Surface Passivation of Crystalline Silicon by Sputtered Aluminium Oxide

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Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university and that, to the best of my knowledge, it does not contain any material previously published or written by another person except where due reference is made in the text. The work in this thesis is my own, except for the contributions made by others as described in the Acknowledgements.

Tsu-Tsung Andrew Li
Before I begin this thesis, I would like to recognise and express my appreciation to the many people who have contributed to its creation.

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Abstract

Efficient and inexpensive solar cells are necessary for photovoltaics to be widely adopted for mainstream electricity generation. For this to occur, the recombination losses of charge carriers (i.e. electrons or holes) must be minimised using a surface passivation technique suitable for manufacturing. In the literature, it has been shown that the aluminium oxide films are negatively charged dielectrics that provide excellent surface passivation of silicon solar cells. Meanwhile, sputtering has been shown to be an inexpensive thin film deposition method that is suitable for manufacturing. This thesis work aims to combine the excellent passivation properties of aluminium oxide with the manufacturing advantages offered by sputtering.

We show—for the first time—that sputtering is capable of depositing negatively charged aluminium oxide films that provide very good surface passivation of crystalline silicon. Effective surface recombination velocities of 24.6 cm/s and 9 cm/s are achieved on 0.8 Ω.cm p-type crystalline silicon and 1 Ω.cm n-type crystalline silicon respectively, with charges in the range of $-10^{11}$ to $-10^{13}$ cm$^{-2}$. We specify the sputtering requirements and processing conditions required for achieving these results, showing the effect of the various deposition and annealing parameters. After investigating the physical characteristics of the sputtered aluminium oxide films using thin film measurement techniques such as Rutherford Backscattering Spectrometry and Secondary Ion Mass Spectroscopy, we conclude that the current levels of surface passivation attained using aluminium oxide films appear to be closely related to the interfacial layer and the presence of hydrogen. In some cases the level of surface passivation is most likely limited by the incorporation of unwanted impurities. We determine the composition and bonding of aluminium oxide films, discussing their significance to the various hypotheses concerning the origin of the negative charge. Finally, we demonstrate that sputtered aluminium oxide can be applied to solar cells by fabricating passivated emitter and rear cells with efficiencies as high as 20.1%. The results of this thesis provide the foundation for the sputtered aluminium oxide technology and its application to industrial solar cells.
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Introduction

“The challenge for commercial [solar] cells is, of course to find a low-cost, high-throughput method that is compatible with the other solar cell fabrication steps and the silicon material used.”
A. G. Aberle, 2000

Thesis Motivation

As humanity moves well into the 21st century, its fundamental need for energy has not changed. The challenge is to maintain and increase the amount of energy available to society even as conventional fossil fuel resources head towards depletion. Photovoltaic (PV), among other forms of renewable energies, offer practical solutions to this challenge. In order for these solutions to be economically viable and widely accepted however, their levelised cost—the overall cost of electrical energy generated from a PV system over its lifetime—must be reduced to levels that are competitive with conventional energy options.

The competitiveness of a particular PV technology can be measured by a ratio of the cost of fabricating the solar cell to its nominal electricity output; the parameter commonly used for measuring this is dollars per Watt peak ($/W_p$). A simplified definition of the $$/W_p is presented in Equation 1:

$$$/W_p = \frac{\text{Facility + Equipment + Operational Expenditures}}{\text{Throughput} \times \text{Solar Cell Efficiency} \times \text{Module Size}} \tag{1}$$

The efficiency of the energy conversion is still an important factor, but it is relative to the cost of production; lower solar cell efficiencies can be offset by lower production costs and vice versa. The motivation and prevailing trajectory of photovoltaic research at this present time is to minimise the $$/W_p of a particular PV technology through both efficiency enhancement and cost reduction. The best technological solutions are low-cost, high-throughput methods that are compatible with the other solar cell fabrication steps and the silicon material used.

Carrier recombination—particularly at the surfaces—has a strong bearing on the performance of crystalline silicon (c-Si) solar cells. The relation between the surface re-
Figure 1: Calculated conversion efficiency of a $p$-type silicon solar cell ($250 \mu m$ $0.5 \Omega.cm$ c-Si($p$) with $100 \Omega/\square$ $n^+$ emitter, 5% reflectance) as a function of (a) the front surface recombination velocity and (b) the rear surface recombination velocity.

Negatively charged aluminium oxide ($AlO_x$) has been identified as a surface passivation technology that can satisfy the various shortcomings of current surface passivation methods [9]. The negative charge avoids the parasitic shunting that would occur with a positively charged dielectric on $p$-type surfaces for $p$-type solar cells [10], while its excellent passivation of $p^+$ emitters [11] allows the fabrication of high efficiency $n$-type solar cells [12]. However, the excellent surface passivation [13, 14] and solar cell results have been achieved using $AlO_x$ deposited by Plasma-Assisted Atomic Layer Deposition (PA-ALD), which is a thin film deposition technique that is not easily adaptable to manufacturing [15]. The throughput and operational cost of using PA-ALD $AlO_x$ are unlikely to be offset by the gains in solar cell efficiency and thus are unlikely to minimise the $$/W_p$ in Equation (1).

On the other hand, PA-ALD can be replaced by alternative deposition techniques such as thermal atomic layer deposition [16, 18], sol-gel [16, 19, 20], Atmospheric Pressure Chemical Vapour Deposition (APCVD) [9], Plasma-Enhanced Chemical Vapour Deposition (PECVD) [17, 21, 22] and sputtering [16, 23]. Even though the surface passivation
results from these deposition techniques have not been as good as that from PA-ALD, they can offer practical advantages in terms of cost and throughput.

The results using PECVD have so far been the most encouraging, as the technique is already widely used in the manufacturing of solar cells and excellent surface passivation has been achieved on both p- and n-type silicon wafers \[17, 21, 22\]. Its deposition rate of 100 nm/min \[21\] is already higher than the minimum 60 nm/min expected by industry \[24\]. Alternatively, sputtering is more attractive for manufacturing due to its low cost and high throughput. It also avoids the use of expensive and dangerous metal organics that are required for Chemical Vapour Deposition (CVD) and Atomic Layer Deposition (ALD) techniques \[25\]; the infrastructure necessary for operating with the hazardous metal organics would also be avoided. Thus, the sputtering of AlO$_x$ has advantages over other deposition methods in meeting the requirements of facility, equipment, operating costs and throughput in Equation 1.

A comprehensive evaluation is needed to establish whether sputtered AlO$_x$ can meet the requirements for the manufacturing of solar cells from the point of view of surface passivation. In previous attempts \[16, 23\] this topic was only briefly explored and thus deserves to be revisited.

Thesis Outline

The work of this thesis provide the groundwork for the application of sputtered AlO$_x$ to industrial solar cells.

Chapter 1. Review of Surface Passivation reviews the physics necessary for understanding the mechanisms that lead to good surface passivation of c-Si solar cells.

Chapter 2. Overview of Characterisation Techniques provides the background to the experimental results presented in this thesis by describing the characterisation techniques used in this work.

Chapter 3. Viability of Sputtering Methods evaluates three sputtering methods and two sputtering systems to deposit AlO$_x$. For the first time, surface passivation suitable for solar cells is demonstrated using sputtered AlO$_x$. We confirm that negative charges \((-10^{11} \text{ to } -10^{13} \text{ cm}^{-2})\) are obtained with sputtered AlO$_x$ films on c-Si after annealing \((\sim400^\circ\text{C in N}_2 \text{ for } >10 \text{ min})\). We specify the main requirements, methods and processes for sputtering AlO$_x$ for surface passivation.
Chapter 4 Material Properties of Sputtered Aluminium Oxide Films analyses sputtered AlO$_x$ films using thin film characterisation techniques. We determine the composition and bonding of sputtered AlO$_x$ films, highlighting the physical characteristics that are likely to influence the surface passivation that is achieved.

Chapter 5 Optimisation of the Surface Passivation optimises the deposition parameters for the sputtering as well as the annealing parameters and we detail their effects on the surface passivation from sputtered AlO$_x$ films. We show that sputtered AlO$_x$ can provide very good surface passivation, with $S_{eff}$ values of 24.6 cm/s and 9 cm/s achieved on 0.8 $\Omega$.cm Float-Zoned (FZ) $c$-Si($p$) and 1 $\Omega$.cm Czochralski (CZ) $c$-Si($n$) respectively, consistent with achieving open-circuit voltages of up to 705 mV.

Chapter 6 Applicability to Solar Cells analyses the applicability of sputtered AlO$_x$ to silicon solar cells, such as the effect of the AlO$_x$ thickness and its ability to withstand firing conditions. We first address the passivation of $p^+$ emitters for $n$-type solar cells and show that sputtered AlO$_x$ can provide acceptable levels of surface passivation of boron-diffused emitters; the best $J_{0E}$ value of 228 fA/cm$^2$ is achieved on a sheet resistance of 88 $\Omega/$$\square$. Next we focus on $p$-type solar cells and demonstrate that sputtered AlO$_x$ can be applied to high-efficiency solar cells, by fabricating PERC solar cells with 20% efficiency.

Ancillary work on the theoretical modelling of surface passivation, but focusing on $a$-Si:H rather than AlO$_x$, is presented in Appendix B. A summary of the main conclusions from this thesis are presented in Summary and Outlook; we outline the direction for further work on sputtered AlO$_x$, on how to develop it into a negatively charged dielectric film that can be regularly applied to industrial solar cells.
Chapter 1

Review of Surface Passivation

“The ultimate performance of many semiconductor devices is limited by the recombination lifetime of the charge carriers.”

R. Häcker and A. Hangleiter, 1994 [26]

1.1 Introduction

In order to evaluate sputtered AlO$_x$ as an effective method of surface passivation, it is necessary to understand how surface recombination occurs and how a dielectric film—such as AlO$_x$—provides surface passivation. This chapter reviews the physics necessary for understanding surface recombination and how it can be minimised. It also presents the background to why sputtering of AlO$_x$ is an attractive surface passivation method for silicon solar cells.

Section 1.2 reviews the three fundamental recombination mechanisms in $c$-Si. We analyse the roles of radiative recombination (Section 1.2.1), Auger recombination (Section 1.2.2) and the recombination through defects in the bandgap (Section 1.2.3) in the $c$-Si bulk and the statistics that quantify the rates at which they occur.

In Section 1.3 we analyse how the recombination mechanisms described in Section 1.2 and the surface band-bending (Section 1.3.1) apply to the recombination at $c$-Si surfaces (Section 1.3.2). The solutions for deducing the surface recombination velocity are grouped into four categories and are reviewed separately (Sections 1.3.3–1.3.6).

In Section 1.4 we review the strategies and techniques currently used for the surface passivation of $c$-Si solar cells. We analyse the advantages and disadvantages of chemical passivation (Section 1.4.1), surface doping (Section 1.4.2) and dielectric films (Section 1.4.3). The information of this chapter provides the background for the investigations into sputtered AlO$_x$ in Chapters 3–6.
1. Literature Review

1.2 Carrier Recombination in Crystalline Silicon

In generation, energy from thermal processes or the absorption of photons provide the means for the transition of electrons from the Valence Band (VB) to the Conduction Band (CB). When this occurs, electron-hole pairs are created in the silicon. It is this fundamental process that enables and establishes the capacity of solar cells to produce electricity. However, this capacity is reduced by the opposite effect, namely recombination. Here, electrons in the conduction band recombine with the holes in the valence band; the electron-hole pair is lost and the excess energy released as photons or phonons. Recombination reduces the density of electrons and holes available for electricity production, subsequently limiting the efficiency of a solar cell.

At equilibrium the concentration of electrons and holes in silicon are $n_0$ and $p_0$ respectively. Their product is related to the intrinsic carrier concentration $n_i$ by the equation:

$$n_0 p_0 = n_i^2$$  \hspace{1cm} (1.1)

When excess electrons ($\Delta n$) and holes ($\Delta p$) are generated, the concentrations of electrons ($n$) and holes ($p$) becomes:

$$n = n_0 + \Delta n \hspace{1cm} p = p_0 + \Delta p$$  \hspace{1cm} (1.2)

Fortunately for solar cells, these excess carriers do not recombine instantly. They continue to be free carriers in the silicon for a limited time, allowing for the formation of currents and voltages that enable the generation of electricity. The average time for an electron-hole pair to recombine after generation is defined as the recombination lifetime ($\tau$):

$$\tau \equiv \frac{\Delta n}{U}$$  \hspace{1cm} (1.3)

where $U$ is defined as the rate of recombination. We have made the assumption here that $\Delta n = \Delta p$, which is generally true in the bulk of c-Si provided that there are no trapping effects or band-bending. At the surfaces however, this assumption is not valid and we will present later in Section 1.3 how Equation (1.3) can be adapted for surfaces.

Reducing the rate of recombination maximises the currents and voltages that can be generated and is therefore very important for improving solar cell efficiencies. In order to reduce the rate of recombination, the following three fundamental recombination mechanisms need to be understood:
1. Radiative recombination (Section 1.2.1)

2. Band-to-band Auger recombination (Section 1.2.2)

3. Recombination through defects in the bandgap (Section 1.2.3)

All of the recombination processes in silicon—in the bulk or at the surfaces—can be derived from the above three mechanisms. Radiative recombination ($U_{\text{rad}}$) and band-to-band Auger recombination ($U_{\text{Auger}}$) are intrinsic to the material and are unavoidable, but recombination through defects ($U_{\text{SRH}}$) can in principle be overcome by eliminating the defects through careful preparation of the sample [26]. Figure 1.1 depicts the fundamental generation and recombination mechanisms in silicon. The combined effect of the different recombination mechanisms gives the total recombination ($U_{\text{eff}}$):

$$U_{\text{eff}} = U_{\text{rad}} + U_{\text{Auger}} + U_{\text{SRH}}$$

(1.4)

Using Equation 1.3 the equivalent effective lifetime ($\tau_{\text{eff}}$) is [27]:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}}$$

(1.5)

Figure 1.1: The three fundamental generation and recombination mechanisms in silicon: generation ($G$), radiative recombination ($U_{\text{rad}}$), band-to-band Auger recombination ($U_{\text{Auger}}$) and recombination through defects in the bandgap ($U_{\text{SRH}}$). The solid arrows represent generation and recombination processes while the dotted arrows represent emission processes that augment the rate of recombination. The curved arrows labelled $h\nu$ recognise the role of phonons.
1.2.1 Radiative Recombination

In radiative recombination, an electron in the conduction band makes a transition to a hole in the valence band and the excess energy is released as a photon with the energy of the bandgap [7]. This intrinsic mechanism is dependent on the concentrations of electrons and holes. The radiative recombination rate is given by:

\[ U_{\text{rad}} = B(n_p - n_i^2) \]  

where \( B \) is the coefficient of radiative recombination equal to \( 9.5 \times 10^{-15} \text{ cm}^3\text{s}^{-1} \) for silicon at 300 K [28]. In an indirect band-gap semiconductor such as silicon, radiative recombination is negligible compared to band-to-band Auger recombination and recombination through defects in the bandgap. Nonetheless, this recombination mechanism can be used to measure surface recombination through the photoluminescence technique (Section 2.2.2).

1.2.2 Band-to-Band Auger Recombination

Auger recombination is a three-particle process where the recombination of an electron-hole pair gives its excess energy and momentum to a third charge carrier [7]. In band-to-band Auger recombination, the involvement of defects is ignored. Subsequently there are two possible ways for this process to occur: the third charge carrier can either be an electron in the conduction band or a hole in the valence band. The former process is labelled eeh while the latter process is labelled ehh. The total band-to-band Auger recombination rate \( (U_{\text{Auger}}) \) is given by the addition of the recombination rate of the eeh process \( (U_{\text{eeh}}) \) and the ehh process \( (U_{\text{ehh}}) \). In the basic model where the charge carriers are assumed to be non-interacting quasi-free particles [29], \( U_{\text{Auger}} \) is given by:

\[ U_{\text{Auger}} = (C_n n + C_p p)(n_p - n_i^2) \]  

where \( C_n \) and \( C_p \) are the electron and hole Auger coefficients respectively.

Band-to-band Auger recombination in reality has a more complicated dependence on material properties and involves the interactions between the charge carriers. By taking into account of the Coulomb interaction between the electrons and holes, the electron and hole Auger coefficients are replaced by \( g_{\text{eeh}} C_n \) and \( g_{\text{ehh}} C_p \), where \( g_{\text{eeh}} \) and \( g_{\text{ehh}} \) are the Coulomb-enhancement factors for the eeh and ehh processes respectively [26, 30]. The Coulomb-enhanced Auger recombination model has reduced the discrepancies between
the theory and experimental results, but the various coefficient values that have been proposed have been insufficient for providing a precise quantification of band-to-band Auger recombination.

Alternatively, experimental measurements have led to detailed parameterisations of band-to-band Auger recombination [31–33]. One of the most widely used is the parameterisation of Kerr and Cuevas [33], which accounts for the enhancement of Auger recombination due to the dopant density, dopant type and the injection level. In this parameterisation, $U_{\text{Auger}}$ is expressed as:

$$U_{\text{Auger}} = (np - n_i^2)(1.8 \times 10^{-24}n_0^{0.65} + 6 \times 10^{-25}p_0^{0.65} + 3 \times 10^{-27}\Delta n^{0.8})$$ (1.8)

### 1.2.3 Recombination through Defects in the Bandgap

Impurities, dislocations and defects generate energy levels in the bandgap. In general, defects with multiple energy levels and charge conditions exist [34, 35] and a variety of recombination processes through these defects are possible. In the $c$-Si bulk however, recombination through defects is dominated by a two-step process, with four possible electron-hole interactions (Figure 1.1). An electron first makes a transition from the conduction band to the defect level, before making its transition to the valence band and completing the process by recombining with a hole. The excess energy is usually released as phonons.

The model for a discrete energy level in the bandgap was independently developed by Shockley and Read [36] and Hall [37]; this became known as Shockley-Read-Hall (SRH) formalism. This is usually sufficient for evaluating recombination through defects in the $c$-Si bulk, but is insufficient for the general case of recombination in semiconductors, particularly for surfaces (Section 1.3). Also, the simplified forms in which the SRH statistics are typically presented [7, 8] hide particular details that are relevant to the recombination due to dangling-bonds (Appendix B) or details that improve the accuracy in the calculation of surface recombination. In this review, we expand on the derivation of the general SRH recombination statistics.

Firstly, we make the assumption that the neighbouring defects do not interact with each other. The defect level is either a acceptor defect or a donor defect [38] and their densities are given by $N_{t,A}(E)$ and $N_{t,D}(E)$ respectively. Acceptor defects can be neutral ($T^0$) or negatively charged ($T^-$) while donor defects can be neutral ($T^0$) or positively
charged ($T^+$). Together they contribute to the total density of defects $N_t(E)$:

$$N_{t,A}(E) + N_{t,D}(E) = N_t(E) \quad (1.9)$$

The nature and charge of the defect are unimportant for the calculation of the rate of recombination through defects ($U_{SRH}$). As a result, SRH recombination statistics are typically presented with the total density of defects and without the distinction between acceptor or donor defects. However, as this distinction is important for calculating surface recombination using the approximate solution of the band-bending problem in Section 1.3.5, we proceed with the derivation of recombination through defects with this distinction.

We follow the common assumption that the capture cross-sections are independent of energy and that the capture cross-sections of electrons ($\sigma_n$) and holes ($\sigma_p$) are defined irrespective of the nature of the defect [36–40]. Hence, the following definitions are made:

$$n = \frac{\nu_{th}}{\pi} n \sigma_n$$
$$p = \frac{\nu_{th}}{\pi} p \sigma_p$$
$$n_0 = \frac{\nu_{th}}{\pi} n_0 \sigma_n$$
$$p_0 = \frac{\nu_{th}}{\pi} p_0 \sigma_p \quad (1.10)$$

where $\nu_{th}$ is the thermal velocity equal to $10^7$ cm/s [41].

In Figure 1.1, $u_{A,1}$ to $u_{A,4}$ refer to the carrier flows of acceptor defects while $u_{D,1}$ to $u_{D,4}$ refer to the carrier flows of donor traps; these are given by [40]:

$$u_{A,1}(E) = \frac{\pi f_D(E) N_{t,A}(E)}{\pi + p + e_n(E) + e_p(E)} = \frac{\pi f_D(E) N_{t,D}(E)}{\pi + p + e_n(E) + e_p(E)}$$
$$u_{A,2}(E) = e_n(E) f_A(E) N_{t,A}(E)$$
$$u_{A,3}(E) = \frac{\pi f_A(E) N_{t,A}(E)}{\pi + p + e_n(E) + e_p(E)}$$
$$u_{A,4}(E) = e_p(E) f_D(E) N_{t,A}(E)$$

$$u_{D,1}(E) = \frac{\pi f_D(E) N_{t,D}(E)}{\pi + p + e_n(E) + e_p(E)}$$
$$u_{D,2}(E) = e_n(E) f_A(E) N_{t,D}(E)$$
$$u_{D,3}(E) = \frac{\pi f_A(E) N_{t,D}(E)}{\pi + p + e_n(E) + e_p(E)}$$
$$u_{D,4}(E) = e_p(E) f_D(E) N_{t,D}(E) \quad (1.11)$$

where the occupation fraction of acceptor defects $f_A(E)$ and donor defects $f_D(E)$ are given by:

$$f_A(E) = \frac{\pi + e_p(E)}{\pi + p + e_n(E) + e_p(E)}$$
$$f_D(E) = \frac{\pi + e_n(E)}{\pi + p + e_n(E) + e_p(E)} \quad (1.12)$$

$$1 = f_A(E) + f_D(E) \quad (1.13)$$

and the emission rates of electrons $e_n(E)$ and holes $e_p(E)$ is dependent on energy of the
defect:

\[ e_n(E) = \nu n \sigma_n N_C \exp[\beta(E - E_C)] \]  

(1.14)

\[ e_p(E) = \nu p \sigma_p N_V \exp[\beta(E_V - E)] \]

We use the standard nomenclature \( \beta = q/kT \), \( N_C \) and \( N_V \) are the effective densities of states at the conduction and valence band edges, while \( E_C \) and \( E_V \) are the energies of the conduction and valence bands respectively.

Finally, the general equation for the rate of recombination through defects (\( U_{SRH} \)) \([39, 40]\) is given by the rate of recombination through acceptor defects (\( U_A \)) and the rate of recombination through donor defects (\( U_D \)):

\[ U_{SRH} = U_A + U_D \]

\[ = \int_{E_V}^{E_C} (u_{A,1} - u_{A,2}) + (u_{D,1} - u_{D,2}) dE \]

\[ = \int_{E_V}^{E_C} \pi f_D(E) N_t(E) - e_n f_A(E) N_t(E) dE \]

(1.15)

\[ = \int_{E_V}^{E_C} \frac{\pi p - e_n(E) e_p(E)}{\pi n + \pi n + e_n(E) + e_p(E)} N_t(E) dE \]

\[ = \int_{E_V}^{E_C} A_{SRH}(E) N_t(E) dE \]

where \( A_{SRH}(E) \) represents the term in the square brackets. It can be easily shown that for a discrete energy level, Equation (1.15) reduces to the various forms of \( U_{SRH} \) that are commonly presented in the literature \([7, 8, 36, 37]\).

Even though the extended solution requires integration and cannot be easily solved, Taylor and Simmons \([40]\) showed that the solution can be simplified by defining quasi-Fermi levels for traps. The quasi-Fermi levels for trapped electrons (\( E_{tn} \)) and holes (\( E_{tp} \)) correspond to the conditions when the electron or hole flows in the re-emission paths are negligible. Thus if a defect level lies below the quasi-Fermi level for trapped holes, the hole will have a greater probability of being emitted to the valence band; if a defect energy level lies above the quasi-Fermi level for trapped holes, the hole will have a greater probability of recombining with an electron from the conduction band. The converse is true with
electrons and the quasi-Fermi level for trapped electrons. These two quasi-Fermi levels for traps are given by [40]:

\[ E_{tn} = E_F - \frac{1}{\beta} \ln \left( \frac{n + p}{n_0} \right) \]

\[ E_{tp} = E_F - \frac{1}{\beta} \ln \left( \frac{n + p}{p_0} \right) \]

where \( E_F \) is the Fermi energy. Only the defect levels between the two quasi-Fermi levels for traps are effective in the recombination process and these are called “recombination centers”. Meanwhile, the recombination at the defect levels outside this region is negligible and these defect levels are called “shallow traps”. It follows that Equation 1.15 can be reduced to [40]:

\[ \hat{U}_{SRH} = \left[ \frac{np}{n + p} \right] \int_{E_{tp}}^{E_{tn}} N_t(E) dE \]

\[ = \hat{A}_{SRH} \int_{E_{tp}}^{E_{tn}} N_t(E) dE \]

where \( \hat{A}_{SRH} \) represents the term in the square brackets and is the “efficacy” [40] of the recombination between the two quasi-Fermi levels for traps. In the case where all of the density of states are between the quasi-Fermi levels for traps, the integration of \( N_t(E) \) is simply equivalent to the total density of defects \( N_T \).

### 1.3 Surface Recombination

Surface recombination \( (U_s) \) describes the recombination of light-generated or injected carriers at the surfaces of a semiconductor. The surface of a c-Si wafer is a large and abrupt discontinuity in the c-Si lattice and a large number of silicon bonds remain unsaturated. The recombination mechanisms are the same as in the bulk of the c-Si (Section 1.2), except that the geometry changes from a three-dimensional volume to a two-dimensional surface, with a large density of defects within the bandgap [8]. As a result, the contribution of radiative (Section 1.2.1) and Auger recombination (Section 1.2.1) become negligible while recombination through defects (Section 1.2.3) is dominant.

Solar cells usually have a diffused emitter and/or a dielectric layer with fixed or mobile charge carriers at the surface of the silicon [7]. This change typically forms an electric field,
resulting in band-bending at surface (Section 1.3.1). Subsequently, the surface concentrations of electrons ($n_s$) and holes ($p_s$) are almost always different to the concentrations of electrons and holes in the bulk (i.e. $n_B$, $p_B$) and are dependent on the surface band-bending ($\psi_s$). The statistics for surface recombination need to be changed as a result (Section 1.3.2). At the present time, there is no easy method for directly measuring $n_s$, $p_s$ or $\psi_s$. A number of methods have been devised for evaluating surface recombination by making particular assumptions. The resulting solutions vary in application as well as their accuracy; they can be divided into four categories:

1. Solutions at a virtual surface (Undiffused) (Section 1.3.3)
2. Solutions at a virtual surface (Diffused) (Section 1.3.4)
3. Approximate solution of the band-bending problem (Section 1.3.5)
4. Exact solution of the complete system (Section 1.3.6)

The knowledge of the surface recombination statistics and the ability to determine the surface recombination are both extremely helpful for the application and analysis of surface passivation techniques (Section 1.4).

1.3.1 Surface Band-bending

Figures 1.2 and 1.3 demonstrate on p-type and n-type silicon respectively how $n_s$, $p_s$, $\psi_s$ and the subsequent calculation of surface recombination are closely related in four characteristic surface conditions. Note that the positive potential of $\psi_s$ is downwards.

We now discuss the silicon surface conditions as for p-type silicon (Figure 1.2). When the charge on the surface—typically negative—is such that the energy bands are bent upwards at the silicon surface, holes are attracted to the surface to form an accumulation layer [Figure 1.2a]]. When there is no bending of the bands anywhere from the silicon bulk to the silicon surface, the silicon is neutral everywhere and flatband conditions are met [Figure 1.2b]].

As the surface charge—in most cases positive—changes such that the energy bands are bent slightly downwards, holes are repelled from the surface while the electron density also remains low. The low concentrations of electrons and holes at the surface leads to a depletion layer [Figure 1.2c]]. Here, the positive charge is not balanced by the electrons, but by the negative acceptor ions in the depleted region. Finally, as the energy bands are bent downwards greatly, nearly all the holes are repelled from the surface while a large
concentration of electrons become attracted to the surface. This forms an inversion layer [Figure 1.2(d)]. Underneath this inversion layer the depletion still exists and away from the surface the silicon is neutral.

Surface recombination (using Equation 1.24 for example) is typically maximal when $n_s$ and $p_s$ are approximately equal, subject to the ratio of $\sigma_n/\sigma_p$. It is useful to note that this tends to occur under depletion conditions and occasionally at flatband conditions.

The same surface conditions exist for $n$-type silicon, except the roles of electrons and holes and the direction of the band-bending are reversed (Figure 1.3). However, the direction of the band-bending as a result of positive or negative charges remains the same.

Figure 1.2: The relative concentrations of electrons and holes as related to the four distinctive surface conditions as on $p$-type silicon: (a) accumulation, (b) flatband, (c) depletion and (d) inversion.
1.3 Surface Recombination

1.3.2 Surface Recombination Statistics

Due to the surface band-bending (Section 1.3.1), the surface concentrations of electrons and holes are generally not equal as assumed in Equation 1.3. Thus, it is necessary to define a surface recombination velocity $S$ [8]. For $p$-type surfaces, this is given by:

$$S = \frac{U_s}{\Delta n_s} \quad (1.18)$$

where $\Delta n_s$ is the excess concentration of electrons at the surface. For $n$-type silicon, $\Delta n_s$ is replaced with the excess concentration of holes at the surface $\Delta p_s$. The latter and the
The surface or interface is a large discontinuity in the lattice that is unlikely to be bare (e.g. due to the presence of a native oxide) or completely planar. As a result there are usually many defect states with various defect energies. Even though this is similar to the recombination statistics of Equation 1.15, the densities of defect levels [i.e. \( N_{t,A}(E) \) \( N_{t,D}(E) \) and \( N_{t}(E) \)] in a three-dimensional volume needs to be replaced with the equivalent densities of interface states. Similar to Equation 1.19, the densities of acceptor interface states \([D_{it,A}(E)]\), donor interface states \([D_{it,D}(E)]\) and the total density of interface states \([D_{it}(E)]\) are related by:

\[
D_{it,A}(E) + D_{it,D}(E) = D_{it}(E) \quad \text{(1.20)}
\]

Also, the carrier concentrations of Equation 1.10 are replaced with the terms of Equation 1.19:

\[
n_s = \nu_{th} n_s \sigma_n \quad p_s = \nu_{th} p_s \sigma_p \quad \text{(1.21)}
\]

It follows that the occupation functions become:

\[
\begin{align*}
\dot{f}_{it,A}(E) & = \frac{\bar{n}_s + e_p(E)}{\bar{n}_s + \bar{p}_s + e_n(E) + e_p(E)} \\
\dot{f}_{it,D}(E) & = \frac{\bar{p}_s + e_n(E)}{\bar{n}_s + \bar{p}_s + e_n(E) + e_p(E)} \\
1 & = \dot{f}_{it,A}(E) + \dot{f}_{it,D}(E) \quad \text{(1.22)}
\end{align*}
\]

The rate of recombination at the surface \( U_s \) is derived in the same way as Equation 1.15 except with the substitution of the above mentioned terms.

\[
U_s = \int_{E_V}^{E_C} \frac{[\bar{n}_s \bar{p}_s - e_n(E)e_p(E)]D_{it}(E)dE}{[\bar{n}_s + \bar{p}_s + e_n(E) + e_p(E)]} \quad \text{(1.24)}
\]

It is important to note that although Equation 1.24 has been the most commonly used and widely accepted statistic for the calculation of surface recombination at a silicon surface, it is by no means the only solution. Depending on the material that is in contact with the silicon surface, defect levels with multiple energy levels and charge conditions \[34, 35\] may become important. Olibet et al. \[42\] for example, recently showed that it was possible to describe the recombination at the silicon surface using the recombination statistics of dangling bonds when the silicon surface was passivated with a layer of hydrogenated
amorphous silicon. This is analysed and discussed in Appendix B.

Independent of the statistics used, \( n_s \) and \( p_s \) need to be known for the calculation of \( U_s \). Alternatively, \( n_s \), \( p_s \) and \( \psi_s \) are neglected and the “effective surface recombination velocity” (\( S_{eff} \)) is calculated at a virtual surface \(^8\). Table 1.1 lists the four categories of solutions for deducing the surface recombination, summarising the parameters that are solved and the surface recombination parameters that are subsequently calculated.

**Table 1.1**: Summary of the assumptions and limitations for the different categories of deducing surface recombination.

<table>
<thead>
<tr>
<th>Surface Recombination Solutions</th>
<th>( S_{eff} )</th>
<th>( J_0 ) ( E ), ( J_0 ) ( surf )</th>
<th>( U_s ), ( S )</th>
<th>( U(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solutions at a Virtual Surface</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Solutions at a Diffused Surface</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Approximate Solution Band-bending Problem</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Exact Solution Complete System</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

**1.3.3 Solutions at a Virtual Surface (Undiffused)**

This method neglects \( n_s \), \( p_s \) and \( \psi_s \) and estimates the surface recombination based upon parameters at a virtual surface within the silicon. This virtual surface is situated where the band-bending \( \psi \) is zero and is indicated on Figures 1.2 and 1.3 as the vertical dashed line. It tends to be the least accurate but the most simple method as it quantifies an effective surface recombination velocity (\( S_{eff} \)) rather than the actual surface recombination (\( U_s \)).
The recombination at the surface is, on a basic level, a process that is independent to recombination in the bulk and thus can be considered as a parallel process:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{1}{\tau_{\text{s.front}}} + \frac{1}{\tau_{\text{s.rear}}}
\]

\[
\frac{1}{\tau_{\text{eff}}} = \left(\frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}}\right) + \frac{1}{\tau_{\text{s.front}}} + \frac{1}{\tau_{\text{s.rear}}}
\]

where \(\tau_{\text{s.front}}\) and \(\tau_{\text{s.rear}}\) are used to distinguish between the surface recombination lifetime \(\tau_s\) of the front and rear surfaces respectively when necessary.

The lifetime in the bulk \(\tau_b\) consists of the three types of recombination processes, as shown in Equation 1.5. However, if one uses Equation 1.18 directly, several assumptions will be invalidated in practice. The excess concentrations of electrons and holes are generally not equal at the surface due to the bending of the bands; an example of this is given in Figure 1.4. Thus, it is necessary to define an effective surface recombination velocity \(S_{\text{eff}}\) at a virtual surface \(x=d_{sc}\) where the assumption \(\Delta n = \Delta p\) is true 8:

\[
S_{\text{eff}} = \frac{U_s}{\Delta n(x=d_{sc})}
\]

We use \(S_{\text{eff.front}}\) and \(S_{\text{eff.rear}}\) when necessary to distinguish between the \(S_{\text{eff}}\) of the two surfaces of a silicon wafer. By calculating the surface recombination rate at the
1.3 Surface Recombination

virtual surface, the term $S_{\text{eff}}$ actually encompasses all the recombination that occurs from $x=0$ to $x=d_{sc}$, whereas $U_s$ is strictly the recombination at $x=0$. Typically, the recombination rate between $x=0$ and $x=d_{sc}$ is negligible compared to the recombination rate at the surface and thus $S_{\text{eff}}$ provides a valid and meaningful description of the surface recombination.

In the general case, it is not always easy to distinguish between the various processes from the dependence of the lifetime on the injection level, nor is it simple to distinguish between $S_{\text{eff,front}}$ and $S_{\text{eff,rear}}$ when the sample is not symmetrical. The presence of SRH recombination in the bulk and possible trapping effects makes it very difficult to extract the surface recombination of a sample based on lifetime measurements in the general case. Thus for the purposes of evaluating surface recombination, a high-quality undiffused $c$-Si wafer that is passivated identically on both sides [Figure 1.5(a)] should be used; the following assumptions are made:

1. $S_{\text{eff,front}} = S_{\text{eff,rear}}$
2. $\tau_{SRH} \to \infty$ in the silicon bulk.
3. The substrate doping [$N_{dop}$, i.e $N_A$ for $c$-Si(p) or $N_D$ for $c$-Si(n)] is uniform everywhere.
4. Uniform photogeneration.

When $S_{\text{eff}}$ is small, it can simply be calculated by combining Equations 1.25 and 1.26:

$$S_{\text{eff}} = \frac{W}{2} \left( \frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_b} \right)$$

(1.27)

where $\tau_b$ consists only of contributions of $\tau_{\text{Auger}}$ and $\tau_{\text{rad}}$ as the SRH recombination is negligible ($\tau_{SRH} \to \infty$) in a high-quality $c$-Si wafer. Both the values of $\tau_{\text{Auger}}$ and $\tau_{\text{rad}}$ are well established in the literature (see Sections 1.2.1 and 1.2.2), while the substrate thickness $W$ and $\tau_{\text{eff}}$ can be measured. Subsequently, $S_{\text{eff}}$ can be deduced using Equation 1.27. Its relative deviation from the exact solution is less than 4% for $S_{\text{eff}} < D_a/4W$ [44], where the ambipolar diffusion coefficient $D_a$ is given by:

$$D_a = \frac{(n + p)}{\left( \frac{n}{D_n} + \frac{p}{D_p} \right)}$$

(1.28)

where $D_n$ and $D_p$ are the electron and hole diffusion coefficients respectively. They can be considered as constant provided that $N_{dop}$ is not too high ($< 10^{16}$ cm$^{-3}$) [7, 45].
It is relevant to note that when a sample has excellent surface passivation, it can be assumed that $S_{\text{eff}} \to 0$; Equation 1.27 can be used to deduce the coefficients for Auger recombination such as with Equation 1.8.

![Figure 1.5: Examples of symmetrical samples for the determination of surface recombination. (a) Undiffused sample (b) Heavily-doped emitter.](image)

On the other hand, as $S_{\text{eff}} \to \infty$, recombination at the surface is limited by the diffusion of carriers to the surface [8, 46]:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \left( \frac{\pi^2}{W^2} \right) D_a \quad \text{for transient conditions}
\]
\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \left( \frac{12}{W^2} \right) D_a \quad \text{for steady-state conditions} \quad (1.29)
\]

In between the two limiting cases of small and large $S_{\text{eff}}$, the $S_{\text{eff}}$ can be approximated relatively accurately with the expression [44]:

\[
S_{\text{eff}} = \frac{\pi^2 D_a W (\tau_b - \tau_{\text{eff}})}{2\pi^2 D_a \tau_b \tau_{\text{eff}} - 2W^2 (\tau_b - \tau_{\text{eff}})} \quad (1.30)
\]

where the relative deviation from the exact solution is less than 5% for the whole range of $S_{\text{eff}}$. Meanwhile, the exact solution of $S_{\text{eff}}$ requires the solving of a transcendental equation where the solution is an infinite sum of modes that decay exponentially with different time constants [47]. When $S_{\text{eff}}$ is < 1000 cm/s, the first mode is clearly dominant and $S_{\text{eff}}$ can be given by:

\[
S_{\text{eff}} = \sqrt{D_a \left( \frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_b} \right) \tan \left[ \frac{W}{2} \sqrt{\frac{1}{D_a} \left( \frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_b} \right)} \right]} \quad (1.31)
\]

provided that $D_a$ is relatively constant during the interval of the measurement [48]. For measurements taken under steady-state or biased light conditions the latter is generally true; for measurements taken under transient conditions the interval over which $d\Delta n/dt$ is extracted needs to be considered. On the other hand at low injection conditions (i.e. $\Delta n \ll N_{\text{dop}}$), $D_a$ is constant with injection level regardless of the measurement conditions and can be simplified to either $D_n$ for $p$-type silicon or $D_p$ for $n$-type silicon [8].
1.3 Surface Recombination

Figure 1.6: A comparison of the $S_{\text{eff}}$ calculated from the different equations on (a) 0.8 $\Omega\cdot\text{cm}$ c-Si($p$) and (b) 1 $\Omega\cdot\text{cm}$ c-Si($n$).

The values $D_a$ used were from the carrier mobility model of Klaassen [45], the values of $\tau_b$ used were based on the parameterisation of Kerr and Cuevas [33], while the thickness of the wafer was 240 $\mu$m. Figure 1.6 demonstrates that in the main region of interest to solar cell research (i.e. wafer resistivity of $\sim$1 $\Omega\cdot\text{cm}$, $S_{\text{eff}}=10–1000$ cm/s), the $S_{\text{eff}}$ as calculated from Equations 1.27, 1.30 and 1.31 are essentially equivalent. Similar results are obtained for different thicknesses, resistivity and minority carrier densities; comprehensive analyses can be found in the original references [44, 47]. Thus, Equations 1.27, 1.30 and 1.31 can all be used with confidence for the calculation of $S_{\text{eff}}$ at a virtual surface within an undiffused wafer.

### 1.3.4 Solutions at a Virtual Surface (Diffused)

The presence of diffused layer at the surface(s) complicates the situation and additional assumptions need to be made. This method neglects $n_s$, $p_s$ and $\psi_s$ as in the previous method (Section 1.3.3) and estimates the surface recombination based upon parameters at a virtual surface within the silicon at the edge of the diffused region.

The additional considerations that need to be made are due to the presence of the $p$-$n$ junction and the band-bending associated with it. An example of a $n^+/p$ junction is given in Figure 1.7. The behaviour of carriers is affected by a number of quasi-neutral and space charge regions and there is also recombination in these regions. The surface recombination is limited by the current going into the lightly doped emitter, which is defined as the emitter saturation current density ($J_{0E}$). Thus, the surface lifetime ($\tau_s$) is
described by the emitter lifetime ($\tau_{\text{emitter}}$) \cite{49}:

$$\frac{1}{\tau_s} = \frac{1}{\tau_{\text{emitter}}} = \frac{J_0 \nu p}{q W n_{i}^{2} \Delta n}$$ \hspace{1cm} (1.32)

Figure 1.8(a) gives an example of how the lifetime curve of a $p^+/n/p^+$ sample can be separated into its various recombination processes. In this general case, the procedure is complicated by the presence of Depletion-Region Modulation (DRM) \cite{50} at low excess carrier densities. In general, many iteration of parameters are needed before the theoretical curve of $\tau_{eff}$ gives a reasonable fit of the measured lifetime. This is because the inability to accurately fit one of the recombination processes using graphical curve fitting leads to subsequent errors in fitting other recombination parameters and so forth.

In general, $J_0E$ can be dependent on the injection level. It describes the recombination between $x=0$ to $x=d_{sc}$; that is, it accounts for a number of recombination processes in addition to surface recombination at $x=0$. The presence of other recombination processes affects the validity of the assumptions behind the extraction of $J_0E$ and in some cases, the injection-dependence of the lifetime cannot be reasonably described by any of the established theories \cite{51}. Thus, the values of $J_0E$ and $S_{eff}$ obtained for the general case may have large margins of error.
1.3 Surface Recombination

There is a relatively simple case where the surface recombination can be evaluated at a virtual surface for a diffused wafer. Firstly, high-quality silicon wafers with identical heavily doped emitters and symmetrical surface passivation should be used [Figure 1.5(b)]. It is still valid to calculate the surface recombination at the virtual surface $x = d_{sc}$ provided that

1. $S_{\text{eff.front}} = S_{\text{eff.rear}}$

2. $\tau_{SRH} \to \infty$ in the silicon bulk.

3. The emitters are equal and heavily doped compared to $N_{dop}$ and are much narrower than the substrate.

4. The material constants (i.e. lifetime and mobility) in the emitters are independent of the minority carrier density.

5. The quasi-Fermi levels are constant across the space-charge region.

6. Generation and recombination in the space-charge regions are negligible.

When the above assumptions are valid, the $J_{0E}$ in Equation [1.32] is independent of the injection level [49]. By measuring the effective lifetime when the bulk is in high injection conditions (i.e. $\Delta n \gg N_{dop}$), the quadratic dependence of $J_{0E}$ on the excess carrier density makes it easily separable from the other recombination processes [49]. We can combine

**Figure 1.8:** (a) By changing the parameters of the theoretical curve until it aligns with the measured data, information concerning the recombination in a $p^+/n/p^+$ sample can be graphically extracted. (b) A $J_{0E}$ of $50 \text{ fA/cm}^2$ is graphically extracted from the slope of the lifetime curve of a $p^+/n/p^+$ sample.
Equations 1.25 and 1.32 to obtain:

\[
\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_b} = \left[ \frac{2J_{0E}}{qn_i^2W} \right] (N_D + \Delta p) \text{ for } n\text{-type} \\
= \left[ \frac{2J_{0E}}{qn_i^2W} \right] (N_A + \Delta n) \text{ for } p\text{-type} \tag{1.33}
\]

The \(J_{0E}\) can then be extracted graphically from the term in the square brackets in Equation 1.33, an example of this is given in Figure 1.8(b). As both the \(J_{0E}\) and \(S_{\text{eff}}\) are calculated at a virtual surface at the edge of the space-charge region, there is a level of equivalence between these two surface recombination parameters. This is the basis for Equation 1.34 which can convert the extracted \(J_{0E}\) to values of \(S_{\text{eff}}\) [8].

\[
S_{\text{eff}} = \frac{J_{0E}np}{qn_i^2\Delta n} \tag{1.34}
\]

Despite using \(\Delta n\) in the above equation, it is valid for both \(p\)-type and \(n\)-type silicon. This is because \(J_{0E}\) and \(S_{\text{eff}}\) are calculated at the virtual surface as defined for this method and thus the assumption \(\Delta n = \Delta p\) is valid.

Even though Equation 1.33 is usually applied to diffused emitters, it can also describe an undiffused surface. This because in both cases the surface recombination is calculated at an equivalent virtual surface as implied through Equation 1.34. In this work, when Equations 1.33 or 1.34 are applied to an undiffused surface, we replace the term \(J_{0E}\) with the term \(J_{0,\text{surf}}\) to distinguish between the diffused and undiffused surface. The physical meaning of the \(J_{0,\text{surf}}\) has not been firmly established and there are likely to be limitations to the validity of applying Equations 1.33 or 1.34 to an undiffused surface, particularly in the regions where the equations for \(S_{\text{eff}}\) differ (Figure 1.8). Therefore, it is a method that appears to be valid empirically—as shown in Section 5.5.1—but the theory behind the use of \(J_{0,\text{surf}}\) requires further clarification.

For the comparison of surface recombination between different samples, the advantage of using \(S_{\text{eff}}\) rather than the measured \(\tau_{\text{eff}}\) is that the comparison is not dependent on the thickness of the lifetime sample. The additional advantage from using \(J_{0,\text{surf}}\) or \(J_{0E}\) is that the comparison is not dependent on the thickness nor the dopant density of the sample. A surface passivation result characterised using \(J_{0,\text{surf}}\) or \(J_{0E}\) can theoretically be translated to any wafer thickness and dopant density through Equation 1.33. This is particularly useful for modelling solar cells where the wafer and dopant density of the substrate need to be changed as part of the optimisation process and these \(J_{0,\text{surf}}\) or \(J_{0E}\) parameters are used in modelling programs such as PC1D [6] and QSS Model [53].
1.3.5 Approximate Solution of the Band-Bending Problem

Whereas the solutions at a virtual surface (Sections 1.3.3 and 1.3.4) neglects the space-charge region and surface, the approximate solution of the band-bending problem considers the space-charge region and surface as a combined surface space-charge region that has constant quasi-Fermi potentials. The values of \( n_s \) and \( p_s \) are determined through the knowledge of the surface band-bending \( \psi_s \). For c-Si surfaces, \( U_s \) is usually calculated using Equation 1.24.

The quasi-Fermi potentials of electrons (\( \Phi_n \)) and holes (\( \Phi_p \)) throughout the surface space charge region \([38, 54]\) can be assumed to be constant provided that the generation and recombination in this region is negligibly small \([54]\). The recombination at the surface can then be calculated by solving the band-bending problem, whereby the band-bending \( (\psi_s) \) at the surface is iterated until the condition of charge neutrality is met \([8, 38, 54]\):

\[
0 = Q_g + Q_f + Q_{it} + Q_{sc} \\
0 = Q_g + Q_f + (Q_{it,A} + Q_{it,D}) + (Q_{sc,f} + Q_{sc,p} + Q_{sc,n})
\] (1.35)

where \( Q_g \), \( Q_f \), \( Q_{it} \) and \( Q_{sc} \) are the charges from the gate (or metal layer), insulator, the interface and the surface space charge region respectively. \( Q_{it} \) can be divided into the contributions of the charge from acceptors \( Q_{it,A} \) and donors \( Q_{it,D} \), while \( Q_{sc} \) can be divided into the contributions of charge from free electrons \( Q_{sc,n} \), free holes \( Q_{sc,p} \) and the fixed ions \( Q_{sc,f} \). The charge distribution and band diagram of a possible scenario is given in Figure 1.39. \( Q_{it,D} \) and \( Q_{sc,D} \) do not appear in Figure 1.39(a) as their contributions are negligible in this case.

For the calculation of Equation 1.35, one begins with the carrier concentrations at the edge of the space charge region, which is by definition the carrier concentrations in the bulk:

\[
n_B = n_0 + \Delta n_B \quad p_B = p_0 + \Delta p_B
\] (1.36)

The above equation is equivalent to Equation 1.22 as we also assume \( \Delta n_B = \Delta p_B \). However, we deliberately distinguish the electron and hole concentrations at the bulk (i.e. \( n_B \) and \( p_B \)) from the electron and hole concentrations at the surface (i.e. \( n_s \) and \( p_s \)) as well as from the general electron and hole concentrations (i.e. \( n \) and \( p \)). The quasi-Fermi levels of holes and electrons are given by:

\[
\Phi_n = \frac{1}{\beta} \ln \left( \frac{n_B}{n_i} \right) \quad \Phi_p = \frac{1}{\beta} \ln \left( \frac{p_B}{n_i} \right)
\] (1.37)
Figure 1.9: An illuminated \( p \)-type silicon wafer passivated with a positively-charged insulator, with a metal gate on the insulator, showing (a) the charge distribution and (b) the band diagram.

and they are assumed to be constant throughout the bulk of the silicon to the silicon surface, as shown in Figure 1.9(b).

The charges in the surface space charge region can be separated into its contribution from electrons \( (Q_{sc,n}) \), holes \( (Q_{sc,p}) \) and fixed charges \( (Q_{sc,f}) \) as given in Equation 1.35. However, this requires complex integration \[43\] and is not directly relevant to the work of this thesis, so we only present the equation for the total charge in the surface space charge region \( (Q_{sc}) \):

\[
Q_{sc} = Q_{sc,f} + Q_{sc,p} + Q_{sc,n} = -Sgn(\psi_s) \sqrt{\frac{2\varepsilon_0 \varepsilon_{Si}}{\beta q}} \left[ p_B(\exp(-\beta \psi_s) + \beta \psi_s - 1) + n_B(\exp(\beta \psi_s) - \beta \psi_s - 1) \right] \quad (1.38)
\]

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_{Si} \) is the dielectric constant of silicon and \( Sgn(\psi_s) \) is the sign of \( \psi_s \). The derivation and forms of \( Q_{sc} \) is discussed in detail in Appendix A.2.
Meanwhile, the charges at the interface are given by:

\[
Q_{it,D} = \int_{E_V}^{E_C} D_{it,D}(E)f_{it,D}(E)dE \\
Q_{it,A} = -\int_{E_V}^{E_C} D_{it,A}(E)f_{it,A}(E)dE
\]  

(1.39)

The fixed charge in the insulator \(Q_f\) is independent of the quasi-Fermi potentials and the band-bending. It is either a known property of the insulator or can be determined (e.g. by capacitance-voltage measurements as described in Section 2.2.3). Finally, the charge at the gate is given by:

\[
Q_g = -\frac{1}{d_i} \left( \frac{Q_f d_f}{2} + \frac{\varepsilon \varepsilon_{\alpha x}}{q} (\psi_s - V_a + \phi_{MS}) \right)
\]  

(1.40)

where \(\varepsilon_{\alpha x}\) and \(d_{\alpha x}\) are the dielectric constant and thickness of the insulator respectively, \(d_f\) is the width of the charge sheet in the insulator, \(V_a\) is the applied gate voltage. The metal-silicon work function \(\phi_{MS}\) is given by [41]:

\[
\phi_{MS} = \phi_M - \chi_{Si} + (E_C - E_i) + (E_i - E_F)
\]  

(1.41)

where \(\phi_M\) is the metal work function, \(\chi_{Si}\) is the electron affinity of silicon and \(E_i\) is the intrinsic Fermi energy.

The charge neutrality condition is solved by numerically iterating \(\psi_s\). When a value of \(\psi_s\) satisfying Equation 1.35 is found, this is used to find the surface concentration of electrons and holes [41]:

\[
n_s = n_B \exp (\beta \psi_s) \quad p_s = p_B \exp (-\beta \psi_s)
\]  

(1.42)

Finally, the values of \(n_s\) and \(p_s\) are in turn substituted into Equation 1.24 to calculate the rate of surface recombination. Even though this method is more complicated than the solutions at a virtual surface (Sections 1.3.3 and 1.3.4) and computers are required for the numerical iteration, it allows the calculation of \(n_s\), \(p_s\) and \(\psi_s\). These parameters offer very useful insight into the conditions at the surface, particular with evaluating the effectiveness of “field-effect passivation” (Section 1.4).
1.3.6 Exact solution of the Complete System

The knowledge of the band-bending $\psi$, $n$ and $p$ everywhere in the silicon [i.e. $\psi(x)$, $n(x)$ and $p(x)$] is found by solving the Poisson equation, the continuity equation for electrons and holes \[41\] and the boundary conditions imposed by the properties of surface. The recombination everywhere in the silicon [$U(x)$], including the surface, is deduced. This exact solution is possible with numerical modelling programs, but there are considerable time and computation hardware requirements.

The numerical modelling programs can be grouped in terms of the number of dimensions it models. An example of a one-dimensional device modelling program is [PC1D 6], while DEvice Simulation for Smart Integrated Systems [DESSIS 55] is an example of a multi-dimensional device modelling program. The higher number of dimensions used increases the precision of the solution, but also increases the complexity of the equations as well as the hardware and time requirements for solving the equations.

1.4 Surface Passivation for Silicon Solar Cells

Surface passivation refers to the techniques employed to reduce and minimise surface recombination. Surface recombination (Section 1.3) is one of the major factors that limit the performance of high-efficiency $c$-Si solar cells and effective surface passivation techniques are required for overcoming these limitations [1, 7]. Based on the statistics of surface recombination, it can be deduced that there are two fundamental strategies for surface passivation [8].

- **Optimisation of the properties of the surface states**—The density of defect states as well as the capture cross-sections have a strong influence on the rate of surface recombination through defects. Depositing or growing an appropriate passivating film will tie up the dangling bonds and reduce the $D_{it}$, subsequently reducing the recombination through defects.

- **Reduction of surface concentration of electrons or holes**—The rate of surface recombination is generally maximised when the surface concentration of electrons and holes are approximately equal. Thus, by reducing the surface concentration of either the electrons or holes, the recombination rate will decrease. This can be realised by the implementation of a doping profile at the surface, or by creating an electric field with electrostatic charges in an overlying insulator. The latter is also known as “field-effect passivation” [56].
There exists a large range of surface passivation methods that utilise one or both of the above surface passivation strategies. A combination of these methods is usually employed for reducing the surface recombination in a solar cell. The surface passivation methods can be grouped into three categories; their ability to address the two surface passivation strategies is outlined in Table 1.2 and are described in the following subsections.

Table 1.2: The utilisation of the two surface passivation strategies by three types of surface passivation techniques.

<table>
<thead>
<tr>
<th>Surface Passivation Technique</th>
<th>Chemical Passivation (Section 1.4.1)</th>
<th>Surface Doping (Section 1.4.2)</th>
<th>Dielectric Films (Section 1.4.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Passivation Strategies</td>
<td>• Optimisation of the properties of the surface states ✓ ✓ ✓</td>
<td>• Reduction of the surface concentration of electrons or holes ✓ ✓ ✓</td>
<td></td>
</tr>
</tbody>
</table>

1.4.1 Chemical Passivation

Chemical methods focus on optimising of the properties of the surface states. By dipping the silicon wafer into particular solutions (e.g., HF, alcoholic iodine solution), very low surface recombination velocities can be achieved. However, this surface passivation is very sensitive to the preparation of the wafer surface and its lack of stability rules out an application to practical solar cells. Nonetheless, these methods are very useful for characterisation purposes.

1.4.2 Surface Doping

Heavy emitter doping and high-low junctions focus on reducing the concentration of either electrons or holes. These methods are usually implemented by the alloying of metals (e.g., Aluminium) or diffusion of dopants (e.g., Boron, Phosphorus) at the surface of the silicon.

The equilibrium equation (Equation 1.1) implies that if one of the carrier types is increased by doping, the concentration of the other carrier is suppressed. Although the minority carrier density increases under illumination, there is still an imbalance in the concentrations of p and n. When a good surface doping scheme is applied, the imbalanced concentrations of the carriers are far from the ideal conditions for SRH recombination; the
potential barrier present between the high and lowly doped regions help to "confine" carriers in the lowly doped wafer—keeping them away from recombination at the surfaces—and the recombination rate can be expected to be lower. As the doping increases however, an increase in Auger recombination in the emitter can be expected. Thus, the emitter surface concentration is typically moderated to $\sim 10^{20}$ cm$^{-3}$ or lower ($5 \times 10^{18}$ to $10^{19}$ cm$^{-3}$ is typical of optimised emitters [8]) to achieve a net reduction in the rate of recombination.

Good suppression of surface recombination in solar cells can be achieved with optimised emitters and high-low junctions. These can cover the entire area of the solar cell (e.g. Aluminium Back Surface Field (Al-BSF) [61]) or are only implemented at the metal contacts ("locally diffused" or "selective" emitters) [1]. These steps are usually incorporated into the formation of the $p$-$n$ junction and the metallisation of the solar cells. In combination with passivating dielectric films (Section 1.4.3) on the doped surfaces, excellent surface passivation can be achieved. This has historically led to a number of record-breaking solar cell efficiencies on crystalline silicon, such as the Passivated Emitter, Rear Locally diffused (PERL) solar cell depicted in Figure 1.10 [12, 60, 62].

The high temperatures (> 800°C) and the long processing times (1–3 h) that are traditionally required for the creation of optimised emitters are unattractive in the manufacturing of solar cells and subsequently their utilisation has been limited. However, alternative methods such as laser doping [63] and silicon inks [64] have become available in recent years and they offer fast and low-temperature solutions for the application of surface doping.
1.4 Surface Passivation for Silicon Solar Cells

1.4.3 Dielectric Films

The deposition or growth of dielectrics typically utilises both surface passivation strategies to reduce the rate of recombination. Table 1.3 lists the key properties of the dielectric films that are reviewed in this section. The given values are approximate, but representative enough to offer a reasonable comparison for the purposes of this review (e.g. the typical values of $Q_{ox}$ are reported rather than the whole range of possible $Q_{ox}$).

Table 1.3: Comparison of the key properties of four dielectric films used for c-Si solar cells.

<table>
<thead>
<tr>
<th>Dielectric</th>
<th>SiO$_2$</th>
<th>SiN$_x$</th>
<th>a-Si:H</th>
<th>AlO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Method</td>
<td>Thermal</td>
<td>PECVD</td>
<td>PECVD</td>
<td>PA-ALD</td>
</tr>
<tr>
<td>$S_{eff}$ (cm/s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• 2 Ω.cm c-Si(p)</td>
<td>6 [51]</td>
<td>5 [8]</td>
<td>3 [43]</td>
<td>3$^{(a)}$ [17]</td>
</tr>
<tr>
<td>• 3.5 Ω.cm c-Si(n)</td>
<td>2.4 [51]</td>
<td>2 [65]</td>
<td>7 [43]</td>
<td>0.8$^{(a)}$ [14]</td>
</tr>
<tr>
<td>$J_{0E}$ (fA/cm$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• 100 Ω/□ (n)</td>
<td>26 [51]</td>
<td>38 [51]</td>
<td>18$^{(c)}$ [68]</td>
<td>N/A</td>
</tr>
<tr>
<td>$Q_{ox}$ (cm$^{-2}$)</td>
<td>+$10^{11}$ [8]</td>
<td>+$10^{12}$ [8]</td>
<td>±$10^{11(d)}$ [69]</td>
<td>−$10^{13(a)}$ [25]</td>
</tr>
<tr>
<td>$D_{it}$ (cm$^{-2}$eV$^{-1}$)</td>
<td>10$^{11}$ [8]</td>
<td>10$^{11}$ [8]</td>
<td>10$^{10(d)}$ [69]</td>
<td>10$^{11(a)}$ [70]</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$)</td>
<td>3.9 [8]</td>
<td>7.5 [8]</td>
<td>11.8 [71]</td>
<td>8.9$^{(a)}$ [72]</td>
</tr>
<tr>
<td>Refractive index ($\hat{n}$)</td>
<td>1.5 [8]</td>
<td>2 [8]</td>
<td>5 [73]</td>
<td>1.6 [17]</td>
</tr>
<tr>
<td>Firing stability (°C)</td>
<td>&lt; 1200 [8]</td>
<td>&gt; 800 [65]</td>
<td>&lt; 820$^{(c)}$ [74]</td>
<td>&gt; 830 [75]</td>
</tr>
<tr>
<td>Deposition rate (nm/min)</td>
<td>&lt; 0.5 [76]</td>
<td>&lt; 600 [8]</td>
<td>&lt; 600 [24]</td>
<td>&lt; 2 [17]</td>
</tr>
</tbody>
</table>

$^{(a)}$ After annealing at 425°C in N$_2$ for > 5 min.
$^{(b)}$ After annealing at 450°C in N$_2$ for 240 min.
$^{(c)}$ Includes the use of a SiN$_x$ capping layer.
$^{(d)}$ Includes the use of doped a-Si:H.

Thermally grown oxide films (SiO$_2$) have traditionally provided the best surface passivation on a wide range of silicon surfaces and doping [41, 77]. As the oxide consumes the silicon at the surface and grows into the wafer, the resulting shift of the interface ensures a low $D_{it}$ while the positive electrostatic charges in the oxide also contribute to surface passivation [78]. Even though they have been a feature of high-efficiency solar cells [12, 60], the high temperatures required and the long oxidation times have limited their adaptation and widespread use in industrial solar cells [79].
Hydrogenated amorphous silicon nitride ($\text{SiN}_x$) deposited by PECVD is the most widely used dielectric layer in c-Si solar cells. The low temperature typically used for its deposition ($< 400^\circ\text{C}$) and the fast deposition times offer practical advantages in the manufacturing of solar cells. In addition, the SiN$_x$ film is compatible with metallisation processes, has ideal anti-reflection properties and is capable of providing excellent surface passivation \cite{8}. With additional high temperature annealing, the hydrogen-rich film can also improve the bulk lifetime of multicrystalline silicon through the hydrogen passivation of defects \cite{80}. Being a positively charged dielectric, SiN$_x$ is well adapted to passivating n-type surfaces \cite{9}. On lowly doped p-type surfaces, however, it can cause shunting at the metal contacts, leading to undesired current losses in a solar cell \cite{43}. Meanwhile on highly doped p-type surfaces, good surface passivation is possible but up to 4 hours of annealing is required \cite{66}, making it impractical for commercial solar cells.

![Figure 1.11: Schematic view of a HIT solar cell \cite{81,82}.
](image)

Intrinsic hydrogenated amorphous silicon (a-Si:H) deposited by PECVD offers similar advantages to SiN$_x$ with the deposition method, but avoids the problems with shunting at the metal contacts. Excellent surface passivation have been achieved on both undiffused \cite{43} and diffused \cite{67} p- and n-type surfaces. In using doped layers of a-Si:H, the resulting Heterojunction with Intrinsic Thin layer (HIT) structure \cite{83} has led to high efficiency heterojunction solar cells (Figure \ref{fig:1.11} \cite{81,82,84,85}. However, only low temperature ($< 300^\circ\text{C}$) processing steps can be used after the deposition of the a-Si:H (see Appendix C) and the layers have significant absorption in the visible part of the solar spectrum. The problems with thermal stability can be overcome by using a thick layer of a-Si:H with a capping layer of SiN$_x$, but then losses at the metal contacts will be a problem \cite{74}.

Aluminium oxide deposited by PA-ALD is a strongly negatively charged dielectric \cite{25} that has provided excellent surface passivation of p-type surfaces and on lowly doped n-


1.4 Surface Passivation for Silicon Solar Cells

type surfaces \[17, 75, 86, 87\] as well as the otherwise difficult to passivate highly doped (diffused) \(p\)-type surfaces \[11\]. The advantage of \(\text{AlO}_x\) being negatively charged is that it can improve on the surface passivation that would be achieved using an \(\text{Al-BSF}\) on \(p\)-type solar cell technologies, while avoiding the shunting losses that would otherwise occur from the use of \(\text{SiN}_x\) \[10\]. Solar cell efficiencies of up to 21.5% have been achieved by using \(\text{AlO}_x\) as the rear side passivation of Passivated Emitter and Rear Cell (PERC) solar cells \[88–91\]. Alternatively, \(\text{AlO}_x\) can be applied to \(n\)-type solar cell technologies by passivating the diffused \(p\)-type emitter. Solar cell efficiencies of up to 23.2% have been achieved by using \(\text{AlO}_x\) to passivate the front boron emitter on a \(\text{PERL}\) solar cell \[12\] and up to 19% when the \(\text{AlO}_x\) is used to passivate the rear aluminium emitter on Back-Junction Back-Contact (BJBC) solar cells \[92\].

Even though the anti-reflection properties of \(\text{AlO}_x\) are not as ideal as that of \(\text{SiN}_x\), \(\text{AlO}_x/\text{SiN}_x\) double layers \[75\] have been successfully applied to achieve excellent anti-reflection properties. Alternatively, the solar cell can be designed such that the \(\text{AlO}_x\) layer is on the rear of the solar cell \[88\]. The main limitation preventing the adaptation of \(\text{PA-ALD}\) \(\text{AlO}_x\) into manufacturing is the low deposition rate of \(< \, 2\, \text{nm/min}\), whereas the deposition rates need to be \(> \, 60\, \text{nm/min}\) to be relevant to manufacturing \[24\].

\(\text{AlO}_x\) as a material can meet the shortcomings of \(\text{SiO}_2\), \(\text{SiN}_x\) and \(n\)-\(\text{Si:H}\), but the deposition method of \(\text{PA-ALD}\) is unlikely to be able to meet the requirements for manufacturing. The use of ultrathin layers \[14, 75, 100\] and \(\text{AlO}_x/\text{SiN}_x\) stacks \[75, 93\] have been presented as possible solutions for utilising \(\text{PA-ALD}\) \(\text{AlO}_x\). Alternatively, deposition methods such as thermal ALD \[17, 18, 23\], sol-gel \[16, 19, 20\], APCVD \[9\], PECVD \[17, 21, 22\], sputtering \[16, 23\], thermal evaporation \[101\] and Molecular Beam Epitaxy (MBE) \[102\] can be used.

The \(\text{AlO}_x\) in its as-deposited state provides very poor surface passivation and a post-deposition anneal—typically \(\sim 425^\circ\text{C}\) in \(\text{N}_2\) for \(> 5\, \text{min}\)—is required for achieving a good level of surface passivation. Table 1.4 compares the key differences of the different deposition methods. The deposition methods are not differentiated into its various forms (e.g. the different methods of ref. \[17\] and ref. \[21\] in depositing \(\text{AlO}_x\) using PECVD). The given values are for after a post-deposition anneal; they are approximate and representative values that offer a reasonable comparison between the current capabilities of the different deposition methods. It is quite possible that the \(\text{AlO}_x\) from the various deposition methods will be improved in the near future.

PECVD and sputtering are the two most promising solutions, as they are deposition methods that are most suitable and already widely used in solar cell manufacturing.
Table 1.4: Comparison of AlO$_x$ deposited by different methods.

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>PA-ALD</th>
<th>Thermal ALD</th>
<th>Sol-gel</th>
<th>APCVD</th>
<th>PECVD</th>
<th>Sputtering$^{(a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{eff}$ (cm/s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• 2 Ω.cm c-Si(p)</td>
<td>2.6 [93]</td>
<td>4 [17]</td>
<td>100$^{(c)}$ [16]</td>
<td>210 [9]</td>
<td>2.9 [17]</td>
<td>N/A</td>
</tr>
<tr>
<td>• 3.5 Ω.cm c-Si(n)</td>
<td>0.8 [14]</td>
<td>2 [14]</td>
<td>N/A</td>
<td>N/A</td>
<td>0.8 [17]</td>
<td>N/A</td>
</tr>
<tr>
<td>$J_{0E}$ (fA/cm$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• 100 Ω/$\square$ (p)</td>
<td>10 [11]</td>
<td>20 [91]</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>• 100 Ω/$\square$ (n)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$Q_{ox}$ (cm$^{-2}$)</td>
<td>$10^{12}$–$10^{13}$ [25]</td>
<td>$10^{12}$–$10^{13}$ [25]</td>
<td>$(1–5)\times10^{12}$ [20]</td>
<td>$3\times10^{12}$ [9]</td>
<td>$(2–6)\times10^{12}$ [17, 21]</td>
<td>$\pm1\times10^{11}$ [94]</td>
</tr>
<tr>
<td>$D_{it}$ (cm$^{-2}$eV$^{-1}$)</td>
<td>$2\times10^{11}$ [70]</td>
<td>$10^{11}$–$10^{12}$ [25]</td>
<td>N/A</td>
<td>$8\times10^{10}$ [9]</td>
<td>$(2–5)\times10^{10}$ [21]</td>
<td>$&lt;5\times10^{10}$ [95]</td>
</tr>
<tr>
<td>$\bar{n}$</td>
<td>1.6–1.65 [17]</td>
<td>1.6–1.65 [17]</td>
<td>1.55–1.7$^{(c)}$ [16]</td>
<td>1.65 [9]</td>
<td>1.5–1.65 [17, 21]</td>
<td>1.6–2.1 [96]</td>
</tr>
<tr>
<td>Deposition rate (nm/min)</td>
<td>$&lt;2$ [17]</td>
<td>$&lt;1$ [17]</td>
<td>$&lt;300^{(d)}$ [20]</td>
<td>N/A</td>
<td>$&lt;100$ [21]</td>
<td>$&lt;146$ [99]</td>
</tr>
<tr>
<td>Dangerous materials</td>
<td>Yes$^{(e)}$</td>
<td>Yes$^{(e)}$</td>
<td>No</td>
<td>Yes$^{(e)}$</td>
<td>Yes$^{(e)}$</td>
<td>No</td>
</tr>
</tbody>
</table>

$^{(a)}$ Prior to the results of this thesis.

$^{(b)}$ Includes the use of a AlO$_x$/SiO$_x$ stack.

$^{(c)}$ (Al$_2$O$_3$)$_x$(TiO2)$_{1-x}$ pseudo-binary alloy.

$^{(d)}$ Does not account for the time required for drying or annealing after deposition (~2 h).

$^{(e)}$ Requires the use of various alkyl aluminium, alkyl aluminium hydride and alkyl amino aluminium precursors that are usually pyrophoric.
PECVD is the dominant deposition method for SiNₓ and a-Si:H while sputtering is used for the deposition of Transparent Conductive Oxides (TCO) [81, 103, 104]. The best results so far have been with PECVD AlOₓ, with deposition rates of 100 nm/min and $S_{\text{eff}}$ values of around 10 cm/s [21]. Sputtering can achieve rates of up to 150 nm/min for the deposition of AlOₓ [99], although its surface passivation capabilities are unknown. It remains to be seen whether PECVD or sputtering will be the dominant method for depositing AlOₓ in solar cell manufacturing. In either case, negatively charged dielectric films are becoming available for surface passivation of commercial c-Si solar cells.
Chapter 2

Overview of Characterisation Techniques

“Characterization techniques that allow the spatial variation of the material quality to be assessed quantitatively, quickly and without being affected by artefacts can be invaluable tools in the development of high efficiency solar cells and for effective process monitoring.”

T. Trupke et al., 2006 [103]

2.1 Introduction

The characterisation techniques used in this thesis are reviewed and discussed in this chapter to provide a basis for interpreting the experimental data presented in Chapters 3–6. Section 2.2 reviews the techniques for evaluating surface passivation provided by the AlO$_x$ films, while Section 2.3 reviews the techniques used for the physical analyses of the AlO$_x$ films.

2.2 Evaluating Surface Passivation

The surface recombination (Section 1.3) resulting from a surface passivation method (Section 1.4) can be measured or deduced from a variety of characterisation techniques. Table 2.1 lists the techniques used for evaluating surface passivation in this thesis and summarises the parameters that are measured. The different parameters that are measured and calculated from the different characterisation techniques offer valuable but incomplete information concerning the surface passivation technique. The various characterisation techniques can be used in parallel—either on the same sample or on a sister sample—to provide a more comprehensive analysis of a surface passivation method.
Table 2.1: Summary of techniques used for the evaluation of surface passivation in this thesis. Only the parameters relevant to this thesis have been listed.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Parameters Changed</th>
<th>Measured Parameters</th>
<th>Calculated Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoconductance (Section 2.2.1)</td>
<td>Illumination, time</td>
<td>$\Delta n$, $\tau_{eff}$</td>
<td>$\tau_{SRH}$, $S_{eff}$, $J_0$, $J_{0, surf}$</td>
</tr>
<tr>
<td>Photoluminescence (Section 2.2.2)</td>
<td>Illumination, time</td>
<td>$\Delta n$, $\tau_{eff}$</td>
<td>$\tau_{SRH}$, $S_{eff}$</td>
</tr>
<tr>
<td>Capacitance-Voltage (Section 2.2.3)</td>
<td>$V_a$, $C_{tot}$, $Q_{ox}$</td>
<td>$Q_{ox}$, $\psi_s$, $D_{it}$</td>
<td></td>
</tr>
<tr>
<td>Kelvin Probe (Section 2.2.4)</td>
<td>–</td>
<td>$V_a$</td>
<td>$Q_{ox}$</td>
</tr>
<tr>
<td>Corona-Lifetime (Section 2.2.5)</td>
<td>$Q_{surface}$, $V_a$, $\Delta n$, $\tau_{eff}$</td>
<td>$Q_{ox}$, $S_{eff}$</td>
<td></td>
</tr>
</tbody>
</table>

2.2.1 Photoconductance Techniques

![Figure 2.1: The arrangement for measuring photoconductance using (a) transient photoconductance and (b) microwave-detected photoconductance decay.](image)

Transient photoconductance is the primary method used to determine the effective carrier lifetime ($\tau_{eff}$) of the c-Si samples used in this work. A Sinton Consulting WCT-100 lifetime tester is used and the general arrangement for this measurement is shown in Figure 2.1(a). An appropriate calibration sample is first placed on the coil and the capacitor and resistor are adjusted to balance the coil. After this, the calibration sample is replaced with the sample to be measured. The sample is temporarily illuminated with a flash lamp; after the photogeneration has decreased to small levels, the excess photoconductance ($\sigma_L$)
of the sample is measured over time with an oscilloscope or Radio-Frequency (RF) bridge circuit:

\[ \sigma_L(t) = q \Delta n(t)(\mu_n + \mu_p)W \]  

(2.1)

where \( \mu_n \) and \( \mu_n \) are the electron and hole mobility respectively. The values of \( \Delta n \) are deduced from the measured values of \( \sigma_L \), which are then converted to values of \( \tau_{\text{eff}} \):

\[ \tau_{\text{eff}} = -\frac{\Delta n}{d\Delta n/dt} \]  

(2.2)

After this relationship between \( \tau_{\text{eff}} \) and \( \Delta n \) is determined, the surface recombination can be deduced as described in Section 1.3. The measured data is typically graphed as the dependence of the \( \tau_{\text{eff}} \) on \( \Delta n \) [Figure 2.2(a)] or can be graphed as the dependence of the \( S_{\text{eff}} \) on \( \Delta n \) [Figure 2.2(b)]. For the comparison of the surface passivation between a large set of samples, the value of \( \tau_{\text{eff}} \) or \( S_{\text{eff}} \) at \( \Delta n = 10^{15} \text{ cm}^{-3} \) is generally quoted by convention (see for example, ref. [17, 43]).

![Figure 2.2: The photoconductance results for a 1 Ω cm FZ c-Si(n) wafer passivated with 50 nm of a-Si:H on both sides. (a) The dependence of the measured \( \tau_{\text{eff}} \) on the excess carrier density. (b) The dependence of the calculated \( S_{\text{eff}} \) on the excess carrier density, after subtracting Auger and radiative recombination.](image)

Alternatively, it is possible to compare the values of implied open-circuit voltage \( (iV_{\text{oc}}) \). This is because the measurement of the excess minority carrier density implies an equivalent voltage that would be measured. This is given by [106]:

\[ iV_{\text{oc}} = \frac{1}{\beta} \ln \left( \frac{np - n_i^2}{n_i^2} \right) \]  

(2.3)

Even though the transient photoconductance method will have difficulty in analysing low
lifetime samples, for high lifetime samples it is more accurate and reliable than Quasi-Steady-State Photoconductance (QSSPC) or generalised photoconductance methods. This is because the optical properties of the sample and the use of a reference solar cell in QSSPC and generalised photoconductance methods introduce additional assumptions and uncertainties that may reduce the accuracy of the measurement.

Figure 2.3: A microwave photoconductance image of passivated wafer, showing the spatial dependence of the lifetime.

The spatial dependence of the lifetime can be mapped using Microwave-detectected Photoconductance Decay (MWPCD); the general arrangement for this measurement is shown in Figure 2.1(b). The sample is illuminated from above with a diode laser ($\lambda = 904$ nm), while microwaves ($\omega = 22$ GHz) are directed through a waveguide to the bottom of the wafer. As only a small area of the wafer (3–22 mm$^2$) is illuminated by the laser, the reflected microwaves yield information on the photoconductance and thus the lifetime of the particular area. By scanning the entire surface of the wafer, the spatial dependence of the lifetime is mapped. An example is given in Figure 2.3 where a quarter of a 4" $n$-type wafer is passivated with AlO$_x$ deposited by thermal ALD. The area of highest lifetime is in the middle, while the lifetime decreases towards the edge of the wafer due to additional recombination at the edge of the wafer.

2.2.2 Photoluminescence Techniques

Quasi-Steady-State Photoluminescence (QSSPL) can also be used to determine the relationship between $\tau_{eff}$ and $\Delta n$ to determine surface recombination. Rather than the use of a flash lamp as with photoconductance (Section 2.2.1), the illumination from a Light-Emitting Diode (LED) array is controlled such that the electronic properties of the silicon sample will reach an effective steady-state or "quasi-steady-state". Then, $\Delta n$ is determined by measuring the photons emitted from the sample due to radiative
2.2 Evaluating Surface Passivation

The relative Photoluminescence (PL) intensity \( I_{PL,rel} \) is directly related to \( \Delta n \) by [110]:

\[
A_i I_{PL,rel} = B(N_D + \Delta n)\Delta n
\]  
(2.4)

where \( A_i \) is a calibration factor. The relationship between \( \tau_{eff} \) and \( \Delta n \) is then determined by [109]:

\[
\tau_{eff} = \frac{\Delta n(t)}{f_{PL}G_{rel}(t) - \frac{d\Delta n(t)}{dt}}
\]  
(2.5)

where \( f_{scale} \) is a scaling factor and \( G_{rel}(t) \) is the relative generation rate, both of which are determined using a self-consistent calibration method [109].

\[\text{Figure 2.4:}\] The generalised photoconductance and QSSPL results for a \( p^+/n/p^+ \) structure, passivated with 50 nm of a-Si:H on both sides.

QSSPL has several major advantages over photoconductance techniques: it is not affected by DRM [50, 111, 112] or minority carrier traps [113, 114]. It is able to accurately determine \( \tau_{eff} \) to very low \( \Delta n \), but for practical reasons related to the LED, the measurements are currently unable to determine the \( \tau_{eff} \) to high \( \Delta n \). Given the complementing range of \( \Delta n \) that can be measured by photoconductance and photoluminescence techniques, an extended range of \( \tau_{eff} \) can be reliably determined using an appropriate combination of the two measurement techniques. Figure 2.4 gives an example of how the photoconductance and photoluminescence measurements of a particular sample can complement each other.

Photoluminescence imaging uses the same principles as QSSPL. Rather than quantifying the \( \tau_{eff} \) and \( \Delta n \) as values averaged over the whole sample, the relative lifetime across the sample is spatially resolved [113]. Also, the LED is typically replaced with a
2. Overview of Characterisation Techniques

Figure 2.5: A PL image of a 4” boron-diffused wafer, identifying surface defects.

Laser (\(\lambda=808\,\text{nm}\)) for the illumination of the sample. The image allows the identification of local areas with low lifetimes. If a high-quality c-Si wafer is used, \(\tau_b\) can be assumed to be high and spatially uniform; thus the local areas with low lifetimes identify areas with high surface recombination \[65\]. A BT Imaging LIS-R1 system was used for this work. Figure 2.5 gives an example of PL image identifying surface passivation issues in a 4” boron-diffused wafer passivated with sputtered AlO\(_x\). The scale given in the image is a relative scale with arbitrary units, with the brighter areas indicate regions of higher lifetime, while the shape and the location of the dark marks can help identify the causes of low lifetime \[65\]. The black marks on the top left corner is due to the scribing of the wafer label, while the marks at the centre of the wafer is most likely from scratching of the surface during some of the processing steps.

2.2.3 Capacitance-Voltage Measurements

The Capacitance-Voltage (C-V) measurement—and the parallel measurement of the Conductance-Voltage (G-V)—of a Metal-Oxide-Semiconductor (MOS) capacitor has been a common technique for characterising the surface passivation quality of oxides \[77\]. The technique is also applicable to other dielectric films provided that the leakage current is small. For consistency with the terms and equations found in various texts (e.g. Nicollian and Brews \[77\], Schroder \[27\]), we have kept the use of term “oxide” and its related nomenclature, even if the dielectric evaluated is not strictly an oxide. Similarly, the silicon capacitance (\(C_{Si}\)) actually refers the the capacitance of the surface space-charge region, but we maintain the use of term “silicon capacitance” here.
2.2 Evaluating Surface Passivation

Figure 2.6: (a) The standard MOS structure used for this work and (b) an enlarged cross-section showing a simple equivalent circuit.

Figure 2.6 shows the typical structure of a MOS used for C-V measurements. An undiffused silicon wafer is passivated on one side with the dielectric film to be evaluated. The metal contacts on the dielectric need to be a defined area and thickness—their required values depend on the properties of the dielectric—while the metal chosen for the ohmic contact on the rear must ensure the series resistance kept to acceptable levels (< 20 Ω). The band diagram for this structure is the same as in Figure 1.9.

A number of different charges are typically present in the oxide. They may be positive or negative and are usually the result of various structural defects, impurities, or trapped electrons or holes [27]. In this work, only the independent contribution of \( Q_{it} \) and its related capacitance \( C_{it} \) are important for surface passivation; the remaining charges in the oxide are summarised as the oxide charge \( Q_{ox} \) and its related capacitance \( C_{ox} \). The latter is related to the area of the metal (\( A_{metal} \)), the thickness of the oxide (\( d_{ox} \)) as shown in Figure 2.6 and the dielectric constant of the oxide (\( \varepsilon_{ox} \)) by:

\[
C_{ox} = \frac{\varepsilon_0 \varepsilon_{ox} A_{metal}}{d_{ox}}
\]  

The total capacitance (\( C_{tot} \)) is defined as the change in the total charge (Equation 1.35) due to a change in the applied voltage (\( V_a \)), which is then related to \( C_{ox} \), \( C_{it} \) and \( C_{Si} \) by the equation [27, 77]:

\[
\frac{dV_a}{dQ_{tot}} = \frac{1}{C_{tot}} = \frac{1}{C_{Si}(\psi_s) + C_{it}(\psi_s)} + \frac{1}{C_{ox}}
\]  

where \( C_{it} \) and \( C_{Si} \) are dependent on the band-bending \( \psi_s \). The relation between \( \psi_s \) and \( V_a \) can be solved using the approximate solution of the band-bending problem as described in Section 1.3.5). By measuring \( C_{tot} \) and \( V_a \) in the C-V measurement and deducing the values of \( \psi_s \), \( C_{it} \) and \( C_{Si} \), it is possible to deduce surface passivation characteristics such
as the $D_{it}$ and the charges at the various parts of the MOS (Appendix A). There are typically two levels of changes in the voltage during a $C-V$ measurement:

1. Change in $V_a$

   The applied Direct Current (DC) voltage $V_a$ is stepped over time. This is typically done under equilibrium conditions (i.e. $t_{step}$ is sufficiently long) such that all carriers respond to this change in voltage. When $V_a$ is changed rapidly (i.e. $t_{step}$ is very short) with insufficient time for inversion charge generation, deep depletion conditions occur.

2. Change in $\Delta V_a$

   A small Alternating Current (AC) voltage superimposed on $V_a$; the amplitude $a$ is much smaller than $V_{step}$ while the frequency $\omega$ typically ranges from 100 Hz to 1 MHz. The term “high frequency” refers to the conditions when the frequency of the measurement is sufficiently high that neither the interface traps nor minority carriers follow the AC gate voltage. On the other hand, “low frequency” refers to the conditions when the frequency of the measurement is sufficiently low that the interface traps and minority carriers immediately respond to AC gate voltage.

![Figure 2.7](image)

**Figure 2.7:** Measurement of a MOS structure. (a) An small AC voltage is superimposed on the DC gate bias voltage, which is stepped over time. (b) The different types of $C-V$ measurements relative to the measurement conditions.

The two levels of changes in the voltage are shown graphically in Figure 2.7(a), while Figure 2.7(b) depicts the relation of high frequency, low frequency and deep depletion conditions with respect to the measurement parameters. The $C-V$ measurements relevant to this thesis are when the change in $\Delta V_a$ constitutes high frequency or low frequency conditions, while $V_a$ is changed under steady-state conditions. Figure 2.8(a) gives an
example of a C-V sample measured at various frequencies. The C-V curve measured at 19.911 kHz is in high frequency conditions, while the C-V curve measured at 0.111 kHz is in low frequency conditions. At the frequencies in between, the interface traps are responding to the AC gate voltage at varying rates.

The high frequency and low frequency C-V curves are graphed again in Figure 2.8(b), but with the ideal high frequency, low frequency and deep depletion theoretical C-V curves. The ideal C-V curves are known (Appendix A.3) and they represent the C-V curves without the influence of $C_{it}$. Thus from the comparison of the measured and ideal C-V curves, various parameters of interest can be extracted [27, 77]. In particular, the position of flatband voltage ($V_{FB}$) allows the determination of charge, while the “stretchout” [77] allows the determination of the $D_{it}$.

$$V_{FB} \equiv \phi_{MS} - \frac{Q_{ox} + Q_{it}(0)}{C_{ox}} \quad (2.8)$$

In Equation 2.8, $V_{FB}$ is usually calculated from the high frequency C-V measurements, as $Q_{it}(0) \approx 0$ compared to low frequency conditions where $Q_{it}$ is maximised. Several methods of deducing $V_{FB}$ are described in detail in Appendix A.4.

The other useful parameter in the evaluation of dielectric layers for surface passivation

Figure 2.8: The C-V curves of an AlO$_x$ MOS structure. (a) The C-V curves resulting from measurement over a range of frequencies. (b) The measured high and low frequency C-V curves (symbols) and the corresponding ideal C-V curves (solid lines).
is the $D_{it}$, which is related to $C_{it}$ by [77]:

$$D_{it} = qC_{it}$$  \hspace{1cm} (2.9)

The values of $D_{it}$ determined through Equation 2.9 will vary depending on the measurement condition from which $C_{it}$ is obtained, due to the various levels of measurement accuracy and assumptions used. Several of these methods for the determination of $D_{it}$ are described in detail in Appendix A.5. Figure 2.9 graphs the $D_{it}$ of the sample in Figure 2.8 as calculated from the various methods.

![Diagram](image.png)

**Figure 2.9:** The $D_{it}$ of the sample in Figure 2.8 as calculated from the various methods described in Appendix A.5.

C-V measurements of MOS structures is a powerful and versatile technique for characterising the surface passivation quality of oxides. However, as shown in Appendix A.3, the equations are complex and their validity depends on various assumptions [116]. There are also practical limitations in the range of frequencies and voltages that C-V curves can be measured due to the limitations of the measurement equipment and non-ideal MOS structures. For example, it is not always possible to attain true high or low frequency conditions, while errors and uncertainty in the measurements are also important considerations [77]. All of these must be taken into account when measuring, interpreting and analysing C-V results.
2.2 Evaluating Surface Passivation

2.2.4 Kelvin Probe Measurement

The Kelvin Probe (KP) measures the work function (in the case of metals) or the surface potential (in the case of non-metals) between a conducting sample and a vibrating tip. When the conducting sample and the vibrating tip are brought close together—but not touching—an electric field is induced in the air gap due to the work function/surface potential. By applying a voltage to nullify the electric field, the work function/surface potential can be quantified. It is a non-contact and non-destructive technique that is extremely sensitive to the conditions at the surface.

In the work of this thesis, the Kelvin Probe is used to quantify the charge on the surface of a dielectric layer. For a stack of dielectric layers, the surface charge $Q_{\text{surface}}$ can be approximated by $[32]$:

$$Q_{\text{surface}} = \varepsilon_0 \frac{V_a}{q} \left( \frac{1}{d_1 + \frac{d_2}{\varepsilon_1 + \frac{d_2}{\varepsilon_2 + \ldots}}} \right)$$

(2.10)

where $d_1, d_2, \ldots$ and $\varepsilon_1, \varepsilon_2, \ldots$ are the thicknesses and dielectric constants of the various dielectric layers respectively. In this case, $V_a$ is the voltage applied by the Kelvin probe. Through the knowledge of this surface charge, the charge of the dielectric layer can be deduced using the Corona-Lifetime technique (Section 2.2.5).

Equation (2.10) neglects the potential drop across the space-charge region $[117]$ and $Q_{it}$, both of which can become considerable if $D_{it}$ is on the same scale as $Q_{\text{surface}}$. To solve this, an adaptation of the approximate solution of the band-bending problem (Section 1.3.5) is required. The air gap between the Kelvin probe and the surface of the stack of dielectric layers is treated as a dielectric layer with the properties of air, while the charge at the edge of this layer on the side closer to the silicon is $Q_{\text{surface}}$. Equation (2.10) is solved iteratively as with the approximate solution of the band-bending problem, but $Q_{\text{surface}}$ is solved such that $Q_g = 0$ and $\psi_s = 0$.

An example of the different values of $Q_{\text{surface}}$ that can be calculated from $V_a$ is shown in Figure 2.10(a). The error in the use of Equation (2.10) rather than the use of the approximate solution of the band-bending problem is expressed as the vertical difference between the blue and red lines for a particular $V_a$ in Figure 2.10(a). The actual size of the error will differ from sample to sample, but the example shown in Figure 2.10(a) is fairly typical. For large positive and negative values of $V_a$, the error in the calculated $Q_{\text{surface}}$ is relatively small, but for values of $V_a$ between -2 V and 2 V, the error in the calculated
Figure 2.10: (a) Theoretical calculations of $Q_{\text{surface}}$ from $V_a$ using the different methods for a SiO$_2$/c-Si(n) structure. (b) Schematic diagram of a needle corona charger.

$Q_{\text{surface}}$ can be larger than an order of magnitude. Thus, Equation 2.10 can be reliably used when the measured values of $V_a$ are large, but extra considerations need to be made for values of $V_a$ that are closer to zero.

### 2.2.5 Corona-Lifetime Technique

In the Corona-Lifetime technique, the silicon surface condition of a lifetime sample is modified by changing the charge at the surface ($Q_{\text{surface}}$). As surface recombination is related to the silicon surface condition (Section 1.3.1), there is subsequently a correlation between $Q_{\text{surface}}$ and $\tau_{\text{eff}}$.

A corona charger is used to deposit ionised air molecules onto the surface of a sample to change $Q_{\text{surface}}$; a schematic diagram of a needle corona charger is shown in Figure 2.10(b). A potential of several kilovolts is applied to a source needle, multiple needles, wire or a mesh of wires above (0.1–1 cm) the sample surface, while the sample remains grounded. The strong electric field surrounding the source ionises the surrounding air molecules; depending on the polarity of the potential the predominant ionic species are CO$_3^-$ or H$_3$O$^+$. The source forces the ionised molecules along the electric field lines of the inhomogeneous electric field between the source and the sample. The molecules have very little kinetic energy; it is generally assumed that the ionised molecules do not damage or penetrate the sample surface, but only become deposited on the surface.

Provided that the sample is insulating, the deposited ions become a temporary surface charge on the sample. This surface charge will slowly decrease over time, or can be removed
immediately by washing the sample with water \[118\] or isopropanol \[119\].

Photoconductance and Kelvin probe measurements are made after each step of corona charging; this is repeated to graph the relationship between \(\tau_{\text{eff}}\) and \(V_a\) as \(Q_{\text{surface}}\) changes from accumulation to inversion [Figure 2.11(a)]. This technique is often used to determine the charge \(Q_{\text{ox}}\) in various dielectric layers to evaluate their field-effect passivation capabilities \[17, 25, 97, 117\]. A good approximation of \(Q_{\text{surface}}\) can be obtained through Equation 2.10 and thus \(\tau_{\text{eff}}\) can be graphed against \(Q_{\text{surface}}\). The minimum of \(\tau_{\text{eff}}\) corresponds to when the sum of the charges is zero:

\[
Q_{\text{surface}} + Q_{\text{ox}} = 0 \quad (2.11)
\]

and subsequently \(Q_{\text{ox}}\) is simply the negative of \(Q_{\text{surface}}\). The dependence of \(\tau_{\text{eff}}\) on \(Q_{\text{ox}}\) as calculated from the measurement in Figure 2.11(a) is given in Figure 2.11(b).

Figure 2.11: (a) The measured \(\tau_{\text{eff}}\) and corresponding \(V_a\) from the Kelvin probe at each point of corona charging. (b) The change in \(\tau_{\text{eff}}\) as related to \(Q_{\text{surface}}\) resulting from the applied corona charge. The minimum of \(\tau_{\text{eff}}\) corresponds to flatband conditions and \(Q_{\text{ox}}\) is subsequently deduced.

For a more accurate determination of \(Q_{\text{surface}}\), the approximate solution of the band-bending problem (Section 1.3.5) can be used. However, this is much more complicated as additional bulk and surface recombination parameters need to be known or else fitted. Also, rather than just calculating \(Q_{\text{surface}}\) for \(\tau_{\text{eff}}\) at a particular injection level as in Figure 2.11(b), the fitting needs to be done for the complete injection-dependent lifetime curve at each \(V_a\). The additional bulk and surface recombination parameters used need to consistently fit all of the complete injection-dependent lifetime curves for the complete range of \(V_a\). This method can be very useful for theoretical modelling, but not practical for the fitting of measured data.
The Corona-lifetime technique is used in Section 3.5. As the measured $V_a$ relevant to the determination of $Q_{ox}$ is large enough, Equation 2.10 is used for the determination of $Q_{ox}$.

2.3 Surface and Thin Films Analysis

The surface passivation provided by dielectric films is often related to the properties of the film and its interface with the silicon surface. In optimising these, the surface passivation can be improved [65, 81]. The basic principles behind the techniques for characterising surfaces and thin films are shown in Figure 2.12.

---

**Figure 2.12:** Generic schematic of the particles and interactions in surface and thin film analysis.

Incident particles bombard and interact with the surface or the thin film and the particles that are ejected from the sample are monitored. The particles can be ejected in a forward or backward direction and can be a primary particle (i.e. the incident particle) or secondary particle (i.e. a particle from the sample). The ejected particles carry the information concerning the interactions, which can yield a range of information regarding the surface or thin film. In most cases, the measurements are made in an ultra-high vacuum environment to prevent interaction of the particles with the ambient; this increases the accuracy and the sensitivity of the measurement.

The possible combinations of incident and monitored particles as shown in Figure 2.12 is theoretically very large, given that any atom from the periodic table, the ions arising
from the latter, or photons from any part of the spectrum are allowable. On a practical level however, there are limitations to the generation and acceleration of incident particles and not all monitored particles yield useful information. Thus, a number of particular techniques have been developed over time for specific applications and information.

Table 2.2 summarises the techniques used in this work for surface and thin film analysis in relation to solar cells; they are described in detail in the following subsections. Note that the table does not comprehensively list the particles, interactions and information that occur from the measurement, but gives the ones that are of interest in the measurement.

Table 2.2: Summary of techniques used for the analysis of surface and thin films in this thesis.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Incident Particle</th>
<th>Interaction</th>
<th>Ejected Particle</th>
<th>Information Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBS (Section 2.3.1)</td>
<td>Ions (H or He)</td>
<td>Elastic Scattering</td>
<td>Ions (Primary, Backward)</td>
<td>Elemental (Li to U)</td>
</tr>
<tr>
<td>SIMS (Section 2.3.2)</td>
<td>Ions (O or Cs)</td>
<td>Elastic Scattering</td>
<td>Ions (Secondary, Backward)</td>
<td>Elemental and Thickness</td>
</tr>
<tr>
<td>PAS (Section 2.3.3)</td>
<td>Positrons</td>
<td>Annihilation</td>
<td>Photons (Secondary)</td>
<td>Structural</td>
</tr>
<tr>
<td>FTIR (Section 2.3.4)</td>
<td>Photons (Infra-red)</td>
<td>Absorption</td>
<td>Photons (Primary, Forward)</td>
<td>Bonding</td>
</tr>
<tr>
<td>Spectrophotometry (Section 2.3.4)</td>
<td>Photons</td>
<td>Reflection</td>
<td>Photons (Primary, Backward)</td>
<td>Reflectance</td>
</tr>
<tr>
<td>Ellipsometry (Section 2.3.5)</td>
<td>Photons</td>
<td>Polarisation</td>
<td>Photons (Primary, Backward)</td>
<td>Refractive index</td>
</tr>
<tr>
<td>TEM (Section 2.3.6)</td>
<td>Electrons</td>
<td>Absorption</td>
<td>Electrons (Forward)</td>
<td>Topographic and Thickness</td>
</tr>
</tbody>
</table>

2.3.1 Rutherford Backscattering Spectrometry (RBS)

The elemental aspects of a thin film can be quantitatively determined using Rutherford Backscattering Spectrometry (RBS); the schematic for this is given in Figure 2.13. RBS is done by directing positively charged He or H ions of a known quantity ($Q_{RBS}$, measured as a cumulative charge) and a particular energy ($E_{RBS0}$) towards the sample. These incident ions and the target atoms scatter and recoil respectively following the physics governing the elastic scattering for two charged particles. By measuring the energy of the primary ions and their quantity scattered in the backward direction at a known angle with a detector with a known solid angle and efficiency, it is possible to deduce the elements
and their relative quantity in the thin film.

As the different ions and atoms in the sample have distinct mass and atomic numbers, they have a marked effect on the energy and quantity of the backscattered ions. Subsequently, information on the elemental composition of the sample, their location and the thickness of particular layers can be deduced through graphical curve fitting using computer simulation programs such as RUtherford backscatttering data Manipulation Program (RUMP) [120] or QUantative Analysis of Rutherford Kinematics (QUARK) [121].

It is important to note that the incident ions also impose limitations on the thickness of the dielectric film that can be measured and fitted effectively. Also, the presence of hydrogen and helium in the sample cannot be detected using this method, as they are indistinguishable from the incident ions.

![Diagram of Rutherford backscattering setup](image)

**Figure 2.13:** Schematic representation of the experimental setup for the Rutherford backscattering measurements used in this work.

Figure 2.14 shows the RBS measurement and fitting of two reference samples. The mismatch between the experimental and modelled data at low energies (< 0.3 MeV) is due to the non-linearities of the detector. As the composition and thickness of the layers of these reference samples are known, the fitting of the measured data allows the conversion of the measured channel number (top x-axis) to the actual energy of the backscattered ion (bottom x-axis). The detector solid angle can also be empirically deduced.

The energy and quantity of the incident ions can be adjusted to enhance the distinguishing features of particular elements. Figure 2.15 shows the RBS measurement and fitting of a Al$_2$O$_3$/c-Si sample, measured with two different $E_{RBS}$. In the case of Figure 2.15(a), the low number of features means that the experimental data can be fitted by different stoichiometry of AlO$_x$ and can even be fitted using a SiO$_x$/c-Si structure [c.f. Figure 2.14(b)]; useful information cannot be obtained with the fitting of such experimen-
2.3 Surface and Thin Films Analysis

Figure 2.14: RBS measurements and QUARK fitting of (a) an a-Si/c-Si reference sample and (b) a SiO₂/c-Si reference sample.

Figure 2.15: RBS measurements and QUARK fitting of a Al₂O₃/c-Si sample measured with a beam energy of (a) 1 MeV and (b) 2 MeV.

tal data. Figure 2.15(b) on the other hand, is the same sample but measured with incident ions of a higher energy. Many distinguishing features can be observed in the experimental data, which can only be fitted by very few solutions; thus the elemental composition of the thin film and its areal density can be confidently determined.

In Figures 2.14 and 2.15, the dashed vertical lines give the energy at which a peak is expected for a particular element. When this layer is sufficiently thick, the peak extends to lower energies and these are marked with the arrows in the figures. In Figure 2.15(b) for example, the peak corresponding to Al begins at 1.107 MeV and ends at ∼0.5 MeV,
while the peak corresponding to Si begins at 1.134 MeV and extends to zero.

This technique is used frequently in Chapter 3 for determining the O/Al ratio of aluminium oxide thin films and Chapter 4.4 for identifying contaminants. Typically, 1–2 MeV 4He$^+$ ions were used and a cumulative charge of 20 µC was measured. Information concerning the composition, densities and thicknesses of the AlO$_x$ films were extracted using the simulation program QUARK [12].

2.3.2 Secondary Ion Mass Spectroscopy (SIMS)

Figure 2.16: Schematic representation of the experimental arrangement for the secondary ion mass spectroscopy method used in this work.

Secondary Ion Mass Spectroscopy (SIMS) is a technique that can be used to quantitatively analyse the composition of surfaces and thin films. In this technique, primary ions (typically O, Xe, Ar or Cs) bombard the sample. Instead of measuring the backscattered ions as in RBS (Section 2.3.1), the mass and charge of the various atoms and molecules that are ejected from the surface of the sample in the backward direction are evaluated as shown in Figure 2.16. The secondary ions are filtered and/or separated by the mass analyser; the ions are then detected separately to allow the different elements to be distinguished. The SIMS measurements provide a quantitative measurement regarding the concentration of elements. Either a complete mass spectrum of the surface (~0.5 nm) is measured (static SIMS), or a particular mass is measured as a function of depth (dynamic SIMS).

Figure 2.17 shows an example of dynamic SIMS measurements of a SiO$_2$ layer on a c-Si(p) substrate, after a forming gas anneal. Due to the energy of the primary ions and the resulting sputtering effect, the abrupt change in the concentration of an element at a surface appears as a steep gradient rather than a vertical transition. Nonetheless, the quantification and definition of the surfaces and interfaces can be approximated by these
2.3 Surface and Thin Films Analysis

Figure 2.17: The concentration of various elements as a function of depth as measured by SIMS gradients. In Figure 2.17, the dotted line highlights how the sudden change in the concentrations of oxygen, silicon and hydrogen at ~180 nm can distinguish the approximate interface between a dielectric layer and the silicon substrate. Meanwhile, the jump in the concentration of hydrogen at ~180 nm demonstrates how SIMS can be used to verify the hydrogenation of an interface.

This technique is used in Section 4.5 for determining the concentration of hydrogen and its depth in AlO_x thin films. Dynamic SIMS using a magnetic sector Cameca IMS-4f model was utilized; the samples were bombarded with a Cs ion beam and the negative secondary ions of hydrogen, oxygen, silicon and aluminium were monitored. The concentrations of oxygen and hydrogen were directly measured, while the concentration of silicon was extrapolated from the silicon ion counts of the SIMS measurement by fitting it to a concentration of \(5 \times 10^{22} \text{ cm}^{-3}\) in the bulk. The concentration of aluminium was extrapolated from the aluminium ion counts of the SIMS measurement and from the O/Al ratio as deduced from a RBS measurement (Section 2.3.1) of the same sample.

2.3.3 Positron Annihilation Spectroscopy (PAS)

Positron Annihilation Spectroscopy (PAS) relies on the fact that a positron annihilates with an electron in a solid and releases two \(\gamma\) rays in opposite directions; a schematic representation of this measurement is given in Figure 2.18. The technique exploits the high sensitivity of positrons to the electron density for examining defects in semiconductors [27]. The angular correction and the Doppler broadening of the energy of the \(\gamma\) rays are dependent on the local electronic environment where the annihilation occurs,
yielding information concerning vacancies and the electron momentum distribution at the annihilation site \[122\].

![Schematic representation of the experimental arrangement for the positron annihilation spectroscopy method used in this work.](image)

**Figure 2.18:** Schematic representation of the experimental arrangement for the positron annihilation spectroscopy method used in this work.

The energy broadening of the annihilation line—as shown in Figure 2.19(a)—reflects the momentum state of the electron annihilated by the positron. The measurements are typically normalised to a defect-free reference, allowing the obtained parameters to be compared. Alternatively for the analysis of a surface or thin film, the bulk of the material—which is comparatively defect-free—can be used as the reference.

The valence annihilation parameter (\(S\)-parameter) provides information on the structure of the defect and is determined using Equation 2.12. The interval limits for the \(S\)-parameter are chosen symmetrically around the energy of \(E_{PAS,0}=511\) keV, with \(E_{PAS,S}\) preferably taken at the intersection points of \(f_{PAS}(E)\) and the reference curve to obtain the largest sensitivity for defect-induced change.

\[
S\text{-parameter} = \frac{A_{PAS,S}}{A_{PAS,0}}, \quad A_{PAS,S} = \int_{E_{PAS,0}+E_{PAS,S}}^{E_{PAS,0}-E_{PAS,S}} f_{PAS}(E)dE \quad (2.12)
\]

\[
W\text{-parameter} = \frac{A_{PAS,W}}{A_{PAS,0}}, \quad A_{PAS,W} = \int_{E_{PAS,1}}^{E_{PAS,2}} f_{PAS}(E)dE \quad (2.13)
\]

The core annihilation parameter (\(W\)-parameter) provides information on the chemical surrounding of the annihilation site and is given by Equation 2.13. The energy interval is typically taken in the high-energy side of \(f_{PAS}(E)\), with the interval limits \(E_{PAS,1}\) and \(E_{PAS,2}\) defined such that they do not overlap with the energy interval for the \(S\)-parameter. As this energy interval reflects the annihilation of electrons with higher momentum, a larger \(W\)-parameter can be indicative of an electric field.
2.3 Surface and Thin Films Analysis

Figure 2.19: (a) A example of Doppler-broadening spectra from PAS measurements. The indicated areas $A_{PAS,S}$, $A_{PAS,W}$ and $A_{PAS,0}$ are used to determine (b) the line shape parameters $S$-parameter and $W$-parameter.

By varying the incident energy of the positrons used, the $S$-parameter and $W$-parameter can be extrapolated for a relative depth profile. However, the dependence of the incident positron energy and the depth is usually non-linear, as a constant defect concentration and a constant positron density are required for a linear dependence \[122\]. The incident positron energy gives an indication of the relative depth but cannot be easily converted to an absolute value of depth as a result. Provided that the layers are > 100 nm—such that they are distinguishable from each other in terms of the incident positron energy—the relative concentration of defects from a surface (e.g. diffused junction) or between different layers of material (e.g. dielectric layers) can be compared [Figure 2.19(b)]. Further analysis can be achieved with simulation programs such as Variable Energy Positron FIT (VEPFIT) \[123\], which uses a positron implantation depth profile at each incident energy to calculate an average value the for $S$-parameter and positron diffusion length for each layer.

In this work, we utilise Doppler-broadening spectroscopy to determine the $S$-parameter and $W$-parameter for a relative depth profile in silicon samples passivated with AlO$_x$ films (Section 4.7). In this case, the positrons annihilate with high momentum oxygen electrons, leading to a broader momentum distribution \[124\]. As the analysis is of the AlO$_x$ layer, the silicon bulk is used as the defect-free reference (i.e. $S$-parameter = 1, $W$-parameter = 1 in the silicon bulk). Thus, a lower $S$-parameter and a higher $W$-parameter is to be expected from an AlO$_x$ film compared to the silicon bulk, as seen in Figure 2.19(b). Vacancies trap positrons as well, so a lower $S$-parameter and a higher $W$-parameter can also be caused by defects.
2.3.4 Spectrophotometry

In spectrophotometry, the sample is illuminated and the reflectance is measured at individual wavelengths. A Tungsten lamp provides the photons and the light is passed through a monochromator to transmit only the selected wavelength. The reflected light—specular and diffuse—from the sample is summed in the integrating sphere, before being measured by a photomultiplier detector.

![Diagram of experimental arrangement for reflectance measurements](image)

**Figure 2.20:** Schematic representation of the experimental arrangement for reflectance measurements.

This is repeated over the range of wavelengths to be measured, resulting in the measurement of reflectance over the range of wavelengths. For solar cells, these measurements are commonly made over the range of 200–1200 nm, as this accounts for most of the light that a solar cell absorbs for photovoltaic conversion. Examples of the reflectance from various anti-reflection technologies are given in Figure 2.21. The reflectance needs to be
minimised for this range, particularly at \( \sim 633 \text{ nm} \) as the intensity of light from the sun is highest near this wavelength. A Perkin-Elmer Lambda 1050 \( \text{UV-Vis-IR} \) spectrometer (350–1200 nm) or a Filmetrics F20-\( \text{UV} \) thin-film analyser (200–1100 nm) were used to make reflectance measurements.

### 2.3.5 Ellipsometry

Ellipsometry measures the change in the polarisation of light reflected from a surface. A schematic representation of ellipsometry is shown in Figure 2.22. By modelling this measurement, it is possible to calculate the refractive indices (\( \hat{n} \)), the extinction coefficients (\( \hat{k} \)) and the thicknesses of thin films that have been deposited on a reflective substrate. The accuracy of the measurement is significantly improved by depositing the thin film on a mirror polished silicon substrate to avoid the scattering of the incident light or changes in the polarisation of the light due to surface roughness. Meanwhile, the accuracy of the modelling can be improved if reasonable estimates of \( \hat{n} \), \( \hat{k} \) and the film thicknesses are provided as initial values for the modelling.

<table>
<thead>
<tr>
<th>Analysis Information</th>
<th>Refractive Index</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (1) Source (HeNe laser)</td>
<td>(2) Detector (StokesMeter™)</td>
<td>(3b) Detector (StokesMeter™)</td>
</tr>
<tr>
<td>Incidence Reflection Polarisation</td>
<td>Primary</td>
<td>Primary</td>
</tr>
<tr>
<td>Incident Particle Photons</td>
<td>(4) Analysis Information</td>
<td>Backward Ejected Particle Photons</td>
</tr>
</tbody>
</table>

**Figure 2.22:** Schematic representation of the experimental arrangement for ellipsometry measurements.

A Gaertner LSE ellipsometer at a wavelength of 633 nm and at a fixed angle of 70° was used for the ellipsometry measurements of AlO\(_x\) films deposited on mirror polished silicon substrates. As \( \hat{k} \) can be assumed to be zero for AlO\(_x\) [87], a two layer optical model consisting of the silicon substrate and a AlO\(_x\) layer described by a Cauchy model [125] was used to extract \( \hat{n} \) and the film thickness from the ellipsometry measurements.
2.3.6 Transmission Electron Microscopy (TEM)

In Transmission Electron Microscopy (TEM), a beam of electrons is transmitted through a sufficiently thin (10–100 nm) sample. An image is formed when the transmitted electrons impinge on a photographic plate or phosphor screen. The image contrast depends on the scattering and diffraction of electrons as a result of the structural composition of the sample. A schematic representation of a TEM measurement is given in Figure 2.23.

![Figure 2.23: Schematic representation of the experimental arrangement for transmission electron microscopy.](image)

Figure 2.23: Schematic representation of the experimental arrangement for transmission electron microscopy.

The roughness of the a-Si:H surface contrasts with the evenness of the a-Si:H/c-Si interface, yielding valuable information concerning the quality of the deposition. In this work, TEM was used to determine the thickness of dielectric layers and inspecting interfaces (Section 4.6).

![Figure 2.24: The TEM image of an a-Si:H/c-Si structure.](image)

Figure 2.24: The TEM image of an a-Si:H/c-Si structure.

Figure 2.24 gives an example of how a TEM image can yield spatial information concerning an a-Si:H/c-Si structure. The deduced thickness of the a-Si:H film is 130 nm.
2.3.7 Fourier Transform Infra-Red Spectroscopy (FTIR)

In Fourier Transform Infra-Red spectroscopy (FTIR), the IR absorbance spectra of a sample is measured, as these correspond to molecular vibration energies. The vibration modes (e.g. wagging, stretching, etc.) refer to the way in which the molecule is vibrating after the absorption of a particular IR wavelength. The wavelength of these peaks correspond to particular bonding configuration, thus allowing their identification. The peak area can be used to calculate bond densities.

![Schematic representation of the experimental arrangement for Fourier Transform Infra-Red spectroscopy.](image)

**Figure 2.25:** Schematic representation of the experimental arrangement for Fourier Transform Infra-Red spectroscopy.

Rather than changing the frequency of the IR beam and measuring the corresponding transmission/absorbance spectra of a sample for each frequency, the IR beam is passed through a Michelson interferometer to obtain a interferogram. This interferogram is a single signal that contains information concerning every frequency of the IR beam, resulting in extremely fast measurement as all the frequencies of the IR beam are measured simultaneously. The detected interferogram is resolved through Fourier transformation to graph the absorption by the sample at particular parts of the frequency spectrum (Figure 2.25).

For the evaluation of bond structures and densities in dielectric films, the silicon substrate is first measured without the dielectric film and then measured with the dielectric film deposited. By subtracting the measurement of the blank sample from the sample with the dielectric film, the peaks corresponding to the silicon substrate are eliminated, leaving only the peaks corresponding to the dielectric film. By knowing the approximate elemental composition of the dielectric film, the bond structures can be identified using information from the literature and quantified. By relating the bond densities with surface passivation results of the same dielectric film, the correlation between bond densities and
surface passivation can be established.

An example of the resolved FTIR spectra of an a-Si:H film deposited on a silicon substrate is shown in Figure 2.26(a), while that of an annealed AlO$_x$ layer is shown in Figure 2.26(b). The bonding types, molecular structures and vibration modes relevant to the sample have been highlighted. A Perkin-Elmer Spectrum GX spectrometer over the wavenumber range of 450–3000 cm$^{-1}$ is used in Section 4.8 for identifying the bonding configurations in AlO$_x$ films.


Chapter 3

Viability of Sputtering Methods

"Effective surface passivation techniques, preferably carried out at low temperature, are indispensible for future industrial high-efficiency silicon solar cells."

J. Schmidt et al., 2009 [75]

3.1 Introduction

A review of the literature shows that there are a number of different methods for the sputtering of AlO$_x$ (Section 3.2.1), most of which have been evaluated as an alternative to SiO$_2$ in microelectronic applications (Section 3.2.2). Agostinelli et al. [16, 23] briefly mentions that the achievable combinations of $D_{it}$ and $Q_{ox}$ with sputtered AlO$_x$ were not enough to guarantee good surface passivation and no values of $S_{eff}$ were reported. There has not been a sufficiently comprehensive investigation in the literature establishing whether sputtered AlO$_x$ is suitable for the surface passivation of crystalline silicon.

In this chapter we evaluate two sputtering systems and three sputtering methods for the deposition of AlO$_x$ (Sections 3.5–3.7). We evaluate whether sputtered AlO$_x$ is negatively charged and whether it can provide good surface passivation on both $p$- and $n$-type surfaces. We find that negative charges can be obtained using any of the sputtering systems and methods after annealing the AlO$_x$ film at 400$^\circ$C in N$_2$. However, good surface passivation results are limited to a particular sputtering method and system. Nonetheless, $S_{eff}$ values as low as 124 cm/s and 22 cm/s are obtained on 0.8 Ω.cm CZ $c$-Si($p$) and 1 Ω.cm CZ $c$-Si($n$) respectively after annealing, demonstrating for the first time that sputtered AlO$_x$ is capable of providing good surface passivation.
3.2 Literature Review

This section reviews the literature on sputtered AlO$_x$ for electronic applications. Section 3.2.1 provides the background to the sputtering process and reviews the various methods that can be used for the deposition of AlO$_x$. Section 3.2.2 reviews the electronic properties of sputtered AlO$_x$ films and explains how it may be different to AlO$_x$ films deposited by other deposition methods (e.g. ALD and CVD).

3.2.1 Sputtering of Aluminium Oxide

Sputtering is advantageous to other thin film deposition methods as nearly all types of materials can be sputtered and the deposition can be done at room temperature [76]. The deposition rate with sputtering is also usually higher than the other deposition methods. However, the main disadvantages of sputtering include plasma damage, film contamination by other materials in the sputtering chamber as well as porous and grainy films.

Sputtering is a Physical Vapour Deposition (PVD) process whereby atoms and molecules are ejected from the surface of its source material (called the “target”) through physical collisions, travels through a relative vacuum in vapour form and is deposited as a thin film on an adjacent surface (called the “substrate”) [76]. The target material can be a single element or a compound. An example of a basic DC sputtering arrangement is given in Figure 3.1(a).

The target is attached to the cathode, while the substrate is usually grounded and is the anode. A voltage applied across the two electrodes accelerates free electrons to ionise the gas molecules and subsequently creating a plasma. The immediate start of the sputter power (typically 10% of the maximum power) in a chamber with sufficient pressure (> 20 mTorr) is usually required for initiating the plasma. The pressure is lowered to the working pressure (i.e. the pressure used during the sputter deposition process) and the voltage is increased slowly to avoid any damage to the target or the power source. Since the ionised gas molecules are positively charged, they are accelerated towards the negatively biased target. The resulting collisions of the ionised gas molecules with the target results in the sputtering of target material as well as electrons. The electrons contribute to sustaining the plasma, while the released target atoms and molecules—bearing the kinetic energies and vectors of their initial collisions—travel through the plasma. The target atoms and molecules strike the substrate, where it condenses and forms the deposited film.

A shutter can be placed between the target and the substrate to prevent the target material from being deposited on the substrate. This is usually kept in the “closed”
Figure 3.1: (a) A basic DC sputtering setup showing the four principle processes: (1) gases entering into the vacuum chamber, (2) movement of free electrons due to the voltage between the electrodes, (3) the free electrons ionise the gas molecules, the latter accelerating towards the cathode and impacting the target and (4) the released target material is deposited onto the substrate. (b) In a contemporary DC magnetron sputtering setup, the magnetic field confine the movement of the free electrons of process (2) which enhances process (3). A shutter can be used to restrict process (4).

position (i.e. in between the target and the substrate) during the ignition of the plasma to prevent the deposition of material and “opened” (i.e. no longer between the target and the substrate) to commence deposition on the substrate when the sputtering conditions have reached steady-state. The substrate holder may be rotating to improve the uniformity of the deposition and it may been heated (typically 25–550°C) to assist with the bonding of the deposited material with the substrate. To end the deposition, the shutter is “closed” and the voltage is slowly decreased until the plasma is extinguished.

In the basic DC sputtering arrangement shown in Figure 3.1(a), the deposition rate is slow and the electron bombardment of the substrate is considerable; this usually results in undesired heating as well as damage of the substrate. Figure 3.1(b) gives an example of an improved sputtering arrangement called “magnetron sputtering”, whereby magnets behind the cathode restrict the movement of the electrons away from the cathode. By concentrating the electrons near the cathode, the ionisation of the gases increases, which subsequently increases the sputtering of the target and the deposition rate of the thin film. Also, the concentration of electrons is reduced near the substrate, which minimises the unwanted heating and damage of the substrate.

DC sputtering is limited by the fact that the target must act as an electrode and therefore must also be conductive. This is not a problem for the sputtering of metals and conductive compounds, but prohibits the sputtering of insulators and some semicon-
ductors. The solution to the latter is to use a high-frequency (typically 13.56 MHz) AC voltage that is coupled capacitively through the insulating target to the plasma, which eliminates the need for conducting electrodes. The typical sputtering arrangement for this is similar to Figure 3.1(b), except that the DC power source is replaced with a RF generator and an impedance matching network; this resulting arrangement is called “RF magnetron sputtering”.

Instead of using a target comprised of a particular compound, the individual elements of the compound can be simultaneously sputtered from separate cathodes and the deposited material on the substrate is the desired compound; this is called “cosputtering”. If one or more of the elements of the compound is gaseous (typically O$_2$, N$_2$ or H$_2$), they can be introduced into the sputtering ambient in gaseous form whilst a solid target is being sputtered. The inert gas in its molecular form is disassociated in the plasma into its reactive atomic components, which can then easily react with the vapour of the sputtered target material as it travels through the plasma, resulting in the deposition of compounds formed with atoms from the target and the gases. This is called “reactive sputtering”.

Reactive sputtering is complicated by the fact that the reactive gas can react and deposit on the surface of the target. This can be a serious problem in DC sputtering, whereby the reactive gas bonds with the surface of the conductive target to form a non-conductive compound. The target is “poisoned”; the sputtering process is greatly inhibited and essentially stops. This has historically been called “target oxidation” as the problem usually involved the oxidation of a metal target. RF sputtering avoids this problem as the target can be sputtered even if its surface becomes an insulating material. Alternatively, a pulsed DC power source can be used to repeatedly change the polarity of the target such that target oxidation is avoided.

The different methods of sputtering AlO$_x$ can be grouped into four main categories:

1. **RF sputtering of an Al target**—an Al target is sputtered using a RF power source in an Ar/O$_2$ ambient.

2. **RF sputtering of an Al$_2$O$_3$ target**—an alumina target is sputtered using a RF power source, typically in an Ar or Ar/O$_2$ ambient.

3. **DC sputtering of an Al target**—an Al target is sputtered using a DC power source in an Ar/O$_2$ or O$_2$ ambient.

4. **Pulsed DC sputtering of an Al target**—an Al target is sputtered using a pulsed DC power source in an Ar/O$_2$ ambient.
Table 3.1: Comparison of the reported processing conditions of AlO$_x$ deposited by sputtering.

<table>
<thead>
<tr>
<th>Method</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power source</td>
<td>RF</td>
<td>RF</td>
<td>DC</td>
<td>Pulsed DC</td>
</tr>
<tr>
<td>Target</td>
<td>Al</td>
<td>Al$_2$O$_3$</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>Gases</td>
<td>Ar/O$_2$</td>
<td>Ar or Ar/O$_2$</td>
<td>Ar/O$_2$ or O$_2$</td>
<td>Ar/O$_2$</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>1000–2000 [133]</td>
<td>0–200 [134]</td>
<td>280–1200 [94, 96]</td>
<td>N/A</td>
</tr>
<tr>
<td>Ar flow (sccm)</td>
<td>30 [127]</td>
<td>N/A$^a$</td>
<td>0–30 [94, 96]</td>
<td>40 [99, 132]</td>
</tr>
<tr>
<td>O$_2$ flow (sccm)</td>
<td>1.5–2.3 [127]</td>
<td>N/A$^a$</td>
<td>0–10 [96]</td>
<td>1–40 [131, 132]</td>
</tr>
<tr>
<td>Deposition temperature ($^\circ$C)</td>
<td>25–600 [127, 133]</td>
<td>20–400 [129]</td>
<td>25</td>
<td>25–380 [95]</td>
</tr>
<tr>
<td>Deposition rate (nm/min)</td>
<td>&lt; 10 [135]</td>
<td>&lt; 35 [138]</td>
<td>&lt; 25 [96]</td>
<td>&lt; 146 [99]</td>
</tr>
</tbody>
</table>

$^a$ The reported values were given as a ratio of O$_2$ to Ar (0–50% O$_2$ in Ar [128, 136]).
Significantly higher deposition rates can be achieved with DC power sources, but they may encounter problems with target oxidation \[96, 137\]. Meanwhile, an alumina (Al\(_2\)O\(_3\)) target cannot be sputtered using a DC power source, but it does not require O\(_2\) in the ambient to deposit AlO\(_x\). In one case, an Ar/N\(_2\) ambient was used to sputter an Al\(_2\)O\(_3\) target, although the deposited film may have been AlO\(_x\)N\(_y\) \[138\]. Table 3.2 summarises the ranges of deposition parameters that have been used for the different sputtering methods.

A post-deposition anneal is sometimes necessary to improve the electronic properties of AlO\(_x\) films. The post-deposition anneal has been done in N\(_2\), O\(_2\), Ar, He ambient or in a vacuum \[94, 95, 128, 134, 139\]. The annealing time is typically > 30 min and the temperatures used have ranged from 100–900°C.

The deposition parameters listed in Table 3.1 are used as a guide for the experiments in this chapter to evaluate whether it is possible to use sputtered AlO\(_x\) for surface passivation purposes. The dependence of the surface passivation attained on the wider range of deposition and annealing parameters is investigated and presented in Chapter 5.

### 3.2.2 Electronic Properties of Sputtered Aluminium Oxide

Most of the studies in the literature have evaluated sputtered AlO\(_x\) as an alternative to SiO\(_2\) \[95\], particularly as an insulating layer in Field Effect Transistor (FET) \[99, 127, 128, 130, 132, 140\]. The emphasis has been on its Current-Voltage (IV) characteristics, surface morphology and its higher dielectric constant (\(\varepsilon = 7–9.5\)) compared to SiO\(_2\) (\(\varepsilon = 3.8\)).

The experiments that have reported on the negative charge of sputtered AlO\(_x\) have been aimed at minimising the negative charge for FET applications, whereas the aim for surface passivation in solar cells is to maximise its negative charge. In the experiments that have been aimed at surface passivation with sputtered AlO\(_x\), no values of \(S_{eff}\) were reported \[16, 23\]; it was stated that the achievable combination of surface defect states and interface charges were deemed to be unlikely to lead to good surface passivation.

Given the excellent surface passivation provided AlO\(_x\) films deposited with PA-ALD and thermal ALD \[14\], we can consider its electronic properties as the properties that should ideally be achieved with sputtered AlO\(_x\). Table 3.2 lists the electronic properties of AlO\(_x\) achieved with the various methods of sputtering and compares it with AlO\(_x\) deposited by ALD methods.

It is the strong negative charge that is the distinguishing feature of AlO\(_x\) deposited by PA-ALD and this can be as high as \(-10^{13} \text{ cm}^{-2}\) after annealing in N\(_2\) \[25, 143\]. Meanwhile with sputtered AlO\(_x\), the results are mixed. Salama \[139\] finds only positive charges in
Table 3.2: Comparison of the reported electronic properties of AlO$_x$ deposited by sputtering and ALD methods.

<table>
<thead>
<tr>
<th>Type</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>PA-ALD</td>
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</tr>
<tr>
<td></td>
<td>Thermal</td>
<td>2</td>
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<td>Power Source</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>RF</td>
<td>4</td>
</tr>
<tr>
<td>Target</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>Al</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$Q_{ox}$ (cm$^{-2}$)</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>$-6 \times 10^{12}$ [70]</td>
<td>$-10^{11}-10^{13}$ [25]</td>
</tr>
<tr>
<td>After annealing</td>
<td>$-10^{12}-10^{13}$ [25]</td>
<td>$-10^{12}-10^{13}$ [25]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$D_{it}$ (cm$^{-2}$eV$^{-1}$)</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>$3 \times 10^{13}$ [70]</td>
<td>$10^{11}-10^{12}$ [25]</td>
</tr>
<tr>
<td>After annealing</td>
<td>$2 \times 10^{11}$ [70]</td>
<td>$10^{11}$ [25]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\varepsilon$</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\bar{n}$</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O/Al</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\rho_{mass}$ (g/cm$^3$)</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
the range of $+10^{11}$ to $+10^{13}$ cm$^{-2}$ with the reactive RF sputtering of an Al$_2$O$_3$ target and annealing in a N$_2$ ambient, while Chen [94] finds both positive and negative charges in the range of $10^{11}$ cm$^{-2}$ from DC sputtering of an Al target and after annealing in a He ambient. Meanwhile, Manchanda et al. [95] finds charges in the range of $10^{11}$ to $10^{13}$ cm$^{-2}$ with the pulsed DC sputtering of an Al target, but does not specify the polarity. In all cases however, the annealing resulted in either a shift to negative charges or at least a reduction of positive charges.

With ALD methods, the deposited AlO$_x$ is close to stoichiometric due to its self-limiting reaction [72]. With sputtered AlO$_x$ it is possible to achieve a much wider range of stoichiometry and bonding configurations as the deposition of Al and O atoms can be controlled—to a certain extent—independently, particularly in the reactive sputtering of an Al target. This could explain how a greater range of charges—both in terms of magnitude and polarity—have been achieved with sputtered AlO$_x$. This would also explain the larger range of refractive indices that have been achieved with sputtered AlO$_x$ ($\hat{n} = 1.5$–$2.35$) compared to the range of refractive indices achieved with PA-ALD AlO$_x$ ($\hat{n} = 1.6$–$1.65$). This shows that the electronic properties of sputtered AlO$_x$ can be optimised to match those of PA-ALD AlO$_x$, or alternatively, be adjusted as required for its particular application.

Meanwhile, the dielectric constants achieved are dependent on the thickness of the AlO$_x$ film [141], so the values of the dielectric constants listed in Table 3.2 are not directly comparable. We also note that the density for the AlO$_x$ films deposited by RF sputtering of an Al target can be as low as 1.8 g/cm$^3$, almost half the density compared to AlO$_x$ films deposited by other methods. This is a disadvantage of the sputtering method (Section 3.2.1) and in the experiment of Section 6.3 we discuss how it may be limiting the thermal stability of sputtered AlO$_x$ films.

3.3 Experimental Design

Figure 3.2 gives the generic process flow diagram for the experiments of this chapter in exploring the viability of sputtered AlO$_x$. Both $p$-type and $n$-type silicon wafers were used; their details are listed in Table 3.3. The surface passivation experiments of this work are focused on the 0.8 Ω.cm FZ c-Si($p$) and 1 Ω.cm CZ c-Si($n$) wafers as they are more relevant to the resistivity used for solar cells.

The wafers were saw-damage etched using a 50% NaOH solution for 20 min, followed by a Radio Corporation of America (RCA) clean [144], ~5% HF dip and a Deionised (DI)
Figure 3.2: Process flow diagram for the AlO$_x$ samples fabricated for the experiments of this chapter. The dashed boxes are optional fabrication steps depending on the characterisation method used.
Table 3.3: Summary of the wafers used for the experiments of this chapter.

<table>
<thead>
<tr>
<th>Wafer type</th>
<th>Growth method</th>
<th>Orientation</th>
<th>Resistivity (Ω·cm)</th>
<th>Dopant density (cm⁻³)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si(p)</td>
<td>FZ</td>
<td>&lt;100&gt;</td>
<td>0.5</td>
<td>3.25 × 10¹⁶</td>
<td>250–270</td>
</tr>
<tr>
<td>c-Si(p)</td>
<td>FZ</td>
<td>&lt;100&gt;</td>
<td>0.8</td>
<td>1.92 × 10¹⁶</td>
<td>280–300</td>
</tr>
<tr>
<td>c-Si(p)</td>
<td>FZ</td>
<td>&lt;100&gt;</td>
<td>1.5</td>
<td>9.79 × 10¹⁵</td>
<td>300–320</td>
</tr>
<tr>
<td>c-Si(n)</td>
<td>Cz</td>
<td>&lt;100&gt;</td>
<td>0.5</td>
<td>1.07 × 10¹⁶</td>
<td>220–240</td>
</tr>
<tr>
<td>c-Si(n)</td>
<td>Cz</td>
<td>&lt;100&gt;</td>
<td>1</td>
<td>5.0 × 10¹⁵</td>
<td>220–240</td>
</tr>
<tr>
<td>c-Si(n)</td>
<td>Cz</td>
<td>&lt;100&gt;</td>
<td>3.5</td>
<td>1.33 × 10¹⁵</td>
<td>200–220</td>
</tr>
<tr>
<td>c-Si(n)</td>
<td>Cz</td>
<td>&lt;100&gt;</td>
<td>10</td>
<td>4.53 × 10¹⁴</td>
<td>370–470</td>
</tr>
<tr>
<td>c-Si(n)</td>
<td>Cz</td>
<td>&lt;100&gt;</td>
<td>15</td>
<td>3.0 × 10¹⁴</td>
<td>520–540</td>
</tr>
</tbody>
</table>

(a) After saw-damage etching.

Water rinse. The surfaces were then polished using a 10:1 HNO₃/HF solution. The wafers underwent a RCA clean, ~5% HF dip and a DI water rinse prior to deposition of the AlOₓ film.

The deposition of AlOₓ was performed using two different magnetron sputtering systems. System “A” was an AJA International 2400V system while system “B” was a custom-built system. Neither system “A” or “B” had a pulsed DC power source and so this sputtering method could not be explored. Table 3.4 provides a summary of their specifications and the range of deposition parameters explored in this investigation. The deposition time given is for the deposition of AlOₓ on one side of the sample.

In system “A”, the substrate holder was heated from above using IR lamps and the samples were conductively heated by being in contact with the substrate holder. The samples were deposited at temperatures between 25–500°C. However, the temperature could not be measured by a direct contact with the sample, but was extrapolated from the power of the IR lamps and the calibration constants given by the manufacturer. This provided a reasonable estimate of the deposition temperature, but prior experiments had shown that the actual temperature of the sample could be as much as 10% lower. A Maxtek TM-350 quartz crystal thickness monitor is used to measure the rate of deposition.

Reference AlOₓ samples were deposited using a Cambridge Nanotech thermal ALD reactor. A cycle in the reactor consisted of a 15 ms injection of Al(CH₃)₃ vapour followed by a 5 s N₂ purge. The oxidation step consisted of a 15 ms injection of H₂O vapour followed by a 5 s purge with N₂ resulting in a deposition rate of 1.06 Å/cycle. The deposition temperature was 250°C while a 20 sccm background flow of N₂ was used.
Table 3.4: Details of the sputtering systems, methods and deposition parameters used in this thesis. The range of values gives the range over which a particular parameter was explored while the bracketed value gives the value used when the particular parameter was kept constant.

<table>
<thead>
<tr>
<th>System</th>
<th>“A”</th>
<th>“A”</th>
<th>“A”</th>
<th>“B”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Power source</td>
<td>RF</td>
<td>RF</td>
<td>DC</td>
<td>RF</td>
</tr>
<tr>
<td>Target</td>
<td>Al</td>
<td>AlO$_2$</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>Power (W)</td>
<td>178–300 (300)</td>
<td>300 (300)</td>
<td>244–490 (490)</td>
<td>300–400 (400)</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>83–184</td>
<td>160–205</td>
<td>480–530</td>
<td>160–260</td>
</tr>
<tr>
<td>Base pressure (T)</td>
<td>&lt; 7×10$^{-7}$</td>
<td>&lt; 7×10$^{-7}$</td>
<td>&lt; 7×10$^{-7}$</td>
<td>&lt; 3×10$^{-6}$</td>
</tr>
<tr>
<td>Working pressure (mTorr)</td>
<td>1–7 (3)</td>
<td>1–7 (3)</td>
<td>1–7 (3)</td>
<td>3</td>
</tr>
<tr>
<td>Ar flow (sccm)</td>
<td>0–20 (20)</td>
<td>0–20 (20)</td>
<td>0–20 (20)</td>
<td>50–100 (50)</td>
</tr>
<tr>
<td>O$_2$ flow (sccm)</td>
<td>0–3 (2)</td>
<td>0–1.5</td>
<td>0–20</td>
<td>0–8</td>
</tr>
<tr>
<td>Deposition temperature (°C)</td>
<td>25–500 (25)</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Deposition time (s)</td>
<td>60–600</td>
<td>60–7500</td>
<td>60–130</td>
<td>1800</td>
</tr>
<tr>
<td>Substrate rotation (rpm)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>Magnetron</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Sputter direction</td>
<td>Up</td>
<td>Up</td>
<td>Up</td>
<td>Down</td>
</tr>
<tr>
<td>Shutter</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Load lock</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Thickness monitor</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

For all of the deposition methods, an AlO$_x$ film thickness of 30 nm was targeted unless specified otherwise. RBS measurements (Section 2.3.1) were performed on the samples to determine the O/Al ratio of the as-deposited films. Making the RBS measurements prior to the post-deposition anneal did not affect results as the O/Al ratio of the AlO$_x$ does not change with annealing (Section 4.4). The post-deposition annealing was carried out in a quartz furnace at 400°C in N$_2$ for 30–60 min.

To enable carrier lifetime testing, AlO$_x$ was deposited on both sides of a wafer to create a symmetrical structure; the lifetime samples were then characterised using transient photoconductance (Section 2.2.1) and the values of $S_{ef}$ were calculated using Equation 1.31. For C-V measurements, unannealed and annealed samples with AlO$_x$ on the front side were contacted with aluminium dots (0.7 µm diameter, 0.1 µm thick) on front side and a full area aluminium contact (0.1 µm thick) on the rear side; the C-V samples were then characterised using high-frequency C-V techniques (Section 2.2.3) to calculate the $Q_{ox}$ and the $D_{it}$. A number of these samples were further characterised using PL imaging (Section 2.2.2), MWPCD imaging (Section 2.2.1), SIMS (Section 2.3.2) or the corona-lifetime technique (Section 2.2.5).
3.4 Development of the Sputtering Process

Target oxidation, control of the reactive sputtering process and film uniformity can affect the sputtering and deposition of AlO$_x$ films (Section 3.2.1). Meanwhile, the stoichiometry of the deposited AlO$_x$ film leads to different electronic properties (Table 3.2) and not all sputtered AlO$_x$ films are of suitable electronic quality for surface passivation.

In this experiment we evaluate two sputtering systems and identify the system components that are highly desirable for the deposition of AlO$_x$. We investigate a wide range of deposition parameters to determine the conditions for when AlO$_x$ of suitable electronic quality can be deposited. We formulate sputtering processes that minimises the variation in the reactive sputtering process and these processes are used in the subsequent experiments of this thesis.

3.4.1 Base Pressure

The incorporation of impurities in the sputtered films can be greatly reduced with lower base pressures [ ]. The availability and use of a load lock in system “A” allowed the vacuum chamber to reach low base pressures of $\sim 7 \times 10^{-7}$ Torr as the main chamber was always under high vacuum. Meanwhile in system “B”, the lack of a load lock meant that the whole vacuum chamber needed to be pumped down for each deposition and the chamber could only be pumped to a base pressure of $\sim 3 \times 10^{-6}$ Torr consistently. As will be discussed in Section 4.4, higher concentrations of impurities are likely to be detrimental to surface passivation. It follows that the higher base pressure of system “B” is one of its limiting factors, while it is important to monitor and minimise the base pressure in system “A” in order to achieve the best surface passivation results.

3.4.2 Target Oxidation

Target oxidation was often a problem with the initial depositions of this experiment. It would occur during the middle of a deposition process, invalidating the experiment as a different and undesirable layer of AlO$_x$ (“Oxide Mode” in Section 3.4.6) was deposited on the substrate. The Al or Al$_2$O$_3$ target can be cleaned by sputtering in Ar for 5–10 min, but the experiment would need to be repeated on a new sample. As will be discussed in Section 3.4.6, the availability of a thickness monitor—as with system “A” but not system “B”—can be very helpful with the monitoring of target oxidation.

Target oxidation occurs when the rate of target oxidation is higher than the sputtering
of the same surface (Section 3.2.1). In the initial depositions of this experiment, the concentration of O\textsubscript{2} in the sputtering ambient was the same throughout the deposition process but the voltage was slowly increased (at the beginning of the process) or decreased (at the end of the process) to prevent damage to the target. This meant that the rate of sputtering was often lower than the rate of target oxidation at the beginning and at the end of the deposition process. In many instances, partial oxidation of the target was occurring at the beginning of the deposition process when the rate of sputtering was low, decreasing the rate of sputtering and allowing for further oxidation of the target until it became completely oxidised, stopping the deposition process before it was due to finish.

In order to minimise the instances of target oxidation, the deposition process was changed whereby the O\textsubscript{2} is only introduced into the ambient 30 s before the shutter is

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**Figure 3.3:** An optimised deposition process for system “A” and the deposition parameters at each stage of the process: (a) plasma power, (b) pressure, (c) Ar and O\textsubscript{2} flows and (d) the shutter position.
opened; target oxidation is avoided as a sufficiently high sputtering rate is obtained before the target is exposed to O$_2$. Taking into account of the various considerations discussed above, an optimised deposition process for system “A” is given in Figure 3.3.

3.4.3 Control of the Gas Flow

In both systems “A” and “B”, the Mass Flow Controllers MFC—that control the flow of the gases into the sputtering chamber—did not have sufficient precision; the fluctuations in the oxygen flow during the course of the deposition could be as much as 0.2 sccm. This is problematic when the fluctuations are large compared to the flow of O$_2$. For example, a change in O$_2$ used from 0.5 sccm to 1 sccm can change the O/Al ratio of the AlO$_x$ film from 0.5 to 1.7 (Section 3.5), making it very difficult to target an O/Al ratio of 1.5 for stoichiometric Al$_2$O$_3$. The solution to this is either to utilise a MFC with precise control of the O$_2$, or adjust the amount of aluminium atoms that are deposited by changing the voltage.

However, neither solution were easily applicable to systems “A” and “B” and the existing arrangements were used. This is the reason why the stoichiometric value for AlO$_x$ of 1.5 (i.e. Al$_2$O$_3$) is not attained for some of the experiments of this work, even though it would have been interesting to compare stoichiometric sputtered AlO$_x$ to the stoichiometric Al$_2$O$_3$ deposited by ALD methods in the literature (e.g. Sections 3.3 and 5.3.4).

The problem above regarding the control of the oxygen flow is a disadvantage of the reactive sputtering methods for the deposition of AlO$_x$. A process that requires the control of only one process gas is much more robust and repeatable than one that requires the control and balance of two process gases. Thus in the manufacturing environment, it would be preferable to utilise inert sputtering (e.g. RF sputtering of an Al$_2$O$_3$ target in an Ar ambient) rather than the reactive sputtering methods for the deposition of AlO$_x$.

3.4.4 Film uniformity

The use of substrate rotation was crucial to achieving uniform film depositions. This effect is particularly obvious for thicker films, where a colour gradient can be observed. Figure 3.4 gives an example of sputtered AlO$_x$ films from system “A”, showing when substrate rotation was used resulting in a uniform deposition and when substrate rotation was not used resulting in a highly non-uniform deposition. The AlO$_x$ films deposited by system “A” were uniform through the use of the substrate rotation, while the lack of
3.4 Development of the Sputtering Process

Figure 3.4: Examples of sputtered $\text{AlO}_x$ films from system “A”, showing (a) when substrate rotation was used and (b) when substrate rotation was not used. The semicircles on the edge of the wafers are shadow marks from the substrate holder. The deposition parameters were exaggerated to illustrate the effect.

Figure 3.5: Spatially resolved lifetime imaging of sputtered $\text{AlO}_x$, using (a) PL imaging and (b) MWPCD imaging.

Substrate rotation in system “B” was clearly one of its limitations.

The semicircles on the edge of the samples in Figure 3.4 are shadow marks from the substrate holder and no $\text{AlO}_x$ is deposited in these regions. To investigate how the shadow marks may affect the characterisation of the $\text{AlO}_x$, PL and MWPCD imaging were performed on a number of samples after they had been annealed. Figure 3.5(a) shows the PL imaging of a sample, with the darker regions indicating a lower lifetime compared to the brighter region (relative scale given alongside the image). The darker semicircles on the edges correspond to the shadow marks as seen visually in Figure 3.4(a) and lower lifetimes were expected in these locations as there is no $\text{AlO}_x$ to provide surface passivation. Most importantly however, these regions of low lifetime are limited to the locations of the shadow marks and do not affect the region in the centre of the sample where the $\text{AlO}_x$ is to be characterised. This is confirmed by the MWPCD imaging in
3. Viability of Sputtering Methods

Figure 3.5(b), which maps the lifetime across the sample. The semicircles do not appear in the MWPCD imaging, which demonstrates that the shadow marks did not have a significant effect on the absolute lifetime. Therefore, the shadow marks do not affect the characterisation of the AlO\(_x\) provided that the measurement is taken at the centre of the sample.

A shutter was not available in system “B” and so the target material was deposited on the substrate during all stages of sputtering process. This would not be a major problem if the target only consisted of one element (e.g. Al) being sputtered in an inert ambient (e.g. Ar), as only aluminium would be deposited during in any of the stages. In the case of sputtering AlO\(_x\) where either reactive sputtering or a multi-element target is always required, it is necessary to wait for the sputtering process to reach steady state prior to the deposition of the sputtered material on the substrate. Otherwise, the composition of the deposited film will vary with thickness, particularly at the surface of the substrate during the initial stages of the deposition (e.g. Figure 4.7 in Section 4.5). Thus, a shutter is critical for obtaining consistent AlO\(_x\) films; this is an important component missing from system “B”.

In thin film deposition systems where the direction of the deposition is downwards, particles formed from the deposition process or residue flakes on the chamber walls drop onto the surface of the sample due to gravity. These particles and flakes are usually undesirable as they affect the composition of the deposited thin film and subsequently affect its electronic properties. This is not a problem when the deposition direction is upwards, as the particles fall to the bottom of the vacuum chamber rather than on the sample. Thus, the upward sputtering direction of system “A” is preferable to the downward sputtering direction of system “B”.

3.4.5 Calibration of the Thickness Monitor

The thickness monitor used in system “A” relied on two material calibration constants: the film density (\(\rho_{mass}\)) and the Z-ratio. The Z-ratio is a parameter that corrects the frequency change to thickness transfer function for the effects of acoustic impedance mismatch between the crystal and the deposited material. The density and Z-ratio are well known for stoichiometric Al\(_2\)O\(_3\), but will vary for sputtered AlO\(_x\) depending on the deposition method and the stoichiometry of the deposited film.

As the Z-ratios only change significantly for thin films under high stress—which was not the case here as the sputtered AlO\(_x\) were rather porous—the Z-ratio for the sputtered
3.4 Development of the Sputtering Process

AlO\textsubscript{x} films was assumed to be the same as for Al\textsubscript{2}O\textsubscript{3} (i.e. Z-ratio = 26.28). The results in Table 3.5 show that the deposition rate of AlO\textsubscript{x} from sputtering can be 2–40 times faster than thermal ALD.

By modelling the ellipsometry measurements as described in Section 2.3.5, the approximate thickness of the deposited AlO\textsubscript{x} film was determined. By fitting the RBS measurements—as discussed in Section 2.3.1—with this thickness, the approximate density of the AlO\textsubscript{x} was determined. The approximate density and deposition rates for the different deposition methods are listed in Table 3.5. The detailed information concerning the composition and properties of the AlO\textsubscript{x} films from the RBS and ellipsometry measurements will be presented and discussed in Section 4.4 and Section 6.2 respectively.

**Table 3.5:** The density of deposited AlO\textsubscript{x} films for selected stoichiometry and deposition methods as determined by ellipsometry and RBS measurements.

<table>
<thead>
<tr>
<th>System</th>
<th>ALD “A”</th>
<th>“A”</th>
<th>“A”</th>
<th>“B”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>Thermal</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Stoichiometry (O/Al)</td>
<td>1.6</td>
<td>1.75</td>
<td>1.75</td>
<td>1.5</td>
</tr>
<tr>
<td>(\rho_{\text{mass}}) (g/cm\textsuperscript{3})</td>
<td>3.9 ± 0.1</td>
<td>2.6 ± 0.2</td>
<td>2.7 ± 0.2</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>Deposition rate (nm/min)</td>
<td>0.6</td>
<td>4.3</td>
<td>1.1</td>
<td>25.9</td>
</tr>
</tbody>
</table>

The main result of this evaluation is that \(\rho_{\text{mass}}\) of the sputtered AlO\textsubscript{x} films is less than that deposited by thermal [ALD] which would indicate that the sputtered films are quite porous. This had been identified in Section 3.2.1 as one of the disadvantages of sputtering. Interestingly, it has been reported that \(\rho_{\text{mass}}\) of AlO\textsubscript{x} films deposited by ALD and PECVD methods decreases with lower deposition temperatures \[17\] and at a deposition temperature of 25°C, \(\rho_{\text{mass}}\) is around 2.7 g/cm\textsuperscript{3} \[72\]. This is essentially identical to \(\rho_{\text{mass}}\) of the AlO\textsubscript{x} films deposited by sputtering at 25°C. Thus, the low \(\rho_{\text{mass}}\) obtained with sputtering in this experiment is probably due to the low deposition temperature and higher \(\rho_{\text{mass}}\) may be obtained using higher deposition temperatures.

Meanwhile, the \(\rho_{\text{mass}}\) of the AlO\textsubscript{x} film deposited by thermal ALD in this thesis (3.9 ± 0.1 g/cm\textsuperscript{3}) is effectively the same as the value for crystalline Al\textsubscript{2}O\textsubscript{3} (3.96 g/cm\textsuperscript{3}). This is higher than the \(\rho_{\text{mass}}\) that has been reported in the literature (2.5–3.5 g/cm\textsuperscript{3}) for AlO\textsubscript{x} deposited by thermal ALD \[17\] \[141\] \[142\]. Since the growth rate of AlO\textsubscript{x} deposited by thermal ALD is very precise, the thickness of the film is known explicitly and the uncertainty in the \(\rho_{\text{mass}}\) of the AlO\textsubscript{x} is low. The \(\rho_{\text{mass}}\) obtained in this experiment for AlO\textsubscript{x} deposited by thermal ALD should be accurate, as demonstrated by the good theoretical fit of its RBS measurement in Figure 4.2(a) in Section 4.4. The difference
in the $\rho_{mass}$ obtained is probably due to the different thermal ALD reactors and the deposition conditions used in the literature compared to what has been used in this work.

The values of $\rho_{mass}$ obtained in this experiment for sputtered AlO$_x$ are used as calibration values for the thickness monitor, allowing the estimation of the deposition rates for subsequent experiments. It is important to note that the deposition rates and thicknesses reported here and elsewhere in this thesis should not be interpreted as exact values, but rather as reasonable estimates that highlight the trends in the deposition rate. This is because the density and Z-ratios of the deposited films will vary when the sputtering parameters are changed; the values in Table 3.5 were only determined for selected stoichiometries of AlO$_x$ films. Also, the actual deposition rate may not be strictly linear as assumed. Nevertheless, the estimated deposition rates are extremely useful for identifying target oxidation and for distinguishing between the different modes of sputtering.

### 3.4.6 Characterising the Modes of Sputtering

![Figure 3.6](image)

**Figure 3.6:** The modes of sputtering can be distinguished by the relationship between the percentage of O$_2$ in Ar and its corresponding (a) voltage and (b) deposition rate.

Olsson *et al.* [96] and Jhin *et al.* [127] showed that the electronic properties of reactively sputtered AlO$_x$ films will vary depending on the state of the Al target, whether it was metallic or oxidised. In this section, we extend the concept to characterise three “modes of sputtering”, of which only “dielectric mode” is suitable for surface passivation purposes.

Figure 3.6 shows some of the key parameters that can be used to distinguish the modes
3.4 Development of the Sputtering Process

of sputtering, as for the case of using DC sputtering with an Al target in system “A”. Figure 3.6(a) shows the relationship between the percentage of O\textsubscript{2} in Ar used in system “A” and the voltage used for sputtering. Figure 3.6(b) shows the deposition rate of the sputtered AlO\textsubscript{x}. The vertical dashed lines divide three distinct modes of sputtering, of which only the “dielectric mode” is suitable for surface passivation purposes. The surface passivation results will be presented and discussed in detail in Sections 3.5–3.7.

In “oxide mode”, a high percentage of O\textsubscript{2} in the sputtering ambient results in the oxidation of the surface of the Al target. This can be distinguished by a sharp decrease in the voltage and the deposition rate (Figure 3.6) and the little material that is deposited—as will be presented in Sections 3.5, 3.6—has very high O/Al ratios. By measuring the deposition rate preferably \textit{in-situ} using a thickness monitor—or the voltage—, the sharp decrease in the deposition rate or the voltage can be used to determine if target oxidation has occurred and that the sputtering is in “oxide mode”. In “dielectric mode”, the Al target remains unoxidised and metallic; a high deposition rate is maintained and desirable AlO\textsubscript{x} is deposited.

When the percentage of O\textsubscript{2} in the sputtering ambient is too low, sputtering in “metal mode” occurs. In this mode, there is insufficient O\textsubscript{2} for the formation of AlO\textsubscript{x}. Effectively, only aluminium is deposited and no surface passivation is obtained. This can be seen visually by the deposition of a silvery film rather than a light brown or blue film. In the case of FTIR measurements as will be seen in Section 4.8, the films sputtered in “metal mode” will have much higher absorbance (∼85%) than those sputtered in “dielectric mode” (2–5%).

The modes of sputtering and the trends observed correspond well with what has been previously reported in the literature \cite{96, 127, 132}. Figure 3.7 gives visual examples of the colours that are usually observed from the different modes of sputtering.
Figure 3.8: The relationship between the percentage of $O_2$ in Ar and its corresponding deposition rate as related to the modes of sputtering for the RF magnetron sputtering of an Al$_2$O$_3$ target using system “A”.

Figure 3.9: The changing relationships between the percentage $O_2$ in Ar and its corresponding deposition rate as related to the deposition pressure demonstrates how the sputtering arrangement affects the location of the transition between the different modes of sputtering.

It is not always possible to achieve all three modes of sputtering with a particular sputtering method or set of deposition parameters. In the case of RF magnetron sputtering of an Al$_2$O$_3$ target using system “A” (Figure 3.8), for example, the presence of oxygen in the target has meant that the sputtered film will always contain oxygen and so “metal mode” is never achieved. On the other hand, this extra source of oxygen means that the onset of “oxide mode” occurs at a comparatively low percentage of $O_2$ in Ar.
3.5 Method 1: RF Sputtering with an Al target

Figure 3.9 demonstrates how the deposition pressure can affect the modes of sputtering for the case of using RF magnetron sputtering with an Al target in system “A”. The sharp drop in the rate of deposition, which was previously identified as an indicator of the onset of “oxide mode”, is located at different percentages of \( \text{O}_2 \) in \( \text{Ar} \) for the different deposition pressures.

Figures 3.6, 3.8 and 3.9 show that for different sputtering parameters and methods, the \( \text{O}/\text{Al} \) ratio of the transition between modes of sputtering will be different. This was also found to be the case between systems “A” and “B”, whereby the modes of sputtering are different for the different sputtering arrangements. Therefore, the modes of sputtering and their relationships to the deposition rate and voltage will always need to be determined empirically for the particular deposition parameters of a particular sputtering arrangement.

3.4.7 Summary

Two magnetron sputtering systems were evaluated for the sputtering of \( \text{AlO}_x \). The applicability of system “B” was found to be limited by the lack of a shutter, a load lock, a thickness monitor and substrate rotation. System “A” was found to be suitable for sputtering \( \text{AlO}_x \), although repeatability can be a problem with the reactive sputtering processes. An optimised sputtering process (Figure 3.3) was formulated for controlling target oxidation and the reactive sputtering process; this optimised sputtering process is used in the subsequent experiments.

We have showed how the deposition rate, voltage and the visual appearance of the \( \text{AlO}_x \) film can be used to identify the different modes of sputtering. For the deposition of \( \text{AlO}_x \) of suitable electronic quality for surface passivation purposes, the deposition conditions used must lead to sputtering in “dielectric mode”. The deposition conditions for achieving “dielectric mode” are used in the subsequent experiments (Sections 3.5–3.7) for evaluating the different sputtering methods and systems in attaining strong negative charges and good surface passivation.

3.5 Method 1: RF Sputtering with an Al target

The previous known work on the sputtering of \( \text{AlO}_x \) for surface passivation was conducted using RF sputtering of an Al target [16, 23]. It was reported as being unsuccessful, as the combination of high \( D_H \) and low density of negative charges—or vice versa—was unlikely to lead to good surface passivation. Nonetheless, we begin with this sputtering method
and investigate its ability to achieving negative charges and surface passivation. Negative charges in the range of $-1 \times 10^{12}$ to $-1 \times 10^{13}$ and surface passivation in the range of 20–260 cm/s are obtained after annealing, demonstrating that RF sputtering of an Al target can be used to deposit AlO$_x$ that is suitable for the surface passivation of solar cells.

**Modes of Sputtering**

Figure 3.10(a) shows the percentage of O$_2$ in Ar used in system “A” in order to achieve the corresponding O/Al ratio in the sputtered AlO$_x$ film when using RF sputtering of an Al target. Figure 3.10(b) shows the relationship between the O/Al ratio and the voltage while Figure 3.10(c) shows the deposition rate.

![Figure 3.10](image_url)

**Figure 3.10:** The O/Al ratio of the as deposited AlO$_x$ films from system “A” using RF sputtering of an Al target, as related to (a) the percentage of O$_2$ in Ar used (b) the voltage and (c) the deposition rate.
Surface Passivation

For the samples deposited in “dielectric mode”, good surface passivation is attained after annealing for the samples deposited in system “A”, but not system “B”. Figure 3.11 relates the $\tau_{\text{eff}}$ to the O/Al ratio of the AlO$_x$ film—deposited using System “A”—after 60 min of annealing. The best results on 0.8 $\Omega$.cm FZ $c$-Si($p$) were in the range of 120 $\mu$s and 120 cm/s for the $\tau_{\text{eff}}$ (at $\Delta n = 10^{15}$ cm$^{-3}$) and the calculated $S_{\text{eff}}$ respectively. The best results on 1 $\Omega$.cm Cz $c$-Si($n$) were in the range of 500 $\mu$s and 22 cm/s. These results are acceptable for the surface passivation of solar cells and confirm that surface passivation can be achieved using AlO$_x$ films deposited by RF sputtering of an Al target.

![Figure 3.11](image.png)

**Figure 3.11:** The dependence of $\tau_{\text{eff}}$ on the excess carrier density for samples passivated with AlO$_x$ from System “A”, annealed at 400°C in N$_2$ for 60 min. On (a) 0.8 $\Omega$.cm FZ $c$-Si($p$) and (b) 1 $\Omega$.cm Cz $c$-Si($n$).

Negative Charge

Negative charges are obtained in the AlO$_x$ films from both system “A” and “B” after annealing. Figure 3.12 shows the high frequency C-V curves of the $p$- and $n$-type wafers passivated with an AlO$_x$ film from system “A”, as deposited and after annealing at 400°C in N$_2$ for 60 min. On the $p$-type sample, the negative charge ($Q_{\text{ox}}$) was greatly enhanced with annealing, changing from $-3.4 \times 10^{12}$ cm$^{-2}$ to $-9.8 \times 10^{12}$ cm$^{-2}$. Meanwhile, on the $n$-type sample, the change was from a positive charge of $+8.8 \times 10^{11}$ cm$^{-2}$ as deposited to a negative charge of $-2.7 \times 10^{12}$ cm$^{-2}$ after annealing. The charge from the AlO$_x$ films with various O/Al ratios are summarised in Figure 3.13. Note that the scale in Figure 3.13(b) changes between positive and negative charges.

The charges on the $n$-type samples are positive as deposited and a negative charge is
observed after annealing. This effect had been previously observed on AlOₓ films deposited by other methods \[101, 145\] and the possible mechanism for this will be discussed later in Section 4.7. No clear trends between $Q_{ox}$ and the O/Al ratio are easily observable here; the results in Section 5.3.4 will show that the $S_{eff}$ is dependent on the $Q_{ox}$, both of which are independent of the O/Al ratio.

![Figure 3.12](image-url) The measured and ideal high frequency C-V curves of AlOₓ passivation. Deposited using RF sputtering of an Al target with system “A” on (a) 0.8 Ω.cm FZ c-Si(p) and (b) 1 Ω.cm c-Si(n).

![Figure 3.13](image-url) The relationship between the O/Al ratio to the charge from AlOₓ films as deposited and after annealing at 400°C in N₂ for 60 min. Deposited using RF sputtering of an Al target with system “A” on (a) 0.8 Ω.cm FZ c-Si(p) and (b) 1 Ω.cm c-Si(n).

The high $D_{it}$ in the AlOₓ films—as will be presented in Figure 3.16—can affect the extraction of the flatband voltage and consequently of the fixed charge density. Thus, to verify the levels of negative charge in AlOₓ films deposited by RF sputtering of an Al...
3.5 Method 1: RF Sputtering with an Al target

results confirm both the polarity and magnitude of $Q_{\text{ox}}$ (Figure 3.13). The negative charge is around $-2.3 \times 10^{12}$ cm$^{-2}$ on both the $p$- and $n$-type substrates. These results confirm both the polarity and magnitude of $Q_{\text{ox}}$ found from the C-V measurements (Figure 3.13).

Figure 3.14: The change in $\tau_{\text{eff}}$ resulting from the corona charge for samples passivated with RF sputtered AlO$_x$ after 150 min of annealing at 400°C in N$_2$ on (a) 0.8 Ω.cm FZ $p$-Si and (b) 1 Ω.cm $n$-Si. The dashed lines indicate the $Q_{\text{surface}}$ corresponding to the minimum $\tau_{\text{eff}}$.

Figure 3.15: The measured and ideal high frequency C-V curves of AlO$_x$ passivation. Deposited using RF sputtering of an Al target with system “B” on 0.5 Ω.cm FZ $p$-Si.

Figure 3.15 shows the high frequency C-V curves of 0.5 Ω.cm FZ $p$-Si passivated with an AlO$_x$ film from system “B”, as deposited and after annealing at 400°C in N$_2$ for 30 min. The charge for this AlO$_x$ as deposited was $+4.3 \times 10^{12}$ cm$^{-2}$ and this changed to $-3.7 \times 10^{11}$ cm$^{-2}$ after annealing. The $D_{it}$ decreased from $2.2 \times 10^{12}$ cm$^{-2}$eV$^{-1}$ to
6.1 \times 10^{11} \text{ cm}^{-2} \text{eV}^{-1} at midgap after annealing. Despite the negative charge and lowering of the $D_{it}$, the surface passivation achieved with the AlO$_x$ films of system “B” did not reach acceptable levels. This is believed to be due to the limitations of this system (Section 3.4) as well as the high concentrations of Ar that were incorporated into the deposited films (Section 4.4).

Density of Interface States

The $D_{it}$ from the AlO$_x$ films deposited using system “A”, with various O/Al ratios are summarised in Figure 3.16. The values of $D_{it}$ for the n-type samples could not be confidently determined and are not presented. The $D_{it}$ of the sample in Figure 3.12(a) is presented as function of the energy in the bandgap in Figure 3.17. In this case, the $D_{it}$ decreased very slightly, from $2.6 \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1}$ to $1.4 \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1}$ at midgap after annealing.

![Figure 3.16: The relationship between the O/Al ratio to the $D_{it}$ at midgap from AlO$_x$ films as deposited and after annealing at 400°C in N$_2$ for 60 min. Deposited using RF sputtering of an Al target with system “A” on 0.8 Ω.cm FZ c-Si(p).](image)

Summary

The results show that AlO$_x$ deposited by the RF sputtering of an Al target is capable of achieving negative charges after annealing in the range of $10^{11}$ to $10^{13} \text{ cm}^{-2}$ were achieved after annealing. Even though surface passivation was not obtained with the AlO$_x$ deposited by system “B”, good surface passivation was achieved with the AlO$_x$ deposited by system “A”. Values of $S_{eff}$ (at $\Delta n=10^{15} \text{ cm}^{-3}$) as low as 125 cm/s and 22 cm/s were obtained on $p$- and $n$-type silicon wafers respectively in this initial experiment. As will be
3.6 Method 2: RF Sputtering with an Alumina Target

As reviewed in Section 3.2.1, the RF sputtering of an Al$_2$O$_3$ target can be used to deposit AlO$_x$. Compared to using an Al target as in Section 3.5, the advantage in using an Al$_2$O$_3$ target is that the use of O$_2$ is not required. Sputtering with an inert gas—usually Ar—can be used and the complications of reactive sputtering—such as control of the Ar/O$_2$ ambient, target oxidation, etc. as discussed in Section 3.4—can be avoided. In this experiment, we investigate the negative charge and surface passivation from AlO$_x$ films deposited by RF sputtering of an Al$_2$O$_3$ target.

Modes of Sputtering

Figure 3.18(a) shows the percentage of O$_2$ in Ar used in the RF sputtering of an Al$_2$O$_3$ target in order to achieve the corresponding O/Al ratio in the deposited AlO$_x$ film. Figures 3.18(b) and 3.18(c) show the relationship between the O/Al ratio to the voltage and rate of deposition respectively. The deposition rates of < 1 nm/min is clearly much lower than that obtained using the other sputtering methods; it is even less than the deposition rates of ~2 nm/min on PA-ALD [17, 25]. On the other hand, deposition rate as high as...
Figure 3.18: The O/Al ratio of the as deposited AlO$_x$ films from system “A” using RF sputtering of an Al$_2$O$_3$ target, as related to (a) the percentage of O$_2$ in Ar used (b) the voltage and (c) the deposition rate.

35 nm/min had been obtained using this sputtering method in the literature [138], so it may be an issue particular to system “A” being a laboratory system. In any case, the deposition rate will definitely need to be higher than 2 nm/min in order for this sputtering method to have significant advantages over the ALD methods.

Surface Passivation

Acceptable levels of surface passivation was not attained using AlO$_x$ deposited using RF sputtering with an Al$_2$O$_3$ target. The $Q_{ox}$ and $D_{it}$ obtained using this sputtering method (Sections 3.6–3.6) are similar to what was obtained through RF sputtering with Al target (Section 3.5–3.5), so it would be expected that similarly good surface passivation results would be obtained. As will be shown in Section 4.4, the incorporation of impurities during the sputtering process is the likely cause for the poor levels of surface passivation. The elimination of these impurities from the sputtering process should lead to good surface passivation being achieved with AlO$_x$ films deposited using RF sputtering of an Al$_2$O$_3$ target.
Figure 3.19: The measured and ideal high frequency \(|C-V|\) curves of AlO\(_x\) passivation. Deposited using RF sputtering of an Al\(_2O_3\) target with system “A” on (a) 0.8 \(\Omega\).cm FZ \(p\)-Si(p) and (b) 1 \(\Omega\).cm Cz \(n\)-Si(n).

**Negative Charge**

Figure 3.20: The relationship between the O/Al ratio to the charge from AlO\(_x\) films as deposited and after annealing at 400\(^\circ\)C in N\(_2\) for 30 min. Deposited using RF sputtering of an Al\(_2O_3\) target with system “A” on (a) 0.8 \(\Omega\).cm FZ \(p\)-Si(p) and (b) 1 \(\Omega\).cm Cz \(n\)-Si(n).

Figure 3.19 shows the high frequency \(|C-V|\) curves of the \(p\)- and \(n\)-type wafers passivated with an AlO\(_x\) film with a O/Al ratio of 1.75, as deposited and after annealing at 400\(^\circ\)C in N\(_2\) for 30 min. On the \(p\)-type sample, a positive charge of \(+9.8 \times 10^{11}\) cm\(^{-2}\) in the AlO\(_x\) film as deposited changed to a negative charge of \(-4 \times 10^{12}\) cm\(^{-2}\) after annealing. Similarly on the \(n\)-type sample, the change was from a positive charge of \(+1 \times 10^{12}\) cm\(^{-2}\) as deposited to a negative charge of \(-3.1 \times 10^{12}\) cm\(^{-2}\) after annealing. The charge from
the AlO$_x$ films with various O/Al ratios are summarised in Figure 3.20. Even though there is one sample with positive charges when the AlO$_x$ is as deposited, the charge is always negative after annealing.

Density of Interface States

Figure 3.21: The relationship between the O/Al ratio to the $D_{it}$ at midgap from AlO$_x$ films as deposited and after annealing at 400°C in N$_2$ for 30 min. Deposited using RF sputtering of an Al$_2$O$_3$ target with system “A” on 0.8 Ω.cm FZ c-Si(p).

Figure 3.22: The $D_{it}$ as a function of the bandgap energy for the sample in Figure 3.19(a), as deposited and after annealing at 400°C in N$_2$ for 30 min.

The $D_{it}$ from the AlO$_x$ films with various O/Al ratios are summarised in Figure 3.21. The values of $D_{it}$ for the n-type samples could not be confidently determined and are not
presented. The $D_{it}$ of the sample in Figure 3.19(a) is presented as function of the energy in the bandgap in Figure 3.22. In this case, the $D_{it}$ decreased from $1.4 \times 10^{12}$ cm$^{-2}$eV$^{-1}$ to $8.2 \times 10^{11}$ cm$^{-2}$eV$^{-1}$ at midgap after annealing. The decrease in the $D_{it}$ with the post-deposition anneal is the greatest at 0.4 eV, which probably corresponds to the annealing out of a particular defect at that energy level.

Summary

In this experiment, AlO$_x$ films deposited with RF sputtering of an Al$_2$O$_3$ target was investigated. Negative charges were found after annealing, along with reduction in $D_{it}$. However, no surface passivation was obtained on any of the samples. Nevertheless, surface passivation is likely to be achieved if various impurities (Section 4.4) are not incorporated into the AlO$_x$ film.

If we consider that stronger negative charges, excellent surface passivation and higher deposition rates have already been achieved using PA-ALD [11, 13, 14], this sputtering method in its current arrangement is inadequate for the surface passivation of solar cells. In order for the RF sputtering of an Al$_2$O$_3$ target to be competitive, much higher deposition rates—possibly through the use of inline sputtering systems—and excellent surface passivation must be achieved.

3.7 Method 3: DC Sputtering with an Al Target

If the negative charges and the surface passivation achieved with DC sputtering is the same or better than from RF sputtering, then the higher deposition rates usually achieved with DC sputtering (Table 3.1) would always be preferable. In this experiment we evaluate the negative charge and surface passivation capabilities of AlO$_x$ films using DC sputtering of an Al target.

Modes of Sputtering

Figure 3.23(a) shows the percentage of O$_2$ in Ar used in system “A” in order to achieve the corresponding O/Al ratio in the sputtered film when using DC sputtering of an Al target. Figure 3.23(b) shows the relationship between the O/Al ratio and voltage while Figure 3.23(c) shows the corresponding deposition rate. As a wider range of voltages was available with DC sputtering compared to RF sputtering, it was easier to control the O/Al ratio in these AlO$_x$ films. The deposition rates achieved here with the DC sputtering of an
Al target (∼26 nm/min) are more than five times higher than that from the RF sputtering of an Al target (∼5 nm/min), which highlights the significant advantage of DC sputtering for the manufacturing of solar cells.

Figure 3.23: The resulting O/Al ratio from system “A” using DC sputtering of an Al target and its corresponding (a) percentage of O₂ in Ar (b) voltage and (c) deposition rate.

Surface Passivation

None of the lifetime samples showed acceptable levels of surface passivation as deposited or after annealing. The increase in the $D_{it}$ (Section 3.7) with annealing indicates that the AlOₓ films deposited by DC sputtering is different compared to RF sputtering. As will be shown in Section 4.5, it is possible that the higher voltages used in DC sputtering compared to RF sputtering causes significant plasma damage (Section 3.2.1).

Negative Charge

Figure 3.24 shows the C-V measurements on selected p- and n-type samples. On the p-type sample, the charge changed from $+2.7 \times 10^{12}$ cm$^{-2}$ to $-3.9 \times 10^{12}$ cm$^{-2}$ after annealing, while on the the n-type sample, the charge changed from $+1.1 \times 10^{11}$ cm$^{-2}$
to $-9.7 \times 10^{11}$ cm$^{-2}$ after annealing. The range of charges from the AlO$_x$ films for the various O/Al ratios are summarised in Figure 3.25.

![Figure 3.24: The measured and ideal high frequency C-V curves of AlO$_x$ passivation. Deposited using DC sputtering of an Al target with system “A” on (a) 0.8 Ω cm Cz c-Si(p) and (b) 1 Ω cm Cz c-Si(n).](image)

![Figure 3.25: The relationship between the O/Al ratio to the charge from AlO$_x$ films as deposited and after annealing at 400°C in N$_2$ for 30 min. Deposited using DC sputtering of an Al target with system “A” on (a) 0.8 Ω cm FZ c-Si(p) and (b) 1 Ω cm Cz c-Si(n).](image)

**Density of Interface States**

The $D_{it}$ from the AlO$_x$ films with various O/Al ratios are summarised in Figure 3.26. The values of $D_{it}$ for a number of the $p$- and $n$-type samples could not be confidently determined and are not presented. Of the few values of $D_{it}$ that could be calculated, the $D_{it}$ from the as deposited AlO$_x$ film ($8 \times 10^{11}$ cm$^{-2}$eV$^{-1}$) is similar to the values obtained.
in the literature \((10^{11} \text{ to } 10^{12} \text{ cm}^{-2}\text{eV}^{-1})\) [94]. After annealing however, the values of \(D_{it}\) increases \((10^{12} \text{ to } 10^{13} \text{ cm}^{-2}\text{eV}^{-1})\), which is higher than the observed values in the literature \((10^{11} \text{ to } 10^{12} \text{ cm}^{-2}\text{eV}^{-1})\) [94]. The high \(D_{it}\) would explain why no acceptable levels of surface passivation was achieved after annealing.

![Figure 3.26: The relationship between the O/Al ratio to the \(D_{it}\) at midgap from AlO\(_x\) films as deposited and after annealing at 400°C in N\(_2\) for 30 min. Deposited using DC sputtering of an Al target with system “A” on 0.8 Ω.cm FZ c-Si(p).](image)

**Figure 3.26:** The relationship between the O/Al ratio to the \(D_{it}\) at midgap from AlO\(_x\) films as deposited and after annealing at 400°C in N\(_2\) for 30 min. Deposited using DC sputtering of an Al target with system “A” on 0.8 Ω.cm FZ c-Si(p).

**Summary**

The deposition rates achieved in this laboratory sputtering system (~26 nm/min) are already relevant to manufacturing; even higher deposition rates can be expected for industrial inline DC sputtering systems. Even though negative charges were clearly present after annealing, no acceptable levels of surface passivation were obtained as deposited or after annealing. The negative charges and the manufacturing advantages of DC sputtering cannot be utilised unless surface passivation is achieved.

**3.8 Chapter Summary**

In this chapter, we reviewed the literature in the area of sputtered AlO\(_x\) (Section 3.2), most of which were focused on its application to microelectronic devices. For surface passivation purposes, only a small range of deposition parameters and methods had been evaluated and the sputtered AlO\(_x\) had been found to be inadequate for solar cell applications. As shown by the work on microelectronic devices, a much wider range of deposition parameters and methods can be explored and evaluated for surface passivation and so these were
### Table 3.6: Summary of Chapter 3 results.

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</tbody>
</table>

(a) After annealing at 400°C in N$_2$ for $> 30$ min.
(b) Using the stoichiometry specified in Table 3.5.
Three of the methods for sputtering AlO$_x$ and two different sputtering systems were investigated. The influence of the sputtering arrangement and importance of the controlling the reactive sputtering process were analysed and discussed. The different modes of sputtering define when desirable AlO$_x$ could be obtained; the modes can be identified visually, by the deposition rate or by the sputtering voltage. The charge and surface passivation from each of the sputtering systems and method were evaluated and the results are summarised in Table 3.6.

Even though all of the three sputtering methods investigated led to the formation of negative charges after annealing, good surface passivation was only achieved using RF sputtering of an Al target using System “A” (Table 3.6). Using this method, $S_{eff}$ values as low as 124 cm/s and 22 cm/s were obtained on 0.8 Ω.cm c-Si(p) and 1 Ω.cm c-Si(n) respectively after annealing at 400°C in N$_2$. With further optimisation of the deposition and annealing parameters, $S_{eff}$ values as low as 24.6 cm/s and 9 cm/s are obtained on 0.8 Ω.cm c-Si(p) and 1 Ω.cm c-Si(n) are obtained in Chapter 5.
Material Properties of Sputtered Aluminium Oxide Films

"The question arises as to what effect hydrogen has in these oxides."

P. W. Peacock and J. Robertson, 2003

4.1 Introduction

The level of surface passivation obtained with AlO$_x$ films is related to its physical and electronic properties. For AlO$_x$ films deposited by methods other than sputtering, these physical and electronic properties have been found to depend on the incorporation of impurities (Section 4.2.1) as well as the types of atomic bonding within the AlO$_x$ film (Section 4.2.4). The negative charge and the surface passivation attained with the AlO$_x$ film have been linked with the interfacial layer that is in contact with the silicon. Also, it has been hypothesised that various interstitials and vacancies are responsible for the negative charge (Section 4.2.3). Even though the exact mechanisms for the formation of negative charge have not been established, it is reasonable to infer that the desirable characteristics are those observed on AlO$_x$ films that attain strong negative charges and excellent surface passivation (e.g. AlO$_x$ deposited by thermal ALD).

In Chapter 3 it was shown that RF sputtering of an Al target in system “A” is capable of depositing negatively charged AlO$_x$ and achieving good surface passivation on both $p$- and $n$-type silicon wafers. Even though the other sputtering methods were also capable of depositing negatively charged AlO$_x$, it is unclear why similar levels of surface passivation were not achieved. Also, the surface passivation achieved with sputtered AlO$_x$ (> 25 cm/s) is not as good as those achieved with AlO$_x$ deposited by ALD and CVD methods (∼2 cm/s). These results indicate that AlO$_x$ deposited by the various sputtering methods are lacking some of the desirable characteristics that are found in AlO$_x$ films.
deposited by [ALD] and [CVD] methods.

In this chapter, we use various thin film and surface analysis methods (Section 2.3) to study the physical characteristics of sputtered AlO$_x$. We highlight how the levels of surface passivation attained with sputtered AlO$_x$ are likely to depend on the incorporation of impurities (Section 4.4), the incorporation of hydrogen (Section 4.5) and the nature of the interfacial layer (Section 4.2.2). We also discuss how the results from [PAS] and [FTIR] measurements of sputtered AlO$_x$ films (Sections 4.7 and 4.8) address the various hypotheses in the literature concerning the origin of the negative charge in AlO$_x$ films.

4.2 Literature Review

Aluminium oxide has been frequently and widely used in materials engineering, but its application as a thin film for electronic devices is much more recent. In this thesis, we are interested in AlO$_x$ as a thin film for surface passivation purposes; we review in this section the compositional and bonding properties of AlO$_x$ thin films for electronic applications.

4.2.1 Composition of Aluminium Oxide

To create thin films for electronic applications, the deposition of the AlO$_x$ usually relies on the reaction between an aluminium containing material and an oxygen containing material, with some exceptions (e.g. sputtering of an Al$_2$O$_3$ target as in Section 3.6). A large variety of methods and combinations of reactants can be used for the deposition of AlO$_x$ films. Table 4.1 summarises the various deposition temperatures, reactants and ambient that are commonly used for depositing AlO$_x$.

With most of the deposition methods in Table 4.1 amorphous AlO$_x$ is deposited. At deposition or annealing temperatures above 750°C however, crystalline $\gamma$-Al$_2$O$_3$ may be formed [102, 148].

As can be seen in Table 4.1 many of the possible reactants include elements other than aluminium and oxygen. These elements can become incorporated during the deposition processes [17, 72, 143, 150] or from the post-deposition processes [93, 102, 151, 152]. With the ALD methods for example, elements such as carbon and hydrogen are often incorporated in the AlO$_x$ films during the deposition process due to the use of various alkyl aluminium, alkyl aluminium hydride and alkyl amino aluminium precursors [e.g. Al(CH$_3$)$_3$, Al(C$_4$H$_9$O)] as well as H$_2$O [143, 149, 153]; the concentration of carbon and hydrogen in the AlO$_x$ films were found to be dependent on the deposition temperature.
Table 4.1: Summary of the typical deposition conditions for the prevalent methods of depositing AlO\(_x\) thin films for electronic applications.

<table>
<thead>
<tr>
<th>Type</th>
<th>Method</th>
<th>Ref.(^{(a)})</th>
<th>Temperature (°C)</th>
<th>Aluminium Source</th>
<th>Oxygen Source</th>
<th>Ambient(^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD</td>
<td>PA-ALD</td>
<td>[25]</td>
<td>25–300</td>
<td>TMA(^{(c)})</td>
<td>O(_2)</td>
<td>Ar, N(_2)</td>
</tr>
<tr>
<td></td>
<td>Thermal</td>
<td>[14]</td>
<td>25–800</td>
<td>TMA(^{(c),(d)})</td>
<td>H(_2)O, O(_3)</td>
<td>Ar, N(_2)</td>
</tr>
<tr>
<td>CVD</td>
<td>PECVD</td>
<td>[14]</td>
<td>25–300</td>
<td>TMA(^{(c)})</td>
<td>O(_2), N(_2)O</td>
<td>Ar, H(_2)</td>
</tr>
<tr>
<td></td>
<td>APCVD</td>
<td>[9]</td>
<td>290–900</td>
<td>Al(C(_3)H(_7))(_3)(^{(d),(e)})</td>
<td>N(_2), Ar, H(_2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MOCVD</td>
<td>[147]</td>
<td>25</td>
<td>TMA(^{(c),(d)})</td>
<td>O(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>Epitaxy</td>
<td>MBE</td>
<td>[102]</td>
<td>750</td>
<td>Al</td>
<td>N(_2)O</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RF</td>
<td>[128]</td>
<td>25–300</td>
<td>Al, Al(_2)O(_3)(^{(c)})</td>
<td>O(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td></td>
<td>DC</td>
<td>[95]</td>
<td>25–380</td>
<td>Al</td>
<td>O(_2)</td>
<td>Ar</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Thermal</td>
<td>[101]</td>
<td>&lt; 400</td>
<td>Al</td>
<td>O(_2)</td>
<td>N(_2)</td>
</tr>
<tr>
<td>Sol-gel</td>
<td></td>
<td>- [19]</td>
<td>25–350(^{(f)})</td>
<td>Al(C(_3)H(_4))(_3)(^{(e)})</td>
<td>C(_3)H(_8)O, H(_2)O</td>
<td>air</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Selected references.
\(^{(b)}\) Refers to gases that may present but not central to the required reaction. Includes purging gases, carrier gases and gases necessary for sustaining plasmas.
\(^{(c)}\) Trimethylaluminium (TMA) [Al(CH\(_3\))\(_3\)]
\(^{(d)}\) Can substituted with various alkyl aluminium, alkyl aluminium hydride and alkyl amino aluminium precursors.
\(^{(e)}\) Also an oxygen source.
\(^{(f)}\) Deposited at room temperature, but higher temperatures are required for drying (~80°C) and pyrolysis (350–750°C).

Other materials that are not directly related to the reaction but present during the deposition process can also be incorporated into the film. This includes gases used for sustaining plasmas, carrier gases and purging gases that are required to support the reaction, or chemicals that remain on the surface of the sample as a result of wet chemical surface preparation steps. In sputtering for example, Ar—acting as the sputtering ambient—is often incorporated into the deposited film [96, 138] and this is also observed with the sputtered AlO\(_x\) films of this work in Section 4.4.

Various post-deposition annealing conditions have been used with AlO\(_x\) films. A typical low temperature anneal is ~425°C for 30 min [21, 25, 148]. Meanwhile, as a firing step for solar cells the AlO\(_x\) is annealed at 800–900°C for a few seconds [75, 93, 154]. The most common annealing ambient used are N\(_2\) and forming gas (~5% H\(_2\) in Ar or N\(_2\)), while the annealing can also take place in Ar, O\(_2\), H\(_2\), air or in a vacuum [25]. Oxygen and nitrogen atoms—when using a O\(_2\) and N\(_2\) annealing ambient respectively—have been found to diffuse through the AlO\(_x\) film at annealing temperatures > 700°C [102].
4. Material Properties of Sputtered Aluminium Oxide Films

The composition of AlO$_x$ films can vary depending on all of the processing steps prior, during and after deposition. Thus when comparing the physical and electronic properties of AlO$_x$ films deposited by different methods, it is important to remember that the composition of the AlO$_x$ films may not be the same and that the different characteristics may be explained by the incorporation of additional elements.

4.2.2 Interfacial Layer

An interfacial layer is often formed between the deposited AlO$_x$ and the silicon surface. It can be formed during deposition [22, 143], formed during the post-deposition annealing treatment by the diffusion of oxygen to the interface [147, 155], or is the residual native oxide [156]. Alternatively in a very limited number of cases, no interfacial layer is reported as having formed [157], although the presence of the interfacial layer may have been obscured by a lack of contrast in the TEM measurements. The formation of the interfacial layer—or lack thereof—can be controlled by the deposition temperature [102], the reactants used [149, 158] or the surface preparation [157]. Even though the interface is usually chemically abrupt [149, 156, 157], it influences but does not necessarily ensure good electronic properties [148].

The presence of this interfacial layer is verifiable with TEM measurements (see Section 4.3 for example). A thin (< 2 nm) interfacial SiO$_x$ layers is typically observed with AlO$_x$ deposited by ALD methods [25, 155, 156] or PECVD AlO$_x$ [159] while a thicker (~5 nm) layer has been observed with deposition by Metal-Organic Chemical Vapour Deposition (MOCVD) [147]. The interfacial layer has been reported to consist of SiO$_x$ [25, 143, 147, 149, 155, 156] or AlSi$_x$O$_y$ [160]. Due to the use of different deposition methods in the literature, it is possible that the composition of the interfacial layers depend on the deposition process.

4.2.3 Origin of the Fixed Charge

The negative charge associated with AlO$_x$ films has been deduced to be located at this interfacial layer [22, 148] and relatively unaffected by the thickness of the AlO$_x$ [14, 100]. The strong reduction in the $D_{it}$ after annealing [9, 151] is also likely to be related to the changes at these interfaces [22]. The exact configuration for this negative charge is yet to be determined, but it has been proposed that tetrahedrally coordinated Al in AlO$_4^-$ units [161] is dominant at the interface and the latter is the origin of the negative charge in AlO$_x$ films [155]. Meanwhile, Al vacancies, O interstitials [162] and interstitial H [146]...
have also been proposed as the origin of the negative charge in AlO$_x$ films.

Conversely, Al interstitials and O vacancies have been proposed to be a source of positive charges \[162\]. The changes to the state of Al and O in the AlO$_x$ films with annealing may then explain why positive charges are sometimes observed in as-deposited AlO$_x$ films and negative charges are observed after annealing (Chapter \[3\]).

### 4.2.4 Bonding of Aluminium Oxide

The bulk of the AlO$_x$ films mainly consist of O–Al–O and Al–O bonds \[156, 163\], though Al=O may also be present \[147, 156\]. However, additional bonding types are usually present due to the incorporation of other elements in the AlO$_x$ film (Section \[4.2.1\]). Table \[4.2\] lists the bonds that are commonly observed in AlO$_x$ films and their corresponding wavenumbers in FTIR measurements.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Bond Type</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>400–530</td>
<td>Al–O</td>
<td>Stretching in isolated AlO$_6$ octahedra [19, 164]</td>
</tr>
<tr>
<td>500–680</td>
<td>Al–O</td>
<td>Stretching in condensed AlO$_6$ octahedra [19, 156, 164]</td>
</tr>
<tr>
<td>590–700</td>
<td>O–C=O</td>
<td>Bending [163]</td>
</tr>
<tr>
<td>640–750</td>
<td>O–Al–O</td>
<td>Bending [19, 156, 163]</td>
</tr>
<tr>
<td>650–800</td>
<td>Al–O</td>
<td>Stretching in isolated AlO$_4$ tetrahedra [19, 156, 164]</td>
</tr>
<tr>
<td>700–900</td>
<td>Al–O</td>
<td>Stretching in condensed AlO$_4$ tetrahedra [163–165]</td>
</tr>
<tr>
<td>850</td>
<td>Al–O–Al</td>
<td>[166]</td>
</tr>
<tr>
<td>1060</td>
<td>Al–O</td>
<td>Stretching, localised at surface [165]</td>
</tr>
<tr>
<td>1060–70</td>
<td>Si–O–Si</td>
<td>Stretching [147, 156]</td>
</tr>
<tr>
<td>1000–1200</td>
<td>Al–CH$_3$</td>
<td>[158, 163, 166]</td>
</tr>
<tr>
<td>1345</td>
<td>Al=O</td>
<td>[147, 156]</td>
</tr>
<tr>
<td>1500–1700</td>
<td>AlC=O</td>
<td>Stretching in Al–COOH [163, 166]</td>
</tr>
<tr>
<td>2600–3800</td>
<td>O–H</td>
<td>Stretching in Al–OH [163, 165, 167]</td>
</tr>
<tr>
<td>3000</td>
<td>Al–CH$_3$</td>
<td>Stretching [158, 166]</td>
</tr>
</tbody>
</table>

Hydrogen is often present due to the use of hydrogen containing reactants and are usually found in the form of O–H groups \[72, 93, 143, 150\]. Meanwhile, various carboxylates may be present if carbon is incorporated into the film during deposition \[163, 166\].

As can be seen in Table \[4.2\] many of the bonds overlap in their wavenumbers, making them difficult to distinguish. The most important of these is the bond at $\sim$1060 cm$^{-1}$: the relatively large change in the density of this bond with annealing and its position
between the AlO$_x$ and the silicon (Section 4.2.2) makes this bond the most likely cause of the increase in the negative charge and improvement in surface passivation after annealing [23]. This bond has been interpreted as a stretching Si–O–Si bond, or as a stretching Al–O bond localised at the surface.

In the first interpretation, this bond at $\sim$1060 cm$^{-1}$ corresponds to the transverse optical phonon associated with the asymmetric stretch of the O in the Si–O–Si bridging bond, as seen in good quality SiO$_2$ [25, 143, 144, 156]. This hypothesis is supported by agreeable interpretations of Electron Energy-Loss Spectroscopy (EELS) measurements [147, 155], X-ray Photoelectron Spectroscopy (XPS) measurements [149, 156] and optical Second-Harmonic Generation (SHG) measurements [143].

In the second interpretation, this bond at $\sim$1060 cm$^{-1}$ corresponds to some Al–O stretching bonds localised at the surface brought about by crystal truncation and surface dehydroxylation (i.e. loss of O–H groups) [168]. This surface defect arises from the disappearance of free alumina hydroxyl groups at temperatures $>$ 400$^\circ$C and is not affected by the introduction of O$_2$ or H$_2$ [169]. The surface defect can then be removed through adsorption processes that rebuild the surface hydrated layer [165]. This hypothesis is supported by FTIR data whereby the bond density at $\sim$1060 cm$^{-1}$ increases with dehydroxylation and decreases with rehydration of the AlO$_x$ surface when there was no silicon available in these samples for the formation of Si–O–Si bonds [168, 169]. Interestingly, the FTIR data of some of the literature that support the hypothesis of the SiO$_x$ layer also show dehydroxylation with annealing at temperatures $>$ 400$^\circ$C [25]. On the other hand, the fact that the samples were not on a silicon surface may mean that this effect from dehydroxylation and rehydration is not applicable to the AlO$_x$/Si interfaces of this work.

Both interpretations have valid supporting evidence for their hypotheses and it may be that both effects occur at the interface between the AlO$_x$ and silicon. Thus, both interpretations are discussed in relation to the experimental results of this thesis.

4.3 Experimental Design

The preparation of the wafers for the experiments of this chapter are as described in Section 3.3, except that 10 k$\Omega$.cm, (100), FZ p-type silicon wafers were used for the FTIR measurements in Section 4.8. The deposition of the AlO$_x$ films using sputtering systems “A” and “B” or using thermal ALD and the post-deposition anneal were also carried out as described in Section 3.3.

Various AlO$_x$ film thicknesses were deposited depending on the characterisation tech-
nique used in order to enhance measured features or to provide certainty to the modelling. The various thin film characterisation techniques performed on the AlO$_x$ were carried out as described in Section 2.3.

4.4 Impurity Analysis

The incorporation of elements other than aluminium and oxygen can affect the physical and electronic properties of the AlO$_x$ film (Section 4.2.1). In this experiment, we investigate the composition of sputtered AlO$_x$ films using RBS measurements (Section 2.3.1) and identify any additional elements that are incorporated. We compare the composition of the AlO$_x$ films deposited by the different sputtering methods and thermal ALD and discuss how their differences may influence the surface passivation obtained.

Table 4.3: Summary of the atomic percentage of impurities found in the AlO$_x$ deposited by various methods and the corresponding $S_{eff}$ for the particular deposition method.

<table>
<thead>
<tr>
<th>Method</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>Thermal</td>
<td>“A”</td>
</tr>
<tr>
<td>Power Source</td>
<td>-</td>
<td>RF</td>
</tr>
<tr>
<td>Target</td>
<td>-</td>
<td>Al</td>
</tr>
<tr>
<td>RBS Measurement</td>
<td>Fig. 4.2(a)</td>
<td>Fig. 4.1</td>
</tr>
<tr>
<td>O/Al</td>
<td>1.6</td>
<td>1.75</td>
</tr>
<tr>
<td>Argon (at.%)</td>
<td>0</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Ge (at.%)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pt (at.%)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lifetime Measurement</td>
<td>Sect. 5.4.3</td>
<td>Sect. 3.5</td>
</tr>
<tr>
<td>$S_{eff}$ (cm/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• 0.8 Ω.cm c-Si(p)</td>
<td>7.2</td>
<td>125</td>
</tr>
<tr>
<td>• 1 Ω.cm c-Si(n)</td>
<td>2.2</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 4.3 lists the various deposition methods used in this experiment and summarises the approximate atomic percentage concentrations of argon and other impurities found in the deposited AlO$_x$ films using RBS measurements. The energy of the RBS measurements was high enough to detect heavy metals such as silver and platinum, which are sometimes used in the same sputtering systems. However, the RBS measurements cannot detect hydrogen and SIMS measurements are used to measure the concentrations of hydrogen; the results are presented in Section 4.5.

The concentrations of impurities found in the AlO$_x$ films of a particular deposition
method were essentially the same and independent of the O/Al ratio. Since the surface passivation results of Chapter 3 did not show a strong correlation between surface passivation and the O/Al ratio, we deem that the O/Al ratio is not important in this analysis. Thus, the values listed in Table 4.3 and the selected RBS measurements presented in Figures 4.1–4.4 are representative of the AlO<sub>x</sub> films of a particular deposition method.

A comparison of the AlO<sub>x</sub> films as deposited and after annealing showed that any changes to the O/Al ratio, film thickness and density were negligible. An example comparing the composition of an AlO<sub>x</sub> as deposited and after annealing is given in Figure 4.1.

![Figure 4.1: The measured and fitted RBS data of AlO<sub>x</sub> deposited system “A” by RF sputtering of an Al target (a) as deposited (b) after annealing at 400°C in N<sub>2</sub> for 30 min.](image)

In the AlO<sub>x</sub> films deposited using RF sputtering with an Al target, the only impurity detected was argon. This incorporation of Ar was expected, given that the sputtering ambient was predominantly Ar and the effect had been observed in the literature [128, 138]. The incorporation of impurities in the sputtered films is known to reduce with lower base pressures [76]. Thus, the higher base pressure of system “B” (3 × 10<sup>-6</sup> Torr) compared to system “A” (7 × 10<sup>-7</sup> Torr) can explain the higher (< 5 at.%) incorporation of Ar in the AlO<sub>x</sub> films deposited by system “B” compared to system “A” (< 0.2 at.%).

From Table 4.3, we can observe a correlation between the surface passivation achieved and the amount of Ar incorporation. Excellent surface passivation was achieved with the AlO<sub>x</sub> films deposited using thermal ALD with no incorporation of Ar, while good surface passivation was achieved by the films deposited by system “A” over a wide range of O/Al ratios with less than 0.2 at.% incorporation of Ar. On the other hand, no surface passivation was achieved by any of the AlO<sub>x</sub> films deposited by system “B”, which had up to 5 at.% incorporation of Ar. The major difference between the AlO<sub>x</sub> films deposited
using the above-mentioned systems is the incorporation of Ar and so it appears that the incorporation of Ar is strongly detrimental to surface passivation.

In order to minimise Ar incorporation, the sputtering system needs to be capable of achieving low base pressures and longer pumping times may be needed to bring the base pressures to $< 7 \times 10^{-7}$ Torr as in system “A”. Alternatively, in order to avoid Ar incorporation altogether, it may be possible to do the sputtering in a different ambient such as an N$_2$ ambient or a He ambient. However, the incorporation of N$_2$ or He in the deposited AlO$_x$ films may lead to other undesirable effects.

![Figure 4.2](image_url)

Figure 4.2: The measured and fitted RBS data of AlO$_x$ deposited by (a) thermal ALD and (b) RF sputtering of an Al target using system “B”.

The AlO$_x$ films deposited in system “A” using RF sputtering of an Al$_2$O$_3$ target (Figure 4.3) showed a slightly higher concentration of Ar ($< 0.5$ at.%) than when an Al target was used ($< 0.2$ at.%) and not nearly as high as when using system “B” ($< 5$ at.%). It seems unlikely that the small difference in the concentration of Ar can account for the large difference in the surface passivation obtained.

The RBS measurements in Figure 4.3 (b) show that in the samples deposited by RF sputtering of an Al$_2$O$_3$ target, minute traces of germanium ($< 0.05$ at.%), platinum ($< 0.07$ at.%) were detected alongside argon. These elements are known to have been used in system “A” and have sometimes been used in the same RF sputtering gun prior to the use of the Al$_2$O$_3$ or Al target. In bulk silicon, platinum can act as a strong recombination center and even minute concentrations can strongly limit the lifetime. At present there is no established physical explanation linking the presence of the impurities and surface recombination, but nevertheless the incorporation of germanium and platinum should be avoided. Where possible, only the Al and Al$_2$O$_3$ target should be used in the
4. Material Properties of Sputtered Aluminium Oxide Films

No obvious impurities were detected in the DC sputtered AlO\(_x\) films (Figure 4.4). Even though this should have inferred that good surface passivation would be achieved, this was not the case. However as seen in Figure 4.3(b), there are some features that may be carbon peaks. These peaks are difficult to distinguish as they are convoluted with the
4.5 Hydrogen Concentration

The incorporation of hydrogen in the AlO$_x$ films—deposited by methods other than sputtering—can change the composition of the film as well as the types of bonds that are formed (Section 4.2). It is believed that the incorporation has a positive effect on surface passivation achieved, both in terms of hydrogenation of defects [25] or from the formation of negative charges [146]. In this experiment, we use SIMS measurements to investigate the incorporation of hydrogen in sputtered AlO$_x$ films. The presence of hydrogen in sputtered AlO$_x$ films is confirmed and the concentration of hydrogen decreases after annealing. We discuss how the results may be explained by the various hypotheses outlined in the literature review (Section 4.2).

Table 4.4 lists the various deposition methods used in this experiment and summarises the approximate atomic percentage concentrations of hydrogen found in the AlO$_x$ films as deposited and after annealing. The different O/Al ratios do not affect the outcomes of this experiment as we are investigating the presence of hydrogen in the sputtered AlO$_x$ films and not the dependence of the hydrogen concentration on the O/Al ratio.

Figure 4.5(a) shows the SIMS measurement of an AlO$_x$ film deposited by thermal ALD while Figures 4.5(b)-4.7 show the SIMS measurements of various AlO$_x$ films deposited by the different sputtering methods and systems. Note that the concentration of argon and other impurities as found in Section 4.4 were not assessed in the SIMS measurements as...
Table 4.4: Summary of the atomic percentage of hydrogen found in the \( \text{AlO}_x \) deposited by various methods and the corresponding \( S_{\text{eff}} \) for the particular deposition method.

<table>
<thead>
<tr>
<th>Method</th>
<th>ALD</th>
<th>Sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>Thermal</td>
<td>“A” “A” “A” “B”</td>
</tr>
<tr>
<td>Power Source</td>
<td>-</td>
<td>RF RF DC RF</td>
</tr>
<tr>
<td>Target</td>
<td>Al</td>
<td>( \text{Al}_2\text{O}_3 ) Al Al</td>
</tr>
<tr>
<td>O/Al ratio</td>
<td>1.6</td>
<td>1.75 1.75 1.5 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SIMS measurement</th>
<th>Fig. 4.5(a)</th>
<th>Fig. 4.5(b)</th>
<th>Fig. 4.6(a)</th>
<th>Fig. 4.6(b)</th>
<th>Fig. 4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (at.%)</td>
<td></td>
<td></td>
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only a limited number of elements could be measured. The trails of oxygen, hydrogen and aluminium into the silicon substrate in Figures 4.5(b)–4.7 are most likely measurement artefacts, remnants of the sputtering and knock-on effects associated to the heavy Cs ions used for these SIMS measurements (Section 2.3.2). They are unlikely to be from the deposition process using RF or DC sputtering as the trails are also observed when the \( \text{AlO}_x \) is deposited by thermal ALD [Figure 4.5(a)].

The SIMS measurements show a strong presence of hydrogen in both the \( \text{AlO}_x \) films deposited by thermal ALD [Figure 4.5(a)] and sputtering [Figures 4.5(b)–4.7]. Even though higher concentrations of hydrogen—up to 15 at.%—have been found in the \( \text{AlO}_x \) films deposited by ALD and PECVD methods [16, 72], its presence and incorporation into sputtered \( \text{AlO}_x \) films is a significant result. This is because ALD and CVD methods use reactants that contain hydrogen (Section 4.2.1), but for sputtering hydrogen is not intentionally introduced into the process. High purity gases and targets have been used in our sputtering process and the RBS measurements above have shown that the \( \text{AlO}_x \) films are unlikely to be contaminated with any other elements that may have been bonded with hydrogen.

The most likely source of this hydrogen is water vapour, which can remain in the vacuum chamber even when the base pressure is \(< 10^{-7} \text{ Torr} \). All the \( \text{AlO}_x \) films of this work showed hydrogen incorporation independent of the sputtering system or method used, which suggests that hydrogen incorporation can be expected with any sputtering system.
4.5 Hydrogen Concentration

Figure 4.5: The composition of an AlO$_x$ film as deposited and after annealing, deposited by (a) thermal ALD and (b) RF sputtering of an Al target.

Figure 4.6: The composition of AlO$_x$ films deposited using system “A” with (a) RF sputtering of an Al$_2$O$_3$ target and (b) DC sputtering of an Al target.

or method used. In this experiment, the concentrations of hydrogen in the sputtered AlO$_x$ films were around $3\times10^{21}$ cm$^{-3}$, which are even higher than the $\sim 1.3 \times 10^{21}$ cm$^{-3}$ in the AlO$_x$ films that are deposited by thermal ALD. As summarised in Table 4.4, this equates to 0.6–2 at.% of hydrogen in the sputtered AlO$_x$ films, compared to 0.6–0.8 at.% in the AlO$_x$ films deposited by thermal ALD in this experiment.

A post-deposition anneal is essential to improve the surface passivation to acceptable levels (Section 3.2). This means that the presence of hydrogen in the as-deposited films is not a guarantee of good passivation, although it probably is a prerequisite. It is therefore important to evaluate possible changes caused by the annealing. In both thermal
and sputtering, the concentration of hydrogen in the bulk of the AlO$_x$ film decreases after annealing (Figure 4.5). Even though this decrease seems contradictory with the idea that a higher concentration of hydrogen should lead to better surface passivation, a similar contradiction has been found for PECVD SiN$_x$, where the density of the film, not just its hydrogen content, is a key determinant for passivation [170].

The results in this experiment clearly show that with AlO$_x$ films deposited by either thermal ALD or RF sputtering with an Al target, the improvement in surface passivation with annealing (Section 3.5) coincides with a decrease in the hydrogen concentration (Figure 4.5). This does not necessarily rule out the effect of hydrogenation of the interface in the surface passivation with AlO$_x$ as a sufficiently high concentration of hydrogen remains after annealing, but indicates that there must be another mechanism involved that improves the surface passivation with annealing.

It is possible to observe some differences at the surface of the silicon, where the film deposited by thermal ALD appears to retain the same concentration of hydrogen [Figure 4.5(a)], while this concentration clearly decreases for the sputtered film, compared to the as-deposited state (Figure 4.5). It is possible that the behaviour of interfacial hydrogen upon annealing is different in the ALD and sputtered films. It is likely that the greater reduction of interfacial hydrogen in the AlO$_x$ films deposited by sputtering compared to thermal ALD correlates to the higher $D_t$ typically found with sputtered AlO$_x$ (Table 1.4). It would explain why the AlO$_x$ films deposited by thermal ALD achieved better surface passivation than the AlO$_x$ films deposited by sputtering.

As reviewed in Section 4.2.4 FTIR measurements have shown that dehydroxylation
occurs at the surface of AlO\textsubscript{x} after annealing at \(> 400^\circ\text{C}\) \cite{25,165}. This would agree with the decrease in the concentration of hydrogen at the interface between the AlO\textsubscript{x} and silicon after annealing (Figure 4.5). Meanwhile, the dip and the nearby peak in the concentrations of the elements is likely to be an interfacial layer that is present as deposited [\(\sim 45–55 \text{ nm in Figure 4.5(a) and } \sim 100–115 \text{ nm in Figure 4.5(b)}\)] and is most likely the SiO\textsubscript{x} interfacial layer agreed on by the majority of the literature (Section 4.2.4). Thus, the SIMS results here can be interpreted to agree with both hypotheses concerning what is occurring at the interface.

Peacock and Robertson \cite{146} proposed that the origin of the negative charge in AlO\textsubscript{x} films is due to interstitial H at the interface. It would seem more likely that the hydrogen concentration at the interface should have increased to account for the increase in the magnitude of the negative charge from the sputtered AlO\textsubscript{x} film after annealing (Section 3.5), but instead we observe a decrease in the hydrogen concentration. However, it is important to note that the SIMS measurements cannot inform us whether the hydrogen at the interface is bonded or interstitial. Whereas a complete lack of hydrogen at the interface would have disproved this hypothesis, this hypothesis remains plausible given that significant concentrations of hydrogen were detected in all of the sputtered AlO\textsubscript{x} films after annealing.

The SIMS results showed that hydrogen is incorporated into sputtered AlO\textsubscript{x} films are in concentrations similar—and in this specific experiment they are actually higher—to AlO\textsubscript{x} films deposited by thermal ALD. Even though hydrogen is not intentionally part of the sputtering process and its origin is unclear, the results here show that hydrogen can be expected to be incorporated in all sputtered AlO\textsubscript{x} films, independent of the sputtering method or arrangement. Even though the presence of hydrogen as measured by SIMS cannot directly inform us of its role, its presence in the AlO\textsubscript{x} films is consistent with the various proposed hypotheses. Further investigations are required to verify the role of hydrogen in sputtered AlO\textsubscript{x} films.

### 4.6 Interface Analysis

A thin interfacial layer is often present between the AlO\textsubscript{x} and the silicon after deposition and this layer can change in thickness with the post-deposition anneal (Section 4.2.2). It is believed that this interfacial layer plays an important role in the surface passivation from AlO\textsubscript{x} films, particularly in increasing the negative charge \cite{23,148}. In this experiment, we utilise TEM (Section 2.3.6) measurements to confirm the presence of an interfacial
layer. We match one of the TEM images with its corresponding SIMS measurement from Section 4.5 and analyse the characteristics of the interfacial layer in sputtered AlO\textsubscript{x} films.

Figure 4.8 shows a TEM image of an AlO\textsubscript{x} film on a silicon substrate after annealing. In this case, the thickness of the AlO\textsubscript{x} film is \(\sim 150\) nm and was deposited using DC sputtering of an Al target. The contrast of the interfacial layer can be observed between AlO\textsubscript{x} and the silicon substrate in the TEM images. The gradient in the contrast makes it difficult to confirm the edge of the interfacial layer visually with the TEM image only. Nonetheless, we can compare the TEM image with the SIMS profile of its sister sample and obtain a confident approximation of the surfaces and interfaces on both the TEM image and the SIMS profile (Figure 4.9).

![Figure 4.8](image_url)

**Figure 4.8:** A TEM image showing the interfacial layers between the deposited AlO\textsubscript{x} and the silicon substrate.

The location of the surfaces and interfaces can be approximately estimated based on the abrupt changes in the elemental concentrations shown by the SIMS profiles (Section 2.3.2). In Figure 4.9, the plateau of the silicon concentration and the corresponding drop in the concentrations of aluminium, oxygen and hydrogen at \(\sim 170\) nm is a good indication that the silicon surface is at this location, while the dip in the concentrations of oxygen, aluminium and hydrogen at \(\sim 160\) nm is an indication of another interface. A comparison of the SIMS measurement with its corresponding TEM image shows that the interfacial layer as approximated by the SIMS measurement aligns with the darker grey layer in the TEM image. The independent results of the TEM image and the SIMS measurement
Figure 4.9: The TEM image from Figure 4.8 is superimposed with the SIMS profile of its sister sample from Figure 4.6(b), showing the approximate location of surfaces and interfaces.

agree and it can be confidently assumed that the interface at $\sim$160 nm and the silicon surface at $\sim$170 nm define an interfacial layer for this particular sample. The results here show that an interfacial layer can be expected to be formed when sputtering is used to deposit AlO$_x$.

The SIMS and TEM results are unable to define the exact composition of this interfacial layer. Nonetheless, based on the minute concentrations of impurities observed with RBS measurements (Section 4.4) and the results in the literature (Section 4.2.2), the interfacial layer is either the SiO$_x$ interfacial layer that is most commonly observed, or an AlSi$_x$O$_y$ layer. Given that no obvious Al–O–Si bonds are observed in the FTIR measurements (Section 4.8) and that AlO$_x$ deposited by sputtering and thermal ALD are overall very similar in composition (Sections 4.4 and 4.5), it is most likely that this is a SiO$_x$ interfacial layer.

There are various uncertainties regarding the thickness estimations from the TEM or SIMS data, but it is clear that the interfacial SiO$_x$ layer observed here is definitely much thicker than the thin ($< 2$ nm) interfacial SiO$_x$ layers observed with AlO$_x$ deposited by ALD methods [23, 155, 156] or PECVD AlO$_x$ [159]. It is also thicker than the 5 nm SiO$_x$ layer observed with deposition by MOCVD [147]. As seen in Figure 4.8, the interfacial
SiO$_x$ layer in sputtered AlO$_x$ is also not as abrupt as any of the above mentioned deposition methods. Since better surface passivation has been achieved with the AlO$_x$ films deposited by [ALD] and [PECVD] this would infer that the interfacial SiO$_x$ layer should ideally be abrupt and very thin. This is certainly not the case for sputtering and improvements need to be made in this area.

Compared to [ALD] which is a precisely controlled depositions where one atomic layer is deposited after another, sputtering involves the high energy impact of atoms during deposition, leading to the deposition of a porous amorphous material (Section 3.2.1). It can be expected that disordered and defective interfaces result from the high energy deposition. This would explain the thicker interfacial layer observed here and the higher $D_{it}$ that is typically obtained with sputtering compared to other deposition methods for AlO$_x$ (Section 5.5.3). It may be possible to control the thickness of this layer and the surface damage from sputtering by limiting the voltage used, but there will be a compromise with the deposition rate.

The interfacial layer observed between the AlO$_x$ and the silicon surface is most likely the SiO$_x$ interfacial layer that is commonly observed in the literature. Compared to the interfaces of the AlO$_x$ films deposited by [ALD] and [CVD] methods, this interfacial layer appears to be much thicker and not as abrupt. This is most likely caused by the higher energy of the sputtering process and the damage it causes. The results of this experiment indicate that better control of the sputtering process and its optimisation are required to improve the AlO$_x$/SiO$_x$/Si interfaces and subsequently improve the surface passivation attained.

### 4.7 Defect Analysis

The origin of the fixed charge in AlO$_x$ films is likely to be related to Al, O and H vacancies and interstitials (Section 4.2.3). Most interestingly, it has been shown theoretically that Al interstitials and O vacancies tend to be positively charged, while Al vacancies and oxygen interstitials tend to be negatively charged. The change in the concentration of vacancies and interstitials with annealing could explain why positive charges are sometimes observed in an AlO$_x$ film as deposited, while negative charges are observed after annealing.

Positrons are a sensitive probe to detect oxygen-related defects, which are not observable by electron microscopy [171]. Thus, [PAS] (Section 2.3.3) is a technique that may allow the determination of the role of oxygen vacancies with regard to the fixed charge in AlO$_x$ films. In this experiment, we use [PAS] measurements to analyse AlO$_x$ films deposited
cannot be used to infer the depth profile of the sample (Section 2.3.3), it shows that the 

*\( x \)*

respond to the thickness of the AlO

4.11, this is at the positron energy of 10 keV and the interval from 0–10 keV would correspond from the measured Doppler-broadening spectra. The thickness of the deposited AlO

x

indicates the transition from the AlO

S

x

could indicate a movement of oxygen from the AlO

Figure 4.10: The *S*-parameter of an AlO

x

film on (a) 0.8 Ω.cm c-Si(p) (b) 1 Ω.cm c-Si(n).

Figure 4.11: The *W*-parameter of an AlO

x

film on (a) 0.8 Ω.cm c-Si(p) (b) 1 Ω.cm c-Si(n).

by sputtering. The results show a change related to oxygen in the AlO

x

films, which could indicate a movement of oxygen from the AlO

x

film to the interface or a reduction of vacancies.

Figures 4.10 and 4.11 show the *S*-parameter and *W*-parameter respectively as calculated from the measured Doppler-broadening spectra. The thickness of the deposited AlO

x

films was 1.1 µm, to ensure that the AlO

x

film would be distinguishable from the silicon bulk. As reviewed in Section 2.3.3 the sudden change in the *S*-parameter or *W*-parameter indicates the transition from the AlO

x

film to the silicon substrate. For Figures 4.10 and 4.11 this is at the positron energy of 10 keV and the interval from 0–10 keV would correspond to the thickness of the AlO

x

film (i.e. 1.1 µm). Even though the latter thickness cannot be used to infer the depth profile of the sample (Section 2.3.3), it shows that the
trail from 10–30 keV is unlikely to define the < 10 nm interfacial layer as seen in the TEM measurements (Section 4.6) and is more likely be a measurement artefact related to the poor depth resolution of PAS measurements. On both the p- and n-type samples, the S-parameter increased [Figure 4.10(a)] while the W-parameter decreased [Figure 4.10(b)] for the AlO<sub>x</sub> film (i.e. positron energy < 10 keV) after annealing.

**Figure 4.12:** (a) A example of the measured Doppler-broadening spectra. (b) The oxygen response for the AlO<sub>x</sub> film as deposited and after annealing.

An example of the measured Doppler-broadening spectra used to calculate the S-parameter and W-parameter is presented in Figure 4.12(a). Instead of normalising the measured spectra to the silicon bulk, it is possible to normalise the measured spectra to a pure Al reference. Subsequently, the response of oxygen in the PAS measurements can be isolated at ∼514.2 eV [172]. In Figure 4.12(b), we compare the oxygen response in the p-type sample as deposited and after annealing, showing that the oxygen response decreases after annealing.

The results from Figures 4.10–4.12 can indicate a diffusion of oxygen to the interface and/or a reduction in the concentration of defects in the bulk of the AlO<sub>x</sub> film with annealing. The diffusion of oxygen to the interface is consistent with the hypotheses that this diffusion is responsible for the formation of the interfacial layer [147]. Alternatively, the reduction in the concentration of defects is consistent what is expected with low temperature annealing of oxides. It is possible that both effects are occurring in parallel.

The line shape parameters of the annealed samples in Figures 4.10 and 4.11 are graphed in Figure 4.13 to highlight the different between the p- and n-type samples at the interval between the AlO<sub>x</sub> bulk and the silicon bulk (i.e. positron energy = 10–25 keV). The difference is a result of the different momentum of electrons in that region, indicating
a difference in the electric field between the $p$- and $n$-type samples near the interface between the AlO$_x$ film and the silicon surface. Even though the magnitude and polarity of the electric field cannot be determined using Figure 4.13, the results are nonetheless consistent with a particular fixed charge in a thin film inducing a different electric field on the silicon surface, depending on whether the surface is $p$- or $n$-type (Section 1.3.1).

The results here demonstrate the potential of PAS measurements in determining the origin of the negative charge in AlO$_x$ films. The drawback of PAS measurements is that the oxygen vacancies can be neutral or positively charged [162], so the PAS measurements need to be complemented with other thin film measurement techniques to determine the charge of the oxygen vacancy [173]. More precise PAS measurements can be expected from abrupt and uniform AlO$_x$ films deposited by ALD compared to the sputtered AlO$_x$ films analysed here; further PAS measurements should be made on AlO$_x$ films deposited by ALD methods for investigating the origin of the negative charge.

4.8 Atomic Bonding Analysis

The bonding in the AlO$_x$ films typically consist of aluminium and oxygen related bonds, but the incorporation of elements other than aluminium and oxygen can lead to other bonding types (Section 4.2.4). This can subsequently affect the surface passivation achieved. In this experiment, we use FTIR (Section 2.3.7) to analyse the bonding types in AlO$_x$ films deposited by sputtering methods as well as from thermal ALD. We find that there are no obvious differences in the bonding types between AlO$_x$ films deposited...
by sputtering or thermal ALD. The results here support the hypotheses, that the increase in the bond density at 1060 cm$^{-1}$ is indicative of improvements in surface passivation.

Figures 4.14 and 4.15 show the FTIR spectra of AlO$_x$ films with various O/Al ratios after annealing for 30 min. The FTIR spectra have been grouped in terms of the sputtering system and method used. Particular wavenumbers of interest and their corresponding bond types—as reviewed in Section 4.2.4—have been highlighted. The main aluminium oxygen bonding types observed in these annealed AlO$_x$ films are the O–Al–O bending bond at 668 cm$^{-1}$ and the various Al–O stretching bonds at 500–800 cm$^{-1}$. The Al–O–Al bond at
850 cm\(^{-1}\) and Al=O bond at 1345 cm\(^{-1}\) were not observed in any of the spectra, while no peaks corresponded to Al–O–Si bonds. No carbon related bonds are observed other than the peaks at \(\sim 2400\) cm\(^{-1}\) which are linked to residual CO\(_2\) in the ambient during the FTIR measurement. The bond at \(\sim 1060\) cm\(^{-1}\) has been attributed to the Si–O–Si stretching bond following the majority of the literature.

The sample with an O/Al ratio of 0.6 in Figure 4.14(a) was sputtered in “metal mode”; its FTIR spectra is clearly different, with absorption \(\sim 85\%\) and the absence of any strongly distinguishable peaks. Meanwhile, the sample sputtered with an O/Al ratio of 1.1 in Figure 4.15(b) is probably close to the transition between “dielectric mode” and “metal mode”, as it has the FTIR features of the other AlO\(_x\) films but with a higher absorption of up to 15%. The remainder of the samples from both systems were sputtered in “dielectric mode”, with absorption in the range of 2–5% and very much similar to the FTIR spectra of AlO\(_x\) films deposited by thermal ALD [Figure 4.15(a)] as well as in the literature [25, 147, 156, 163]. This is another aspect where AlO\(_x\) films deposited by sputtering is similar to AlO\(_x\) films is deposited by other methods and thus supporting the hypothesis that sputtered AlO\(_x\) relies on the same surface passivation mechanism as AlO\(_x\) films deposited by other methods.

The absorption features for the Al–O stretching bonds are very similar for most of the AlO\(_x\) films deposited using RF sputtering and thermal ALD. As seen in Figures 4.16 and 4.17(a), the Al–O bond densities do not change significantly over the time of annealing. When DC sputtering was used, there was a much higher initial Al–O bond density as deposited, which decreases after annealing [Figure 4.17(b)]. This suggests that the bonding in DC sputtered AlO\(_x\) films behave differently to that deposited by RF sputtering or thermal ALD and could explain why no surface passivation is achieved when DC sputtering is used.

Meanwhile, the O–Al–O bond density varies between the different sputtering methods and systems as well as over the annealing time. Despite the significant changes in the absorption of this bond, there is no clear trend linking it with either the O/Al ratio of the film or with the annealing time. However, we note that it is a very sharp feature that is not commonly observed in the FTIR spectra of AlO\(_x\) films, whereas the Al–O and Si–O–Si features are commonly observed in the literature [25, 147, 156, 163]. It is possible that it is a measurement anomaly from the wafers or FTIR system used in this experiment. On the other hand, the measurement of such a sharp feature may not have been possible with the older FTIR system used in the literature, or could have been averaged out during data manipulation.
Figure 4.16: FTIR spectra of AlO\textsubscript{x} films over the time of annealing, deposited using (a) thermal ALD and (b) system “A” using RF sputtering of an Al target.

Figure 4.17: FTIR spectra of AlO\textsubscript{x} films over the time of annealing, deposited using system “A” with (a) RF sputtering of an Al\textsubscript{2}O\textsubscript{3} target and (b) DC sputtering of an Al target.
Due to the size of the peak at 1060 cm\(^{-1}\) compared to its neighbouring Al–O peaks, it is difficult to quantify the change in the bond densities. However, the increase of this peak appears to indicate good surface passivation will be achieved while the decrease of this peak appears to indicate the converse. By comparing Figures 4.18(a) and 4.18(b), we observe the increase or decrease in absorption after annealing. We note that the samples that experience an increase in absorption are the Al\(_2\)O\(_x\) films deposited by thermal ALD and from RF sputtering of an Al target, which happens to correspond to surface passivation being achieved; a similar observation was made by Hoex et al.\(^{[25]}\). Meanwhile, we note here that the converse also appears to be true: the samples that experience a decrease in absorption were the methods where surface passivation was not attained. FTIR measurements of Al\(_2\)O\(_x\) films deposited by a larger variety of deposition methods will need to be made to verify this hypothesis.

**Figure 4.18:** FTIR spectra of Al\(_2\)O\(_x\) films, emphasising the feature at 1060 cm\(^{-1}\). (a) As deposited. (b) After annealing at 400\(^\circ\)C in N\(_2\) for 30 min.

As reviewed in Section 4.2.4, the bond at 1060 cm\(^{-1}\) has been interpreted as an interfacial SiO\(_x\) layer that is restructured upon annealing, leading into an increase in absorption intensity of this Si–O–Si peak. On the other hand, this peak has also been observed with Al\(_2\)O\(_x\) layers that were not bonded with silicon, thus making a Si–O–Si bond impossible and has instead been attributed to a truncated Al–O bonds localised at the surface. The FTIR results showing the increase and decrease of the peak at 1060 cm\(^{-1}\), along with the loss of hydrogen at the interface with annealing in the SIMS results (Section 4.3) support the hypothesis regarding the truncated Al–O bonds. Meanwhile, the TEM image of the interfacial layer and the results in the literature strongly support the presence of a SiO\(_x\) layer and thus the peak at 1060 cm\(^{-1}\) is representative of Si–O–Si bonds. Considering
that the experimental results have so far not contradicted either of these hypotheses, it is possible that the peak at 1060 cm$^{-1}$ consists of both Al–O and Si–O–Si bonds.

The FTIR spectra of a variety of AlO$_x$ films spanning a range of O/Al ratios, deposition methods, deposition systems, annealing ambient and annealing times have been measured, showing that similar bonding occurs in the various AlO$_x$ films. The exception to this is when the sputter deposition has been done in “metal mode”, whereby a high absorption is observed throughout the FTIR spectra; the layer displays the characteristics of aluminium rather than AlO$_x$. Nonetheless, the AlO$_x$ films that are sputtered in “dielectric mode” are similar to the AlO$_x$ films deposited by other methods.

The FTIR results here support the hypothesis that the bond at 1060 cm$^{-1}$ is an indication of surface passivation. Even though we cannot clearly define this peak as a truncated Al–O or a Si–O–Si bond, an increase in this peak—shown both here and in the literature—appears to indicate an improvement in the surface passivation from the AlO$_x$ films, while a decrease implies poorer surface passivation. This bond could be used to differentiate between samples that have greater potential for achieving good surface passivation. Further experiments and alternative thin film characterisation techniques are required for determining the physical mechanism of the surface passivation and the reasons for the increase of this peak.

4.9 Chapter Summary

In this chapter, we have investigated the composition and bonding in sputtered AlO$_x$ films using a variety of thin film analysis techniques. These were analysed in parallel with the results of Chapter 3 in order to find the correlations between the composition and bonding of the sputtered AlO$_x$ films to the surface passivation that is subsequently attained on the silicon substrates.

The RBS measurements in Section 4.4 revealed the incorporation of germanium, argon and platinum in various concentrations in the AlO$_x$ films. The effect of these impurities in the AlO$_x$ films has not been clearly established, but the results indicate that their presence is unlikely to be beneficial for surface passivation and should be avoided. Their incorporation appears to be dependent on the sputtering arrangement. Low base pressures (< 7 × 10$^{-7}$ Torr) are preferable while the use of other materials in the same sputtering machine should be avoided to minimise the incorporation of impurities.

In the SIMS measurements of Section 4.5 hydrogen was not only detected in all of the sputtered AlO$_x$ films, but in concentrations comparable to what was found in AlO$_x$ films.
deposited by thermal ALD. Hydrogen is usually expected in ALD and CVD processes, as it is present in large quantities in the gas precursors used. However, its presence and concentration in the sputtered AlO$_x$ was not expected, since hydrogen is not intentionally introduced into any of the sputtering processes. As seen in the as deposited AlO$_x$ films, the presence of hydrogen does not guarantee that surface passivation is achieved. However, the decrease in hydrogen after annealing correlates with the strong improvement in surface passivation. Further investigations need to be made to identify the source of this hydrogen and its particular role in surface passivation using sputtered AlO$_x$ films.

The TEM images of Section 4.6 show that an interfacial layer is present after annealing sputtered AlO$_x$ films on silicon. The interfacial layer of sputtered AlO$_x$ (∼10 nm) is thicker than the interfacial layer from other deposition methods (typically < 2 nm) [22, 25, 155, 156]; this is most likely due to the comparatively high energy nature of the sputter deposition process. The thicker interfacial layer is probably an indication of the non-ideal arrangement of the bonds in that region and subsequently the higher $D_{it}$ that may be limiting the surface passivation from sputtered AlO$_x$ films.

The results of Section 4.7 could indicate that annealing either reduces the concentration of defects in the AlO$_x$, or that there is a diffusion of oxygen to the interface. Further PAS measurements on AlO$_x$ films deposited by ALD may yield more information concerning the origin of the negative charge.

The FTIR measurements of Section 4.8 show that the bonding of the AlO$_x$ films deposited by sputtering is very similar to the AlO$_x$ films deposited by other methods. This tends to support the hypothesis that sputtered AlO$_x$ films relies on the same surface passivation mechanisms as the AlO$_x$ films deposited by other methods. In particular, the changes in the bond at 1060 cm$^{-1}$ with annealing appear to be indicative of the surface passivation: increases in this bond would indicate improvement in surface passivation, while a decrease would indicate poorer surface passivation. Further experiments on a wider variety of samples need to be made to verify this hypothesis.

The results of this chapter show that AlO$_x$ films deposited by sputtering is very similar in composition and bonding to AlO$_x$ films deposited by other methods and the results are compatible with a number of hypotheses in the literature concerning the origin of the negative charge. Further analyses of AlO$_x$ films with thin film measurement techniques are required for verifying the hypotheses and to confirm the origin of the negative charge.
Chapter 5

Optimisation of the Surface Passivation

“Al₂O₃ is a versatile high-κ dielectric that has excellent surface passivation properties on crystalline silicon.”
B. Hoex et al., 2008 [25]

5.1 Introduction

In Chapter 3, it was shown that RF sputtering of an Al target is capable of depositing negatively charged AlOₓ and achieving surface passivation on both p- and n-type silicon wafers. In this chapter, we systematically investigate the deposition and annealing conditions to further optimise the surface passivation attained. Thanks to this optimisation, $S_{eff}$ values as low as 24.6 cm/s and 9 cm/s have been obtained on 0.8 Ω.cm c-Si(p) and 1 Ω.cm c-Si(n) respectively.

The deposition conditions of AlOₓ using CVD and ALD methods have been shown to influence the composition of the deposited AlOₓ and subsequently affect the surface passivation achieved [17, 22]. In Section 5.3, we investigate the influence of the deposition temperature and discuss the optimum deposition conditions that were deduced from the experiments in Section 3.4. The best surface passivation results are achieved with depositions at room temperature and do not appear to be dependent on the O/Al ratio.

The annealing of the AlOₓ films after deposition is sometimes used to enhance the desired electronic properties for microelectronic applications [102, 151, 152]. As mentioned in Section 1.4.3, this post-deposition anneal—typically at ~400°C in N₂ for > 5 min—has so far proven to be crucial for achieving excellent surface passivation with AlOₓ deposited by CVD [16, 25] and ALD methods [21, 22] and in Section 3.3, we showed that this was also the case for sputtered AlOₓ. Temperatures ranging from 400–800°C and ambient such
as N₂, O₂ and forming gas have been used [25] for the annealing of AlOₓ films. Effects such as hydrogen passivation [151] and interfacial oxide formation [25, 102] have been reported in the literature. In Section 5.4, we investigate the effect of the annealing time, annealing temperature and the annealing ambient on the surface passivation obtained from sputtered AlOₓ. The results show that a post-deposition anneal at 425°C in N₂ for > 30 min provides consistent and excellent surface passivation with sputtered AlOₓ.

5.2 Experimental Design

The general process for the experiments of this chapter are as described in Section 3.3. The deposition of the AlOₓ films is restricted to using thermal ALD or using sputtering system “A” with RF sputtering of an Al target. The post-deposition annealing was done over a larger range of parameters: the annealing temperature ranged from 300–500°C, the annealing time ranged from 5–180 min, while the ambient used include N₂, O₂, forming gas (~5% H₂ in Ar), Ar and in a vacuum. The range of parameters used for each optimisation experiment is specified in their respective sections.

5.3 Optimisation of the Deposition Parameters

5.3.1 Sputter Power and Voltage

In reactive sputtering where the target may become oxidised, there is a minimum sputter power below which target oxidation would occur, as the rate of target oxidation becomes higher than the sputtering of the target surface (Section 3.2.1). On the other hand, higher sputtering powers may cause damage to the target or the deposited thin film. In the case of system “A” where the control of the reactive sputtering process is limited by the precision of the MFC in controlling the gas flows (Section 3.4.3), the situation would worsen as the fluctuations in the gas flow are enhanced relatively with a lower sputter power. The maximum sputter power of 300 W was used in Section 3.5 without any obvious problems to the surface passivation due to plasma damage, so for system “A” the maximum sputter power of 300 W should be used as the optimum deposition condition.

The voltage is dependent on the sputter power; this is usually consistent for a particular set of deposition parameters unless the target becomes oxidised, in which case the voltage drops significantly (Section 3.4.6). This was observed to be true for consecutive depositions. However, Figure 5.1 shows that for the case of RF sputtering of an Al target with system “A”, the voltage gradually decreased over time and a sudden increase in the
5.3 Optimisation of the Deposition Parameters

The voltage for a particular set of deposition parameters over time for the Al target in system “A”.

Figure 5.1: The voltage for a particular set of deposition parameters over time for the Al target in system “A”.

5.3.2 Deposition Temperature

In AlO$_x$ films deposited by CVD and ALD methods, the optimum deposition temperature was $\sim 200^\circ$C for achieving the best surface passivation results [17]. As the deposition temperature was kept at room temperature ($\sim 25^\circ$C) for the surface passivation results in Section 3.5, in this section we vary the deposition temperature and observe its effect on surface passivation.

Figure 5.2 compares the effective lifetime of the samples where the AlO$_x$ film was deposited at room temperature and 500$^\circ$C, as deposited and after 30 min of annealing at 500$^\circ$C in N$_2$. Acceptable surface passivation ($\sim 550$ cm/s) was achieved as deposited on the sample where the AlO$_x$ was deposited at 500$^\circ$C, while very poor surface passivation was achieved as deposited on the sample where the AlO$_x$ was deposited at 25$^\circ$C. Figure 5.3 summaries the surface passivation from AlO$_x$ deposited with various deposition temperatures.
Figure 5.2: The dependence of $\tau_{eff}$ on the excess carrier density for AlO$_x$ passivated samples deposited at room temperature and 500°C, as deposited and after 30 min of annealing at 500°C in N$_2$ on (a) 0.8 Ω.cm FZ c-Si(p) and (b) 1 Ω.cm CZ c-Si(n).

Figure 5.3: The $S_{eff}$ at $\Delta n = 10^{15}$ cm$^{-3}$ for samples passivated AlO$_x$ deposited using RF sputtering of an Al target, deposited over a range of deposition temperatures and annealed at 500°C in N$_2$ over 180 min of annealing. On (a) 0.8 Ω.cm FZ c-Si(p) and (b) 1 Ω.cm CZ c-Si(n).

temperatures as values of $S_{eff}$ and shows that acceptable surface passivation is achieved as deposited only when the AlO$_x$ is deposited at 500°C.

At the deposition temperature of 500°C, the AlO$_x$ film is probably undergoing the same changes as during a post-deposition anneal while the deposition is still in progress. At lower deposition temperatures, the surface passivation is very poor. This can explained by the fact that the deposition conditions do not meet the requirements for achieving good surface passivation with the post-deposition anneal (Section 5.4). The deposition time (~3 min) and the deposition temperature (< 400°C) fall short of the annealing times...
5.3 Optimisation of the Deposition Parameters

(> 5 min) and annealing temperatures (> 400°C) that are required, while the higher deposition temperature of 500°C appears to have compensated for the shorter annealing time.

Nonetheless, the best passivation results are achieved in all cases after a post-deposition anneal. In Figure 5.2, the surface passivation of the samples where the AlOₓ was deposited at 500°C improved [403 cm/s on c-Si(p) and 168 cm/s on c-Si(n)], but were ultimately not as good as the samples where the AlOₓ was deposited at 25°C [273 cm/s on c-Si(p) and 15 cm/s on c-Si(n)]. In Figure 5.3 we can see how the above observation similarly applies to the range of deposition temperatures. The results from Figures 5.2 and 5.3 show that for the aim of achieving the best surface passivation possible, a post-deposition anneal is needed and this cannot be replaced with a higher deposition temperature.

![Figure 5.4: The dependence of the $S_{eff}$ at $\Delta n = 10^{15} \text{cm}^{-3}$ on the deposition temperature for AlOₓ films deposited by various methods. On (a) c-Si(p) and (b) c-Si(n). The dashed lines have been drawn to guide the eye.](image)

The surface passivation that is obtained using sputtered AlOₓ is dependent on the deposition temperature and cannot be compensated by a longer annealing time. This dependence on the deposition temperature is made clear in Figure 5.4 by plotting the relation between the surface passivation and the deposition temperature. On both the c-Si(p) and c-Si(n) substrates, the best surface passivation results were achieved on the samples where the AlOₓ was deposited at 25°C. As highlighted by the dashed guiding lines, the surface passivation achieved is worse as the deposition temperature increases.

This is in contrast to the optimised deposition temperatures for CVD and ALD methods, which are typically ~200°C as seen in Figure 5.4(a). Even though better surface passivation results are achieved following the optimisations of this chapter [e.g. at a de-
position temperature of 25°C, an $S_{eff}$ of 24.6 cm/s as achieved in Section 5.5.1 rather than the 168 cm/s as given in Figure 5.4(a)], the dependence of the $S_{eff}$ on the deposition temperature is unlikely to change.

There is likely to be an effect that occurs with ALD and CVD methods that leads to an optimum deposition temperature of ∼200°C, but this effect does not occur with sputtering. The poor surface passivation provided by AlO$_x$ deposited by CVD and ALD methods at < 50°C may be due to the significant amount of carbon (∼4 at.%) that is incorporated at those temperatures [22, 72]. For sputtered AlO$_x$ on the other hand, carbon is not involved in the deposition process (Section 4.2.1) and no detectable amounts of carbon have been found to be incorporated into sputtered AlO$_x$ films (Section 4.4). The precise effects of carbon incorporation in AlO$_x$ films are unknown, but it is unlikely to be beneficial to surface passivation. Thus, carbon incorporation may explain the difference in optimum deposition temperatures between AlO$_x$ deposited by CVD, ALD and sputtering methods.

The results here show that the deposition temperature has a significant influence on the surface passivation achieved with AlO$_x$ films deposited by RF sputtering of an Al target. Even though acceptable surface passivation can be achieved as deposited with high deposition temperatures (> 500°C), the best surface passivation results were achieved with the lowest deposition temperatures (25°C) after the post-deposition anneal. Thus, the optimum deposition temperature is at 25°C, provided that a post-deposition anneal (> 400°C for > 5 min) is carried out.

### 5.3.3 Working Pressure

High working pressures should be avoided as this can lead to sputtering in “oxide mode” and target oxidation. This is because the deposition rate decreases greatly and the deposited AlO$_x$ is usually too oxide-rich for an AlO$_x$ film (Section 3.4.6). On the other hand, there are problems with sustaining the plasma at low working pressures. These two limits (i.e. sputtering in “oxide mode” and sustaining the plasma) are dependent on the sputtering arrangement and so the working pressure needs to be optimised for each sputtering arrangement. The working pressure of 3 mTorr was found to be the best compromise for system “A”.

### 5.3.4 Gas Flow

The optimum Ar and O$_2$ gas flows are strongly dependent on the sputtering arrangement, such as the size of the vacuum chamber, location of the gas inlet or the working pressure...
used. Thus, it is more logical to report and optimise the resulting O/Al ratio of the AlO$_x$ film, as this information is not limited to the sputtering arrangement used and should be transferable to other sputtering arrangements. The main experimental work showing the dependence of the surface passivation on the O/Al ratio was presented in Section 3.5. No obvious trends were observed between the O/Al ratio and the surface passivation achieved with AlO$_x$ films deposited by RF sputtering of an Al target.

This appears to be in contrast to the results in the literature, where better surface passivation results had been achieved with AlO$_x$ films that were close to stoichiometric [17, 72]. However, we note that the stoichiometry of the AlO$_x$ films deposited by CVD and ALD methods is affected by carbon and hydrogen incorporation. Rather than the $S_{eff}$ being dependent on the O/Al ratio, it is possible that both the $S_{eff}$ and the O/Al ratio are dependent on carbon and hydrogen incorporation.

![Figure 5.5](image)

**Figure 5.5:** (a) The $S_{eff}$ at $\Delta n = 10^{15}$ cm$^{-3}$ for samples passivated with AlO$_x$ of various O/Al ratios, annealed at 400°C in N$_2$ over 180 min of annealing. (b) The $Q_{ox}$ of the various AlO$_x$ films, as a function of the O/Al ratio.

Figure 5.5(a) graphs the surface passivation on the O/Al ratio of the sputtered AlO$_x$ films after annealing for up to 180 min. There is still no clear trend between the surface passivation and the O/Al ratio but the results highlight an interesting asymmetry between the surface passivation of the $p$- and $n$-type wafers. The O/Al ratios at which the $p$-type wafers have the best surface passivation lead to the worst surface passivation for the $n$-type wafers and vice versa. This asymmetry can correspond to different surface carrier concentrations as a result of the field-effect passivation (Section 1.3.1). This is verified by the relation $Q_{ox}$ and the O/Al ratio is shown in Figure 5.5(b), where trends followed by $Q_{ox}$ crossover for the $p$- and $n$-type wafers. This indicates that there is a direct relationship between the $S_{eff}$ and $Q_{ox}$ as will be shown and discussed in Section 5.5.2.
5.4 Optimisation of the Annealing Conditions

5.4.1 Annealing Time

In the literature it has been shown that surface passivation from some dielectric layers can improve with longer annealing time. In the case of highly doped, boron-diffused, $p$-type surfaces passivated with SiN$_x$, for example, good surface passivation was only achieved after 2–3 hours of annealing [66]. In this experiment we extend the annealing time of the samples from Section 3.5 and we observe the changes in surface passivation over 180 min of annealing.

Figure 5.6 shows the $S_{eff}$ at $\Delta n = 10^{15}$ cm$^{-3}$ for films having different O/Al ratios. $S_{eff}$ values as low as 73 cm/s and 22 cm/s were obtained on $c$-Si($p$) and $c$-Si($n$) respectively. The latter $S_{eff}$ values were obtained after 180 min of annealing, showing that longer annealing times do improve the surface passivation from sputtered AlO$_x$ films.

![Figure 5.6: The $S_{eff}$ at $\Delta n = 10^{15}$ cm$^{-3}$ for samples passivated with AlO$_x$ from system “A”, annealed at 400°C in N$_2$ over 180 min of annealing on (a) 0.8 Ω.cm FZ $c$-Si($p$) and (b) 1 Ω.cm Cz $c$-Si($n$).](image)

On the $c$-Si($p$), the surface passivation from the AlO$_x$ films with the higher O/Al ratios (i.e. 1.95, 2.1 and 2.5) remained fairly constant over the 180 min of annealing, whereas the surface passivation from the sample with the low O/Al ratio (1.7) greatly improved over the annealing time. The converse occurs on $c$-Si($n$), where the surface passivation from the AlO$_x$ films with the lower O/Al ratios (i.e. 1.7, 1.95, 2.1) remained fairly consistent over the 180 min of annealing, whereas the surface passivation from the sample with the high O/Al ratio (2.5) improved over the annealing time. This asymmetry may be related to the field-effect passivation as discussed in Section 5.3.4 since it is possible that $Q_{ox}$
5.4 Optimisation of the Annealing Conditions

changes over the annealing time.

The results of Figure 5.6 show that good surface passivation can be achieved after 30 min of annealing. In Figure 5.7, we observe that surface passivation can be achieved as quickly as after 10 min of annealing. We note however that in all cases, the surface passivation is not optimal with the short annealing times and longer annealing times of between 30–90 min are generally required.

5.4.2 Annealing Temperature

The annealing temperature has a strong influence on the surface passivation obtained on AlO\textsubscript{x} films deposited by CVD and ALD methods [14, 22]. In this experiment we investigate here the effect of the annealing temperature on the surface passivation that is obtained from sputtered AlO\textsubscript{x} films.

Figure 5.7: The \( S_{\text{eff}} \) at \( \Delta n = 10^{15} \text{ cm}^{-3} \) for samples passivated AlO\textsubscript{x} deposited using RF sputtering of an Al target, annealed at 300–500°C in \( \text{N}_2 \) or forming gas over 180 min of annealing. Deposited on (a) c-Si\((p)\) and (b) c-Si\((n)\).

Figure 5.7 shows the surface passivation from AlO\textsubscript{x} deposited using RF sputtering of an Al target as related to the annealing temperature and the annealing time. Examples of the dependence of the lifetime on the minority carrier density is shown in Figure 5.8. The measured lifetimes of some of the samples annealed at 300°C were very low and do not appear in the figures.

The best surface passivation was obtained at the annealing temperature of 425°C, with similar values of \( S_{\text{eff}} \) (at \( \Delta n = 10^{15} \text{ cm}^{-3} \)) for both the annealing in \( \text{N}_2 \) and forming gas. The difference between annealing in the different ambient will be discussed in Section 5.4.3. The \( S_{\text{eff}} \) was \( \sim 25 \text{ cm/s} \) on the 0.8 Ω.cm FZ c-Si\((p)\) and \( \sim 9 \text{ cm/s} \) on the 1 Ω.cm Cz c-Si\((n)\);
5. Optimisation of the Surface Passivation

**Figure 5.8:** The dependence of $\tau_{eff}$ on the excess carrier density for AlO$_x$ passivated samples after 30 min of annealing in N$_2$ at 300–500$^\circ$C on (a) 0.8 Ω.cm FZ c-Si($p$) and (b) 1 Ω.cm Cz c-Si($n$).

The level of surface passivation is very poor achieved with annealing at 300$^\circ$C and does not improve to the levels of surface passivation obtained at the other annealing temperatures despite 150 min of annealing. Similar results had been obtained on AlO$_x$ deposited by ALD [14] and CVD [22] methods. This shows that the annealing temperature is a critical factor for achieving acceptable surface passivation and that a lower annealing temperature cannot be compensated with a longer annealing time.

**Figure 5.9:** The dependence of $S_{eff}$ on the annealing temperature for surface passivation from AlO$_x$ films deposited by various deposition methods on (a) c-Si($p$) and (b) c-Si($n$). The dashed lines have been drawn to guide the eye.

Meanwhile at higher annealing temperatures > 500$^\circ$C, the surface passivation is not as
5.4 Optimisation of the Annealing Conditions

good as annealing at \( \sim 425^\circ C \). The results of this experiment agree with the results in the literature, where the optimum annealing temperature is between 350–450°C (Figure 5.9).

5.4.3 Annealing Ambient

In this experiment, we investigate the effect of the annealing ambient on the surface passivation achieved. Firstly, we investigate the effect of annealing \textit{in-situ} in the sputtering chamber after deposition. We then evaluate the use of N\(_2\), forming gas, O\(_2\) and Ar as the annealing ambient for the post-deposition anneal of sputtered AlO\(_x\) films and compare these results to AlO\(_x\) films deposited by thermal ALD.

**Figure 5.10**: The \( S_{eff} \) at \( \Delta n = 10^{15} \) cm\(^{-3}\) for samples passivated with AlO\(_x\) deposited by RF sputtering of an Al target, highlighting the effects of annealing \textit{in-situ}. On (a) 0.8 \( \Omega \cdot \text{cm} \) FZ c-Si(p) and (b) 1 \( \Omega \cdot \text{cm} \) Cz c-Si(n).

Figure 5.10 shows the \( S_{eff} \) determined for samples passivated with RF sputtered AlO\(_x\) over 120 min of annealing. No significant surface passivation was observed when the AlO\(_x\) was initially deposited, nor when the samples were annealed \textit{in-situ} immediately after deposition for 30 min. Good surface passivation is achieved as quickly as 15 min for all samples after annealing in either \( N_2 \) or forming gas. It is possible that higher annealing temperatures are needed for achieving good surface passivation when annealing \textit{in-situ}, as demonstrated in Section 5.3.2 where acceptable surface passivation could only be achieved with the higher deposition temperatures (500°C).

The dependence of \( \tau_{eff} \) on the injection level with and without the in-situ annealing is shown in Figure 5.11. Annealing \textit{in-situ} clearly has a negative effect on surface passivation. Even though some surface passivation was obtained after a post-deposition anneal in either \( N_2 \) or forming gas, it did not improve to the levels of surface passivation achieved...
Figure 5.11: The dependence of $\tau_{eff}$ and the subsequent calculated $\xi_{eff}$ on the excess carrier density for samples passivated with 40 nm of RF sputtered AlO$_x$ as deposited and after 60 min of annealing at 400$^\circ$C in forming gas or N$_2$ on (a) 0.8 $\Omega$.cm FZ c-Si($p$) and (b) 1 $\Omega$.cm Cz c-Si($n$).}

by the samples without the in-situ anneal, despite two hours of annealing.

Meanwhile, different ambient for the post-deposition anneal affect the surface passivation that is achieved. Figure 5.12 shows the dependence of $\tau_{eff}$ on the injection level after annealing sputtered AlO$_x$ in various ambient. Oxygen is clearly the preferred ambient for the $p$-type substrate, but the least preferable for the $n$-type substrate. However, if we observe the results of AlO$_x$ deposited by thermal ALD (Figure 5.13), N$_2$ is the clearly preferred ambient. There is no single ambient that is clearly preferable for all AlO$_x$ deposition methods and substrate types. However, if we temporarily ignore the results from annealing in an O$_2$ ambient, then the results show that N$_2$ is generally the preferred ambient to use, closely followed by forming gas and then Ar.

Though both argon and N$_2$ are commonly considered as inert ambient, the results show a clear difference, with the AlO$_x$ films annealed in N$_2$ always achieving better surface passivation than those annealed in Ar. In the case of AlO$_x$ deposited by thermal ALD, the difference in the surface passivation achieved is significant and thus cannot be explained by experimental error. Either the Ar ambient or N$_2$ ambient—or both—are not inert and are reacting with the AlO$_x$ film.

Even though the results in the literature have reported the incorporation of N$_2$ and its positive effects [102, 152], the presence of N$_2$ was not detected in the RBS measurements of Section 4.4 nor was the annealing done at the high temperatures (> 500$^\circ$C) where nitridation was previously observed [102]. Thus, a positive interaction between the N$_2$ ambient and the AlO$_x$ films is not likely. Meanwhile, the results of Section 4.4 had
5.4 Optimisation of the Annealing Conditions

Figure 5.12: The dependence of $\tau_{\text{eff}}$ on the excess carrier density for samples passivated with AlO$_x$ using RF sputtering of an Al target and annealed in various ambient, on (a) 0.8 $\Omega$.cm FZ c-Si(p) and (b) 1 $\Omega$.cm CZ c-Si(n).

Figure 5.13: The dependence of $\tau_{\text{eff}}$ on the excess carrier density for samples passivated with AlO$_x$ using thermal ALD and annealed in various ambient, on (a) 0.8 $\Omega$.cm FZ c-Si(p) and (b) 1 $\Omega$.cm CZ c-Si(n).

suggested that Ar incorporation in AlO$_x$ films is detrimental so a negative reaction between the Ar and the AlO$_x$ films is more likely. In any case, it is clearly preferable to use N$_2$ rather than Ar in the annealing ambient.

The hydrogen from the forming gas was expected to contribute to hydrogenation and thus strongly improve surface passivation. When compared to the AlO$_x$ films annealed in N$_2$ however (Figures 5.7, 5.10–5.13), better surface passivation results are sometimes achieved with annealing in N$_2$ and sometimes with forming gas, without any clear trend. However, we note that the forming gas used here consists of $\approx$95% argon and $\approx$5% H$_2$. The
contribution of H$_2$ clearly has a positive effect compared to than using only Ar. However, if Ar has a negative reaction with the AlO$_x$ as suggested above, there will be a competition between the positive effects of H$_2$ and the negative effects of Ar, thus explaining the varied surface passivation results that has been obtained with annealing in forming gas.

As it is possible to use forming gas mixtures of N$_2$ and H$_2$, it would be preferable to use such a mixture rather than the mixture of argon and H$_2$ that was used in this experiment. In the literature, it has been reported that the use such a forming gas ambient (~5% H$_2$ in N$_2$) has given the same surface passivation results as from using a pure N$_2$ ambient [75].

The results in Figures 5.12 and 5.13 suggest that the O$_2$ ambient is reacting differently with the different AlO$_x$ films and becomes incorporated in them. As it has been hypothesised that the charge in AlO$_x$ films is linked to O interstitials and O vacancies (Section 4.2.3), the reaction of the O$_2$ ambient with the AlO$_x$ may be changing the charge in the film and thus explaining the different surface passivation results on c-Si(p) and c-Si(n).

The results here show that the use of an N$_2$ ambient provides the most consistent and desirable surface passivation results. Better surface passivation may be achieved with the use of an O$_2$ ambient or a forming gas mixture of N$_2$ and H$_2$. However, further experiments and understanding of the reactive ambient are needed before they can be confidently used to provide consistent surface passivation results.

### 5.5 Comparison to Other Deposition Methods

#### 5.5.1 Surface Passivation

Using the optimised deposition and annealing parameters as determined in this chapter, $S_{eff}$ values (at $\Delta n = 10^{15}$ cm$^{-3}$) of 24.6 cm/s and 9 cm/s were obtained on 0.8 Ω.cm c-Si(p) and 1 Ω.cm c-Si(n) respectively. The dependence of $\tau_{eff}$ on the excess carrier density for these surface passivation results are graphed in Figure 5.14(a). The best surface passivation result achieved on 0.8 Ω.cm c-Si(p) in this work is a $S_{eff}$ of 17.3 cm/s, but as discussed in Section 5.4.3 the variability of the O$_2$ annealing ambient as used for this result needs to be addressed.

The surface passivation results in the literature regarding AlO$_x$ deposited by various methods have been reported on various wafer resistivities. By converting the resistivity to its corresponding dopant density, we graph in Figure 5.14(b) the relationship between $S_{eff}$ and the dopant density for the best AlO$_x$ passivation results in the literature and
Figure 5.14: (a) The dependence of $\tau_{eff}$ on the excess carrier density for samples passivated with AlO$_x$ using the optimised deposition and annealing parameters. (b) The dependence of $S_{eff}$ on the dopant density of the wafer for AlO$_x$ deposited by various methods.

The best passivation results from sputtered AlO$_x$ of this work. Note that the results for RF sputtering of an Al target are not necessarily the best achievable results as optimised in Chapter 5, but correspond to the best surface passivation results attained over the range of dopant densities throughout the experimental work of this thesis. The values for sputtered AlO$_x$ presented in Figure 5.14(a) are limited to the results where the post-deposition anneal was carried out in an N$_2$ ambient, to allow an equivalent comparison to the AlO$_x$ reported in the literature which were also annealed in an N$_2$ ambient.

It can be observed that in the doping range $> 10^{16}$ cm$^{-3}$, $S_{eff}$ is linearly proportional to the dopant concentration, that is, $S_{eff} \propto N_{dop}$. The linearity is lost at lower doping, partly because the $S_{eff}$ data are reported at an excess carrier density $\Delta n = 10^{15}$ cm$^{-3}$ and the samples are not in low injection.

Even though there is no diffused emitter on the wafer surfaces, it is possible to use the concept of saturation (or recombination) current density $J_{0,surf}$ to describe the recombination at the surface (Section 1.3.2). The dashed blue line in Figure 5.14(a) gives the values of $S_{eff}$ corresponding to a $J_{0,surf}$ of 40 fA/cm$^2$, providing a reasonable correlation with the $S_{eff}$ for the AlO$_x$ deposited by RF sputtering of an Al target. The sample with the dopant density $3 \times 10^{14}$ cm$^{-3}$ is an outlier for this fit, possibly due to non-negligible bulk recombination or because the dopant density is dominated by the minority carrier density term in Equation 1.34. Meanwhile, the dashed brown line graphs the $S_{eff}$ corresponding to a $J_{0,surf}$ of 500 fA/cm$^2$, which can be used to model the $S_{eff}$ for the AlO$_x$ deposited by APCVD or sol-gel methods. The best surface results using AlO$_x$ as
5. Optimisation of the Surface Passivation

deposited by PECVD, PA-ALD or thermal ALD methods can be described by a $J_{0,\text{surf}}$ of 7 fA/cm$^{-2}$ as given by the dashed purple line.

Figure 5.14(a) demonstrates how the $J_{0,\text{surf}}$ value of 40 fA/cm$^{-2}$ can be used to extrapolate the $S_{\text{eff}}$ for sputtered AlO$_x$ across a broad range of dopant densities and wafer thicknesses. This parameter can be used in computer programs such as PC1D [6] and Spreadsheet for simulating QSSPC lifetime measurements (QSS Model) [53] to model and predict the performance of solar cells using sputtered AlO$_x$ for surface passivation.

5.5.2 Negative Charge

From the results of Section 3.5, the average concentration of negative charges from sputtered AlO$_x$ of this thesis ($-10^{11}$ to $-10^{13}$ elementary charges) are in the same range as the negative charges obtained with AlO$_x$ deposited by thermal ALD, PECVD, APCVD and sol-gel methods (Table 1.4). However, it is smaller—on average—than the negative charge achieved with AlO$_x$ deposited by PA-ALD which can be as high as $-1.3 \times 10^{13}$ cm$^{-2}$ [25]. A graphical representation of the values of $Q_{\text{ox}}$ and $D_{\text{it}}$ achieved with AlO$_x$ deposited by various methods is given in Figure 5.15; the references for the values from the literature are provided in Table 1.4.

![Figure 5.15: A graphical representation of the values of $Q_{\text{ox}}$ and $D_{\text{it}}$ achieved with AlO$_x$ deposited by various methods.](image)

In Section 5.3.4 we discussed how neither $S_{\text{eff}}$ nor $Q_{\text{ox}}$ depend on the O/Al ratio in the sputtered AlO$_x$ films. Rather, the values of $S_{\text{eff}}$ and $Q_{\text{ox}}$ are related to each other, independently of the O/Al ratio. This relationship is made clearer in Figure 5.16 where the $S_{\text{eff}}$ results of Section 5.5 are graphed as a function of $Q_{\text{ox}}$. 

<table>
<thead>
<tr>
<th>Charge $Q_{\text{ox}}$ (cm$^{-2}$)</th>
<th>$D_{\text{it}}$ (cm$^{-2}$ eV$^{-1}$) at midgap</th>
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<tr>
<td>$10^{10}$</td>
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<td>$10^{12}$</td>
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<tr>
<th>Process</th>
<th>$Q_{\text{ox}}$ (cm$^{-2}$)</th>
<th>$D_{\text{it}}$ (cm$^{-2}$ eV$^{-1}$)</th>
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<td>$10^{10}$</td>
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<tr>
<td>Thermal ALD</td>
<td>$-10^{12}$</td>
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<td>APCVD</td>
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<td>PA-ALD</td>
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<td>PECVD</td>
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</tbody>
</table>
Figure 5.16: The negative charge from the AlO$_x$ films as related to the $S_{eff}$ at $\Delta n = 10^{15}$ cm$^{-3}$ after annealing on (a) 0.8 Ω.cm FZ c-Si(p) and (b) 1 Ω.cm Cz c-Si(n).

As expected, there is a direct correlation between higher $Q_{ox}$ and better surface passivation; this is highlighted by the dashed lines. Interestingly, the correlation observed with the sputtered AlO$_x$ films of this work show a $1/Q_{ox}^{1/2}$ dependence on both the $p$- and $n$-type samples, although the proportionality factors are different. Meanwhile, computer simulations have shown that a $1/Q_{ox}^{2}$ dependence can be expected for $Q_{ox} > 5 \times 10^{11}$ cm$^{-2}$ [25]. It is unclear at this point why the sputtered AlO$_x$ films show a $1/Q_{ox}^{1/2}$ dependence rather than the theoretical $1/Q_{ox}^{2}$ dependence. There has not been sufficient experimental data from the other deposition methods relating $S_{eff}$ and $Q_{ox}$, so it is currently not possible to determine if this observed $1/Q_{ox}^{1/2}$ dependence is restricted to sputtered AlO$_x$ or applies to AlO$_x$ films in general. Further investigations in this area would be helpful in understanding the surface passivation from charged dielectric films.

5.5.3 Density of Interface States

In terms of surface passivation results, sputtered AlO$_x$ is definitely much better that the sol-gel and APCVD techniques, but not as good as the ALD and PECVD techniques [Figure 5.14(a)]. From Figure 5.14(a) we observe a significant difference in the values of the $D_{it}$: AlO$_x$ deposited by ALD and PECVD methods have $D_{it}$ in the range of $2 \times 10^{11}$ cm$^{-2}$eV$^{-1}$, while the $D_{it}$ of the AlO$_x$ deposited by the RF sputtering of this work is around ten times higher, at $2 \times 10^{12}$ cm$^{-2}$eV$^{-1}$. This would explain why the sputtered AlO$_x$ has not achieved so far the same surface passivation results as from the AlO$_x$ deposited by PECVD. From this comparison it is clear that reducing the $D_{it}$ is necessary for improving the surface passivation from sputtered AlO$_x$ in the future.
5.6 Chapter Summary

In this chapter, we optimised a number of deposition and annealing conditions for surface passivation from AlO$_x$ films deposited by RF sputtering of an Al target. The optimal deposition temperature is 25°C, while the sputter power, gas flows and working pressure will depend on the sputtering arrangement used (Section 5.3). Meanwhile, the preferred annealing conditions for achieving excellent and consistent surface passivation results is to anneal at 425°C in N$_2$ for 30–90 min (Section 5.4). The optimum deposition and annealing conditions as found in this thesis are summarised in Table 5.1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Details and discussion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power source</td>
<td>RF</td>
</tr>
<tr>
<td>Target</td>
<td>Al</td>
</tr>
<tr>
<td>Sputter power (W)</td>
<td>300</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>100–120</td>
</tr>
<tr>
<td>Base pressure (Torr)</td>
<td>&lt; 7 × 10$^{-7}$</td>
</tr>
<tr>
<td>Working pressure (mTorr)</td>
<td>3</td>
</tr>
<tr>
<td>Ar flow (sccm)</td>
<td>20</td>
</tr>
<tr>
<td>O$_2$ flow (sccm)</td>
<td>2</td>
</tr>
<tr>
<td>Deposition temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Substrate rotation (rpm)</td>
<td>40</td>
</tr>
<tr>
<td>Magnetron</td>
<td>Yes</td>
</tr>
<tr>
<td>Sputter direction</td>
<td>Up</td>
</tr>
<tr>
<td>Shutter</td>
<td>Yes</td>
</tr>
<tr>
<td>Load lock</td>
<td>Yes</td>
</tr>
<tr>
<td>Thickness monitor</td>
<td>Yes</td>
</tr>
<tr>
<td>Annealing time (min)</td>
<td>30–90</td>
</tr>
<tr>
<td>Annealing temperature (°C)</td>
<td>425</td>
</tr>
<tr>
<td>Annealing ambient</td>
<td>N$_2$</td>
</tr>
</tbody>
</table>

Some of the limitations of the current sputtering arrangement—as discussed in Sections 3.4 and 5.3—remain to be addressed. However, these limitations could only be removed through substantial physical changes to the current sputtering machine or the use of a new one, which were beyond the scope of this thesis. Meanwhile, an understanding of the reactions between the forming gas and O$_2$ ambient with AlO$_x$ may also provide better surface passivation results in the future. Thus, further optimisation is possible and better surface passivation from sputtered AlO$_x$ films can be expected.
Using the optimised deposition and annealing parameters as provided in Table 5.1, $S_{eff}$ values (at $\Delta n = 10^{15}$ cm$^{-3}$) of 24.6 cm/s and 9 cm/s were obtained on 0.8 $\Omega$.cm $c$-Si($p$) and 1 $\Omega$.cm $c$-Si($n$) respectively. The levels of surface passivation achieved with this optimisation are consistent with the possibility of achieving open-circuit voltages—modelled using the QSS Model—of up to 705 mV on both 0.8 $\Omega$.cm $c$-Si($p$) and 1 $\Omega$.cm $c$-Si($n$) wafers. It is therefore fair to say that these levels of surface passivation are already acceptable for high efficiency solar cells. This is confirmed by the fabrication of 20.1% efficient PERC solar cells in Section 6.5.
Applicability to Solar Cells

“For passivation of highly doped p-type c-Si, a dielectric containing a fixed negative-charge density without any absorption in the visible part of the solar spectrum would be ideal.”

J. Benick et al., 2008

6.1 Introduction

In the area of surface passivation of industrial c-Si solar cells, there are two main applications for AlO$_x$. The first application is the passivation of the rear, undiffused surface of a p-type silicon solar cell. The AlO$_x$ can provide effective “field-effect passivation” (Section 1.4) of the p-type surface without the parasitic shunting effects that occur from SiN$_x$ or the high temperature processes involved in thermal oxides. In this form of application, PERC solar cells with efficiencies of > 20% have been achieved using AlO$_x$ deposited by thermal ALD. The second application is the passivation of the front, boron-diffused surface of an n-type silicon solar cell. PA-ALD AlO$_x$ has provided the best surface passivation of the diffused p-type surface seen so far and PERL solar cells with efficiencies of 23.2% have been attained.

In Chapter 3, it was shown that RF sputtering of an Al target is a viable technique for depositing negatively charged AlO$_x$ and achieving surface passivation on both p- and n-type silicon wafers. The processing conditions were optimised in Chapter 5 to bring the surface passivation from sputtered AlO$_x$ films to levels suitable for high-efficiency solar cells.

In the design of solar cells, compromises need to be made between the $S_{eff}$ attained and the other considerations (e.g. anti-reflection, metallisation, diffusion times) in order to minimise production costs and maximise the solar cell efficiency. Thus in this chapter we investigate the implications of the film thickness (Section 6.2) and the firing stability (Section 6.3) have on the solar cell design. The applicability of AlO$_x$ to n-type solar cells...
is explored with the passivation of boron diffusions (Section 6.4), while the applicability to p-type solar cells is demonstrated with 20.1% efficient PERC solar cells (Section 6.5).

6.2 Effect of the Film Thickness

In the surface passivation of silicon surfaces with dielectric films, the film thickness is an important consideration. In the case of industrial solar cells using SiN$_x$ films for example, the film thickness affects the UV stability, the resilience at high temperature “firing” conditions, the anti-reflection properties and the surface passivation achieved [8, 80]. Also, the deposition time is important for throughput considerations for industrial solar cells, which results in various compromises involving the film thickness.

In this experiment, we investigate the effect of the film thickness of sputtered AlO$_x$ films on the surface passivation and anti-reflection properties. We find that film thicknesses of $>10$ nm are sufficient for achieving the necessary surface passivation ($S_{eff} < 37$ cm/s), while film thicknesses of $>110$ nm are suitable for anti-reflection (8.6% reflection at $\lambda = 633$ nm) as well as surface passivation ($S_{eff} < 20$ cm/s). The refractive index of sputtered AlO$_x$ films is around 1.6.

6.2.1 Experimental Design

The preparation of samples, the AlO$_x$ deposition using RF sputtering of an Al target in system “A” and annealing was done as described in Section 3.3 using the optimised deposition and annealing conditions given in Table 5.1. Various samples were characterised using transient photoconductance (Section 2.2.1), spectrophotometry (Section 2.3.4) and ellipsometry (Section 2.3.5) techniques.

6.2.2 Results and Discussion

In Figure 6.1(a), we can observe the thickness dependence of the $S_{eff}$ for AlO$_x$ films deposited by RF sputtering of an Al target as well as from ALD methods [14]. Note that the values of $S_{eff}$ from the different deposition techniques in Figure 6.1(a) should not be directly compared as the wafer resistivity used (0.8 $\Omega$.cm for the sputtered AlO$_x$ and 2.2 $\Omega$.cm for AlO$_x$ deposited by ALD methods) and the annealing conditions ($425^\circ$C for 30 min for the sputtered AlO$_x$ and $400^\circ$C for 10 min for AlO$_x$ deposited by ALD methods) were different. The thickness dependence of the $S_{eff}$ from sputtering is similar to that from thermal ALD [14, 91], whereby the surface passivation from sputtered AlO$_x$ films is
6.2 Effect of the Film Thickness

Effect of the Film Thickness on \( S_{\text{eff}} \) and \( \tau_{\text{eff}} \)

The injection level dependence of the lifetime of the sample passivated with various thicknesses of sputtered \( \text{AlO}_x \) can be seen in Figure 6.1(b). The injection level dependence of the lifetime does not appear to be influenced by the thickness of the sputtered \( \text{AlO}_x \). The best surface passivation results are attained with 110 nm \( \text{AlO}_x \) films, giving \( S_{\text{eff}} \) values of \( \sim 20 \text{ cm/s} \). For film thicknesses between 10–50 nm, the values of \( S_{\text{eff}} \) are \( \sim 30 \text{ cm/s} \).

![Figure 6.1](image1)

**Figure 6.1:** (a) The dependence of the \( S_{\text{eff}} \) on the \( \text{AlO}_x \) film thickness. The dashed lines have been provided to guide the eye. (b) The dependence of \( \tau_{\text{eff}} \) on the excess carrier density for samples passivated with various \( \text{AlO}_x \) film thicknesses.

The injection level dependence of the lifetime of the samples passivated with various thicknesses of sputtered \( \text{AlO}_x \) can be seen in Figure 6.1(b). The injection level dependence of the lifetime does not appear to be influenced by the thickness of the sputtered \( \text{AlO}_x \). The best surface passivation results are attained with 110 nm \( \text{AlO}_x \) films, giving \( S_{\text{eff}} \) values of \( \sim 20 \text{ cm/s} \). For film thicknesses between 10–50 nm, the values of \( S_{\text{eff}} \) are \( \sim 30 \text{ cm/s} \).

![Figure 6.2](image2)

**Figure 6.2:** The measured and modelled reflectance of a 0.6 \( \mu \text{m} \) \( \text{AlO}_x \) film deposited by sputtering, yielding a refractive index of 1.57.
Ellipsometry measurements showed that the sputtered AlO$_x$ films had refractive indices of about 1.65. This was supported by modelling the reflectance of a particularly thick (0.6 µm) AlO$_x$ layer, as shown in Figure 6.2, which yielded a refractive index of 1.57. These values of refractive index are consistent with AlO$_x$ films deposited by other methods [17].

Even though the anti-reflection properties of sputtered AlO$_x$ films are not as ideal as those of SiN$_x$, it can still be an effective part of an anti-reflection scheme. For example, a thin (~10 nm) AlO$_x$ layer can be combined with a SiN$_x$ layer (~70 nm) to provide anti-reflection on the front surface of solar cells, while a thick AlO$_x$ layer (~110 nm) is suitable as the rear reflector. Figure 6.3 shows the reflectance of the sputtered AlO$_x$ films with 6–110 nm thickness. For AlO$_x$ film thicknesses < 20 nm, the reflection is essentially the same as a bare planar silicon surface (~34% reflection at $\lambda = 633$ nm). For the AlO$_x$ film thickness of 110 nm, the reflection is very low (8.6% reflection at $\lambda = 633$ nm). On a textured surface the reflection from this 110 nm AlO$_x$ layer would be < 1%.

![Figure 6.3: The reflectance of sputtered AlO$_x$ films with various film thicknesses.](image)

Nevertheless, the deposition time for the 110 nm AlO$_x$ film is 11 times longer than for the 10 nm AlO$_x$ film. As high throughputs are preferable in solar cell fabrication, the use of a 10 nm AlO$_x$ film in a stack of dielectric films may offer a better compromise between the deposition rate, surface passivation and anti-reflection properties than the use of the 110 nm AlO$_x$ film with texturing.
6.3 Firing Stability

For the application of sputtered AlO$_x$ to solar cells, it is preferable that the surface passivation qualities are maintained despite being momentarily subjected to “firing” conditions (800–900°C for ∼3 s) that are typically used for the metallisation of solar cells. Otherwise, the use of sputtered AlO$_x$ may be limited to solar cell designs that have low-temperature processes. In the literature, it has been shown that AlO$_x$ deposited by ALD methods is capable of maintaining good surface passivation after firing [75, 91, 93, 154], which suggest that sputtered AlO$_x$ should also have similar stability under firing conditions.

In this experiment, we evaluate the tolerance of sputtered AlO$_x$ to firing conditions. These initial results show that sputtered AlO$_x$ does not maintain an acceptable level of surface passivation after firing. However, it is likely that firing stability will be achieved in future experiments with the optimisation of the sputtered AlO$_x$ film—such as the film density—for firing conditions.

6.3.1 Experimental Design

![Process flow diagram](image)

Figure 6.4: Process flow diagram for evaluating the firing stability of sputtered AlO$_x$.

Figure 6.4 gives the generic process flow diagram for evaluating the firing stability of sputtered AlO$_x$. The preparation of samples and the AlO$_x$ deposition—using RF sputtering of an Al target in system “A”—was done as described in Section 3.3 using the optimised deposition and annealing conditions given in Table 5.1. One set of samples were fired immediately, while another set of samples were annealed with the optimised low-temperature post-deposition anneal as given in Table 5.1 prior to firing. The firing was done in a Rapid
Thermal Processing (RTP) furnace (Unitemp UTP–1100) at 800°C for 3 s in a N₂ ambient. A constant ramp-up rate of 50°C/s was used, while the wafers were quickly cooled down (cooling rate of ~100°C/s until ~400°C) by removing all illumination sources and flushing the chamber with high flows of N₂.

The samples were characterised mainly using transient photoconductance techniques (Section 2.2.1). When the surface passivation was very poor, the generalised photoconductance method was used with an optical constant of 0.7.

6.3.2 Results and Discussion

Figure 6.5: The dependence of τ_{eff} on the excess carrier density for samples passivated with sputtered AlOₓ after annealing and firing processes. (a) 20 nm AlOₓ (b) 110 nm AlOₓ.

Figure 6.5(a) shows the lifetime of the sample passivated with 20 nm of AlOₓ in response to the annealing and firing processes, while Figure 6.5(b) shows the lifetime of the sample passivated with 110 nm of AlOₓ. In both cases, good surface passivation is achieved after the low-temperature post-deposition anneal. The calculated values of S_{eff} (at Δn = 10^{15} cm⁻³) were 100 cm/s for the 20 nm AlOₓ and 41 cm/s for the 110 nm AlOₓ. Although these surface passivation results are not as good as those in Chapter 5, the outcomes of this experiment are not affected.

The lifetime results in Figure 6.5 show a clear decrease in the surface passivation after firing. Even though the 110 nm AlOₓ film showed a higher tolerance to firing than the 20 nm AlOₓ film, the levels of surface passivation are very poor in all cases after firing and are unacceptable for the surface passivation of solar cells. The results show that the sputtered AlOₓ films using the current set of optimised deposition conditions are not firing stable.
Table 6.1: Summary of temperature tolerance experiments on AlO\(_x\) films deposited \(\text{PA-ALD}\) or sputtering. Values are reported as \(S_{\text{eff}}\) (cm/s) for undiffused \(p\)-type surfaces and \(J_{0E}\) (fA/cm\(^2\)) for diffused \(p\)-type surfaces; a dash means that the processing step was not carried out.

<table>
<thead>
<tr>
<th>Method</th>
<th>Passivation scheme</th>
<th>Reference</th>
<th>(1) Annealing step (in N(_2))</th>
<th>(2) Firing step (in forming gas) (&gt; 800(^\circ)C for ~3 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-ALD AlO(_x) on (c)-Si((p))</td>
<td>30 nm AlO(_x)</td>
<td>[93]</td>
<td>2.6 cm/s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>27 nm AlO(_x)</td>
<td>[154]</td>
<td>–</td>
<td>~1 cm/s</td>
</tr>
<tr>
<td></td>
<td>30 nm AlO(_x)/70 nm SiN(_x)</td>
<td>[93]</td>
<td>2.8 cm/s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>30 nm AlO(_x)/70 nm SiN(_x)</td>
<td>[93]</td>
<td>–</td>
<td>11.5 cm/s</td>
</tr>
<tr>
<td></td>
<td>27 nm AlO(_x)</td>
<td>[154]</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10 nm AlO(_x)/60 nm SiN(_x)</td>
<td>[176]</td>
<td>–</td>
<td>24 fA/cm(^2)</td>
</tr>
<tr>
<td></td>
<td>10 nm AlO(_x)/60 nm SiN(_x)</td>
<td>[176]</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sputtered AlO(_x) on (c)-Si((p))</td>
<td>20 nm AlO(_x)</td>
<td>this</td>
<td>100 cm/s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>110 nm AlO(_x)</td>
<td>work</td>
<td>41 cm/s</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>110 nm AlO(_x)</td>
<td></td>
<td>–</td>
<td>~1100 cm/s</td>
</tr>
</tbody>
</table>
Table 6.1 compares the results of this work to AlO,
 films deposited by PA-ALD [93, 154]. It includes the results from the evaluation of AlO,
/SiNx stacks in the literature, which showed a substantially improved tolerance of firing conditions, particularly for very thin (< 10 nm) layers of AlO,
. It may be possible to use AlO,
/SiNx stacks for sputtered AlO,
 to improve its thermal stability.

In the literature, it has been shown that the firing stability of SiNx is dependent on the silicon nitride bond density [65] and this subsequently increased the density of the film [80]. It was hypothesised that the higher film density is necessary for maintaining the hydrogen in the SiNx film for surface passivation purposes.

The above hypothesis regarding achieving firing stability with SiNx may also be applicable to achieving firing stability with AlO,
. From Section 3.4.5, we note that the density of AlO,
 films deposited by RF sputtering of an Al target is ∼2.6 g/cm³, which is less than the density of ∼3 g/cm³ for AlO,
 films deposited by PA-ALD [17]. From Section 4.5, we note that the AlO,
 film with the higher film density loses less hydrogen (from 0.8 at.% to 0.6 at.%) compared to the AlO,
 film with the lower density (from 1.9 at.% to 1 at.%). The results in Table 6.1 agree with the above hypothesis as the AlO,
 film with the higher film density (deposited by PA-ALD) achieves good firing stability, whereas the AlO,
 film with the lower film density (deposited by sputtering) is not firing stable.

In this experiment, the better tolerance of the 110 nm AlO,
 film to firing compared to the 20 nm AlO,
 film also agrees with the hypothesis, as less hydrogen is expected to be lost from the thicker AlO,
 film. All of these results indicate that AlO,
 films behave similarly to SiNx films for the purposes of achieving firing stability, that higher film densities are required for preventing the loss of hydrogen. This suggests that if the film density of sputtered AlO,
 films can be increased through optimisation of the deposition and annealing conditions, it would be possible to achieve firing stability with sputtered AlO,
 films.

### 6.4 Passivation of Boron-diffused Surfaces

The best surface passivation of boron-diffused emitters have been attained with AlO,
 deposited by PA-ALD [11]. The excellent surface passivation results have been attributed to a low Dit and/or that the dominant interface defect has a relatively low σn. Even though sputtered AlO,
 is unlikely to achieve similar surface passivation results on boron-diffused surfaces due to its higher Dit, it may still be superior to the use of other dielectrics. In this experiment, we investigate the passivation of various boron-diffused surfaces using AlO,
 deposited by RF sputtering of an Al target. J0E values as low as 228 fA/cm² across sheet
resistances of 88–210 Ω/□ are achieved in this initial experiment; better surface passivation can be expected with the optimisation of the boron diffusion and AlOₓ deposition.

### 6.4.1 Experimental Design

![Figure 6.6](image_url)

Figure 6.6: Process flow diagram for evaluating the surface passivation of boron-diffused emitters using sputtered AlOₓ. The dashed boxes highlights that the use of the drive-in step depended on the targeted sheet resistance.

Figure 6.6 gives the generic process flow diagram for evaluating the surface passivation of boron-diffused emitters using sputtered AlOₓ. Twelve, 4” round, 10 Ω.cm, (100) Cz n-type silicon wafers were saw-damage etched using a 50% Tetramethylammonium Hydroxide (TMAH) solution. The surfaces were polished using a 10:1 HNO₃/HF solution and the final wafer thicknesses were between 370–470 µm. The wafers underwent a RCA clean, ∼5% HF dip and a DI water rinse prior to the boron diffusion process. A set of dummy wafers [4” round, 500 Ω.cm, (100) FZ p-type silicon] was also prepared to accompany each of the different sets of diffusion parameters and annealing processes.

The boron diffusion was done by exposing both sides of the wafers in a quartz tube furnace to BBr₃. For six of the wafers, the boron diffusion was done at 865°C for 60 min, while for the other six wafers, the boron diffusion was performed at 900°C for 60 min. All boron glass was removed using alternating steps in hot HNO₃ and HF solutions. The
wafers were dipped in 10% HF for 2 min, followed by immersion in a 110°C 70% HNO₃ for 10 min and then dipped in the HF solution again; this was repeated until the surfaces became hydrophobic.

To obtain a range of sheet resistances, same wafers underwent different annealing processes. The wafers underwent a RCA clean, ~5% HF dip and a DI water rinse prior to loading into a Trichloroethane [RCA] cleaned quartz tube furnace. Six wafers were put aside, four wafers were annealed at 1000°C in N₂ for 3 h and two wafers were annealed at 1000°C in N₂ for 18 h. The boron emitters where no drive-in step was carried out corresponds to an “industrial type” of emitter [177], with a high surface doping and a relatively shallow profile that is not ideal for solar cell performance but suitable for manufacturing. The boron emitters that underwent a drive-in step are closer to an optimised emitter shape, a “laboratory type” of emitter with low surface doping and a deep profile that leads to high solar cell efficiencies. The sheet resistance of the boron-diffused surfaces were measured on the dummy wafers using a four-point probe [27].

The 4” wafers were quartered to provide a set of samples for passivation with sputtered AlOₓ and a set of control wafers for passivation with a nitric acid SiO₂/SiNX stack. The wafers underwent a RCA clean, ~5% HF dip and a DI water rinse prior to the passivation processes. The AlOₓ deposition using RF sputtering of an Al target in system “A” and the post-deposition annealing was done as described in Section 3.3 using the optimised deposition conditions given in Table 5.1. The control wafers were passivated with an ultrathin SiO₂ layer formed by Nitric Acid Oxidation of Silicon [NAOS] and capped with a layer of PECVD SiNx using the same facilities and method as Mihailetchi et al. [178] at the Energy Research Centre of the Netherlands [ECN].

To enable carrier lifetime testing, AlOₓ was deposited on both sides of a wafer to create a symmetrical structure; these were then characterised using transient photoconductance techniques (Section 2.2.1). The values of J₀E were calculated as described in Section 1.3.4. The iVOC for the n-type solar cells that could be fabricated was calculated using the QSS Model [53].

### 6.4.2 Results and Discussion

Figure 6.7 (a) shows the results for the surface passivation of boron-diffused emitters using sputtered AlOₓ or using a NAOS SiO₂/PECVD SiNₓ stack, while Figure 6.7 (b) shows the best results for the surface passivation of boron-diffused emitters in the literature using various dielectrics. No clear trend can be observed between the surface passiva-
Figure 6.7: The dependence of the $J_{0E}$ on the sheet resistance for the surface passivation of boron-diffused emitters (a) in this experiment (Section 6.4) and (b) in the literature.

For the “industrial type” of emitter, the best value of $J_{0E}$ using sputtered AlO$_x$ is 349 fA/cm$^2$ at the sheet resistance of 100 Ω/□. This is consistent with achieving open-circuit voltages of up to 655 mV in n-type (1 Ω.cm) solar cells with a boron emitter. The corresponding control sample that had been passivated with the NAOS SiO$_2$/PECVD SiN$_x$ stack achieved a $J_{0E}$ of 155 fA/cm$^2$, which is not a great surface passivation result either. This shows that for the “industrial type” of emitter, the surface passivation results achieved with these samples (i.e. with no drive-in step) have been limited by the boron diffusion. It gives an indication of the surface passivation capabilities of sputtered AlO$_x$ of boron-diffused surfaces but by no means representative of the best surface passivation results that may be achieved.

For the “laboratory type” of emitter, the best value of $J_{0E}$ using sputtered AlO$_x$ is 228 fA/cm$^2$ at the sheet resistance of 88 Ω/□. This is consistent with achieving open-circuit voltages of up to 665 mV in n-type (1 Ω.cm) solar cells with a boron emitter. The control samples that had been passivated with the NAOS SiO$_2$/PECVD SiN$_x$ stack
(e.g. \( J_{0E} = 25 \, \text{fA/cm}^2 \) at \( 210 \, \Omega/\square \)) are comparable to the best results in the literature [Figure 6.7(b)], indicating that the surface passivation results achieved with these samples (i.e. with a drive-in step) are not limited by the boron diffusion. These results show that the surface passivation from sputtered \( \text{AlO}_x \) is not as good as the other surface passivation methods and further optimisation is required.

**Figure 6.8**: Process flow diagram for the PERC solar cells fabricated in this work.
6.5 Application of Sputtered Aluminium Oxide to Solar Cells

In order to verify the suitability of sputtered AlO$_x$ for the surface passivation of silicon solar cells, $p$-type PERC solar cells are fabricated using sputtered AlO$_x$ for the rear surface passivation.

6.5.1 Experimental Design

The PERC solar cells were fabricated as described by the process flow diagram in Figure 6.8. The AlO$_x$ was deposited using RF sputtering of an Al target in system “A” as described in Section 3.3, using the optimised deposition and annealing conditions given in Table 5.1. The other fabrication steps were carried out at the Institute for Solar Energy Research HameIn/Emmerthal (ISFH) using the same facilities and method as Schmidt et al. [88, 91].

6.5.2 Results and Discussion

Table 6.2: One-sun parameters measured under standard testing conditions of 290 $\mu$m thick PERC type silicon solar cells with 110 nm AlO$_x$, 20 nm AlO$_x$/100 nm SiN$_x$ or thermal SiO$_2$ rear surface passivation. The aperture cell area is 4 cm$^2$. Average values and standard deviations for the best three cells processed in the batch are also provided.

<table>
<thead>
<tr>
<th>Rear passivation</th>
<th>Cell no.</th>
<th>$V_{OC}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 nm AlO$_x$</td>
<td>3, 4</td>
<td>651</td>
<td>39.1</td>
<td>79.1</td>
<td>20.1$^{(a)}$</td>
</tr>
<tr>
<td>Average of 3</td>
<td></td>
<td>651.9±1.2</td>
<td>38.16±0.44</td>
<td>78±2.2</td>
<td>19.4±0.45</td>
</tr>
<tr>
<td>20 nm AlO$_x$/100 nm SiN$_x$</td>
<td>5, 3</td>
<td>654.2</td>
<td>37.92</td>
<td>78.8</td>
<td>19.6</td>
</tr>
<tr>
<td>Average of 3</td>
<td></td>
<td>653.4±4.9</td>
<td>38.16±0.55</td>
<td>78±3.3</td>
<td>19.4±0.6</td>
</tr>
<tr>
<td>Thermal SiO$_2$ [88]</td>
<td>7, 1</td>
<td>656</td>
<td>38.9</td>
<td>80.3</td>
<td>20.5</td>
</tr>
<tr>
<td>Average of 4</td>
<td></td>
<td>655±1</td>
<td>38.4±0.5</td>
<td>80.3±1.3</td>
<td>20.2±0.3</td>
</tr>
</tbody>
</table>

$^{(a)}$ Independently confirmed at Fraunhofer ISE CalLab.

The solar cells results are presented in Table 6.2. The best result with sputtered AlO$_x$ is achieved using 110 nm of AlO$_x$, achieving an efficiency of 20.1%. Meanwhile, the best result using the 20 nm AlO$_x$/100 nm SiN$_x$ stack is 19.6%. The IV curves of the former and the latter PERC cells are given in Figure 6.9.

The average efficiency of the solar cells with sputtered AlO$_x$ were 19.4% while the reference solar cells using thermal SiO$_2$ as rear surface passivation achieved an average
efficiency of 20.2% \cite{88}. Even though the solar cells using sputtered AlO\textsubscript{x} are not as good as the solar cells using thermal SiO\textsubscript{x}, we have clearly shown here that sputtered AlO\textsubscript{x} can be a low temperature, high throughput alternative to thermal SiO\textsubscript{x} for high efficiency solar cells.

![Figure 6.9: The IV curves of PERC solar cells, with rear surface passivation using a 110 nm AlO\textsubscript{x} film or a 20 nm AlO\textsubscript{x}/100 nm SiN\textsubscript{x} stack.](image)

Table 6.3 lists the one-sun parameters of the solar cells passivated with the sputtered AlO\textsubscript{x} of this experiment alongside the one-sun parameters of solar cells in the literature that have used AlO\textsubscript{x} deposited by ALD and CVD methods. Note that the solar cell structures used are not the same, so the one-sun parameters only provides a rough comparison between the use of AlO\textsubscript{x} deposited by the different deposition methods. The limiting parameter for the solar cells with sputtered AlO\textsubscript{x} appears to be the \( V_{OC} \), which is consistent with the fact that the surface passivation from sputtered AlO\textsubscript{x} is not as good as the surface passivation from AlO\textsubscript{x} deposited by ALD and CVD methods.

### 6.6 Chapter Summary

In this chapter, we evaluated the suitability of sputtered AlO\textsubscript{x} for application to solar cells. An AlO\textsubscript{x} film thickness of 10 nm is sufficient for achieving excellent surface passivation (Section 6.2). A 110 nm layer of sputtered AlO\textsubscript{x} can be combined with surface texturing to minimise the total reflectance, or a thin layer of AlO\textsubscript{x} capped with other dielectric layers can be used as a compromise between the deposition rate, surface passivation and anti-reflection properties.
### Table 6.3: Comparison of the best solar cell efficiencies achieved using AlO$_x$ passivation deposited by the different methods. The AlO$_x$ passivates the undiffused $p$-type surface on the $p$-type solar cells or passivates the diffused $p$-type surface on the $n$-type solar cells.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Cell type</th>
<th>Passivation structure</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-type PERC [179]</td>
<td>$p$-type PERC</td>
<td>AlO$_x$/$SiO_x$</td>
<td>664</td>
<td>40.7</td>
<td>79.4</td>
<td>21.4</td>
</tr>
<tr>
<td>PA-ALD</td>
<td>$n$-type BJBC $^a$ [92]</td>
<td>AlO$_x$</td>
<td>636</td>
<td>37.9</td>
<td>78.7</td>
<td>19</td>
</tr>
<tr>
<td>Thermal ALD</td>
<td>$n$-type PERL $^b$ [12]</td>
<td>AlO$_x$/$SiN_x$</td>
<td>703.6</td>
<td>41.2</td>
<td>80.2</td>
<td>23.2</td>
</tr>
<tr>
<td>PECVD</td>
<td>$p$-type PERC [90]</td>
<td>AlO$_x$/$SiO_x$</td>
<td>618</td>
<td>40.73</td>
<td>80</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>$p$-type PERC [90]</td>
<td>AlO$_x$/$SiN_x$</td>
<td>662</td>
<td>40.6</td>
<td>76.9</td>
<td>20.7</td>
</tr>
<tr>
<td>Sputtering$^c$</td>
<td>p-type PERC (this experiment)</td>
<td>AlO$_x$</td>
<td>651</td>
<td>39.1</td>
<td>79.1</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>p-type PERC (this experiment)</td>
<td>AlO$_x$/$SiN_x$</td>
<td>654.2</td>
<td>37.92</td>
<td>78.8</td>
<td>19.6</td>
</tr>
</tbody>
</table>

$^a$ Rear aluminium-diffused emitter.  
$^b$ Front boron-diffused emitter.  
$^c$ RF sputtering of an Al target.

An initial investigation into the thermal stability of sputtered AlO$_x$ films (Section 6.3) found that they—using the current optimisation of deposition parameters—were not sufficiently firing stable ($> 800^\circ$C for $\sim$3 s). Based on the results in the literature, we believe that firing stability can be achieved with sputtered AlO$_x$ that have a higher density. For boron-diffused surfaces, the best $J_{0E}$ value of 228 fA/cm$^2$ was achieved on a sheet resistance of 88 $\Omega$/$\square$ (Section 6.4).

Finally, sputtered AlO$_x$ was applied to PERC solar cells as the rear surface passivation (Section 6.5). An average solar cell efficiency of 19.4% was achieved, with the best solar cell achieving an efficiency of 20.1%. This demonstrates that sputtered AlO$_x$ is applicable to high efficiency solar cells.
Summary and Outlook

Summary

The work of this thesis was divided into studying the viability (Chapter 3), understanding (Chapter 4), optimising (Chapter 5) and applying (Chapter 6) sputtered AlO$_x$ for the surface passivation of silicon solar cells. Each of these areas were investigated experimentally and the main conclusions are summarised below.

In determining the viability of sputtered AlO$_x$ for surface passivation, two sputtering systems and three sputtering methods were investigated in Chapter 3. The main conclusions of this investigation were:

• Good surface passivation can definitely be achieved using RF sputtering of an Al target. $S_{eff}$ values as low as 124 cm/s and 22 cm/s were obtained on 0.8 Ω.cm c-Si($p$) and 1 Ω.cm c-Si($n$) respectively after annealing at 400°C in N$_2$.

• Negative charges—in the range of $-10^{11}$ to $-10^{13}$ cm$^{-2}$—can be obtained on AlO$_x$ deposited by all of the sputtering methods and systems.

• We explain how the components of a sputtering arrangement—such as the base pressure, substrate rotation and the availability of a shutter—affect the deposition of the AlO$_x$ and the surface passivation that is subsequently achieved.

• Of the three modes of sputtering, only the parameter space defined by “dielectric mode” is suitable for depositing AlO$_x$ for surface passivation purposes.

To understand the levels of surface passivation and negative charges achieved with AlO$_x$ deposited by the different sputtering methods, a number of thin film and surface analysis techniques were performed on sputtered AlO$_x$ films in Chapter 4. The analyses showed that:

• Impurities such as argon, germanium and platinum were found in some of the sputtered AlO$_x$ films and we hypothesise that this is limiting the surface passivation in the latter samples.
Summary and Outlook

- Hydrogen concentrations of < 2 at.\% was present in all of the sputtered AlO\(_x\) films, even though hydrogen was not intentionally included in the deposition process.

- The hydrogen concentration decreased after the low-temperature post-deposition process, which coincided with large improvements in surface passivation. This supports the hypotheses that hydrogen has an important role in the surface passivation from AlO\(_x\) films, but the exact mechanism is yet to be understood.

- The interfacial layer—most likely a SiO\(_x\) layer based on what has been reported in the literature—is thicker in sputtered AlO\(_x\) films (as thick as 10 nm) compared to the interfacial layers associated with AlO\(_x\) films deposited by ALD and CVD methods (~2 nm).

- An increase in the bond density at 1060 cm\(^{-1}\) in FTIR measurements after the post-deposition anneal is associated with improvement in the surface passivation, while a decrease is likely to indicate very poor surface passivation.

To optimise the surface passivation from AlO\(_x\) films deposited by the RF sputtering of an Al target, the following parameters were investigated in Chapter 5:

- Deposition temperature: It is preferable to deposit the sputtered AlO\(_x\) at ~25°C.

- O/Al ratio: There is no clear dependence of the surface passivation on the O/Al ratio of the AlO\(_x\) film. The results however showed a \(S_{\text{eff}} \propto 1/Q_{\text{ox}}^{1/2}\) relationship, demonstrating that the levels of surface passivation achieved with sputtered AlO\(_x\) has a dependence on the negative charge attained.

- Annealing time: The sputtered AlO\(_x\) should be annealed for 30–90 min to attain the best surface passivation.

- Annealing temperature: The optimal temperature for the post-deposition anneal is ~425°C.

- Annealing ambient: N\(_2\) is the preferred annealing ambient to be used for the best and most consistent results. Other ambient such as O\(_2\) and forming gas (~5% H\(_2\) in N\(_2\)) can lead to better results but their reaction with the AlO\(_x\) needs to be understood.

- Very good surface passivation is achieved using RF sputtering of an Al target using system “A”. \(S_{\text{eff}}\) values as low as 24.6 cm/s and 9 cm/s were obtained on 0.8 Ω.cm c-Si(p) and 1 Ω.cm c-Si(n) respectively after annealing at 425°C in N\(_2\).
• The $J_{0,\text{surf}}$ value of 40 fA/cm$^{-2}$ can be used to describe surface passivation from sputtered AlO$_x$ for modelling purposes.

In investigating the applicability of AlO$_x$ films deposited by the RF sputtering of an Al target to solar cells, we investigated some of the parameters relevant to solar cell design in Chapter 6. The main findings of this section were:

• We showed that sputtered AlO$_x$ can provide acceptable levels of surface passivation of boron-diffused emitters; the best $J_{0E}$ value of 228 fA/cm$^{-2}$ is achieved on a sheet resistance of 88 Ω/$\Box$.

• An AlO$_x$ film thickness of 10 nm is sufficient for surface passivation purposes.

• Sputtered AlO$_x$ films have refractive indices of around 1.6.

• The current sputtered AlO$_x$ films are not firing stable, but firing stability may be achieved with films with higher densities (> 3 g/cm$^3$).

• PERC solar cells with efficiencies of up to 20.1% were fabricated, demonstrating that sputtered AlO$_x$ can be applied to high-efficiency solar cells.

The work of this thesis has demonstrated that sputtered AlO$_x$ is suitable for the surface passivation of high-efficiency solar cells and has the potential of being applied to commercial solar cells. Ultimately, the advantages of sputtered AlO$_x$—over AlO$_x$ deposited by other methods—will come through its application to the fabrication of commercial solar cells and this should be the direction of future research work on sputtered AlO$_x$.

**Suggestions for Future Work**

From this work, there are a number of areas that warrant further investigation in the shorter term. They include:

• A re-evaluation of the surface passivation capabilities of AlO$_x$ deposited using RF sputtering of an Al$_2$O$_3$ target (i.e. Section 6). This re-evaluation must eliminate the incorporation of impurities that had occurred during the deposition processes of this work (Section 4).

• Evaluate the surface passivation capabilities of AlO$_x$ deposited using pulsed DC sputtering of an Al target.
• Investigate the effect of different annealing ambient on AlO$_x$ films deposited by various deposition processes (e.g. PA-ALD, PECVD). This includes evaluating the negative charges and surface passivation achieved, as well as observing if there are any changes to the composition of the AlO$_x$ film.

• Determine if sputtered AlO$_x$ films with higher densities demonstrate firing stability.

• Determine if an AlO$_x$/SiN$_x$ stack (sputtered AlO$_x$, PECVD SiN$_x$) can provide firing stability and desirable anti-reflection properties for the passivation of the front surface of a solar cell.

• Determine if an AlO$_x$/SiO$_x$ stack (sputtered AlO$_x$, PECVD SiO$_x$) can provide firing stability and desirable anti-reflection properties for the passivation of the rear surface of a solar cell.

• Determine the stability (e.g. UV, humidity) of the AlO$_x$ layers.

• Optimise the deposition and annealing conditions of sputtered AlO$_x$ for the passivation of boron-diffused emitters.

In the longer term, the sputtered AlO$_x$ technology of this work needs to be adapted to an industrial sputtering system for it to be relevant to the manufacturing of solar cells. The sputtering arrangements will be different and there will be additional considerations of cost and throughput; a new set of optimised deposition and annealing conditions will need to be developed to meet the requirements of industry. The sputtered AlO$_x$ must also be compatible with commercial solar cell designs and processes.

For repeatable and reliable results in manufacturing, the RF sputtering of an Al$_2$O$_3$ target is preferable as it avoids the balancing of parameters that is required with reactive sputtering. Meanwhile for the highest throughput, pulsed DC sputtering of an Al target would be preferable. However, neither of these sputtering methods have been shown to deposit AlO$_x$ that provides good surface passivation. Thus, priority should be placed on investigating these two sputtering methods in industrial sputtering systems, for the application of sputtered AlO$_x$ in the manufacturing of solar cells.
Appendix

A Capacitance-Voltage Equations and Methods

The Capacitance-Voltage (C-V) technique relies on the fact that the width of the space charge region in the silicon is dependent on the applied voltage. The conditions at the silicon surface as deduced from C-V measurements (e.g. $\psi_s$, $D_{it}$) depend strongly on accurate knowledge of the silicon capacitance ($C_{Si}$). Thus the calculation of the latter needs to be precise; assumptions should be avoided unless necessary.

As the C-V techniques were developed primarily for microelectronic applications, the equations have often been derived and simplified for the dark case and the carrier concentrations were strongly correlated with the density of a particular dopant [77, 118]. Even though the use of illumination has not been widely incorporated into C-V measurements [180], their usefulness and importance for characterisation solar cell structures is likely to be realised in the near future.

Firstly, we present here the generalised equations for the dimensionless electric field, $Q_{sc}$ and $C_{Si}$ as relevant to C-V measurements. The derivation of these equations are not new, but the various forms in which they are presented [8, 38, 77, 118] are often for $p$-type substrates only, or have included simplifications that do not allow inclusion of illumination or multiple dopant. Rederiving from the Poisson equation where necessary, we deduce and present here a more complete set of equations in the generalised forms that allow for the inclusion of illumination and multiple dopant.

We then present a number of methods for the determination of $V_{FB}$ and $D_{it}$. The detailed description and analysis of these various methods have been regularly presented in textbooks [8, 77, 118]; we present a description of them here as relevant to the work of this thesis.
A.1 Dimensionless Electric Field

In order to allow for the use of illumination or multiple dopant, we find that it is best to use the form of $F$ as a function of $\psi_s$, $p_B$ and $n_B$ \[181\]. This is because while $\psi_s$, $p_B$ and $n_B$ may need to be calculated differently to account for illumination or multiple dopants, the expressions of $F$, $Q_{sc}$ and $C_{Si}$ will remain unchanged.

The dimensionless electric field under equilibrium conditions $F_{Eq}$ is given by:

$$F_{Eq}(\psi_s, p_B, n_B) = \sqrt{\frac{2}{p_B + n_B}}[p_B(\exp(-\beta\psi_s) + \beta\psi_s - 1) + n_B(\exp(\beta\psi_s) - \beta\psi_s - 1)]$$ (A.1)

If $V_a$ is changed rapidly \[Figure 2.7(b)\] with insufficient time for inversion charge generation, the structure is not in steady-state and the deep depletion curve results. This can be modelled by removing the contribution of electrons in the derivation of the dimensionless electric field for $p$-type structures, or removing the contribution of holes in the derivation of the dimensionless electric field for $n$-type structures. Thus the dimensionless electric field for deep depletion $F_{DD}$ is given by:

$$F_{DD}(\psi_s, p_B, n_B) = \sqrt{\frac{2}{p_B + n_B}}[p_B(\beta\psi_s) + n_B(\exp(\beta\psi_s) - \beta\psi_s - 1)]$$ for $n$-type (A.2)

$$F_{DD}(\psi_s, p_B, n_B) = \sqrt{\frac{2}{p_B + n_B}}[p_B(\exp(-\beta\psi_s) + \beta\psi_s - 1) + n_B(-\beta\psi_s)]$$ for $p$-type (A.3)

Note that though Equations A.1 and A.2 are similar and dimensionless like the other forms of $F$ presented elsewhere \[8, 38, 77, 118\], the equations are actually not equivalent. This because of the different variables and definitions used for the derivation. However, provided that the variables and definitions are kept consistent in the subsequent derivations $Q_{sc}$ (Section A.2) and $C_{Si}$ (Section A.3), the various forms of $Q_{sc}$ and $C_{Si}$ will equate for dark conditions.
A.2 Silicon Charge

As the charge deep in the bulk is assumed to be neutral, the only charge in the silicon that needs to be accounted for is the charge in the space-charge region \((Q_{sc})\). The latter is related to the dimensionless electric field by [38]:

\[
Q_{sc} = -Sgn(\psi_s) \sqrt{\frac{\varepsilon_0 \varepsilon_{Si}}{\beta q \lambda_{D,e}}} F(\psi_s, p_B, n_B)
\] (A.4)

where \(Sgn(\psi_s)\) is the sign of \(\psi_s\) and the steady-state extrinsic Debye length \(\lambda_{D,e}\) is given by [181]:

\[
\lambda_{D,e} = \sqrt{\frac{\varepsilon_0 \varepsilon_{Si}}{\beta q (n_B + p_B)}}
\] (A.5)

In steady-state conditions, the silicon charge is given by:

\[
Q_{sc,Eq} = -Sgn(\psi_s) \sqrt{\frac{\varepsilon_0 \varepsilon_{Si}}{\beta q \lambda_{D,e}}} F_{Eq}(\psi_s, p_B, n_B)
\]

\[
= -Sgn(\psi_s) \sqrt{\frac{2 \varepsilon_{Si}}{\beta q} [p_B(\exp(-\beta \psi_s) + \beta \psi_s - 1) + n_B(\exp(\beta \psi_s) - \beta \psi_s - 1)]}
\] (A.6)

while in deep depletion conditions this is given by:

\[
Q_{sc,DD} = -Sgn(\psi_s) \sqrt{\frac{\varepsilon_0 \varepsilon_{Si}}{\beta q \lambda_{D,e}}} F_{DD}(\psi_s, p_B, n_B)
\]

\[
= -Sgn(\psi_s) \sqrt{\frac{2 \varepsilon_{Si}}{\beta q} [p_B(\beta \psi_s) + n_B(\exp(\beta \psi_s) - \beta \psi_s - 1)]} \quad \text{for } n\text{-type} \quad \text{(A.7)}
\]

\[
= -Sgn(\psi_s) \sqrt{\frac{2 \varepsilon_{Si}}{\beta q} [p_B(\exp(-\beta \psi_s) + \beta \psi_s - 1) + n_B(-\beta \psi_s)]} \quad \text{for } p\text{-type}
\]

A.3 Silicon Capacitance

Capacitance relates to the change in the charge as a result of the change in voltage [77, 118]. However, keeping in mind that the change in the voltage can be due to the change of \(V_a\) or \(\Delta V_a\) (Section 2.2.3), the capacitance for the various conditions [Figure 2.7(b)] need to be derived from different starting conditions.

When both \(V_a\) and \(\Delta V_a\) change slow enough such that equilibrium is maintained, this low frequency capacitance \((C_{Si,LF})\) is given by:
\begin{equation}
C_{Si,LF} = -\beta \left( \frac{\delta (qQ_{sc,Eq})}{\delta \psi_s} \right)
= \text{Sgn}(\psi_s) \frac{n_B \exp(\beta \psi_s) - 1 + p_B [1 - \exp(-\beta \psi_s)]}{\lambda_{D,e}(n_B + p_B) F_{Eq}}
\end{equation}

Meanwhile, if \( V_a \) changes too quickly for inversion charge generation, deep depletion conditions occur regardless of \( \Delta V_a \); this deep depletion capacitance \( (C_{Si,DD}) \) is given by:

\begin{equation}
C_{Si,DD} = -\beta \left( \frac{\delta (qQ_{sc,DD})}{\delta \psi_s} \right)
= \text{Sgn}(\psi_s) \frac{n_B \exp(\beta \psi_s) - 1 + p_B [1 - \exp(-\beta \psi_s)]}{\lambda_{D,e}(n_B + p_B) F_{DD}}
\end{equation}

for \( n \)-type

\begin{equation}
C_{Si,DD} = \text{Sgn}(\psi_s) \frac{-n_B + p_B [1 - \exp(-\beta \psi_s)]}{\lambda_{D,e}(n_B + p_B) F_{DD}}
\end{equation}

for \( p \)-type

When \( V_a \) is changing slow enough for inversion charge generation, but \( \Delta V_a \) is changing too quickly for the minority carriers in the inversion charge to follow the AC signal, high frequency conditions are attained. The minority carriers move spatially at the silicon surface in response to \( V_a \) and to account for this the high frequency capacitance \( C_{Si,HF} \) needs to be re-derived starting from the solution of the Poisson equation. The reason why the dimensionless electric field and \( Q_{sc} \) for high frequency conditions has not been presented separately in the previous sections (Sections \[A.1\] and \[A.2\]) is because they are essentially equivalent to \( F_{Eq} \) and \( Q_{sc,Eq} \); only \( C_{Si,HF} \) is markedly different from \( C_{Si,LF} \).

\begin{equation}
C_{Si,HF} = \text{Sgn}(\psi_s) \frac{n_B \exp(\beta \psi_s) - 1 + p_B [1 - \exp(-\beta \psi_s)]}{\lambda_{D,e}(n_B + p_B) F_{Eq}}
\end{equation}

for \( n \)-type

\begin{equation}
C_{Si,HF} = \text{Sgn}(\psi_s) \frac{1 + \delta_n}{\lambda_{D,e}(n_B + p_B) F_{Eq}}
\end{equation}

for \( p \)-type

where \( \delta_p \) and \( \delta_n \) accounts for the constancy of inversion layer charge and its spatial redistribution for \( n \)-type and \( p \)-type substrates respectively. This factor \( \delta_p \) is given by [182]:

\begin{equation}
\delta_p = \frac{\exp(-\beta \psi_s) + \beta \psi_s - 1}{\lambda_{D,e}(n_B + p_B)}
\end{equation}

for \( \psi_s > 0 \)

\begin{equation}
\delta_p = 0
\end{equation}

for \( \psi_s \leq 0 \)
while $\delta_n$ is given by:

$$\delta_n = \frac{\exp \beta \psi_s - \beta \psi_s - 1/F_{E_0}(\psi_s, p_B, n_B)}{\int_0^{\psi_s} \frac{p_B[1 - \exp(-\beta \psi)](\exp(\beta \psi) - \beta \psi - 1)}{(n_B + p_B)[F_{E_0}(\psi, p_B, n_B)]^3} d\psi} \quad \text{for } \psi_s < 0$$

$$\delta_n = 0 \quad \text{for } \psi_s \geq 0$$

(A.12)

### A.4 Flatband Voltage

We outline three methods for deducing $V_{FB}$:

- **Second-derivative Method**

  After taking the second-derivative of $(1/C_{HF})^2$ or $(C_{ox}/C_{HF})^2$, where $C_{HF}$ is the capacitance from a high frequency C-V measurement, the voltage at which the maximum value occurs is the $V_{FB}$ [Figure A.1(a)].

- **Conductance Method**

  The conductance of a MOS structure is maximum at flatband conditions; the voltage at which the maximum conductance occurs gives the $V_{FB}$ [Figure A.1(b)].

- **Flatband Capacitance Method**

  Alternatively, the flatband capacitance ($C_{FB}$) can be first calculated using the equation [77]:

  $$C_{FB} = \frac{1}{\left(\frac{\lambda_{D,e}}{\varepsilon_0 \varepsilon_{Si}} + \frac{1}{C_{ox}}\right)}$$

  (A.13)

  $V_{FB}$ is usually extracted from the measured high frequency C-V curve to minimise any contribution of $C_{it}$.

The assumptions of the flatband capacitance method quickly become invalidated when the doping of the structure is not uniform to the interface, or when true high frequency conditions are not attained. The second-derivative and the conductance method on the other hand are more accurate and reliable as they are determined from the experimental data without requiring the knowledge of the variables in Equation (A.13).
Figure A.1: From the sample in Figure 2.8(a), $V_{FB}$ corresponds to the voltage of the sharp peak of either (a) the second derivative of $(1/C_{HF})^2$ as calculated from the high frequency C-V curve or (b) the high frequency G-V curve.

However, the use of the second-derivative method or the conductance method will lead to an offset between $V_{FB}$ and the ideal high frequency C-V curve; this can be seen in Figure 2.8(b). This is due to the difficulty in attaining true high frequency conditions in the measurement at flatband conditions, even at frequencies as high as 1 MHz \cite{77}; $C_{it} (\psi_s = 0)$ is not negligible as assumed. Conversely, the use of the flatband capacitance method renders $C_{it} (\psi_s = 0)$ as zero, but can subsequently lead to an incorrect extrapolation of $V_{FB}$.

### A.5 Density of Interface States

The density of interface states $D_{it}$ can be determined using one of the following methods:

- **High Frequency Capacitance Method**

  The frequency of the measurement in high frequency conditions mean that the interface traps do not follow the AC voltage, but they still follow the changes in the gate bias. The influence of interface states results in the “stretchout” [Figure 2.8(b)] of the high frequency capacitance curve along the gate bias axis. Terman \cite{184} developed the method whereby the relationship between $\psi_s$ and $V_a$ is found for the measured C-V data from comparison with the ideal C-V curves; the $D_{it}$ is then given by:

$$D_{it} = \frac{C_{ox}}{q} \left[ \left( \frac{d\psi_s}{dV_a} \right)^{-1} - 1 \right] - \frac{C_{Si}(\psi_s)}{q}$$

(A.14)
A Capacitance-Voltage Equations and Methods

• Low Frequency Capacitance Method

At low frequency conditions, the interface traps immediately respond to the AC gate voltage and they contribute an additional capacitance \( (C_{it}) \) to the circuit. The total capacitance at low frequency conditions \( (C_{LF}) \) is given by (c.f. Equation 2.7):

\[
\frac{1}{C_{LF}(V_a)} = \frac{1}{C_{Si}(\psi_s)} + \frac{1}{C_{it}(\psi_s)} + \frac{1}{C_{ox}} \tag{A.15}
\]

Berglund [185] developed the method whereby the relationship between \( \psi_s \) and \( V_a \) is found using the integral:

\[
\psi_s = \psi_{s0} + \int_{V_{a0}}^{V_a} \left[ 1 - \frac{C_{LF}(V_a)}{C_{ox}} \right] dV_a \tag{A.16}
\]

Even though the boundary conditions \( (\psi_{s0}, V_{a0}) \) can be chosen arbitrarily, we recall that the definition of \( V_{FB} \) is when \( \psi_{Si0} = 0 \) and thus \( (0, V_{FB}) \) is a convenient boundary condition to use. The \( D_{it} \) is then given by:

\[
D_{it} = \left[ q \left( \frac{1}{C_{LF}(\psi_s)} - \frac{1}{C_{ox}} \right) \right]^{-1} - \frac{C_{Si}(\psi_s)}{q} \tag{A.17}
\]

• Combined High-Low Capacitance Method

By combining the measured high and low frequency \( C-V \) curves, Castagné and Vapaillie [186] showed that the \( D_{it} \) could be calculated without the need for ideal \( C-V \) curves or \( V_{FB} \).

\[
D_{it} = \left[ q \left( \frac{1}{C_{LF}} - \frac{1}{C_{ox}} \right) \right]^{-1} - \left[ q \left( \frac{1}{C_{HF}} - \frac{1}{C_{ox}} \right) \right]^{-1} \tag{A.18}
\]

This method is more accurate than the methods above as it removes the uncertainty related to the derivation of the ideal \( C-V \) curves. However, the range of \( D_{it} \) values obtained is limited by the fact that Equation A.18 is not valid for gate biases in or near inversion.

• Conductance Method

The \( D_{it} \) can also be determined from the conductance, provided that \( C-V \) and \( G-V \) measurements are made over a sufficient range of frequencies. These values then need to be converted to terms of \( <G_P>/\omega \):

\[
\frac{<G_P>}{\omega} = \frac{\omega C_{ox}^2 G_m}{G_m^2 + \omega^2 (C_{ox} - C_m)^2} \tag{A.19}
\]
where $C_m$ is the measured capacitance and $G_m$ is the measured conductance corresponding to the frequency $\omega$. This is plotted against $\omega$, allowing for the extraction of the peak $f_p$ and two points on either side of the peak, typically at $f_p/5$ and $5f_p$. A number of complicated integrations are then required to extract parameters for a function $f_D$; details of these steps can be found in various textbooks [77]. The $D_{it}$ is then given by:

$$D_{it} = \left(\frac{\left< G_P \right>}{\omega}\right)_{f_p} [qA_{metal}f_D]^{-1} \quad (A.20)$$

The $D_{it}$ derived from $f_p/5$ is labelled the low ratio conductance method and The $D_{it}$ derived from $5f_p$ is labelled the high ratio conductance method in Figure 2.9.

In all of the above cases, the $D_{it}$ can be matched to its corresponding energy in the bandgap ($E_{it}$) by:

$$E_{it} = E_F + \psi_s \quad (A.21)$$
B Recombination at a-Si:H/c-Si Interfaces

Hydrogenated amorphous silicon (a-Si:H) has long been used as a semiconductor material for thin film solar cells, but its application to the surfaces of silicon wafers for surface passivation purposes has been more recent. The interest in this area was greatly increased by the excellent surface passivation achieved on both undiffused [43] and diffused [67] surfaces and the high efficiencies of HIT solar cells [81, 82].

Olibet et al. [69] showed that the recombination at these a-Si:H/c-Si interfaces is better described by the recombination statistics of dangling bonds DB rather than the SRH statistics that have been commonly used. By adapting the simplified dangling-bond recombination model of Hubin et al. [187] for recombination in a-Si:H bulk, Olibet et al. [69] were able to quantify and improve the understanding of the recombination at a variety of a-Si:H/c-Si interfaces [42, 69, 188, 190]. However, the hypotheses behind the models of Hubin et al. [187] and its adaptation by Olibet et al. [69] have a limited range of validity and can be easily misused.

In this appendix we first revisit the recombination in bulk a-Si:H and analyse the hypotheses made by Hubin et al. [187] that permit the use of the simple closed-form solution. We find that the latter model needed to be revised with the appropriate quasi-Fermi levels for traps [191]. Following this, we analyse its adaptation by Olibet et al. [69] and discuss representative examples to illustrate the validity and limitations of the simple model. We show that the invalidation of the hypotheses can occur at excess carrier densities that are highly relevant to the analyses of recombination in solar cells and can have a substantial impact due to the potentially large errors.

B.1 Review of Dangling-Bond Recombination Statistics

Hydrogenated amorphous silicon contains an amphoteric DB defect that can be neutral ($D^0$), positively charged ($D^+$) or negatively charged ($D^-$) [192, 193]. The defect’s energy level depends on its charge state and there are two energy levels for the dangling-bond in a-Si:H (Figure B.2). Consequently, the recombination rate associated with the dangling bond ($U_{DB}$) does not follow SRH statistics or its extension to allow for a distribution of energy states (Section 1.2.3). Instead, $U_{DB}$ follows the statistics of correlated electrons [191, 192], which is more complicated and requires knowledge of the defect density, as well as the emission and capture rates at each of the different energy levels.

Figure B.2 illustrates DB recombination as presented by Vaillant and Jousse [193]. We assert that it is a depiction of the multiple states of a single defect level and not multiple
adjacent defects. It contains two energy states ($E_{DB}$ and $E_{DB} + E_u$), three charge states ($D^+, D^0, D^-$) and eight carrier flows ($u_{DB,1} - u_{DB,8}$). In this representation, $E_{DB}$ and $E_{DB} + E_u$ are discrete, but the following derivation permits a distribution of $E_{DB}$ with energy.

To determine the recombination rate of the dangling-bond model $U_{DB}$, we make the common assumptions that all carrier flows are in steady-state and that neighbouring defects do not interact. In the case of $a$-Si:H, the latter assumption is valid when the total density of defects $N_{DB}$ is $< 10^{16}$ cm$^2$, which is equivalent to an average separation of $d > 300$ Å.

The recombination and re-emission paths can then be divided into two parallel processes:

$$D^+ + e \leftrightarrow D^0$$
$$D^+_0 + e \leftrightarrow D^-$$  \hspace{1cm} (B.22)

the first consisting of $u_{DB,1}, u_{DB,3}, u_{DB,5}$ and $u_{DB,7}$ and the second consisting of $u_{DB,2}, u_{DB,4}, u_{DB,6}$ and $u_{DB,8}$. The flows $u_{DB,1}$ to $u_{DB,8}$ are given by [193]:

$$u_{DB,1}(E) = \pi^+ f^+(E) N_{db}(E) \hspace{1cm} u_{DB,2}(E) = \pi^0 f^0(E) N_{db}(E)$$
$$u_{DB,3}(E) = e_n^0(E) f^0(E) N_{db}(E) \hspace{1cm} u_{DB,4}(E) = e_n^-(E) f^-(E) N_{db}(E)$$
$$u_{DB,5}(E) = \nu^0 f^0(E) N_{db}(E) \hspace{1cm} u_{DB,6}(E) = \nu^- f^-(E) N_{db}(E)$$
$$u_{DB,7}(E) = e_p^+(E) f^+(E) N_{db}(E) \hspace{1cm} u_{DB,8}(E) = e_p^0(E) f^0(E) N_{db}(E)$$  \hspace{1cm} (B.23)
where $N_{db}(E)$ is the density of defects. The terms $f^+(E)$, $f^0(E)$ and $f^-(E)$ are the occupation functions of the $D^+$, $D^0$, $D^-$ states, given by [192, 193]:

$$
f^+(E) = \frac{1}{1 + \frac{e_p^+(E) + \pi^+}{e_n^0(E) + \bar{p}^0} \left( 1 + \frac{e_p^0(E) + \pi^0}{e_n^+(E) + \bar{p}^-} \right)}
$$

$$
f^0(E) = \frac{e_p^+(E) + \pi^+}{e_n^0(E) + \bar{p}^0} f^+(E)
$$

$$
f^-(E) = \frac{e_p^+(E) + \pi^+}{e_n^0(E) + \bar{p}^0} \left( \frac{e_p^0(E) + \pi^0}{e_n^+(E) + \bar{p}^-} \right) f^+(E)
$$

The electron emission coefficients of $D^0$ and $D^-$ are $e_n^0$ and $e_n^-$ while the hole emission coefficients of $D^+$ and $D^0$ are $e_p^+$ and $e_p^0$ [193]:

$$
e_n^0(E) = \frac{\pi_n^+}{2 \exp[\beta(E_F - E)]}
$$

$$
e_n^-(E) = \frac{2\pi_n^0}{\exp[\beta(E_F - E - E_u)]}
$$

$$
e_p^+(E) = 2\pi_p^0 \exp[\beta(E_F - E)]
$$

$$
e_p^0(E) = \frac{1}{2\pi_p^-} \exp[\beta(E_F - E - E_u)]
$$

Equations B.23–B.26 include the convenient definitions [40]:

$$
\pi^+ = \nu_{th} n \sigma_n^+ \quad \pi^0 = \nu_{th} n \sigma_n^0 \quad \bar{p}^0 = \nu_{th} p \sigma_p^0 \quad \bar{p}^- = \nu_{th} p \sigma_p^-
$$

$$
\pi_n^+ = \nu_{th} n \sigma_n^+ \quad \pi_n^0 = \nu_{th} n \sigma_n^0 \quad \bar{p}_n^0 = \nu_{th} p \sigma_p^0 \quad \bar{p}_n^- = \nu_{th} p \sigma_p^-
$$

where $\sigma_n^+$ and $\sigma_n^0$ are the electron capture cross-sections of $D^+$ and $D^0$, $\sigma_p^0$ and $\sigma_p^-$ are the hole capture cross-sections of $D^0$ and $D^-$. Note that we follow the common assumption that the capture cross-sections are independent of energy [42, 69, 187, 190, 193, 197].

When the interaction between neighbouring defects is negligible as assumed, $N_{db}(E)$ can be considered as a continuum of defects with discrete energy levels. The total recomb-
bination rate $U_{DB}$ can be given by integrating over energy:

$$U_{DB} = \int_{E_V}^{E_C} (u_{DB,1} + u_{DB,2} - u_{DB,3} - u_{DB,4})dE$$

$$= \int_{E_V}^{E_C} \left[ \frac{n^+ f^+(E) + n^0 f^0(E) - e^{-}(E)f^{-}(E)}{e^{+}(E)f^{+}(E)} - e^{-}(E)f^{-}(E) \right] N_{db}(E)dE \quad (B.27)$$

$$= \int_{E_V}^{E_C} A_{DB}(E)N_{db}(E)dE$$

where $A_{DB}(E)$ represents the term in the square brackets. Note the similarities between the derivation for $DB$ recombination (Equation B.27) and SRH recombination (Equation 1.15). As such, the concept of quasi-Fermi levels for traps can be applied here to distinguish between recombination centers and shallow traps [39] and simplify the integration of Equation B.27 [191]. Even though the the quasi-Fermi levels for traps as derived by Taylor and Simmons [40] for a monovalent defect are the most well known and often referenced, they are not directly applicable to the case of dangling-bonds and its correlated states. Longeaud and Kleider [191] showed that a different set of quasi-Fermi levels for traps are required:

$$E_{tn}^0 = E_F - \frac{1}{\beta} \ln \left( \frac{\pi_0^+}{2\pi_0^{-} + 2\pi_0^{+}} \right)$$

$$E_{tp}^+ = E_F - \frac{1}{\beta} \ln \left( \frac{\pi^+ + \pi^0}{2\pi_0^0} \right)$$

$$E_{tn}^- = E_F - E_u - \frac{1}{\beta} \ln \left( \frac{2\pi_0^0}{\pi^0 + \pi} \right)$$

$$E_{tp}^0 = E_F - E_u - \frac{1}{\beta} \ln \left( \frac{2\pi_0^0 + 2\pi^-}{\pi_0^-} \right)$$

(B.28)

The quasi-Fermi levels for traps correspond to the conditions where the flows of either $u_{DB,3}$, $u_{DB,4}$, $u_{DB,7}$ or $u_{DB,8}$ is negligible. When the energy level of a single defect being considered $E_{DB}$ is below the quasi-Fermi level for trapped electrons $E_{tn}$ for example, the probability of thermal re-emission to the conduction band via the corresponding flow (i.e. $u_{DB,3}$ for this case) is negligible. This similarly applies to $E_{tn}^-$ for electrons via $u_{DB,4}$ and conversely for $E_{tp}^+$ and $E_{tp}^0$ for holes via $u_{DB,7}$ and $u_{DB,8}$ respectively.

The classification of shallow traps and recombination centers for the possible scenarios for dangling-bond recombination is depicted in Figure B.3(b)–(d). In the case of two quasi-Fermi levels for traps (Section 1.2.3), a defect level will always either be a shallow trap or
a recombination centre [Figure B.3(a)]. On the other hand, the existence of four quasi-Fermi levels for traps complicates the classification of the shallow traps and recombination centers as there are defect levels that cannot be defined as either [Figure B.3(b)–(c)]. The reason for this is because there are two parallel recombination processes (Equation B.22).

Figure B.3: The quasi-Fermi levels for traps and the subsequent classification of shallow traps and recombination centers in the cases of (a) SRH recombination statistics and (b)–(d) DB recombination statistics. The numbers (see Table B.1) match the equivalent energy intervals in the cases of dangling-bond recombination statistics with (b) a positive $E_u$, (c) a strongly positive $E_u$ and (d) where $E_u$ is negative.

When the defect level is at a energy where both recombination processes are active (i.e. all thermal re-emission flows are negligible), the defect level acts as a recombination center. When the defect level is at a energy where neither recombination processes are active, the defect level acts as a shallow trap. However, when the defect level is at a energy where only one of the recombination processes is active, the defect level is neither a shallow trap or a recombination center. Table B.1 summarises the conditions that need to be met for the defect level to be characterised in one of the six regions are shown in Figure B.3(b)–(d).

When $E_u$ is positive, in nearly all cases there will be regions where defect levels are neither recombination centers or shallow traps; the exception to this is if $E_{ta} = E_{ta}^0$ and $E_{tp} = E_{tp}^0$ to create the conditions of Figure B.3(a). For the cases where $E_u$ is negative [Figure B.3(d)], these regions are never present and the scenario conveniently reduces to that of two quasi-Fermi levels for traps as in Figure B.3(a).

The multiple scenarios and increased complexity of the quasi-Fermi levels for traps unfortunately means that Equation B.27 can only be simplified slightly to a piecewise so-
Table B.1: List of conditions that define the different classes of dangling bonds.

<table>
<thead>
<tr>
<th>Region</th>
<th>Energy Conditions</th>
<th>Defect Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$E_C &gt; E_{DB} &gt; E_{tn}^0$</td>
<td>Shallow Trap</td>
</tr>
<tr>
<td>(2)</td>
<td>$E_{tn}^0 &gt; E_{DB} &gt; E_{tn}^- &gt; E_{tp}^+$</td>
<td>N/A</td>
</tr>
<tr>
<td>(3)</td>
<td>$E_{tn}^- &gt; E_{DB} &gt; E_{tp}^+$ and $E_{tn}^0 &gt; E_{DB} &gt; E_{tp}^0$</td>
<td>Recombination Center</td>
</tr>
<tr>
<td>(4)</td>
<td>$E_{tn}^- &gt; E_{tp}^+ &gt; E_{DB} &gt; E_{tp}^0$</td>
<td>N/A</td>
</tr>
<tr>
<td>(5)</td>
<td>$E_{tp}^0 &gt; E_{DB} &gt; E_V$</td>
<td>Shallow Trap</td>
</tr>
<tr>
<td>(6)</td>
<td>$E_{tp}^+ &gt; E_{DB} &gt; E_{tn}^-$</td>
<td>Shallow Trap</td>
</tr>
</tbody>
</table>

Table B.2: The simplified occupation functions for the energy intervals as shown in Figure B.3.

<table>
<thead>
<tr>
<th>Energy interval</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{f}^+$</td>
<td>$\frac{p_0}{p_0 + p_+}$</td>
<td>$\frac{\bar{p}^-}{\bar{p}^- + \bar{p}^0}$</td>
<td>$\frac{\bar{p}^0}{\bar{p}^- + \bar{p}^0}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\hat{f}^0$</td>
<td>$\frac{\pi_+}{\pi_0 + \pi_+}$</td>
<td>$\frac{\bar{p}^-}{\bar{p}^- + \bar{p}^0}$</td>
<td>$\frac{\bar{p}^0}{\bar{p}^- + \bar{p}^0}$</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$\hat{f}^-$</td>
<td>0</td>
<td>0</td>
<td>$\frac{\pi_+}{\pi_0 + \pi_+}$</td>
<td>$\frac{\bar{p}^-}{\bar{p}^- + \bar{p}^0}$</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
The main advantage of using the quasi-Fermi levels for traps for dangling-bond recombination lies with the simplification of the occupation functions (Table B.2), as they become constant and independent of $E_u$. However, this does not extend to the calculation of $U_{DB}$, as $E_u$ is still required for calculating the quasi-Fermi levels for traps that define the limits of the integral.

In this section we have reviewed the recombination statistics of dangling-bonds, where there are three charge states and two energy levels. We highlight the additional complexities involved in the calculation of the dangling-bond recombination compared to SRH recombination (Section 1.2.3), as well as in the application of the appropriate quasi-Fermi levels for traps. The concepts and equations presented in this section are used to analyse and evaluate the validity of a simple closed-form solution and its adaptation to interface recombination in the following sections.

B.2 Revision of a Simple Closed-Form Solution

The recombination statistics of dangling bonds is not usually applied in its full form due to its mathematical complexity; the knowledge of various parameters and numerical solutions are needed [194, 198], making them difficult to apply. Some of the complications can be resolved through the use of quasi-Fermi levels for traps [191], as seen in the previous section (Section B.1), but the latter remains difficult to apply due to the number of possible scenarios that need to be considered. As a result, assumptions are often made to further simplify the calculations for dangling bond recombination.

A simple closed-form solution given by Hubin et al. [187] has become a popular choice among researchers [193, 197] due to its simplicity; the number of parameters that need to be known are reduced and an integration is avoided. However there are several points concerning the validity of this solution that can be misleading, particularly in the application of the appropriate quasi-Fermi levels for traps as discussed in the previous section (Section B.1). As a result, the limitations for the application of the simple closed-form solution becomes uncertain and requires clarification. In addition, the simple closed-form solution and the relevant quasi-Fermi levels for traps were derived independently and it had not been demonstrated how the latter could be used to verify the valid use of the former.

Firstly, we review the three hypotheses made by Hubin et al. [187] in their model and present the derivation of the simple closed-form solution. After making the necessary clarifications, the hypothesis in question is revised. We apply the appropriate quasi-Fermi
level for traps to the model and compare it with the original model from which it was derived (Section B.1); we find that the revised hypothesis is both conceptually valid and consistent mathematically. Finally, we establish a process for verifying the acceptable use of the simple closed-form solution and using several representative examples, we demonstrate the importance of checking the validity of the hypothesis.

The Simple Closed-Form Solution

In this section, we begin by quoting the three hypotheses as presented by Hubin et al. [187] and present the simple closed-form solution as derived by Hubin et al. [187]. Following this, the contentious points of the second hypothesis are addressed and discussed.

Hubin et al. [187] simplified the equations for recombination in the dangling bonds by presenting three hypotheses for their model:

1. The steady-state condition is fulfilled independently at each energy level.

2. The illumination level is high enough that the demarcation levels for electrons and holes lie outside the distribution of the dangling-bond states. The concept of demarcation levels, as defined by Taylor and Simmons [40] and called “quasi-Fermi levels for traps” in that article, means that the states in the energy interval \((E_{tn}, E_{tp})\) act as “recombination centres” and not as “traps”; in fact, the thermal re-emission from such recombination centres can be neglected. With this hypothesis, all the dangling-bond states act as recombination centers only.

3. The capture cross-sections of the dangling-bond states are independent of the energy level.

Compared to previous simplifications, it is the second hypothesis that distinguishes the model as put forward by Hubin et al. [187] and makes simple closed-form solution possible. By making the hypothesis that the sample is sufficiently illuminated that the quasi-Fermi levels for traps lie outside \(N_{db}(E)\), all defects act as recombination centres and the re-emission flows (i.e. \(u_{DB,3}, u_{DB,4}, u_{DB,7}, u_{DB,8}\)) are negligible; this is shown in Figure B.4. As evident in Equation B.24, when the emission terms are neglected, the
occupation fractions become independent of $E_F$, $E_{DB}$ and $E_u$, giving:

$$
\dot{f}^+ = \frac{p^- p^0}{p^- p^0 + n^+ p^- + n^+ n^0} \\
\dot{f}^0(E) = \frac{n^+ p^-}{p^- p^0 + n^+ p^- + n^+ n^0} \\
\dot{f}^-(E) = \frac{n^+ n^0}{p^- p^0 + n^+ p^- + n^+ n^0}
$$

and consequently, the dangling-bond recombination can be described by an analytic solution $\dot{U}_{DB}$:

$$
\dot{U}_{DB} = \int_{E_V}^{E_C} (u_{DB,1} + u_{DB,2}) dE
$$

$$
= \left[ \pi^+ \dot{f}^+ + \pi^0 \dot{f}^0 \right] \int_{E_V}^{E_C} N_{db}(E) dE
$$

$$
= \dot{A}_{DB} N_{DB}
$$

where $\dot{A}_{DB}$ represents the term in the square brackets and $N_{DB}$ is the total density of states.

Even though the simple closed-form solution greatly simplified the calculation of recombination in dangling-bonds, there are two parts of the second hypothesis that can be misleading and we clarify them here:
• Hubin et al. [187] considers demarcation levels [199] and quasi-Fermi levels for traps to be equivalent, but they are in fact different. The concept of quasi-Fermi levels for traps are more appropriate for this context [39] and therefore the reference to demarcation levels should be removed.

• The second hypothesis can also be misleading in that while it is correct to apply the concept of quasi-Fermi levels for traps as described by Taylor and Simmons [40], it is inappropriate to directly apply the equations for $E_{tn}$ and $E_{tp}$ as presented in that paper. As discussed in Section B.1 the appropriate quasi-Fermi levels for traps for DB recombination are from the equations presented by Longeaud and Kleider [191].

The use of the quasi-Fermi level for traps as defined by Taylor and Simmons [40] is conceptually correct, but the hypothesis can be misleading in that it references $E_{tn}$ and $E_{tp}$. As discussed in the previous section (Section B.1), the appropriate quasi-Fermi levels for traps are $E_{tn}^-, E_{tn}^0, E_{tp}^0, E_{tp}^+$ as derived by Longeaud and Kleider [191].

With the above points of clarification in mind, the second hypothesis should be rephrased as such:

2. The illumination level is high enough that all four quasi-Fermi levels for traps lie outside the entire distribution of the dangling-bond states. Dangling-bond states act as recombination centers in this energy interval and it follows that if all dangling-bond states are within this energy interval, then all dangling-bond states act as recombination centers only.

An example of this is shown in Figure B.5(a); the second hypothesis is valid and thus it is appropriate to use $\hat{U}_{DB}$. On the other hand, when all of the quasi-Fermi levels for traps do not lie outside the distribution of $N_{db}(E)$, then the conditions for the hypothesis are not met. In Figure B.5(b) for example, all defects between $E_{tn}^- - E_{tp}^+$ are recombination centers but only some defects between $E_{tn}^-$ and $E_{tn}^0$ are recombination centers. Since not all of $N_{db}(E)$ are recombination centers, the hypothesis is invalid and $\hat{U}_{DB}$ should not be used.

A comparison of the occupation functions in Equation B.30 and those given in Table B.2 reveals that that the model of Hubin et al. [187] is a special case of the simplifications made by Longeaud and Kleider [191]. It is the case where the entire distribution of $N_{db}(E)$ lie within the energy interval as defined by region (3) as displayed graphically.
Figure B.5: (a) The second hypothesis is valid and $\tilde{U}_{DB}$ is applicable when all the quasi-Fermi levels for traps are outside $N_{db}(E)$. (b) One of the quasi-Fermi level for traps is not outside $N_{db}(E)$; the hypothesis invalid and $\tilde{U}_{DB}$ should not be used.

In terms of recombination statistics this can be shown for $E_u > 0$:

$$\tilde{U}_{DB} = \pi^+ \tilde{f}^+(E) \int_{E_{t^-}}^{E_{t^+}} N_t(E) dE$$

$$+ (\pi^+ \tilde{f}^+ + \pi^0 \tilde{f}^0) \int_{E_{tp}}^{E_{tn}} N_{db}(E) dE$$

$$= 0 + (\pi^+ \tilde{f}^+ + \pi^0 \tilde{f}^0) N_{DB}$$

$$= (\pi^+ \tilde{f}^+ + \pi^0 \tilde{f}^0) N_{DB}$$

$$= \tilde{U}_{DB}$$

as well as for $E_u < 0$:

$$\tilde{U}_{DB} = (\pi^+ \tilde{f}^+ + \pi^0 \tilde{f}^0) \int_{E_{tp}}^{E_{tn}} N_{db}(E) dE$$

$$= (\pi^+ \tilde{f}^+ + \pi^0 \tilde{f}^0) N_{DB}$$

$$= (\pi^+ \tilde{f}^+ + \pi^0 \tilde{f}^0) N_{DB}$$

$$= \tilde{U}_{DB}$$
Thus, the use of the appropriate quasi-Fermi levels for traps in our rephrasing of the second hypothesis is not only conceptually valid, but the recombination statistics are also mathematically consistent.

Validity of the Simple Closed-Form Solution

Equations \(B.32\) and \(B.33\) demonstrate the validity of the the model of Hubin et al. \(187\) when the hypotheses are true, but they do not demonstrate the significance of the hypotheses. We do not ascertain whether the quasi-Fermi levels for traps are convenient mathematically or whether they impose stringent conditions for the application of the simple closed-form solution. This is important because the simple closed-form solution \(\bar{U}_{DB}\) has been applied to various a-Si:H structures \(42, 69, 195–197\), assuming, without clear verification, that the quasi-Fermi levels for traps were outside \(N_{db}(E)\). Thus we aim to establish here the importance of using the quasi-Fermi levels for traps for validating the use of the simple closed-form solution. This can be demonstrated graphically by comparing the mathematical error between \(\bar{U}_{DB}\) and \(U_{DB}\) as well as their energy-dependence to the quasi-Fermi levels for traps.

<table>
<thead>
<tr>
<th>Table B.3: List of modelling parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_0 = p_0 \text{ (cm}^{-3}\text{)})</td>
</tr>
<tr>
<td>(\Delta n = \Delta p \text{ (cm}^{-3}\text{)})</td>
</tr>
<tr>
<td>(\sigma^0_p = \sigma^0_n \text{ (cm}^2\text{)})</td>
</tr>
<tr>
<td>(\sigma^-_p = \sigma^+_n \text{ (cm}^2\text{)})</td>
</tr>
<tr>
<td>(E_C - E_V \text{ (eV)})</td>
</tr>
<tr>
<td>(E_F \text{ (eV)})</td>
</tr>
<tr>
<td>(E_u \text{ (eV)})</td>
</tr>
<tr>
<td>(v_{th} \text{ (cm/s)})</td>
</tr>
</tbody>
</table>

We present examples using a Gaussian function for \(N_{db}(E)\) (Equation \(B.34\)): the numerical integration was done at 0.05 eV intervals and the total density of states \(N_{DB}\) resulting from the numerical integration of this function was \(2.51 \times 10^{14} \text{ cm}^{-3}\). Typical values from literature \(73, 193, 194\) were used for the variables in Equations \(B.25\) and \(B.26\); these are listed in Table B.3.

\[
N_{db}(E) = 10^{15} \exp \left[ -\frac{(E - 0.85)^2}{0.02} \right] \quad (B.34)
\]
Figure B.6 graphs the energy-dependence of $\bar{U}_{DB}$ and $U_{DB}$. The grey area in Figure B.6(b) graphically represents $\bar{U}_{DB}$ by multiplying the functions of $N_{db}(E)$ and $\bar{A}_{DB}$ in Figure B.6(a) with $v_{th}$ as in Equation B.31 we obtain the function ($u_{DB,1} + u_{DB,2}$) and the grey area under this function is equivalent to the integral (i.e. $\bar{U}_{DB}$). Similarly the cross-hatched area graphically represents $U_{DB}$: multiplying the functions of $N_{db}(E)$ and $A_{DB}(E)$ in Figure B.6(d) with $v_{th}$ as in Equation B.27 gives ($u_{DB,1} + u_{DB,2} - u_{DB,3} - u_{DB,4}$) in Figure B.6(a) and the integral of this gives the numerical solution of $U_{DB}$.

Figure B.6: (a) Energy-dependence of $\bar{U}_{DB}$ and $U_{DB}$ and the corresponding quasi-Fermi levels for traps in a case where the quasi-Fermi levels for traps do not lie outside the distribution of $N_{db}(E)$. (a) The functions of $N_{db}(E)$, $A_{DB}(E)$, its corresponding function of $\bar{A}_{DB}$ and the corresponding quasi-Fermi levels for traps. (b) The areas under the curves give the numerical and the simple closed-form solutions to the total recombination in the dangling bonds.

In Figure B.6(d), we can clearly see that the discrepancy between the grey and cross-hatched areas (i.e. $\bar{U}_{DB}$ and $U_{DB}$ respectively) occurs precisely where the quasi-Fermi levels for traps do not lie outside the distribution of $N_{db}(E)$. The percentage error of using $\bar{U}_{DB}$ rather than $U_{DB}$ is given by:

$$\%\text{error} = \frac{U_{DB} - \bar{U}_{DB}}{U_{DB}}$$

and is about 49.3% (global error) in this case, demonstrating the inadequacy of the simple closed-form solution when the hypothesis in question is not valid.

According to Hubin et al. [187], the second hypothesis is valid with the illumination is sufficiently high and the excess carrier density is also high, but eventually becomes invalid as the illumination decreases. Here, we can confirm their predictions on the effect of excess carrier generation.
Figure B.7: (a) At low illumination the quasi-Fermi levels for traps are very close in energy; the hypothesis is invalid and the use of $\tilde{U}_{DB}$ will lead to large errors. (b) At sufficiently high illumination, all the quasi-Fermi levels for traps lie outside the distribution of $N_{db}(E)$; the areas under the curves are almost the same, demonstrating that it is appropriate to use the $\tilde{U}_{DB}$ solution.

In Figure B.7, we show the effect of (a) low ($\Delta n = \Delta p = 10^{11} \, \text{cm}^{-3}$) and (b) high illumination ($\Delta n = \Delta p = 5 \times 10^{14} \, \text{cm}^{-3}$) using $N_{db}(E)$ as in Figure B.6(a). In Figure B.7(a) we can see that the hypothesis is invalid at low illumination due to the fact that the quasi-Fermi levels for trapped electrons and holes are close to each other and do not lie outside $N_{db}(E)$. The error of $\tilde{U}_{DB}$ is very high, at 51.3%. In Figure B.7(b) we show the case when the illumination is high enough such that the hypothesis is valid. The splitting between the quasi-Fermi levels for traps is very large and outside $N_{db}(E)$, making the hypothesis valid and reducing the error of the simple closed-form solution to 0.4%.

The value of $E_u$ used in the modelling will change the values of the quasi-Fermi levels for traps and subsequently influence the illumination level at which the hypothesis in question becomes invalid. Increasing the value of $E_u$ for example will shift the quasi-Fermi levels for traps $E_{tn}^-$ and $E_{tp}^0$ to lower energies. This will narrow the region in which all the defect levels act as recombination centers, thus increasing the error. For example, a change in $E_u$ from 0.1 eV [Figure B.7(b)] to 0.35 eV [Figure B.8(a)] increases the error from 0.4% to 16.7%. A higher illumination is needed ($\Delta n = \Delta p = 10^{18} \, \text{cm}^{-3}$) for the hypothesis to be valid for this value of $E_u$ [Figure B.8(b)] and the error reduces to 0.5%.

Changing the values of the other parameters such as the capture cross-sections will also affect the values of the quasi-Fermi levels for traps and subsequently influence the illumination level at which the second hypothesis of Hubin et al. [187] becomes invalid. So far, the effect appears to be negligible for the range of values that have been reported in the literature for these parameters.
Recombination at a-Si:H/c-Si Interfaces

Figure B.8: The effect of increasing $E_u$: (a) $E^+_{tn}$ and $E^+_{tp}$ will be closer in energy and the region of validity will be smaller. (b) A higher illumination is needed to make the hypothesis valid.

By comparing $\tilde{U}_{DB}$ with the numerical solution of $U_{DB}$, we have shown how the correct set of quasi-Fermi levels for traps strictly define the limitations of $\tilde{U}_{DB}$. When the second hypothesis is not valid, the application of simple closed-form solution using Equations B.26, B.24 and B.31 can lead to large errors in the calculation of recombination in the dangling-bonds. Subsequently, it is improper to apply the model of Hubin et al. [187] without verifying its validity through the use of the quasi-Fermi levels for traps.

The parameters that were made redundant by the second hypothesis (i.e. $N_{db}(E)$, $E_u$ and $E_F$) are needed for calculating the quasi-Fermi levels for traps and justify the use of $\tilde{U}_{DB}$. Estimates for their values can be made from a theoretical [73, 193, 194] or an experimental basis [73, 200], but they cannot be ignored by not verifying the valid use of the simple closed-form solution. In addition, we have demonstrated how the quasi-Fermi levels for traps are affected by illumination and by the various parameters of the material. It follows that assuming and using the wrong parameters can result in the inappropriate justification of the use of the simple closed-form solution.

Alternatively, the same parameters needed for calculating the quasi-Fermi levels for traps enable the calculation of $U_{DB}$ using the numerical solution (Equations B.23, B.27), providing a more accurate determination of the recombination in the dangling-bonds. Given the capabilities of modern computing, the additional calculations that arise from using the numerical solution of $U_{DB}$ should not be a problem and it would be advantageous to avoid any errors that would arise from the use of $\tilde{U}_{DB}$. 

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Alternatively, the same parameters needed for calculating the quasi-Fermi levels for traps enable the calculation of $U_{DB}$ using the numerical solution (Equations B.23, B.27), providing a more accurate determination of the recombination in the dangling-bonds. Given the capabilities of modern computing, the additional calculations that arise from using the numerical solution of $U_{DB}$ should not be a problem and it would be advantageous to avoid any errors that would arise from the use of $\tilde{U}_{DB}$.
Summary

Hubin et al. [187] greatly simplified the calculations for the recombination in the dangling bonds, where there are three charge states and two energy levels by making several hypotheses leading to a simple closed-form solution. This approximate solution reduces the number of parameters that need to be known and simplifies the calculations enormously, but the limitations for the validity of this model were not clearly defined.

We make clarifications on the model of Hubin et al. [187] and revise the relevant hypothesis. We show that the quasi-Fermi levels for traps are suitable and important for defining the limitations of the model. We establish that it is necessary to ensure the validity of the model in order to avoid potentially large mathematical errors. We point out that this unfortunately requires the same parameters that were supposed to become negligible with the simplified model and thus we encourage the use of the numerical solution of $U_{DB}$.

B.3 Revision of a Novel Model for a-Si:H/c-Si Interface Recombination

Olibet et al. [42] developed a novel method for the modelling of a-Si:H/c-Si interface recombination by adopting the three hypotheses and the dangling bond statistics as formulated by Hubin et al. [187]. It has proven to be a simple and useful method, as the model has been able to fit experimentally measured injection level dependent lifetimes on various combinations of intrinsic, $\mu$ doped (“micro doped”), or internally polarized $a$-Si:H(i) layers on a wide range of wafer doping ($p$, $n$ and intrinsic) and the parameters relevant to the passivation could be extracted [42, 69, 188–190].

In light of the relation between the appropriate set of quasi-Fermi levels for traps and the hypotheses as discussed in the previous section (Section B.2), we discuss the validity of this novel model for $a$-Si:H/c-Si interface recombination.

Model for $a$-Si:H/c-Si Interface Recombination

We quote the hypotheses, equations and method used by Olibet et al. [42] in this section. Firstly, the three hypothesis of Hubin et al. [187] as presented in Section B.2 are utilised. Then, Equation B.31 is adapted to model the recombination at the interface between the $a$-Si:H and the c-Si wafer and is subsequently given by:

$$
\dot{U}_S = \frac{(n_s + n_1)\sigma_n^0 + (p_s + p_1)\sigma_p^0}{(p_s + p_1)\sigma_p^0 + 1 + \frac{(n_s + n_1)\sigma_n^0}{(p_s + p_1)\sigma_p^0}} v_{th} D_{IT}
$$

(B.36)
where \( D_{IT} = \int D_{it}(E)dE \) is the total surface state density. The thermally emitted carrier densities of \( n_1 \) and \( p_1 \) are given by:

\[
\begin{align*}
n_1 &= n_i \exp \left[-\beta \psi_s\right] \\
p_1 &= n_i \exp \left[\beta \psi_s\right]
\end{align*}
\] (B.37)

For \( |\psi_s| \geq 125 \text{ meV} \), \( \psi_s \) is restricted to \( \pm 125 \text{ meV} \). Note that \( n_1 \) and \( p_1 \) is the thermal emission from the \( c \)-Si bulk; the thermal emission from the dangling-bond states at the surface had been assumed to be negligible as a result of the hypotheses of Hubin et al. [187].

The approximate solution to the band-bending problem as described in Section 1.3.5 is then adapted. Most importantly, Equation 1.24 is replaced with Equation B.36. The contribution of charge from the dangling-bonds at the interface \( Q_{it} \) and the bandtails is set to be independent of the injection level and thus is equivalent to a fixed charge \( Q_f \). The gate charge \( Q_g \) is neglected as no metal gate is used. Subsequently the equation of charge neutrality necessary for the approximate solution to the band-bending at the surface (Equation 1.35) becomes:

\[ 0 = Q_f + Q_{sc} \] (B.38)

The values of \( \psi_s \), \( n_s \), and \( p_s \) are determined by iteration and the \( S_{\text{eff}} \) is calculated using Equation 1.27. The parameters \( D_{IT} \) and the surface charge \( Q_f \) are varied until the calculated surface recombination velocity provides a reasonable fit of the experimental measured \( S_{\text{eff}} \).

**B.4 Validity of the Interface Recombination Model**

In Section B.2 we showed how the second hypothesis of Hubin et al. [187] could be validated by using the quasi-Fermi levels for traps as derived by Longeaud and Kleider [191]. This procedure is necessary, as the errors in the modelling can become very large with the invalidation of the hypothesis.

The \( a \)-Si:H/\( c \)-Si interface recombination model of Olibet et al. [42] also utilises the hypotheses in the same way. We highlight the fact that Olibet et al. [42] had observed discrepancies between their experimental data and their modelling of \( a \)-Si:H/\( c \)-Si interfaces at low carrier densities and had attributed this to the invalidation of second hypothesis. It follows that the interface recombination model needs to be similarly validated as
demonstrated in Section B.2 to ensure that all the dangling-bonds at the interface act as recombination centers.

Unfortunately, the calculation of the quasi-Fermi levels for traps require the knowledge of addition parameters such as the distribution of the dangling bonds \(N_{db}(E)\) and the correlation energy \(E_u\). As these parameters are unknown for the various experimental works where this model had been applied \[42, 69, 188–190\], we are not able to directly evaluate if the simple model had been used appropriately.

Nonetheless, the discrepancy between the experimental data and the modelling can be interpreted as the invalidation of the second hypothesis. However, this discrepancy will add uncertainty to the confidence of the fitting, particularly if the differences are large. Thus, validity of the second hypothesis should be evaluated using \(N_{db}(E)\) and the quasi-Fermi levels for traps prior to application of this \(a\)-Si:H/\(c\)-Si interface recombination model.

**Thermal Emission Processes**

Without the inclusion of \(n_1\) and \(p_1\) in Equation B.36, the surface recombination approaches zero when \(n_s\) and/or \(p_s\) become very small. Even though the latter situation can occur for intrinsic or lightly-doped silicon, it does not occur in practice [Figure B.10(b)]. Since the thermal emission processes from the dangling-bonds at the interface were negligible due to the assumptions of the model, Olibet et al. \[42\] included the thermal emission processes from the bulk of Equation B.37 to account for the discrepancies.

**Figure B.9:** A 60 Ω.cm \(c\)-Si(n) wafer is passivated with 40 nm of \(a\)-Si:H(i) \[42\]. (a) The modelled concentrations of \(n_s + n_1\) and \(p_s + p_1\) according using the model of Olibet et al. \[42\] compared to the concentrations of \(n_s\) and \(p_s\) if the contributions of \(n_1\) and \(p_1\) were excluded. (b) The effect of the contributions of \(n_1\) and \(p_1\) on the modelling of the measured \(S_{eff}\).
Figure B.10: A > 15 kΩ.cm c-Si(n) wafer is passivated with 40 nm of a-Si:H(i) \cite{42}. (a) The modelled concentrations of $n_s + n_1$ and $p_s + p_1$ according using the model of Olibet \textit{et al.} \cite{42} compared to the concentrations of $n_s$ and $p_s$ if the contributions of $n_1$ and $p_1$ were excluded. (b) The effect of the contributions of $n_1$ and $p_1$ on the modelling of the measured $S_{eff}$ is particularly apparent at low excess carrier densities.

Figures B.9–B.11 give three examples from the experimental work of Olibet \textit{et al.} \cite{42}. The values of $n_s + n_1$ and $p_s + p_1$ are compared to the case where $n_s$ and $p_s$ are calculated without the contributions of $n_1$ and $p_1$. Note that this is not the same as subtracting $n_1$ and $p_1$ from the values of $n_s + n_1$ and $p_s + p_1$; this is because the contributions of $n_1$ and $p_1$ affect the value of the iterated $\psi_s$, which subsequently changes the values of $n_s$ and $p_s$ that are deduced.

In Figure B.9(a), we observe that the contributions of $n_1$ and $p_1$ are small compared to the values of $n_s$ and $p_s$ in this case, with only a slight difference between the concentrations of $p_s + p_1$ and $p_s$ at low excess carrier densities. In turn, the modelling of the $S_{eff}$ differs slightly at low excess carrier densities, as seen in Figure B.9(b). In Figure B.10(a) however, the contribution of $p_1$ is large compared to the value of $p_s$ at low excess carrier densities. Correspondingly in Figure B.10(b), the modelling of the $S_{eff}$ differs greatly at low excess carrier densities. Similar results are observed in Figure B.11 except that the large difference in the surface concentration of carriers is between $n_s + n_1$ and $n_s$ as the substrate is c-Si(p). The results demonstrates how the surface passivation does not experimentally tend to zero and that thermal emissions need to be accounted for at low excess carrier densities.

As the modelling of Olibet \textit{et al.} \cite{42} matches well with the experimental data as seen in Figures B.9 and B.10 it would appear that it is necessary to account for the thermal emission from the bulk. However, while we agree that it is necessary to account...
A 130 Ω cm c-Si(p) wafer is passivated with 10 nm of a-Si:H(i) and 40 nm of a-Si:H(n) \[42\]. (a) The modelled concentrations of \(n_s + n_1\) and \(p_s + p_1\) according using the model of Olibet et al. \[42\] compared to the concentrations of \(n_s\) and \(p_s\) if the contributions of \(n_1\) and \(p_1\) were excluded. (b) The effect of the contributions of \(n_1\) and \(p_1\) on the modelling of the measured \(S_{eff}\) is particularly apparent at low excess carrier densities.

for emission processes at low excess carrier densities, we find that the solution used by Olibet et al. \[42\] is invalid in two ways:

- The addition of \(n_1\) and \(p_1\) as defined in Equation \ref{B.37} into Equation \ref{B.36} does not actually account for thermal emission from the bulk.

In SRH recombination statistics (Section \ref{1.2.3}) the emission flows of Equation \ref{1.14} can be reduced to the equations for \(n_1\) and \(p_1\) as presented in Equation \ref{B.37}. This is because the capture cross sections related to the emission flows are the same as the capture cross sections related to the recombination flows and they are factorised out for simplicity.

In the model of Olibet et al. \[42\] on the other hand, the emission from the defects in the c-Si bulk are independent of the dangling-bonds recombination flows. The capture cross-sections of the dangling-bonds (i.e. \(\sigma_n^+, \sigma_n^0, \sigma_p^0\) and \(\sigma_p^-\)) are different from the capture cross sections of the SRH-type defects in the c-Si bulk (\(\sigma_n, \sigma_p\)). However, as \(\sigma_n\) and \(\sigma_p\) are not found anywhere in Equation \ref{B.36}, \(n_1\) and \(p_1\) can only be utilising the capture cross-sections of the dangling bonds. Thus, even though Olibet et al. \[42\] intended that \(n_1\) and \(p_1\) accounted for emission from SRH-type defects in the c-Si bulk, they in fact are mathematically accounting for emission from the dangling bonds.
For a defect at midgap in the c-Si bulk, recombination processes cannot be neglected. As explained in Section 1.2.3, recombination and emissions flows are competing flows for any defect levels in the bandgap. Above the quasi-Fermi levels for trapped electrons and below the quasi-Fermi level for trapped holes, the recombination flows can be properly neglected. However, a defect at midgap is almost always between the quasi-Fermi levels for trapped electrons and holes; the recombination through this defect cannot be neglected. In fact, in a recombination center it is the emission flows that can usually be neglected. Thus, it is improper to account for emission processes from a defect at midgap in the c-Si bulk without considering the recombination processes. When the recombination processes are properly accounted for, one would find the emission processes negligible.

From the two points above, any mismatch between the modelling and measured $S_{eff}$ at low excess carrier densities indicates some sort of thermal emission process that requires consideration, but the latter is unlikely to be the thermal emission from the bulk. There are a number of alternative explanations for the sources extra carriers:

1. Thermal emission from the dangling-bonds.

Given that the thermal emission processes from the dangling bonds were neglected from Equation B.36 due to the hypothesis used for the model, it is more likely that the mismatch between the modelling and measured $S_{eff}$ represents the invalidation of the hypothesis: the illumination level is no longer sufficiently high for all the dangling bonds to be recombination centers and thus the thermal emission processes from the dangling-bonds are no longer negligible.

In Figure B.10(b) for example, the illumination level, which can be represented by the excess carrier density, is sufficiently high for the hypothesis to be valid at $\Delta n > 2 \times 10^{14} \text{ cm}^{-3}$. However, for excess carrier densities lower than this, the hypothesis is not valid; hence the discrepancy between the measured $S_{eff}$ and the modelling of the blue dashed line. The illumination at which the hypothesis becomes invalid differs for different samples and different modelling parameters; for the case of Figure B.9(b) for example, the excess carrier density at which the hypothesis becomes invalid is at $\Delta n > 1 \times 10^{13} \text{ cm}^{-3}$.

As the $N_{db}(E)$ and the values of $E_u$ and $E_F$ of the experimental work of Oli-bet et al. [42] are unknown, it is not possible to calculate the thermal emission from the dangling-bonds from Equation B.25 and observe its effect on the modelled $S_{eff}$.
2. Thermal emission from the $a$-Si:H bandtails.

The bandtail states in $a$-Si:H are shallow traps that do not contribute to recombination. However, the trapped carriers in these bandtails contribute to the charges in the system \cite{69} and affect the number of free carriers in the $a$-Si:H bulk. Due to the wider bandgap of $a$-Si:H compared to $c$-Si, the energy levels of some of these bandtail states are the same as either the conduction or valence bands of the $c$-Si. Even though the bandtail states deep in the bulk of the $a$-Si:H are too far away to interact with the carriers in the conduction and valence bands of the $c$-Si, bandtail states next to the $a$-Si:H/$c$-Si interface can become shallow traps for carriers in the $c$-Si. It is possible that the thermal emission from these bandtail states account for the discrepancy in the number of carriers at the surface at low excess carrier densities.

3. Carriers from the $a$-Si:H bulk.

Another assumption which is typically made and was implicit in this model is that the generation of carriers in the $a$-Si:H layer and its contribution to the carrier densities at the interface is negligible \cite{201}. Indeed, as the bandgap is larger and the carrier diffusion coefficients are much smaller in $a$-Si:H, any generation and contribution of carriers from the $a$-Si:H layer will still remain negligible compared to that from the $c$-Si bulk.

Unfortunately, none of the above possibilities can be tested or verified, as the parameters required are unknown. Nonetheless, we explain why it is invalid to use $n_1$ and $p_1$ in the current form in Equation B.36 and why the thermal emission of carriers is unlikely to be from the $c$-Si bulk. We propose a number of possibilities that can explain the results observed, all of which imply that various assumptions become invalidated and it is inappropriate to apply the modelling at that point.

Summary

In an adaptation of the dangling bond recombination model by Hubin et al. \cite{187}, Olibet et al. \cite{42} utilised the same hypotheses and recombination statistics to calculate recombination at $a$-Si:H/$c$-Si interfaces. As in the model of Hubin et al. \cite{187}, the deviation of the modelling from the experimental data in the model of Olibet et al. \cite{42} can be interpreted as the invalidation of the second hypothesis. The examples in this section show that this can be occurring at excess carrier densities of importance to the analyses of the recombination at $a$-Si:H/$c$-Si interfaces. We emphasise that the quasi-Fermi levels
for traps can be and ought to be used to evaluate the validity of this \textit{a-Si:H/c-Si} interface recombination model.

We discuss the addition of $n_1$ and $p_1$ in this model to account for thermal emission of carriers from defects in the \textit{c-Si} bulk. We find the application of this to be mathematically and conceptually inappropriate and propose other possibilities. In any case, the discrepancies between the modelling and the experimental data represents a shortcoming of the simple model. As such, it is best that it is not redressed with additional assumptions and equations, but be acknowledged as part of the inadequacy of the simplified \textit{a-Si:H/c-Si} interface recombination model.

\section*{B.5 Modelling \textit{a-Si:H/c-Si} Interfaces using Dangling-Bond Recombination}

In the previous section (Section \[B.3\]), we discussed the use of a novel \textit{a-Si:H/c-Si} interface recombination model. We highlighted the discrepancies between the model and experimental data that typically occur at low excess carrier densities and recognised the shortcomings of this simple model. However, some of these shortcomings can be addressed by the use of the dangling-bond recombination model from Section \[B.1\].

In this section, we implement the more complete dangling-bond recombination equations from Section \[B.1\] to \textit{a-Si:H/c-Si} interfaces. We apply this model to the experimental work of Olibet \textit{et al.} \cite{42}. We graph a range of possible values for $E_u$ and demonstrate how the use of the $U_{DB}$ statistics can provide a better fit of the experimental data and possibly account for the discrepancies at low excess carrier densities.

\section*{Method of Analysis}

The method used for calculating the recombination at the \textit{a-Si:H/c-Si} interface is as in Section \[B.3\] except that $\bar{U}_S$ (Equation \[B.36\]) is replaced by an adaptation of $U_{DB}$ (Equation \[B.27\]) to the surface.

The distribution of dangling-bonds states over the bandgap at the interface can be accounted for by using the integration in $U_{DB}$, but it adds additional complications to the modelling of the experimental work of Olibet \textit{et al.} \cite{42} as the distribution of DB states are unknown. Thus, we use a $\delta$ function at midgap, which is equivalent to the assumption made concerning the DB states in the model of Olibet \textit{et al.} \cite{42}. This effectively consigns all the DB states to be recombination centers and thus the thermal emission from the dangling-bond states will not be modelled. However, this method allows the variation of
Table B.4: List of experimental and modelling parameters [42].

<table>
<thead>
<tr>
<th>Sample no. [42]</th>
<th>Figure B.12</th>
<th>Figure B.13</th>
<th>Figure B.14</th>
<th>Figure B.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H layer(s)</td>
<td>40 nm i</td>
<td>40 nm i</td>
<td>40 nm pdop p</td>
<td>10 nm i + 40 nm n</td>
</tr>
<tr>
<td>Substrate</td>
<td>60 Ω.cm c-Si(n)</td>
<td>130 Ω.cm c-Si(p)</td>
<td>60 Ω.cm c-Si(n)</td>
<td>130 Ω.cm c-Si(p)</td>
</tr>
<tr>
<td>( \sigma_n^0 / \sigma_p^0 )</td>
<td>1/20</td>
<td>1/20</td>
<td>1/20</td>
<td>1/20</td>
</tr>
<tr>
<td>( \sigma_n^+ / \sigma_n^- = \sigma_p^- / \sigma_p^+ )</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>( D_{IT} ) (cm(^{-2}))</td>
<td>( 2 \times 10^{10} )</td>
<td>( 4 \times 10^{10} )</td>
<td>( 3 \times 10^{10} )</td>
<td>( 1 \times 10^{10} )</td>
</tr>
<tr>
<td>( Q_f ) (cm(^{-2}))</td>
<td>( 2 \times 10^{10} )</td>
<td>( 2 \times 10^{10} )</td>
<td>( 2 \times 10^{10} )</td>
<td>( -9 \times 10^{10} )</td>
</tr>
<tr>
<td>( v_{th} ) (cm/s)</td>
<td>( 2 \times 10^7 )</td>
<td>( 2 \times 10^7 )</td>
<td>( 2 \times 10^7 )</td>
<td>( 2 \times 10^7 )</td>
</tr>
</tbody>
</table>

\( E_u \) compared to the model of Olibet et al. [42] and we focus on its effect on \( S_{eff} \).

As recombination is only calculated for one energy level and integration is not required, the surface recombination in this case (\( \tilde{U}_S \)) is given by:

\[
\tilde{U}_s = [\pi^+ f^+(E_{DB}) + \pi^0 f^0(E_{DB}) - \epsilon_n^0 f^0(E_{DB}) - \epsilon_n^- f^-(E_{DB})] D_{IT} \quad (B.39)
\]

where the terms have the same definitions as in Section B.3. However, the emissions flows and occupation functions only need to be calculated for the defect energy of \( E_{DB} \). This expression of \( \tilde{U}_s \) is inserted into the approximate solution to the band-bending problem (Section 1.3.5) as done in Section B.3.

We utilise the same fitting parameters as used by Olibet et al. [42] for the fitting of the experimental data and these are listed in Table B.4. We graph the experimental data and the modelling of Olibet et al. [42] and compare it to the modelling with various values of \( E_u \). The modelling of Olibet et al. [42] should be equivalent to this model when \( E_u = 0 \) eV, but this does not occur at low excess carrier densities as the contributions of \( n_1 \) and \( p_1 \) have not been included in this model (see the discussion in Section B.4).

### B.6 Surface Passivation Examples

The example given in Figure B.12 is a 60 Ω.cm c-Si(n) wafer while the example given in Figure B.13 is a 130 Ω.cm c-Si(p) wafer; both have 40 nm a-Si:H(i) on both its surfaces to achieve surface passivation.

By comparing the fitting using the model of Olibet et al. [42] and the the \( S_{eff} \) calcu-
Figure B.12: The experimental data and the application of the model of Olibet et al.\cite{42} on an $a$-Si:H(i)/c-Si(n) interface is compared to the $S_{eff}$ calculated from $U_DB$ for (a) various positive values of $E_u$ and (b) various negative values of $E_u$.

Figure B.13: The experimental data and the application of the model of Olibet et al.\cite{42} on an $a$-Si:H(i)/c-Si(p) interface is compared to the $S_{eff}$ calculated from $U_DB$ for (a) various positive values of $E_u$ and (b) various negative values of $E_u$.

lated using $\bar{U}_s$, we can see in Figures B.12 and B.13 that $E_u$ does not make a significant impact for values between $-0.1$–$-0.2$ eV. However, for values of $E_u$ outside this range, the modelled $S_{eff}$ can change significantly; the values for $S_{eff}$ are much lower at low excess carrier densities for positive values of $E_u$, while the values for $S_{eff}$ increases at particular excess carrier densities for negative values of $E_u$.

From the observation of the experimental data in Figure B.12 (a), the value of $E_u$ could possibly be $\sim 0.3$ eV; for Figure B.13 (a) the value of $E_u$ could possibly be $\sim 0.2$ eV. Thus, even though we show that the discrepancies from the modelling using the simple
a-Si:H/c-Si interface recombination model at low excess carrier densities could be due to the neglect of \( E_u \).

However, we have to keep in mind that we have not accounted for the thermal emission from the dangling-bonds, nor considered varying the capture cross-sections, all of which can affect the value of \( E_u \) that is extracted. Thus, there are too many parameters in this a-Si:H/c-Si interface recombination model for the fitting to be simple and effective. On the other hand, the modelling demonstrates the effect of \( E_u \); if the latter can be controlled in the deposition of the a-Si:H(\( i \)) layer in the experimental work, the recombination can be dramatically reduced at low excess carrier densities.

**Heterojunction Examples**

![Figure B.14](image-url)

**Figure B.14:** The experimental data and the application of the model of Olibet *et al.* [42] on an a-Si:H(\( \mu dop \ p \))/c-Si(\( n \)) structure is compared to the \( S_{eff} \) as calculated from \( U_{DB} \) for (a) various positive values of \( E_u \) and (b) various negative values of \( E_u \).

Figure B.14 shows a 60 \( \Omega \cdot cm \) c-Si(\( n \)) wafer with 40 nm a-Si:H(\( \mu dop \ p \)) on both its surfaces to create a symmetrical heterojunction test structure. A much larger deviation between the experimental data and the modelling of Olibet *et al.* [42] at low excess carrier densities can be observed; the \( E_u \) of the a-Si:H(\( i \)) layer in this example could possibly be \( \sim 0.3 \) eV. This demonstrates that the consideration of \( E_u \) is probably even more important for evaluating doped a-Si:H layers and heterojunctions.

Figure B.15 shows a 130 \( \Omega \cdot cm \) c-Si(\( n \)) wafer with 40 nm a-Si:H(\( n \)) on both its surfaces to create a symmetrical structure similar to that used in heterojunction solar cells. Surprisingly, large changes in the positive value of \( E_u \) do not lead to any significant differences in the \( S_{eff} \). Instead, the \( E_u \) in this sample is probably negative, possibly around \( -0.12 \) eV.
We show that by accounting for $E_u$ using $\bar{U}_s$, it is possible to account for the discrepancies from the modelling using the simple $a$-Si:H/c-Si interface recombination model at low excess carrier densities. However, details concerning the distribution of $D_{it}(E)$ and capture cross-sections need to be established before one can be confident about the extracted values of $E_u$.

**B.7 Summary**

Recently, Olibet et al. [42] showed that the surface passivation from $a$-Si:H/c-Si interfaces can be effectively evaluated using an adaptation of a simplified dangling-bond recombination model proposed by Hubin et al. [187]. The validity of both models depended on three important hypotheses.

In this appendix we began by reviewing the DB recombination statistics and analysed the relationships between the latter and the three hypotheses. We found that there were
two misleading points concerning the second hypothesis and we clarified the situation. We specify the appropriate quasi-Fermi levels for traps for validating the second hypothesis and demonstrated their application. We showed that large errors in the calculation of dangling-bond recombination can occur if the second hypothesis is not valid.

In the application of a-Si/c-Si interface recombination model of Olibet et al. [42] to their experimental work, discrepancies were observed between the modelling and their experimental data at low excess carrier densities. We add to their discussion, showing how $E_u$, $n_1$ and $p_1$ affected the modelling and could account for the discrepancies. We establish that the discrepancies represent the invalidation of the second hypothesis. As this is occurring at excess carrier densities highly relevant to the analyses of the recombination for a-Si:H/c-Si interfaces and its related solar cells, we highlight the need for validating the relevant assumptions and ensure that the model is being used appropriately.

The simplified model of Hubin et al. [187] and its adaptation by Olibet et al. [42] has provided an easy and convenient means to analyse recombination in dangling-bonds and a-Si:H/c-Si interfaces respectively. However, we have shown that the hypotheses utilised for formulating these models need to be carefully considered and should not be overlooked, as their validity can have a substantial impact on the modelling and analyses.
C Thermal Stability of $a$-Si:H for Heterojunction Solar Cells

Intrinsic hydrogenated amorphous silicon has been found to provide excellent surface passivation $c$-Si and has been a key feature of high efficiency heterojunction solar cells [81, 82, 85]. In addition, the focus has been on $n$-type heterojunction solar cells, as the $a$-Si:H/$c$-Si($n$) structure is preferable to the converse [203] and has historically yielded higher cell efficiencies [81, 82, 201, 204]. These have been achieved by depositing $a$-Si:H on $n$-type silicon using various types of PECVD systems.

However, $a$-Si:H is well known to have problems with thermal stability [74, 84, 85, 205–210]. Previous investigations have shown that the $a$-Si:H in heterojunction cells do not degrade under light-soaking or at typical cell operating temperatures [84, 85]. However, temperatures can be much higher during post-deposition fabrication steps and it is important that these temperature limitations are known in order to avoid and minimise any degradation of the $a$-Si:H surface passivation.

In the case of surface passivation with $a$-Si:H, the focus is on the recombination at the $a$-Si:H/$c$-Si interface; the bulk of the $a$-Si:H is relatively insignificant as the generation of minority carriers in the latter and any injection of carriers from the $c$-Si can be neglected [201]. As many of the previous studies have focused on the thermal stability of $a$-Si:H as the bulk material [205–207, 209], they may not be directly applicable to the case of $a$-Si:H surface passivation. In $a$-Si:H/$c$-Si interfaces, it was found that the abruptness of the interface affected the thermal stability characteristics of the surface passivation [211]. An abrupt interface is one where instant $a$-Si:H deposition on $c$-Si occurred without initial epitaxial growth. According to De Wolf et al. [211], $a$-Si:H surface passivation that had an abrupt interface initially had very poor surface passivation after deposition, but improved to very good surface passivation with higher temperatures of annealing ($\sim 280^\circ$C). Conversely, those that had initial epitaxial growth started with very good surface passivation after deposition, but degraded with higher temperatures of annealing.

However, all of these previous studies in the thermal stability $a$-Si:H surface passivation have used different methods of deposition, deposition parameters or substrate materials to this work. The thermal stability of the amorphous silicon can change with some of these aspects [205] and it was also suggested that some of the previous work may have inadvertently had initial or total epitaxial growth in their $a$-Si:H deposition [212]. The latter is not necessarily undesirable, as it was reported to be preferable for heterojunction solar cells [212]. However, the general concept for heterojunction solar cells regards abrupt
interfaces as preferable [213]. Nonetheless, these factors would lead to different thermal stability characteristics of the surface passivation and it is uncertain how applicable they are to the thermal stability of a-Si:H deposition on n-type silicon using microwave PECVD.

The previous research highlight some key temperatures for a-Si:H and we use these to determine the annealing temperatures that we use to test the thermal stability of the a-Si:H surface passivation. At ∼50°C, no apparent degradation occurs in the a-Si:H surface passivation [84, 85]. At temperatures around 200°C, the breaking of the Si–H bonds [206] is likely to cause degradation for samples with initial epitaxial growth or result in improvement for samples with an abrupt interface [211]. At temperatures above 340°C, epitaxial regrowth begins to occur and this can lead to degradation in the electric properties of the a-Si:H/c-Si(n) interface [208]. From the a-Si:H layer, there is evolution of weakly bonded hydrogen at ∼365°C and evolution of strongly bonded hydrogen at ∼696°C [206].

In this work, we investigate the thermal stability of a-Si:H surface passivation on n-type silicon, deposited using a microwave PECVD system at various temperatures. Thermal annealing is then carried out at various temperatures and times to simulate possible subsequent thermal processes in the fabrication of heterojunction solar cells. The thermal behaviour of the surface passivation and the lifetime behaviour of the samples are studied, while the activation energy for the thermal degradation is determined using Arrhenius plots. The results indicate that the annealing temperature is the main factor that determines the thermal stability of the a-Si:H surface passivation. At a given annealing temperature, the level of degradation can be limited by restricting the annealing time. Comparatively, the dependence on the deposition temperature is very small and can be neglected.

C.1 Experimental Design

Several batches of 1 Ω.cm, (100), FZ n-type silicon wafers were saw-damage etched using NaOH, RCA cleaned, HF dipped and underwent a DI water rinse prior to the PECVD deposition. The same a-Si:H layer was deposited on both sides of a sample using a Roth & Rau AK400 PECVD which is a remote microwave PECVD system. The deposition parameters of the a-Si:H films were the same except for the different deposition temperatures ($T_{depo}$) of 200°C, 250°C, 300°C and 400°C. A silane flow of 30 sccm and an argon flow of 30 sccm were used. The chamber was kept at 0.2 mbar and the times of the depositions ($t_{depo}$) were 65 s.
The final thicknesses of the wafers were around 240 µm and the deposited a-Si:H layers were around 50 nm. Thermal annealing was carried out in a N\textsubscript{2} ambient at temperatures ($T_{\text{ann}}$) of 200°C, 300°C, 330°C, 350°C and 450°C. The samples were then characterised at various annealing times ($t_{\text{ann}}$) using the QSSPC and transient photoconductance lifetime testing techniques as described in Section 2.2.1. The values of $S_{\text{eff}}$ calculated using Equation 1.31 were used to evaluate the thermal stability of the a-Si:H layer surface passivation.

C.2 Results

The extracted $S_{\text{eff}}$ for the as-deposited films are shown in Figure C.16(a). They have an average value of 8.6 cm/s, with one sample having a $S_{\text{eff}}$ as low as 2.4 cm/s. This demonstrates that excellent surface passivation can be achieved on 1 Ω.cm FZ c-Si(n) using a-Si:H films. Previously, very low effective surface recombination velocities of 3 cm/s were obtained on a higher wafer resistivity of 1.6 Ω.cm by Dauwe et al. [201], also using a microwave PECVD reactor.

Despite keeping all deposition parameters constant, the $S_{\text{eff}}$ values measured on the several samples used at each deposition temperature were slightly different. For a particular deposition temperature, the samples were not necessarily all processed together in the chemical steps or in the same PECVD run. Thus, it is likely that such differences in the $S_{\text{eff}}$ are the result of experimental variability.

As shown in Figure C.16(a), there is not a clear dependence of the as-deposited $S_{\text{eff}}$ on the deposition temperature. The optimum temperature appears to be 300°C, but the
spread in the $S_{eff}$ from wafer to wafer is almost as large as the effect of the deposition temperature. Therefore, it is unlikely that the deposition temperature will have a significant effect on the investigation of the thermal stability of the a-Si:H surface passivation.

Figure C.16(b) shows the behaviour of the surface passivation provided by the a-Si:H to the first 30 min of annealing at different temperatures for the samples deposited at 250°C; this behaviour is typical of all the samples used in the experiment irrespective of their deposition temperatures. We observe that the wafers with comparatively worse as-deposited surface passivation initially improve with annealing. As a result, the spread in the $S_{eff}$ found for as-deposited wafers is practically removed after approximately 15 min of annealing. Note however, that no improvement was observed in the samples annealed at 450°C; on the contrary, the surface passivation degraded very rapidly.

In Figure C.17(a), we show the behaviour of the surface passivation provided by the a-Si:H at annealing time of 10 min, which is within the time period of the observed initial improvements in the $S_{eff}$. If we consider the initial improvements, the optimum deposition temperature would be 300°C. However, we will show in the next section that this dependence on the deposition temperature is negligible when longer annealing times are considered.

The initial improvements in the $S_{eff}$ for some of the samples show that annealing does not always result in degradation of the a-Si:H surface passivation. Therefore, limited post-deposition thermal processing for making n-type heterojunction solar cells can be beneficial, provided it is at moderate temperatures for a total time period of less than

**Figure C.17:** The $S_{eff}$ at $\Delta n = 10^{15}$ cm$^{-3}$ deposited at various deposition temperatures and annealed at various temperatures for (a) 10 min and (b) over 180 min. Dashed guiding lines have been added to highlight the trends at the different annealing temperatures.
15 min. Other researchers \cite{208,211} have found that $S_{\text{eff}}$ can improve significantly upon annealing.

Figure C.17(b) shows the change in surface passivation provided by the $a$-Si:H layers over 180 min of annealing. The different symbols represent the different deposition temperatures, while the different colours represent the different annealing temperatures. Coloured dashed lines have been added to guide the eye for the different annealing temperatures.

We observe in Figure C.17(b) that the level of degradation is strongly dependent on the annealing temperature. It is strongest and fastest at the annealing temperature of 450°C, with $S_{\text{eff}}$ degrading to $\sim 700$ cm/s after only 30 min of annealing. At temperatures lower than 350°C, the $a$-Si:H surface passivation degrades initially and then tends to stabilise to a final value. As the temperature is reduced, the degradation is slower and the stable value is lower. At 350°C and 330°C, the $S_{\text{eff}}$ increases to $\sim 200$ cm/s and $\sim 70$ cm/s respectively after 180 min, although full stability is not reached. At 300°C and 200°C, the $a$-Si:H surface passivation stabilises to $\sim 23$ cm/s and $\sim 14$ cm/s respectively after 120–180 min.

Using the mathematical expressions of the guiding lines in Figure C.17(b), it is estimated that the samples annealing at 450°C will reach an $S_{\text{eff}}$ value of $\sim 10^6$ cm/s by $\sim 80$ min, while the samples at 350°C and 330°C will stabilise at $\sim 470$ cm/s and $\sim 300$ cm/s respectively after $\sim 50$ h of annealing. As highlighted by the guiding lines, the main factor that determines the thermal stability of the $a$-Si:H surface passivation is the annealing temperature. At a given temperature, the level of degradation before stabilisation can be limited by restricting the annealing time. In comparison, the dependence on the deposition temperature is very small and can be neglected.

These results are in agreement with the results of Dauwe et al. \cite{201} for $a$-Si:H surface passivation on $p$-type silicon, who found that the $a$-Si:H is thermally stable at 250°C and unstable at 375°C. An increase in the degradation with higher annealing temperatures corresponds well with the observation by Arendse et al. \cite{209} that the structural disorder of the $a$-Si:H increases with annealing. Mitchell et al. \cite{208} observed that the critical limit for the thermal stability of the $a$-Si:H surface passivation to be at $\sim 340$°C. Our results show that the $a$-Si:H surface passivation annealed at 330°C and 350°C tend to become stable over a period of time longer than 3 h. Nevertheless, for maintaining good surface passivation by the $a$-Si:H, the temperature for further processing should preferably be low, less than 300°C.

The lifetime testing technique used gives information on the dependence of $S_{\text{eff}}$ on the
Figure C.18: Examples of the dependence of the \( S_{\text{eff}} \) on the excess carrier density as-deposited and over 180 min of annealing: (a) a sample showing the typical changes in the dependence over time, (b) a sample showing how the dependence does not change over a particular time period after it becomes thermally stable.

excess carrier densities \( \Delta n \). An example of this is shown in Figure C.18(a). The shape of the \( S_{\text{eff}} \) vs. \( \Delta n \) curve changes considerably for the first 120 min of annealing. However, when thermally stability is reached, the values of \( S_{\text{eff}} \) and the dependence of \( S_{\text{eff}} \) on \( \Delta n \) remains practically identical. An example of this is shown in Figure C.18(b), where the values of \( S_{\text{eff}} \) are practically identical between 120 and 180 min of annealing.

The \( S_{\text{eff}} \) at \( \Delta n = 10^{15} \) cm\(^{-3}\) does not show the complete change in the \( a\)-Si:H surface passivation over the annealing time, but nonetheless it is a sufficient indicator of the thermal stability of the \( a\)-Si:H surface passivation. The changing shape of the curves in Figure C.18 indicate a modification of surface defects or the creation of new ones at the interface between the \( c\)-Si wafer and the \( a\)-Si:H.

From the Arrhenius plot of \( S_{\text{eff}} \) as a function of inverse annealing temperature, the activation energy (\( E_A \)) for the thermal degradation can be determined. Arrhenius plots were made for all the annealing times from 0–30 min and Figure C.19 shows the plot for the case of 30 min. For annealing times in excess of 30 min, there was insufficient data for the extraction of \( E_A \). For all the samples, \( S_{\text{eff}} \) remained practically constant (i.e. \( E_A = 0 \)) for a range of temperatures up to \( \sim 313^\circ \text{C} \) and Arrhenius behaviour commenced at higher temperatures. The exponential fits to determine \( E_A \) were, therefore, made for the data excluding that at \( T_{\text{ann}} = 200^\circ \text{C} \).

As can be seen in Figure C.19, the slopes for different deposition temperatures are very similar. The corresponding activation energies are practically the same, as shown
Figure C.19: Arrhenius plot of the $S_{eff}$ in dependence of the inverse of the annealing temperature at the annealing time of 30 min. The top axis shows the corresponding $T_{ann}$ in °C. The dashed lines are linear fits for the data excluding that at $T_{ann} = 200$°C. The region where the $E_A$ changed from zero to the Arrhenius behaviour is labelled the “points of change in $E_A$”.

in Figure C.20(a); that is, $E_A$ is practically independent of the deposition temperature. Nevertheless, when the process is repeated for other time intervals, different values of $E_A$ are found. As shown in Figure C.20(b), the extracted activation energy appears to decrease approximately linearly with the annealing time. The fact that the extracted $E_A$ depends on the annealing time means that care must be taken when comparing different experimental determinations of $E_A$. Considering the typical behaviour during the first 30 min of annealing shown in Figure C.16(b), the most meaningful values of $E_A$ in our case are those corresponding to 20–30 min, that is, an activation energy of the order of -1 eV.

The above observations support the conclusions drawn from Figure C.17(b), that the thermal stability of the $a$-Si:H surface passivation is strongly dependent on the annealing temperature and the annealing time and not the deposition temperature of the $a$-Si:H. Also, the points of change in $E_A$ can be considered an indicator of the critical annealing temperature for the thermal stability of the $a$-Si:H. Below this critical temperature for annealing, the $a$-Si:H surface passivation is generally stable and above it, the $a$-Si:H surface passivation appears unstable and will continue to degrade. The points of change in $E_A$ from the Arrhenius plots has approximately been 313°C, which supports the recommendation of this paper that temperatures should only reach a maximum of 300°C during post-deposition processing.
C.3 Discussion

De Wolf et al. [211] proposed a method by which the abruptness of the a-Si/c-Si interface may be determined by lifetime measurements. Samples with a negative $E_A$—which degrade upon annealing—would have had initial epitaxial growth during the first stages of the a-Si:H deposition; only those with a positive $E_A$—which improve upon annealing—would have abrupt a-Si/c-Si interfaces. Nevertheless, the range of annealing temperatures used in the latter work were 120–260°C, whereas the annealing temperatures used in this work have ranged from 200–450°C. In addition, the work was on $p$-type silicon and used a RF PECVD system, which could have led to different a-Si:H layers to this work. These differences suggest that the method proposed by De Wolf et al. [211] might not be directly applicable to our samples.

Unlike the results of De Wolf et al. [211], who used a constant annealing time of 30 min we observe from Figure C.20(a) that there is little dependence of $E_A$ on the deposition temperature. For the annealing time of 30 min, we obtain activation energies of approximately -1.2 eV for deposition temperatures between 200°C and 300°C. According to the method of De Wolf et al. [211], this negative $E_A$ would indicate that our samples had an initial epitaxial growth, but this is inconsistent with the excellent level of surface passivation shown by our as-deposited a-Si:H layers, comparable to or better than the samples with abrupt interfaces in the experiments of De Wolf et al. [211]. In actual fact our samples show a zero activation energy over the range of annealing temperatures explored by De Wolf et al. [211].

The results of this work and the method proposed by De Wolf et al. [211] are not nec-
C Thermal Stability of $a$-Si:H for Heterojunction Solar Cells

Essarily incompatible despite the many differences in the processing parameters. However, the method by De Wolf et al. [211] needs to be extended to higher deposition and annealing temperatures before it may be applied to this work. The question of whether there had been initial epitaxial growth during the first stages of the $a$-Si:H deposition or possibly epitaxial regrowth from annealing in the $a$-Si:H surface passivation of this work would be best resolved by taking a TEM image (Section 2.3.6) of the $a$-Si:H/$c$-Si interfaces.

C.4 Summary

Hydrogenated amorphous silicon provides excellent surface passivation on n-type silicon and is a crucial part of n-type heterojunction solar cells. However, the thermal stability of the $a$-Si:H places limitations on the temperatures that may be reached for subsequent processing steps in the fabrication of heterojunction solar cells.

In this work, we have shown that the degradation in the surface passivation provided by the $a$-Si:H deposited by microwave PECVD is strongly dependent on the temperature used for further processing, while the deposition temperature of the $a$-Si:H layers themselves makes little difference. The rate of degradation increases as the annealing temperature increases. Initial annealing for time periods less than 15 min causes little degradation and in some cases can improve the $a$-Si:H surface passivation. At annealing temperatures $> 300^\circ C$, the $a$-Si:H surface passivation appears to stabilise after 3 h; at other annealing temperatures, the $a$-Si:H surface passivation is still unstable, but is likely to reach stability after a longer annealing time.

Most importantly, the final stable level of surface passivation varies greatly with annealing temperature. Thus, it is recommended that the times for further processing steps should be short and the temperatures should only reach a maximum value of 300$^\circ$C, with even lower temperatures preferable.
## List of Symbols

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<th>Symbol</th>
<th>Definition</th>
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<td>$\beta = q/kT$</td>
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<td>$\sigma_p$</td>
<td>Capture cross-section of holes</td>
<td>10 $cm^2$</td>
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</table>
σ_p^- Capture cross-section of holes for $D^-$, page 177 \( \text{cm}^2 \)

σ_p^0 Capture cross-section of holes for $D^0$, page 177 \( \text{cm}^2 \)

τ Carrier lifetime, page 6 \( \text{s} \)

τ_{Auger} Auger recombination lifetime, page 7 \( \text{s} \)

τ_{SRH} \text{SRH recombination lifetime, page 7} \( \text{s} \)

τ_b Recombination lifetime of the bulk, page 19 \( \text{s} \)

τ_{eff} Effective lifetime, page 7 \( \text{s} \)

τ_{rad} Radiative recombination lifetime, page 7 \( \text{s} \)

τ_{s,front} Surface recombination lifetime of the front surface, page 18 \( \text{s} \)

τ_{s,rear} Surface recombination lifetime of the rear surface, page 18 \( \text{s} \)

τ_s Surface recombination lifetime, page 18 \( \text{s} \)

v_{th} Thermal velocity, page 10 \( \text{cm/s} \)

ε Dielectric constant, page 68 \( \text{—} \)

ε_0 Permittivity of free space, page 26 \( \text{F/cm} \)

ε_1, ε_2, \ldots Dielectric constants of a stack of dielectric layers, page 47 \( \text{—} \)

ε_Si Dielectric constant of silicon, page 26 \( \text{—} \)

ε_{ox} Dielectric constant of the insulator layer, page 27 \( \text{—} \)

$/W_p$ Dollars per Watt peak, page 1 \( \$/\text{W} \)

$\ddot{A}_{DB}$ Integrand of $\ddot{U}_{DB}$, page 183 \( \text{s}^{-1} \)

$A_{DB}(E)$ Integrand of $U_{DB}$, page 178 \( \text{s}^{-1} \)

A_i Calibration factor for QSSPL measurements, page 41 \( \text{—} \)

AlO_x Aluminium oxide, page 2 \( \text{—} \)

A_{metal} Area of the metal dot for the CV measurement, page 43 \( \text{cm}^2 \)

A_{PAS,0}, A_{PAS,S}, A_{PAS,W} Area parameters for PAS measurements, page 56 \( \text{eV} \)

$a$-Si:H Hydrogenated amorphous silicon, page 32 \( \text{—} \)
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$E_{tp}$ Quasi-Fermi levels for trapped holes for $D^-$, page 178 eV

$E_{tp}^0$ Quasi-Fermi levels for trapped holes for $D^0$, page 178 eV

$E_u$ Correlation energy for recombination, page 175 eV

$E_V$ Energy of the Valence Band, page 11 eV

$\bar{\tilde{f}}^+(E)$ Simplified occupation fraction of $D^+$, page 183 —

$f_+(E)$ Occupation fraction of $D^+$, page 177 —

$\bar{\tilde{f}}^-(E)$ Simplified occupation fraction of $D^-$, page 183 —

$f_-(E)$ Occupation fraction of $D^-$, page 177 —

$\tilde{f}^0(E)$ Simplified occupation fraction of $D^0$, page 183 —

$f_0(E)$ Occupation fraction of $D^0$, page 177 —

$f_A(E)$ Occupation fraction of acceptor defects, page 10 —

$f_D(E)$ Occupation fraction of donor defects, page 10 —

$F_{DD}$ Dimensionless electric field under deep depletion conditions, page 168 —

$F_{Eq}$ Dimensionless electric field under equilibrium conditions, page 168 —

$f_{it,A}(E)$ Occupation fraction of acceptor interface states, page 16 —

$f_{it,D}(E)$ Occupation fraction of donor interface states, page 16 —

$f_p$ Peak frequency from G-V measurements, page 174 Hz

$f_{PAS}(E)$ Doppler-broadening spectra from PAS measurements, page 56 —

$f_{PL}$ Scaling factor for QSSPL measurements, page 41 —

$G$ Generation rate of carriers, page 7 cm$^{-3}$s$^{-1}$

$g_{eeh}$ Coulomb-enhancement factor for $U_{eeh}$, page 8 —

$g_{ehh}$ Coulomb-enhancement factor for $U_{ehh}$, page 8 —

$G_m$ The measured conductance from G-V measurements, page 174 Ω$^{-1}$

$<G_p>/\omega$ Parameter for calculating $D_{it}$ from G-V measurements, page 174 —

$G_{rel}(t)$ Relative generation rate for QSSPL measurements, page 41 cm$^{-3}$s$^{-1}$
List of Symbols

\( I_{PL,rel} \)  Relative photoluminescence intensity, page 41  \( \text{cm}^{-3}\text{s}^{-1} \)

\( iV_{oc} \)  Implied open-circuit voltage, page 39  \( \text{V} \)

\( J_{0E} \)  Emitter saturation current density, page 21  \( \text{fA/cm}^2 \)

\( J_{0,\text{surf}} \)  Saturation current density for an undiffused surface, page 24  \( \text{fA/cm}^2 \)

\( J_{sc} \)  Short-circuit current density, page 159  \( \text{A/cm}^2 \)

\( k \)  Boltzmann constant, page 11  \( \text{J/K} \)

\( \hat{k} \)  Extinction coefficient, page 59  —

\( \Delta n \)  Excess concentration of electrons, page 6  \( \text{cm}^{-3} \)

\( \pi \)  Electron parameter for \[ \text{SRH} \] recombination, page 10  \( \text{s}^{-1} \)

\( n \)  Concentration of electrons, page 6  \( \text{cm}^{-3} \)

\( \pi^+ \)  Electron parameter for \[ \text{DB} \] recombination, page 177  \( \text{s}^{-1} \)

\( \pi^0 \)  Electron parameter for \[ \text{DB} \] recombination, page 177  \( \text{s}^{-1} \)

\( \pi_0 \)  Electron parameter for \[ \text{SRH} \] recombination at equilibrium, page 10  \( \text{s}^{-1} \)

\( n_0 \)  Concentration of electrons at equilibrium, page 6  \( \text{cm}^{-3} \)

\( \pi^+_0 \)  Electron parameter for \[ \text{DB} \] recombination at equilibrium, page 177  \( \text{s}^{-1} \)

\( \pi^0_0 \)  Electron parameter for \[ \text{DB} \] recombination at equilibrium, page 177  \( \text{s}^{-1} \)

\( n_1 \)  Density of thermally emitted electrons, page 191  \( \text{cm}^{-3} \)

\( \hat{n} \)  Refractive index, page 59  —

\( N_A \)  Acceptor concentration, page 19  \( \text{cm}^{-3} \)

\( \Delta n_B \)  Excess concentration of electrons in the bulk, page 25  \( \text{cm}^{-3} \)

\( n_B \)  Concentration of electrons in the bulk, page 13  \( \text{cm}^{-3} \)

\( N_C \)  Effective densities of states at the Conduction Band, page 11  \( \text{cm}^{-3} \)

\( N_D \)  Donor concentration, page 19  \( \text{cm}^{-3} \)

\( N_{DB} \)  Total density of \[ \text{DB} \] defects, page 175  \( \text{cm}^{-3} \)

\( N_{db}(E) \)  Energy-dependent density of dangling bond defects, page 177  \( \text{cm}^{-3} \)
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<td>Net rate of [SRH] recombination involving acceptor defects, page 11 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$U_{\text{Auger}}$</td>
<td>Net rate of Auger recombination, page 8 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$u_{D,1}$-$u_{D,4}$</td>
<td>Carrier flows for donor defects [SRH], page 10 cm$^{-3}$eV$^{-1}$s$^{-1}$</td>
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<tr>
<td>$U_D$</td>
<td>Net rate of [SRH] recombination involving donor defects, page 11 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$\ddot{U}_{DB}$</td>
<td>Simple closed-form solution of $U_{DB}$, page 183 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$\hat{U}_{DB}$</td>
<td>Piecewise solution for $U_{DB}$, page 180 cm$^{-3}$s$^{-1}$</td>
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<td>$u_{DB,1}$-$u_{DB,8}$</td>
<td>Carrier flows for [DB] defects, page 177 cm$^{-3}$eV$^{-1}$s$^{-1}$</td>
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<tr>
<td>$U_{DB}$</td>
<td>Net rate of [DB] recombination, page 178 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$U_{\text{ech}}$</td>
<td>Rate of Auger recombination involving two electrons and a hole, page 8 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$U_{\text{eff}}$</td>
<td>Net effective rate of recombination, page 7 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$U_{\text{ehh}}$</td>
<td>Rate of Auger recombination involving two holes and an electron, page 8 cm$^{-3}$s$^{-1}$</td>
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<tr>
<td>$U_{\text{rad}}$</td>
<td>Net rate of Radiative recombination, page 8 cm$^{-3}$s$^{-1}$</td>
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<td>$\ddot{U}_s$</td>
<td>Net rate of surface recombination using the [DB] model, page 198 cm$^{-2}$s$^{-1}$</td>
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<tr>
<td>$U_s$</td>
<td>Net rate of surface recombination, page 15 cm$^{-2}$s$^{-1}$</td>
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<td></td>
</tr>
</tbody>
</table>
List of Symbols

\(U_{SRH}\)  Net rate of SRH recombination, page 11 \(\text{cm}^{-3}\text{s}^{-1}\)

\(U(x)\)  Net recombination rate at \(x\), page 28 \(\text{cm}^{-3}\text{s}^{-1}\)

\(\Delta V_a\)  Small AC voltage superimposed on \(V_a\), page 44 \(V\)

\(V_a\)  Applied voltage, page 27 \(V\)

\(V_{FB}\)  Flatband voltage, page 45 \(V\)

\(V_{oc}\)  Open-circuit voltage, page 159 \(V\)

\(V_{step}\)  Voltage step for a C-V measurement, page 44 \(V\)

\(W\)  Thickness of the silicon substrate, page 19 \(\text{cm}\)

\(W\)-parameter  Core annihilation parameter in PAS measurements, page 56

\(Z\)-ratio  Correction factor for quartz thickness monitor, page 78
## List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>Al-BSF</td>
<td>Aluminium Back Surface Field</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>ANU</td>
<td>the Australian National University</td>
</tr>
<tr>
<td>APCVD</td>
<td>Atmospheric Pressure Chemical Vapour Deposition</td>
</tr>
<tr>
<td>BJBC</td>
<td>Back-Junction Back-Contact</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
<td>Cz</td>
<td>Czochralski</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance-Voltage</td>
</tr>
<tr>
<td>DB</td>
<td>Dangling Bond</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DESSIS</td>
<td>DEvice Simulation for Smart Integrated Systems</td>
</tr>
<tr>
<td>DI</td>
<td>Deionised</td>
</tr>
<tr>
<td>DRM</td>
<td>Depletion-Region Modulation</td>
</tr>
<tr>
<td>ECN</td>
<td>Energy Research Centre of the Netherlands</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy-Loss Spectroscopy</td>
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<tr>
<td>ENEA</td>
<td>Italian national agency for new technologies, energy and sustainable economic development</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------------------------------------------------</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-Red spectroscopy</td>
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<tr>
<td>FZ</td>
<td>Float-Zoned</td>
</tr>
<tr>
<td>G-V</td>
<td>Conductance-Voltage</td>
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<tr>
<td>HIT</td>
<td>Heterojunction with Intrinsic Thin layer</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
</tr>
<tr>
<td>ISE</td>
<td>Instituts für Solare Energiesysteme</td>
</tr>
<tr>
<td>ISFH</td>
<td>Institute for Solar Energy Research HameIn/Emmerthal</td>
</tr>
<tr>
<td>IV</td>
<td>Current-Voltage</td>
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<tr>
<td>KP</td>
<td>Kelvin Probe</td>
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<tr>
<td>LED</td>
<td>Light-Emitting Diode</td>
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<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
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<tr>
<td>MOCVD</td>
<td>Metal-Organic Chemical Vapour Deposition</td>
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<tr>
<td>MOS</td>
<td>Metal-Oxide-Semiconductor</td>
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<tr>
<td>MWPCD</td>
<td>Microwave-detected Photoconductance Decay</td>
</tr>
<tr>
<td>NAOS</td>
<td>Nitric Acid Oxidation of Silicon</td>
</tr>
<tr>
<td>N/A</td>
<td>Not Available</td>
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<tr>
<td>PAS</td>
<td>Positron Annihilation Spectroscopy</td>
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<td>PA-ALD</td>
<td>Plasma-Assisted Atomic Layer Deposition</td>
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<tr>
<td>PC1D</td>
<td>Name of a one-dimensional numerical semiconductor simulation program</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma-Enhanced Chemical Vapour Deposition</td>
</tr>
<tr>
<td>PERL</td>
<td>Passivated Emitter, Rear Locally diffused</td>
</tr>
<tr>
<td>PERC</td>
<td>Passivated Emitter and Rear Cell</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>PV</td>
<td>Photovoltaic</td>
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<td>Acronym</td>
<td>Description</td>
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<tr>
<td>PVD</td>
<td>Physical Vapour Deposition</td>
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<td>QSSPC</td>
<td>Quasi-Steady-State Photoconductance</td>
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<tr>
<td>QSSPL</td>
<td>Quasi-Steady-State Photoluminescence</td>
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<td>QSS Model</td>
<td>Spreadsheet for simulating QSSPC lifetime measurements</td>
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<td>QUARK</td>
<td>QUantative Analysis of Rutherford Kinematics</td>
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<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry</td>
</tr>
<tr>
<td>RCA</td>
<td>Radio Corporation of America</td>
</tr>
<tr>
<td>RF</td>
<td>Radio-Frequency</td>
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<tr>
<td>RTP</td>
<td>Rapid Thermal Processing</td>
</tr>
<tr>
<td>RUMP</td>
<td>RUtherford backscattering data Manipulation Program</td>
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<tr>
<td>SHG</td>
<td>Second-Harmonic Generation</td>
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<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
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<tr>
<td>SRH</td>
<td>Shockley-Read-Hall</td>
</tr>
<tr>
<td>TCA</td>
<td>Trichloroethane</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent Conductive Oxide</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>TMA</td>
<td>Trimethylaluminium</td>
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<tr>
<td>TMAH</td>
<td>Tetramethylammonium Hydroxide</td>
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<tr>
<td>UNSW</td>
<td>University of New South Wales</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>VB</td>
<td>Valence Band</td>
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<td>Vis</td>
<td>Visible</td>
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<tr>
<td>VEPFIT</td>
<td>Variable Energy Positron FIT</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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List of Publications

Publications arising from the work in this thesis

Refereed journal papers


Papers presented at international conferences


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