifetime curve was seen to occur at an injection level of approximately $\Delta n = 2.5 \times 10^{15} \text{ cm}^{-3}$, thereafter the lifetime effectively plateaus and remains constant when the sample moves into high injection conditions.

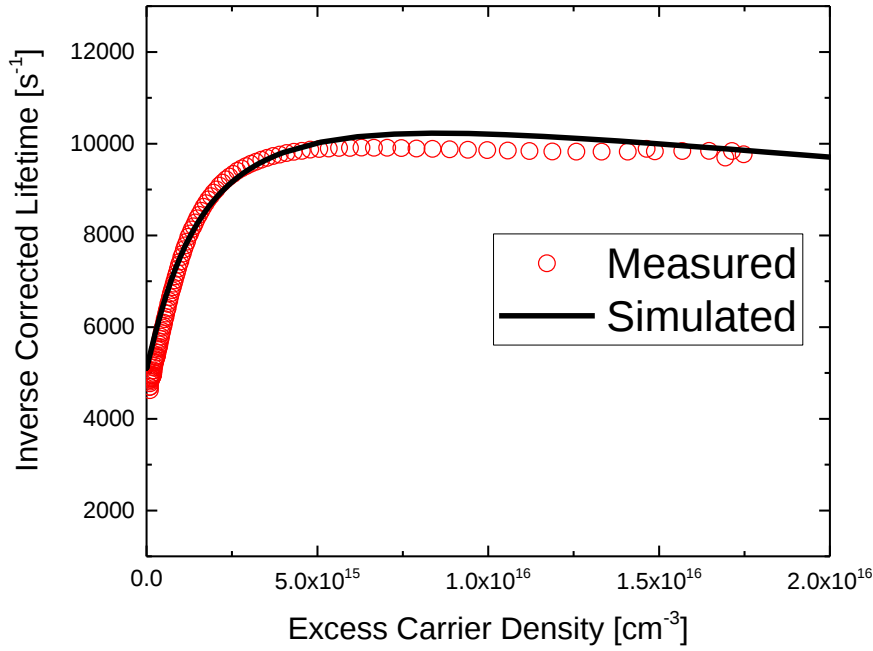


Figure 5.5 Modelled vs. measured inverse Auger-corrected lifetime curves showing good agreement in the high injection region. Parameters used in this simulation include $\sigma_p = \sigma_n = 10^{-17} \text{ cm}^2$, $D_{it} = 7.5 \times 10^{11} \text{ cm}^{-2}$, $Q_f = 3.0 \times 10^{12} \text{ cm}^{-2}$ and a mid-gap trap level.

The main recombination mechanisms and their lifetime contributions in the simulated sample in Figure 5.5 are shown in Figure 5.6. In the plot, $1/\tau_{\text{Bulk}}$, SRH accounts for SRH recombination processes in the bulk, $1/\tau_{\text{Bulk}}$, Auger accounts for Auger recombination in the bulk only, $1/\tau_{\text{Radiative}}$ accounts for radiative recombination in the whole substrate, $1/\tau_{\text{Surface (front)}}$ and $1/\tau_{\text{Surface (rear)}}$ account for SRH recombination at the front and rear surfaces of the solar cell, and $1/\tau_{\text{front doping}}$, Auger and $1/\tau_{\text{rear doping}}$, Auger, account for the Auger recombination in the diffused front and rear regions respectively. For this sample, SRH recombination at the front illuminated p^+ surface was the dominant recombination mechanism over a broad range of injection levels, which indicates that the non-linear lifetime behaviour in high injection was related to recombination processes at the surfaces. It follows that this trend will be observed provided the samples are corrected for bulk Auger recombination processes, and limited by SRH recombination at the surface and near surface regions. Similarly, if the sample is well passivated, the sample is less likely to be limited by surface SRH processes, and instead may be limited by, for instance, bulk SRH recombination processes. Furthermore, for heavier doping levels in the emitter, the Auger recombination mechanisms in this region may begin to dominate the wafer—requiring an additional

correction to the lifetime measurement. This sensitivity to the doping levels in the emitter, and surface passivation is explored in more detail in Chapter 6.

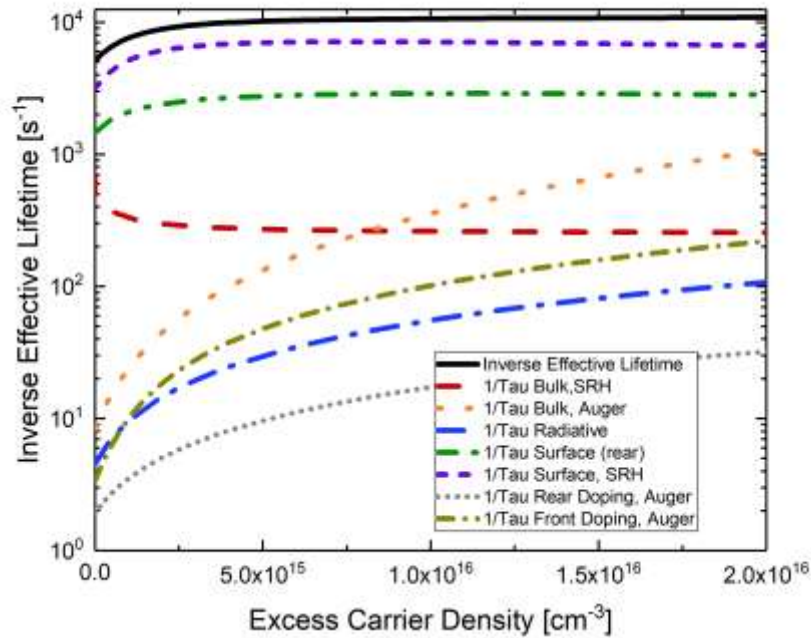


Figure 5.6 Breakdown of the various recombination mechanisms and their corresponding lifetime components in the symmetrical lifetime sample as a function of the injection level. The results indicate that the effective lifetime was dominated by surface SRH recombination for the broad range of injection levels of interest.

5.4 Analysis

The previous section shows that the effective lifetime behaviour at high injection conditions can be modelled by SRH recombination which specifies the trap level, concentration, carrier capture cross-section of the defect(s) and the interface fixed charge. Further analysis of the individual recombination processes within the wafer suggest that surface recombination was the mechanism affecting this behaviour, however, to understand why the recombination rate was non-linear requires exploration of the carrier concentrations at the surface as a function of injection level.

The simulated concentration of holes and electrons as a function of depth into the silicon away from the surface for various injection levels is shown in Figure 5.7, for the structure fitted in Figure 5.5, which was diffused with the ECV profile displayed in Figure 5.3. It shows the concentration of electrons at the surface increasing with injection level, eventually surpassing the hole concentration at the surface in high injection conditions

(as defined when the carrier concentrations in bulk are equal). The ‘swapping’ of minority carrier was is combined result of increasing hole concentration in the bulk from illumination, and the simultaneous depletion of holes and accumulation of electrons at the surface, induced by the fixed charge at the SiN_x film. For low injection levels in the bulk, the positive fixed charge in the SiN_x increases the minority carrier (electron) concentration by several orders of magnitude resulting in an equivalent increase in the recombination rate. As the sample moves from low injection to medium injection in the bulk, the surface concentration of electrons increases further, whereas the hole concentration at the surface remains relatively fixed as, due to the magnitude of p^+ background doping, changes in injection level on the overall concentration are relatively negligible, i.e., $p_d = N_a + \Delta p \approx N_a$. For high injection conditions in the bulk (e.g. $\Delta n > 1 \times 10^{16} \text{ cm}^{-3}$) the minority charge carrier changes polarity and the surface recombination rate is limited by the hole concentration at the surface, rather than the electron concentration at the surface.

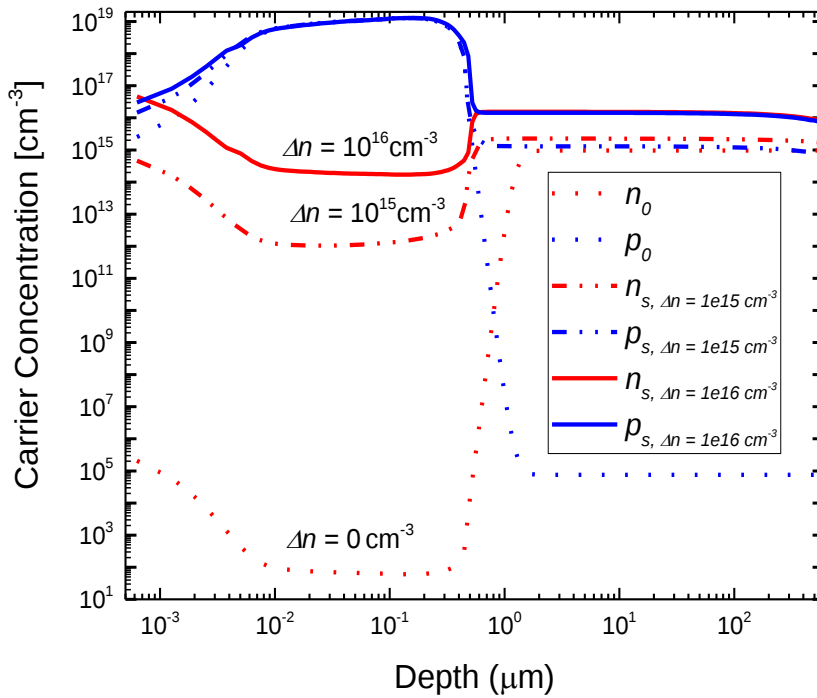


Figure 5.7 Concentration of electron and holes as a function of depth, for varying injection levels. A transition of the surface from depletion to inversion due to the fixed positive charge at the surface interface as the sample moves into high injection is evident. The depth is plotted on a logarithmic scale to give insight to the mechanisms close to the surface affected by surface charge. The simulations reveal an inverted surface is formed at high injection where $\Delta n > 10^{16} \text{ cm}^{-3}$.

This trend in injection dependent lifetime was evident in simple analytical expressions which were derived from 1) the general formula for J_{0s} ; 2) the relationship between surface charge, band-bending and carrier concentrations and; 3) the formulae for carrier concentrations at the surface. In the following derivations, the general definition of J_{0s} is used [76], whereby

$$J_{0s} = \frac{qn_{ie}^2}{\frac{p_s+p_1}{s_{n0}} + \frac{n_s+n_1}{s_{p0}}}, \quad \text{Eq. (5.3)}$$

and the surface concentrations are taken from the same reference and expressed as;

$$n_s = \frac{n_{is}}{n_{id}} n_d e^{\frac{\psi_s}{V_T}}, \quad \text{Eq. (5.4)}$$

$$p_s = \frac{p_{is}}{p_{id}} p_d e^{-\frac{\psi_s}{V_T}}, \quad \text{Eq. (5.5)}$$

where V_T is the thermal voltage equal to kT/q , n_{is} and n_{id} are the intrinsic electron concentrations at the surface, s and distance d , p_{is} and p_{id} are the equivalent expressions for holes. The relationship between the carrier concentrations, surface potential and surface charge can be found assuming charge neutrality [46],

$$p_s - p_d + n_s - n_d + (N_A - N_D) \frac{\psi_s}{V_T} = \frac{Q^2}{2q\epsilon_{Si}V_T}. \quad \text{Eq. (5.6)}$$

To derive these expressions, the following general assumptions were made:

- 1) The quasi-Fermi levels in the space-charge region at the surface are flat.
- 2) The fixed charge, Q_f is positive and non-negligible ($Q_f > 10^{12} \text{ cm}^{-2}$), i.e. $n_d \ll n_s$ and $p_s \ll p_d$.
- 3) The sample is boron doped near the surface, with a surface concentration of $N_s = 10^{19} \text{ cm}^{-3}$ as confirmed by ECV measurements and hence $N_a = N_s \gg N_d$.

The first assumption was believed to introduce insignificant error given the width of the surface depletion region. This would introduce negligible variations of carrier concentrations relative to that introduced by band bending for the high levels of fixed charge with depth under illumination or due to doping.

There are two general scenarios depicted in Figure 5.7 corresponding to various injection levels:

- i. Case 1: Low injection where $n_s, n_d \ll p_s, p_d$

ii. Case 2: ‘Moderate’ to high injection where $n_s \approx p_s$

For Case 1, the sample is in low injection; $n_s, n_d \ll p_s, p_d$. Therefore Eq. 5.6 can be written as,

$$p_s = \frac{Q^2}{2q\epsilon_{Si}V_T} - \frac{N_A\psi_s}{V_T} + p_d. \quad \text{Eq. (5.7)}$$

due to p^+ doping, $p_d = N_a + \Delta p \approx N_a$. Substituting Eq. 5.7 into Eq.5.3 gives:

$$J_{0s} = \frac{qn_{ie}^2 S_{n0}}{\frac{Q^2}{2q\epsilon_{Si}V_T} + N_A \left(1 - \frac{\psi_s}{V_T}\right)}. \quad \text{Eq. (5.8)}$$

Note that the terms p_1 and n_1 were omitted in this step and throughout in line with the assumptions made and qualified by McIntosh and Black [76]. Rearranging Eq. 5.5 to make ψ_s the subject and substituting into Eq. 5.8 produces

$$J_{0s} = \frac{qn_{ie}^2 S_{n0}}{\frac{Q^2}{2\epsilon_{Si}kT} + N_A \left[1 - \ln\left(\frac{p_s p_{id}}{p_d p_{is}}\right)\right]}. \quad \text{Eq. (5.9)}$$

It was noted that Eq. 5.9 reduces to the expression presented by McIntosh and Black [76]. for the case of negligible Q_f such that $p_s \approx p_d$. For the second intermediate to high injection case where $n_s \approx p_s \gg n_d$, we follow a similar approach, rearranging and simplifying Eq. 5.6 to become:

$$n_s = \frac{Q^2}{2q\epsilon_{Si}V_T} + \left(1 - \frac{\psi_s}{V_T}\right) N_A - p_s. \quad \text{Eq. (5.10)}$$

Substituting into Eq. 5.3, the expression becomes,

$$J_{0s} = \frac{qn_{ie}^2 S_{n0} S_{p0}}{(S_{p0} - S_{n0})p_s + S_{n0} \left[\frac{Q^2}{2\epsilon_{Si}kT} + \left(1 - \frac{\psi_s}{V_T}\right) N_A\right]}. \quad \text{Eq. (5.11)}$$

These equations are summarised in Table 5.2

Table 5.2 Simplified expressions for J_{0s} for positive charge on p^+ doped surfaces.

Condition	J_{0s}
Low injection: $n_s, n_d \ll p_s, p_d$	$J_{0s} = \frac{qn_{ie}^2 S_{n0}}{\frac{Q^2}{2\epsilon_{Si}kT} + N_A \left(1 - \frac{\psi_s}{V_T}\right)}$
Moderate to high injection: $n_s \approx p_s$	$\frac{qn_{ie}^2 S_{n0} S_{p0}}{(S_{p0} - S_{n0})p_s + S_{n0} \left[\frac{Q^2}{2\epsilon_{Si}kT} + \left(1 - \frac{\psi_s}{V_T}\right) N_A \right]}$

Equivalent expressions can be derived in the case that Q_f is negative and non-negligible, and the sample is negatively doped, such that $N_d = N_s \gg N_a$. These equations are summarised in Table 5.3 below.

Table 5.3 Simplified expressions for J_{0s} for negative charge on n^+ doped surfaces.

Condition	J_{0s}
Low injection: $p_s, p_d \ll n_s, n_d$	$J_{0s} = \frac{qn_{ie}^2 S_{p0}}{\frac{Q^2}{2\epsilon_{Si}kT} + N_D \left(1 - \frac{\psi_s}{V_T}\right)}$
Moderate to high injection: $n_s \approx p_s$	$\frac{qn_{ie}^2 S_{n0} S_{p0}}{(S_{n0} - S_{p0})n_s + S_{p0} \left[\frac{Q^2}{2\epsilon_{Si}kT} + \left(1 - \frac{\psi_s}{V_T}\right) N_D \right]}$

The change in minority carrier from holes to electrons at the surface explains the non-linear shape of the corrected inverse lifetimes measured for these samples. The SRH recombination rate $U_{SRH, surface}$ is directly related to the electron and hole concentration at the surface. For increasing injection levels in the bulk, the hole concentration changes only moderately relative to the level of the p^+ doping, whereas the electron concentration steadily increases. Close to the surface, there is the presence of a surface depletion region introduced by the fixed charge, which causes band bending [48]. The result is that in the presence of fixed charge, n_s is initially several orders of magnitude lower than p_s , and the recombination rate at the surface is limited by the electron concentration. As the sample moves into higher injection, n_s increases to approach parity with p_s , and it is at this point that the slope in the inverse effective lifetime curve begins to change, producing the characteristic ‘bend’. With a further increase in injection level, n_s can exceed p_s , shifting

the recombination behaviour to be dominated by the hole concentration, which has become the minority carrier at the surface.

The lifetime component associated with SRH at the surface is defined as:

$$\frac{1}{\tau_{Surface}} = \frac{\Delta n}{U_{SRH, Surface}}. \quad \text{Eq. (5.12)}$$

When SRH processes at the surface are the main recombination mechanism limiting the effective lifetime, the injection dependent lifetime curve gradient will be dominated by recombination behaviour at the surface, which as previously outlined, is related to the minority carrier transition from electrons to holes due to the surface inversion induced by the fixed interface charge. The plateau of the inverse lifetime curve shown in Figure 5.4 and Figure 5.5 reflect that the concentration of holes in the p^+ region remaining relatively constant with injection level, as a result of the fixed positive charge induced surface depletion region.

5.5 Conclusion

The recombination rate at high injection for SiN_x passivated p^+np^+ structures was shown to be the result of a transition from electron to hole limited surface recombination as the structure moves from low to high injection. This transition occurs due to the fixed positive charge at the surface, which depletes the concentration of holes, and increases the concentrations of electrons. The gradient of the inverse lifetime curve in high injection reflects the change in concentration of holes and electrons at the surface, which produces the non-linear lifetime behaviour, which makes J_{0e} extraction using the Kane-Swanson method invalid. Agreement between QSSPL and QSSPC measurements show this phenomenon was not a measurement artefact and intrinsic to the electronic properties at the c-Si/ SiN_x interface. The injection level dependent recombination rate was reproduced in Sentaurus TCAD with positive interface charge and modelling SRH recombination at the surface. This chapter broadens the current understanding of how the electrostatics at the diffused silicon surface can influence surface passivation, as is evidenced in changes to the lifetime behaviour due to interface charge. In the following chapter, this thesis investigates the potential to extract interface parameters Q_f , S_{n0} and S_{p0} from fitted measurement curves using this simulation technique.

6 EXTRACTION OF INTERFACE PARAMETERS FROM PHOTOCONDUCTANCE MEASUREMENTS

INTRODUCTION

This chapter applies the findings of the Chapter 5 and presents a new method for the extraction of the interface parameters, S_{n0} , S_{p0} and Q_f from the injection level dependent inverse corrected lifetime curves of samples with heavily diffused layers (such as n^+ electron collectors). This was previously not possible on doped samples with commonly used techniques to measure the interface parameters, such as singular CV measurements, nor has it been demonstrated previously with PC lifetime measurements alone. The method of interface parameter estimation presented in this work involves reproducing the measured injection level dependent lifetime curves using Sentaurus TCAD, and is applied to diffused silicon wafers passivated with AlO_x , SiN_x and HfO_x .

The general conditions of substrate doping, interface charge polarity and magnitude, and injection level, which give rise to the non-linear lifetime behaviour was investigated. This was achieved through the development of a MATLAB model of the surface concentration of electrons and holes fully taking into account the effects of BGN; Fermi-Dirac statistics, and interface charge at the surface. With the surface concentration of electrons and holes calculated, the surface potential and its impact on the ratio of holes and electrons, as a function of injection level, interface charge and underlying substrate doping, was used to present the substrate conditions which lead to non-linear lifetime at high injection. This was analysed by calculating the injection level J_{0s} for a range of interface charge and doping levels, showing the conditions for which the non-linear lifetime occurs. As a

result, a novel method which enables the extraction of S_{n0}/S_{p0} and Q_f is presented which uses the inexpensive and commonly applied PC technique.

6.1 Review: extraction of interface charge density from semiconductor surfaces

In practice, surface passivation of c-Si solar cells is commonly achieved by applying a thin charged dielectric such as SiO_x , SiN_x or AlO_x on a diffused substrate surface [39, 314]. These dielectrics are designed to reduce recombination by chemical and charge-effect passivation [313], and therefore the characterisation of the passivation properties on doped surfaces is particularly relevant for solar cell development.

As outlined in Chapter 2, when attempting to characterise the performance of a passivating dielectric, effective parameters such as S_{eff} or J_{0s} are often extracted [39, 105]. These parameters, which measure the aggregated value of surface recombination, are limited since they do not give insight into the surface passivation mechanism, rather they give insight to the quality of passivation achieved. Furthermore, as outlined by McIntosh and Black, there are certain common conditions of substrate doping and dielectric induced interface charge whereby these parameters gain sensitivity to the underlying substrate conditions, limiting their applicability for comparison of surface passivation results on varying substrates [76]. Therefore, it is of significant interest to both research and industry to be able to directly measure Q_f and D_{it} (or S_{n0}/S_{p0}) on doped surfaces. These interface properties give direct insight into the passivation mechanism, enable direct comparison between different substrates and dielectrics, and can be used as input into semiconductor device modelling packages.

Measurement of Q_f and D_{it} is commonly achieved via the analysis of the CV characteristic of metal-oxide-semiconductor (MOS) structures with an ohmic base contact [105], or via the contactless corona oxide characterisation of semiconductor (COCOS) method [315], which can be applied to some unmetallised semiconductor-oxide samples. In a typical measurement using a MOS structure with ohmic contact, a depletion region is created, which interacts with the surface electric fields, and the capacitance of this region is measured. In the case of a COCOS measurement, corona charging is used to modulate the depletion region, as opposed to the gate voltage in the MOS technique. The underlying principle behind these measurements is to sweep the CV characteristic of the sample, and through measurement of the flatband voltage shift and the slope of the characteristic

curve, extract interface parameters Q_f and D_{it} . However, in the presence of an additional diffused region, the large voltages required to transition the sample between inversion and accumulation can result in dielectric breakdown. Furthermore, the interface capacitance appears in parallel with substrate capacitance, making their separate resolution difficult. This means that these measurements cannot be performed on samples with a ‘heavily’ diffused ($N_s > 10^{17} \text{ cm}^{-3}$) pn junction. Another general limitation of this method is that the CV curve cannot be meaningfully extracted if the dielectric does not hold the deposited charge well, as is the case for some ‘leaky’ SiN_x films, and semiconductors such as amorphous silicon, both of which are of strong interest to PV research and commercial activities. This is in addition to the downside that the fabrication of dedicated MOS structures requires extra processing resources and effort and can even affect the electronic properties of the sample. Recently, a technique which utilises a combination of CV measurements, conductance measurements and frequency techniques to determine the key interface parameters Q , S_{n0} and S_{p0} on diffused and passivated surfaces was demonstrated [75]. Although comprehensive, this technique relies on the ability for the dielectric to hold charge, the fabrication of dedicated test structures, and the analysis is non-trivial.

When trying to assess the performance of dielectrics on doped surfaces with CV techniques, monitor samples are placed in-situ with the product sample. These samples are undiffused and a non-trivial assumption of equivalence between the undiffused ‘monitor’ samples and the ‘product’ diffused samples of interest is made and the interface parameters are inferred. However, this assumption loses validity in the instances of non-uniform deposition throughout the reactor deposition chamber, and the fabrication and measurement of monitor samples takes time and resources. This can be problematic for researchers and engineers trying to characterise and optimise a novel surface passivation process.

An alternative technique for extracting fixed charge from dielectrics on silicon is Electric Field-Induced Second Harmonic generation (EFISH). EFISH is a non-linear optical technique which exploits the interface sensitivity of second harmonic generation from centrosymmetric materials to detect the significant electric field arising in the c-Si from interface charge [47]. However, this method requires complex analysis and expensive experimental setups and requires each measurement to be calibrated through, for instance, a CV measurement. Consequently, it is not widely adopted.

Fixed charge can also be assessed by corona lifetime measurements [316, 317], and a sophisticated method of modelling the surface recombination rate which enables the estimation of interface parameters D_{it} , σ_n and σ_p from the fitting of the PC lifetime measurements, has recently been demonstrated [317]. This approach was shown to accurately model the recombination at the Si-SiO₂ interface without the need to invoke the assumption of a surface damaged region [318]. In this technique, the sample undergoes a sequence of corona charging, lifetime measurement, and Kelvin probe measurements, and the resulting measurement results are fitted to extract S_{eff} curves over a range of Kelvin probe surface potentials. From these results, the trend in S_{eff} for varying Kelvin probe surface potential is modelled using a parameterisation for S_{eff} which takes into account bulk recombination, a distribution of defects and enables the capture cross sections to be resolved. A key limitation of this technique is that it relies on the dielectric charge being stable within the film for the duration of the measurement, and thus dielectrics which do not hold charge are not likely able to be characterised by this technique. Furthermore, the surface recombination behaviour of diffused surfaces is not reported in this work and the model used to simulate the effective lifetime does not account for recombination in the diffused regions, which currently limits this technique to undiffused samples.

Consequently, a simple method to extract the interface parameters S_{n0} , S_{p0} and Q parameters from dielectrics deposited on doped surfaces was developed. This method is based on the fitting of the Auger-corrected inverse lifetime curve over a range of minority carrier injection levels, as demonstrated in Chapter 5. This technique can be applied directly to doped surfaces, does not require corona charging and uses an inexpensive PC stage found in most photovoltaic research laboratories.

Through quantitative analysis and fitting the inverse corrected lifetime of inverted, SiN_x passivated, p^+np^+ samples, it was revealed that Q and S_{n0}/S_{p0} have unique signatures, showing that these parameters are not correlated and thus can be extracted independently. Finally, the applications of this technique to as-deposited and annealed ALD deposited AlO_x and hafnium oxide (HfO_x) films on phosphorus diffused p -type wafers, and SiN_x passivated boron diffused n -type wafers was demonstrated.

6.2 Modelling the surface concentration of electrons and holes

It was shown in Chapter 5 that a transition of minority carrier species as result of high values of Q and increasing injection level can cause the non-linear lifetime behaviour observed in the PC lifetime measurements of SiN_x passivated, boron diffused lifetime structures [301, 319]. This transition was a complex result of Q , substrate doping (and hence the concentration of carriers at the surface) and injection level. This section explores the general conditions of the aforementioned parameters in which this minority carrier transition will occur. This was achieved by numerically modelling the surface concentration and resulting recombination rate using Fermi-Dirac statistics at two finite one-dimensional points which are representative of the surface conditions. In doing so, ψ_s , carrier concentrations, and J_{0s} values were calculated, which show clearly the range of surface conditions in which this non-linearity can be observed, and the extraction technique applied to extract surface recombination parameters and fixed charge. The calculation method of carrier concentrations at equilibrium and steady state follows the procedure outlined in Refs. [320, 321], with minor variances in the calculation method and semiconductor models used, as will be outlined in the following text. These carrier populations were then input into the calculation of Q , which was evaluated numerically according to the method outlined in Ref. [46]. This effectively evaluates the concentration of electrons and holes at two finite points; firstly at some distance from the surface, d , unaffected by interface charge; and at the actual surface denoted by subscript, s . The calculation procedure was as follows:

- 1) The temperature dependent band gap of silicon, $E_g(T)$, was calculated according to Eq. 23 of Ref. [322], valid for the temperature range 2-415 K.
- 2) The intrinsic carrier concentration, n_i , was calculated as outlined in Ref. [323] where n_i was calculated as per the expression,

$$n_i = AT^B e^{-\frac{C}{T}}, \quad \text{Eq. (6.1)}$$

with $A = 1.54 \times 10^{15}$, $B = 1.712$ and $C = E_g(T)/2k_b$. This temperature dependent model was chosen specifically for its compatibility with the band gap model of Ref. [322] used in step 1. The density of states in the valence and conduction band N_c and N_v , were then calculated according to Eq. 4, 5, 18 and 19 in Ref. [322].

- 3) The E_i , was calculated as per the relation

$$E_i = \frac{E_g}{2} + \frac{kT}{q} \ln \frac{N_v}{N_c}, \quad \text{Eq. (6.2)}$$

and the conduction and valence band energy are defined relative to the mid-band gap

$$E_c^i = E_g - E_i, \quad \text{Eq. (6.3)}$$

$$E_v^i = 0 - E_i. \quad \text{Eq. (6.4)}$$

With the intrinsic characteristics calculated, the equilibrium and steady state concentrations were calculated, assuming 100 % ionisation of dopants. The following steps assume a p -type doped surface on an n -type substrate, although equivalent expressions may be derived for n -type doping on a p -type substrate. As a note, the bracketed superscript/subscript “(0)” denotes a parameter which takes on equilibrium or steady-state values, according to whether equilibrium or steady-state calculations were performed. It is referenced herein for conciseness.

- 4) Initial guesses of the equilibrium carrier concentrations were calculated [99], with

$$p_0 = \frac{1}{2} (N_D - N_A + \sqrt{(N_A - N_D)^2 - (4n_i^2)}), \quad \text{Eq. (6.5)}$$

$$n_0 = \frac{n_i^2}{p}. \quad \text{Eq. (6.6)}$$

Initial guesses of steady state values were made by specifying an excess carrier density, and forcing $\Delta n = \Delta p$ such that $p = p_0 + \Delta n$, and $n = n_0 + \Delta n$.

- 5) The effects of BGN due to doping was modelled according to Schenk [113] by calculating the reduction in energy at the valence and conduction band edge, $\Delta E_{v, BGN}$ and $\Delta E_{c, BGN}$, with input of N_A , N_D , $p_{(0)}$ and $n_{(0)}$. The value of the conduction and valence band are then updated;

$$E_c^{(0)} = E_c^i - \Delta E_{c, BGN}, \quad \text{Eq. (6.7)}$$

$$E_v^{(0)} = E_v^i + \Delta E_{v, BGN}. \quad \text{Eq. (6.8)}$$

Note the values $E_c^{(0)}$ and $E_v^{(0)}$ were defined as the energy levels at the conduction and valence band edge at either equilibrium or steady-state conditions taking into account the shift due to BGN, and not as they are defined in Ref. [324], as the intrinsic energy level at the conduction and valence band edges respectively.

- 6) Fermi-Dirac statistics, as opposed to Boltzmann statistics, were employed in these calculations. The Fermi-Dirac integral of order j , is defined as

$$F_j(x) = \frac{1}{\Gamma(j+1)} \int_0^\infty \frac{\epsilon^j}{1 + \exp(\epsilon - x)} d\epsilon. \quad \text{Eq. (6.9)}$$

For the forward half-integral, the short series approximation of Refs [325, 326] was applied with accuracy 10^{-5} . When calculating the inverse Fermi-Dirac half-integral, $X_{1/2}$, the rational function approximations of Ref. [327] were used, with $m_1 = 4$, $k_1 = 3$, $m_2 = 6$, $k_2 = 5$ —see Table 6 of Ref. [327]—corresponding to a maximum error of 4.19×10^{-19} . These are the same numerical approximations for the calculation of the forward and inverse half-integral used by the solar cell device simulator PC1D v6.2 [328, 329] and emitter simulation tool EDNA2 [321]. The Fermi level of electrons and holes was then calculated as:

$$E_{fp}^{(0)} = E_v^{(0)} - X_{\frac{1}{2}} \left(\frac{p_{(0)}}{N_v} \right) \frac{k_b T}{q}, \quad \text{Eq. (6.10)}$$

$$E_{fn}^{(0)} = E_c^{(0)} + X_{\frac{1}{2}} \left(\frac{n_{(0)}}{N_c} \right) \frac{k_b T}{q}. \quad \text{Eq. (6.11)}$$

The Fermi level was then defined as:

$$E_f^{(0)} = \frac{1}{2} \left\{ E_v^{(0)} + E_c^{(0)} + \left[X_{\frac{1}{2}} \left(\frac{n_{(0)}}{N_c} \right) - X_{\frac{1}{2}} \left(\frac{p_{(0)}}{N_v} \right) \right] \frac{k_b T}{q} \right\}, \quad \text{Eq. (6.12)}$$

- 7) Factors to account for the change in n_i on account of band gap narrowing (γ_{BGN}), degeneracy (γ_{DEG}) and non-equilibrium (γ_{neq}) were then calculated, as outlined by Altermatt *et al.* in Ref. [320] where

$$\gamma_{DEG} = \frac{F_{\frac{1}{2}} \left(-q \frac{E_c^i - E_{fn}}{k_b T} \right)}{\exp \left(-q \frac{E_c^i - E_{fn}}{k_b T} \right)} \times \frac{F_{\frac{1}{2}} \left(-q \frac{E_{fp} - E_v^i}{k_b T} \right)}{\exp \left(-q \frac{E_{fp} - E_v^i}{k_b T} \right)}. \quad \text{Eq. (6.13)}$$

For equilibrium conditions $E_{fn} = E_{fp} = E_{f0}$, and therefore a simplification can be made:

$$\gamma_{DEG} = \frac{F_{\frac{1}{2}} \left(-q \frac{E_c^i - E_f}{k_b T} \right) \times F_{\frac{1}{2}} \left(-q \frac{E_f - E_v^i}{k_b T} \right)}{\exp \left(q \frac{E_g}{k_b T} \right)}. \quad \text{Eq. (6.14)}$$

The factor to calculate BGN takes into account doping both n -type and p -type doping, and is defined as

$$\gamma_{BGN} = \frac{F_{\frac{1}{2}} \left(q \frac{E_{fn} - E_c^i + \Delta E_{c,BGN}}{k_b T} \right)}{F_{\frac{1}{2}} \left(-q \frac{E_{fn} - E_c^i}{k_b T} \right)} \times \frac{F_{\frac{1}{2}} \left(-q \frac{E_{fp} - E_v^i - \Delta E_{v,BGN}}{k_b T} \right)}{F_{\frac{1}{2}} \left(-q \frac{E_{fp} - E_v^i}{k_b T} \right)} \quad \text{Eq. (6.15)}$$

and

$$\gamma_{neq} = \exp\left(-\frac{q(E_{fp}-E_{fn})}{k_bT}\right), \quad \text{Eq. (6.16)}$$

noting that $\gamma_{neq} = 1$ at equilibrium.

- 8) The pn product was then calculated from

$$p_0 n_0 = n_i^2 \times \gamma_{DEG} \times \gamma_{BGN} \times \gamma_{neq}, \quad \text{Eq. (6.17)}$$

and $n_{i,eff}$ was calculated by:

$$n_{i,eff} = \sqrt{n_i^2 \times \gamma_{DEG} \times \gamma_{BGN}}, \quad \text{Eq. (6.18)}$$

with this revised value of $n_{i,eff}$, $n_{(0)}$ and $p_{(0)}$ were recalculated as per Eq. 6.5 and Eq. 6.6. Recently an updated revision to the calculation of BGN and degeneracy was proposed [330], however this model will not affect the present results, as the expression for the pn product remains unchanged in this more recent work.

- 9) In the same manner as outlined in Ref. [321], Steps 4-8 were iterated to obtain more accurate values of $n_{i,eff}$, $p_{(0)}$ and $n_{(0)}$ by calculating the difference, δ , until the following condition was met:

$$\delta = 10^{-10} > \frac{n_{i,eff} - n_{i,eff \text{ previous}}}{n_{i,eff \text{ previous}}}. \quad \text{Eq. (6.19)}$$

- 10) At this point, p and n (p_0 and n_0 in the equilibrium case) were set to be the carrier concentrations at the edge of the surface depletion region, i.e. $p = p_d$ and $n = n_d$.

- 11) The surface concentration of carriers was then calculated by numerically solving the equation [46].

$$p_s - p_d + n_s - n_d + (N_A - N_D) \frac{\psi_s}{V_T} = \frac{Q^2}{2q\epsilon_{Si}V_T}, \quad \text{Eq. (6.20)}$$

where Q represents the net sum of charge present at the interface from interface traps and fixed charge at the surface contained, for instance, in a dielectric layer.

- 12) Finally, p_s and n_s were calculated by the simple expressions:

$$n_s = n_d \exp(-\beta\psi_s), \quad \text{Eq. (6.21)}$$

$$p_s = p_d \exp(\beta\psi_s) \quad \text{Eq. (6.22)}$$

6.3 Modelling the effect of interface charge on doped surfaces

With ψ_s , n_s and p_s calculated, the effect of interface charge on the surface recombination rate and its dependence on doping and injection level was explored. The presence of

interface charge introduces an additional potential ψ_s , and the value of ψ_s as a function of interface charge, injection level for various acceptor doping levels is shown in Figure 6.1.

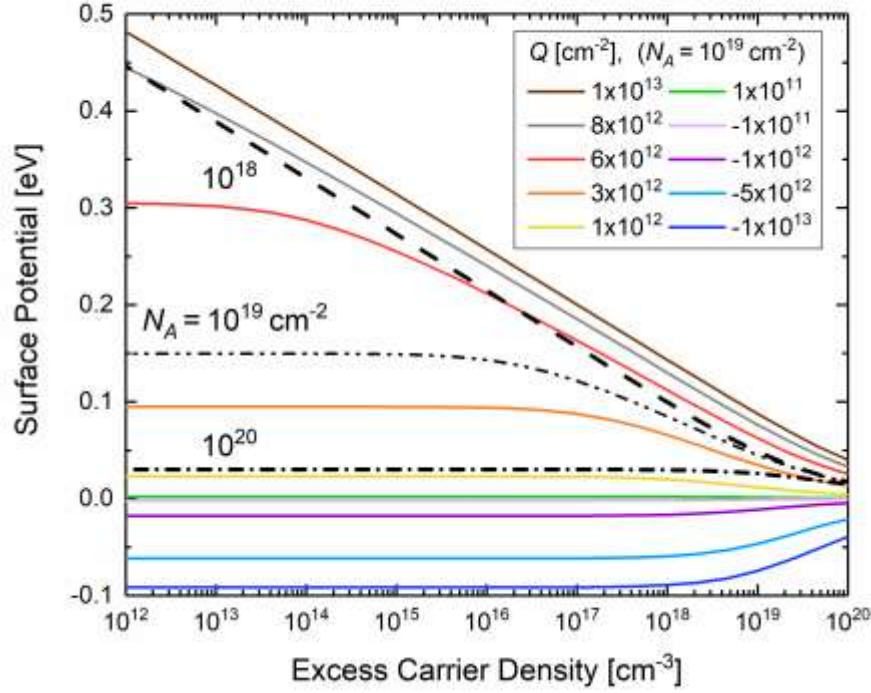


Figure 6.1 Surface potential as a function of excess carrier density, calculated using the method outlined in Ref. [46] for a range of net interface charge values (solid lines) with $N_A=10^{19} \text{ cm}^{-3}$. Two curves with varying doping levels are simulated with $Q = 4 \times 10^{12} \text{ cm}^{-2}$ (dashed lines) for comparison. In this plot, Schenck's BGN model and Fermi-Dirac statistics are used to calculate the carrier concentration at steady state.

Figure 6.1 shows that when p -type doping was present at the surface:

- 1) For high values of positive Q , the surface bending was large and scales with injection level.
- 2) For low to high values of negative Q , the surface potential was relatively constant, until very high levels of injection are achieved when the surface potential increases towards zero.
- 3) For a given substrate doping level, there were intermediate values (for $N_a = 10^{19} \text{ cm}^{-3}$ and $Q = 1\text{--}8 \times 10^{12} \text{ cm}^{-2}$) of positive Q whereby the surface potential ranges from being constant to decreasing towards zero with increasing injection level. The value of fixed charge for which this effect can be observed was affected by the substrate doping level, where higher doping levels experience less band bending for a given value of Q .

Having calculated ψ_s , the concentration of electrons and holes at the surface was calculated to assess the effect of Q on the population of electrons and holes at the surface, since this in turn drives the surface recombination rate. An expression for the ratio p_s/n_s was derived and plotted to assess the values of Q where the carrier concentrations approach parity. For a given doping level,

$$\frac{p_s}{n_s} = \frac{p_d \exp(\beta \psi_s)}{n_d \exp(-\beta \psi_s)}. \quad \text{Eq. (6.23)}$$

Substituting $n_d = n_0 + \Delta n$ and $p_d = p_0 + \Delta n$ ($\Delta n = \Delta p$, which is valid since this was at the edge of the quasi-neutral region in the emitter), the expression becomes;

$$\frac{p_s}{n_s} = \frac{p_0 + \Delta n}{n_0 + \Delta n} \frac{\exp(\beta \psi_s)}{\exp(-\beta \psi_s)}. \quad \text{Eq. (6.24)}$$

Since for large N_A , $n_0 \ll \Delta n$ and $N_A \gg \Delta n$, the above expression was simplified to

$$\frac{p_s}{n_s} = \left(\frac{N_A}{\Delta n} + 1 \right) \exp \left(- \frac{2\psi_s(\Delta n)}{V_T} \right). \quad \text{Eq. (6.25)}$$

A similar expression was derived for n -type doped surfaces with large N_D ;

$$\frac{n_s}{p_s} = \left(\frac{N_D}{\Delta p} + 1 \right) \exp \left(\frac{2\psi_s(\Delta p)}{V_T} \right) \quad \text{Eq. (6.26)}$$

Figure 6.2 plots Eq. 6.25 as a function of injection level for a fixed doping concentration and varying Q , showing the full range surface conditions (accumulation, depletion, and inversion) of a given sample, due to varying injection levels and interface charge values. In this calculation, extremely high injection levels were plotted to show the overall trend, despite these levels being difficult to achieve in reality. Interestingly, Figure 6.2 shows that the sample can move through conditions of depletion and inversion, as a result of increasing injection level; and through the full range of accumulation, depletion and inversion depending on the polarity and magnitude of charge deposited. In particular, Figure 6.2 shows:

- 1) With increasing injection level, the carrier concentrations approach parity at very high injection levels. This was evident for an interface without charge present (black dotted line in Figure 6.2).
- 2) For large values of positive $Q > 10^{13} \text{ cm}^{-2}$, the sample was heavily inverted over the entire injection level range.

- 3) There was an intermediate case where the sample moves from mild depletion, into severe depletion, and for some samples, into inversion, despite the large concentration of dopants at the surface.
- 4) As the doping level increases, larger values of fixed positive charge are required to move the sample into inversion, which in turn implies that the non-linear injection level is unlikely observed for heavily doped samples.

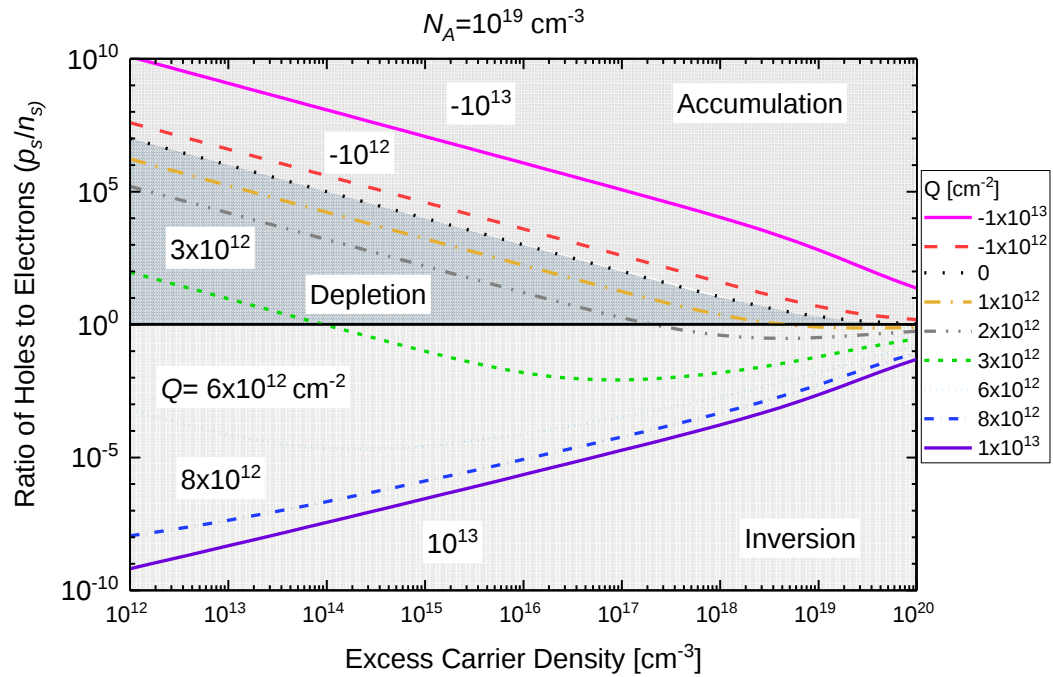


Figure 6.2 Ratio of holes to electrons, for a range of Q values, as a function of excess carrier density. The conditions where the surface condition is in accumulation, depletion or inversion are shaded, and the curves trace where surface condition transitions occur due to changing excess carrier density. In these calculations, the doping levels are $N_A = 10^{19} \text{ cm}^{-3}$ and $N_D = 10^{15} \text{ cm}^{-3}$

To illustrate the effect of background doping on the relative carrier concentration at the surface, Figure 6.3 plots the hole to electron ratio at a constant Q value as a function of background doping.

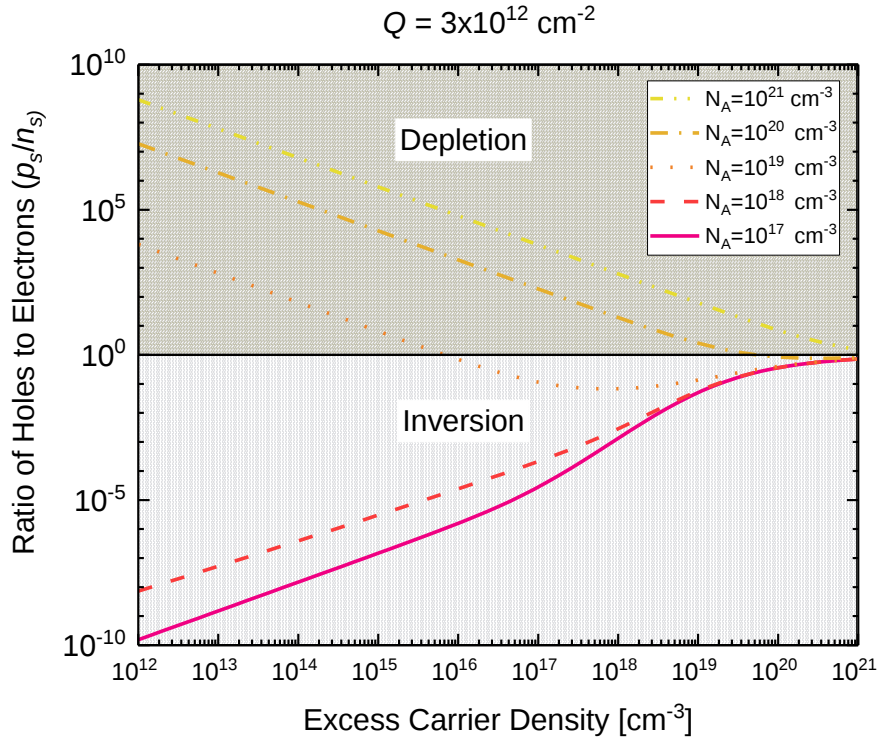


Figure 6.3 Ratio of holes to electrons, for a range of N_A values, as a function of excess carrier density. In these calculations, $Q = 3 \times 10^{12} \text{ cm}^{-3}$. The conditions where the surface is in depletion or inversion are shaded, and the curves trace where transitions in surface condition occur due to changing excess carrier density.

The non-linear curvature of the inverse effective lifetime curve can now be explained by modelling J_{0s} as a function of injection level for various Q values. Figure 6.4 shows that for certain values of Q , there was a varying J_{0s} with excess carrier density, particularly in the range $\Delta n = 10^{15} - 10^{17} \text{ cm}^{-3}$, in which J_{0e} is typically extracted using the Kane-Swanson method[109]. J_{0e} is representative of SRH recombination at the surface, Auger recombination in the diffused region and SRH in the diffused region. Assuming the surface recombination rate is limiting J_{0s} (or J_{0e} as applicable) which is true in the case of a surface passivation limited sample, the lifetime behaviour will reflect the surface recombination behaviour J_{0s} . Therefore, varying J_{0s} will affect the shape of the inverse lifetime curve in a surface limited sample, as is evident upon inspection of Eq. 2.62, which shows that J_{0e} is the gradient of the inverse effective lifetime curve in a plot of excess carrier density vs. Auger-corrected inverse effective lifetime. Therefore a varying J_{0s} as plotted in Figure 6.4 would imply a non-linear Auger-corrected inverse effective lifetime curve in high injection, which can explain the non-linear lifetime behaviour observed in previous studies [301, 319, 331] and in the previous work of Chapter 5. Due to the unique combination of interface charge, substrate doping and increasing injection level, the

surface of the sample is in a range where the recombination rate becomes affected by the SRH recombination parameters of both the majority and minority carrier, because the sample is transitioning into deep depletion, or in some cases, beyond deep depletion and into inversion. This has the effect of producing a varying recombination rate, which is reflected in the varying J_{0s} and hence the linear injection level dependence of the inverse corrected lifetime at high injection is lost, and the behaviour becomes non-linear.

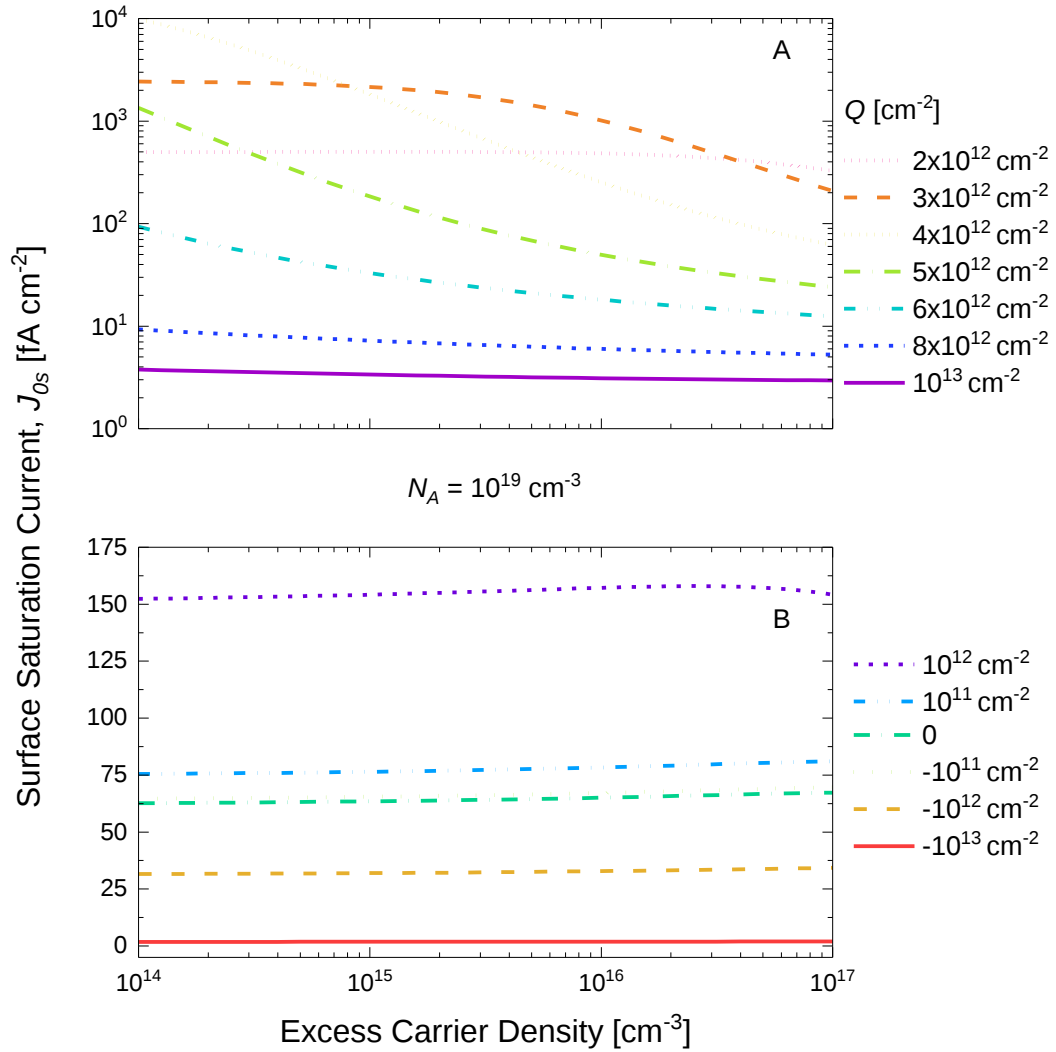


Figure 6.4 Calculated J_{0s} values as a function of excess carrier density, for a range of Q values. Plot A (top) shows that there is a range of values which produce a non-constant J_{0s} which produces non-linear inverse lifetime behaviour, whilst a range of positive and negative values produce the characteristic constant J_{0s} (bottom). These calculations are performed with $S_{n0} = S_{p0} = 5000$ cm/s, a single trap level at the mid-gap for donors and acceptors, and acceptor doping density $N_A = 10^{19}$ cm⁻³.

Modelling the effect of varying S_{n0} and S_{p0} on J_{0s} values revealed a different trend in comparison to the effect of varying Q . Three scenarios were modelled in the following

analysis; equal S_{n0} and S_{p0} and varying $S_{n(p)0}$ whilst $S_{p(n)0}$ was kept constant, for a fixed doping and Q at varying injection levels. The results are shown in Figure 6.5, where varying S_{n0} and S_{p0} values appear to shift the curve along the y -axis with increasing values increasing J_{0s} , without affecting the overall ‘shape’ of the curve. Similarly, a comparison of the curves with non-equal capture cross sections, shows that there is a transition in minority carrier limited recombination as a function of injection level, which corresponds to the conditions presented in Figure 6.2. This can be inferred from the divergence and convergence of the curves as a function of injection level.

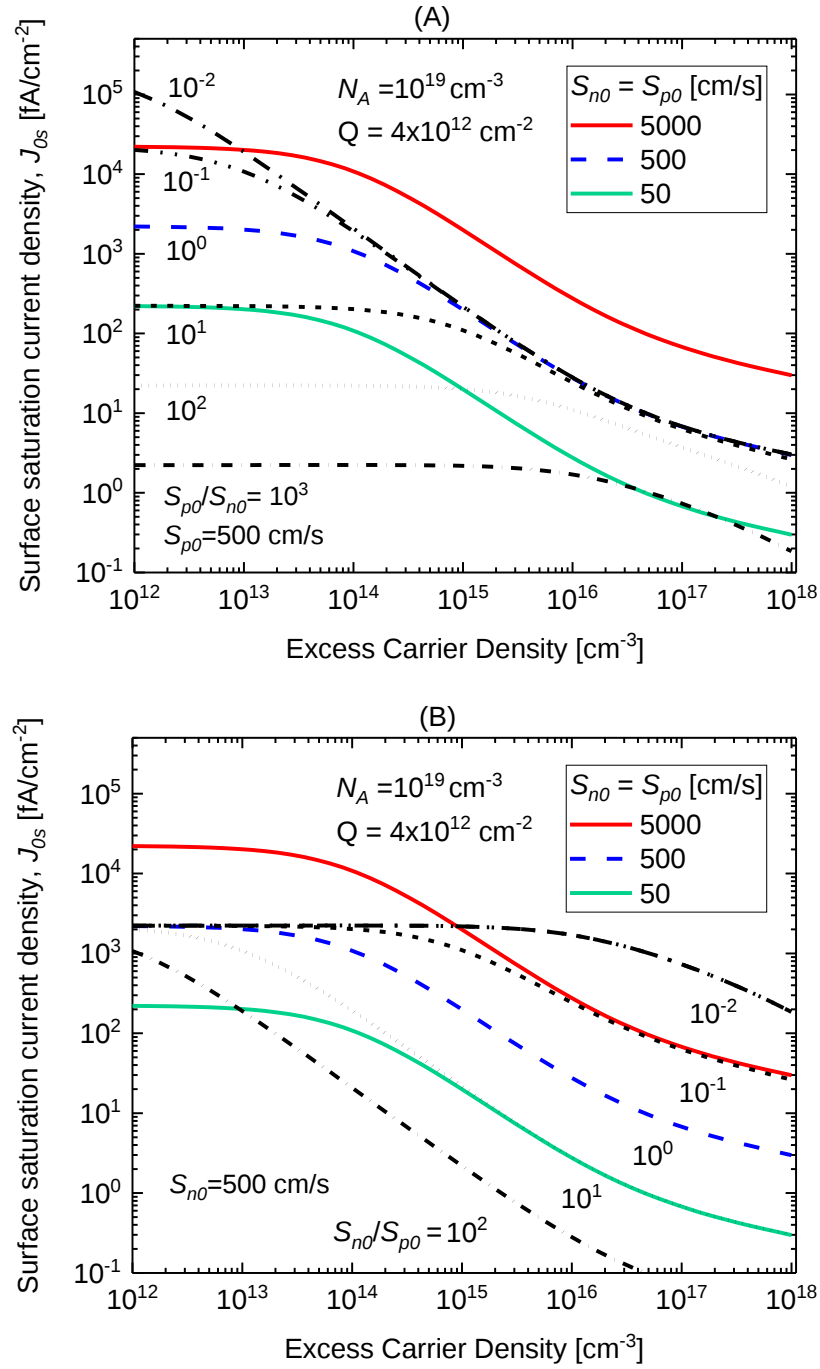


Figure 6.5 The effect of equal (coloured lines) and varying (dotted lines) S_{n0} and S_{p0} values on J_{0s} , for a p -type doped surface with $N_A = 10^{19} \text{ cm}^{-3}$ and $Q = 4 \times 10^{12} \text{ cm}^{-2}$ due to variances in S_{n0} (left, A) and S_{p0} (right, B). The trend in the coloured lines where $S_{n0} = S_{p0}$ is varied shows how the overall recombination trend shifts along the y-axis – which is distinct to the trend in Figure 6.4. Alternatively, the dotted lines where S_{n0} or S_{p0} is varied relative to a fixed S_{n0} (plot A), S_{p0} (plot B) = 500 cm/s, show that for a broad range of unequal capture cross sections until $S_{p0} / S_{n0} \approx 10^2$, the recombination rate in high injection is independent of S_{n0} , and is governed by S_{p0} (the minority carrier in high injection).

The non-linear lifetime behaviour occurs within an injection level range in which the relative concentrations of minority carriers at the surface is changing due to Q and increasing injection level. This has a corresponding effect on the effective lifetime behaviour. Furthermore, comparing Figure 6.4 and Figure 6.5 shows that variances in S_{n0} , S_{p0} and Q produce distinct trends in recombination behaviour with increased injection level, herein referred to as ‘signatures’. This suggests that the variances of Q and S_{n0}/S_{p0} are unique and can be extracted independently. This was explored in the proceeding experimental section.

The previous analysis in Figure 6.2 and Figure 6.3 presents conditions for inversion at the sample surface as the sample transitions from low into high injection, and hence exhibit the non-linear lifetime behaviour which enables the extraction of Q . This transition from strong depletion into inversion was a function of doping density, injection level and Q . Higher (lower) levels of doping concentration require higher (lower) values of interface charge to move the sample from depletion into inversion conditions. The following analysis calculated the value of interface charge values required to observe a transition in minority carrier type for a full range of surface carrier concentrations. In the analysis, the following restrictions were made.

- 1) For surface doping concentrations less than 10^{17} cm^{-3} , an un-diffused boron doped surface ($N_A = N_s$, $N_D = 0$) was simulated. For surface doping concentrations greater than 10^{17} cm^{-3} , a p -type diffusion $N_A = N_s$, on an n -type wafer $N_D = 10^{14}$ was simulated.
- 2) The transition from depletion to inversion conditions occurred in the range of $\Delta n = 10^{15}$ - 10^{16} cm^{-3} . This can be expressed as:
 For $\Delta n < 10^{15} \text{ cm}^{-3}$, $p_s > n_s$
 For $\Delta n > 10^{16} \text{ cm}^{-3}$, $p_s < n_s$.
- 3) Flat quasi-Fermi levels.

The scenario in point 2 above outlines a transition in minority carrier type and the surface moving from depletion to inversion. It can be shown that for $n_s = p_s$, this is achieved when;

$$E_{fn} + E_{fp} = 2\psi_s, \quad \text{Eq. (6.27)}$$

where E_{fn} and E_{fp} are the electron and hole Fermi levels located at the surface, in steady state conditions. In Figure 6.6a, the ratio of holes to electrons at the surface is shown as a

function of surface doping for various Q densities at $\Delta n = 10^{15} \text{ cm}^{-3}$ and $\Delta n = 10^{16} \text{ cm}^{-3}$. This range was chosen as it is relatively easily accessible using standard PC lifetime measurements, and of high enough injection for the extraction of J_{0e} for most bulk doping levels. Figure 6.6 shows that the polarity of the minority carrier at the surface strongly depends on the surface dopant concentration, injection level, and Q . In this case the specific parameters where the minority carrier changes polarity between $\Delta n = 10^{15}$ - 10^{16} cm^{-3} were of interest, as these measurements have the ‘desired’ injection level dependent recombination rate which allows the extraction of the interface electronic properties. These narrow regions of interest are marked by yellow bands in Figure 6.6. This study provides guidance to researchers interested in using this technique for extracting the Q from dielectric films on highly doped surfaces. If, for example, a Q density of 10^{12} cm^{-2} is expected, a surface concentration of $1\text{-}2 \times 10^{18} \text{ cm}^{-3}$ will give maximum sensitivity if the measurement range is between $\Delta n = 10^{15}$ - 10^{16} cm^{-3} . When a higher Q is expected, higher surface concentrations will enable optimal sensitivity. It should be noted that similar studies could be performed using different injection level ranges resulting in other optimal experimental combinations.

A method of extracting the interface parameters is presented in the following sections. Symmetrically passivated and diffused p^+np^+ and n^+pn^+ lifetime structures were fabricated to test the extraction of interface properties for both n -type and p -type diffused surfaces. The p^+np^+ samples were passivated with the negatively charged dielectric, AlO_x , and the n^+pn^+ samples were passivated with the positively charged dielectrics HfO_x and SiN_x , to create depleted conditions at the surface. The following sections outline the fabrication procedure and fitting results.

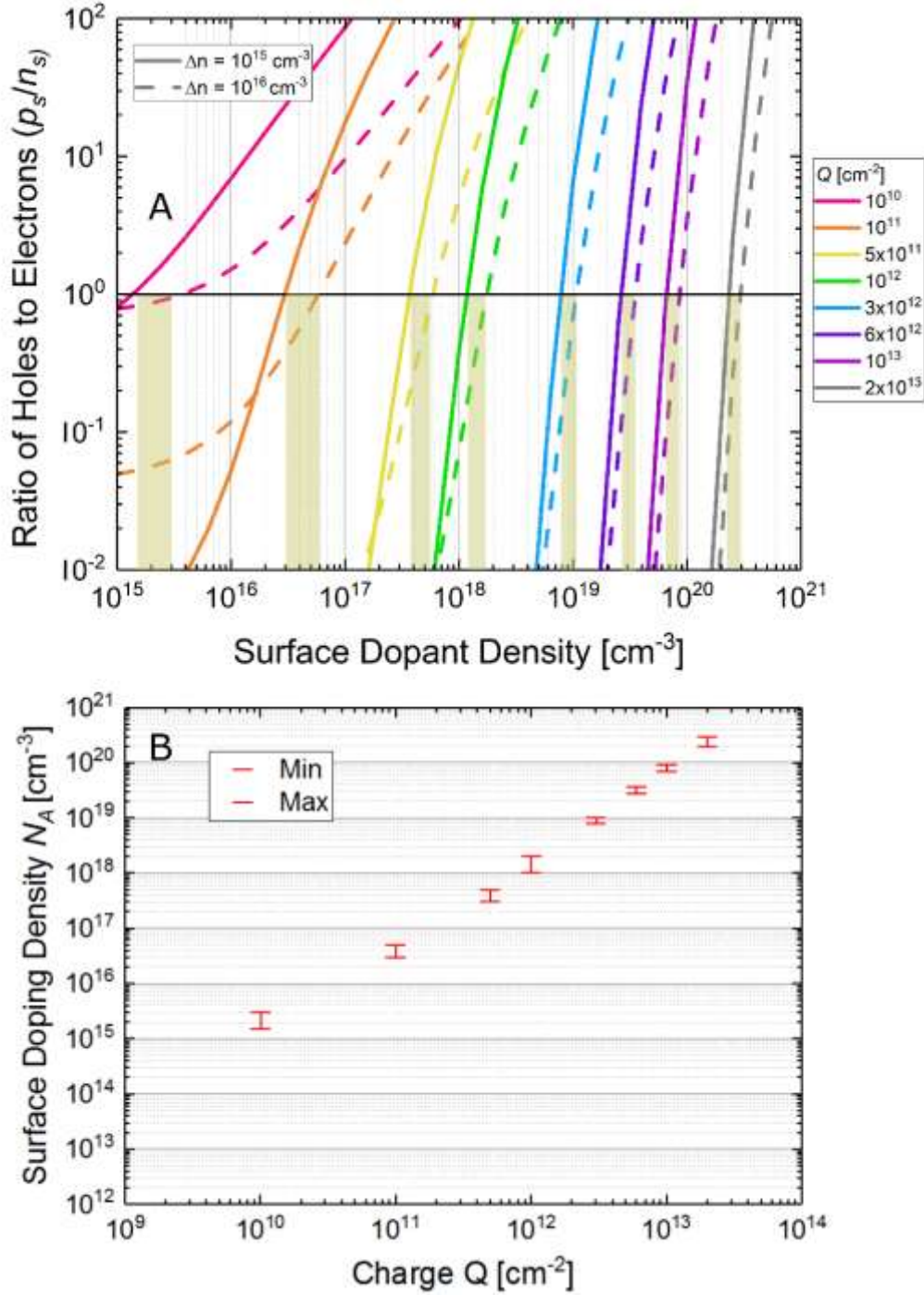


Figure 6.6 The above plot (a) shows the ratio of holes to electrons (n_s/p_s) calculated at two specific injection levels ($\Delta n = 10^{15} \text{ cm}^{-3}$ and $\Delta n = 10^{16} \text{ cm}^{-3}$) as a function of substrate doping, for various interface charge densities. Sensitivity to the non-linear lifetime behaviour is achieved when the sample moves from depletion to inversion between the injection level range $10^{15} - 10^{16} \text{ cm}^{-3}$. For the transition to occur at $\Delta n = 10^{15} \text{ cm}^{-3}$, for a given charge level, the $p_s/n_s > 1$ (i.e. the curve is above the black line), and for $\Delta n = 10^{16} \text{ cm}^{-3}$ $p_s/n_s < 1$ (i.e. the curve is below the black line), which signifies the surface moving into inversion in this injection level range. The yellow shaded regions are used as guides for the eye to the corresponding substrate p -type doping level, for sensitivity to the interface charge. The lower plot (b) plots the range of surface dopant density highlighted in yellow and plots it as a function of Q , for greater clarity.

6.4 Experimental

SiN_x passivated p^+np^+ lifetime structures were fabricated using, 660 μm thick, 4.5 $\Omega\cdot\text{cm}$ phosphorus doped n -type float zone (FZ) $\langle 100 \rangle$ planarised wafers. After a standard RCA cleaning procedure and short immersion in 1 % w/v hydrofluoric (HF) acid, the samples were diffused in a commercial tube diffusion furnace (TS8603, Tempres Systems) using boron tribromide (BBr₃) as the boron source. ECV profiling of a sister monitor wafer was performed, revealing the active boron concentration at the surface to be $N_A = 1.3 \times 10^{19} \text{ cm}^{-3}$ with junction depth of approximately 475 nm ($\pm 50 \text{ nm}$). The samples then underwent double-sided SiN_x deposition in a Roth & Rau MAiA remote PECVD deposition tool, resulting in an 85 nm thick SiN_x layer with refractive index $n=2.03$. The samples underwent an anneal sequence at 400 °C in a N₂ ambient, and were subsequently cleaved into quarters. The samples were divided into two groups, each receiving separate treatments to observe the resulting shift in injection level dependent lifetime. The first group underwent an anneal process, which involved the monochromatic illumination of the samples on a hot plate at two different temperatures. The second group of wafers underwent corona charging for varying time intervals to study the effect of increasing levels of deposited negative charge.

A strong non-linear recombination rate for some experimental conditions was observed in the work of Hoex *et al.*, which studied the lifetime behaviour of phosphorus diffused, symmetrically passivated n^+pn^+ AlO_x passivated samples [156]. Measured ECV and PC measurements were provided by the authors of Ref. [156] to facilitate the fitting of the lifetime curves, and full processing details of those samples can be found in the Ref. [156]. It is noted herein that these samples were fabricated on high lifetime, polished FZ wafers, making them ideal samples for this study.

The HfO_x passivated lifetime samples were fabricated on 280 μm thick, 100 $\Omega\cdot\text{cm}$, phosphorus doped, FZ $\langle 100 \rangle$, polished c-Si wafers. The samples were cleaned in a standard RCA procedure followed by a short HF dip. The samples were then boron diffused in a tube diffusion process with liquid BBr₃ source. Following BSG removal, thin HfO_x layers were deposited via ALD (TFS200, BENEQ) on both sides, using a liquid tetrakis hafnium (TEMAH) precursor and deionized water at 250 °C. Layers approximately 15 and 30 nm thick were grown with 200 and 400 deposition cycles respectively. The samples were then annealed in forming gas at 350 °C for 15 minutes. The electronic properties of this HfO_x film is discussed in detail in Ref. [236].

The active dopant profile, wafer thickness, generation rate were used as inputs into the simulation. The wafer resistivity and active boron depth profile for each sample was determined by ECV (WEP, CVP21) measurements, calibrated by 4-point-probe sheet resistance measurements. The generation rate was simulated using OPAL2 [104], by fitting the measured reflectance curves to simulated curves, and the optical constant estimated by fitting transient to generalised QSSPC measurements by varying the optical constant in the generalised measurement over a range of injection levels. QSSPC measurements were performed using a Sinton WCT-120 lifetime tester.

The simulation of the injection level dependent lifetime using Sentaurus TCAD method and models was identical as that presented in Chapter 5.

6.5 Results

6.5.1 SiN_x passivated p^+np^+ samples

The Auger-corrected, injection dependent inverse lifetime curves for the SiN_x passivated p^+np^+ samples after various sequential anneal treatments is shown in Figure 6.7. The simulated lifetime curves are overlaid on the measurements and the surface parameters corresponding to each simulated curve fit are listed in Table 6.1. The variation in inverse lifetime was fitted by changing S_{n0} , which suggests that a consistent shift along the y-axis of the inverse lifetime curve is primarily associated with changes in the values of S_{n0} and S_{p0} (noting in this case $S_{n0} = S_{p0}$), in agreement with Figure 6.5. To investigate the possibility that the poor fit was a result of the assumption of equal capture cross section, lifetime curves with varying S_{n0} and S_{p0} values were simulated, and the average difference between the measured and simulated lifetime was calculated as the average residual value (A), given by the equation,

$$A [\%] = \sum_{j=1}^n \frac{\tau_{measured,j} - \tau_{simulated,j}}{\tau_{measured,j}} / n, \quad \text{Eq. (6.28)}$$

Where $\tau_{measured}$ and $\tau_{simulated}$ is the measured and simulated corrected lifetime at the same injection level respectively, m is the number of discrete injection level values at which the calculation is performed, in this case equal to 13. The average residual values for lifetime curves simulated with varying S_{n0} and S_{p0} values is shown in Fig. 7b. A minimum was obtained for $S_{n0} = S_{p0} = 48 \text{ cm}^2/\text{s}$, indicating the best fit was obtained with equal capture cross sections. Hence the discrepancy between measured and simulated curves

may be a result of the neglect of other effects and is discussed further in the discussion section.

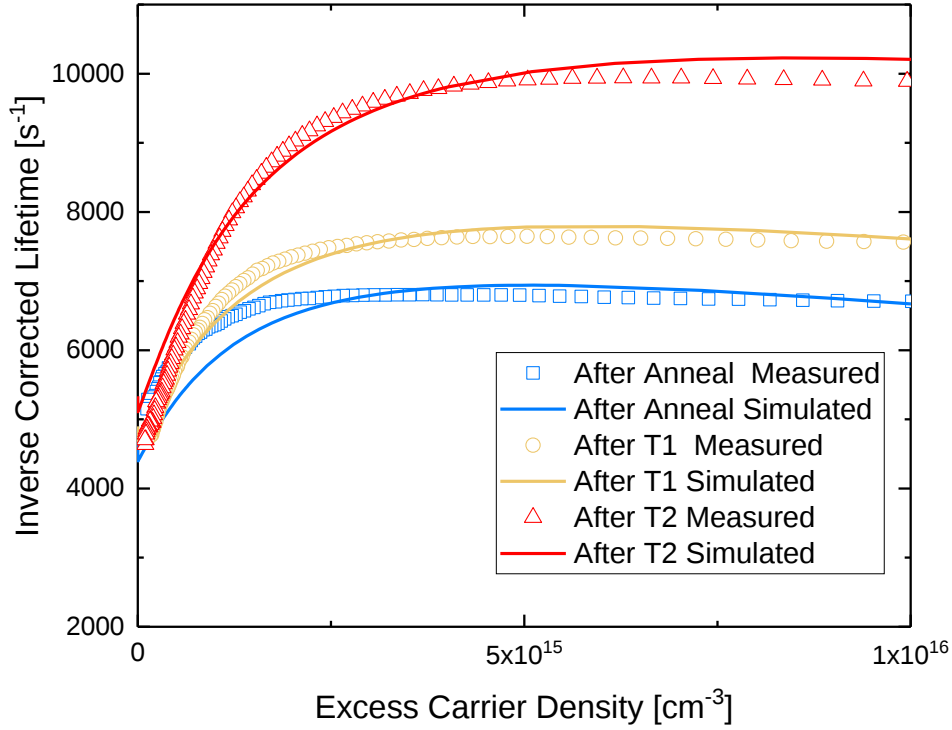


Figure 6.7 Measured and modelled corrected inverse effective lifetime curves for SiN_x passivated p^+np^+ samples after annealing treatments.

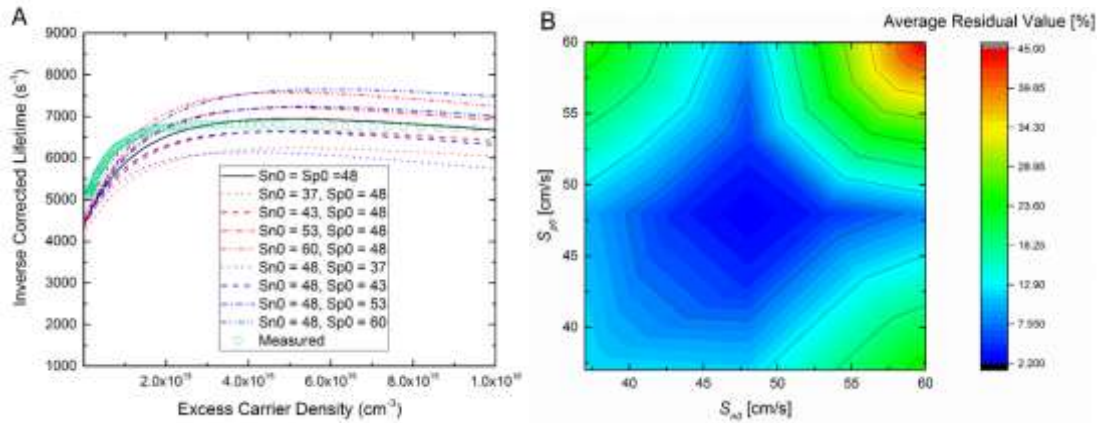


Figure 6.8 Measured and modelled lifetime curves of varying capture cross sections (Plot A) indicating the best fit was achieved for an assumption of equal capture cross section. The average residual values for lifetime curves fitted with varying S_{n0} and S_{p0} (right) indicating the best fit was achieved for $S_{n0} = S_{p0} = 48$ cm/s for the sample after anneal (Plot B).

In comparison to the samples which underwent varying thermal treatments, the trend in injection dependent lifetime due to corona charging shown in Figure 6.9 exhibit a clearly different trend. By varying the simulated Q value whilst keeping S_{n0} constant, the effect

of changing Q during corona charging was demonstrated, and matches well with the measured curves—with the exception of the curve with 4 minutes of charging, which was fitted with a higher S_{n0} value. During corona charging, the amount of negative charge deposited on the surface increased, effectively compensating the positive charge in the SiN_x film at the interface. As a result, the gradient of the curve ‘flattened’, manipulating the shape of the inverse lifetime curve towards the expected linear trend. This effect is noticeably distinct compared to the trend exhibited in Figure 6.5 and Figure 6.7 where S_{n0} was varied. This was also consistent with the trend in the calculated J_{0s} curves shown in Figure 6.4 and a previous study of the recombination behaviour of inverted p^+np^+ diffused lifetime structures [331].

Table 6.1 Extracted interface parameters Q_f and $S_{n0}=S_{p0}$, for SiN_x passivated samples.

Corona Charged Samples			Annealed Samples		
Cumulative charge duration (min)	S_{n0} [cm/s]	Q [cm ⁻²]	Anneal Process	S_{n0} [cm/s]	Q [cm ⁻²]
0	75	3.0×10^{12}	Before T1 and T2	48	3.2×10^{12}
4	82	3.0×10^{12}	After anneal T1	55	3.2×10^{12}
8	75	2.6×10^{12}	After anneal T2	75	3.2×10^{12}
12	75	2.4×10^{12}			
20	75	2.35×10^{12}			

A comparison of Figure 6.7 and Figure 6.9 shows that variations in S_{n0} and Q are reflected in unique trends in the shape of the inverse lifetime behaviour, in support of the previous modelling. As the effect on the shape was distinct, this technique can be used to identify trends in Q , S_{n0} and S_{p0} independently.

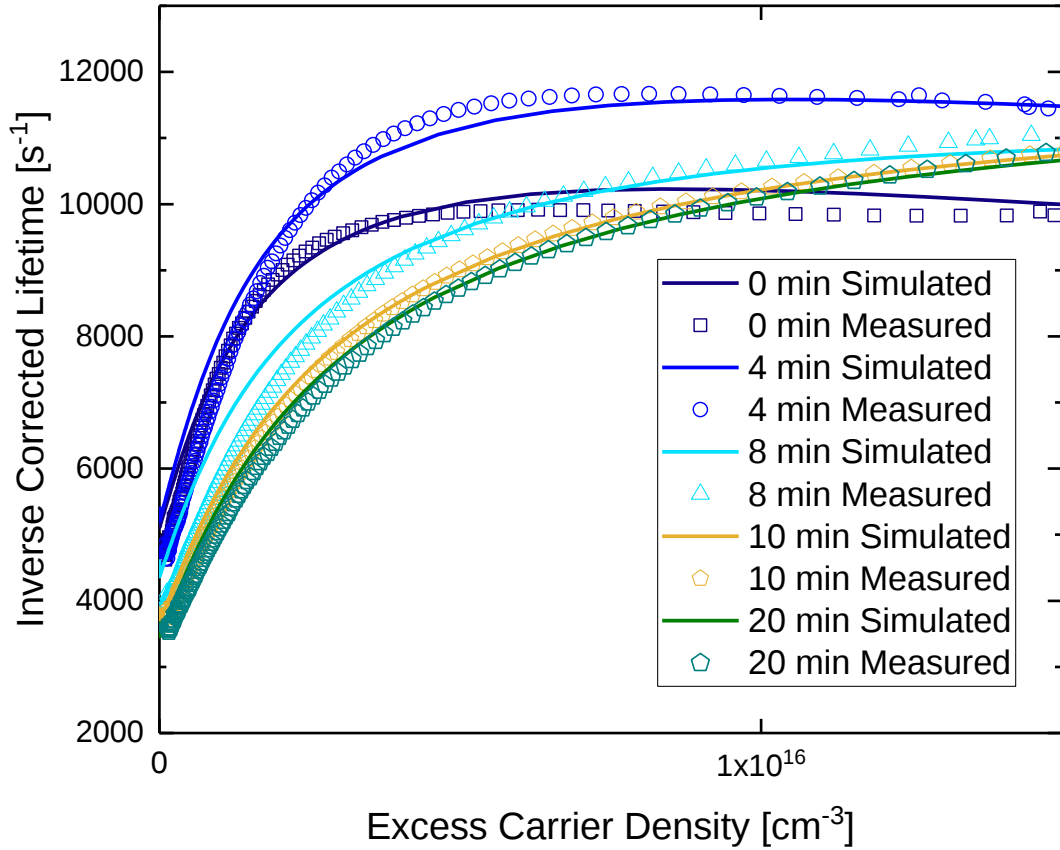


Figure 6.9 Measured and fitted corrected inverse effective lifetime curves for SiN_x passivated p^+np^+ samples after various intervals of negative corona charging on both surfaces.

6.5.1.1 Estimating uncertainty in the extracted parameters S_{n0} , S_{p0} and Q

To estimate the uncertainty of the extracted parameters S_{n0} , S_{p0} and Q , a reduced-Chi² goodness of fit parameter Q^2 was calculated, as this metric gives allows for the comparison of the uncertainty of the fitted curves relative to the inherent measurement uncertainty (note that usually the reduced-Chi² metric is denoted as Q , however it is herein referred to as Q^2 to distinguish the metric from the interface charge, Q). This metric is given by the equation

$$Q^2 = \frac{\sum_{i=1}^N \left(\frac{x_i - \mu_i}{\sigma_i} \right)^2}{DOF} \quad \text{Eq. (6.29)}$$

Where σ_i is the variance in the measurement, x_i and μ_i are the inverse corrected lifetime of the model and measured data respectively, DOF is the degrees of freedom, calculated as the difference between the number of fitted measurement points N , and the number of fitting parameters used in the model r . The value of Q^2 is a dimensionless ratio of the error associated with the fitting model and the variability of the measured data. A Q^2

value greater than one signifies a poor fit where the residual error from fitting is greater than the error introduced from measurement variability. A value less than one suggests the data is over fit, as the fit is within the measurement variability. A Q^2 value of one is ideal, and suggests that a good fit to the data was achieved within the measurement variability. Furthermore, the variance in the measurement σ_i and the DOF will have a significant effect on the goodness of fit. As σ_i increases, a lower value of Q^2 is more easily obtained. Similar trends are observed as the number of fitting points N are increased, or if the number of free fitting variables r is reduced.

In this work, Q^2 was calculated with $N = 36$ over an injection level range of $5 \times 10^{14} \text{ cm}^{-3} < \Delta n < 1.5 \times 10^{14} \text{ cm}^{-3}$ for the “after anneal” sample in Figure 6.7, as this had the poorest fit and is therefore likely to be an ‘extreme case’. A value of $\sigma_i = 5\%$ was calculated from Monte Carlo method simulations of the uncertainty of the measured lifetime from the uncertainty of the input parameters, using the Photoconductance Uncertainty Calculator software[332]. The variances in S_{n0}/S_{p0} and Q were assessed separately by simulating a range of lifetime curves whereby either S_{n0} ($S_{n0} = S_{p0}$) was varied, whilst Q remained constant—or vice versa in the case of calculating the uncertainty in Q —and then calculating the Q^2 from the resulting range of curves. The S_{n0}/S_{p0} and Q values which resulted in a Q^2 value less than one was calculated was taken as the range of the uncertainty, as within this range of values, any improvements within the fit are within the variance expected from the measurement variability, and therefore do not yield greater accuracy in the extracted parameters.

The results from this simulation are shown in Figure 6.10, and the ranges $2.9 \times 10^{12} \text{ cm}^2 < Q < 3.1 \times 10^{12} \text{ cm}^2$ and $47 \text{ cm/s} < S_{n0} < 50.7 \text{ cm/s}$ were calculated to produce Q^2 values less than or equal to 1. This corresponds to an uncertainty range of 4.7 % and 7.7 % for Q and S_{n0}/S_{p0} respectively. These values, although extracted for a single example are believed to be representative of all samples used in this work, as the same measurement technique and fitting techniques are applied in all subsequent fitting analysis.

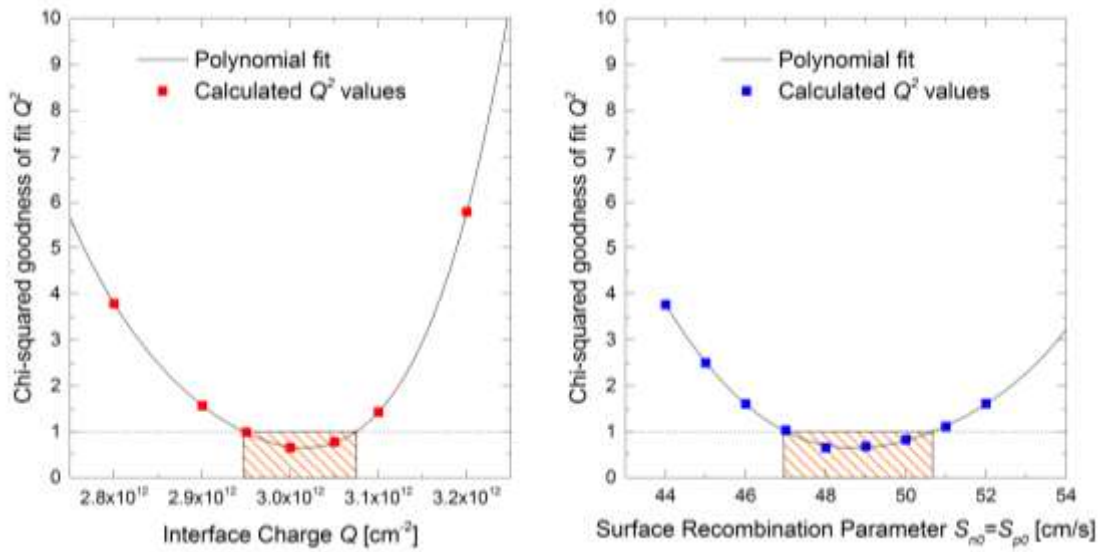


Figure 6.10 Calculated Q^2 values for a range of lifetime curves simulated with varying Q (left) and S_{n0} values ($S_{n0} = S_{p0}$) values, fitted with a 6th order polynomial function to extract the Q and S_{n0} ranges for which $Q^2 < 1$.

6.5.2 HfO_x passivated p^+np^+ Samples

The measured and simulated Auger-corrected inverse lifetime curves for the passivated p^+np^+ structures before and after annealing for the 15 nm and 30 nm thicknesses are shown in Figure 6.11. Whilst the Q value increased, The 15 nm film was fitted with an increasing S_{n0} and S_{p0} value, suggesting the improvement in passivation was a result of improved charge-effect passivation. In comparison, the improvement in lifetime observed for the 30 nm film after annealing was attributed primarily to the decrease in S_{n0} and S_{p0} , since the fitted Q value decreased between treatments. That the decrease in Q for the 30 nm film was larger than the increase in Q for the 15 nm film, suggests that as S_{n0} and S_{p0} became smaller, the sample was less reliant on charge-effect passivation since the number of defect sites was low and hence the overall lifetime was still higher in comparison to the as-deposited state.

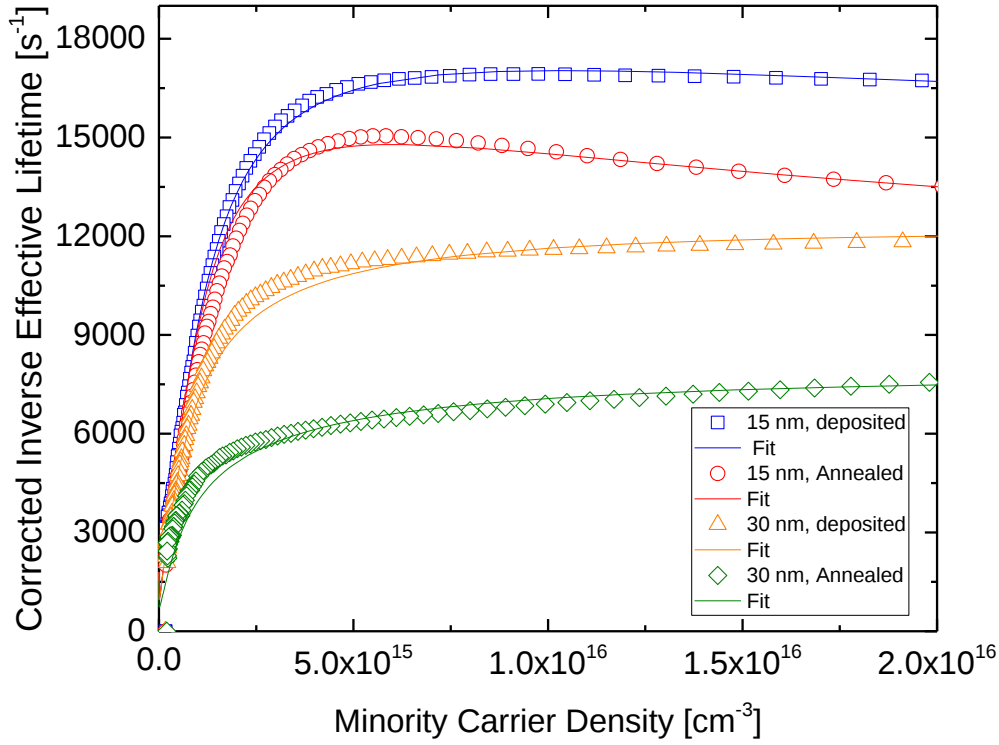


Figure 6.11 Measured and fitted inverse corrected lifetime curves as a function of injection level for HfO_x passivated samples.

The fitting results in Figure 6.11 show that the method can be applied to HfO_x passivated films, in addition to SiN_x films, due to the fixed positive charge inherent in the film. The extracted parameters in Table 6.2 show that although the surface passivation improved for both the 15 nm and 30 nm films, the underlying mechanism was different.

Table 6.2 Extracted interface parameters from HfO_x passivated samples.

Thickness	Parameter	Deposited	After Anneal
15 nm	Q	$1.4 \times 10^{12} \text{ cm}^{-2}$	$1.8 \times 10^{12} \text{ cm}^{-2}$
	S_{n0}	135 cm/s	152 cm/s
30 nm	Q	$3 \times 10^{11} \text{ cm}^{-2}$	$2 \times 10^{11} \text{ cm}^{-2}$
	S_{n0}	65 cm/s	40 cm/s

6.5.3 AlO_x passivated n^+pn^+ Samples

In this section the fitting and analysis of the resulting lifetime curves from AlO_x passivated samples was restricted to the samples exhibiting the non-linear behaviour,

herein referred to as Sample A and Sample B. ECV measurements (shown in Figure 6.12) found the active surface concentrations of phosphorus to be $N_D = 1.96 \times 10^{19} \text{ cm}^{-3}$ and $N_D = 3.74 \times 10^{19} \text{ cm}^{-3}$ for Samples A and B respectively. The fitted and measured curves are shown in Figure 6.13, with the extracted interface parameters listed in Table 6.3. As was the case with the inverted p -type surface, the non-linear recombination was effectively modelled with an inverted surface condition, induced by high negative charge at the interface. These results are the first fitting results of n^+pn^+ inverted structures passivated with ALD AlO_x , and show this methodology is not limited solely to p -type diffused surfaces.

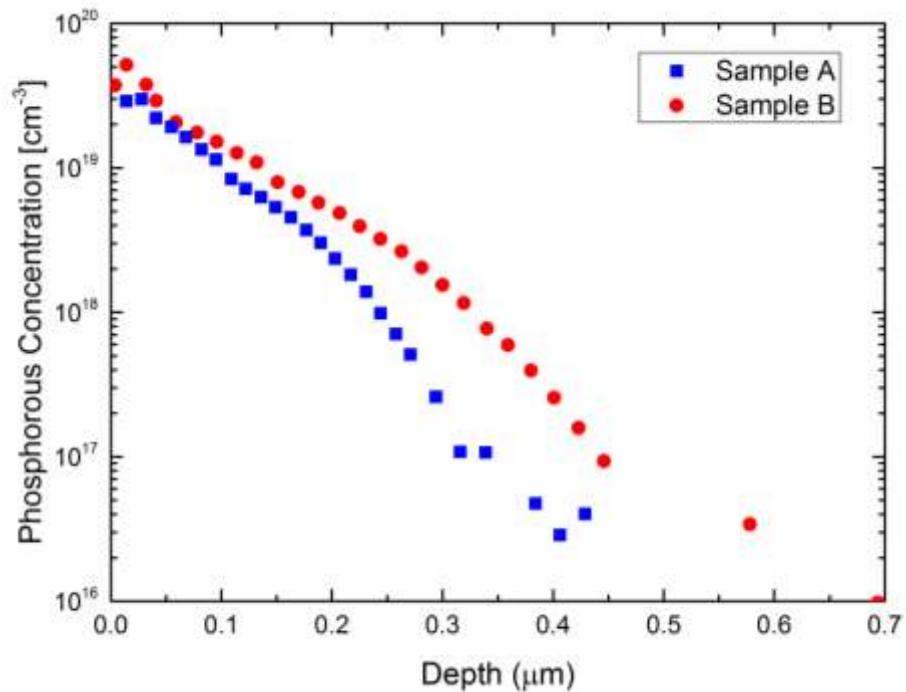


Figure 6.12 Electrically active phosphorus concentration as a function of depth for the n^+pn^+ structures, Sample A and Sample B, extracted via ECV measurements.

Table 6.3 Extracted interface parameters from AlO_x passivated samples.

Sample	S_{n0} [cm/s]	Q [cm ⁻²]
A	40	-6.35×10^{12}
B	200	-1.0×10^{12}

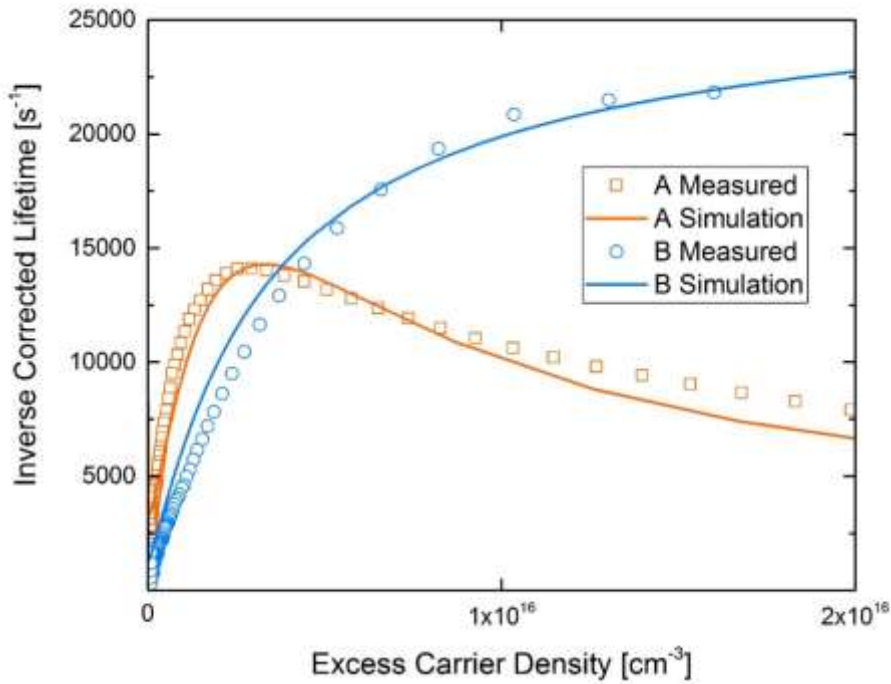


Figure 6.13 Measured and simulated Auger-corrected inverse lifetime curves for AlO_x passivated n^+pn^+ samples. In this plot, the non-linear recombination trend was reproduced by modelling a high density of negative Q at the silicon surface.

The fitted parameters for these samples show that S_{n0} increased with the surface concentration. It should, however, be noted that this does not necessarily imply a correlation between the interface parameters and surface carrier concentration, noting that prior studies have found S_{n0} to be independent of surface doping [75]. A possible explanation for this variance is differences in sample handling leading to surface contamination, as the D_{it} is very sensitive to surface preparation and handling prior to deposition. Unfortunately the samples are not available for further analysis and so this could not be verified.

6.6 Discussion

In Section 6.5, the modelling was performed without assuming flat quasi-Fermi levels, and therefore any gradients in the quasi-Fermi levels at the surface were taken into account. An exponential parameterisation of the measured dopant concentration at the surface was used to account for the finite depth intervals of the ECV measurement. However the analysis in Section 6.3 assumed that the quasi-Fermi levels are flat, i.e. the doping concentration was constant over the entire width of the surface depletion region. This is valid provided that the dopant concentrations vary negligibly over the width of the

depletion region, which is affected by the interface charge and carrier concentrations. To assess the validity of this assumption, the depletion region width was calculated according to Eq. 53 in Ref. [48], and shown in Figure 6.14 at an injection level $\Delta n = 5 \times 10^{15} \text{ cm}^{-3}$. Figure 6.14 shows that the depletion width was less than 2 nm for $N_A > 5 \times 10^{18} \text{ cm}^{-3}$, for the full range of interface charge investigated in this work and therefore this assumption was expected to introduce minimal uncertainty.

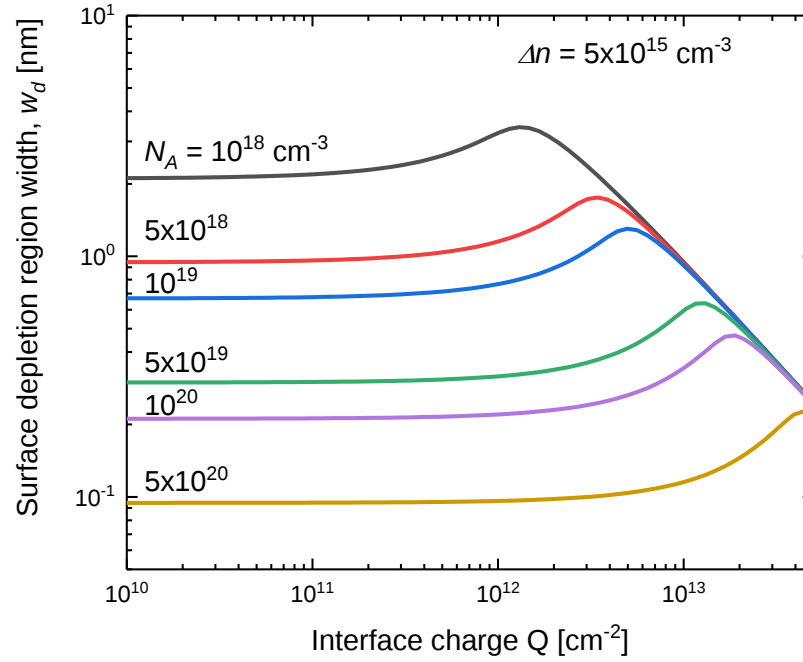


Figure 6.14 Surface depletion width as a function of Q for a p -type surface with varying doping levels N_A calculated according to Eq. 53 from Ref. [48]

In Section 6.5, a single defect for donors and acceptors respectively with $S_{p0} = S_{n0}$ was used in the simulations. However, it is well known that the Si-SiO₂ interface present at SiN_x and AlO_x passivated silicon surfaces features a distribution of defect states across the band gap, with varying density and capture cross sections which are commonly approximated using a Gaussian distribution [83, 88, 317]. The simulation of a single mid-gap trap level was used for simplicity, however this simplification has an effect on the overall goodness of fit. Firstly, SRH statistics are such that recombination at defect sites at the band edges are less impactful on the overall recombination rate in comparison to a mid-gap state. Therefore a simulation mid-band gap state may result in an underestimation of S_{n0}/S_{p0} . A recent study found that donor and acceptor tail states at the edge of the valence and conduction band respectively had an impact on the overall modelled S_{eff} dependence on Q_f for symmetrically passivated, undiffused c-Si wafers [317]. Therefore some error is produced by assuming a single mid-band gap trap state for

acceptors and donors. With regard to the assumption of setting S_{n0} and S_{p0} equal, it is not suggested from these findings that the parameters S_{n0} and S_{p0} , are in fact equal. Rather that these results show that when S_{n0} and S_{p0} are equal the simulations are able to reproduce the non-linear lifetime measurements presented, in addition to modelling of the residual error in the fitting for varying S_{n0} and S_{p0} values in Figure 6.15, suggests that the assumption was reasonable and that the differences in S_{n0} and S_{p0} do not significantly affect the lifetime behaviour in the injection level range of interest and in the examples presented above, do not achieve greater fit.

As the surface concentrations approach parity, unless there is a significant asymmetry between S_{n0} and S_{p0} , both parameters will affect the overall recombination rate and therefore the accuracy of assuming equal capture cross sections is assessed in the quality of fit. Alternatively, in the instances that the surface becomes heavily inverted and/or there is significant asymmetry in S_{n0} and S_{p0} such that the recombination is driven by the minority carrier parameter in high injection, then it should be noted that the majority carrier parameter is not accurately resolved (since it can take a range of physical values without affecting the overall lifetime behaviour in this regime). One exception to this is if the sample is surface recombination limited in the injection level ranges corresponding to when the carriers are close to parity and the surface is in strong depletion—which can be determined with accurate device simulation—as in this regime the majority carrier surface recombination parameter will affect the overall recombination rate, and therefore the quality of fit in this regime will give guidance towards an accurate majority carrier surface recombination parameter value.

Furthermore, both edge recombination present at the unpassivated cleaved edge and non-uniformity of the surface passivation were not accounted for in these simulations. These non-uniformities were present in some PL images of the samples after annealing and corona charging, which revealed a minor variance in counts at the edges, and in localised spots, likely to be surface contamination. The effect of edge recombination has a significant effect on the effective lifetime at low injection, where for inverted samples, carriers can diffuse via a surface inversion channel to the edges and recombine [75, 333-336]. Since this work was focused on an effect which occurs at high injection, where the sample was predominantly affected by surface recombination, edge effects at low injection have been overlooked in this work. Approaches which take into account the

edge recombination via the circuit simulations[336], numerical modelling [333, 335], and by an analytical resistive network [75] are referenced herein.

The influence of microscopic fluctuations in the surface potential due to the discrete nature of the surface charge and dopants was also neglected in this work [337]. Consideration of this effect was demonstrated to have a broadening effect on the slope of the injection dependent lifetime behaviour of AlO_x passivated phosphorus diffused surfaces [75], and therefore additional modelling of this effect may have the effect of improving the fit quality of the results in Section 6.5. The implementation of this effect, allows for an additional degree of freedom, via Gaussian scaling, to be fitted to the measured lifetime behaviour.

In addition to this simplification of the interface parameters, an additional error was introduced in the measurement error of the lifetime tool, which for the tool studied has been shown to be $<2\%$ repeatability error for the injection level range of interest [338]. Furthermore, non-uniformities inherent in the sample from the fabrication process, which can produce variances in, for instance, the optical absorption, active dopant surface concentration, and the interface parameters are aggregated over the sensor area in the lifetime measurement—these latter considerations were addressed in the Monte Carlo method simulations. As a result, when using this method to fit a lifetime curve with S_{n0}/S_{p0} , the extracted fit and interface parameters represent the cumulative effects of all the variances across the sample, which limit the lifetime behaviour for any given injection level. The effect of aggregating the non-uniformities over an area is inherent in all measurement techniques which are spatially dependent. Therefore, despite being able to reproduce the macro trend in recombination behaviour with injection level, the cumulative effects of measurement error, non-uniformities in the wafer, edge recombination, and the use of a single defect level, are likely to account for the minor deviations between the fitted and measured curves. Quantifying the goodness of fit to account for the uncertainty in taking these simplifications is an area of future work.

6.7 Conclusion

A model for the surface concentration of carriers at the surface as they were affected by Q , heavy doping effects and interface charge was developed, taking into account BGN effects and Fermi-Dirac statistics was presented. This model was used to highlight the particular combinations of Q , surface doping and injection level which result in the

sample moving from depletion into inversion with increasing injection level. It was shown that in this parameter space, the carrier selectivity of the surface was highly variable, with a non-constant J_{0s} . This results in the corresponding non-linear lifetime behaviour at high injection.

Furthermore, in this regime, it was found that variances in Q , S_{p0} , or S_{n0} have unique ‘signatures’ on the overall lifetime curve and can therefore be resolved independently during fitting. The general conditions of surface doping and interface charge which have sensitivity to this effect was calculated. This understanding was then applied to demonstrate a method of extracting the interface parameters Q , S_{n0} and S_{p0} , from the inverse injection dependent lifetime curve on samples with heavily diffused surfaces has been demonstrated. The interface parameters of heavily diffused p -type surfaces, passivated with SiN_x and HfO_x , and heavily diffused n -type surfaces passivated with AlO_x , have been extracted. This method overcomes the current limitations in dielectric/interface characterisation techniques, which cannot resolve the interface parameters on diffused silicon surfaces.

In the analysis, assumption of a mid-gap trap level and equal S_{n0} and S_{p0} was invoked to enable fast calculations. This assumption was able to reproduce the measured lifetime trend, although the error inherent in this method may be reduced in future work by modelling a distribution of asymmetric trap concentrations over the band gap, edge effects, minor variations in surface potential and the effects of non-uniformities. Quantifying the goodness of fit in this method, and the simulation of these additional effects is an area of future work. Future work could focus on the further development of the numerical method herein to allow for the accurate and fast simulation of the lifetime measurement and interface parameter extraction. This would remove the need for TCAD simulations and improve the broader availability of this methodology.

7 DIFFUSED HOMOJUNCTION INTERDIGITATED BACK CONTACT SOLAR CELLS

7.1 Introduction

The highest homojunction silicon wafer based solar cell power conversion efficiencies reported to date have been achieved with the interdigitated back contact (IBC) architecture. With the exception of the Tunnel Oxide Passivated Contact (TOPCon) [339] and PERL solar cell [16] architectures, this type of silicon wafer based solar cell structure is the only architecture to achieve or exceed 25 %. The IBC architecture is the dominant architecture for all silicon wafer based solar cells with efficiencies over 25 % [17]. The highest efficiency IBC solar cell has been fabricated with a heterojunction structure with a energy conversion efficiency of $> 26.63\%$ [340], whilst the highest known diffused homojunction IBC structures has achieved a conversion efficiency of 24.4% [341], the polysilicon on oxide (POLO) cell which recently achieved 25.0% with doped-polysilicon on SiO_2 passivated contacts [342] and the most recent SunPower X-series cell, which reached 25.2% [343]. There are several advantages of the IBC architecture over the more commonly fabricated front and rear contact design;

- 1) the elimination of front grid shading, allowing for potentially higher short circuit currents,
- 2) the elimination of front surface doping allows for a wider range of front surface texturing and light trapping schemes to be deployed on the front surface [344, 345] and
- 3) the IBC solar cell is ideal for mechanically stacked tandem cells with higher band gap technologies such as perovskites.

However, a key drawback of this technology is the significantly more complicated fabrication procedure required to isolate and fabricate the interdigitated carrier selective collector regions—although there have been numerous attempts to simplify this

fabrication through selective etching [346] and laser processing [341, 347]. The second issue with this structure is the requirement for high minority carrier lifetime wafer material to ensure that the photogenerated electron-hole pairs can diffuse to the rear contacts, which mainly affects carriers generated near the front side of the cell. A third issue is the complications with rear surface passivation design and optimisation, due to the presence of dual polarities of dopants on the rear side of the solar cell, which is typically passivated by a single dielectric material. This final issue creates a significant challenge when optimising the rear passivation for enhanced carrier selectivity within the device, since the optimisation of the effects of interface charge Q on the both the heavily doped p -type and n -type regions is required. The current state-of-the-art rear surface passivation designs used on IBC solar cells to optimise rear surface carrier selectivity are shown schematically in Figure 7.1 and listed as follows:

- 1) Using passivating dielectrics with a very low interface defect density such as thermally grown SiO_2 [341, 345, 348] or hydrogenated amorphous silicon (a-Si) [349] on the rear side of the device. This has the effect of reducing S_{n0} and S_{p0} , and hence the peak J_{0s} (Figure 7.1a).
- 2) Eliminating the un-diffused surface area at the rear of the device, such that the heavily diffused n -type and p -type regions are adjacent or overlapping (Figure 7.1b).[350].
- 3) The fabrication of a heterojunction at the rear of the solar cell (Figure 7.1c) [18, 295, 351, 352].

The third approach avoids the formation of a dual polarity diffused surface and moves the hole and electron selective regions out of the base material, and onto the rear surface where they are isolated. Note that the second approach has been adopted in the heterojunction architectures, whereby the p -a-Si layer is adjacent to the n -a-Si layer [352]. In this case, due to the low lateral mobility within the thin doped a-Si layers, the contact between the n -type and p -type a-Si is not device limiting.

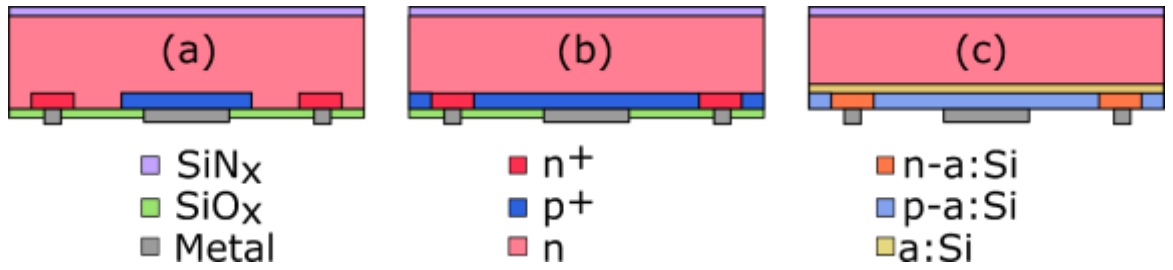


Figure 7.1 Schematic of an IBC solar cell showing the various approaches to rear diffused region layout and passivation strategies.

Modelling of the state-of-the-art homojunction diffused IBC solar cell found a total 0.6 % absolute loss in efficiency on account of rear recombination [341]. However the modelling software used (Quokka), with assumptions of conductive boundaries, does not take into account the recombination in the surface depletion region, and therefore does not directly account for this effect. The purpose of the work in this chapter was to understand, through device fabrication and simulation, the effect of varying Q values on the rear surface recombination rate of IBC solar cells, and the effect this has on the overall cell performance, taking into account recombination in the surface depletion region. The second objective was to simulate the effect of the technologies developed in the previous chapters, as a guide for how the current state-of-the-art approaches can be applied to IBC solar cells.

7.2 Surface recombination at the rear of IBC solar cells

For a diffused homojunction IBC solar cell structure, the carrier selective collector regions of both carrier species are located on the rear of the device, and therefore surface regions with doping of both polarities exist. At the edge of these areas a surface depletion region forms due to the transition of the heavily diffused electron (hole) collector into the p -type (n -type) bulk regions as the diffused surface dopant concentration decays. This is exacerbated for structures where the dopants are thermally diffused into the wafer, since the dopants will diffuse laterally to a similar extent that they diffuse vertically into the solar cell bulk regions (with the difference being due to different rates of diffusion along various planes within the silicon). This process, depicted in Figure 7.2a, creates a diffusion profile at the surface which decays in concentration around the perimeter of all locally diffused regions in the device. After the diffusion process, a final depletion region of width W is formed within the bulk and at the surface of the device around the region where the metallurgical junction formed (Figure 7.2b). Therefore, at the boundary of the

diffused region a depletion region, characterised by a depleted concentration of electrons and holes at the surface occurs. These surface depletion regions are potential sites for high surface recombination, due to the lack of charge-effect passivation from doping, and the presence of potential surface defect sites. This presents a significant obstacle to high performance diffused homojunction devices.

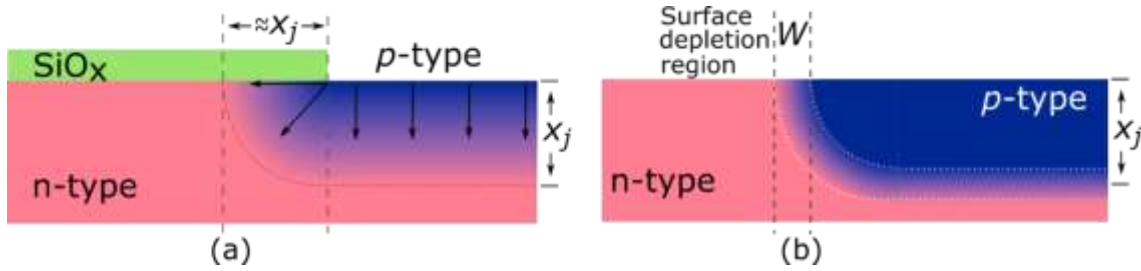


Figure 7.2 Schematic depiction of the formation of a surface depletion. The left image (a) depicts the formation of the localised metallurgical junction of depth x_j during an SiO_x masked thermal diffusion. This leads to the formation of a depletion region of width W within the device at and at the surface (b).

To investigate how carrier selectivity can be engineered to reduce the recombination in these regions, an analysis of the recombination at the rear surface of diffused homojunction IBC solar cells was conducted. The recombination in this region is limited by the concentration of electrons and holes able to diffuse into the area to recombine, the concentration of defects at the surface D_{it} and their corresponding capture cross sections $\sigma_{n/p}$. Interface charge at the surface will affect the concentration of holes and electrons in the region, and therefore the overall recombination rate. To give insight into the recombination rate at the surface, J_{0s} was calculated as a function of acceptor and donor dopant concentrations for a range of positive and negative Q values, and the results are shown in Figure 7.3. The model outlined in Section 6.2 was used for the calculations assuming an n -type sample with bulk doping $N_D = 10^{15} \text{ cm}^{-3}$, a fixed excess carrier density $\Delta n = 10^{15} \text{ cm}^{-3}$; and an interface with a single mid-gap defect with $S_{n0} = S_{p0} = 10^4 \text{ cm/s}$.

For surfaces with zero or low values of Q , J_{0s} increases as the doping level decreases, to a maximum value where, in this case, the doping density approaches the bulk doping density. As a result, J_{0s} increases due to the lack of carrier selectivity in suppressing the minority carrier concentration. Conversely, for these low values of Q , J_{0s} is minimal at high doping levels, showing the effect of dopant induced carrier selective surface passivation. As the absolute magnitude of Q increases, for accumulated surfaces (Plots b

and c), the surface recombination rate tends to decrease with increasing doping level, demonstrating the effect of charge-effect passivation. However, for depleted and inverted surfaces (Plots a and d), there is a clear peak in the surface recombination rate, which corresponds to the point at which the surface transitions into inversion since in this simulation S_{n0} and S_{p0} are set to be equal.

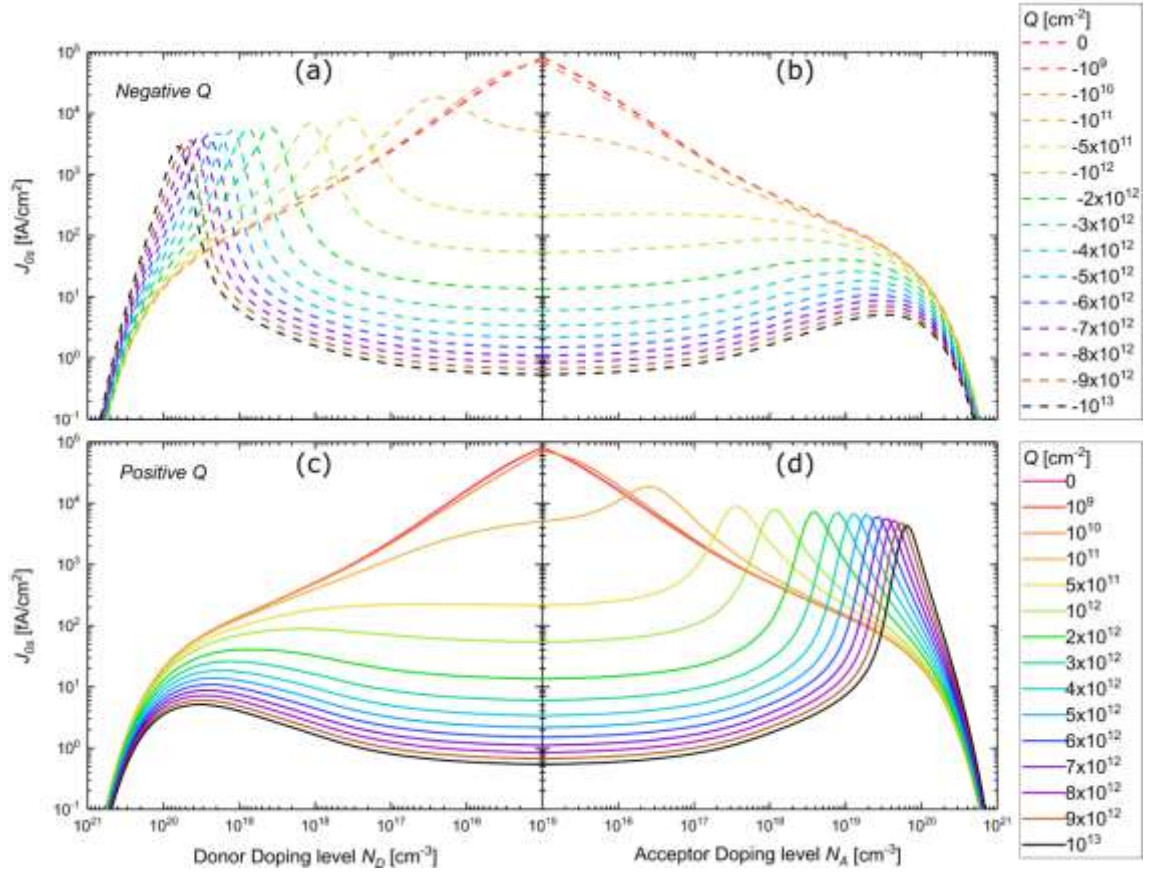


Figure 7.3 Rear surface J_{0s} as a function of doping level and Q calculated $\Delta n = 10^{15} \text{ cm}^{-3}$, taking into account Fermi-Dirac statistics, band gap narrowing and degeneracy. The values of J_{0s} were calculated with $S_{n0}=S_{p0}=10^4 \text{ cm/s}$ for a single mid-band gap trap state. Electrostatics at the interface were solved analytically according to Ref. [46]

To verify that this peak in recombination occurs when the surface has equal carrier concentrations, the relative concentration of carriers at the surface as a function of doping level for positive values of Q was calculated and plotted in Figure 7.4. It shows that the acceptor doping concentration corresponding to the peak J_{0s} level for a given Q in Figure 7.3 corresponds to the point at which the carrier concentrations are equal (intersection with solid black line) in Figure 7.4. The peak J_{0s} in Figure 7.3 corresponds to an increased surface doping concentration as the Q increases. This suggests that a higher value of Q is required to reduce the carrier selective suppression of the minority carriers due to doping.

In other words, this peak recombination position shift is a function of surface doping, Q and injection level.

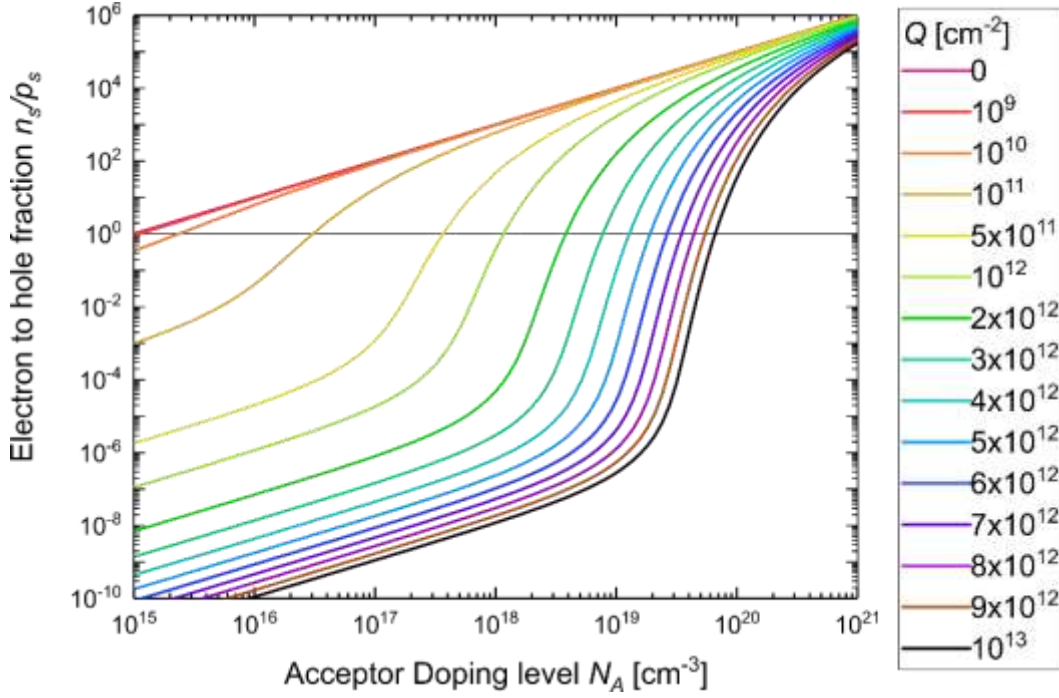


Figure 7.4 Calculated ratio of electrons and holes at the surface as a function of Q and acceptor doping level for $\Delta n = 10^{15} \text{ cm}^{-3}$. The plot shows the minority carrier transition from electrons (lower portion, $p_s > n_s$) to holes (upper portion, $n_s > p_s$). The values were calculated using the method outlined in ref. [46] taking into account Fermi-Dirac statistics, band gap narrowing and degeneracy effects.

Auger and SRH processes in the underlying diffused regions were not simulated in Figure 7.3, to have maximum sensitivity to the effects of J_{0s} on the overall recombination rate. Therefore a plot of J_{0e} , may have a different trend taking into account intrinsic and SRH recombination processes in the underlying diffused layer. Consequently, the drop off in J_{0s} at the extreme doping levels is likely to be countered by an increase in recombination in the diffused regions, as Auger and radiative recombination processes increase. However, the magnitude of the peak surface recombination, as evident in the peak values $> 1000 \text{ fA/cm}^2$, suggests that in these regions the recombination rate at the surfaces will dominate, and therefore this plot accurately reflects the high recombination potential in these regions.

Similarly, the fact that the peak in recombination occurs when the carrier concentrations are equal is related to the simulation of equal capture cross sections, and is not the case when there is a large asymmetry in the capture cross section of electrons and holes. When S_{n0} is greater (less) than S_{p0} , this will shift the peak to occur at lower (higher) acceptor

doping densities. When S_{n0} and S_{p0} both increase (decrease), this will shift the observed trend up (down) the y-axis.

Figure 7.3 and Figure 7.4 suggest that a peak in surface recombination will occur provided there is a depletion region present at the surface. By introducing Q , the region at the surface where the depletion exists can be manipulated. For instance, Figure 7.3d suggests that if the acceptor doping level can be reduced significantly in the non-metallised diffused regions, and the charge density is positive and sufficiently large, then this peak can be altogether avoided. For instance, a peak acceptor concentration of 10^{19} cm^{-3} has a corresponding $J_{0s} < 10 \text{ fA.cm}^2$ for $Q = 10^{13} \text{ cm}^{-3}$, suggesting if the surface concentration of acceptors is $N_{A,s} = 10^{19} \text{ cm}^{-3}$, then the large peak surface recombination values can be avoided entirely. Furthermore, the breadth of the peak J_{0s} —which appears artificially narrow due to the x-axis scaling in Figure 7.3—will be affected by the diffusion profile. For instance when there is a long tail in the diffusion profile where the concentration is in a range where the maximum peak occurs, this results in extending the surface area over which the depletion region is present. This could increase the effective recombination rate at the surface. In these instances, it may be preferable to select a dielectric with lower Q , such that the peak surface recombination rate corresponds to a much thinner region where the diffusion profile decays, and seek to reduce the overall J_{0s} by reducing S_{n0} and S_{p0} decreasing the amount of defective surface states via, for instance, hydrogenation.

7.3 Simulation of a diffused wafer IBC Solar Cell

In the following section, the simulated performance of diffused wafer IBC solar cells is presented. The simulations are based on the simulation of an IBC solar cell baseline developed as part of this thesis, and outlined in Appendix A, and the state of the art diffused wafer IBC solar cell outlined in Refs. [142, 341].

An optimised solar cell geometry was developed using Sentaurus TCAD simulations to optimise the rear contact fraction and diffused region geometry. The details of this optimisation and simulation parameters used is outlined in the Appendix. The simulated cell—referred to within this thesis as Cell X—was simulated to achieve 24.9 % efficiency, and was verified with simulations of the state-of-the-art ANU solar cell [341] in both Quokka and TCAD to ensure consistency between simulation platforms. The ANU cell was simulated using the performance parameters listed in Ref. [142] Cell X is

used in the following simulations to represent the potential of the IBC solar cell architecture developed in Appendix A.

An n -type IBC solar cell with the optimised geometry of Cell X was fabricated in a procedure also outlined in Appendix A. This baseline cell, referred to as Cell B, was fabricated with a planar front surface and achieved a measured conversion efficiency of 18.3 %. Cell B was fully characterised, taking measurements from process monitors and the measured performance characteristics of the cells using, QSS and transient PC, four-point-probe calibrated ECV, Light I - V , Suns- V_{oc} , Quantum Efficiency and Dark I - V measurements. The extracted performance parameters are listed in Table 7.1, and were input into both Sentaurus and Quokka simulations to simulate the device performance in this chapter.

Table 7.1 Extracted parameters for the computer simulation of a baseline IBC solar cell, Cell B.

Parameter	Cell B 18.3 %	Characterisation method description
Cell thickness	280 μm	Measured with micrometer
Wafer resistivity	2.5 $\Omega\cdot\text{cm}$	Measured via PC dark conductance
Bulk SRH Lifetime	5 ms	PC measurement (see Appendix A)
p^+ surface concentration $N_{A,s}$	$1.4 \times 10^{-19} \text{ cm}^{-3}$	Four-point probe calibrated ECV
p^+ R_{sheet}	114 $\Omega/\square$	Four-point probe measurement
p^+ J_{0e}	18.95 fA/cm^2	PC measurement on process monitor
p^+ contact J_{0c}	1160 fA/cm^2	Simulated in EDNA2 [89], with the ECV profile input and $S = 10^7 \text{ cm/s}$
p^+ contact resistivity ρ_c	3.6 $\text{m}\Omega\cdot\text{cm}^2$	CTLTM measurement
n^+ surface concentration $N_{D,s}$	$4.3 \times 10^{-19} \text{ cm}^{-3}$	Four-point probe calibrated ECV
n^+ R_{sheet}	26 $\Omega/\square$	Four-point probe measurement
n^+ J_{0e}	160 fA/cm^2	PC measurement on process monitor
n^+ contact J_{0c}	186 fA/cm^2	Simulated in EDNA2 [89], with the ECV profile input and $S=10^7 \text{ cm/s}$
n^+ contact resistivity ρ_c	0.76 $\text{m}\Omega\cdot\text{cm}^2$	CTLTM measurement
Rear undiffused J_{0s}	2.89 fA/cm^2	PC measurement on process monitor
Front undiffused J_{0s}	8.55 fA/cm^2	PC measurement on process monitors

Reflection	Planar	UV-VIS measurement, generation profile extracted using OPAL2[104]
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The cell structure and input parameters, unless stated otherwise, was identical to the optimised geometry developed in Appendix A, and therefore the simulations model the potential impact of variances of a particular parameter on a cell structure which has very similar performance to a state-of-the-art diffused homojunction IBC solar cell. The focus of these simulations brought together the results of the previous chapters, and is divided into three separate sections:

- 1) A study of the effect of varying rear surface passivation using Sentaurus TCAD.
- 2) The effect of varying ρ_c using Sentaurus TCAD.
- 3) The effect of varying J_{0c} using Quokka.

To accurately model the electrostatics at the rear surface, Sentaurus TCAD simulations were used in the study outlined in Point 1 above. Quokka simulations were used in Point 3 as this allows for the input of J_{0c} values (Sentaurus does not accept input of J_{0c} , and has fixed models for metal-silicon recombination), which were directly relatable to the results of Chapter 4. The simulations described in Point 1 above simulated the work studied in Chapter 5 and 6, and Points 2 and 3 applied the results of Chapter 4.

7.3.1 Effect of rear surface passivation

As outlined earlier in this chapter, the dual polarity of dopants present at the rear of IBC solar cells presents a unique challenge when engineering the carrier selective charge-effect passivation. In particular, the presence of the surface depletion region produces a region of enhanced surface recombination due to the similar concentrations of electrons and holes in this region. To demonstrate this effect, Cell X in Appendix A was simulated under 1 sun illumination with a rear surface recombination velocity $S = 1000 \text{ cm.s}^{-1}$ and a negative $Q = -10^{11} \text{ cm}^{-2}$. The recombination spatially in the structure was resolved in the device and depicted in Figure 7.5, which shows the surface recombination rate spatially across the diffused regions. The maximum recombination rate (red region) corresponds to the undiffused region underneath the metal, which has similar doping level corresponds to the peak J_{0s} value shown in Figure 7.1, $Q = -10^{11} \text{ cm}^{-2}$. (Note that the dark horizontal red line demarcates the metallurgical junction, and confusingly, was set to a

dark red colour by default in the software; importantly it does not represent a recombination maximum, as would be inferred from the colour scale). This shows that the location of the peak surface recombination rate can be locally defined by manipulating the rear Q . This was achieved by manipulating the location of the surface depletion region, away from the metallurgical junction where the maximum surface recombination rate occurs for $Q = 0 \text{ cm}^{-3}$. In this case, a large region was selected to show how this surface recombination can be maximised, however for solar cell performance optimisation, the area of this region should be reduced.

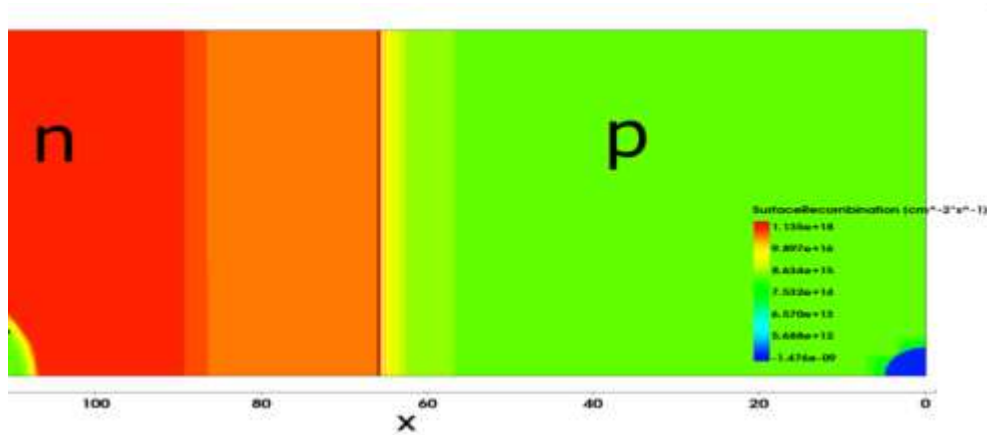


Figure 7.5 Spatial map of the surface recombination rate on the rear side of the simulated IBC solar cell, Cell X, calculated and visualised in Sentaurus. The vertical dark red line demarcates the metallurgical junction (i.e. not to be confused with a representation of the maximum value of surface recombination) and the dark blue dots are the metallised contact regions.

This approach was then broadened by sweeping a range of Q , S_{n0} and S_{p0} values on the rear of the device. Since Q , S_{n0} and S_{p0} are a function of the interface passivation method, they can be assumed to be constant across the entire surface despite local variations in doping level. In reality, there would be variations in SRH recombination within diffused regions which may be generated due to, for instance, the introduction of lattice interstitials, silicon-dopant precipitates, and lattice dislocations. However, these issues were neglected in this analysis since these are highly process specific and thus outside the scope of this study; which aims to focus on the effect of manipulating the carrier selectivity at the rear surface via variations in the rear electrostatics. As a result, these simulations take into the intrinsic recombination processes in the diffused regions and SRH recombination processes at the surface, assuming an equal mid-gap trap density with $S_{n0} = S_{p0}$. The neglect of SRH in the diffused regions in these simulations implies that these results can be considered as an upper lower-limit scenario.

Figure 7.6 plots the simulated efficiency (a), V_{oc} (b), FF (c) and J_{sc} (d) of Cell X for a range of rear Q and rear S values under 1 sun illumination conditions. All the plots in this figure reflect a general trend that the solar cell performance is increased as S is decreased since this suppresses the overall number of recombination sites. Furthermore, as the absolute magnitude of Q increases (i.e. becomes more negative or more positive) there is a trend towards higher efficiency. Finally, for this structure, there was a skew towards higher efficiencies being achieved with positive Q values for any given value of $S > 100$ cm/s. This was correlated with the skew towards lower FF (Plot c) and J_{sc} (Plot b) with $-10^{12} < Q < -10^{10}$ cm⁻²; whereas the trend in V_{oc} (Plot b) also reflects this trend, although to a lesser extent. This is the range of Q values which corresponds to the surface depletion region—and hence a maximum surface recombination rate—being located at the surface of the undiffused regions, and in the tail regions of the n^+ diffusion profile, around the n^+ contact diffusions. This had a strong impact on charge separation and carrier selectivity of the rear surface, enhancing minority carrier recombination as the carriers diffused towards the contacts such that the collection efficiency was reduced, affecting J_{sc} and FF .

The peak surface recombination rate was found to be a function of the surface doping concentration and profile at the surface. Therefore, in addition to tailoring the Q , modifying the surface concentration and profile presents an alternate approach to improving the carrier selectivity at the rear and improve device performance. To study the effect of varying the doping profiles on the IBC solar cell performance, a range of diffusion profiles of varying peak dopant concentrations with Gaussian profile and fixed depth of 0.75 μ m, was input into the simulations. In these simulations, the solar cell performance was simulated at 1 sun illumination, for a range of p^+ peak doping $N_{A,s}$ and positive/negative Q values, for constant $S = 5000$ cm/s. This was performed for the diffused p^+ region (hole collector) only, as this represents the largest diffused area, and the doping concentration affects the minority carrier selectivity and collection. The results of this simulation are shown in Figure 7.7.

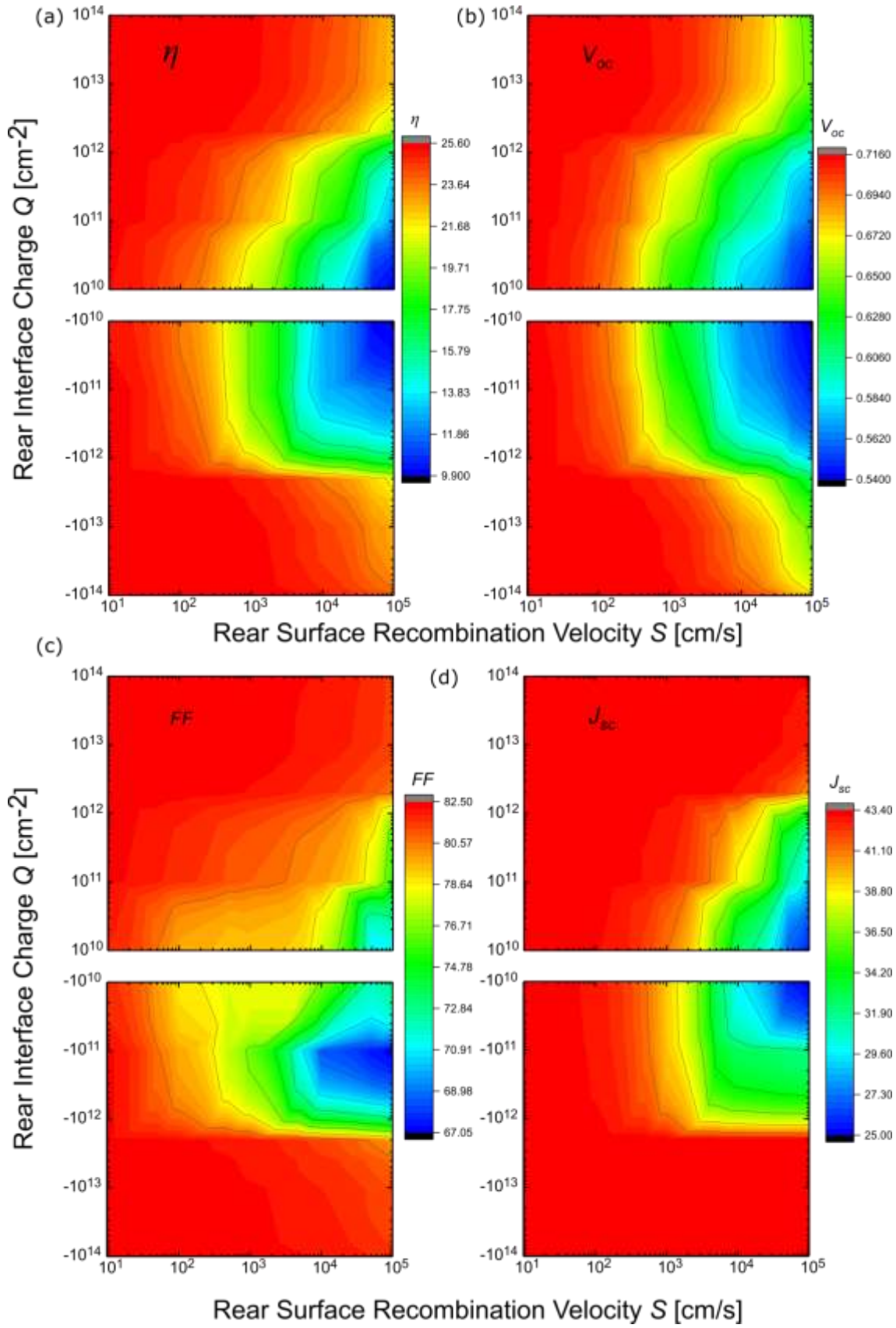


Figure 7.6 Simulated efficiency (a), V_{oc} (b), FF (c) and J_{sc} (d) of a diffused homojunction IBC solar cell for a range of rear Q and S values.

Figure 7.7 plots the efficiency (a), V_{oc} (b), FF (c) and J_{sc} (d) of Cell X for varying $N_{A,s}$ and Q values, simulated at 1 sun efficiency. The result depict a stronger response to variances in Q than $N_{A,s}$ and therefore the subsequent analysis was divided into three distinct ranges of Q :

1) For large positive $Q > 2 \times 10^{12} \text{ cm}^{-2}$:

The V_{oc} (Plot b) and J_{sc} (Plot c) peaks around $N_{A,s} = 5 \times 10^{19} \text{ cm}^{-3}$, and this results in a similar trend being evident in the efficiency (Plot a). This was because the p^+ region transitions between depletion and inversion in this regime. At higher $N_{A,s}$ values Auger recombination begins to dominate, hence the peak at an intermediate value of $N_{A,s} = 5 \times 10^{19} \text{ cm}^{-3}$. As the surface doping decreases, surface recombination increases as at these larger values of Q , the surface depletion region was located in the p -diffused regions (see J_{0s} peaks in Figure 7.3d and Figure 7.4). This surface depletion region affects the carrier selectivity by reducing both the surface passivation—affecting V_{oc} —and charge extraction since carriers recombine before reaching the carrier selective diffused regions—affecting J_{sc} . Furthermore, the previous suggestion that by minimising the peak dopant concentration on the inverted surface performance may be improved, was not evident in Plot b which models a lower FF , J_{sc} and V_{oc} in this range, due reduced carrier selectivity.

2) For large negative $Q > -2 \times 10^{12} \text{ cm}^{-2}$:

A similar trend was observed in the case of high positive Q , with a peak $N_{A,s} = 5 \times 10^{19} \text{ cm}^{-3}$ which decreases with increased doping due to Auger recombination. Note that the J_{sc} was relatively high and constant in this region, unlike the case for large negative Q , since the minority carrier collection in the diffused p^+ regions was unaffected in this regime since the p^+ region was accumulated for all values of Q . The n^+ diffused region was sufficiently diffused to be unaffected.

3) For intermediate Q ; $Q > 2 \times 10^{12} \text{ cm}^{-2}$ and $Q < -2 \times 10^{12} \text{ cm}^{-2}$:

Higher FF values were achieved for positive as opposed to negative charge densities since for negative charge, surface recombination was maximised in the undiffused region—as shown in Figure 7.5. This had a clear impact on all solar cell parameters, since the minimum for all cell performance parameters corresponds to moderate to low values of negative Q . The trend in this intermediate range was largely independent of doping

concentration, with the exception of the FF in low to moderate values of negative Q , and the overall performance parameters are relatively constant with $N_{A,s}$ in this range.

This simulation was repeated for $S = 10, 10^2, 10^3$ and 10^4 cm/s, and whilst the magnitude of efficiency scaled as expected with S , the relative trends with Q and $N_{A,s}$ was observed to be identical for all S values and therefore not depicted separately herein.

As the final part of this section of analysis, the interface values for S and Q for a range of dielectrics, as presented in Ref. [313] were overlaid on an identical plot of Figure 7.6a, displayed separately for clarity in Figure 7.8. The D_{it} values presented in Ref. [313] were related to the S values used in the simulation since $S = D_{it}\sigma_{n/p}v_{th}$, and taking $\sigma_{n/p} = 10^{-17}$ cm² and $v_{th} = 10^7$ cm/s. From this analysis, the suitability of PECVD a-Si:H and thermal SiO₂ were clearly presented, as these dielectrics typically produce the low S values required for high performance devices. HfO_x, with an intermediate range of S and Q , was not suited for the cell structure modelled in this work. Interestingly, the plot suggests that comparable high performance could be achieved with AlO_x and SiN_x passivation layers, if high values of dielectric fixed charge and reasonable chemical passivation could be achieved. This has potential advantages since thermally grown SiO₂ redistributes the dopants during the process and the high-temperature process risks further bulk degradation. Furthermore, AlO_x and SiN_x do not, unlike a-Si:H, suffer from degradation mechanisms such as the Staebler-Wronski effect, which adversely affects module power output. Figure 7.8 shows that there are a range of dielectrics available which can be used to manipulate the carrier selectivity at the rear of the diffused homojunction IBC solar cells studied.

As previously suggested, this analysis does not take into account SRH recombination in the diffused regions. To accurately model this effect, a series of diffusion profiles with the optimised $N_{A,s}$ could be developed, and symmetrically passivated samples with a range of dielectrics of varying Q and S values—accounting for asymmetries in σ_n and σ_p . The Auger and SRH recombination rate can be isolated with ECV and PC measurements, producing a lumped surface and diffused bulk SRH value, which can then be related to an effective S value as above, provided the diffused region bulk SRH recombination rate has a similar injection level dependence. In this way, more accurate insight of the cell performance of a fabricated device can be gained in future work.

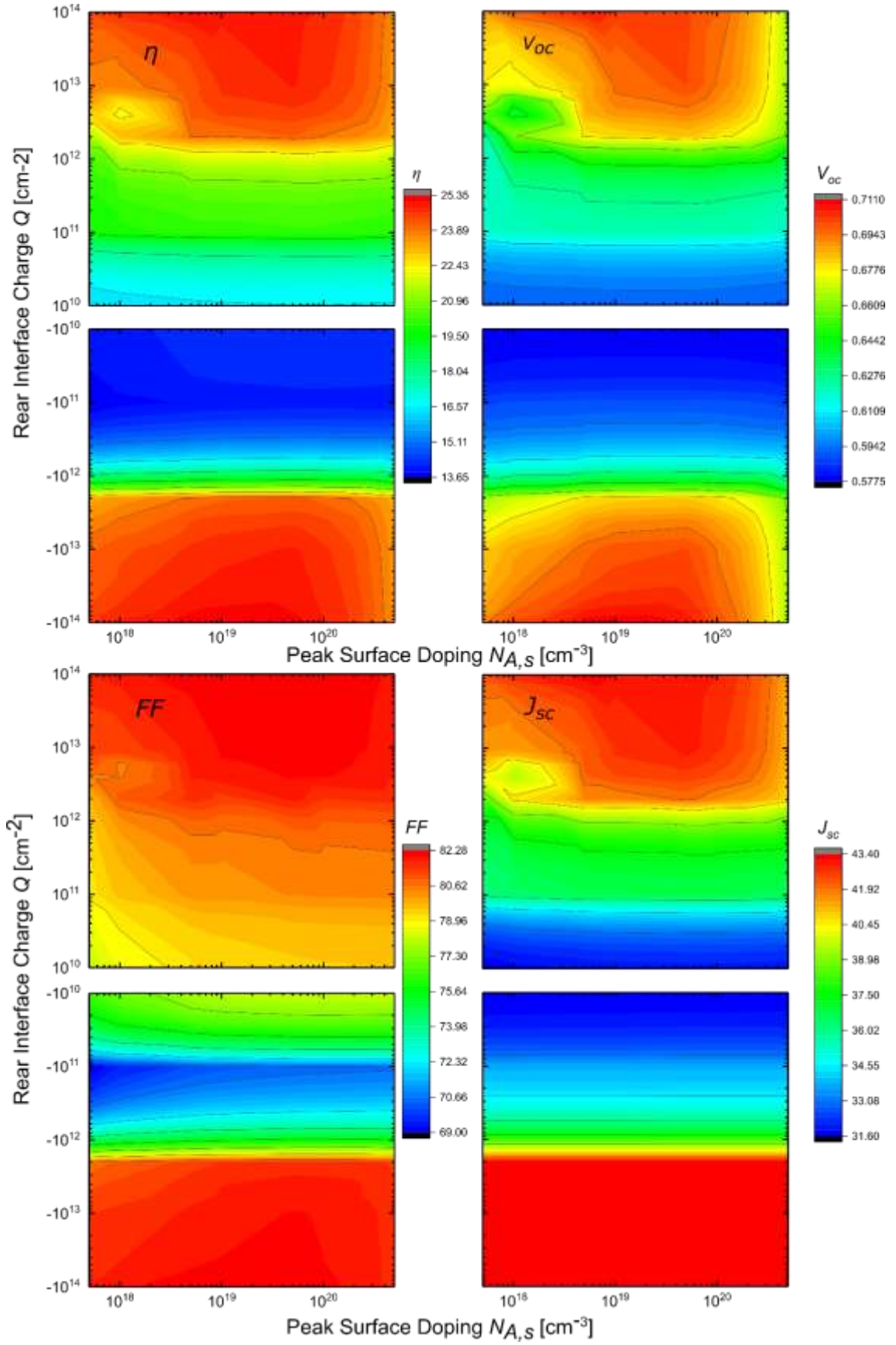


Figure 7.7 Simulated efficiency (a), V_{oc} (b), FF (c) and J_{sc} (d) of a diffused homojunction IBC solar cell for a range of rear Q and $N_{A,s}$ values.

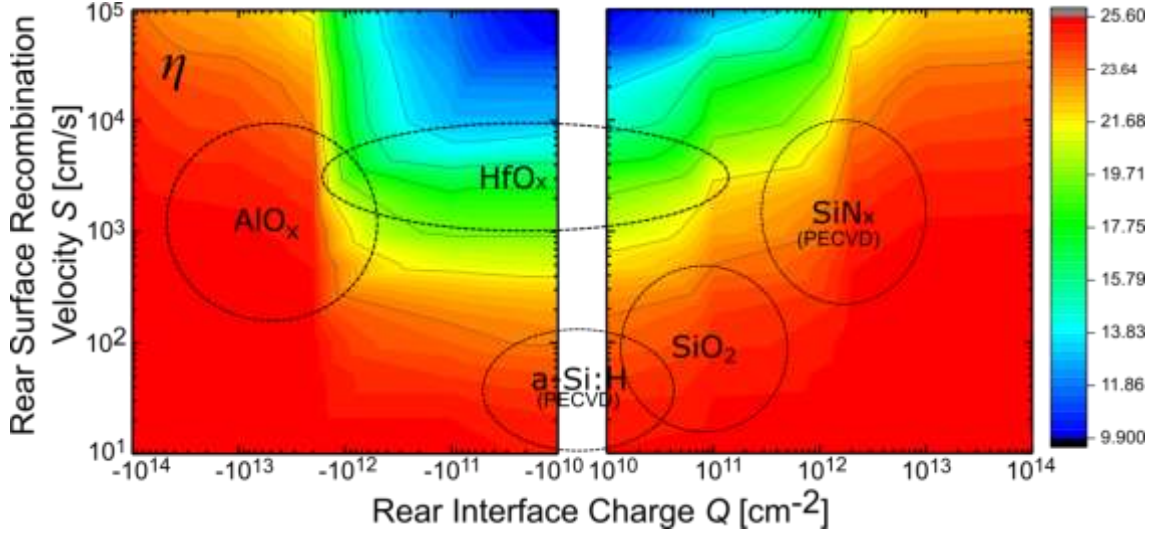


Figure 7.8 Conversion efficiency of a diffused homojunction IBC solar cell for a range of rear S and Q values, with typical interface values of a range of dielectrics, sourced from [313] imposed over the image to indicate the potential performance of an actual cell fabricated with those materials on the rear.

7.3.2 Effect of nickel plated contacts on simulated IBC solar cell performance

In this section, the ρ_c and J_{0c} values measured on electroless nickel plated p -Si-Ni boron contacts in Chapter 4 were input into IBC solar cell simulations, to assess the potential effect of such contacts on the diffused solar cell performance. As previously mentioned, TCAD simulations were used for the study of varying ρ_c , whereas Quokka simulations were performed to enable simulation of J_{0c} .

7.3.2.1 Simulated performance of a nickel plated IBC solar cell.

The Sentaurus TCAD simulations simulate the effect of an external resistance as seen at the metal-silicon interface. Therefore, to simulate the effect of varying ρ_c , the contact resistance and metal grid resistance need to be calculated externally and then combined as a single lumped parameter R_{metal} for input into the simulations. In this section, the effect of varying ρ_c at the p^+ and n^+ metal-silicon interface was simulated for the baseline Cell B to assess the potential impact of integrating the nickel plated contacts developed in Chapter 4 on the current baseline solar cell. The same simulation was performed using the model and input parameters for Cell X to assess the potential impact on cell performance of these contact incorporated into a high performance diffused homojunction IBC solar cell. Given that the study in Chapter 4 was focused on the p -type contact, the simulations assume a Ni/Cu stack on the p^+ contact, and the existing aluminium evaporated contact on the n -type contact. For the simulations, the contact resistance was

calculated with varying ρ_c range of 0.1-2500 m Ω .cm² and 1-2500 m Ω .cm² for the p^+ contact and n^+ contact respectively to encompass the range of values measured in Chapter 4. The aluminium and copper finger resistance was calculated using values of 2.8×10^{-3} m Ω .cm and 1.76×10^{-3} m Ω .cm for the aluminium and copper fingers respectively, assuming a contact height of 1 μ m with rectangular geometry.

The simulated cell efficiency as a function of varying n^+ and p^+ ρ_c is shown for Cell B and Cell X in Figure 7.9a and Figure 7.9b respectively. Shaded boxes which correspond to the maximum and minimum ρ_c values measured for samples plated with (P8) and without (P3 and M1) prior surface activation are superimposed over the plots to highlight the range of efficiencies which could potentially be achieved assuming the ρ_c values were substituted directly onto the actual solar cell. These samples were chosen for the comparison as the $N_{A,s}$ measured on these samples ($N_{A,s} = 1.40 \times 10^{19}$ cm⁻³ for M1 and P3 and $N_{A,s} = 1.51 \times 10^{19}$ cm⁻³ for P8) was similar to the $N_{A,s}$ measured on Cell B ($N_{A,s} = 1.4 \times 10^{19}$ cm⁻³)

Figure 7.9a shows that nickel plated contacts with activation (Sample P8) would not have a significant impact on the cell performance of Cell B for the lower range of ρ_c values extracted. In contrast, integration of the ρ_c values achieved without prior Pd/Sn activation would lead to lower efficiency relative to the current aluminium evaporated process, in the instance that the process of Sample P3 was repeated. When the performance of these contacts were simulated within Cell X, the current ρ_c results achieved for Samples P3 and P8 would significantly limit the performance of the device. Sample M1 demonstrates the potential of this technology at its current best, with a maximum efficiency of 24.7 % achieved with the minimum value of ρ_c measured on sample M1. This efficiency was, however, lower than the baseline case with evaporated aluminium contacts, which has efficiency potential > 25 % when the extracted p -Si/Al ρ_c value, measured in Chapter 4, was input into the simulation. The above inferences are valid provided the n^+ ρ_c was low ($\rho_c < 10$ m Ω .cm² for Cell B and $\rho_c < 1$ m Ω .cm² for Cell X). A dedicated CTLM test structure to measure the ρ_c of the n^+ Al/Si contact in Cell B, measured $\rho_c < 1$ m Ω .cm². Similarly, ρ_c values less than 1 m Ω .cm² measured on electroless plated nickel contacts to phosphorus diffused silicon of similar surface concentration as the diffused n^+ regions on Cell B have been reported [353]. These results suggest that if the electroless plated nickel-silicon contact to p^+ silicon could be improved, the technology has potential to be integrated within structures with efficiency > 25 % with fully plated nickel contacts. As

a final comment, although the best results of M1 and P8 were not likely to limit the performance of the current baseline process, the process reliability and minimum ρ_c for electroless nickel plated contacts need to be improved for this technology to be compatible with high efficiency IBC structures.

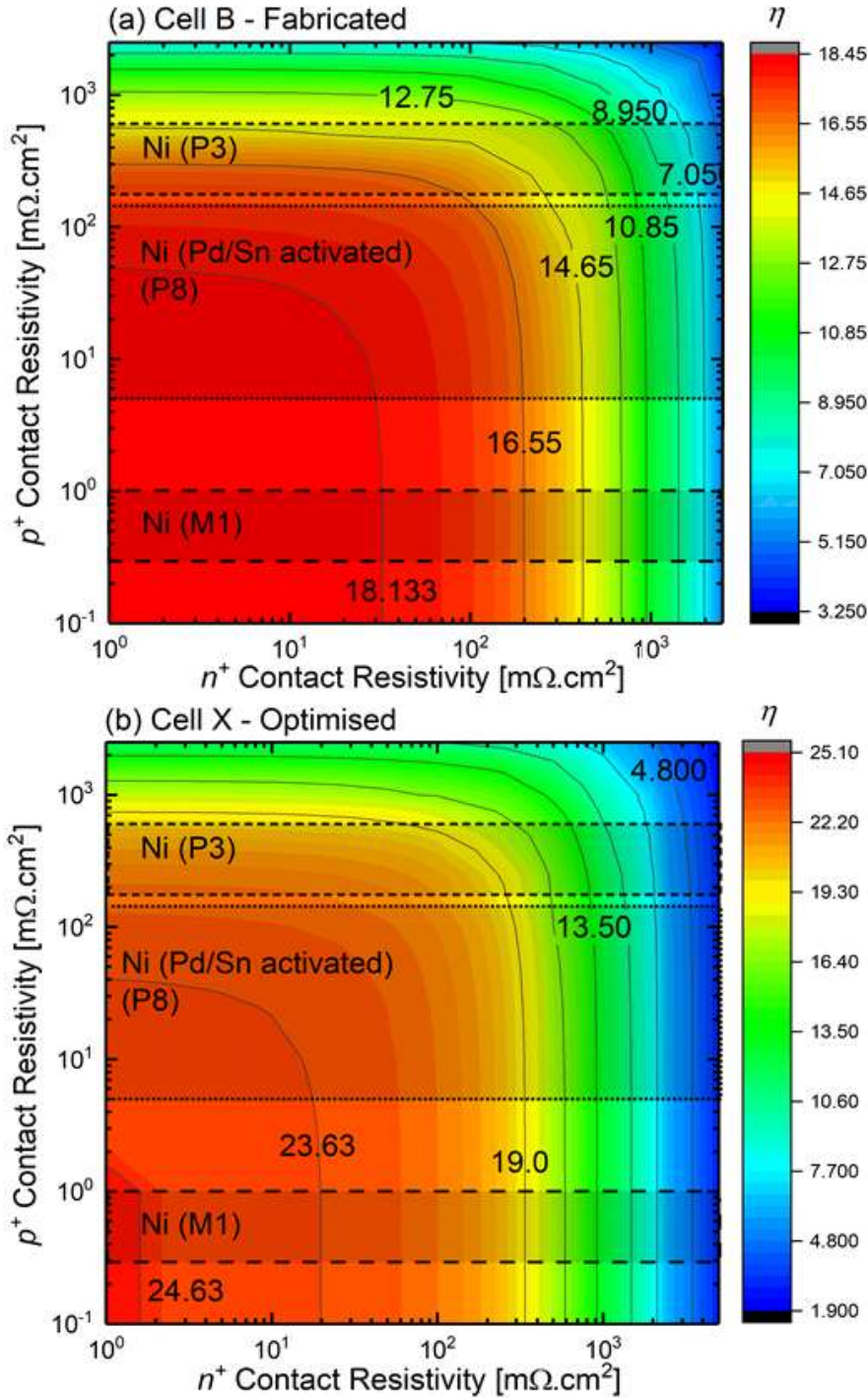


Figure 7.9 Simulated efficiency for varying n^+ and p^+ contact resistivity values for Cell B (a) and Cell X (b) respectively. Shaded boxes highlight the maximum and minimum ρ_c values, and the corresponding simulated efficiency ranges, measured for the nickel plated samples in Chapter 4.

7.3.2.2 Simulated effect of varying J_{0c} on IBC solar cell performance

The effect of varying J_{0c} at the p^+ and n^+ metal-silicon interface was simulated using a Quokka model for Cell B and Cell X. In these simulations, the contact recombination was varied over a range of $10^2 - 10^5$ fA/cm² to encompass the minimum and maximum J_{0c} values extracted for both aluminium evaporated and nickel plated contacts in Chapter 4. The input parameters for Cell B are listed in Table A.1, and the input parameters for Cell X is listed in the Table A.2 in Appendix A.

The simulated efficiency for Cell B and Cell X as a function of J_{0c} at the diffused n^+ and p^+ surface ($J_{0c,n}$ and $J_{0c,p}$ respectively) is shown in Figure 7.10a and Figure 7.10b respectively. Shaded boxes are imposed on Figure 7.10a and b which highlight the extracted J_{0c} values of sample P3 and E3, chosen for the similar surface concentration of dopants between the two samples and Cell B. Figure 7.10a shows that for Cell B, the current range of $J_{0c,p}$ values extracted on both the aluminium evaporated and nickel plated contacts would not limit the device performance, with a maximum efficiency potential of 18.3 %. The maximum efficiency potential for further reductions in $J_{0c,p}$ are not significant, suggesting that Cell B currently is not $J_{0c,p}$ limited. Figure 7.10b demonstrates the potential of these contacts, with the current best minimum J_{0c} values able to achieve efficiency > 24 % when integrated into Cell X. The simulations suggest a maximum efficiency of 24.6 % can be achieved with the existing minimum J_{0c} value achieved. Further reductions in J_{0cp} will continue to increase the cell performance to a maximum 24.7 %, achieved for $J_{0c,p} = 700$ fA/cm² and $J_{0c,n} < 2000$ fA/cm². Reductions in either J_{0c} value beyond these values do not produce further benefits as the cells become limited by other losses within the device.

Both figures show that the cell efficiency was more sensitive to low values of $J_{0c,p}$ since higher efficiencies can be achieved at higher equivalent values of $J_{0c,n}$ than $J_{0c,p}$. This was likely due to the difference in carrier selectivity of the underlying diffused regions; the n^+ region was more heavily diffused and the dopants were diffused deeper into the material than at the p^+ region. As a result, the minority carrier conduction was significantly reduced in the vicinity around the contact, restricting the flow of minority carriers to the contacted region where they may recombine and hence the higher tolerance to increased J_{0c} at the n^+ interface. Furthermore, it was noted that this effect was more pronounced on Cell X than on Cell B, since this cell is more sensitive to variances in J_{0c} since other loss mechanisms have been minimised.

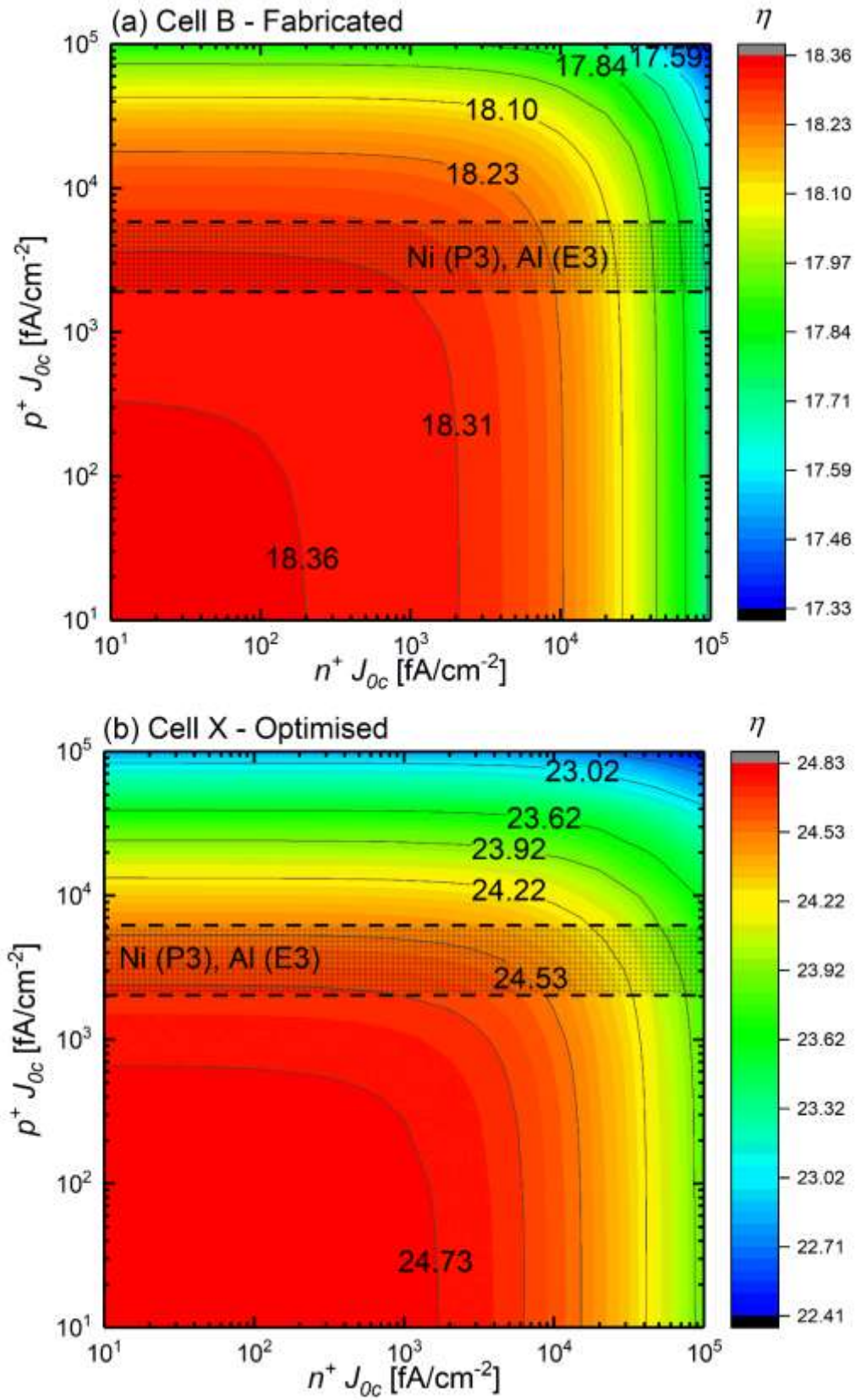


Figure 7.10 Simulated efficiency for varying n^+ and $p^+ J_{0c}$ values for Cell B (a) and Cell (x) respectively. Shaded boxes highlight the maximum and minimum J_{0c} values extracted from Samples E3 and P3 in Chapter 4.

7.4 Conclusion

The intricacies of optimised carrier selectivity on the rear surface of IBC solar cells was presented in this chapter. Modelling of the rear J_{0s} revealed a sharp peak in surface recombination, due to the formation of a surface depletion region from the dual polarity of doping on the rear surface. The peak J_{0s} , as it was affected by the surface doping and the magnitude and polarity of Q , was explored with numerical simulations.

Simulation of the effect of Q and S on the solar cell performance, shows that the rear Q can be used to spatially define the surface depletion region, and affect the carrier selectivity at the rear of the solar cell. It was found that the charge collection was severely hindered when the surface depletion region was located in the undiffused bulk surface regions, which for the n -type IBC structure simulated occurs for low values of negative Q . Due to the enhanced recombination in these areas, the V_{oc} was reduced, whilst the current was reduced as the carriers generated in this region recombine before extraction at the carrier selective regions. By tailoring rear magnitude and polarity of Q , the simulations suggest that carrier selectivity can be enhanced such that comparable performance can be achieved for IBC cells passivated with high fixed charge dielectrics, such as AlO_x and SiN_x in place of the more commonly used $a\text{-Si:H}$ and SiO_x . This can be verified with further device fabrication and measurements. An alternate method could involve sequential corona charging of the rear surface to invoke a range of negative and positive Q values, followed by light I - V testing of the cell performance in response.

Sentaurus TCAD and Quokka simulations were conducted to assess the potential effect of the nickel plated contacts developed in Chapter 4 on a baseline and state-of-the-art optimised IBC solar cell. Simulation of the ρ_c results achieved for plated contacts showed that only the lowest values achieved on sample M1 would not adversely impact on the current baseline solar cell, and that these results have an efficiency potential of 24.7 % when integrated into Cell X. Both cells were more tolerant to higher values of J_{0c} , with the current nickel plated contacts not limiting the baseline cell, with efficiency potential up to 24.6 %, at which the solar cell became limited by some other factor. Future work could focus on the integration of these contacts into the fabricated baseline device.

With reference to work covered in Appendix A, to observe the effect of varying interface passivation schemes, three solar cells were partially fabricated with varying rear surface passivation dielectrics to manipulate the rear surface Q . These cells were abandoned due

to poor process uniformity; contamination from the boron diffusion and alkaline etch process; and a failure of the AlO_x passivation due to blistering. Consequently, there is significant potential for future work in demonstrating the effects of this chapter, through device fabrication, process development and further simulation.

8 CONCLUSION

The aim of this thesis was to investigate methods of improving the carrier selectivity of diffused silicon wafer solar cells. This was explored by a study of the majority and minority carrier properties at metallised and diffused silicon interfaces, and by investigating the surface recombination at diffused depleted and inverted silicon surfaces. The resulting developments demonstrate potential approaches for improved diffused silicon solar cell devices.

Carrier selectivity at the metal-silicon contacts formed on both n^+ and p^+ silicon was studied. For phosphorus diffused n^+ silicon electrons collectors, a key issue related to the fabrication of passivated emitter and rear cell (PERC) solar cells—the wrap-around deposition of aluminium oxide (AlO_x) at the edges of the front silicon nitride (SiN_x) antireflection coating (ARC) before screen printing—was assessed. The key findings were that; 1) a 3 and 5 nm AlO_x layer can actually improve the contact resistivity (ρ_c) of silver screen-printed contacts by one order of magnitude and, 2) the negative effects of thicker AlO_x layers and wrap-around extents can be mitigated to an extent by changing paste formulation. These findings have potential implications for the further development of low cost, high performance industrial PERC solar cells, as this enables more flexibility in the design of low-cost, high throughput thin-film deposition tools.

For boron diffused p^+ silicon hole collectors, an investigation into electroless nickel plated p -type contacts was conducted; recognising the potential advantages of an electroless deposition of nickel-seed layers in next-generation high performance bi-facial solar cell fabrication. The test structures extracted high values and variance of both the contact recombination saturation density (J_{0c}) and the ρ_c , on nickel plated contacts, relative to aluminium evaporated structures. This was related to a combination of poor process repeatability and the inherent limitations of the J_{0c} extraction method utilised. The presence of an interfacial oxide of varying thickness formed during the galvanic displacement reaction was suggested as a likely cause for the high ρ_c measured. This work highlights the difficulty in achieving a reliable, high performance electroless nickel plating (ENP) process on boron diffused silicon. Nevertheless, promising results were

demonstrated, with an average $\rho_c < 1 \text{ m}\Omega\cdot\text{cm}^2$ for low $N_{A,s} = 1.4 \times 10^{19} \text{ cm}^{-3}$, which shows the potential for electroless nickel contacts formed on p^+ silicon.

Subsequently, the work focused on the surface recombination at diffused and inverted silicon surfaces. In Chapter 5, modelling using Sentaurus TCAD of identical symmetrically passivated samples during photoconductance (PC) measurement was able to, for the first time, reproduce the injection level dependent lifetime behaviour, even though this effect was reported by various groups previously. This work was extended in Chapter 6 where, via simulation of the carrier concentrations at the silicon surface as a function of N_s and interface charge (Q), it was shown that variances in Q and S_{n0}/S_{p0} have distinct effects on the injection level lifetime behaviour. This understanding was applied to develop a novel method of estimating Q , S_{n0} and S_{p0} from the injection level dependent lifetime curves of diffused silicon samples in depletion/inversion condition—something which was not possible with existing characterisation techniques. This technique was able to; 1) reproduce the lifetime behaviour of SiN_x and HfO_x passivated p^+np^+ structures, and AlO_x passivated n^+pn^+ lifetime structures, and 2) estimate the sample interface parameters, with comparable results to those obtained via conventional methods. Such extracted parameters are particularly useful for researchers assessing the passivation performance and charge selectivity mechanism of dielectric films, and/or for use in device simulation.

Chapter 7 applied the results and understanding gained in the Chapters 4, 5 and 6 to a diffused homojunction IBC solar cell structure, to assess how the carrier selectivity of this solar cell would be impacted by the findings of those chapters. Through Sentaurus TCAD and Quokka simulations of 1) a baseline diffused IBC cell developed in this work and 2) a simulated state-of-the-art diffused IBC solar cell, it was found that high values of positive or negative Q , and low values of S produce high IBC solar cell performance characteristics. It was also shown that for the geometry developed in this work, high performance, comparable to that achieved with the more common a-Si:H or SiO_2 passivation stacks, may be achievable when a high- Q_f AlO_x or SiN_x dielectric is used instead. Simulation of the best comparable J_{0c} and ρ_c results achieved for plated contacts in Chapter 4 were not found to limit the efficiency of the baseline IBC solar cell. For the optimised structure, the best comparable ρ_c is non-limiting for an IBC cell structure up to 24.7 %, whereas the nickel plated J_{0c} will need to be reduced to enable cell efficiencies greater than 24.6 %.

8.1 Original contributions

The original contributions resulting from this work are summarised below:

- 1) A study of the effect of varying firing temperature, firing speed and silver paste formulation on the ρ_c of screen-printed silver contacts fired through $\text{SiN}_x/\text{AlO}_x$ stacks deposited on industrial screen-printed n^+ electron collectors via ladder TLM measurements.
- 2) Demonstration, via FEM simulation and solar cell fabrication, of the potential effects of 3, 5, 7 and 10 nm thick AlO_x wrap-around on p -PERC and Al/BSF solar cell performance
- 3) Development of an electroless nickel plating process on silicon without prior Pd/Sn activation. This process was found to have a steady growth rate of 1.76 nm/s after nucleation.
- 4) Assessment of the carrier selectivity of electroless nickel plated contacts on a range of boron diffused silicon samples, via extraction of the ρ_c and J_{0c} , and compared against aluminium evaporated samples. It was found that the plated nickel-silicon contacts had higher ρ_c and J_{0c} values in comparison to aluminium evaporated contacts.
- 5) Verification that the non-linear injection level dependent inverse lifetime behaviour at high injection observed on heavily diffused depleted/inverted samples is not a measurement artefact of the PC lifetime measurement technique.
- 6) Calculation of the general conditions whereby a heavily diffused silicon surface will experience a transition in minority carrier species—as it is affected by interface charge, doping level and injection level—and the effect this has on the surface recombination rate J_{0s} .
- 7) Development of a method for extracting Q , S_{n0} and S_{p0} from the injection level dependent lifetime curves of diffused silicon samples in depletion/inversion condition.
- 8) The demonstration of this technique on SiN_x and HfO_x passivated p^+np^+ structures, and AlO_x passivated n^+pn^+ lifetime structures.
- 9) Sentaurus TCAD simulation of the effect of varying Q and S on the rear of diffused homojunction IBC solar cells, demonstrating how the carrier selectivity within the device—and overall solar cell performance—is affected by these parameters.

- 10) The potential for high Q AlO_x or SiN_x dielectrics to achieve high IBC solar cell performance, that is comparable with a-Si:H and SiO_x rear passivation, was demonstrated.
- 11) The simulated effect of electroless nickel plated contacts on IBC solar cell performance, demonstrating that the best comparable contacts developed in Chapter 6 have efficiency potential up to 24.6 %.

8.2 Future work

The key results of this work demonstrate methods in which the carrier selectivity of diffused silicon wafer solar cells can be improved. However, there remains further potential to develop these results and demonstrate their broader potential in the PV industry.

In the first instance, the underlying mechanisms which reduce/improve ρ_c depending on the AlO_x thickness, firing condition and paste formulation has not been studied in this work. The understanding gained from these insights may help realise satisfactory results on 5-10 nm AlO_x thicknesses. This could assist in the development of screen-print pastes which can achieve a low contact resistance on surfaces with lower surface phosphorus concentrations.

The results of Chapter 6 highlight the performance potential and processing difficulty of electroless nickel plating to heavily diffused p^+ silicon layers. Further characterisation of the current samples to infer the elemental composition and interface properties of the nickel deposits is required to identify the cause of the variance in ρ_c , and account for the higher J_{oc} relative to the aluminium evaporated samples. The repeatability of the process needs to be improved, and key to this is a deeper understanding of the initial surface reactions at the silicon surface during plating. The characteristics of these contacts as they would occur in an actual solar cell—as for instance a plated Ni/Cu stack—needs to be demonstrated, and characteristics such as line resistance and adhesion evaluated.

A key assumption of the work in Chapters 5 and 6 was the use of a mid-gap trap of equal capture cross section during fitting. Furthermore, the distribution of acceptor and donor states throughout the interface was simplified to a single state for acceptors and donors respectively. This was done to simplify the fitting process, however more accurate insights are likely to be gained if the simulations can account for the specific nature of the interface traps. Furthermore, Sentaurus TCAD simulations were used in this work as

it is the most complete semiconductor simulation package. However, this software is not universally accessible, and therefore future work could focus on expanding the model developed in Chapter 6 to have sufficient accuracy by; 1) not taking the flat quasi-Fermi level approximation; 2) modelling the full diffusion profile and solving the continuity equations within a simulation mesh; 3) simulating a range of defect states and their distributions across the band gap; and 4) implementing models for the other lifetime components present in the device, allowing for full simulation of the effective lifetime outside of the Sentaurus TCAD package.

Finally, the applicability of the simulated IBC solar cell performance may be enhanced with the input of process specific data, such that the performance of actual processes can be simulated in a potential device. The work contained in Appendix A, which outlined an incomplete attempt at the fabrication of a diffused homojunction IBC solar cell with varying rear dielectrics could be continued to realise the fabrication of high performance devices. Alternatively, the effect of varying interface charge at the rear could also be studied by sequential corona charging of the rear surface and light I - V testing of a completed IBC solar cell. Similarly, baseline solar cells with nickel plated contacts may be fabricated to directly assess the potential for other low-cost metallisation technologies on the rear of the device. If the ρ_c and J_{0c} of the nickel plated contacts could be reduced, this would provide an alternate low-cost metallisation approach for high performance IBC solar cells. Combined with the potential for high-performance rear passivation from stable, low-temperature deposition dielectrics such as AlO_x , this presents further potential for lower-cost high-performance carrier selective diffused homojunction IBC solar cells.

PUBLICATIONS ARISING FROM THIS THESIS

Journal Publications

To, A., Ma, F., & Hoex, B. (2017). Improved understanding of the recombination rate at inverted p⁺ silicon surfaces. *Japanese Journal of Applied Physics*, 56(8S2), 08MB05.

To, A., Tahir, S., Garavaglia, A., Li, W. M., Li, X., & Hoex, B. (2017). The Effect of Bifacial AlO_x Deposition on PERC Solar Cell Performance. *IEEE Journal of Photovoltaics*, 7(6), 1528-1535.

To, A., & Hoex, B. (2017). Extracting dielectric fixed charge density on highly doped crystalline-silicon surfaces using photoconductance measurements. *Journal of Applied Physics*, 122(19), 195301.

Rahman, T., To, A., Pollard, M. E., Grant, N. E., Colwell, J., Payne, D. N., ... & Boden, S. A. (2017). Minimising bulk lifetime degradation during the processing of interdigitated back contact silicon solar cells. *Progress in Photovoltaics: Research and Applications*.

Conference Publications

To, A., Li, W. M., Li, X., & Hoex, B. (2017). The effects of bifacial deposition of ALD AlO_x on the contact properties of screen-printed contacts for p-type PERC solar cells. *Energy Procedia*, 124, 914-921.

To, A., Cui, J., Hoex, B. (2017) Extracting the fixed charge density in HfO_x films grown on highly-doped p-Si samples. *IEEE Photovoltaic Specialists conference (PVSC44)* Washington D.C.

Appendix A

A1.1 Development of a planar diffused wafer IBC cells

The following sections outlines the design, fabrication and process development of a planar, diffused homojunction IBC solar cell. The cells fabricated in this work were fabricated without front surface texturing to (a) simplify the fabrication procedure as the effects studied in this work are independent of the front side light trapping and (b) enable the cells to be fabricated with novel light trapping structures. The author would like to acknowledge the contribution of T. Rahman, who performed the Sentaurus TCAD simulations in collaboration with the author, who provided the guidance on the input parameter values and feedback on the simulation set-up.

A1.1.1 Development, simulation and verification of an optimised IBC solar cell geometry

The geometry for the IBC solar cell used in this work was simulated and verified in Sentaurus TCAD, and compared against the geometry outlined in Ref. [341]. A 3D unit-cell with varying geometries for the hole and electron collector geometries was simulated to find the optimum geometry to maximise the cell efficiency, V_{oc} , J_{sc} and FF . This was achieved in two steps:

- 1) Find the optimised area fraction for the rear diffused hole collector (emitter) for a simplified geometry with rectangular diffusions for the diffused hole and electron collector regions.
- 2) With the optimised diffused hole collector fraction calculated, find the optimised geometry for an equivalent diffused area ratio using point contact geometries for the electron collector (BSF) regions, whilst maintaining a rectangular hole collector geometry.

To validate the Sentaurus model, both the cell in this work, and the state-of-the-art diffused IBC solar cell reported in Ref. [341] was reproduced in both Quokka and Sentaurus TCAD. In this way, the simulation method was checked for consistency using published physical results and using multiple simulation software packages. The rendered

unit cell geometry is shown in Figure A.1a and the input parameters for the geometry sweep (bullet point 1 above) is listed in Table A.1.

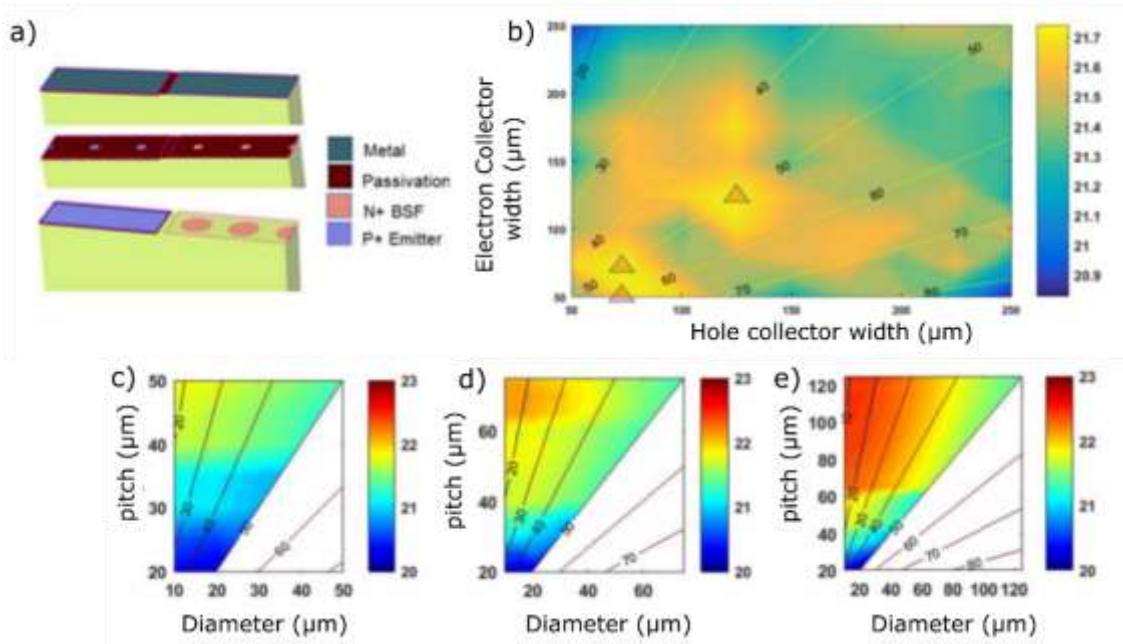


Figure A.1 a) Schematic of the unit cell used to simulate the IBC solar cell and b) efficiency plots for varying widths of hole and electron collector as a function of rear back surface field diameter and pitch for hole:electron collector ratios c) 75 μm : 75 μm , d) 75 μm : 50 μm and e) 125 μm : 125 μm .

Figure A.1b plots the efficiency as a function of hole and electron collector width, with triangles superimposed on the graph to highlight the efficiency maxima, corresponding to hole:electron collector width ratios of 75 μm : 75 μm , 75 μm : 50 μm and 125 μm : 125 μm (the corresponding area fractions are a function of the unit cell length in units of microns). These parameters were then used to find the optimised geometry for the localised back surface field (n^+ diffused region) contact holes and the resulting simulations for the ratios are shown in Figure A.1, Plot c, Plot d and Plot e respectively. The results from the simulations found an optimised geometry, with hole collector diffusion width of 125 μm , electron collector diameter of 30 μm and a pitch of 100 μm .

Table A.1 Input parameters for Sentaurus TCAD IBC model sweep

Fixed Parameters		Variable Parameters	
Parameter	Value	Parameter	Value
Cell Thickness	280 μm	p^+ Hole Collector (Emitter) width	50 – 250 μm
Bulk doping	$1.5 \times 10^{15} \text{ cm}^{-3}$	n^+ Electron Collector (BSF) diameter	10 – 120 μm
Bulk Lifetime	5 ms	n^+ Electron Collector (BSF) pitch	20 – 125 μm
Front $S_{n,p}$	10 cm/s	Contact diameter	10 μm
Rear $S_{n,p}$	10 cm/s	Contact pitch	20 – 125 μm
Surface charge, front	$4 \times 10^{11} \text{ cm}^{-2}$		
Rear surface Charge	$4 \times 10^{11} \text{ cm}^{-2}$		
Auger Model	Altermatt <i>et al.</i> [67]		
Mobility Model	Klaassen [308, 309]		

Table A.2 lists the simulated performance characteristics of the optimised geometry relative to the state of the art geometry in Ref. [341], simulated in both Sentaurus TCAD and Quokka, using inputs published in Ref. [341] and [167]. In this instance, a cell with equivalent light trapping was simulated for consistency. The results from the simulation show consistency with the modelling results of Ref. [341] and also show a modest improvement in V_{oc} for the parameters simulated.

Table A.2 Optimised Geometry parameters and simulated performance.

	Efficiency	FF	V_{oc}	J_{sc}
	[%]	[%]	[mV]	[mA. cm^{-2}]
Cell X This Work (TCAD)	24.9	83.6	709	42.0
Cell Y Ref. [341] (TCAD)	24.7	83.3	705	42.0
Cell X This Work (Quokka)	24.5	83.9	703	41.6
Cell Y Ref [341] (Quokka)	24.4	83.8	700	41.6

A1.2 Fabrication of an IBC solar cell

In this section, the fabrication of an IBC solar cell and the various process related issues as they were uncovered in this work are outlined. Specifically, the effect of damage induced from reactive ion etching used in patterning steps, damage induced from electron-beam evaporation processes and the effect of bulk lifetime stabilisation processes are discussed. With regards to the bulk lifetime stabilisation work, the samples were fabricated by the author, however, the super-acid passivation process and measurements were conducted by N. Grant at Warwick University. All other cell fabrication work was performed by the author, except for the photolithography patterning and metallisation steps, in which the author assisted M. Pollard.

The cell fabrication process is depicted in Figure A.2 as a numbered sequence with corresponding cell schematic, and these numbered steps are referenced in the following description of the processing sequence. The devices in this work were fabricated on 280 μm thick 4" phosphorus doped n -type FZ wafers, with resistivity 2-4 $\Omega\cdot\text{cm}$ and with both sides with polished surface condition. All wafers were initially cleaned in a standard RCA cleaning process [172], followed by a short immersion in $\sim 2\%$ (w/v) HF solution to leave a hydrophobic surface. The wafers receiving the bulk stabilisation treatment underwent a dry oxidation for 30 minutes at 1050 $^{\circ}\text{C}$ in a mixed oxygen/nitrogen ambient in a (TS8603, Tempress) and the resulting thermal SiO_2 layer was subsequently removed in a 5% (w/v) HF acid solution (Step 1 and 2). All subsequent processing for the stabilised and un-stabilised wafers was therein identical. A diffusion mask was grown by subjecting the wafers to a 45 minute wet-oxidation process at 1000 $^{\circ}\text{C}$, producing an approximately 230 nm thick SiO_2 layer. Circular openings to expose the underlying silicon for the formation of the n^+ electron collector was performed via photolithography and either wet or RIE etching of the SiO_2 layer (Step 3). This was performed by either 1) wet etching in buffered HF (7:1) solution for 5-6 minutes until visibly hydrophobic at room temperature, or 2) a plasma process with a CF_4/O_2 ambient (OPT Plasmalab System 100, 35/3 s ccm, 165 W, 380 V DC bias, for 6 minutes). The positive lithography process for the electron collector mask used AZ6632 resist spun at 4000 rpm, soft baked on a hotplate for 1 minute at 110 $^{\circ}\text{C}$, exposed with a broadband UV source at a total fluence of 130 mJ/cm^2 , developed in MIF AZ826 for 30 s, and finally hard baked at 145 $^{\circ}\text{C}$ for 10 minutes on a hotplate. The resist in both instances was removed via rinsing in acetone followed by isopropyl alcohol (IPA) and DI water rinsing. Phosphorus diffusion of the local n^+

electron collector was performed in a tube furnace (TS8603, Tempress) with a liquid POCl_3 source (Step 4). This process consisted of a deposition step at 795 °C for 25 minutes in 1:1:16 $\text{POCl}_3\text{:O}_2\text{:N}_2$ gas ambient, followed by a 1-hour drive-in process at 920 °C. The diffusion mask and phosphosilicate glass (PSG) were then removed with a dilute HF acid solution. The formation of the p^+ hole collector regions consisted of the growth of a SiO_2 diffusion mask on both sides, photolithographic patterning to define the diffused area (step 5), and a dry or wet etching procedure to open the SiO_2 dielectric (Step 6). The fabrication for these processes was identical to that used in the formation of the electron collector regions outlined previously. The formation of the p^+ layer was via thermal diffusion in a tube furnace (TS8063, Tempress) using a liquid BBr_3 source (Step 7). This consisted of a deposition step at 850 °C in a 1:1:19 $\text{O}_2\text{:BBr}_3\text{:N}_2$ gas ambient, followed by a drive-in at 920 °C and an in-situ dry oxidation at the same temperature for 30 minutes in order to dissolve any potential boron rich layer (SiB_6) formed during the process. The borosilicate glass (BSG) layer and diffusion mask were then removed in a dilute HF acid solution (Step 8). To passivate the wafers, an ALD AlO_x capped by PECVD SiN_x was grown on the rear, and the front side was passivated with PECVD SiN_x only (Step 9). The ALD AlO_x layer was deposited in a thermal ALD system (Savannah, Cambridge) at 200 °C using 110 ALD cycles. This layer was capped with a 60 nm thick PECVD $\text{SiN}_x\text{:H}$ layer, grown in a remote PECVD system (AK400, Roth & Rau)—Step 10. The wafers then underwent a short RCA 2 cleaning procedure to remove the unintentional AlO_x deposition onto the front side of the wafers, followed by a short (<10 s) immersion in ~2 % (w/v) HF acid solution to restore the H-terminated, hydrophobic silicon surface. Shortly after wafer drying, the front side of the wafers were passivated with an 80 nm thick PECVD $\text{SiN}_x\text{:H}$ layer, in the same PECVD tool. To activate the surface passivation, the wafer was subsequently annealed for 10 minutes at 400 °C in a rapid-thermal-anneal tool in an N_2 ambient. The metal contact openings were then patterned in the same photolithography procedure using positive photoresist as outlined previously (Step 11), however the wet etch time increased to 15 minutes to fully remove the $\text{AlO}_x\text{/SiN}_x$ stack (Step 12). With the contact openings fabricated, a metallisation mask to define the metal contact area via lift-off was deposited on the samples (Step 13). This consisted of resist spinning (AZ nLOF 2035 at 3000 RPM for 30s), soft bake on a hotplate for 1 min at 110 °C, exposure (i-line, 72 mJ/cm²), development in MIF AZ826 for 60s) and a hotplate hard bake for 150 °C for 5 minutes. Immediately before metal deposition, the samples

received a short immersion in 7:1 buffered HF to remove any native oxide formed on the surface. A 1 μm thick aluminium layer was subsequently deposited via e-beam evaporation, or thermal evaporation using a 99.999 % pure pellet Al source (Step 14). Lift off was performed by soaking the wafers in acetone using ultrasonic agitation (Step 15). Finally, the samples were sintered for 1 minute at 350 °C in an N₂ ambient in a rapid thermal annealing furnace to lower the contact resistance.

The wafers were characterised via numerous techniques, and the extracted parameters were used as inputs in subsequent device modelling of the resulting cells to assist in fault diagnosis and further optimisation. The passivation quality and effective minority carrier lifetime were measured using either transient or QSS PC measurements (WCT-120 PC lifetime tester, Sinton Instruments), in addition to PL imaging (LIS-R1, BT imaging) throughout the fabrication process, on the finished cells and process monitor wafers. The accuracy of the PL images was improved by applying point spread function deconvolution [286]. AlO_x layers deposited via ALD were used as a passivating dielectrics to assess the damage induced by RIE processes. PC measurements were also performed on some finished cells that were subsequently de-passivated via HF and alkaline etching to remove the diffused regions, to investigate bulk lifetimes. All stated carrier lifetimes were extracted from PC measurements at an excess carrier density $\Delta n = 10^{15} \text{ cm}^{-3}$. The *I-V* measurements were measured taken using a triple-A class solar simulator (Sun 3000, ABET Technologies) with a source measurement unit on a custom made jig to probe the rear contacts without temperature control.

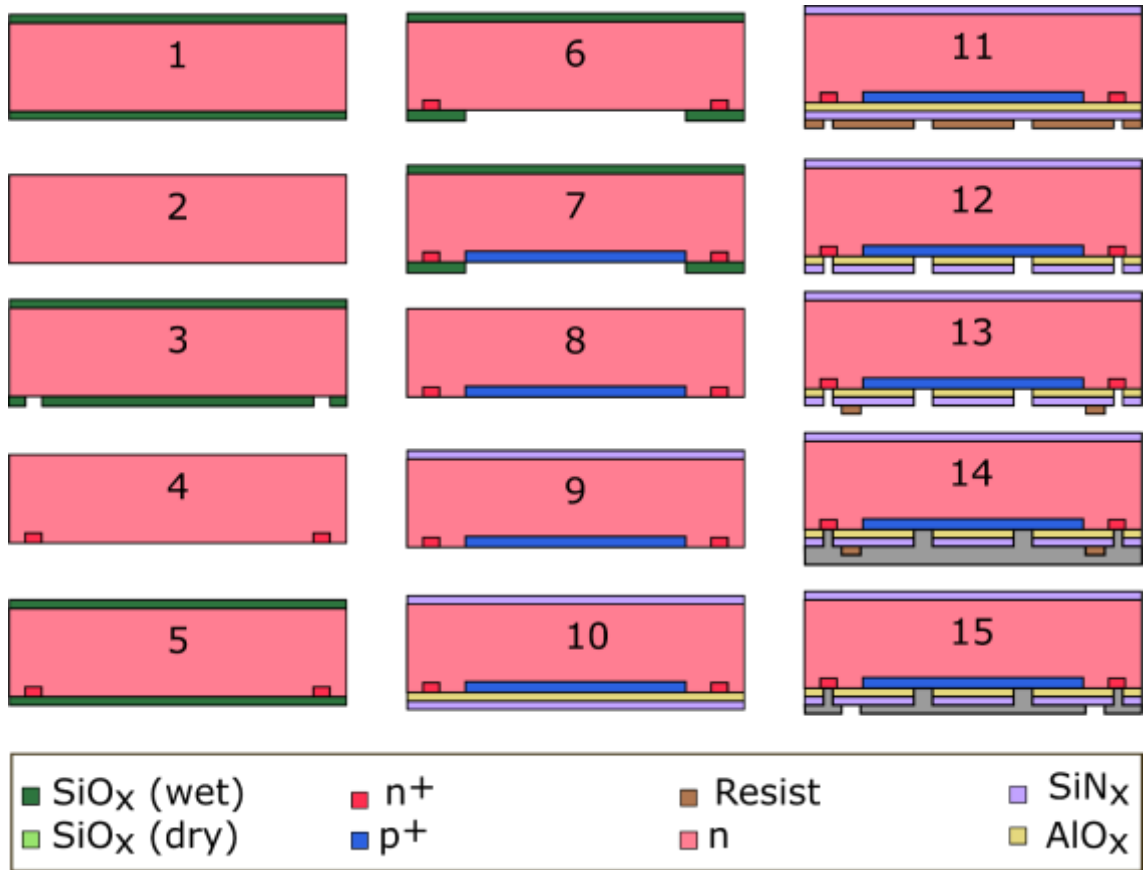


Figure A.2 Schematic diagram of the fabrication flow of the diffused wafer homojunction IBC solar cell used in this work

A1.2.1.1 Effect damage from electron beam evaporation of metal contacts

The PL images of a processed wafer after e-beam evaporation before (left half image) and after (right half image) sintering, is shown in Figure A.3. Both images are taken with the same imaging conditions (1 sun exposure for 1 second) and are presented with identical colour scales. The left-hand image presents strong lifetime degradation across the entire wafer—including the unmetallised passivated regions—suggesting the presence of defects which promote non-radiative recombination in all regions of the device. This was likely due to X-rays emitted during the evaporation of the aluminium source, which are known to increase the concentration of oxide traps, charges and surface states on evaporated MOS structures [354-356]. An increase in the PL signal was observed after the annealing process, especially in the undiffused edge regions, suggesting that some of this damage had been reversed. Further improvements in the PL signal and overall cell performance were made by replacing this process with a thermal evaporation process, which avoids the generation of the damaging X-rays during the metallisation process.

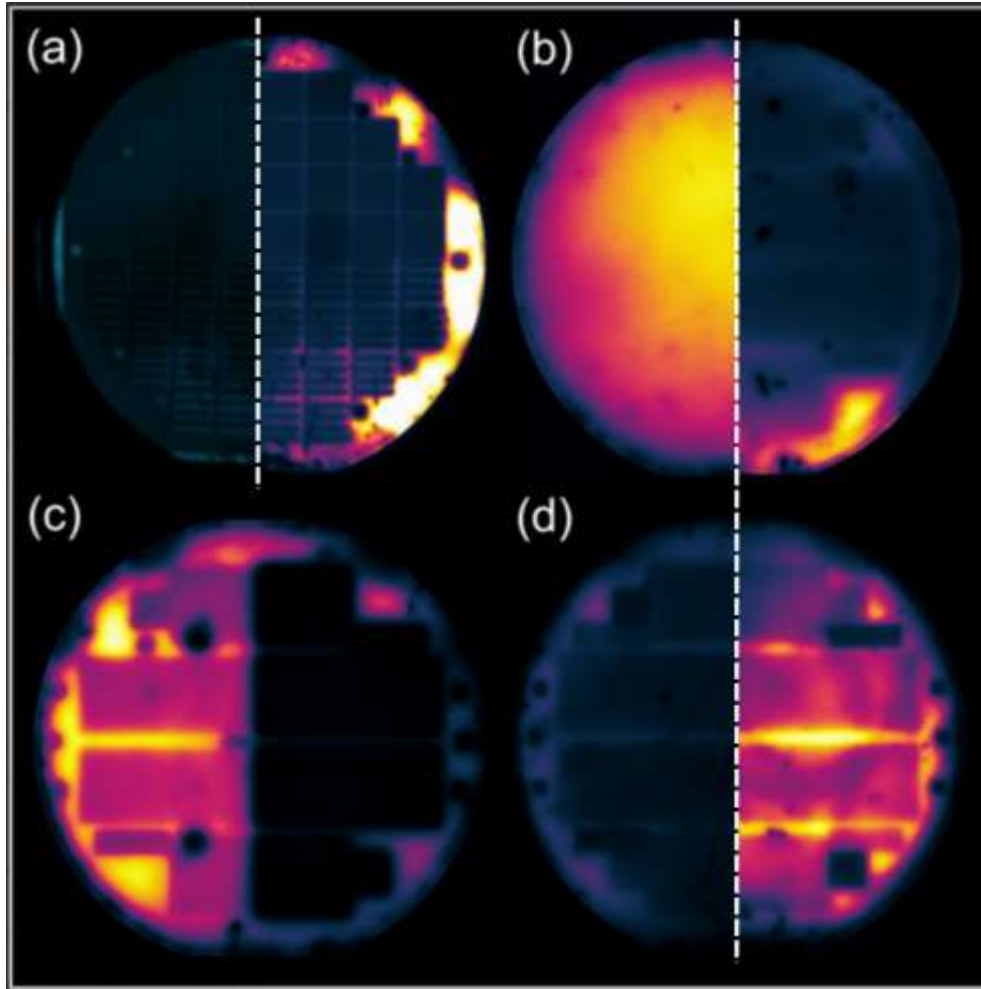


Figure A.3 PL image of a wafer after e-beam evaporation, pre (left) and post (right) sintering. b) PL image of a wafer repassivated after one half was subject to RIE exposure (right) whilst the other side was masked from RIE exposure (left). c) PL image of wafer using buffered HF etch (left) and RIE etch (right) passivated with AlO_x after boron diffusion. d) PL image of wafer without (left, Cell A) and with (right, Cell B) bulk FZ treatment. All wafers are 4" in diameter. All images are at 1 sun, with exposure times of 1s for (a) and 0.1s for (b), (c), and (d), and have been deconvolved using [286]

A1.2.1.2 Effect of RIE damage

Throughout processing, it was observed that the diffused regions patterned via dry etching had significantly lower PL counts than the diffusion monitor wafers. These diffusion monitors had undergone the same diffusion and passivation processes (these wafers were processed in the same batch) however did not undergo any dry etch patterning processes. RIE-induced damage of the exposed areas was suspected, since shallow implantation of reactive ions as well as lattice damage has resulted in surface degradation in silicon [357-360]. To confirm that the RIE process was causing the damage two tests were performed to;

- 1) assess the effect of RIE damage on raw silicon, and
- 2) measure the lifetime of regions which have been boron diffused after RIE patterning.

To assess if the RIE inherently damaged silicon, a wet oxide mask was grown in an identical procedure to the cell fabrication process on an *n*-type FZ wafer, which was then patterned in two different ways on each half; one half was patterned via wet etching, whilst the other side was patterned via the RIE process used in cell fabrication. Note that the non-target half was completely masked during each process to avoid RIE etching in the wet etched half, and to avoid wet etching on the RIE etched half. This wafer was then passivated with a 30 nm thick ALD AlO_x dielectric. The PL image of this wafer, shown in Figure A.3b, after anneal shows that the RHS of the wafer, which received the RIE etch, has lower PL signal than the LHS of the wafer, which was wet etched. This shows that the RIE process damaged the silicon at the surface, whereas no evidence of damage is evident on the wet etched silicon.

To test the effect of boron diffusion through RIE patterned regions on the sample lifetime, an identical experiment was performed with one half of the wafer patterned via RIE etching and the other half of the wafer was patterned via wet etching. In this case, the sample underwent a boron diffusion process before repassivation with ALD AlO_x. The oxidation growth, photolithographic patterning, dry and wet etch processes and boron diffusion processes were performed in an identical procedure to that which is outlined in Section A1.2. The PL image of the wafer in Figure A.3c shows that the side which received wet etching (LH half image) had much higher PL counts in comparison to the side which received RIE etching (RH half image). Furthermore, PC measurements shown in Figure A.4 of the partially processed cells after passivation and before metallisation openings (after Step 9) measured the corrected effective lifetime to be < 100 μs for cells processed with dry etching, whereas the cells with wet etch processing recorded an effective lifetime of 460 μs. Since the PC measurement is an area aggregated measurement, effects in the diffused damaged region are aggregated with the undiffused, undamaged regions and therefore the bulk lifetime in the damaged regions was likely to be lower than measured and therefore overestimated in the figure.

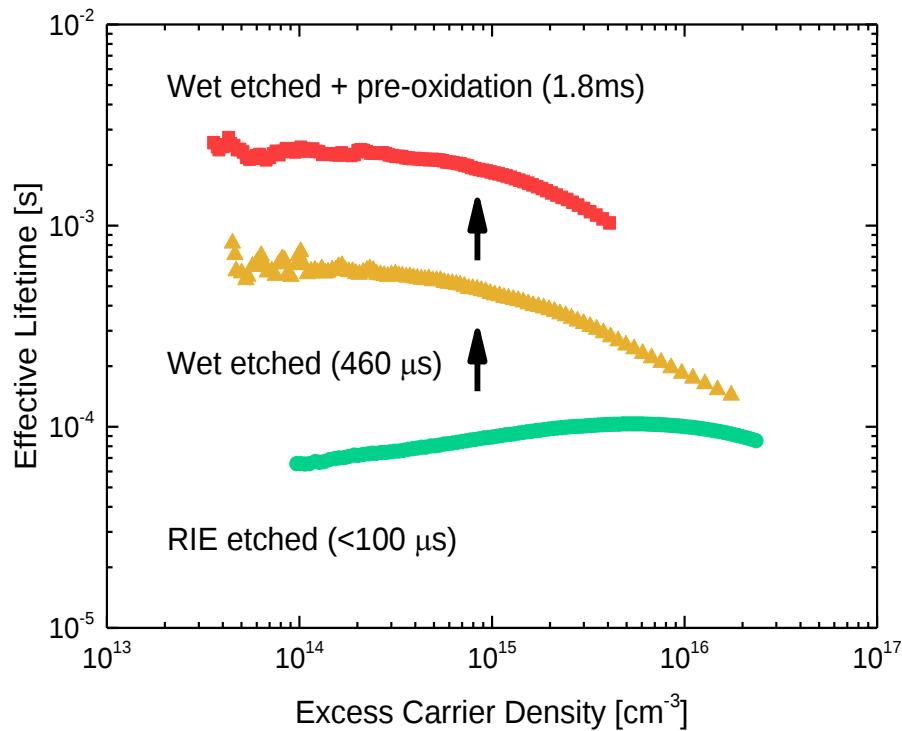


Figure A.4 Measured effective minority carrier lifetime of cells on FZ 3.2 Ω -cm *n*-type silicon wafer (prior to metallisation) for RIE etched cells, wet etched cells (Cell A) and wet etched cells with bulk FZ treatment (Cell B).

A1.2.1.3 Effect of bulk anneal

Grown-in defects limiting the bulk lifetime of commercially manufactured FZ silicon have been shown to become recombination-active after treatment at moderate (450-750 °C) temperatures [281, 361, 362]. In order to explore the influence of an initial bulk FZ treatment on mitigating the effect of such defects on the processed IBC cell performance, two wafers were put through the processing procedure with one wafer receiving no bulk stabilisation treatment (Cell A), and the other wafer (Cell B) receiving the stabilisation treatment in Section A1.2. PL images of Cell A and Cell B after passivation anneal and prior to contact opening is shown in the RHS and LHS of Figure A.3 respectively. The treated wafers had much higher PL signal prior to contact openings (which in this case were opened via wet etching processes). Similarly, PC measurements of the wafers in Figure A.4 taken prior to metallisation and after anneal show a significant difference in the injection level dependent effective lifetime, with an effective lifetime of 1.8 ms for the treated wafer, relative to 460 μ s for the untreated wafer. The effects at the completed cell level are shown Figure A.5, which shows the *I*-*V* curve and key performance parameters of Cell A and Cell B. A 28 % relative increase (from 14.3 % to

18.3 % absolute efficiency) is observed between the two cells, with the only processing difference being that one wafer received a pre-stabilisation treatment.

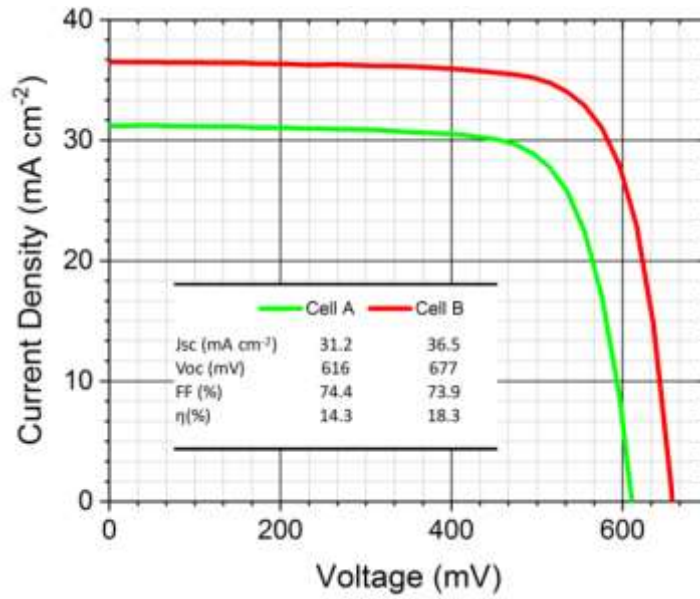


Figure A.5 One-sun I - V measurement for solar cells with (Cell B) and without (Cell A) bulk FZ treatment.

Further investigation of the bulk lifetime and edge effects was carried out to quantify the effect of edge recombination, such that this effect can be removed from the effective lifetime measurement and give greater accuracy on the actual bulk lifetime. The effective lifetime was measured by PC measurements of two IBC cells with (Cell B) and without (Cell A) the bulk treatment before metallisation. After the remaining fabrication steps and characterisation, the passivation and diffused regions of the two cells were removed by a HF acid immersion, followed by an alkaline etch in 25 % TMAH solution. The samples were then passivated in a superacid (SA) solution of trifluoromethanesulfonimide dissolved in dichloroethane (2 mg/ml) in the procedure outlined in Ref. [292].

The effect of edge recombination on the 2×2 cm IBC cell samples was found by comparing the lifetime of two 270 μm thick, n -type FZ samples with bulk resistivity of 2.6 $\Omega\cdot\text{cm}$, one sample with 2×2 cm dimension, and the other being a quarter sample of the 4-inch wafer. Both samples were passivated with the SA solution. PC lifetime measurements taken on these wafers are shown in Figure A.6, which shows an effective lifetime of ~ 5 and ~ 4 ms for the quarter and 2×2 cm sample respectively. This difference is attributed to the impact of different edge geometries, which produces a total effective edge recombination velocity (S_{edge}) equal to ~ 0.7 cm/s via calculations outlined in Ref. [363]. The effect of surface and edge effects of the 2×2 cm etched and SA passivated

samples were removed from the effective lifetime measurements, producing the bulk lifetimes and accounting for differences in the bulk doping. This bulk lifetime is shown in Figure A.6, where the calculated difference in untreated and treated bulk lifetime is ~ 2 ms once external recombination mechanisms are accounted for.

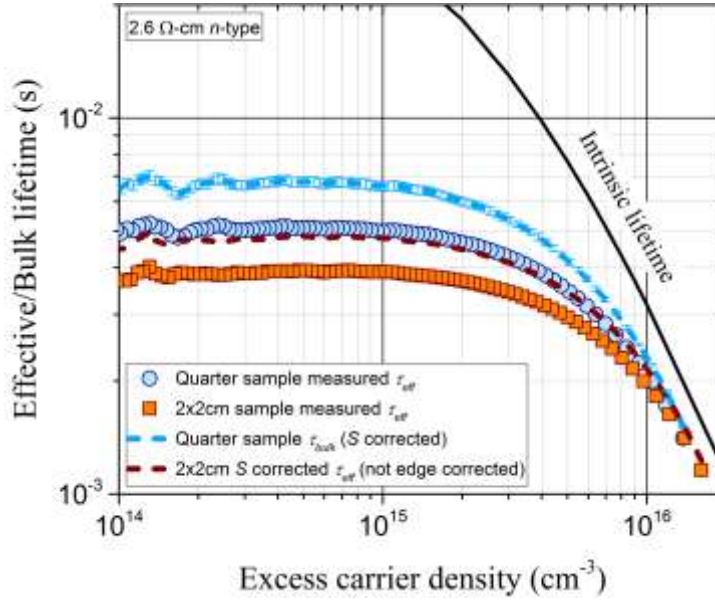


Figure A.6 Effective/bulk lifetime of 2.6 Ω -cm *n*-type FZ silicon, SA passivated control samples. Blue circles: τ_{eff} measurement on a quarter sample; blue dashed line: bulk lifetime after correcting for $S_{edge}=0.65\pm0.05$ cm/s; orange squares: τ_{eff} measurement of a 2 $\times$ 2 cm sample from the same wafer; brown dashed line: 2 $\times$ 2 cm *S* corrected lifetime, but without edge recombination correction. The black line corresponds to the intrinsic limit [364]

The bulk lifetime reduction during processing was quantified by measuring the as-received wafer with SA passivation and comparing this to a sister wafer which underwent the same boron diffusion process of this work. It was found that a significant reduction in the bulk lifetime occurred due to the boron diffusion process, which had a lifetime lower than 2 ms following this process. This is lower than the measured cell bulk lifetimes, which is possibly due to the getting of impurities into the phosphorus diffused regions which had occurred previously in Ref. [365]. The degradation from the boron diffusion process could potentially be mitigated by using a wet chemical process to strip the BRL layer, to prevent the release of any impurities gettered to the BRL layer and released back into the wafers as it was dissolved during the in-situ oxidation process [261]. Also, it is known that boron diffusions can form dislocations which diffuse into the bulk material, which have a dependence on the BRL thickness. Therefore, a potential strategy to reduce this impact is to further optimise the boron diffusion, to balance the degradation associated with BRL formation, and its getting properties. This can be enhanced by using

a front surface phosphorus diffusion to act as a getting site throughout processing, which is subsequently removed before passivation. The fabrication of an IBC cell outlined in the following section integrates some of these approaches and discusses the implications of these changes on the overall cell processing sequence and performance.

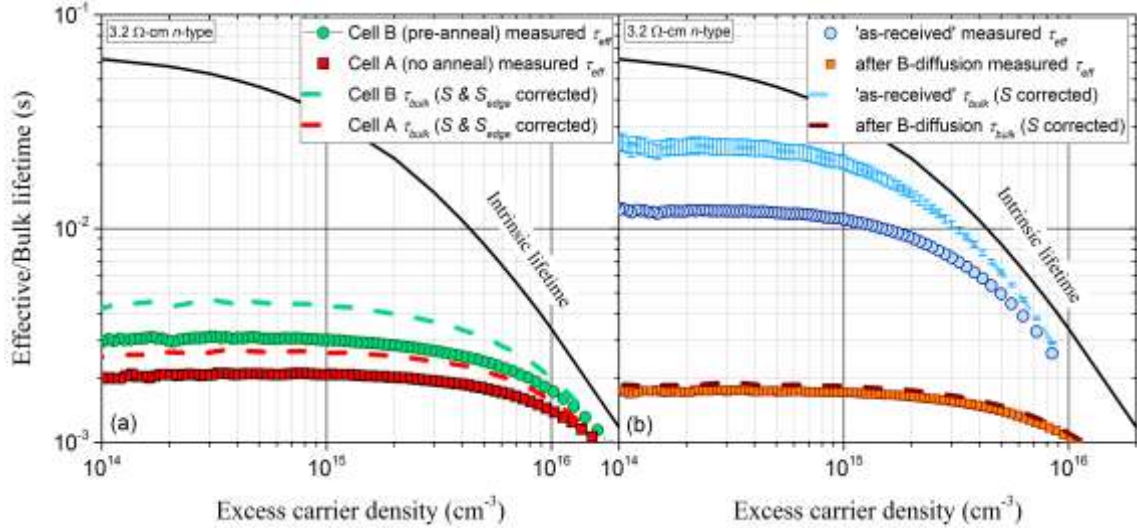


Figure A.7 SA passivated effective/bulk lifetime of FZ 3.2 Ω-cm *n*-type silicon. (a) τ_{eff} measurement of 2×2 cm Cell A (no bulk FZ treatment, red squares) and Cell B (bulk FZ treatment -green circles). The figure also plots τ_{bulk} for Cell A (red dashed line) and Cell B (green dashed line) after correcting for both S and S_{edge} . (b) τ_{eff} (solid symbols) and τ_{bulk} (dashed lines) of two silicon wafers, in the (i) as-received condition and (ii) after a boron diffusion, which was subsequently etched away prior to SA passivation. The black lines represent the intrinsic limit [364].

A1.3 Fabrication of IBC solar cell with varying rear passivation

Having developed a planar IBC solar cell baseline, an experiment was designed to test the effect of different rear passivating dielectrics on the carrier selectivity at the rear of diffused homojunction IBC solar cells, to test the effect of varying rear Q and D_{it} values. This was achieved by fabricating separate IBC solar cells with rear passivation from either an AlO_x/SiN_x stack, SiO_x/SiN_x stack or a single SiN_x layer. All other processing parameters were kept as identical as possible to isolate the effect of this variance in rear passivation.

A1.3.1 Fabrication methodology.

The fabrication sequence utilised identical processes to those developed in the previous section, with two notable differences; 1) the rear passivation stack was varied and 2) a gettering phosphorus diffusion was performed on the front side of the cell and carried

through processing to act as a collection site for impurities introduced during high-temperature processing. This is to mitigate any potential bulk degradation processes from the boron diffusion outlined in the previous section, and has also been used by other groups fabricating IBC solar cells [341, 346]. Furthermore, the furnace processes (POCl_3 diffusion, and dry/wet oxidation) were performed in a different furnace (TS8063, Tempress Systems), due to equipment maintenance and repairs on the original furnace. Three cells with different rear surface passivation schemes were fabricated, labelled Cell D ($\text{AlO}_x/\text{SiN}_x$ rear), Cell E (SiN_x rear) and Cell F ($\text{SiO}_x/\text{SiN}_x$ rear) and a schematic diagram of their final structure before metallisation is shown in Figure A.8.

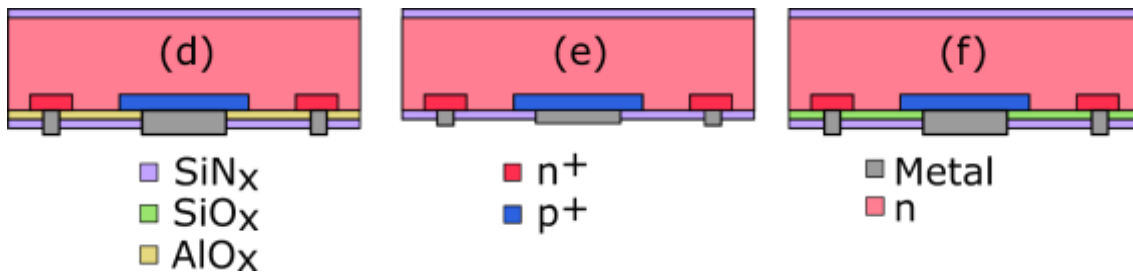


Figure A.8 Schematic of three different IBC cells structures with varying rear passivation schemes, including an $\text{AlO}_x/\text{SiN}_x$ stack (d), SiN_x only (e) and a $\text{SiO}_x/\text{SiN}_x$ stack (f).

The processing sequence is depicted in Figure A.9 and the corresponding steps are numbered corresponding to the following text. The starting substrates were $280\ \mu\text{m}$ thick phosphorus doped n -type FZ wafers with double sided polished texture, and bulk resistivity of $2\text{--}3\ \Omega\cdot\text{cm}$. As the processing details were in most cases identical to the process outlined extensively in Section A1.2, the process is only outlined briefly herein, with the key differences highlighted:

- 1) RCA cleaning and HF dip, followed by the bulk stabilisation oxidation process. The thin oxide layer grown was subsequently removed in dilute HF acid (Steps 1 and 2).
- 2) A wet oxide mask for the heavily diffused n^+ region was grown and patterned via photolithography. During patterning, the oxide mask on the front side of the wafer was removed, allowing for a full area diffusion on the front side of the wafer (Step 3).
- 3) Phosphorus diffusion to form the n^+ regions, followed by a PSG layer and oxidation mask removal in dilute HF acid (Step 4).

- 4) Growth of the diffusion mask for the p^+ hole collector regions via a wet oxidation process and patterning of the mask via photolithography to define the p^+ diffused regions (Step 5).
- 5) Boron diffusion of the p^+ regions, followed by removal of the BSG layer and oxidation mask (Step 6). This recipe was modified to reduce the in-situ oxidation duration to 10 minutes (from 30 minutes), to lessen the likelihood of redistribution of impurities getterred during BRL formation.

At this point, the processing sequence deviates from that outlined in Section A1.2, with the goal to fabricate three structures whereby the only difference is the rear passivation dielectric. First, all the cells all received a high temperature dry thermal oxidation in a tube furnace (Step 7). This process consisted of a dry oxidation process in a mixed O_2 : N_2 ambient at 1000 °C for 25 minutes, followed by an anneal for 30 minutes in N_2 . Although Cell A and Cell B do not feature a SiO_x layer, this process was performed on these samples to ensure that the diffusion profiles and thermal history were consistent across all samples. A 60 nm thick SiN_x mask was deposited on top of the SiO_x layer on the rear side of the wafer in a PECVD deposition (MAiA, Roth and Rau)—Step 8. Then, positive photoresist was spun on top of the SiN_x layer (AZ6632, 3000 RPM 30s, soft baked at 110 C for 1 minute) to act as a wet etch mask. The front side SiO_x layer was then subsequently removed in a dilute HF (10 % w/v) acid dip, and the photoresist removed with a sequential acetone/IPA clean, followed by a rinse in DI water. The heavily diffused n^+ layer was then removed in an alkaline etch process, aimed to remove 4 μm of silicon from the front surface (Step 9). This process was performed in a solution of 25 % (v/v) NaOH solution at 75 C for 2 minutes, with ultrasonic agitation to try to preserve the polished surface condition on the front. Following this process, the samples were immersed in a cleaning solution of HF:HCl for 1 minute. All samples then underwent a full RCA clean procedure followed by short HF dip, followed by a SiN_x PECVD deposition to deposit a 75 nm front side SiN_x ARC. Cell F is now fully passivated (Step 10). Cell D and E then underwent a rear passivation removal by masking the front side of the wafer with positive photoresist and then etching off the rear SiO_x/SiN_x stack in a buffered HF solution (Step 11). An ALD AlO_x layer was deposited on the rear of Cell D in a thermal ALD deposition at 200 C, 110 cycles (Savannah, Cambridge NanoTech) (Step 11a). This layer was then capped with a 75 nm PECVD SiN_x layer (AK400, Roth & Rau), followed by an RCA1 cleaning step to remove the unintentional wrap-around

AlO_x layer (Step 13a and b). Cell B underwent an identical procedure, omitting the AlO_x deposition procedure and RCA1 cleaning step. All cells were then annealed at 400 °C for 10 minutes in an N₂ environment and imaged via PL and QSSPC (Step 14).

PL images were taken of the cells after SiO_x passivation (Step 9) and after anneal (Step 12) and are shown in Figure A.10a and Figure A.10b respectively. Whilst in Figure A.10a the cells have reasonable PL signal and present good process uniformity—as indicated by the bright and uniform PL counts within the active regions of the cells and across wafers, notwithstanding the upper dark edges which appear to not affect significant portions of most cells—there are regions of poor lifetime at this stage and after anneal as depicted in Figure A.10b, where the PL signal in the bright regions have deteriorated. There are three distinct regions of low PL, listed separately as follows:

- 1) Dark regions in the upper edges are present in the cells after SiO_x passivation in Figure A.10a. These appear to remain after dielectric passivation (Figure A.10b), although it is masked by an overall reduction in the PL counts across the undiffused regions of the whole wafer.

Specifically in Figure A.10b,

- 2) the undiffused regions surrounding the cells are extremely dark.
- 3) The PL signal in cell A seems to have significantly deteriorated relative to the other wafers.

Consequently, further cell processing was abandoned, and effort was instead focused on determining the cause of the high recombination observed in the separately highlighted regions. These are addressed systematically in the following sections.

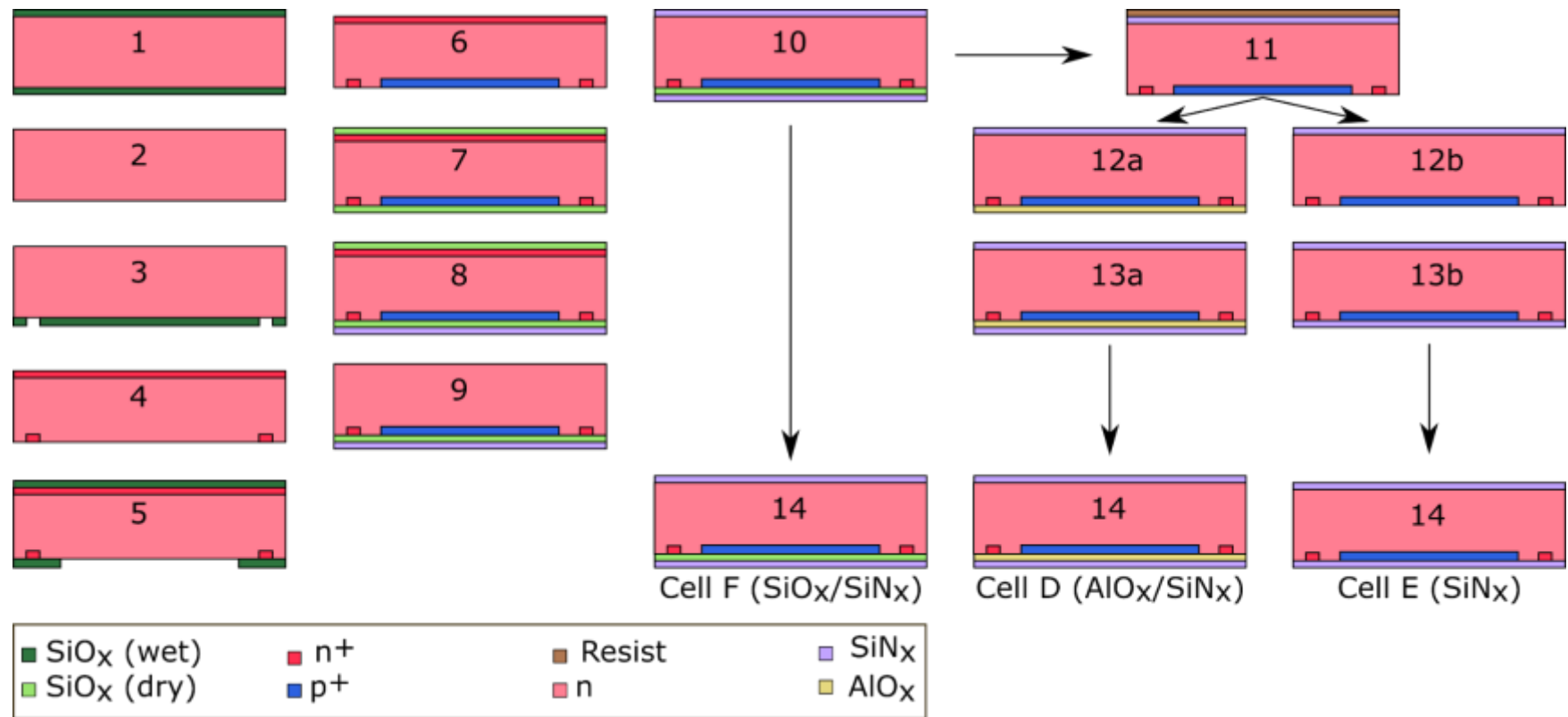


Figure A.9 Cell fabrication sequence for cells D, E and F with three different rear passivating dielectric stacks. The processing sequence was designed to ensure the same diffused carrier profiles and high temperature thermal history across all wafers.

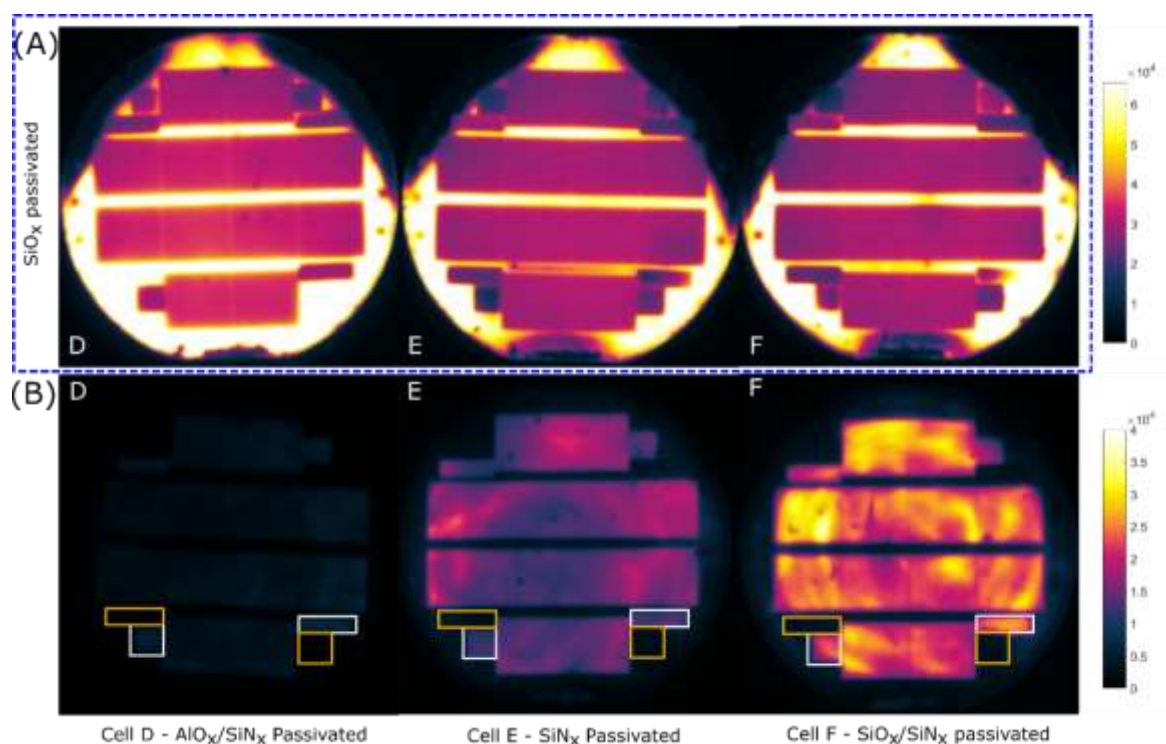


Figure A.10 PL images of the cells D,E and F after SiO_x passivation (step 10) and after anneal (Step 14) shown in the top (a) and bottom (b) rows respectively. The top row of cells were imaged at 1 sun illumination with an exposure time of 1 s and are presented without normalisation. The bottom row of cells were imaged at 1 sun with an exposure time of 1s and are normalised.

A1.3.1.1 Dark regions on the cell edge.

Dark regions along the upper edges of the wafers were observed in all cells in Figure A.10b and were also present in PL images of the boron diffusion monitor, which is depicted in Figure A.11a. These bands were not evident on PL images of the POCl_3 diffusion monitor (Figure A.11b), or the SiO_x passivation monitor (Figure A.11c) which avoided exposure to boron diffusion. This was because the POCl_3 monitor was masked with a wet oxide and therefore not exposed to the boron dopants during the boron diffusion process, and the SiO_x monitor only received the SiO_x passivation process. Therefore, these dark regions were induced during the boron diffusion process, as this is the unique process that the Cells A, B and C have in common with the boron diffusion monitor. Note that the dark band around the edges of the POCl_3 monitor may contribute as a potential source of the poor PL signal in the upper edge regions in Figure A.10. This was ruled out as the cause since the dark region extends around the whole wafer edge in Figure A.11b, whereas the effect in Figure A.10 the darker regions were isolated to the top edge. Second, the edge regions on the cells—the same regions which are darker on the POCl_3 monitor—were masked by an SiO_x layer during the POCl_3 diffusion and

therefore any damage induced by the phosphorus diffusion is avoided on the product cells. All wafers were loaded with the long flat edge towards the top of the diffusion furnace and therefore the consistency across the wafers suggests two potential sources for this nonuniformity:

- 1) Gas flow non-uniformity during the process.
- 2) Contamination from the contact points with the quartz wafer holder in the furnace.

The approximate contact points to the wafer points are circled on the boron diffused wafer in Figure A.11c.

It was observed that these regions of both the solar cells and monitor wafers were hydrophilic after BSG removal. This was ignored during processing as a concern since the hydrophilic region was estimated to be a few millimetres thick along the edge and therefore negligible, however as is evident from the PL images, this effect extends far greater than a few millimetres from the edge. The hydrophilic region suggests the formation of a BRL, which can occur if the BSG deposition is thicker in this region of the cell. In addition, since the in-situ oxidation process was significantly reduced during this process, it is possible any BRL formed in this region was not properly dissolved if it was significantly thicker in these regions, or if oxygen flow was restricted in these areas.

As a result, future work is required to optimise the boron diffusion process to balance the requirements of gettering from a BRL layer, with the damage induced from the presence of a BRL layer, whilst also addressing any potential gas flow non-uniformity during the process. Replacement or cleaning of the quartzware is also recommended as a precaution against contamination.

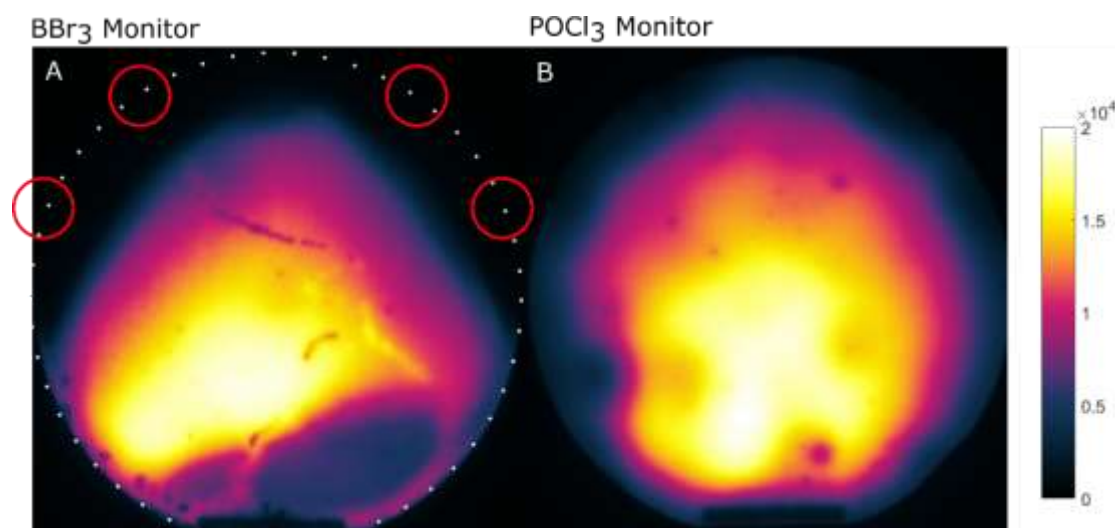


Figure A.11 PL images of the diffused (a) BBr_3 monitor and (b) POCl_3 SiO_x passivation monitor wafers, imaged at 1 sun illumination and 0.1s exposure (BBr_3 monitor) and 1s exposure (POCl_3 monitor). The white dots roughly indicate the edges of the wafer not visible in the image due to low PL signal, and the red circles indicate the approximate location of the points of contact with the furnace quartzware.

A1.3.1.2 Dark regions in Cell A relative to the other cells.

The PL signal between wafers after SiO_x in Figure A.10a are relatively uniform, compared to images after repassivation and annealing in Figure A.10b, whereby Cell A has significantly lower PL signal compared to the other wafers. Furthermore, given the negative fixed charge inherent in the AlO_x dielectric, one would expect the p -type diffused boxes (orange boxes in Figure A.10b) to be brighter than the n -type diffused boxes (white boxes). This was because the p -type region was lower doped and forms an accumulated surface. In contrast, the n -type diffused region was heavily doped and the minority carrier concentration in this region was increased assuming negative Q_f exists at the interface. Consequently, higher Auger recombination in this region and an elevated minority carrier concentration was expected to outweigh any benefits in carrier selectivity from the heavily diffused regions. However, the heavily diffused n -type regions are much brighter than the boron diffused regions, suggesting the charge-effect mechanisms had failed. In this instance, the detrimental Auger recombination was outweighed by the charge-effect passivation from doping which was significant in the boron diffused region. Therefore, a failure of the AlO_x passivation was expected. Visual inspection of the wafers under the microscope revealed extensive blistering across the entire rear surface of Cell A. This blistering was not evident on Cell B and Cell C. The blistering of $\text{AlO}_x/\text{SiN}_x$ stacks has previously been reported to reduce the effective lifetime of AlO_x passivated

silicon surfaces [366]. The blistering was therefore the likely cause of the poor PL signal in the p^+ diffused regions of Cell A.

A1.3.1.3 Dark regions in the un-diffused regions in all cells.

Between SiO_x passivation and annealing in Step 12, a significant deterioration in the PL signal in the undiffused regions indicating an increase in non-radiative recombination in these regions is observed consistently for all cells. This deterioration was not observed in the passivation process monitors, which all reveal high PL signals, suggesting that the deterioration was not a result of poor rear surface passivation. PL images of the passivation monitors are shown on Figure A.12, which depicts the undiffused AlO_x (a), SiN_x (b) and SiO_x (c) wafers after anneal.

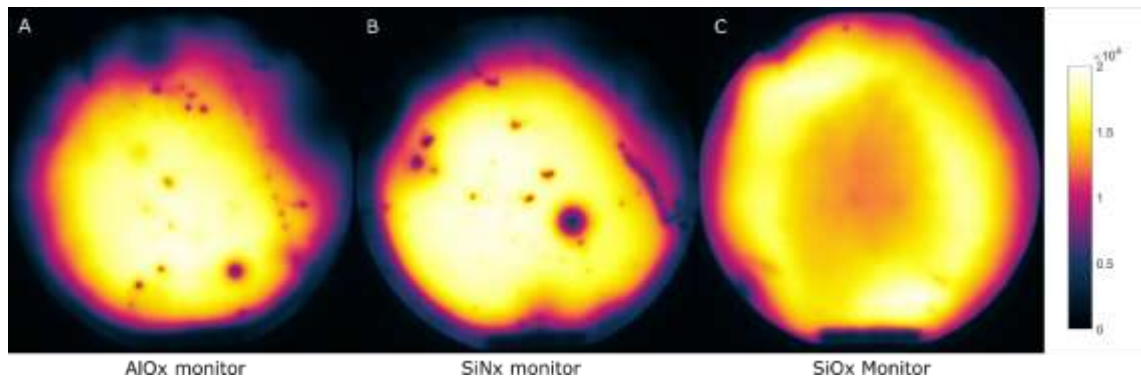


Figure A.12 PL images of the undiffused (a) AlO_x , (b) SiN_x and (c) SiO_x passivation monitors after annealing. The PL images were taken at 1 sun with 0.1s exposure.

Furthermore, since the wafers were processed in the same cleaning baths and deposited in the same deposition run, it is unlikely that handling errors were the cause. Handling errors do not present as uniform regions of non-uniformity, but rather spots or scratches—as is evident in the AlO_x and SiN_x passivation monitors in Figure A.12. The remaining point of difference is that the front side of the Cells D, E and F were etched back in an alkaline etch back procedure consisting of a NaOH solution. Contamination from potassium and sodium ions have been previously discussed as a disadvantage of KOH and NaOH texturing processes [367] and sodium contamination of silicon has been studied in the microelectronics industry. To test the effect of the etch back process on the sample lifetime a simple experiment was conducted. The SiO_x monitor wafer (depicted in Figure A.12) was laser cleaved and broken into smaller pieces. The SiN_x passivation was stripped in dilute HF acid, and one set of samples underwent a repeat of the etch back process (Sample B). Both samples were then cleaned in a standard RCA cleaning procedure, followed by a HF dip, and then repassivated with PECVD SiN_x and annealed.

The PL images of the samples without alkaline etching a) and with alkaline etching b) are shown in Figure A.12. The PL images show that the cleaning process used after NaOH etching was not sufficient to remove any process related surface contamination, which has produced the darker PL regions in image b). The brightness of image a) suggests that the dielectric passivation was not at fault, since both samples were in the same PECVD deposition and closely spaced. Therefore, contamination of the wafer surface from the alkaline etch process was concluded to be the likely cause of the observed lifetime degradation in Figure A.10 across all wafers.

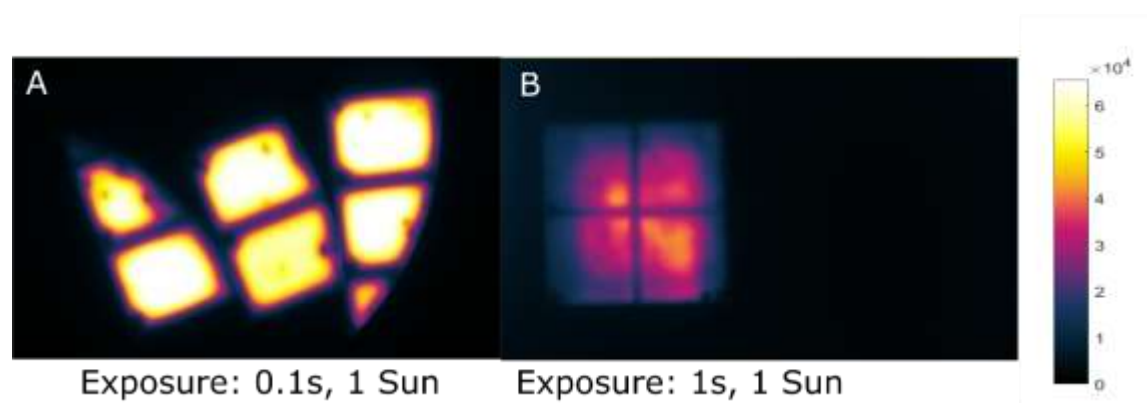


Figure A.13 PL images of SiNx passivated wafer pieces. Image B underwent an alkaline etch process prior to repassivation, Image A did not undergo an alkaline etch and acts as a control for the SiNx passivation process. Note the difference in exposure duration between images (a) and (b).

To overcome this issue, alternative etching solutions which are metal-ion free could be used in future, such as TMAH. Due to time limitations these results were not able to be remedied in a subsequent batch, or by repassivating and cleaning the wafers via a further etch back process with adequate cleaning. Remedying the performance of these samples and the fabrication of optimised devices is therefore an area of future work.

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