Impact of dopant compensation on the electrical properties of silicon for solar cell applications

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Declaration

I certify that this thesis does not incorporate, without acknowledgement, any material previously submitted for a degree or a 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.

Fiacre Emile Rougieux
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To my grandparents Frances and Martin, Paule and Victor
and to mam, dad, Paul, Maura and Celeste.
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Abstract

This thesis aims at understanding the mechanisms limiting the efficiency of compensated silicon solar cells (containing boron and phosphorus in the bulk). Such dopant compensation is common in solar grade materials, especially in silicon from the metallurgical route, and can potentially lead to a degradation of the materials electronic properties.

We experimentally show that a thermal oxidation can create an n-type layer at the surface of compensated p-type silicon. This n-type layer is further shown to interfere with device performance and material characterization.

We investigate the impact of compensation on the minority carrier lifetime, in particular for recombination through defects. Metastable defects such as chromium-boron pairs and the boron-oxygen defect are shown to degrade the lifetime of compensated n-type silicon. The boron-oxygen defect in compensated n-type silicon is then experimentally investigated. It is shown that if not mitigated, the boron-oxygen defect leads to a strong reduction in implied $V_{OC}$. The defect is also shown to be fundamentally different in compensated n-type silicon compared to p-type silicon. Its concentration does not depend on the net doping and its recombination activity is dominated by a shallow defect rather than a deep defect.

Through a theoretical investigation, we show that the carrier mobility is also affected by compensation. Both theory and experiments confirm that the mobility is reduced by the combined presence of acceptors and donors. Compensation not only increases the amount of ionized impurities and decreases the amount of free carriers, it also affects the scattering cross section of ionized impurities and free carriers. Theoretical calculations show a relatively weak influence of the compensating impurities on the mobility. However experimental results suggest a stronger influence of compensating impurities. This results in mobilities slightly lower than predicted by advanced model such as Klaassen’s model.
A new method to measure the sum of the majority and minority carrier mobility in silicon is introduced. Measurement of the influence of dopant density, injected carriers and temperature on the mobility sum are made and compared to data available in the literature.
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Introduction

Thesis Motivation

The photovoltaic industry has enjoyed exponential growth in the past decade. Government subsidies have been a key to such a fast growth and have therefore driven the large manufacturing investments of solar cell manufacturers. However, recent changes in government policies have led to a reduction in subsidies, partly motivated by economic reasons. Additionally the fast scaling up of solar cell manufacturing companies has created an oversupply of modules. In order to remain competitive, most module manufacturers have now reduced their profit margin, with some operating at a loss. This has already caused some industry players to close, including some leading manufacturers. The photovoltaic industry is therefore looking more than ever at new ways to reduce costs and survive this temporary volatility in the market.

![Figure 1: Cost breakdown of solar module with solar-grade crystalline silicon](image)

Figure 1 shows that module assembly and cell processing contribute to approximately 40% and 27% of the solar module cost respectively [1]. Therefore the prime
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An approach to decrease production costs is to increase efficiencies at the cell and module level. Indeed, an increase in efficiency has an indirect net benefit on the production cost. New technologies, such as selective emitter (ion implantation, laser doping, ink-jet doping, chemical etching), localized back surface field (laser fired or ablated contacts and the above) and back contact cells (interdigitated back contact, emitter and metal wrap through) are now not only increasing efficiencies but also reducing the materials and processing costs.

The second approach to obtain lower production costs is to decrease manufacturing costs. This approach has been successfully conducted in recent years through massive scaling up of the industry. Figure 1 also shows that feedstock contributes to approximately 14% of the total solar panel cost [1]. Therefore, manufacturing costs can also be reduced through the use of cheaper and less energy intensive feedstocks. Indeed, currently, the most widely used process to produce silicon for electronic and solar applications is the Siemens process which is both energy intensive and requires heavy initial investments.

This process operates in two steps. First trichlorosilane $HSiCl_3$ is prepared by hydrochlorination of metallurgical grade silicon [2]. The volatile trichlorosilane is then mixed with hydrogen in a deposition reactor to produce highly pure polysilicon. The total reaction is [2]:

$$Si(s) + 3HCl \rightarrow HSiCl_3 + H_2$$  \hspace{1cm} (1)

$$HSiCl_3 + H_2 (high\ purity) \rightarrow Si(s) + 3HCl$$  \hspace{1cm} (2)

In order to avoid the high thermal budget and expensive infrastructures of the Siemens process, several alternatives processes have recently been developed. These processes are all performed in the solid or liquid phase, contrary to the Siemens process which is performed in the gas phase.

One of the most basic ways to purify metallurgical grade silicon is through directional solidification. Indeed, during directional solidification, most impurities tend to segregate in the liquid phase. Directional solidification therefore allows one to concentrate impurities in the last fraction solidified. Removing this last fraction leads
to a reduction of the impurity content in the remaining silicon. Table 1 shows the

<table>
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<th>Dopants</th>
<th>$k_0$</th>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$8 \times 10^{-6}$</td>
<td>B</td>
<td>0.8</td>
</tr>
<tr>
<td>Al</td>
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<td>P</td>
<td>0.35</td>
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<td>$1 \times 10^{-5}$</td>
<td>Sb</td>
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<tr>
<td>Co</td>
<td>$8 \times 10^{-6}$</td>
<td></td>
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</tr>
</tbody>
</table>

Table 1: Equilibrium segregation coefficients $k_0$ of common metals and dopants in silicon [4; 5].

segregation coefficient of common metals and dopants in silicon [4; 5]. From table 1, it is clear that metallic impurities have a segregation coefficient small compared to unity. Therefore metallic impurities are easily removed during directional solidification. However, boron and phosphorus have relatively high segregation coefficients and are therefore not easily removed using directional solidification. Note that, by contrast, the use of the gas phase in the Siemens process is effective at removing all impurities, including these dopants. There exist however alternative ways of removing boron and phosphorus from silicon.

Boron removal can be performed by slag treatment or by volatilization of Boron compounds [6; 7]. When adding calcium to the silicon melt, one separates the impurities from the melt. By removing the slag phase one obtains low levels of boron in the silicon. Boron removal can also be performed using volatilization of Boron compounds [7]. A plasma torch composed of a mixture of argon and water oxidizes the boron in the silicon melt. The boron oxides are volatile and easily extracted [7].

Phosphorus removal can be performed by volatilization under vacuum or by slagging [6; 7]. Volatilization can be performed in a vacuum furnace with electron beam heating. Phosphorus having a high vapor pressure easily evaporates in the furnace under vacuum [7]. One can combine the advantages of impurity volatilisation with those of directional solidification by melting a small zone of the material and moving it along the material [8].
Introduction

Figure 2: Process used by some current UMG producers and their corresponding projected costs and energy budget [6; 9; 10; 11; 12; 13; 14].

Figure 2 shows the processes used by some current Upgraded Metallurgical Grade silicon (UMG) producers in order to purify silicon [6; 9; 10; 11; 12; 13; 14]. The corresponding projected cost and energy budget is also shown. While the Siemens process has a very high thermal budget of 200kWh/kg, metallurgical processes have thermal budgets 10 times smaller.

As seen in figure 1 the feedstock contributes to approximately 14% of the total solar module cost [1]. Assuming a 30% cost advantage of UMG silicon over standard silicon, leads to a 4.2% reduction of the total module production costs. This cost advantage may seem an ambitious target when the spot price of Siemens silicon has fallen to an average US$24 per kg in 2012 [20]. However, as seen above, some UMG silicon producers aims at selling silicon for US$ 15 per kg [12; 21]. This price represents more than a 30% cost advantage when compared to standard silicon. In addition, it is quite likely that the spot price of silicon feedstock will increase in the coming years as the photovoltaic market recovers which would increase the attractiveness of UMG silicon.

Note, however, that a 30% reduction in silicon price does not necessarily trans-
Figure 3: (a) Possible influence of using UMG feedstock on the cost breakdown of a solar module in analogy to figure 1(b) Best cell efficiencies using 100% UMG silicon.

late into a 30% lower ingot price. While the feedstock cost is reduced, the ingot cost may be increased as illustrated in figure 3(a) in analogy to figure 1. Indeed UMG silicon contains much more boron and phosphorus, and therefore the doping profile increases more rapidly than in non-compensated silicon. This in turns reduces the amount of usable silicon to make wafers and therefore reduces the ingot yield. However, recent advances in compensation engineering allow one to obtain ingot yield similar to standard silicon [22].

The cost advantage of UMG silicon is clear, but is UMG silicon a wise choice in order to decrease the $/Wp? Indeed typical boron and phosphorus concentrations in UMG silicon are on the order of $\approx 1 \times 10^{16} cm^{-3}$ to $2 \times 10^{17} cm^{-3}$ and therefore much higher than in silicon from the Siemens process. This higher content of dopants of both polarities (compensation) in UMG silicon can lead to a degradation of the electronic properties of the wafer and a potential reduction in the final cell efficiency. Early use of UMG silicon in solar cells processes proved to be unsuccessful, with low cell efficiencies. However, recently, UMG silicon quality was improved significantly.

In recent years, UMG silicon has raised interests again with several laboratories and companies producing record efficiencies as shown in figure 3(b) [14; 23; 24; 25; 26;
In 2011, Q-Cells achieved comparable cell efficiencies using UMG silicon 18.35% (prior to light induced degradation, LID) and standard polysilicon 18.45% (prior to LID) [26]. In 2012, Apollon Solar and Roth and Rau achieved 19% (prior to LID) on monocrystalline n-type silicon which is the current record [27] for cells made with 100% UMG silicon.

Can we break the 20% efficiency (stabilised, after LID) barrier using UMG silicon? What are the specific mechanisms that could lead to lower efficiencies of UMG silicon over Siemens silicon? Is there any way to mitigate those mechanisms?

Compensation plays a key role in many recombination and resistive loss mechanisms. It is the purpose of this thesis to clarify and better understand the relationship between compensation and the electronic properties of the material in order contribute to the advent of high efficiency solar cells using UMG silicon.

As shown in this thesis, the presence of additional dopants could potentially influence the result of processing steps such as oxidation. It could also have a negative influence on the carrier mobility. Finally compensation could also lead to an increased concentration of the lifetime-degrading boron-oxygen defect in compensated silicon.

Additionally the presence of additional metallic impurities in the silicon can lead to a reduction in the carrier lifetime and thus the cell efficiency. This challenge can be tackled through the introduction of an additional gettering step which effectively removes metallic impurities from the material. However, the additional processing step can in turn increase the cell processing cost as shown in figure 3(a).

**Thesis Outline**

Chapter 1 reports on the formation of a lightly-doped p-n junction at the surface of compensated p-type silicon wafers, caused by dopant segregation during thermal oxidation. Experimental evidence and characterization of the junction is obtained by secondary ion mass spectrometry and hot probe measurements. For the first time the impact of the unexpected junction on the characterization of metal-oxide-semiconductor structures with capacitance-voltage measurements is measured and explained via simulation.
Chapter 2 summarises the different scattering and recombination mechanisms affected by compensation in silicon. Metastable defects such as chromium-boron pair and the boron-oxygen defect are shown to alter the carrier lifetime especially in compensated n-type silicon. The increased concentration of ionized impurities in compensated silicon is also shown to lead to a reduction of the carrier mobility. Compensation is also shown to increase the scattering cross section and therefore further reduce the mobility. The impact of dopant compensation on the majority, minority and sum of the majority and minority carrier mobility is then modelled.

In chapter 3, different lifetime and mobility measurement techniques are introduced. We present a new method to determine the simultaneous injection and temperature dependence of the sum of the majority and minority carrier mobilities in silicon wafers. The technique is based on combining transient and quasi-steady-state photoconductance measurements. It does not require a full device structure or contacting, but only adequate surface passivation. The mobility dependence on both carrier injection level and temperature, as measured on several test samples, is discussed and compared to well-known mobility models. The potential of this method to measure the impact of dopant concentration, compensation ratio, injection level and temperature on the mobility is demonstrated.

In Chapter 4, the influence of compensation on the carrier lifetime and mobility is determined experimentally. The conductivity mobility for majority carrier holes in compensated p-type silicon is determined by combined measurement of the resistivity and the net doping, the latter via electrochemical capacitance-voltage measurements. The minority electron mobility was also measured with a technique based on measurements of surface-limited effective carrier lifetimes. While both minority and majority carrier mobilities are found to be significantly reduced by compensation, the impact is greater on the minority electron mobility. The Hall factor, which relates the Hall mobility to the conductivity mobility, has also been determined using the Hall method combined with the capacitance-voltage measurements. Our results indicate a similar Hall factor in both compensated and non-compensated samples.

In Chapter 5 fundamental aspects of the boron-oxygen defect formation and recombination activity are presented. We then present experimental data regarding the
concentration of the boron-oxygen complex in compensated n-type silicon when subjected to illumination. We find that the defect density is independent of the net dopant concentration and is strongly dependent on the minority carrier concentration during illumination. We show that annealing at temperatures in the range 500°C - 700°C permanently reduces the defect density, possibly via a decrease in the oxygen dimer concentration. We also present experimental data regarding the recombination activity and concentration of the boron-oxygen complex in compensated n-type silicon. Our results suggest the dominant defect level in our doping range to be a shallow level \( E_C - E_T = 0.15 \text{ eV} \). Due to the strong lifetime reduction observed we suggest that this material might not be suited to make high efficiency n-type solar cells, unless practical strategies for reducing the defect concentration can be developed.
Chapter 1

Oxidation-induced inversion layer in compensated p-type crystalline silicon

1.1 Introduction

The properties of compensated silicon wafers, and their behaviour during device fabrication, are of considerable interest. An important characterisation tool is the measurement of the capacitance-voltage (C-V) characteristics of metal insulator semiconductor (MIS) structures constructed on the silicon. This allows important properties of the insulator semiconductor interface to be derived, for example the density of interface states and the fixed charge in the film. However, when attempting to apply C-V methods to characterize thermally grown SiO$_2$ on compensated Si, an unexpected problem arises.

In this chapter we demonstrate that thermal oxidation of compensated p-type silicon wafers can lead to the creation of an unwanted n-type layer at the surfaces, caused by dopant segregation during the oxide growth. We also show how this parasitic n-layer can interfere with device performance and material characterization such as capacitance-voltage measurements and electrochemical capacitance-voltage measurements.
1.2 Formation mechanism

Dopant redistribution during oxide growth is affected by several mechanisms: diffusion in Si, diffusion in SiO$_2$, and segregation at the Si/SiO$_2$ interface. The equilibrium segregation coefficient $m$ is expressed as the ratio of the concentration of impurity in the silicon over the concentration of impurity in the oxide at equilibrium, $m = C_{\text{silicon}}/C_{\text{oxide}}$. The equilibrium segregation coefficient of boron at the Si/SiO$_2$ interface is approximately $m_{\text{boron}} = 0.3$, meaning that the oxide accepts boron [28]. On the other hand the segregation coefficient of phosphorus at the Si/SiO$_2$ interface is approximately $m_{\text{phosphorus}} = 10$, meaning that the oxide rejects phosphorus [28].

As a result of their different segregation properties, boron tends to become depleted from the silicon during oxide growth, while phosphorus tends to pile up just below the surface. In non-compensated p-type material this effect leads to a depletion of boron in the Si near the interface. But in compensated p-type material, it also leads to an accumulation of phosphorous. After sufficient time the effect may be so great that the dominant species near the interface is no longer boron, but phosphorus. The semiconductor has thus changed from p to n-type near the interface. It should be noted that this inversion of conductivity type can only occur in p-type compensated silicon. In n-type compensated silicon the depletion of boron and accumulation of phosphorus will only increase the concentration of n-type dopants. Phosphorous, antimony or arsenic doped samples will act in a similar way as their segregation coefficients are very similar [28].

1.3 Doping profile

1.3.1 Experimental method

The samples used in this study were cleaved sections of 155 × 155 mm pseudo-square, p-type, <100>-oriented Czochralski-grown silicon wafers. There were wafers from two control ingots (non-compensated), which were boron-doped and had resistivities of $1.20 \pm 0.08 \Omega \cdot cm$ and $0.40 \pm 0.08 \Omega \cdot cm$, and also two compensated ingots, doped with both boron and phosphorus, with resistivities of $1.6 \pm 0.1 \Omega \cdot cm$ and
More details of these samples are provided in chapter 4. After surface etching and cleaning, samples for Secondary Ion Mass Spectrometry (SIMS) measurements were thermally oxidized at 1100°C for 1 hour in steam (wet oxidation). A simulation of the oxidation and dopant re-distribution processes during this thermal step was then made using the 2D process simulator silvaco-ATHENA [29; 30].

### 1.3.2 SIMS profile

![Figure 1.1: Measured (SIMS) and simulated dopant profiles after a 1 hour 1100°C wet oxidation in a strongly compensated p-type sample \((N_A = 3.25 \times 10^{16} cm^{-3}, N_D = 2.75 \times 10^{16} cm^{-3})\).](image)

To experimentally demonstrate the formation of the junction, a SIMS dopant profile was performed. Figure 1.1 presents the SIMS profile within the first 1.7\(\mu\)m of both boron and phosphorus in the strongly compensated (1.6\(\Omega\).cm) sample after a 1 hour wet oxidation at 1100°C. This sample was expected to have dopant concentrations of around \(N_A = 4 \times 10^{16} cm^{-3}\) and \(N_D = 3 \times 10^{16} cm^{-3}\), based on previous studies [31]. The secondary ion intensity dropped after 0.4\(\mu\)m showing that the oxidation grew a 0.4\(\mu\)m thick oxide. The figure shows that this oxide caused a large change in dopant concentration near the interface. Deep in the material the doping density is constant with \(N_A > N_D\), making it p-type. Closer to the Si/SiO\(_2\) interface the concentration...
of boron decreases while the concentration of phosphorus increases. At (0.8\(\mu m\) from the interface, the semiconductor becomes perfectly compensated \(N_A = N_D\), and then switches to n-type \(N_D > N_A\). In this sample an n-layer of approximately 0.7\(\mu m\) depth and with a peak net doping density of \(2 \times 10^{16} cm^{-3}\) has formed after oxidation.

### 1.3.3 Simulated profile

To further study the formation of the junction, a numerical simulation of the process was made using the 2D process simulator silvaco-ATHENA [30]. Figure 1.1 plots the results from a 1 hour 1100\(^\circ\)C wet oxidation in a strongly compensated p-type sample with an acceptor concentration of \(N_A = 3.25 \times 10^{16} cm^{-3}\) and a donor concentration of \(N_D = 2.75 \times 10^{16} cm^{-3}\). These dopant concentrations were chosen based on the SIMS measurements deep in the wafer, and vary only slightly from those reported previously for similar wafers \((N_A = 4 \times 10^{16} cm^{-3}, N_D = 3 \times 10^{16} cm^{-3})\) [31]. The simulated dopant distributions in the silicon and the junction depth after oxidation are in good agreement with the SIMS data. Simulation shows that several parameters can be adjusted to reduce the junction depth and doping density, such as reducing the oxidation temperature and time, and using dry oxidation. At a constant net doping density \((N_A - N_D)\), simulations indicate that as \(N_A\) and \(N_D\) increase, the junction becomes deeper and more heavily doped.

### 1.4 Influence on material characterization

The electrochemical capacitance-voltage (ECV) and capacitance-voltage (CV) technique are commonly used to measure net doping concentrations. Hence our interest in using them for compensated silicon. This section demonstrates the impact of the oxidation-induced inversion layer on those two techniques.

#### 1.4.1 Experimental method

The impact of the unwanted junction on electrochemical capacitance-voltage measurements was measured after etching the oxide using a CPV21 ECV profiler with InGa paste for the back ohmic contact. The area of the ECV crater was measured
1.4 Influence on material characterization

externally by a pin profiler (Dektak). This allowed for the correction of the calculated dopant density as explained by Bock et al [32]. The impact of the unwanted junction on Capacitance-Voltage (CV) measurements was demonstrated by high frequency (1MHz) CV measurements on Metal Oxide Semiconductor structures (MOS) with a mercury probe (775µm diameter Hg dots). Four control and four compensated samples were fabricated. These wafers had been first submitted to a wet oxidation at 1050°C for 15 min, 30 min, 1 hour and 2 hours. The potential within the device was simulated using silvaco-ATLAS [29].

1.4.2 Electrochemical Capacitance-Voltage measurements

1.4.2.1 Schottky barrier depletion capacitance

The ECV technique measures the doping density profile using the capacitance-voltage characteristics of a Schotky contact at a constant DC bias. The Schottky contact is achieved with an electrolyte and the profiling is accomplished by electrolytically etching the semiconductor. When a negative voltage is applied on the p-type silicon, the energy band diagram shifts downward and increases the barrier height for holes. The depletion region therefore increases. The width of the depletion region \( x_p \) is [33]:

\[
x_p = \sqrt{\frac{2\epsilon_S}{qP_0} (V_{bi} - V_A)}
\]  

(1.1)

with \( \epsilon_S \) the silicon dielectric constant, \( V_{bi} \) the built-in voltage and \( V_A \) the applied voltage. The depletion region created is like the insulator of a parallel plate capacitor, with the metal and the semiconductor bulk being the electrode.

\[
C(depl) = \frac{\epsilon_S A}{x_p}
\]  

(1.2)

From equation 1.1 the depletion capacitance can be written as:

\[
C = \frac{A}{\sqrt{\frac{2(V_{bi}-V_A)}{qP_0\epsilon_S}}}
\]  

(1.3)
This can be inverted to give [33]:

\[
\frac{1}{C^2} = \frac{2(V_{bi} - V_A)}{q\rho_0\epsilon_S A^2} \quad (1.4)
\]

Therefore the carrier concentration at a distance \( x_p \) from the surface is inversely proportional to the slope of \( 1/C^2 \):

\[
p_0 = \frac{-2}{q\epsilon_S A^2 \frac{d(1/C^2)}{dV}} \quad (1.5)
\]

By measuring the CV characteristics and etching the silicon the dopant profile is thus obtained.

1.4.2.2 Doping profile

ECV measurements were taken on two non-compensated samples and two compensated samples.

![Doping profile graph](image)

Figure 1.2: Measured (ECV) and simulated dopant profiles after a 1 hour 1100°C wet oxidation in two non-compensated p-type sample (a) \( N_A = 2.4 \times 10^{16} cm^{-3} \) (b) \( N_A = 8.5 \times 10^{15} cm^{-3} \).

Figure 1.2 shows the measured and the simulated doping profile after a 1 hour
oxidation step in non-compensated p-type silicon. Near the Si/SiO$_2$ interface the B concentration reduces as expected. Because the doping is quite low, the depletion width $x_p$ is quite large (eq 1.1). For a doping of $N_A = 2.4 \times 10^{16} cm^{-3}$ the zero bias depletion width is nearly 0.2 $\mu$m, therefore the first 0.2 $\mu$m of material cannot be probed (figure 1.2(a)). Similarly with lower doping $N_A = 8.5 \times 10^{15} cm^{-3}$ the first 0.4 $\mu$m of silicon cannot be probed (figure 1.2(b)).

The simulation is performed with the same parameters as in the previous section and the results are in relatively good agreement. This gives some confidence in the simulation results.

Figure 1.3: Measured (ECV) and simulated dopant profiles after a 1 hour 1100$^\circ$C wet oxidation in a (a) weakly compensated p-type sample ($N_A = 8.15 \times 10^{16} cm^{-3}, N_D = 3.10 \times 10^{16} cm^{-3}$) (b) strongly compensated p-type sample ($N_A = 3.25 \times 10^{16} cm^{-3}, N_D = 2.75 \times 10^{16} cm^{-3}$).

Figure 1.3 shows the net doping in two compensated p-type silicon sample of different compensation ratio. In the weakly compensated sample, the measurement follows the simulation (note that incomplete ionization is taken into account in the determination of the net doping). The sample is p-type (empty symbols) with no inversion detected but the decrease of the net doping is noticeably sharper than the non-compensated samples in figure 1.2. However in the strongly compensated san-
ple the measurement indicates that both the n-layer and the samples are n-type (full symbols). The ECV technique is commonly used to profile pn junctions thus it should theoretically be able to measure this low doped pn junction.

Figure 1.4: Measured IV curve in sample with and without the oxidation-induced inversion layer.

To ensure that the dopant density measured is accurate one must ensure that the Schottky contact is ideal and non-leaky. Figure 1.4 shows the IV curve for a sample with and without the n-layer. For the sample where a n-layer was present the leakage current is one order of magnitude stronger. This could in turn mask the capacitive current and explains the erroneous net doping displayed in figure 1.3(b).

1.4.3 Capacitance-Voltage measurements

1.4.3.1 Metal-oxide-semiconductor depletion capacitance

Similarly to the ECV technique the CV technique allows for the determination of the doping density of a substrate. In p-type silicon, when a negative voltage is applied on the gate, the energy band diagram shifts upward. Electrons are repelled from the surface and holes accumulate at the surface. Hence there is no depletion region and
the only capacitance is due to the oxide $C_0$.

$$C(\text{acc}) = C_0 = \frac{\epsilon_{\text{ox}}A}{x_0} \quad (1.6)$$

with $\epsilon_{\text{ox}}$ the SiO$_2$ dielectric constant, $A$ the gate area and $x_0$ the oxide thickness. When a positive voltage is applied on the gate, the energy band diagram shifts downward. Holes are repelled from the surface, the surface becomes depleted of holes. As the voltage increases the depletion width increases. The width of the depletion region is [34]:

$$W = \frac{\epsilon_S}{\epsilon_{\text{ox}} x_0} \sqrt{1 + \frac{V_A}{V_\delta} - 1} \quad (1.7)$$

with $\epsilon_S$ the silicon dielectric constant and:

$$V_\delta = \frac{q}{2} \frac{\epsilon_S x_0^2}{\epsilon_{\text{ox}}} p_0 \quad (1.8)$$

The oxide $C_0$ and the depletion region $C_\delta$ are like two parallel plate capacitors in series. The depletion capacitance is thus.

$$C(\text{depl}) = \frac{C_0 C_\delta}{C_0 + C_\delta} = \frac{C_0}{1 + \frac{\epsilon_{\text{ox}} W}{\epsilon_S x_0}} \quad (1.9)$$

The capacitance can be expressed as [34]:

$$C = \frac{C_0}{\sqrt{1 + \frac{V_\delta}{V_\delta}}} \quad (1.10)$$

Using eq 3.21 and 3.20 one can obtain the doping density of the samples.

### 1.4.3.2 Capacitance-Voltage measurements

High Frequency (1MHz) Capacitance-Voltage (CV) measurements were conducted on Metal Oxide Semiconductor structures (MOS) fabricated on four control and four compensated samples.

Table 1.1 shows that the accumulation capacitances $C_{\text{acc}}$ are similar in the compensated and control wafers, indicating that the oxide thicknesses were similar for
Table 1.1: Measured accumulation capacitance $C_{acc}$ (pF) and corresponding oxide thickness $x_0$ ($\mu m$) for different oxidation times

<table>
<thead>
<tr>
<th>Oxidation time</th>
<th>Control $C_{acc}$</th>
<th>Control $x_0$</th>
<th>Compensated $C_{acc}$</th>
<th>Compensated $x_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>85</td>
<td>0.24</td>
<td>86</td>
<td>0.24</td>
</tr>
<tr>
<td>30 min</td>
<td>58</td>
<td>0.36</td>
<td>59</td>
<td>0.35</td>
</tr>
<tr>
<td>1 hr</td>
<td>40</td>
<td>0.52</td>
<td>40</td>
<td>0.52</td>
</tr>
<tr>
<td>2 hrs</td>
<td>28</td>
<td>0.74</td>
<td>28</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 1.1: Measured accumulation capacitance $C_{acc}$ (pF) and corresponding oxide thickness $x_0$ ($\mu m$) for different oxidation times each oxidation time. The oxide thickness $x_0$ was calculated using the capacitance in accumulation (eq: 1.6).

Figure 1.5: Measured normalized high frequency capacitance voltage curves on Metal Oxide Semiconductor devices after different oxidation times (15 min, 30 min, 1 hour, 2 hours), (a) CV curves for a 1.2 $\Omega.cm$ non-compensated bulk ($N_A = 1.7 \times 10^{16} cm^{-3}$), (b) CV curves for a 1.6 $\Omega.cm$ compensated bulk ($N_A = 4 \times 10^{16} cm^{-3}, N_D = 3 \times 10^{16} cm^{-3}$). The circled number correspond to the voltages of the different features of the CV curve. Those number will be referred to further in the text in order to explain the shape of the CV curve.

Figure 1.5 plots the measured CV curves, showing qualitatively different curves for (a) the control and (b) the compensated samples. In contrast to the control samples, the CV curves of the compensated samples have a distinct minimum and are
increasingly shifted to more negative voltages. Such minima have been found to occur when the entire surface of the semiconductor was inverted either by charge in the oxide near the p-type silicon [35], or by an implanted layer under the oxide [36]. Since these minima do not occur in our control samples, any charge in the oxide is negligible in terms of inducing an inversion layer below the surface, and so should not affect the compensated samples either.

1.4.3.3 Capacitance-Voltage measurements simulation

Sigmond et al. have examined the case of a p-type implanted layer between an n-type bulk and an oxide [36]. In their study a model with an oxide capacitance in series with one surface and one junction depletion capacitance was used. In our case the situation is similar. To analyse precisely the junction coupled with the MOS, the dopant profiles obtained using the process simulator silvaco-ATHENA were entered into the semiconductor characterization simulator silvaco-ATLAS [30; 29].

Figure 1.6: Simulated charge density in the device for different applied gate voltage, the oxide \(d_{ox}\), the surface depletion \(W_S\) and junction depletion \(W_J\) regions lead to the oxide capacitance \(C_{ox}\), surface capacitance \(C_S\) and the junction capacitance \(C_J\) represented at the top, the different gate voltage (1-6) represent the different sections of the CV curve numbered in Figure 1.5.
Oxidation-induced inversion layer in compensated p-type crystalline silicon

Figure 1.7: (a) Simulated charge density profile in the p-side of the junction showing the increase of the junction depletion width $W_{S+J}$ with increasing gate voltage. (b) Simulated charge density profile in the n-side of the junction near the silicon/oxide interface showing the decrease of the surface depletion width $W_S$ with increasing gate voltage.

In the simulation, a voltage ramp was then applied to the gate (-15V to 5V) at high frequency (1MHz). The simulated curves are less stretched-out than the experimental ones. This is due to the simplification in the modelling with zero density of interface states and means that experimental and simulated gate voltages differ. For simplification purposes the values of experimental voltages corresponding to the accumulation minimum and inversion are used in the explanation of the simulation. The simulation allowed for the extraction of the potential, electric field and charge density in the device for different gate voltage (Figure 1.6,1.7).

Due to the presence of the n-layer in compensated samples, inversion for a control p-type sample becomes accumulation for a compensated p-type sample. For the following analysis the terms inversion, depletion and accumulation will refer to the voltage induced charged density in the n-layer not the p-type bulk. This means that positive gate voltage induces accumulation (of electrons) and negative voltage induces inversion (appearance of holes at the surface). Large negative gate voltage not only attracts holes to the surface but also repels electrons on the p-side of the junction (Fig-
1.4 Influence on material characterization

Figure 1.6, 1.7a, \( V_G = -14 \text{V} \). Variations in the gate voltage exclusively induce changes in the charge density of the inversion layer. Hence the surface-junction depletion region \((W_S + J)\) neither expands nor shrinks. The total capacitance is therefore constant (Figure 1.7b, \( V_G = -14 \text{V} \)).

As the gate voltage increases, the inversion layer disappears and electrons start to flow back to the p-side of the p-n junction (Figure 1.6, \( V_G = -14 \text{V} \) to \( -8 \text{V} \)). This results in an increase of the surface-junction depletion region (Figure 1.7a, \( V_G = -14 \text{V} \) to \( -8 \text{V} \)). Consequently the total capacitance decreases as seen in Figure 1.5. \( V_G = -14 \text{V} \) to \(-8 \text{V}\). The depletion region increases with increasing gate voltage until the surface depletion region \((W_S)\) separates itself from the junction depletion region \((W_J)\) (Figure 1.6, 1.7a \( V_G = -8 \text{V} \)).

After this point of separation, the surface become less and less depleted with increasing voltage, thus the surface depletion shrinks (Figure 1.7b, \( V_G = -8 \text{V} \) to \( 0 \text{V} \)). This in turns leads to an increase of the total capacitance as seen in Figure 1.5b \( (V_G = -8 \text{V} \) to \( 0 \text{V} \)). Further increase in the gate voltage results in an accumulation of electron at the surface (Figure 1.7b, \( V_G = 4 \text{V} \)). The junction depletion does not vary much with gate voltage leading to the stabilisation of the total capacitance seen in Figure 1.5b \( (V_G = 4 \text{V} \).

It is interesting to note that for longer oxidation times, thus more heavily doped n-layers, the point of separation occurs at larger negative voltage (Figure 1.5b). For more heavily doped n-regions the junction and surface depletion regions are smaller. Not only are these depletion regions more distant from each other, but the surface depletion region expands more slowly with negatively increasing gate voltage. Therefore larger negative gate voltages are required for the surface depletion region to reach the junction depletion region.

At similar resistivity, samples that have a higher compensation ratio will have a higher n-layer doping. By looking at the shift of the CV curve one can deduce which sample has a higher compensation ratio. This cannot be done by traditional methods such as four point probe where compensated samples with similar resistivities cannot be discriminated. Nevertheless, the fact that the main region affected by the applied gate voltage is the n-region implies that no quantitative data concerning the net dop-
ing of the bulk can be obtained using CV on thermally oxidised compensated samples. The fact that the junction induces a shift of the CV curve also makes it difficult to extract information about the density of interface states using the CV method.

These simulations also explain the difficulty in measuring this layer with ECV in figure 1.3. With the depletion region extending all the way to the surface the ECV technique should not be able to measure the dopant profile of this junction. In order to measure by ECV, the junction would need to be more heavily doped, leading to a smaller junction depletion region. This would also lead to a higher junction capacitance, allowing its contribution to the overall capacitance to be neglected.

1.5 Hot Probe measurements

Finally, a relatively quick and easy way to detect the presence of an oxide-induced junction is to measure the conductivity type of the samples surface by removing the oxide and using the hot probe method [37]. In this measurement, one hot probe and one cold probe are contacted to the sample. The thermal gradient generates a majority carrier current in the semiconductor, and depending on whether the semiconductor is n-type or p-type, the current will be negative or positive.

<table>
<thead>
<tr>
<th>( \rho ) (( \Omega \cdot \text{cm} ))</th>
<th>RC</th>
<th>Surface Polarity After Oxidation</th>
<th>Ideality of CV curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>1 (non-compensated)</td>
<td>p</td>
<td>Ideal</td>
</tr>
<tr>
<td>1.2</td>
<td>1 (non-compensated)</td>
<td>p</td>
<td>Ideal</td>
</tr>
<tr>
<td>0.5</td>
<td>3.5 (compensated)</td>
<td>Not detectable</td>
<td>Non ideal</td>
</tr>
<tr>
<td>1.6</td>
<td>7 (compensated)</td>
<td>n</td>
<td>Non ideal</td>
</tr>
</tbody>
</table>

Table 1.2: Surface polarity after oxidation of p-type samples after oxidation using the hot probe method compared with the ideality of the CV curve obtained.

Table 1.2 shows the results of the hot probe method on our wafers after a 1 hour 1100°C wet oxidation step (the compensation ratio is defined as \( R_C = (N_A + N_D)/(N_A - N_D) \)). While the surface of the non compensated samples \( (R_C=1) \) remains p-type after oxidation, the surface changes to n-type for the highly compensated sample \( (R_C=7) \). Due to a lower compensation ratio \( (R_C=3.5) \), and therefore insufficient surface inversion, the less compensated sample shows no detectable current. The hot
probe method is thus useful to quickly determine whether a relatively heavy inversion layer has been formed. Combined with an oxidation the hot probe method can be used to identify strongly compensated p-type samples.

1.6 Summary

In conclusion, SIMS, hot probe measurements, and numerical simulations, are in agreement and reveal the formation of a surface n-type layer after thermal oxidation in highly compensated p-type silicon.

This n-layer interferes with characterization techniques that require a thermal oxidation such as CV measurements on MOS structures. In a high frequency CV curve the surface n-layer introduces a dip in the CV curve that is due to the separation of the junction and surface depletion regions. This prevents the determination of the bulk doping density or the density of interface defects from such CV measurements. It is thus preferable to use ECV to obtain bulk doping densities, since the requirement for an oxidation is avoided.

Similarly the junction capacitance is likely to dominate the capacitance measured by the ECV technique. This in turn will undermine the determination of the doping profile using this technique. However, due to high leakage current we were not able to prove this hypothesis nor to profile the doping of the junction.

Nevertheless, the CV curve on MOS structures can not only be used to determine whether a sample is compensated or not but also to discriminate two compensated samples with similar resistivity but different compensation ratios. This oxidation induced n-layer could also create significant problems in compensated silicon solar cells involving thermal oxidation for surface passivation. Due to the segregation mechanism involved, this inversion layer can only occur when \( N_A > N_D \) (p-type material). It is also more likely to occur in heavily-doped and highly-compensated material.

The relatively low doping of the resulting n-layer on our samples means that it is unlikely to be useful as an emitter in a solar cell device. Nevertheless it could potentially act as a non-contacted floating junction, repelling minority carriers from the surface, and thus decreasing surface recombination.
More generally this effect could have potential applications in devices requiring a low-doped diffused layer (n-) with an oxide on top, such as CCDs or Buried-Channel MOSFETs, the simple oxidation process potentially making phosphorus implantation unnecessary.
Theoretical investigation and review of the carrier lifetime and mobility in compensated silicon

In this chapter the principles of recombination and scattering mechanisms are summarised and the impact of compensation is considered in detail. Fundamentals of capture and scattering mechanisms are introduced in the first section. The next section summarizes the effects of compensation on the carrier lifetime. Close attention is paid to metastable defects in both compensated p-type and n-type silicon. The impact of compensation on the carrier mobility is then analysed. The concentration of ionized impurities and free carriers is shown to be significantly affected by compensation. The Coulomb field of ionized impurities and free carriers is shown to be enhanced by compensation. The potential emergence of compensation-related scattering mechanisms is also explored. Throughout the chapter, in order to allow a fair comparison, non-compensated and compensated samples are compared at similar net doping $N_D - N_A$ (where $N_D$ and $N_A$ are the total dopant concentrations for n-type silicon).

2.1 Capture and Scattering in silicon

Without an applied electric field, carriers exhibit random motion due to scattering events and frequently change direction. When there is a carrier gradient, or an electric field, $\xi$, is applied, the random motion still occurs, but in addition, there is on average
a net motion along the direction of the field. Due to their different charge, holes move on average in the direction of the applied field, while electrons move in the opposite direction. Carriers will collide with lattice atoms, impurities or defects in the crystal structure leading to different capture and scattering mechanisms. This section briefly introduces those mechanisms.

2.1.1 Collision cross section

![Collision diagram](image)

Figure 2.1: Cylindrical volume travelled by an electron at a velocity $v_{th}$ in a time $t$.

Figure 2.1 shows an electron traveling along a cylinder of arbitrary cross section of area $A$ at its thermal velocity $v_{th}$.

$$v_{th} = \sqrt{\frac{3kT}{m^*}}$$

(2.1)

with $k$ the Boltzmann constant, $T$ the temperature and $m^*$ the effective mass. During a time $t$, it therefore sweeps a volume $A v_{th} t$. There are $N$ centers per $cm^{-3}$ that will scatter or absorb the electron. The total number of centers in this volume is thus $N A v_{th} t$. The area of the plane covered by a center is $\sigma_n = \pi r^2$ with $r$ the radius of the center, therefore the total area covered by centers is $N A v_{th} \sigma_n t$. The fraction of the area
covered by centers is:

\[ \text{Fraction} = \frac{N A v_{th} \sigma_n t}{A} = N v_{th} \sigma_n t \]  \hspace{1cm} (2.2)

The number of centers scattering or absorbing electrons per second is therefore:

\[ N_{\text{scattering,absorbing}} = \frac{N v_{th} \sigma_n t}{t} = N v_{th} \sigma_n \]  \hspace{1cm} (2.3)

The collision time can thus be defined as:

\[ \tau = \frac{1}{N v_{th} \sigma} \]  \hspace{1cm} (2.4)

### 2.1.2 The carrier lifetime

Once a free carrier is within the collision cross section of a center, several mechanisms can happen. The electron can be absorbed by the center or trap, that is the center will capture the electron. For such a process the capture cross section is defined as the effective area of the center for capturing the electron. The electron is then either released by the trap (trapping) or annihilated by the capture of an opposite charge carrier (recombination). Provided there is no trapping, from eq 2.4, the electron or hole lifetime is defined as:

\[ \tau = \frac{1}{N v_{th} \sigma_{\text{capture}}} \]  \hspace{1cm} (2.5)

### 2.1.3 The relaxation time

The electron can also be scattered by the center. Such a collision will tend to randomize the electron’s motion, meaning it will tend to reduce the excess velocity that the electron picked up in the applied electric field. This will therefore perturb the carrier distribution within the crystal. The relaxation time approximation assumes that the rate at which the distribution returns to equilibrium \( f_0 \) is proportional to the extent to which it is perturbed.

\[ \frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau_{\text{relaxation}}(k)} \]  \hspace{1cm} (2.6)
The solution of this equation is:

\[ f(t) = f_0 + [f(0) - f_0]e^{-t/\tau_{\text{relaxation}}(k)} \]  

(2.7)

The time between collisions \( \tau_{\text{scattering}} \) is of the order of the relaxation time \( \tau_{\text{relaxation}} \). It is determined by the random thermal velocity of the particle. From eq 2.4, the scattering time can be defined as:

\[ \tau_{\text{scattering}} = \frac{1}{N\nu_{\text{th}}\sigma_{\text{scattering}}} \]  

(2.8)

### 2.1.4 The carrier mobility

If we assume a simple collision mechanism, the carrier is uniformly accelerated by the electric field until it is scattered by a center. The average velocity increase of the particle between collisions caused by the field is called the drift velocity, and can be identified as:

\[ v_d = a t = \frac{e\tau_{\text{scattering}}}{m^*} \xi \]  

(2.9)

with a the acceleration. The carrier mobility can then be defined as the velocity to field ratio:

\[ \mu = \frac{v_d}{\xi} = \frac{e}{m^*\tau_{\text{scattering}}} \]  

(2.10)

The mobility of a particle in a semiconductor is therefore expected to be large if its mass is small and the time between scattering events is large. With eq 2.8 the carrier mobility can then be defined as:

\[ \mu = \frac{e}{N(2m^*kT)^{1/2}\sigma_{\text{scattering}}} \]  

(2.11)

Note however that scattering mechanisms are often more complicated than a simple collision and therefore the above expression is a simplified one. Moreover one often has to take the impact of the energy band on the mobility into account. The relation between the mobility and the scattering time taking into account each band separately
can be written [16]:

\[
\mu = \frac{q}{3} \left( \frac{\langle \tau_{\text{longitudinal}} \rangle}{m^*_{\text{longitudinal}}} + 2 \frac{\langle \tau_{\text{transversal}} \rangle}{m^*_{\text{transversal}}} \right) \tag{2.12}
\]

where the average scattering time is the Maxwellian average over the energy:

\[
\langle \tau \rangle = \frac{4}{3kT\sqrt{\pi}} \int_0^\infty e^{-E/kT} \frac{E^{3/2}}{kT} \tau(E) dE \tag{2.13}
\]

### 2.1.5 The effective lifetime

Several capture mechanisms often operate in parallel, therefore one needs a lifetime that will take all these mechanisms into account. The effective lifetime is the inverted sum of the inverted lifetime components.

\[
\frac{1}{\tau_{\text{effective}}} = \sum_i \frac{1}{\tau_i} \tag{2.14}
\]

The above equation then allows one to compare the influence of each mechanism on the lifetime. The total effective lifetime itself can be calculated as the inverted sum of the inverted lifetimes.

### 2.1.6 The effective scattering time

Similarly, provided there are no inelastic scattering mechanisms, the scattering time can be calculated as the inverted sum of all the individual scattering times corresponding to each scattering mechanism.

\[
\frac{1}{\tau_{\text{scattering, total}}} = \sum_i \frac{1}{\tau_{\text{scattering, } i}} \tag{2.15}
\]

### 2.1.7 The effective mobility Matthiesen’s rule

If all the scattering mechanisms have the same energy dependence, one can do a Maxwellian average of each scattering mechanism and therefore obtain the mobility
of each scattering mechanism [16].

\[
\frac{1}{\mu_{\text{total}}} = \sum_i \frac{1}{\mu_i}
\] (2.16)

The above equation then allows one to compare the influence of each scattering mechanisms on the mobility. The total mobility itself can be calculated as the inverted sum of the inverted mobilities.

### 2.1.8 Conclusion

The different components of the lifetime and the mobility can be added to each other to obtain the total lifetime or mobility. This will convenient in the next section where we will study the impact of compensation on each scattering or capture mechanism to finally study the impact of compensation on the lifetime or mobility. A mobility or lifetime reduction can be expected when either the density of center N is increased or their capturing or scattering cross section \( \sigma \) is increased. In the next two sections we investigate the influence of compensation on the density of centers and their cross section.

### 2.2 Recombination mechanisms at similar net doping

There are three main recombination mechanisms in semiconductors, Radiative recombination, Auger recombination and recombination through defects. The 3 recombination mechanisms are explained below and the potential influence of compensation on them is discussed. More detailed study of the effect of compensation on the carrier lifetime can be found in the literature [38; 39; 40; 41].

#### 2.2.1 Radiative recombination and compensation

Radiative recombination is the fall of a conduction band electron into a vacant valance band state with the energy released as a photon. Figure 2.2(a) shows that, silicon being an indirect bandgap semiconductor, the process also involves the emission of a phonon in order to conserve both energy and momentum. It is therefore a four particle
2.2 Recombination mechanisms at similar net doping

Figure 2.2: Band diagram showing the momentum and energy conservation during (a) Radiative recombination (b) Auger recombination.

recombination mechanism and its impact on the effective lifetime is small compared to direct semiconductors such as GaAs and InP.

The radiative annihilation of an electron-hole pair is the inverse process of optical absorption. The radiative recombination rate depends on the concentration of electrons and holes.

\[ U_{\text{rad}} = Bnp \]  \hspace{1cm} (2.17)

with \( n \), the concentration of free electrons, \( p \), the concentration of free holes and \( B \), the radiative recombination coefficient.

At room temperature \( B = 9.5 \times 10^{-15} \text{cm}^3\text{s}^{-1} \) [42]. In n-type silicon, compensated or not, the radiative recombination lifetime becomes:

\[ \tau_{\text{radiative}} = \frac{\Delta p}{U_{\text{rad}}} \]  \hspace{1cm} (2.18)

\[ \tau_{\text{radiative}} = \frac{\Delta p}{B(n_0 + \Delta p) \times \Delta p} \]  \hspace{1cm} (2.19)

\[ \tau_{\text{radiative}} = \frac{1}{B(n_0 + \Delta p)} \]  \hspace{1cm} (2.20)
with \( n_0 = N_D - N_A \) the net doping. Therefore at similar net doping a non-compensated and compensated material have the same radiative lifetime. However, starting from a material with a doping concentration \( n_0 = N_D \) and gradually compensating with acceptor \( N_A \), one not only reduces the net doping \( n_0 = N_D - N_A \) but also increases the radiative lifetime.

### 2.2.2 Auger recombination

Auger recombination is the fall of a conduction band electron into a vacant valance band state with the energy released through thermalization of a third carrier. Figure 2.2(b) illustrates the energy and momentum conservation during this process. This is a three particle process and therefore is quite important in silicon. The Auger recombination rate is:

\[
U_{\text{Auger}} = C_n n^2 p + C_p p^2 n
\]  
(2.21)

The third particle is a majority carrier in low injection, in n-type this means that the energy is transferred to an electron:

\[
U_{\text{Auger,li}} = C_n n_0^2 \Delta p
\]  
(2.22)

\[
\tau_{\text{Auger,li}} = \frac{1}{C_n n_0^2}
\]  
(2.23)

with \( n_0 = N_D - N_A \) the net doping. At high injection the Auger recombination rate becomes:

\[
U_{\text{Auger,hi}} = C_n \Delta p^3 + C_p \Delta p^3
\]  
(2.24)

\[
\tau_{\text{Auger,hi}} = \frac{1}{C_n \Delta p^2 + C_p \Delta p^2}
\]  
(2.25)

In n-type silicon the Auger lifetime becomes [43]:

\[
\tau_{\text{Auger}} = \frac{\Delta n}{np(1.8 \times 10^{-24} n_0^{0.65} + 3 \times 10^{-27} \Delta_n^{0.8})}
\]  
(2.26)

Therefore again, at similar net doping, similar Auger lifetimes are thus expected to be obtained in compensated and non-compensated silicon.
2.2.3 Recombination through defects

2.2.3.1 Recombination through metallic impurities

Recombination through defects is the capture of carriers by a defect. This has been treated extensively in compensated silicon [38; 39; 40; 41]. As shown in equation 2.4 the electron and hole lifetime can be defined:

\[ \tau_{p0} = \frac{1}{N v_{th} \sigma_p} \]  
\[ \tau_{n0} = \frac{1}{N v_{th} \sigma_n} \]  

(2.27)  
(2.28)

If the defect density N is small compared to the injection level \( \Delta n \) and the doping density \( n_0 \) or \( p_0 \) the SRH lifetime can be defined as [44]:

\[ \tau_{SRH} = \frac{\tau_{n0}(p_0 + p_1 + \Delta n) + \tau_{p0}(n_0 + n_1 + \Delta n)}{n_0 + p_0 + \Delta n} \]  

(2.29)

with \( n_1 \) and \( p_1 \), the equilibrium concentrations of electrons and holes, when the Fermi level coincides with the energy of the recombination center \( E_T \):

\[ n_1 = N_C \exp\left(\frac{E_T - E_C}{kT}\right) \]  
\[ p_1 = N_V \exp\left(\frac{E_C - E_G - E_T}{kT}\right) \]  

(2.30)  
(2.31)

Similarly to the two preceding mechanisms, at similar net doping and defect densities, similar electron and hole lifetimes are expected and therefore similar SRH lifetimes. However at similar net doping there is more boron in compensated silicon. Because many metallic impurities and oxygen dimers are known to pair with boron it is conceivable that the defect density of such pairs would increase and therefore the SRH lifetime decreases. This point is explored in p and n-type compensated silicon in the next sections. Note that surface recombination being a special case of SRH recombination a similar expression can be obtained for the surface recombination velocity.
2.2.3.2 Recombination through metallic impurities paired with acceptors in compensated p-type silicon

Figure 2.3: Charge of interstitial (a) Iron and (b) Chromium in p-type silicon and formation of pair with acceptors.

Figure 2.3(a) shows that in p-type silicon, the Fermi level is below the energy level of interstitial iron [45]. Iron therefore possess a positive charge. Iron is thus able to bond to negative acceptors such as Boron or Gallium with a reaction [46; 47]:

\[ \text{Fe}^+_i + B^- \rightleftharpoons \text{FeB} \quad (2.32) \]

\[ \text{Fe}^+_i + Ga^- \rightleftharpoons \text{FeGa} \quad (2.33) \]

\[ \text{Fe}^+_i + In^- \rightleftharpoons \text{FeIn} \quad (2.34) \]

Similarly, figure 2.3 shows that the Fermi level is below the energy level of interstitial Chromium in p-type silicon therefore interstitial Chromium is positively charged [48; 49]. Chromium is thus also able to negative acceptors such as Boron, Gallium or Aluminum with the reaction [48; 50]:

\[ \text{Cr}^+_i + B^- \rightleftharpoons \text{CrB} \quad (2.35) \]
§2.2  Recombination mechanisms at similar net doping

\[ Cr_i^+ + Ga^- \rightleftharpoons CrGa \]  \hspace{1cm} (2.36)

\[ Cr_i^+ + Al^- \rightleftharpoons CrAl \]  \hspace{1cm} (2.37)

CrB pairs are highly recombination active and therefore have a great impact on the SRH lifetime. At room temperature in p-type silicon with [B] \( > 1 \times 10^{14} \text{cm}^{-3} \) all of the iron is able to bond with the boron or the gallium present, since the iron concentration is generally less than \( 1 \times 10^{13} \text{cm}^{-3} \) [51]. This means that the boron or gallium concentration does not influence the iron-acceptor pair concentration. Therefore at room temperature similar SRH lifetimes are expected for samples containing similar net doping and iron concentration, regardless of the acceptor concentration.

2.2.3.3  Recombination through metallic impurities paired with boron in compensated n-type silicon

We showed in the previous section that similar SRH lifetimes are to be expected in compensated p-type silicon limited by metallic impurities paired with acceptors. Non-compensated n-type silicon does not contain boron, therefore if pairs where to form in compensated n-type silicon one could expect a different SRH lifetime in the two materials. Figure 2.4(a) shows that in n-type silicon doped at \( 1 \times 10^{16} \text{cm}^{-3} \) the Fermi level is above the energy level of both interstitial iron and chromium. Therefore iron and chromium are both neutral and are not able to pair with negative boron or gallium. For lower doping \( 1 \times 10^{15} \text{cm}^{-3} \), figure 2.4(b) shows that the charge state of interstitial chromium is positive. Therefore Chromium is able to pair with negative boron atoms in compensated n-type silicon. The capture cross section for holes is larger for CrB compared to interstitial Chromium [49]. Therefore, the SRH lifetime of Chromium containing, lightly-doped compensated n-type silicon is thus expected to be lower than in non-compensated n-type silicon. This has not been observed experimentally to date.
Figure 2.4: Charge of interstitial Iron and Chromium in n-type silicon doped at (a) $n_0 = 1 \times 10^{16} \text{cm}^{-3}$ and (b) $n_0 = 1 \times 10^{15} \text{cm}^{-3}$

### 2.2.3.4 Recombination through the Boron-oxygen defect

Boron with a negative charge is also known to pair with positive oxygen dimers. The reaction creates the boron-oxygen complex. The recombination activity of such a complex depends on the net doping. However its concentration has been shown to depend on the boron concentration in p-type silicon. Therefore one could expect a greater boron-oxygen defect density in compensated p-type silicon and a lower SRH lifetime. This is however not the case, as will be shown in chapter 5. Moreover the nature and formation mechanism of the boron-oxygen defect in compensated n-type silicon remains largely unknown and will be explored in chapter 5.

### 2.2.3.5 Recombination through shallow donors and acceptors

Shallow donors and acceptors such as phosphorus and boron, could also potentially contribute to the carrier recombination [52; 53; 39]. Because ionized dopants have a high capture cross section for minority carriers (due to coulomb attraction), it is the capture cross section of neutral dopants for majority carriers that limits the recombination process. The capture cross section of neutral boron is estimated to be
\[ \sigma_n = 10^{-19} - 10^{-17} \text{cm}^2, \] therefore recombination through shallow dopants can be significant at relatively high dopant concentrations [53; 54]. As seen above, in non-compensated silicon, at such doping the minority carrier lifetime is dominated by Auger recombination due to the high free carrier concentration [53; 39]. However, in compensated silicon, not only the ionized impurity is increased but the free carrier concentration is also decreased leading to a decrease in Auger recombination [53; 39]. In such a case recombination through shallow donors or acceptors can indeed dominate the total recombination and has been recently measured in highly doped compensated p-type silicon [54].

### 2.3 Scattering mechanisms at similar net doping

#### 2.3.1 Introduction

The particles responsible for scattering in semiconductors are phonons, impurities and other carriers. Phonon scattering is due to the deformation of the perfect crystal by phonons. This scattering is either due to the deformation potential mechanism or through the electrostatic forces produced by the polarization waves. Impurities can be neutral or ionized. Neutral impurity interactions with carriers are short range, thus the effect of neutral centres is usually very small. On the other hand, ionized impurities and carriers interactions with other carriers are of Coulomb type and thus long range. Therefore the effect of charged impurities on carriers is much stronger.

We first summarise the basic scattering mechanisms taking place in silicon. We then investigate the influence of compensation on the concentration of scattering centers, namely ionized impurities, neutral impurities and free carriers. We also investigate the influence of compensation on the scattering cross section of those mechanisms, with a focus on the coulomb cross section of charged particles. Finally we introduce two additional scattering mechanisms that are created in compensated silicon, dipole scattering and space-charge-region scattering.
2.3.2 Scattering mechanisms in silicon

2.3.2.1 Phonon Scattering

2.3.2.1.1 Phonon concentration  Phonon scattering is very effective at high temperature and when carriers have high energies. There are two types of phonon, acoustic phonons and optical phonons. Acoustic phonons occur when the two atoms on the unit cell vibrate along the same direction. Optical phonons occur when the two atoms on the unit cell vibrate in opposite directions. Both acoustic and optical phonon can be longitudinal or transversal. Figure 2.5(a) shows the longitudinal and transversal mo-

![Image showing acoustical and optical phonons and phonon dispersion in Si from [15].]

Figure 2.5: (a) Acoustical and optical phonon (b) Dispersion relation in Si from[15].

This means that the phonon population decreases with increasing phonon frequency. One can see that near k=0, the frequency of acoustic phonons (TA, LA) is quite small.
Therefore acoustic phonons are present at both low and high temperature. On the other hand, near k=0, the energy of optical phonons (TO, LO) is quite large, thus optical phonons are present only at high temperature.

2.3.2.1.2 Phonon interactions with electrons  Phonon interactions with electrons can be electrostatic or due to a deformation-potential. However, silicon being a non-polar semiconductor, electrostatic interaction due to phonon scattering mechanisms (polar and piezoelectric scattering) do not take place and are therefore not discussed here. Phonon interactions with electrons and holes lead to different type of electronic transitions. Figure 2.6 shows the different electronic transitions due to phonon scattering [16].

![Silicon band diagram showing the electronic transitions in silicon due to scattering mechanisms](image.png)

Figure 2.6: Silicon band diagram showing the electronic transitions in silicon due to scattering mechanisms [16].

2.3.2.1.3 Electron Intravalley, Hole Intraband Scattering  As an acoustic or optical phonon propagates through the lattice, the lattice spacing changes momentarily. This in turn induces a temporary change in the bandgap, the conduction and the valence band edge thus fluctuate. This fluctuation in the band edge then scatters the electron (or hole). This is shown in figure 2.6. This is physically described as a short range potential referred to as the deformation potential. These scattering mechanisms are
inelastic (some energy is exchanged between the phonon and the electron). This is shown in figure 2.6 where most transitions operate with an exchange of energy and momentum.

2.3.2.1.4 Electron Intervaly, Hole Interband scattering Acoustic and optical phonons with shorter wavelength can induce an electron (or hole) transition between two different valleys (or bands). The phonon wavevector is usually close to the distance between the two valleys. These mechanisms are shown in figure 2.6. This scattering mechanism is also inelastic.

2.3.2.1.5 Compensation on phonon scattering Compensation does not have a direct impact on phonon scattering, thus we do not further analyze this mechanism in this chapter.

2.3.2.2 Ionized impurity scattering

As a carrier travels through the semiconductor it encounters the Coulomb field of other charged impurities and other carriers. Ionized impurity scattering is elastic in nature. Figure 2.7 shows the effect of such interactions on a positive hole. The positive

![Figure 2.7: Free carrier deflection by positive or negative ions.](image-url)
hole is attracted by the negative donor and repelled by the positive acceptor. Ionized impurity scattering is more effective at low temperature and when the carrier energy decreases. This scattering mechanism dissipates momentum but not energy.

2.3.2.3 Neutral impurity scattering

Impurities such as carbon and oxygen can scatter carriers. Carrier scattering from neutral impurities is also important at very low temperature where freeze-out of dopants occur. Non-ionized acceptors or donors are like the neutral hydrogen center. This results in a short range potential. Therefore neutral impurities are less effective than ionized impurities as their scattering cross section is very small.

2.3.2.4 Carrier-carrier scattering

2.3.2.4.1 Electron-hole scattering  An electron in the conduction band can interact with a hole in the valence band. This interaction is of Coulombic nature and thus similar to the ionized impurity scattering action. Electron-hole scattering does not dissipate energy but dissipates momentum. Electron-hole scattering affects mainly minority carriers as the concentration of majority carriers is too high to be affected by scattering events with minority carriers.

2.3.2.4.2 Electron-electron scattering  Electron-electron scattering is a second order scattering mechanism. Electron-electron scattering does not lead to a loss of energy or momentum but can redistribute the momentum of electrons. This means that highly energetic electrons will give their energy to lower energy electrons. This in turns give the electron distribution as a function of energy a maxwellian form.

2.3.3 Compensation impact on the concentration of scattering centers

2.3.3.1 Introduction

The phonon concentration purely depends on the temperature in silicon. Therefore, phonon concentration is not affected by compensation. However, ionized impurities, neutral impurities and free carriers are affected by compensation. The next three
sections evaluates the impact of compensation on the concentration of those three scattering centers.

### 2.3.3.2 Compensation impact on the ionized impurity concentration

![Figure 2.8: Influence of (a) temperature and (b) dopant density on the ionized dopant concentration in a non-compensated sample and a sample compensated at 90% ($N_A/N_D=0.9$).](image)

At similar net doping there is more ionized impurities in a compensated silicon sample compared to a non-compensated silicon sample. Figure 2.8 shows the influence of temperature and dopant density on the ionized dopant concentration in a non-compensated sample and a sample compensated at 90% ($N_A/N_D=0.9$). One can clearly see that the ionized impurity concentration is greatly increased in the compensated sample. Because the compensated sample contains more impurities, it has a bigger pool of dopants that can be neutral. Indeed at room temperature all the electrons on the donor level are in the conduction band. However at lower temperature or when the concentration of dopant is very large the thermal energy does not excite all the electrons on the donor level. This leads to incomplete ionization of dopants. This effect in compensated silicon is well documented in the literature [54; 55].
total ionized dopant concentration in non-compensated n-type silicon is:

\[ n_0 = N_D^+ = \frac{N_D}{1 + g_D e^{(E_F - E_D)/kT}} = N_C \exp\left(\frac{-E_C - E_F}{kT}\right) \]  \hspace{1cm} (2.39)

With \( g_D \) the donor degeneracy factor. In compensated n-type silicon as all the acceptors are ionized this becomes:

\[ n_{0,\text{compensated}} = N_D^{+\text{,compensated}} - N_A = \frac{N_D}{1 + g_D e^{(E_F - E_D)/kT}} - N_A = N_C \exp\left(\frac{-E_C - E_F}{kT}\right) \]  \hspace{1cm} (2.40)

In non-compensated silicon the dopants are completely de-ionized at very low temperature. Therefore the ionized impurity scattering is negligible at very low temperature. In compensated silicon, there are much more ionized impurities at very low temperature. At those low temperature ionized impurity scattering remains the dominant scattering mechanism [54; 55; 56; 57].

2.3.3.3 Compensation impact on the neutral impurity concentration

As seen above, as the temperature decreases, dopants become neutral due to freeze-out.

![Figure 2.9: Influence of (a) temperature and (b) dopant density on neutral dopant density in a non-compensated sample and a sample compensated at 90% (\( N_A/N_D=0.9 \)).](image-url)
Theoretical investigation and review of the carrier lifetime and mobility

Figure 2.10: Influence of (a) temperature and (b) dopant density on the net doping in a non-compensated sample and a sample compensated at 90% \( (N_A/N_D=0.9) \).

Figure 2.9 shows the influence of temperature and dopant density on the neutral dopant density. Figure 2.9 clearly shows that there are more neutral impurities in compensated silicon. The reason being that there are more impurities in compensated silicon therefore there are more impurities that can become neutral. Note that the donor energy level is closer to conduction band leading to a proportionally reduced incomplete ionization. However the concentration of neutral dopant is still much less than the concentration of interstitial oxygen in Cz material ([O\text{\textsubscript{i}}]=1 \times 10^{18} cm^{-3}). Moreover, in non-compensated silicon the effect of neutral impurities is only important at very low temperature. In compensated silicon at very low temperature ionized impurity scattering dominates. Therefore the mobility is almost never limited by neutral impurity scattering in compensated silicon.

2.3.3.4 Compensation impact on the free carrier concentration

Figure 2.10 shows that at similar \( N_D - N_A \), the net doping is slightly lower in compensated silicon. This is because there are slightly more non-ionized donors in compensated silicon as explained above. Compensation has a large influence on minority carriers as it reduces the amount of majority carriers. Therefore, for a given donor
concentration, there are less majority carriers to scatter minority carriers which on its own is beneficial for the minority carrier mobility.

### 2.3.4 Compensation impact on the Coulomb scattering cross section

#### 2.3.4.1 Introduction

The interaction between phonons and electrons in silicon is not of Coulomb nature, therefore the scattering cross section of phonons is not altered by compensation. Similarly the interaction between neutral impurities and electrons is not of coulomb nature and hence not affected by compensation. However ionized impurity-carrier and carrier-carrier interactions are of coulomb nature and are thus potentially affected by compensation. The next sections explore the implications of increased Coulombic scattering cross sections in compensated silicon.

#### 2.3.4.2 Scattering by positive and negative center

The scattering cross section is thought to be smaller for minority impurities compared to majority impurities. This is due to the coulomb repulsion between minority impurity and majority carrier. Indeed acceptors being negatively charged (donors being positively charged) have repulsive (attractive) coulomb interaction with holes. Therefore, acceptors have a larger scattering cross section than donors for hole scattering. Phillips unified mobility model (Klaassen’s model) takes into account the difference between hole-donor scattering and hole-acceptor scattering through a factor $G(P)$ which represent the scattering cross section ratio between scattering by majority impurity and minority impurity [58; 59]. This was evaluated from quantum mechanical phase shifts calculations.

$$ G(P) = \frac{\sigma_{s,\text{repulsive}}}{\sigma_{s,\text{attractive}}} = \frac{\mu_{h,A}}{\mu_{h,D}} \quad (2.41) $$

Figure 2.11 shows the scattering cross section ratio for repulsive and attractive center calculated by Klaassen. As the doping increases, the scattering cross section of repulsive centers decreases faster than the scattering cross section of attractive centers. Therefore the mobility of repulsive centers decreases less than the mobility of
Theoretical investigation and review of the carrier lifetime and mobility

2.3.4.3 Screening and scattering cross section

It has been shown above that compensation increases the ionized impurity concentration. Compensation will also affect the ionized impurity scattering cross section. For a comprehensive review of ionized impurity scattering in silicon see [60]. In this section we introduce the ionized impurity scattering cross section in order to understand how compensation might affect its cross section. The carrier deflection will depend on the strength of the electrostatic interaction and the length of time the carrier feels the potential. In a simple model one would expect the electrostatic potential around a charge Ze to be:

\[ V(r) = \frac{1}{4\pi\epsilon_0} \frac{Ze}{r} \]  

(2.42)

This potential is called the bare potential. Theoretically this means that the scattering cross section is infinite. However scattering processes are essentially two body...
processes, involving the free carrier and the fixed impurity. Therefore one must find an alternative to reduce this potential to only allow two-body interactions. Moreover when the charge is surrounded by positive ions, holes and negative ions and electrons, those charges in turn screen the potential of the charge at the centre. This means that with screening, the potential decreases much more rapidly than in $1/r$. A screened coulomb potential is thus more appropriate.

$$V(r) = \frac{1}{4\pi\varepsilon_0} \frac{Ze}{r} \exp\left(-\frac{r}{L_D}\right) \tag{2.43}$$

With $L_D$, the debye length, a measure of the electrostatic screening. At low dopant concentration mainly free carriers contribute to screening while at higher concentration ionized impurities also contribute to screening. The Debye length is defined as:

$$L_D = \sqrt{\frac{\varepsilon_0 k_B T}{(n + p)e^2}} \tag{2.44}$$

Figure 2 shows the doping dependence of the Debye length. Typical values are between 1000nm at $1.7 \times 10^{13} \text{cm}^{-3}$ and 10nm at $1.6 \times 10^{17} \text{cm}^{-3}$. There are two main approaches to deal with the scattering cross section, the Conwell-Weisskop and the Brooks-Herring approach. Those two approaches are described in the following sec-
2.3.4.4 Conwell-Weisskopf

In order to avoid three-body interactions, Conwell and Weisskopf introduced an impact parameter that limits spatially the range of the impurity potential. Conwell-Weisskopf approximate the impact parameter to half the average separation distance of the impurities [61]:

\[ b = \frac{N_I^{-1/3}}{2} \]  

(2.45)

With \( N_I \), the impurity concentration. This means that the electron only scatters with the nearest impurity centre. Effectively the Conwell-Weisskopf model doesn’t take screening into account. It is thus the more appropriate model when screening does not dominate. Figure 2.13 shows the space dependence of the bare and the cut-off Coulomb potential.

![Figure 2.13: Space dependence of the ionized impurity bare and cut-off Coulomb potential.](image)

Coulomb potential. The scattering cross section is [61]:

\[ \sigma = \pi b_{\text{max}}^2 \]  

(2.46)
The mobility is then expressed as [61; 60]:

\[ \mu_{CW} = \frac{\mu_0}{\ln(1 + \beta_{CW})} \]  

(2.47)

with

\[ \mu_0 = \frac{64\pi^{1/2}e^2(2kT)^{3/2}}{(N_D + N_A)Z^2e^3m^{1/2}} \]  

(2.48)

and

\[ \beta_{CW} = \frac{144\pi^2e^2k^2T^2}{Z^2e^4(N_D + N_A)^{2/3}} \]  

(2.49)

### 2.3.4.5 Brooks-Herring

The approach of Brooks and Herring is to take into account screening of the impurities Coulomb field by other carriers. A screened Coulomb potential is introduced. Figure 2.14 shows the space dependence of the bare and a screened Coulomb potential.

![Figure 2.14: Space dependence of the ionized impurity bare and screened Coulomb potential.](image)

The scattering cross section is [62]:

\[ \sigma = \frac{4\pi(\mu/q_0)^2}{1 + (q_0/2k)^2} \]  

(2.50)
Figure 2.15: Doping dependence of the mobility with the model of (a) Conwell-Weisskopf and (b) Brooks-Herring in non-compensated silicon and compensated silicon.

Similarly to the Conwell-Weisskopf, the mobility is then expressed as [62; 60]:

\[
\mu_{BH} = \frac{\mu_0}{\ln(1 + \beta_{BH}) - \beta_{BH}/(1 + \beta_{BH})}
\]  

(2.51)

with

\[
\mu_0 = \frac{64 \pi^{1/2} e^2 (2kT)^{3/2}}{(N_D + N_A)N Z^2 e^3 m^{1/2}}
\]

(2.52)

and

\[
\beta_{BH} = \frac{24 m e (kT)^2}{n_{sc} e^2 h^2}
\]

(2.53)

\[
n_{sc} = n + (1 - (n + N_A)/N_D)(n + N_A)
\]

(2.54)

In the above equations 2.47 and 2.51 the part in the logarithm deals with the screening. Figure 2.15 shows the mobility as a function of the net doping in non-compensated and compensated n-type silicon for the model of Brooks-Herring and Conwell-Weisskopf. The mobility (\(\mu_{total}\)) and its component due to lattice (phonon) scattering (\(\mu_L\)) and ionized impurity scattering (\(\mu_{CW}\) and \(\mu_{BH}\)) are shown. Figure 2.15(a) represents the electron mobility using Conwell-Weisskopf model. In that
Scattering mechanisms at similar net doping

Figure 2.16: Temperature dependence of the mobility with the model of (a) Conwell-Weisskopf and (b) Brooks-Herring in non-compensated and compensated silicon.

Model compensation merely leads to a shift of the whole mobility curve downward. This illustrates the fact that Conwell-Weisskopf does not take screening into account. Figure 2.15(b) demonstrates the impact of screening in the model of Brooks-Herring. The non-compensated sample with equal amount of donors and acceptors is well screened and therefore possesses high mobility. The compensated silicon samples possess more impurities and the same amount of free carriers. Therefore the curve is not only shifted downward, it also is steeper, underlying the importance of screening at high impurity concentrations.

The $\mu_0$ part of the equation deals with the impurity scattering. One can easily see that its dependence is on $T^{3/2}$ which is typical for ionized impurity scattering. Figure 2.16 shows the temperature dependence of the the mobility. It illustrates the $T^{3/2}$ dependence of the mobility in the Conwell-Weisskopf and Brooks-Herring model. Note that at very low dopant density the mobility becomes very high in non-compensated silicon, while it decreases in compensated silicon. This is because compensated silicon contains $N_D^+ = N_A^-$ ionized impurities while in non compensated silicon there are virtually no ionized impurities as seen above.

We have shown above that at similar net doping ionized impurities are much
more screened in non-compensated silicon compared to compensated silicon. Indeed in compensated silicon the Debye length is much larger than the interionic distance. This is illustrated in figure 2.17 showing the doping dependence of the Debye length and the interatomic distance. In effect screening reduces the range of the ionized impurity potential and thus their effectiveness at scattering carriers. However in the case of week screening, for example high compensation, the Brooks-Herring Screened Coulomb potential comes back to the form of the bare potential.

\[
L_D = \sqrt{\frac{\epsilon_0 k_B T}{(n+p) e^2}} \to \infty
\]

\[
V(r) = \frac{1}{4\pi\epsilon_0} \frac{Ze}{r} \exp\left(-\frac{r}{L_D}\right) \to V(r) = \frac{1}{4\pi\epsilon_0} \frac{Ze}{r}
\]

On the one hand, the model of Brooks-Herring includes screening but when there is a lack of screening the potential still has an infinite nature, which then allows more than two body interactions. On the other hand, the model of Conwell-Weisskopf ensures that only two-body interactions can occur by cutting the potential at half the average inter-ion distance. However it doesn’t take into account screening and disregards the effect of the potential outside the impact parameter. In compensated silicon this potential can be significant. There is thus a need to reconcile those two models into one more general model.

### 2.3.4.6 Reconciliation of the Brooks-Herring and the Conwell-Weisskopf models

To overcome the limitations of these models, Ridley developed a new model that reconciles those two models. The model of Brooks-Herring and Conwell-Weisskopf becomes limiting cases of this model at high and low screening respectively. The mobility is expressed as [63]:

\[
\mu_R = \frac{\mu_0}{\exp(\alpha\beta/(1+\beta))(E_1(\exp(\alpha\beta/(1+\beta))) - E_1(\alpha\beta)) - \exp(-\alpha\beta/(1+\beta)) + \exp(-\alpha\beta)}
\]
2.3 Scattering mechanisms at similar net doping

Figure 2.17: Doping dependence of the Debye Length and the interionic distance in silicon (a), at low doping (low screening), the model of Conwell-Weisskopf yields better results. At high doping (high screening), the model of Brooks-Herring yields better results. In compensated silicon (b) we are always in low screening therefore the model of Conwell-Weisskopf should be used.

with

\[ \mu_0 = \frac{64\pi^{1/2}\epsilon^2(2kT)^{3/2}}{NZ^2e^3m^{1/2}} \]  

(2.59)

and

\[ \alpha = \frac{Z^2e^4Na}{576\pi\epsilon^2(kT)^2} \]  

(2.60)

and

\[ \beta_R = \frac{24me(kT)^2}{ne^2h^2} \]  

(2.61)

This is the model used in further simulations. This model is used as part of Klaassen’s model [58; 59]. It is questionable whether screening is rightly taken into account using this method and whether some potential is disregarded in the process.

2.3.4.7 Falicov-Cuevas

Not only can free carriers screen impurities, but if there are many impurities and few free carriers, impurities will screen each other. In order to take this effect into account
Falicov and Cuevas studied the mobility in compensated germanium at low temperature [56; 57]. The mobility can be expressed as [56; 57]:

\[
\mu_{FC} = \frac{\mu_{FC0}}{\ln(1 + \beta_{FC}) + \beta_{FC}/(1 + \beta_{FC})}
\]  

(2.62)

with

\[
\mu_{FC0} = \frac{2^{7/2}(kT)^{3/2}e^2}{\pi^{3/2}(2N_A)e^3m^{1/2}}
\]  

(2.63)

and

\[
\beta_{FC} = \frac{6(kT)^2m}{\pi^{2/3}\hbar^2 n}
\]  

(2.64)

This equation is useful when the ionized impurity concentration is much larger than the free carrier concentration. This is the case at very low temperature (T<40K). Therefore this equation is not used in this chapter.

### 2.3.5 Compensation Specific scattering mechanisms

#### 2.3.5.1 Dipole scattering

In a compensated semiconductor, two oppositely charged impurities can associate their Coulomb field [64; 65; 66; 67]. These will then scatter electrons like a dipole. The study of Reiss and Fueller focused on dopant compensation near room temperature (300°) using lithium. Indeed lithium is a donor in an interstitial position in the lattice and is mobile at such temperatures. Therefore lithium feels the Coulomb field of atoms such as boron or gallium and readily associates itself with them [68]. Reiss et al. demonstrated that for high gallium concentration \(8 \times 10^{18} cm^{-3}\) all the lithium is paired with the gallium. The situation is different for boron-phosphorus compensated silicon as boron and phosphorus are substitutional impurities and therefore neither of them are mobile at low temperature. During ingot cooling the intrinsic carrier concentration is so high that the coulomb field of both boron and phosphorus atoms is highly screened. For example a sample with \(N_D=6 \times 10^{16} cm^{-3}\) \(N_A=4 \times 10^{16} cm^{-3}\) has an interionic distance of 17nm but much smaller debye length of 2.6nm at 1000°C. At this temperature there is no electrostatic interaction between the two dopants. Therefore boron and phosphorus distribute themselves randomly (assuming that steric ef-
fects are negligibly small). Any dipole subsequently formed at room temperature is the result of this random distribution.

For mobile donors (lithium) Boardmann et al found that the dipole concentration is affected by the coulomb attraction between donors and acceptors thus the number of dipoles formed per unit volume is \[ N_{\text{dipole}} = \frac{N_A}{2} \left( 1 + \frac{1}{\Omega N_A} + \frac{N_D}{N_A} \right) - \frac{N_A}{2} \left( \left( 1 + \frac{1}{\Omega N_A} + \frac{N_D}{N_A} \right)^2 - \frac{4N_D}{N_A} \right)^{1/2} \tag{2.65} \]

whith \( \Omega = \frac{N_{\text{dipole}}}{(N_A - N_{\text{dipole}})(N_D - N_{\text{dipole}})} \)

However as shown previously for boron and phosphorus in compensated silicon there is no coulombic attraction between the ions at the temperature where they are mobile.

The dopant distribution can thus be assumed to be completely random. We can also assume that for a dipole to form between a donor and an acceptor they must be nearest neighbours and have opposite charge. Note that nearest neighbours in this context does not mean that the two dopants are within the lattice constant \( a_0 \) of each others, but rather that there are no dopants in between them. A dopant is the nearest neighbour of another one if it is situated in the shell \( 4\pi r^2 \, dr \) and that the volume \( 4/3\pi r^3 \) is empty of an ions. If \( g(x) \, dx \) is the probability that a nearest neighbour lies in the shell \( 4\pi x^2 \, dx \), the probability that the sphere \( 4/3\pi r^3 \) contains an atom is the integral from 0 to \( r \) of that probability \[ P_{\text{sphere,full}} = \int_0^r g(x) \, dx \tag{2.66} \]

The probability that the sphere is empty is therefore:

\[ P_{\text{sphere,empty}} = 1 - \int_0^r g(x) \, dx \tag{2.67} \]

This can be transformed in \[ P_{\text{sphere,empty}} = \exp(-4\pi \int_0^r x^2(N_A^- + N_D^+) \, dx) \tag{2.68} \]
This becomes \[68\]:

\[
P_{\text{sphere, empty}}(r) = \exp\left(-4\pi r^3(N^-_A + N^+_D)/3\right)
\] (2.69)

Now that we have the probability that two dopants are nearest neighbours, we need those two dopants to be of opposite sign to create a dipole. This requires that the shell \(4\pi r^3\) is occupied by an acceptor in compensated n-type. When the distribution of dopant is random the probability that the shell \(4\pi r^3\) contains an acceptor is \[68\]:

\[
P_{\text{shell, acceptor}} = 4\pi r^2 N^-_A
\] (2.70)

The probability that that a donor has an acceptor as a nearest neighbour in the shell \(4\pi r^2\) is thus the product of those two probabilities \[68\].

\[
g(r) = 4\pi r^2 N^-_A \exp\left(-\frac{4\pi r^3(N^-_A + N^+_D)}{3}\right)
\] (2.71)

An acceptor can be nearest neighbour but not create a dipole.

Figure 2.18: Doping dependence of the proportion of acceptors and donors in the form of dipoles.

Knowing the maximum dipole length \(L_{\text{max}}\) one can calculate the dipole concentra-
2.3 Scattering mechanisms at similar net doping

\[ N_{dipole} = N_D^+ * \int_0^{L_{max}} g(r)dr \]  (2.72)

Figure 2.18 shows the influence of dopant density on the proportion of acceptors and donors in the form of dipole in silicon compensated at 80% assuming different dipole lengths.

If one assumes that the dipole length is of the order of the lattice constant \( a_0 \), dipoles are very unlikely to form and the dipole concentration is very low. This is illustrated in figure 2.18 where the proportion of acceptor paired to donors is shown to be lower than 1% for silicon doped at \( 1 \times 10^{17} cm^{-3} \). Tajima et al. have observed photoluminescence from boron-phosphorus pairs in compensated p-type silicon [69]. They found the separation between donor and acceptor pair to be between 25 and 73 lattice constant, 1.9nm to 3.3nm in their samples [69]. If now we assume that the dipole length can be \( 73 \times a_0 \) we find the dipole concentration to be 11% for silicon doped at \( 1 \times 10^{17} cm^{-3} \). This means that a significant proportion of acceptors could be paired with donors. Note however that this distance is relatively large and therefore acceptors and donors are more likely to act as single scattering centers. In an extreme case one can assume that the dipole length is the Debye length. For obvious reasons this is not a good physical picture. Doing this calculation shows that 50% of boron atoms are paired.

The scattering potential of a dipole is defined as [66]:

\[ V(\vec{r}) = \frac{\vec{M} \cdot \vec{r}}{4\pi \epsilon r^3} \]  (2.73)

Similarly to ionized impurity scattering, dipole scattering can be screened by other carriers. Stratton used a screened potential of the form [65]:

\[ V(\vec{r}) = \frac{\vec{M} \cdot \vec{r}}{4\pi \epsilon r^3} (1 + \frac{r}{L_D}) \exp \left(-\frac{r}{L_D} \right) \]  (2.74)

Figure 2.19 shows the spatial dependence of the dipole scattering potential. Unlike ionized impurity potential the dipole potential is directional and depends on the distance between the two ions and their direction. The dipole scattering cross section is
Theoretical investigation and review of the carrier lifetime and mobility

Figure 2.19: Space dependence of the dipole scattering potential when an electron travels along the axis of the two ions.

also much smaller than for impurity scattering, therefore dipole scattering has a beneficial effect on the mobility as it effectively reduces the number of ionized impurities.

As seen above, provided the dipole length is a few nm, the dipole concentration is negligible in boron-phosphorus compensated silicon except for very high doping concentration. The mobility can then be determined from the ionized dopant concentration minus the dipole concentration.

2.3.5.2 Space-charge region scattering

In heavily compensated semiconductors it is possible that due to slight variations in dopant distributions, the net doping inhomogeneity can be very high. Some areas have higher charge than others. In order to obtain charge neutrality, space-charge regions appear around the inhomogeneities [70; 71]. This in turns leads to spatial fluctuation of the conduction and valence band which scatter electrons. This can be treated as a single collision problem [70]. Figure 2.20 shows the space dependence of the space charge region scattering potential [70].

Due to the nature of the space charge region formation mechanism it is hard to describe qualitatively the relationship between compensation and space-charge region
2.3 Scattering mechanisms at similar net doping

2.3.6 Mobility

2.3.6.1 Majority carrier mobility

Figure 2.21 shows the majority electron mobility as a function of the net doping in non-compensated silicon and compensated silicon according to Klaassen’s model. The different scattering mechanisms are shown, $\mu_{\text{total}}$, the total mobility, $\mu_{e-L}$ the lattice (phonon) scattering, $\mu_{e-D}$ the scattering by donors, $\mu_{e-A}$ the scattering by acceptors and $\mu_{e-h}$ the scattering by holes. We are looking at the majority carrier mobility therefore the latter term is negligible and not present. In non-compensated samples, the mobility initially starts as the phonon limited mobility for low net doping. As the doping increases the mobility becomes limited by donor scattering. In compensated silicon on the other hand, with 10 times more donors, the mobility is already limited by donor scattering at low net doping. It also decreases much faster as the doping increases. This is due to the combined influence of donors and acceptors. Acceptor scattering is very important at high net doping but does not dominate donor scatter-
Theoretical investigation and review of the carrier lifetime and mobility

Figure 2.21: Majority electron mobility using Klaasen’s model as a function of the net doping in (a) non-compensated silicon (b) silicon compensated at 90%.

...ing. Note that Klaassen’s model does not include the possible impact of compensation specific mechanisms such as dipole scattering and space-charge-region scattering.

2.3.6.2 Minority carrier mobility

Figure 2.22 shows the low-injection minority hole mobility as a function of the net doping in non-compensated silicon and compensated silicon. Because electrons are minority carriers they see many holes, whereas holes virtually see no electrons ($p \times n = n^2$). This means that electron-hole scattering is a significant scattering mechanism reducing minority electron mobility in non-compensated silicon. The contribution of the electron-hole scattering is even greater than the contribution of the donors at low doping. In compensated silicon the hole concentration is reduced, leading to a strong reduction of the electron-hole scattering. The contribution of the electron-hole scattering on the total minority carrier mobility becomes negligible. The increased donor and acceptor concentration leads to a much higher ionized impurity scattering in compensated silicon. Interestingly, even though there are more donors present acceptor scattering dominates. This is easily explained by the fact that the scattering of a hole by an impurity with negative charge is more effective than the scattering with
2.4 Summary

In this chapter the influence of compensation on recombination mechanisms has been summarized. At similar net doping one can expect similar carrier lifetime in non-compensated silicon and compensated silicon.

The carrier lifetime can be altered in compensated n-type silicon due to the formation of metastable defects with boron. For example, at low net doping chromium will pair with boron and therefore reduce the carrier lifetime. The boron-oxygen (BO) defect can also reduce the carrier lifetime in compensated silicon and this will be further explored in Chapter 5.

Compensation will also lead to a reduction in the carrier mobility at similar net doping. The main reason is due to the increase in the ionized impurity concentration (both donors and acceptors) in order to lower the net doping. This is made stronger by the fact that ionized impurities are no longer screened by free carriers in compensated silicon. Thus they have much higher scattering cross sections. Simulations
also show that compensating impurities have smaller scattering cross section than the main impurities. This suggests that in theory the mobility reduction is not as great as expected.

The scattering cross section of ionized impurities in compensated silicon is not straightforward to model. Because it is not screened, the potential has a long range (many interionic distance) that can not be treated using conventional models where the assumption of two-body interaction is made.

For minority carriers, compensation also leads to less electron-hole scattering, but not enough to balance the strong increase in ionized impurity scattering.

Finally compensation can potentially lead to new scattering mechanisms such as space charge region scattering and dipole scattering. However those mechanism are likely to be negligible for dopant concentrations below $5 \times 10^{17} cm^{-3}$. The impact of compensation on the carrier mobility will be further explored experimentally in the next Chapter.
3.1 Introduction

The carrier lifetime and mobility are key parameters in determining the performance of silicon solar cells. It is well known that the mobility decreases with increasing doping density [72], carrier injection level [73; 74] and sample temperature[75]. Similarly the lifetime is known to be affected by doping density, carrier injection and temperature. Since solar cells often operate under a wide range of injection levels and temperatures, it is thus fundamental to determine the impact of those parameters on the carrier lifetime and mobility. The following 3 sections present techniques used to measure the impact of those factors on the carrier mobility. Many of those techniques will be used in chapter 4 and 5. We discuss their relative advantages and practicality for our purpose. Then we explain the reasons that lead us to use some of these techniques in the thesis. Finally we present a new technique to determine the impact of dopants, injection and temperature on the mobility sum in silicon.
3.2 Carrier lifetime

When illuminating a sample with photons of sufficient energy one can generate carriers within a semiconductor. The continuity equation describes the carrier concentration change in an element of volume as a function of the incoming and outgoing flux of carriers as well as the generation and recombination.

\[
\frac{\partial \Delta n}{\partial t} = G(x, t) - U(X, t) + \frac{1}{e} \frac{dJ_n}{dx} \tag{3.1}
\]

with \(G\) the generation rate, \(U\) the recombination rate \(\Delta n\) the excess carrier density and \(J_n\) the electron current density. The following section describes two methods to measure the lifetime in a transient regime (\(G=0\)) or in a quasi-static regime (\(\partial \Delta n / \partial t = 0\)).

3.3 Minority carrier lifetime measurements

3.3.1 Inductive coil lifetime measurements

In this method, a flash lamp injects carriers into a sample. This in turns increases the conductance of the wafer. The inductive coil measures the excess conductance \(\Delta \sigma\).

The excess carrier concentration \(\Delta n\) is then obtained using the relation:

\[
\Delta n = \frac{\Delta \sigma}{qW(\mu_n + \mu_p)} \tag{3.2}
\]

where \(\mu_n\) and \(\mu_p\) are the electron and hole mobilities respectively, \(q\) the electronic charge and \(W\) the sample thickness. From the knowledge of the time dependence of the excess carrier concentration, two common measurement methods are used to determine the effective carrier lifetimes in silicon. The first one, referred to as transient photoconductance decay (PCD) measures the rate at which carriers recombine after a short excitation pulse. The lifetime is extracted via:

\[
\tau_{PCD} = -\frac{\Delta n}{\frac{d\Delta n}{dt}} \tag{3.3}
\]
where $\tau_{PCD}$ is the transient lifetime, $\Delta n$ is the excess carrier density and $d\Delta n/dt$ is the variation of excess carrier with time. The second method, quasi-steady-state photoconductance (QSSPC), measures the balance between generation and recombination when a quasi-steady state illumination is maintained. The generalized lifetime [76] is then extracted as:

$$\tau_{QSSPC} = \frac{\Delta n}{G_{QSSPC} - d\Delta n/dt}$$

(3.4)

where $\tau_{QSSPC}$ is the quasi-static lifetime and $G_{QSSPC}$ is the generation within the sample.

3.3.2 Microwave photoconductance decay lifetime measurements

An alternative method is the micro-wave photoconductance decay ($\mu$W-PCD) method. In this method, a laser injects carriers into the silicon wafer. Simultaneously an antenna generates microwaves that are reflected by free carriers in the sample. The reflected microwave signal is thus a measure of the excess carrier density. As previously, the lifetime is extracted as the time constant of the excess carrier decay with time, when a short transient light pulse is imposed on a longer steady-state bias light.

3.4 Carrier mobility

Carrier transport in silicon is caused by two specific physical mechanisms. It can be caused by an externally applied voltage. This transport mechanism is referred as drift. Carriers also move from regions where the carrier density is high to regions where the carrier density is low. This transport mechanism is referred as diffusion. Under the influence of an electric field, the electrostatic force causes the carrier to accelerate to reach a constant velocity $v$. It reaches a constant velocity because of the impurity scattering, electron-hole scattering and phonon scattering. The ratio of the velocity to the applied electric field is called the carrier mobility.
3.4.1 Carrier drift

The drift current for electrons and holes is:

\[ J_n = qnv_d = qn\mu_n\xi \]  \hspace{1cm} (3.5)

\[ J_p = qp\nu_d = qp\mu_p\xi \]  \hspace{1cm} (3.6)

The total current flow is just the sum of these two components [37]

\[ J = qn\mu_n\xi + qp\mu_p\xi \]  \hspace{1cm} (3.7)

3.4.2 Carrier diffusion

The random motion does not yield a net flow of carriers in a material with a uniform carrier density. However if an excess concentration of particles is present it will tend to dissipate itself and thus yield a carrier flow and produce a current. The flux of particles is proportional to the negative of the concentration gradient. As current is proportional to the flux of charged particles, the current density corresponding to a one-dimensional concentration gradient of electrons is [37]

\[ J_n = qD_n \frac{dn}{dx} \]  \hspace{1cm} (3.8)

Where \( D_n \) is a constant known as the diffusion constant. An analogous equation with an opposite sign for holes is:

\[ J_p = -qD_p \frac{dp}{dx} \]  \hspace{1cm} (3.9)

3.4.3 Einstein relations

Despite the fact that diffusion is caused by thermal energy while an externally applied field causes drift, drift and diffusion processes are related. The thermal velocity is defined as the mean free path to relaxation time ratio

\[ v_{th} = \frac{l}{\tau_{relaxation}} \]  \hspace{1cm} (3.10)
3.5 Majority carrier mobility measurements

Thermodynamics demonstrates that electrons carry a thermal energy which equals kT/2 for each degree of freedom. For a one-dimensional situation, this leads to

\[
\frac{kT}{2} = \frac{m^*v_{th}}{2} \tag{3.11}
\]

Combining those two relations

\[
lv_{th} = v_{th}^2\tau_{\text{relaxation}} = \frac{m^*v_{th}^2}{q} \cdot \frac{q\tau_{\text{relaxation}}}{m^*} = \frac{kT}{q}\mu \tag{3.12}
\]

The diffusion constant is defined as

\[
D = lv_{th} \tag{3.13}
\]

This leads to a relation between the drift and the diffusion processes, the connection between the diffusion and mobility constants. These equations are referred as the Einstein relations

\[
D_n = \frac{kT}{q}\mu_n \tag{3.14}
\]

\[
D_p = \frac{kT}{q}\mu_p \tag{3.15}
\]

3.5 Majority carrier mobility measurements

As seen in eq 3.7 the total current flow in the semiconductor is:

\[
J = qn\mu_n\xi + qp\mu_p\xi \tag{3.16}
\]

The conductivity of a material is defined as the current density divided by the applied electric field

\[
\sigma = \frac{J}{\xi} \tag{3.17}
\]

\[
\sigma = q(n\mu_n + p\mu_p) \tag{3.18}
\]
The resistivity is defined as the inverse of the conductivity

\[ \rho = \frac{1}{q(n\mu_n + p\mu_p)} \] (3.19)

Measuring both the resistivity and the carrier density of a sample allows the determination of the majority carrier mobility [37]. Several techniques to measure the dopant concentration are briefly explained below. Those techniques include Capacitance-Voltage (CV), Electrochemical Capacitance-Voltage (ECV), Hall, Low temperature Fourier Transform Infrared Spectroscopy (FTIR), Free Carrier Absorption (FCA), Glow Discharged Mass Spectroscopy (GDMS), Inductively Coupled Mass Spectroscopy (ICPMS), room temperature FTIR, Plasma Resonance and Rutherford Back Scattering.

3.5.1 Electrical measurements

3.5.1.1 Capacitance Voltage characteristics of Metal-Oxide-Semiconductor structures

As shown in section 1.4 capacitance voltage characteristics of Metal Oxide Semiconductor structures or Schottky diodes is a powerful tool to measure the dopant density. For a MOS structure the dopant density can be obtained combining the equations:

\[ p_0 = \frac{q}{2} \frac{\varepsilon_S x_0^2}{\varepsilon_{ox}^2 V_\delta} \] (3.20)

with \( \varepsilon_{ox} \) the \( SiO_2 \) dielectric constant, \( \varepsilon_S \) the silicon dielectric constant, \( x_0 \) the oxide thickness and \( V_\delta \):

\[ C = \frac{C_0}{\sqrt{1 + \frac{V_A}{V_\delta}}} \] (3.21)

with \( C_0 \) the oxide capacitance and \( V_A \) the applied voltage. Figure 3.1 shows the measured high frequency capacitance voltage curve on metal oxide semiconductor devices for 3 different doping densities. As seen in section 1.4 smaller doping leads to a larger depletion region which in turns leads to larger capacitance. From the curves above the doping densities can be calculated using equation 3.20 and 3.21. The re-
3.5 Majority carrier mobility measurements

Figure 3.1: Measured high frequency capacitance voltage curve on metal oxide semiconductor devices for 3 different doping densities.

resulting doping densities are in agreement with other measurements using free carrier absorption [77]. Therefore capacitance-voltage measurements on MOS structure is a very powerful technique for measuring the net doping in non-compensated silicon. However as shown in chapter 1 this is inaccurate in compensated silicon as an inversion layer forms during oxidation. One can avoid the formation of an inversion layer by depositing a dielectric at low temperature (for example less than 600°C). Alternatively, one can use another structure that is commonly used for capacitance voltage measurements. The Schottky diode is explored in the next section.

3.5.1.2 Capacitance Voltage of Schottky diodes and Electrochemical Capacitance Voltage measurements

As seen in section 1.4 the ECV technique is a CV measurement on a Schottky diode with the metallic contact being the electrolyte. Therefore the analysis is the same for both techniques. For a Schottky diode the dopant density is obtained as [37]:

\[
p_0 = \frac{-2}{q\epsilon s A^2 \frac{d(1/C^2)}{dV}}
\]  

(3.22)
with \( \varepsilon_S \) the silicon dielectric constant and \( A \) the gate area.

![Figure 3.2](image.png)

Figure 3.2: Influence of the bulk doping on the inverted square capacitance-voltage characteristics of Palladium Schottky diodes in n-type silicon.

Figure 3.2 shows the inverted square capacitance-voltage characteristics of Palladium Schottky diodes in n-type silicon and illustrates equation 3.22. For a steeper slope of the \( 1/C^2 \) vs V characteristics, a lower doping is obtained. Contrary to the MOS structure this technique can be easily used in compensated silicon since a thermal oxide is not required. However in order to obtain accurate results one must ensure that the diode created is not leaky and that the ideality factor of the diode formed is close to unity (as seen in section 1.4). The mobility obtained using this dopant density will be the conductivity mobility.

### 3.5.1.3 Hall effect

When a magnetic field is applied to a semiconductor perpendicular to the current flow direction, it produces an electric field perpendicular to the magnetic field and the current. In the semiconductor, the Lorentz force acting on the free carriers is described by \[ F = q(E + \vec{v} \times \vec{B}) \] (3.23)
Majority carrier mobility measurements

Since the carriers only flow along the x-direction, the net force is nul along the y and z direction, which leads to [37]

\[ F_y = q(E_y - v_z B_z) = 0 \]  \hspace{1cm} (3.24)

This leads to a relation between the applied magnetic field and the electric field in y, with \( E_y \) called the Hall field [37]

\[ E_y = v_z B_z = \frac{J_x}{q\mu_p} B_z \] \hspace{1cm} (3.25)

The Hall coefficient is defined as [37]

\[ R_h = \frac{E_y}{J_x B_z} \] \hspace{1cm} (3.26)

The angle between the current and the net electric field, the Hall angle is defined as [37]

\[ \tan(\theta) = \frac{E_y}{E_x} = B\mu_p \] \hspace{1cm} (3.27)

With [37]

\[ J_x = q\mu_p E_x tW \] \hspace{1cm} (3.28)

This leads to [37]

\[ p = \frac{1}{qR_h} \text{and} n = -\frac{1}{qR_h} \] \hspace{1cm} (3.29)

Figure 3.3 shows the variation of the Hall coefficient as a function of the sheet carrier concentration. The Hall coefficient drops with increasing carrier concentration. When both holes and electrons are present [37]

\[ R_h = \frac{(p - b^2 n) + (\mu_n B)^2 (p - n)}{q[(p + bn)^2 + (\mu_n B)^2 (p - n)^2]} \] \hspace{1cm} (3.30)

with \( b = \mu_n / \mu_p \). However in silicon at room temperature and with no illumination only one type of carrier is dominant therefore equation 3.29 is always valid. To take into account the energy dependant scattering mechanism the Hall scattering factor
Figure 3.3: Measured Hall coefficient and calculated sheet carrier concentration on different samples. The solid line represents equation 3.29

\[ r = \frac{\tau_{\text{scattering}}}{\tau_{\text{scattering}}} \]

with \( \tau_{\text{scattering}} \) the scattering time, is introduced [37]

\[ p = \frac{r}{qR_h} \]  \hspace{1cm} (3.31)

\[ n = -\frac{r}{qR_h} \]  \hspace{1cm} (3.32)

The Hall mobility is defined as [37]

\[ \mu_h = \frac{R_h}{\rho} \]  \hspace{1cm} (3.33)

The mobility obtained from this dopant density will be the Hall mobility. The relationship between the Hall mobility and the conductivity mobility is defined as [37]

\[ \mu_h = r\mu_p \text{ and } \mu_h = r\mu_n \]  \hspace{1cm} (3.34)

Note that the mobility obtained from the Hall effect can be affected by heterogeneous distribution of dopants. This is particularly important in compensated silicon where large spatial variation in net doping have been observed [78].
3.5.1.4 Magnetoresistance

The resistivity of a semiconductor increases when the sample is placed into a magnetic field, this physical mechanism is called the physical magnetoresistance effect (PMR). The resistance of a semiconductor is also influenced by magnetic field. The magnetic field causes the path of the particle to deviate from a straight line raising the sample resistance. This depends on the sample geometry and is known as the geometrical magnetoresistance (GMR). Magnetoresistance measurements are very interesting for high mobility samples but not interesting for measurement in silicon as the PMR and GMR are negligibly small in silicon [37]. Therefore this technique is not used in this work.

3.5.1.5 Photoluminescence spectroscopy

The concentration of individual dopant species can also be measured using low temperature photoluminescence spectroscopy (PL) measurements. The sample is cooled to temperature near liquid helium (T=4.2K) [37]. The sample is then excited with a laser with energy greater than the bandgap of silicon which generates excess carriers. The excess carriers recombine in radiative or nonradiative recombination mechanisms. A free electron (hole) recombining with a neutral acceptor (donor) emits a photon. The energy of the photon emitted depends on the impurity species. The magnitude of PL signal measured is proportional to the impurity density and therefore allows for measurements of both acceptor and donor species [37].

3.5.2 Optical measurements

3.5.2.1 Free Carrier Absorption

A photon of energy lower than the bandgap does not generate an electron-hole pair, it can however excite free carriers [37]. This is called free carrier absorption. A calibration factor can be obtained to directly link the height of the absorption baseline and the net doping of the sample [37; 77; 79]. Similarly to previous work we assumed a linear relationship between the normalized absorbance and the doping [77]. Figure 3.4 shows dependence of the free carrier absorbance on the doping in 2µm thick
silicon samples. The absorbance is measured at a wavelength of 2400nm. Using the calibration allows us to determine the doping of other samples by measuring their absorbance at 2400nm, provided their thicknesses and surfaces are the same as the reference samples.

### 3.5.2.2 Fourier Transform Infrared Spectroscopy

Using an infrared pulse, an electron can be excited from its donor states into excited states. These transitions in turn produce very sharp absorption in the transmission spectrum. If properly calibrated the height of the peak can be directly related to the concentration of the element (boron, phosphorus...). At low temperature the peaks are very sharp and easy to see. However at room temperature, the peaks are very broad (as most of the electrons are excited) and hard to distinguish from the background free carrier absorption as seen in the previous section. Therefore this technique works best at low temperature. Due to its technical complexity this technique is not used in this work.
3.5.3 Chemical doping measurements

Secondary Ion Mass Spectroscopy (SIMS) is a powerful tool to measure dopants in silicon as shown in section 1.3. SIMS dopant density is obtained by sputtering the samples and measuring the secondary ion ejected from the sample. SIMS is used in this work especially as it allows one to measure each dopant concentration individually.

Another method commonly used is Glow Discharged Mass Spectroscopy (GDMS). In this technique the sample is the cathode of a plasma. Ions are accelerated towards the surface of the sample and erode the sample. The surface atoms are subsequently ionized and analysed using a mass spectrometer. Inductively coupled plasma spectroscopy (ICPMS) uses a plasma to ionize a material ejected from the sample, with the ions subsequently analysed in a mass spectrometer. Contrary to electrical and optical techniques, chemical techniques measure the total dopant density and not the electrically active impurity density.

3.5.4 Sensitivity of the doping measurements

![Sensitivity of different techniques in measuring dopant concentration in silicon](image)

Figure 3.5: Sensitivity of different techniques in measuring dopant concentration in silicon[17; 18].

Figure 3.5 shows the sensitivity of different techniques in measuring dopant con-
centration [17; 18]. The range of bulk doping commonly used in solar cells is displayed in the filled rectangle. Out of all the available techniques, CV, ECV, Hall, Low temperature FTIR, FCA and GDMS are the most sensitive techniques for bulk measurements and therefore the most relevant for this thesis. To detect dopant using room temperature FTIR, Plasma Resonance or RBS, one needs much higher dopant concentrations.

3.5.5 Resistivity measurements

In order to obtain the majority carrier mobility one combines the dopant measurements and a resistivity measurement.

\[ \mu_p = \frac{1}{\rho_q p} \]  

(3.35)

Resistivity measurements are usually done using the four point probe technique. In this technique the resistance of the sample is measured as the voltage drop on two contacts when the current is applied to two other contacts. This technique requires correction factors to take into account the geometry of the sample but does not require any calibration.

Another method to measure the resistivity is to couple inductively or capacitively the sample to a measurement apparatus. The sample will thus change the quality factor of the measurement apparatus. When calibrated this allows a direct conversion between quality factor and resistivity. In this thesis this method is performed using the commercially available Sinton lifetime testers [80]. Figure 3.6 shows the sheet resistance \( R_\square \) as a function of the coil balance voltage. Using the above calibration one can determine the sheet resistance of any wafers by measuring the balance voltage of the coil. The resistivity is subsequently obtained as \( \rho = R_\square \times W \).

3.6 Minority carrier mobility measurement

3.6.1 Time of flight drift mobility

The aim of this experiment is the determination of the minority carrier mobility. It was first demonstrated in the Haynes-Shockley experiment. Figure 3.7 shows the Haynes-
§3.6 Minority carrier mobility measurement

Figure 3.6: Sheet resistance as a function of the coil balance voltage.

![Graph showing sheet resistance as a function of coil balance voltage.]

Figure 3.7: Haynes-Shockley experiment, a pulse of carriers is injected in a semiconductor bar. The pulse drifts due to the electric field and is collected at a distance $d$ and time $t$ from the start.

Shockley experiment, a pulse of carriers is injected in a semiconductor bar. The pulse drifts due to the electric field and is collected at a distance $d$ and time $t$ from the start. The drift velocity is then:

$$v = \frac{d}{t_d}$$  \hspace{1cm} (3.36)
The delay time $t_d$ is determined by measuring the output pulses versus time for varying amplitude input pulses and extrapolating to zero injection. With the velocity given by [37]

$$v = \mu_n \xi$$  \hspace{1cm} (3.37)

The drift mobility (or conductivity mobility) is then [37]

$$\mu_n = \frac{d}{t_d \xi}$$  \hspace{1cm} (3.38)

The time of flight method allows the determination of the minority carrier and majority carrier mobility. However it requires relatively high carrier lifetime as the injected pulse must not recombine before being collected. Moreover the sample geometry is not convenient as one must use relatively thick samples. Hence our attempts at measuring the minority carrier mobility have been unsuccessful using this technique. There are however alternative techniques that can be used, one of them is presented in the next section.

### 3.6.2 Sproul method

This method only requires the knowledge of two quantities, the effective lifetime $\tau_{\text{eff}}$ and the thickness $W$ of the sample[81]. Due to the very high surface recombination velocity the lifetime is dominated in low injection by the diffusion rate of the minority carriers to the surface. For the case of an infinite surface recombination velocity and uniformly generated carriers, the relation between the effective lifetime ($\tau_{\text{eff}}$), the diffusion coefficient ($D_n$), the sample thickness ($W$) and bulk lifetime ($\tau_b$) is[81]:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \left(\frac{\pi}{W}\right)^2 D_n$$  \hspace{1cm} (3.39)

Knowing the thickness and the effective lifetime one can therefore deduce the electron diffusion coefficient. Because some of our samples have quite low resistivity, with low bulk lifetime, the diffusion constant was determined from the slope of a plot of $1/\tau_{\text{eff}}$ vs $(\pi/W)^2$ using samples of different thickness, as explained by Sproul et al[81]. This allows the impact of the bulk lifetime to be eliminated from the analysis. Figure 3.8
Figure 3.8: $1/\tau_{\text{eff}}$ vs $(\pi/W)^2$ showing a steeper slope therefore a larger diffusivity for the sample with lower doping.

shows the characteristics $1/\tau_{\text{eff}}$ vs $(\pi/W)^2$ for two samples with different doping. The sample with lower doping has higher minority carrier mobility.

### 3.7 Sum of majority and minority carrier measurement

#### 3.7.1 Dannhauser method

This method uses a p+pn+ structure. When carriers are injected through an infrared pulse, a charge becomes stored in the nearly intrinsic middle region [19; 82; 73; 74]. Figure 3.9 shows the increased carrier concentration in this region. The mobility is then obtained from:

$$\mu_{\text{sum}} = \frac{i_p(2d)^2}{QV} \frac{d}{L} \quad (3.40)$$

with $i_p$ the hole current, 2d the width of the intrinsic region, Q the charge in the intrinsic region, V the impulse voltage and L the diffusion length. This means that with higher mobility less charge is stored in the intrinsic region.
3.7.2 Neuhaus method

This method combines the use of quasi-steady-state photoconductance measurements (QSSPC) and quasi-steady-state open circuit voltage measurements (QSS-Voc). In both methods, carriers are generated in the bulk using a slowly decaying flash. The carriers generated increase the conductivity of the sample. In the QSSPC technique, this is then measured by an inductive coil. The decay of the carriers generated is then observed as the decay of the excess conductance. The photoconductance $\Delta \sigma$ is:

$$\Delta \sigma = qW\Delta n_{av}\mu_{sum}$$  \hspace{1cm} (3.41)$$

with $q$ the electric charge, $W$ the wafer thickness and $\mu_{sum}$ the mobility sum. In the QSS-Voc technique the open circuit voltage generated by the carriers is monitored. The open circuit voltage is directly dependent on the carrier concentration at the edge of the space charge region as

$$(n_0 + \Delta n_{scr})(p_0 + \Delta n_{scr}) = n_{i,eff}^2 \exp\left(\frac{qV_{OC}}{kT}\right)$$  \hspace{1cm} (3.42)$$
By combining the QSSPC and the QSS-Voc method and using eq 3.41 and eq 3.42 one can obtain the mobility sum as a function of excess carrier density. This method requires a complete solar cell and is therefore not used in this work. It also requires that the excess carrier density at the edge of the space charge region is equal to the average excess carrier density in the base, and so is only applicable with high bulk lifetimes and good surface passivation.

3.8 A new technique to determine the mobility sum in silicon

3.8.1 Introduction

As seen above, Dannhauser and Krausse used a combination of infrared radiation and voltage measurements across a pin diode to extract the injection dependence of the mobility sum [73; 74]. Similarly, Neuhaus et al. used a combination of quasi-steady-state photoconductance (QSS-PC) and quasi-steady-state open-circuit-voltage (QSS-Voc) measurements on a solar cell to determine the injection dependence of the mobility sum [83]. However, both of these methods require a complicated structure and need contacting. In this section we propose and demonstrate a new technique based on contactless photoconductance measurements.

3.8.2 Theoretical principles

As seen above, two common measurement methods are used to determine effective carrier lifetimes in silicon. The first one, referred to as transient photoconductance decay (PCD) measures the rate at which carriers recombine after a short excitation pulse. The lifetime is extracted via:

\[ \tau_{PCD} = -\frac{\Delta n}{\frac{d\Delta n}{dt}} \]  

(3.43)

where \( \tau_{PCD} \) is the transient lifetime, \( \Delta n \) is the excess carrier density and \( \frac{d\Delta n}{dt} \) is the variation of excess carrier density with time. The second method, QSSPC, measures the balance between generation and recombination when a quasi-steady state
illumination is applied. The generalized lifetime [76] is then extracted as:

\[ \tau_{QSSPC} = \frac{\Delta n}{G_{QSSPC} - \frac{d\Delta n}{dt}} \]  

(3.44)

where \( \tau_{QSSPC} \) is the quasi-static lifetime and \( G_{QSSPC} \) is the generation rate within the sample. At this point it is interesting to note that the transient technique requires samples with lifetimes significantly longer than the characteristic decay of the excitation flash. In our case this corresponds to lifetimes higher than 100 \( \mu s \). If a light source with shorter cut-off times is used, this value can be reduced, and lower lifetime samples can be measured with the PCD technique. However, it should also be kept in mind that samples with low effective lifetimes, whether due to either surface or bulk recombination, can easily result in non-uniform carrier profiles throughout the wafer thickness. In such cases, the transient lifetime and the quasi-static lifetime are not expected to be equal [84; 85]. The method described here can only be applied when these two lifetimes are equivalent, which will be the case when the carrier profiles remain approximately uniform during the transient decay. This in turn will be true when the minority carrier diffusion length is greater than the sample thickness, and the initial rapid transient modes are excluded from the analysis. These conditions were satisfied for our samples. Assuming that at the same excess conductance the transient lifetime (\( \tau_{PCD} \)) and quasi-steady state lifetime (\( \tau_{QSSPC} \)) are indeed equal, we have:

\[ \tau_{PCD}(\Delta \sigma) = \tau_{QSSPC}(\Delta \sigma) \]  

(3.45)

\[ \frac{\Delta n}{d\Delta n/dt} = \frac{d\Delta n}{dt} - G_{QSSPC} \]  

(3.46)

The excess carrier concentration \( \Delta n \) is related to the excess conductance \( \Delta \sigma \) by the relation:

\[ \Delta n = \frac{\Delta \sigma}{qW(\mu_n + \mu_p)} \]  

(3.47)
where \( \mu_n \) and \( \mu_p \) the electron and hole mobility respectively, \( q \) the electronic charge and \( W \) the sample thickness. By manipulating these expressions one obtains:

\[
(qW(G_{QSSPC})(\Delta\sigma)(\mu_n + \mu_p)^2
+ \left( \frac{d\Delta\sigma_{PCD}}{dt} + \frac{d\Delta\sigma_{QSSPC}}{dt} \right)(\Delta\sigma)(\mu_n + \mu_p)
+ (\Delta\sigma_{QSSPC}\frac{d(\mu_n + \mu_p)_{QSSPC}}{dt})(\Delta\sigma)
-(\Delta\sigma_{PCD}\frac{d(\mu_n + \mu_p)_{PCD}}{dt})(\Delta\sigma) = 0
\]

(3.48)

However, as the mobility varies only very slightly compared to the other time-dependent quantities, one can neglect the final two terms on the left hand side. One can thus easily extract the mobility sum \( (\mu_n + \mu_p) \) as:

\[
(\mu_n + \mu_p) = \frac{1}{qWG_{QSSPC}} \left( \frac{d\Delta\sigma_{QSSPC}}{dt} - \frac{d\Delta\sigma_{PCD}}{dt} \right)
\]

(3.49)

where \( q \) is the electronic charge, \( W \) is the sample thickness and \( \frac{d\Delta\sigma_{QSSPC}}{dt} \) and \( \frac{d\Delta\sigma_{PCD}}{dt} \) are the variation of conductance with time for the quasi-steady-state and transient excitation respectively.

Figure 3.10 shows the dependence of the above quantities with excess conductance. By comparing the variation with time of the excess conductance (figure 3.10a) and the generation rate (figure 3.10b) for a transient and quasi-steady-state measurement one can thus obtain the excess conductance dependent mobility sum (figure 3.10c). This mobility sum is in turn used to compute the excess carrier density from the excess conductance using equation 5. We estimated an uncertainty of 3\% in the measurement of the generation rate \( G_{QSSPC} \) and an uncertainty of 5\% in the measurement of the conductance \( \Delta\sigma \) [86]. In Fig. 1c, at an excess conductance of \( \Delta\sigma = 7 \times 10^{-2} \Omega^{-1} cm^{-1} \), the uncertainty in the calculated mobility sum is 10\%. However at a lower excess conductance of \( \Delta\sigma = 1 \times 10^{-2} \Omega^{-1} cm^{-1} \), the error increases to 12\%. We found that the mobility sum can be obtained with an uncertainty of 9-14\% above this excess conductance.
3.8.3 Experimental methods

3.8.3.1 Transient and QSSPC measurements

The new method is based on combining quasi-steady-state PhotoConductance (QSSPC) [80] and transient photoconductance decay (PCD) lifetime measurements. The carrier lifetimes measured with such methods rely on a calibrated coil to measure.
the excess conductance and a reference solar cell to measure the generation rate. To obtain a more uniform carrier generation profile, an infrared filter was used to cut off wavelengths below 800 nm. Note however that the large effective lifetimes ensure that the excess carrier density is almost uniform throughout the samples anyway. In order to measure the simultaneous temperature and injection dependence of the mobility we used a purpose built, temperature controlled inductive coil photoconductance instrument from Sinton Instruments[87]. The samples were prepared by saw damage removal and RCA cleaning, followed by surface passivation at 400°C with plasma-enhanced chemical vapour-deposited silicon nitride films. As described above, the data analysis requires the calculation of a derivative with respect to time of the excess conductance signal. Therefore, any noise in this signal will be dramatically amplified. To reduce noise, each transient and QSSPC measurement is thus averaged 60 times before being processed. Such carrier injection can lead to change in the state of metastable defects (activation of boron-oxygen defect, dissociation of iron-boron pairs) which would affect the carrier lifetime and in turn the measurement. However in our samples, repeated measurements showed that those effects were negligible. Another important point is that the QSSPC technique is sensitive to the optical properties of the sample. The QSSPC measurement is usually corrected using an optical scaling factor $f_s$[88].

### 3.8.3.2 Determination of the optical factor

The optical factor can be obtained through self-calibration of the generation in an intermediate photoconductance regime [88] or through direct comparison of the optical properties of the sample and the reference cell used in the lifetime tester[89; 90]. The optical factor will influence the generation rate within the sample. If inaccurate, the whole mobility curve will shift up or down (equation 8), it is thus extremely important to accurately determine the optical factor. We measured the absorption in our wafers using a Perkin-Elmer spectrophotometer. Using the measured absorption we determined the effective optical transmission as described in[90].

Figure 3.11a shows the incident photon flux density as a function of wavelength.
Figure 3.11: (a) Incident photon flux spectral density and photon flux spectral density absorbed in the sample. The ratio of those two integrated quantities will determine the effective optical transmission. (b) Incident photon flux spectral density absorbed into the reference solar cell and AM1.5 photon flux spectral density absorbed into the reference solar cell. The ratio of those two integrated quantities will determine the spectral correction factor.

Also shown is the photon flux spectral density absorbed into the wafer. Using the ratio of (integrated photon density absorbed into the wafer)/( integrated incident photon density) we then determine the effective optical transmission[90]. The spectrum of the unfiltered flash is significantly different from AM1.5, even though the calibration of the reference solar cell is performed under AM1.5 conditions. This difference is made even larger when the flash is filtered by an infrared filter (figure 3.11b)). We thus calculate a spectral correction factor to account for the spectral difference between the AM1.5 spectrum and the filtered flash spectrum as proposed in [89] using the ratio of (integrated AM1.5 photon flux density absorbed into the reference solar...
Finally we combined the effective optical transmission and the spectral correction factor to determine the optical factor. In our wafers coated with SiN, when using an infrared filter (800nm cut-off), we found the optical factor to lie between 0.68 to 0.9 depending mainly on the thickness of the wafer used and the variation in the optical properties of the anti-reflection coating.

Figure 3.12: Measured injection dependence of the mobility sum and impact of the optical factor. An overestimation of the optical factor leads to an underestimation of the mobility sum. The method thus greatly relies on a precise measurement of the optical factor in order to give accurate results.

3.8.4 Results and discussions

3.8.4.1 Accuracy of the method

To demonstrate the accuracy of the method, the mobility sum was measured in samples with similar resistivities (100-1000 $\Omega\cdot$cm, 0.90 $\Omega\cdot$cm p-type) to the sample used by Dannhauser (1000-3000 $\Omega\cdot$cm p-type) [73] and the samples used by Neuhaus et al.
Figure 3.13: (a) Measured injection dependence of the mobility sum in a 100-1000 Ω.cm p-type silicon wafer. Also shown is the data of Dannhauser. (b) Measured injection dependence of the mobility sum in a 0.90 Ω.cm p-type silicon wafer. The data of Neuhaus is also shown. The lines are from the models of Dorkel-Leturcq, Klaassen and Dannhauser.

Within error the measured mobility and the data from Dannhauser (figure 3.13a) and Neuhaus (figure 3.13b) are in agreement. This confirms that the method is accurate in this excess carrier density range. The measured data also fits very well to the models of Dannhauser-Krausse and Klaassen. The model of Dorkel-Leturcq lies a little below the measured values at higher doping densities. Although the measured mobility sum aligns with the models relatively well at medium injection (above $1 \times 10^{15} cm^{-3}$), at lower injection the measurement becomes quite inaccurate. This is due to the fact that the derivatives of the quasi static and transient conductances become very similar thus
the uncertainty in their difference becomes greater, as mentioned above. Therefore, a small uncertainty in one or the other leads to great uncertainties in the calculated mobility (equation 3.49). Moreover the signal/noise ratio of the photoconductance signal itself decreases at low injection, leading to greater errors in the measured mobility. In addition, the mobility is also inaccurate at high injection due to the effective lifetime being reduced (Auger recombination), leading to difficulties in making accurate transient measurements, and potentially causing non-uniform carrier profiles.

### 3.8.4.2 Measuring the influence of dopant density

![Figure 3.14](image)

Figure 3.14: Doping dependence of the mobility sum in n-type silicon. The lines represent the models of Dannhauser, Dorkel-Leturcq and Klaassen.

Figure 3.14 shows the doping dependence of the mobility sum in n-type silicon. The lines represent the models of Dannhauser, Dorkel-Leturcq and Klaassen. We clearly see the increasing influence of ionized impurity scattering on the mobility as the doping increases. This mobility is measured at an injection level of $5 \times 10^{15} cm^{-3}$. Within error we obtain an excellent agreement with the mobility models.
3.8.4.3 Measuring the influence of temperature

An important application of this method is to study the impact of temperature on the carrier mobility sum. Using a temperature controlled inductive coil photoconductance device [87] one can obtain the simultaneous temperature and injection dependence of the mobility.

![Figure 3.15: Temperature dependence of the mobility sum in a 0.55 Ω.cm n-type silicon wafer. The lines represent the models of Dorkel-Leturcq and Klaassen.](image)

Figure 3.15 shows the temperature dependence of the mobility sum at an injection level of $5 \times 10^{15} \text{cm}^{-3}$. At low temperature (153 K) the lattice scattering is very low, leading to a high mobility sum of around $2500 \text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$. At very high temperature (513 K) lattice scattering contributes to a drastic reduction of the mobility sum with an overall mobility of around $485 \text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$. It is interesting to compare the temperature dependence of the mobility sum to mobility models at an injection level of $5 \times 10^{15} \text{cm}^{-3}$. The models of Klaassen and Dorkel-Leturcq are used as a comparison, since the model of Dannhauser does not include temperature dependence. Both Klaassen’s and Dorkel-Leturcq’s models are in relatively good agreement with the experimental data at high temperature. For low temperatures, Klaassen’s model seems to overestimate the mobility sum. Discrepancies between Klaassen’s model and experimental data have been observed before at low (<200 K) or high (>400 K)
temperatures[92]. However, the validity of Klaassen’s model when both injection and temperature vary has not been assessed before.

3.8.4.4 Measuring the influence of compensation

Another important application of this method is to measure the impact of dopant compensation on the carrier mobility sum. Compensation doping has been found to be an efficient way to control ingot resistivity when using solar-grade silicon feedstocks[93; 40; 22]. Carrier recombination, being driven by the net doping rather than the sum of the dopant concentrations, can be improved by compensation[41]. However, the mobility is driven by the sum of the dopant concentrations rather than the net doping[94]. At similar resistivity, a significant reduction in mobility has been observed in compensated silicon[95; 96; 54].

Figure 3.16: Measured injection dependence of the mobility sum in 0.55 Ω.cm non-compensated and a 0.56 Ω.cm compensated silicon sample. The line represents the model of Klaassen.

Figure 3.16 shows the mobility sum reduction due to compensation in two 0.55-0.56 Ω.cm n-type silicon samples, one of which was non-compensated \( N_D = 5 \times 10^{15} cm^{-3} \), and the other compensated \( N_D = 5.3 \times 10^{16} cm^{-3}, N_A = 5 \times 10^{16} cm^{-3} \). Even though both samples have similar resistivities, the compensated sample has more ionized impurities, therefore lower mobility. Note that in this measurement
the mobility measured for the compensated samples is higher than the simulated mobility. However more data is needed in order to assess the accuracy of this mobility model in compensated silicon.

3.9 Conclusion

In this chapter two minority carrier lifetime measurement techniques have been introduced. Using these techniques one can measure the influence of dopant and defect densities on the minority carrier lifetime as we will do in chapter 4 and 5.

Several mobility measurement techniques have also been summarised. They allow the measurement of the majority, minority and the sum of the carrier mobilities. These techniques allow one to gain insight on the influence of dopants, injection and temperature on the carrier mobility. Some of these techniques are well suited to measure the mobility in compensated silicon and will be extensively used in chapter 4 to understand the impact of compensation on the carrier mobility. Focus will be placed on Hall measurements and CV/ECV measurements in order to measure the majority carrier mobility while for the minority carrier mobility the Sproul technique will be used. SIMS measurements will in addition be used to monitor the concentration of each dopant species.

In this chapter we have also demonstrated the potential of a novel contactless method to measure the mobility sum in silicon wafers, based on combining transient and quasi-static photoconductance measurements. To be accurate this method must be used in combination with a spectrophotometer in order to measure the optical properties of the sample used. This method is valid at medium injection where the lifetime and the photoconductance signal/noise ratio both remain high. We show that this method can measure the impact of dopant density, compensation, injection level and temperature on the mobility sum. It is limited to samples with relatively high effective lifetime and thus requires surface passivation, to ensure uniform carrier profiles throughout the sample thickness. However through the use of an infrared LED array for example, this technique could measure samples with lower lifetime. This allows us to measure for the first time, the mobility sum reduction due to temperature
and compensation.
Review of lifetime and mobility measurement techniques in silicon
As seen in chapter 2, an important consequence of the higher impurity concentration in compensated silicon is a lower carrier mobility in such material. This has several consequences concerning the use of compensated silicon for solar cells. Firstly, many measurement techniques rely on mobility models to analyse data under various temperature and injection levels. Those measurement techniques may become less accurate when measuring compensated silicon if the mobility models were not built to take compensation into account. Secondly, the reduced minority carrier mobility will act to reduce the efficiency of solar cells. Until this minority carrier mobility is well characterised, the impact of compensation on the solar cell efficiency remains difficult to predict. The majority carrier mobility reduction may also influence the solar cell efficiency through increased series resistance. Thirdly, the traditional use of resistivity measurements to determine the net doping of a wafer cannot be applied accurately for compensated silicon, due to the majority carrier mobility reduction. The use of Hall measurements to determine the net doping is also uncertain as the Hall Factor could be affected by compensation. The problem of mobility in compensated silicon is thus not straightforward, and experimental data for both majority and minority carrier mobility are needed to ascertain the degree of impact of the various scattering mechanisms.
4.1 Lifetime

4.1.1 Radiative and Auger recombination

The intrinsic lifetime has been shown to essentially depend on the net doping previously \[43; 39; 41\]. Figure 4.1(a) shows the measured doping dependence of the intrinsic lifetime in compensated silicon. The samples had boron concentrations between \(N_A = 5.0 \times 10^{16} cm^{-3}\) and \(N_A = 6.5 \times 10^{16} cm^{-3}\) and phosphorus concentrations between \(N_D = 5.0 \times 10^{16} cm^{-3}\) and \(N_D = 9.9 \times 10^{16} cm^{-3}\). The lifetime fits with the theoretical model when plotted against the net doping (net doping between \(n_0 = 5.7 \times 10^{15} cm^{-3}\) and \(n_0 = 4.0 \times 10^{16} cm^{-3}\)). As expected from the theory the lifetime depends on the net doping and not the donor or acceptor concentration. Figure 4.1(b) shows the measured and simulated injection dependence of the lifetime in two compensated n-type silicon samples. The model of Kerr and Cuevas was used \[43\]. The lifetime of the samples with high net doping is close to the Auger lifetime. This confirms previous data showing that even though compensated silicon contains more impurities, its lifetime is similar to a non-compensated sample of
the same net doping. However, the lifetime of the samples with lower net doping (higher compensation ratio) is below the Auger limit. This could potentially reflect recombination through shallow dopants as seen in other studies [54]. Note that these lifetimes are measured prior to activation of the boron-oxygen defect, which reduces the lifetime significantly as described in chapter 5.

4.2 Mobility

4.2.1 Introduction

In this section data on the majority and minority carrier mobility in silicon is summarised. This allows us to determine the best mobility model for compensated silicon. Data on mobility in compensated silicon are reviewed.

The majority hole conductivity mobility, which is essential to deduce the bulk net doping $p_0$ from resistivity $\rho$ measurements, is measured for different acceptor and donor concentrations. We then experimentally demonstrate the potential increased scattering cross section in compensated silicon at low net doping.

As solar cells are minority carrier devices, it is also of fundamental importance to assess the minority carrier mobility in compensated silicon. Diffusion lengths have been measured in compensated silicon before [39; 97; 93; 98] but until now, no direct experimental data concerning minority electron mobility in compensated p-type silicon has been measured. Such data are presented here.

A common method for measuring the majority carrier mobility is the Hall method. Unfortunately, the Hall method requires knowledge of the Hall factor in order to convert the Hall mobility into the conductivity mobility, which is the parameter of interest for solar cell operation. The Hall Factor has been measured before in lightly doped silicon highly compensated with thermal donors [71]. In our study, the Hall factor is determined by a direct comparison between independent measurements of the Hall mobility and conductivity mobility on the same samples (boron and phosphorus doped).

Finally, it is also of interest for further simulation and characterization to know if conventional mobility models such as Klaassen’s[58; 59] model can be used safely for
Experimental investigation of the carrier lifetime and mobility

4.2.2 Review of the carrier mobility in silicon

4.2.2.1 Majority carrier mobility in silicon

The majority carrier mobility has been measured by Thurber as a function of the net doping in p-type and n-type silicon [99]. The mobility has been measured for both boron and phosphorus dopants. Note that the mobility measurements are made at a certain carrier concentration and not doping concentration. Therefore one must calculate the fraction of ionized dopant before calculating the mobility using the model. This is especially relevant for doping above $1 \times 10^{17} \text{cm}^{-3}$ and at low temperature. Figure 4.2 plots the majority electron and hole mobility as a function of the net doping as measured by Thurber. This data is now used as the standard for conversion between dopant density and resistivity in silicon.
4.2 Mobility

Figure 4.3: (a) Minority hole mobility as a function of the net doping in n-type silicon and (b) minority electron mobility as a function of the net doping in p-type silicon measured by Sproul et al. and Dziewior et al. The data is compared to the model of Klaassen, Reggiani, Arora and Dorkel-Leturcq.

4.2.2.2 Modelling the majority carrier mobility in silicon

Figure 4.2 plots the simulated mobility as a function of the ionized dopant concentration for n- and p-type silicon. The models of Klaassen [58; 59], Reggiani [92], Arora [100] and Dorkel-Leturcq [91] are used. The models of Klaassen and Reggiani are in very good agreement with the data of Thurber et al. On the other hand, the model of Dorkel and Leturcq is in disagreement with the measured majority hole mobility. The model of Arora gives a slight error in the majority electron mobility in n-type silicon.

4.2.2.3 Minority carrier mobility in silicon

In the literature, data on minority carrier mobility in silicon is more scattered. Figure 4.3 shows the minority carrier mobility as a function of dopant density in p and n-type silicon as measured by Sproul et al. [81] and Dziewior and Silber [101].
4.2.2.4 Modelling the minority carrier mobility in silicon

Most mobility models only allow for the calculation of the majority carrier mobility. This is however inaccurate as minority carrier mobilities are limited both by ionized impurity scattering and electron-hole scattering. Therefore one needs to take this into account properly. Klaassen’s model takes into account ionized impurity scattering and electron-hole scattering and as such is more suited to determine minority carrier mobilities. Moreover Klaassen’s model takes into account the reduced scattering cross section for positive-positive or negative-negative scattering. This is important for minority carriers as they have the same charge as the main dopants.

4.2.2.5 Carrier mobility in compensated silicon

In compensated silicon, measurements using Free Carrier Absorption [40; 102], Capacitance Voltage [71; 103; 104], Glow Discharge Mass Spectroscopy [39], or the Hall method [71; 105; 97] have shown that the majority carrier mobility in silicon is strongly affected by compensation. Other measurements in compensated germanium have shown a similar trend for majority carriers [57; 56] and minority carriers [106].

4.2.2.6 Modelling the carrier mobility in compensated silicon

A review of the mobility in compensated silicon by Cuevas et al. [107] and data of Fourmond et al. [102] show that the mobility diverges from the mobility model of Klaassen for increasing compensation ratio. Modelling the carrier mobility in silicon is not trivial as one needs to take into account the influence of donors and acceptor simultaneously. Their effect is however not similar on an electron or a hole as they interact repulsively and attractively with the free carrier.

Figure 4.4 plots the simulated mobility as a function of the compensation ratio \( R_C = (N_A + N_D)/(N_A - N_D) \) for different acceptor concentrations. The models of Klaassen [58; 59], Reggiani [92], Arora [100] and Dorkel-Leturcq [91] are used. Even for non-compensated silicon \( (R_C=1) \), Arora’s model and Dorkel-Leturcq’s model are inaccurate. The variation induced by compensation is also very strong.

This is due to the very simple formulation of those models. Indeed they do not
take into account the separate influence of acceptor and donor but only the influence of the total impurity concentration \((N_A + N_D)\). They also implicitly assume that the free carrier concentration is equal to the total dopant concentration, which is not true in compensated silicon. This applies to other models such as Caughey-Thomas [108], Thurber [109; 110], and Masetti [111]. On the other hand, Klassen’s model and Reggiani’s model agree well for non-compensated silicon, but Reggiani’s model seems to be less influenced by compensation.

Both Klaassen’s model and Reggiani’s model are based on the empirical model of Masetti et al. which itself is based on the data of Thurber et al. They introduce a temperature dependence of the doping related parameters and most importantly they take into account the different scattering cross sections of acceptors and donors. Reggiani’s model fits the experimental data well on non-compensated silicon over a wider range of temperature than Klaassen’s model [92]. Nevertheless at room temperature Klaassen’s model has been shown to be more precise for non-compensated silicon [92]. Moreover Klaassen’s model takes into account electron-hole scattering as well as screening mechanisms. By taking those mechanisms into account Klaassen’s model is thus, in principle, more suited for mobility modelling in compensated si-
icon, even if it makes little difference in practice. Klaassen’s model is based upon non-compensated data, where the acceptor concentration and the majority carrier concentration are equal, in which case it is difficult to differentiate between the effect of acceptors and the effect of holes on the electrons. Therefore Klaassen’s model could potentially overestimate or underestimate electron-hole scattering and screening effects.

4.2.2.7 Mobility sum in silicon

![Figure 4.5: Sum of the electron and hole mobility as a function of compensation ratio with Klaassen model and Dannhauser and Krause model.](image)

Another important implication of altered mobilities in compensated silicon is that many common characterization techniques are set up to measure uncompensated samples. What is the impact of compensation on such characterization techniques? In the Quasi-Steady State Photoconductance technique (QSSPC) for example, the net doping is needed as an input parameter [84]. The mobility model of Dannhauser and Krause [73; 74] is then used to simulate the sum of the electron and hole mobility for different injection levels. Figure 4.5 shows the model of Dannhauser and Krause with the net doping \((N_A - N_D)\) and the dopant sum \((N_A + N_D)\) as input parameter compared to Klaassen’s model. Using the net dopant density as the input parameter
for this model will inevitably yield an overestimation of the carrier mobility, and an underestimation of the lifetime. It is thus necessary to input the dopant sum, as a basic approximation, instead of the resistivity/net doping, in order to obtain reasonable carrier lifetimes.

4.2.3 Majority carrier conductivity mobility

4.2.3.1 Experimental method

The net doping was measured by Electrochemical Capacitance Voltage (ECV) and Free Carrier Absorption (FCA) as explained in chapter 3. The acceptor concentrations $N_A$ were determined using a method based on the association time constant of iron-boron pairs [31]. The donor concentrations $N_D$ were determined using net dopant densities combined with acceptor density values, via $N_D = N_A - p_0$. All the samples were surface etched to remove saw damage. The samples were cut in $1 \times 1\,cm^2$ pieces using a dicing saw. Aluminium contacts were then evaporated at each corner of the samples according to the Van der Pauw structure [112]. The resistivity ($\rho$) was measured using a four point probe setup on the four aluminium contacts. The conductivity carrier concentration ($p_{0,C}$) was then measured on the same samples using a CPV21 ECV profiler.

![Doping profile of two n-type silicon wafers.](image)
Experimental investigation of the carrier lifetime and mobility

Figure 4.7: Experimental majority carrier mobility as a function of acceptor and donor concentration and Klaassen’s model.

with contact on the Al pads. The area of the ECV crater was measured externally by a pin profiler (Dektak). This allowed for the correction of the calculated dopant density as explained by Bock et al [32]. Figure 4.6 shows two doping profiles measured in n-type silicon wafers with different resistivities. The profile was found to stabilize after 0.1-0.7µm depending on the samples. To minimize the uncertainty, more than 30 net dopant measurements were made until a depth of 0.5-3µm was reached. The dopant density value was determined as the mode of the net dopant values. By avoiding the use of the average value, the initial measurements and the local false measurements (mainly due to bubbles in the electrolyte) were excluded. The conductivity mobility was then calculated ($\mu_C = 1/q \rho p_{0,C}$).

4.2.3.2 Results

The results reveal a 5-30% reduction of the hole mobility in the compensated silicon wafers compared to non-compensated silicon samples with similar net doping. Figure 4.7 shows the experimental majority carrier mobility as a function of acceptor and donor concentration and Klaassen’s model. The non-compensated samples show a good agreement with the model of Klaassen. Even if there is a lot of scatter in the
data one can see that as the donor concentration increases, Klassen’s model seems to be unable to reproduce the mobility reduction due to donor scattering. As seen in chapter 3, this could be due to several mechanisms. In the following two sections we explore the possibility of enhanced minority impurity scattering and potential fluctuation scattering.

### 4.2.3.3 Enhanced minority impurity scattering

As seen in chapter 2, the scattering cross section between a positive carrier and a negative acceptor is not the same as the scattering cross section between a positive carrier and a positive donor. Majority impurities are thought to scatter much more effectively than minority impurities. The mobility due to ionized donors can be easily extracted from the data above using Klaassen’s model for lattice scattering and acceptor scattering.

\[
\mu_{h,\text{Donor}} = \frac{1}{\frac{1}{\mu_{\text{measured}}} - \frac{1}{\mu_{\text{lattice}}} - \frac{1}{\mu_{\text{Acceptor}}}} 
\]  

(4.1)

![Figure 4.8: Measured and calculated mobility due to ionized donors in compensated p-type silicon as a function of the donor concentration.](image)

This is illustrated in figure 4.8, showing the measured and calculated mobility due to ionized donor in compensated p-type silicon as a function of the donor concentration. Klaassen takes into account the difference between hole-donor scattering and
hole-acceptor scattering through a factor $G(P)$ which represents the scattering cross section ratio between scattering by majority impurity and minority impurity. This was evaluated from quantum mechanical phase shifts calculations.

$$G(P) = \frac{\sigma_{s,\text{repulsive}}}{\sigma_{s,\text{attractive}}} = \frac{\mu_h A}{\mu_h D} \quad (4.2)$$

Assuming that Klaassen’s model underestimates the influence of minority impurity, we can explain the lower mobility obtained in compensated silicon. However it is possible that this difference between modelled and measured mobility reveals an inability of Klaassen’s model to properly take screening into account.

### 4.2.3.4 Coulomb repulsion and minority impurity scattering

![Figure 4.9: Measured and calculated scattering cross section ratio for repulsive and attractive center in silicon.](image)

Using the experimental mobility measurements and comparing to the majority mobility as modelled by Klaassen, one can easily determine the scattering-cross-section ratio or majority/minority mobility ratio. Figure 4.9 shows the experimental scattering cross section ratio for repulsive and attractive centers. Despite significant scatter, most of the measured scattering cross section ratios are higher than those modeled by Klaassen. The overestimation of the mobility obtained by Klaassen’s model...
Figure 4.10: Majority carrier mobility as a function of the temperature in (a) 10Ω.cm n-type sample and (b) 10Ω.cm compensated n-type sample.

in compensated silicon could therefore arise from an underestimation of the scattering potential of minority impurities. Our measured data also indicate that when the carrier concentration decreases the scattering cross section ratio may increase above unity. This can not be explained from the model and could potentially be due to screening effects. As the net doping decreases, the Debye screening length increases and there is less screening. This in turns leads to more scattering of ionized impurities and therefore could explain the increased scattering cross section ratio for low net doping as shown in figure 4.9. Note that as pointed out in the previous chapter and suggested by other authors [113] other mechanisms could be responsible for the mobility reduction such as space charge region scattering and potential fluctuation scattering.

4.2.3.5 Temperature dependence of the majority mobility in silicon

In order to better understand the influence of compensation on the carrier mobility we measured the temperature dependence of the mobility in several compensated samples. Figure 4.10 shows the majority carrier mobility as a function of the temperature in a 10Ω.cm non-compensated and compensated sample. Note that the displayed mo-
bility here is the Hall mobility and should be accordingly corrected by the temperature dependent Hall factor varying between 0.9 and 1.3 in n-type silicon [114]. However this makes little difference in this logarithmic scale and it is unsure presently how strong compensation will affect the Hall factor at low temperature [114]. As above the measured mobility is lower than modelled by Klaassen in the compensated sample. However if we assume that minority acceptors are 4 times more effective at scattering than majority acceptors, we obtain a far better fit. Note that this value is significantly higher than the previous ones. This is shown in figure 4.11. Again this is one possibility but other effects could be responsible for such a mobility reduction.

4.2.4 Minority carrier conductivity mobility

4.2.4.1 Experimental method

In order to perform minority carrier mobility measurements with the technique developed by Sproul et al. [81] wafers were cut into $4 \times 4 cm^2$ pieces. The wafers were then etched to different thicknesses ranging from $90\mu m$ to $170\mu m$ using a standard $HNO_3 : HF$ etch. This tends to yield non uniform surface thickness near the edges. Nevertheless the $2 \times 2 cm^2$ central part was found to be uniform in thickness. The
surfaces were next abraded to yield infinite surface recombination velocities. The effective lifetimes were then dominated by surface recombination, and their magnitudes determined by the diffusivity (or mobility) of minority carriers, as described below.

These lifetimes were measured using the microwave photoconductance decay (MW-PCD) technique with an excitation wavelength of 904 nm. This is the same wavelength used by Sproul et al. [81] and in these thin wafers will generate almost flat carrier profiles. The lifetime variation due to increasing laser power was monitored in order to achieve a high signal/noise ratio without reaching high-injection conditions, which would affect the mobility. However, as we observed no discernable variation of the effective lifetime with laser power, the maximum laser power was used. The lifetime was measured more than 25 times with averaging over 1024 pulses to get a low standard deviation.

![Figure 4.12: Plot of $1/\tau$ vs $(\pi/W)^2$ to determine the minority carrier mobility. The error in the mobility is determined using the best fit within the error bars.](image)

Figure 4.12 shows the reduction of the measured effective lifetime with thickness, plotted in the manner used by Sproul, allowing the minority carrier electron mobility to be determined on each of the samples. The uncertainty in the mobilities was estimated using a best fit within the error bars of the $1/\tau$ vs $(\pi/W)^2$ data (with W the sample thickness).
4.2.4.2 Results and discussion

Figure 4.13(a) shows the minority electron mobilities plotted as a function of $N_A$. Klaassen’s model is shown for three cases, with $N_D = 0 \text{cm}^{-3}$, $N_D = 2.5 \times 10^{16} \text{cm}^{-3}$ and $N_D = 4.05 \times 10^{16} \text{cm}^{-3}$. The $N_D = 0 \text{cm}^{-3}$ case corresponds to the two control wafers, while the other two curves relate to the two compensated samples. While the control samples are in reasonable agreement with Klaassen’s model, the compensated samples lie well below the curves predicted by it. Figure 4.13(b) shows the minority electron mobilities plotted as a function of $N_A$, in analogy to Figure 4.8. The mobility is lower than predicted by Klaassen, again suggesting the potential underestimation of minority impurity scattering in Klaassen’s model.

4.2.5 Hall Factor in compensated silicon

The Hall factor depends on the carrier type, the dominant scattering mechanisms, temperature and the magnitude of the magnetic field. The Hall factor approaches unity when the magnetic field is strong [115]. However, for practical reasons it is
§4.2 Mobility

often difficult to measure under such high magnetic fields. Therefore it is of fundamental importance to measure the Hall factor $r_H$ in compensated silicon in order to be able to convert low-field Hall mobilities into conductivity mobilities. Moreover the Hall factor is larger than 1 in n-type silicon and smaller than 1 in p-type silicon [115]. This raises uncertainty about the value of the Hall factor when both dopant types are present in the bulk, as is the case for compensated silicon.

4.2.5.1 Experimental Method

The Hall carrier concentration ($p_{0,H}$) was then measured on the Van der Pauw structure using an Accent HL5500PC Hall Effect measurement system with a magnetic field strength of 0.32T (low magnetic field). This allowed for the determination of the Hall mobility ($\mu_H = 1/q\rho p_{0,H}$). Using both Hall and conductivity measurements allows us to determine the Hall mobility and the conductivity mobility, and therefore the Hall factor. By making both carrier concentration measurements at the same place on the same sample, we avoid any uncertainty due to dopant differences between samples.

4.2.5.2 Results and discussion

The relationship between the Hall mobility $\mu_h$ and the conductivity mobility $\mu_c$ is expressed as $\mu_h = r\mu_c$. The resistivity has no part in the determination of the Hall factor, and thus the Hall factor can also be expressed as the ratio of the conductivity carrier density $p_{0_c}$ over the Hall carrier density $p_{0_H}$ as follows: $r_H = p_{0_c}/p_{0_H}$. Using the ECV and Hall carrier concentrations measured in this work, the Hall factor at room temperature was thus determined. Figure 4.14 shows that the Hall factor at room temperature is approximately constant in the $10^{16} cm^{-3}$ to $10^{17} cm^{-3}$ dopant range in p-type silicon. An average value of 0.71 is a good approximation for both control and compensated samples. The values of the Hall factor in the control samples are close to those found in the literature for p-type silicon [37; 72]. In compensated silicon, the Hall factor is close to the value of 0.74 estimated by Libal et al. [105] using Hall and simulated conductivity mobility data. It is also in agreement with the $0.85 \pm 0.15$ Hall coefficient measured in p-type silicon compensated by thermal donors [71]. In com-
Figure 4.14: (a) Measured Hall factor in non-compensated and compensated silicon p-type silicon. The straight line represents the average value of 0.71 for the Hall factor in compensated p-type silicon. (b) Measured Hall factor in non-compensated and compensated silicon compared n-type silicon. The straight line represents the average value of 1.1 for the Hall factor in compensated n-type silicon.

In compensated n-type silicon, a value of 1.1 is a good approximation although more data is needed to confirm this. The data is also close to the data of Otha and Sakata [114] in low-compensated n-type silicon. Using a unity Hall factor would lead to approximately a 30% error in the determination of the conductivity mobility for p-type silicon, which is quite significant.

### 4.3 Impact on current and voltage

Minority carrier transport in silicon solar cells is predominantly by diffusion. In p-type cells, the minority carrier diffusion length can be expressed by the relation:

$$L = \sqrt{D_n \tau}$$  \hspace{1cm} (4.3)

With the diffusion constant:

$$D_n = \frac{kT}{q} \mu_n$$  \hspace{1cm} (4.4)
This leads to

\[ L_n = \sqrt{\frac{kT}{q\mu_n\tau_n}} \]  

(4.5)

A variation in the carrier mobility has a direct impact on the carrier diffusion length. In a perfectly passivated long base device (in which \(L_D << W\)), the short circuit current \((J_{SC})\) is linked to the diffusion length and the generation rate by the relation

\[ J_{SC} = qg_nL_n \]  

(4.6)

This means that any variation on the carrier mobility will have a direct impact on the short circuit current. A variation in the carrier mobility and thus in the diffusion length will change the excess carrier density, for short diffusion length. The open circuit voltage \((V_{OC})\) is defined by the relation

\[ V_{OC} = \frac{kT}{q} \ln\left(\frac{(n_0 + \Delta_n)(p_0 + \Delta_n)}{n_i^2}\right) \]  

(4.7)

A variation in the carrier mobility and thus in the excess carrier density will strongly influence the open circuit voltage. The carrier mobility \(\mu\), as well as the carrier lifetime \(\tau\), have a direct impact on both the open circuit voltage and the short circuit current.

Using PC1D with experimental majority and minority carrier mobilities we modelled the efficiency obtained for a simplified passivated emitter, rear locally-diffused (PERL) cells [116; 117] with a long base \((\tau=500\mu s)\) and short base device \((\tau=10\mu s)\).

The cell parameters and results are shown in table 4.1 and table 4.2. Table 4.2 shows that for the long base device, the efficiencies in the non-compensated samples and compensated samples are very similar at similar net doping (within 0.1%). However for the short base device the efficiency reduction is much stronger between 0.3% and 0.4%. Therefore for this cell structure the mobility reduction only leads to an efficiency reduction for a short-base device as shown in other studies [107].
Experimental investigation of the carrier lifetime and mobility

<table>
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<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Thickness ($\mu$m)</td>
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</tr>
<tr>
<td>Emitter sheet resistance (Ω$\square$)</td>
<td>140</td>
</tr>
<tr>
<td>Surface concentration ($cm^{-3}$)</td>
<td>$8.375 \times 10^{19}$</td>
</tr>
<tr>
<td>Junction depth ($\mu$m)</td>
<td>0.3</td>
</tr>
<tr>
<td>Front SRV (cm/s)</td>
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</tr>
<tr>
<td>Rear SRV (cm/s)</td>
<td>100</td>
</tr>
<tr>
<td>Rear series resistance ($\Omega cm^2$)</td>
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</tr>
<tr>
<td>Front texture facet angle = 54.74°</td>
<td></td>
</tr>
<tr>
<td>ARC</td>
<td>SiN$_x$ (40nm, n=2) SiO$_2$ (30nm, n=1.45)</td>
</tr>
<tr>
<td>Rfront (internal)</td>
<td>95%</td>
</tr>
<tr>
<td>Rback (internal)</td>
<td>95%</td>
</tr>
</tbody>
</table>

Table 4.1: PERL cell parameters used in the PC1D simulation

<table>
<thead>
<tr>
<th>$p_0$ ($10^{16} cm^{-3}$)</th>
<th>$\tau_{bulk} = 500\mu$s</th>
<th>$\tau_{bulk} = 10\mu$s</th>
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</thead>
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<td>20.1</td>
</tr>
<tr>
<td>Compensated</td>
<td>20.1</td>
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</table>

Table 4.2: Efficiency from PC1D simulations for a short and a long base device, taking into account the reduction of mobility in compensated silicon.

### 4.4 Summary

In this chapter we have experimentally confirmed that the intrinsic carrier lifetime is limited by the free carrier concentration and not the ionized impurity concentration.

We have shown that both the minority and majority conductivity mobilities are strongly affected by dopant compensation in silicon. In particular, minority carrier mobilities are more affected than majority carrier mobilities. We also conclude that Klaassen’s mobility model appears to overestimate the majority and minority carrier mobility in compensated silicon.

Our results suggests that minority impurities are stronger scatterers than estimated by Klaassen’s model. This confirms the need to improve the modelling of screening effects for the mobility in silicon.

For similar resistivities, the majority hole mobility is reduced by around 20% in the samples studied here, while the minority electron mobility is reduced by around 40%. This reduction in carrier mobility would, in isolation, have a negative impact on the solar cell efficiency, with minority carrier diffusion lengths reduced by around...
22% due to compensation. Nevertheless, the diffusion length also depends on the carrier lifetime, which is known to increase with compensation \[39; 105\], and which may offset the reduction in mobility.

We have found the Hall factor at room temperature to be similar in compensated and non-compensated silicon, with a value of approximately 0.71 in p-type silicon and 1.1 in n-type silicon. Contrary to previous conjectures \[105\], the decrease of the Hall mobility in compensated silicon can not be explained by an increase in the Hall factor.
5.1 Introduction

Combining the advantages of upgraded metallurgical grade silicon (low cost and embodied energy) and the greater immunity to impurities of n-type silicon [118], boron-phosphorus compensated n-type silicon is a promising material for solar cells. As shown in chapter 4 compensated n-type silicon has lifetimes close to the Auger limit.

In this chapter data on the boron-oxygen (BO) defect in p-type and compensated p-type silicon are summarised and two formation models are discussed. We then investigate the key factors that determine the defect concentration and the defect generation in compensated n-type samples and compare our findings to the models mentioned above.

We demonstrate that the BO defect density appears to be independent of the net doping, and also show that the defect density is approximately proportional to the excess carrier density during illumination. We discuss the potential of this material as a substrate for efficient solar cells, especially the effect of the carrier generation rate on the defect density and expected open circuit voltage $V_{OC}$. We then analyse the implications of our findings for a recent BO model [119], and for the potential of compensated n-type silicon as a material for solar cells.
Additionally we investigate the recombination activity of the BO defect in compensated n-type silicon doped with phosphorus and boron, and attempt to fit the injection dependence of the resulting carrier lifetime with the SRH model. We confirm that a single defect dominates the entire time dependence of the degradation, unlike in p-type silicon, in which a fast and slow-forming defect occur.

Finally we explore the effect of intermediate temperature annealing on the BO defect density and show that a permanent reduction of the defect density can be obtained by such annealing.

5.2 Chemical nature and formation of the BO defect in compensated n-type silicon

5.2.1 Review of the chemical nature and formation of the boron-oxygen in silicon

5.2.1.1 The BO defect in p-type silicon

Schmidt and Bothe determined that the defect only occurs in boron doped Cz silicon [120]. They showed the effective defect density to be proportional to the boron concentration and to increase quadratically with the interstitial oxygen concentration [120]. The interstitial oxygen concentration \([O_i]\) is known to have a quadratic influence on the dimer concentration [121] and thus on the BO defect density [120; 122; 123]. Therefore, the concentration of defect created was found to be jointly proportional to the boron concentration and quadratically related to the interstitial oxygen concentration \((N_I^*\alpha N_A \times [O_i]^2)\).

5.2.1.2 The standard boron-oxygen model

Following on the results of Bothe et al., the standard boron-oxygen model [122] was formulated involving a substitutional boron \(B_S\) and an oxygen dimer \(O_{2i}\). In this model, a mobile positively-charged oxygen dimer \(O_{2i}^+\) was thought to diffuse at room temperature through the capture of holes and electrons, until reaching a negatively charged substitutional boron atom \(B^-\) [124].
5.2.1.3 The BO defect in compensated p-type silicon

However, the validity of the standard boron-oxygen model was questioned when it was shown that the defect density depended on the net doping \( (N_d^* \alpha p_0 \times [O_i]^2) \) rather than the total boron concentration \( (N_d^* \alpha N_A \times [O_i]^2) \) in compensated p-type silicon [125; 77; 39]. The BO defect generation rate was also shown to have a quadratic dependence on the net doping \( (R_{gen} \alpha p_0^2) \) [77]. This could not be reconciled with a model where the substitutional boron concentration determines the defect concentration. Moreover Murin et al. [126] have recently shown that diffusion of oxygen dimers is not expected to occur at room temperature, thus an alternative model for the BO defect was needed.

5.2.1.4 The revised boron-oxygen model

To explain the defect density dependence on the net doping Voronkov et al. [119] presented an alternative model involving interstitial boron \( B_i \) rather than substitutional boron \( B_S \). In this model the oxygen dimers are not mobile at room temperature, but bind to the interstitial boron during ingot cooling. The concentration of \( B_i O_{2i} \) then depends on the \( B_i \) concentration at the freeze-in temperature, which in turns depends on the net doping at the freeze-in temperature \( (N_d^* \alpha p_0 \times [O_i]^2) \). This state of the \( B_i O_{2i} \) defect is thought to be latent, and is subsequently transformed into a recombination active defect under illumination. Macdonald et al. [127] presented an alternative model involving interstitial boron \( B_i \) binding with mobile oxygen dimers at room temperature. Both of these models predict the defect density to be inversely proportional to the net doping in n-type silicon and to be independent of the light intensity during defect generation.

5.2.1.5 The BO defect in compensated n-type silicon

Compensated n-type silicon has recently been shown to degrade due to boron-oxygen (BO) related light induced degradation (LID) [128; 129; 130; 131], which is very well known in boron doped p-type silicon [120; 132]. Schutz-Kuchly et al. first experimentally demonstrated the existence of the defect in boron-phosphorus compensated
n-type silicon [128]. They also showed the defect to have a smaller impact on cell efficiency in compensated n-type than in compensated p-type silicon [130]. Lim et al. [129] revealed the slow kinetics, compared to p-type silicon, of both the generation and the annihilation of the defect in compensated n-Si. They also showed that the defect generation and annihilation processes could not be fitted by a simple exponential function as is the case in p-type silicon. Geilker et al. [131] proposed that the defect concentration depends on the compensation ratio rather than the net doping or the boron concentration. However much remains to be understood about the boron-oxygen complex formation mechanism in compensated n-type silicon. In particular, the effect of net doping on the defect density remains unclear, although it is essential to determine this in order to assess the suitability of compensated n-type Si for solar cell fabrication. Moreover the recombination activity of the defect has not been assessed in compensated n-type silicon.

5.2.2 Experimental method

Figure 5.1: Ingot profile showing boron, phosphorus, net doping and interstitial oxygen concentration. The lines are fits to the data using Scheil’s equation.

The samples used in this study were from a single compensated Cz-Si ingot doped with both boron and phosphorus. The boron and phosphorus concentrations were
measured by Secondary Ion Mass Spectrometry (SIMS). The net doping was measured by Electrochemical Capacitance Voltage (ECV) measurements. The interstitial oxygen concentration was measured using Fourier Transform Infrared Spectroscopy (FTIR) and was found to be between \([\text{O}_i]=6 \times 10^{17} \text{cm}^{-3}\) and \(9 \times 10^{17} \text{cm}^{-3}\). Figure 5.1 shows the boron, phosphorus, net doping and interstitial oxygen concentrations along the length of the ingot. Both the segregation coefficient and initial dopant concentrations in the melt were varied in order to fit the SIMS profile. We found segregation coefficients of \(k_B=0.75\) and \(k_P=0.41\) for boron and phosphorus respectively. The initial boron concentration was found to be approximately \([B]=6.2 \times 10^{16} \text{cm}^{-3}\) and the phosphorus concentration \([P]=1.1 \times 10^{17} \text{cm}^{-3}\). Only samples from the n-type part of the ingot were used in this study. The samples were damage-etched and RCA cleaned. To study the impact of net doping on the defect density, a first batch of samples with a range of net doping values from \(n_0=5.7 \times 10^{15} \text{cm}^{-3}\) to \(4.0 \times 10^{16} \text{cm}^{-3}\) was then subjected to a phosphorus diffusion step to remove fast-diffusing impurities that can affect the lifetime. The gettering layer was then etched in HF/HNO₃. All samples were then RCA cleaned and coated at 450°C with plasma-enhanced chemical vapour-deposited silicon nitride. The BO defect has been shown previously to deactivate very slowly in compensated n-type Si [129]. To ensure full deactivation, the samples were annealed at 200°C for 100 hours. The samples were then degraded under various light intensities and temperatures. Effective lifetime measurements were performed using the quasi-steady-state photoconductance technique (QSSPC) [80]. The measured lifetime after full deactivation is referred to as \(\tau_{\text{annealed}}\) while the degraded lifetime is \(\tau_{\text{degraded}}\). The lifetime measured was extracted at a fixed injection level equal to 10% of the net doping \(n_0\). The effective defect concentration was then determined as \(N_i^*=1/\tau_{\text{degraded}}-1/\tau_{\text{annealed}}\). QSSPC measurements are sensitive to the mobility sum, and as shown in chapter 4 mobility reductions have been observed before in compensated silicon. Therefore we used the sum of acceptor and donor concentrations from the fit to the SIMS data as the input parameter of the mobility model (Dannhauser and Krausse) [73; 74] to obtain reasonable values of the lifetime (cf chapter 4).
5.2.3 Slow degradation in compensated n-type silicon

Figure 5.2: Evolution of the effective lifetime during BO generation in compensated n-type silicon ($n_0 = 1.9 \times 10^{15} \text{ cm}^{-3}$, $G=60 \text{ mW.cm}^{-2}$, $T=60^\circ \text{C}$). The line is a guide to the eye.

Figure 5.2 shows the evolution of the effective lifetime during BO generation in compensated n-type silicon ($n_0=1.9 \times 10^{15} \text{ cm}^{-3}$). At similar net doping, the BO generation process is slower than in p-type silicon. Note that the degradation is not completely saturated, even after more than one month of illumination, reflecting the much slower formation rates compared to p-type silicon. Contrary to p-type silicon, in compensated n-type silicon, the degradation proceeds in one slow lifetime decay as observed before [129; 128], rather than with two distinct time constants.

5.2.4 Doping dependence of the defect

Figure 5.3 shows the lifetime $\tau$ evolution during the defect formation for three compensated n-type Si samples with different net doping under an illumination intensity of 60 mW/cm$^{-2}$. Also shown is a control non-compensated 1$\Omega$.cm n-type Cz silicon sample, whose lifetime remains constant, thus confirming that the surface passivation is stable and does not affect the changes observed in the other samples. Interestingly, the lifetime of the different compensated samples crosses over after a certain time.
§5.2 Chemical nature and formation of the BO defect

Figure 5.3: Evolution of the lifetime during light induced degradation for three samples with different net doping levels \((G=60 \text{ mW.cm}^{-2}, T=60^\circ\text{C})\). The lines are guides to the eye.

Figure 5.4: Normalized effective defect density as a function of the net doping after different illumination times \((1 \times 10^4, 1 \times 10^5 \text{s} \text{ and } 1 \times 10^6 \text{s})\). The lines are guides to the eye.

However, since the interstitial oxygen concentration decreases along the ingot, the effective defect concentration should be normalized by the square of the interstitial oxygen concentration to allow for proper comparison between the samples. Figure 5.4
shows this normalized effective defect density as a function of the net doping after different illumination times. The defect density after a given time appears to be approximately independent of the net doping, indicating that the rate of defect creation is very similar for all net doping values.

5.2.5 Excess carrier density dependence of the defect

For this part of the study the BO defect has been generated using different light intensities. The light induced degradation process has already been shown to be an electronically induced degradation mechanism and as such it is the excess carrier density, rather than the light intensity itself, that creates the defect. A simple way to determine the excess carrier density in a sample under a given generation rate is to measure the carrier lifetime, in this case using an inductive coil. The carrier lifetime is given by $\tau = \Delta n / G$, with $\Delta n$ the excess carrier density in the samples and $G$ the generation rate. Combining the intensity of the bias light during the degradation and the optical properties of the sample, one can easily determine the carrier generation rate $G$ in the sample. Using the lifetime measurement $\tau$ and the generation rate $G$ one can obtain the excess carrier density in the sample during the BO generation $\Delta n_{\text{generation}}$. A temperature controlled inductive coil photoconductance setup was used to measure the excess carrier density in this way at 60°C [87].

Figure 5.5 shows the evolution with time of the carrier lifetime and the implied open-circuit-voltage $V_{OC}$, for two different degradation light intensities at 60°C. The implied $V_{OC}$ is calculated via the excess carrier density measured under an illumination intensity corresponding to 1 sun (100 mW/cm$^{-2}$), and reflects the expected impact of the defect on cell performance. Note that the injection level for the implied 1-sun $V_{OC}$ conditions will usually be quite different to that at which the lifetime is reported in Figure 4. The plot shows that the defect causes a very significant reduction in both the carrier lifetime and 1-sun implied $V_{OC}$, meaning that such material would be less suitable for high efficiency solar cells than non-compensated n-type silicon without any mitigation of the defect. In p-type silicon the injection level during BO generation $\Delta n_{\text{generation}}$ is known to have little effect on the BO defect density $N_t^*$, except
5.2 Chemical nature and formation of the BO defect

Figure 5.5: Evolution of the lifetime (empty symbols) and the implied $V_{OC,1Sun}$ (filled symbols) during light induced degradation at $60^\circ C$ for two different light intensities ($n_0 - 5.7 \times 10^{15} cm^{-3}$). The lines are guides to the eye.

for very low injection levels [133] for which the defect formation rate increases with injection. Specifically, the kinetics of the slow forming defect formation are known to saturate for light intensities greater than 1 mW.cm$^{-2}$ in p-type silicon [133]. In contrast, Figure 5.5 shows that n-type samples degrade faster under a greater light intensity (60 mW.cm$^{-2}$ compared to 8.5 mW.cm$^{-2}$), contrary to p-type silicon. Moreover our data indicates that not only the defect generation rate increases with injection but perhaps also the final defect density, although this is difficult to confirm due to the very slow defect generation.

In terms of expected device voltage $V_{OC}$ the drop in lifetime implies a final $V_{OC}$ of $V_{OC}=586$mV ($\Delta V_{OC}=103$mV) at high generation (G=60 mW.cm$^{-2}$, after $1 \times 10^{6}$s) and $V_{OC}=604$mV ($\Delta V_{OC}=84.8$mV) at low generation (G=8.5 mW.cm$^{-2}$, after $1 \times 10^{6}$s). The implied $V_{OC}$ reduction is very significant when the samples are strongly injected ($\Delta p=2.0 \times 10^{15}cm^{-3}$). However when injecting the material with fewer carriers ($\Delta p=4.7 \times 10^{14}cm^{-3}$) the $V_{OC}$ reduction is less pronounced. Note that the excess carrier density during degradation, $\Delta p$ decreases during the experiment, therefore we choose to quote the $\Delta p$ at the end of the experiment. This is usually when it is more stable.

It may still be possible to make reasonably efficient solar cells with this material,
since solar cells operate at maximum power conditions for which $\Delta p = 1 \times 10^{14} \text{cm}^{-3}$ in general. Moreover, the expected defect density and $V_{OC}$ degradation is likely to depend on the initial bulk lifetime and cell design.

Figure 5.6: Defect density in compensated n-type silicon for two different generation rates ($G=60 \text{ mW.cm}^{-2}$, $T=60^\circ \text{C}$ and $G=0.6 \text{ mW.cm}^{-2}$, $T=30^\circ \text{C}$). The lines are guides to the eye.

In order to determine the extent of the difference in terms of lifetime, defect density and implied $V_{OC}$, we measured the light induced degradation using two different generation rates ($G=60 \text{ mW.cm}^{-2}$, $G=0.6 \text{ mW.cm}^{-2}$) for a range of net doping values. Figure 5.6 shows the defect density in compensated n-type silicon as a function of the net doping for two different generation rates. The defect density more than triples with the increase in carrier generation rate, but is not strongly dependent on the net doping.

To further demonstrate the increased defect density with excess carrier density during BO generation, Figure 5.7 displays the effective defect density as a function of excess carrier density during degradation for three different samples after $1 \times 10^5 \text{s}$ and $1 \times 10^6 \text{s}$ of illumination. Note that the samples in Figure 5.7 have the same oxygen concentration, therefore the effective defect density is not normalized by the interstitial oxygen concentration. Two samples were degraded at $60^\circ \text{C}$ with light intensities of 8.5 mW.cm$^{-2}$ and 60 mW.cm$^{-2}$, and one at $30^\circ \text{C}$ with a light intensity of 8.5 mW.cm$^{-2}$. 
5.2 Chemical nature and formation of the BO defect

Figure 5.7: Effective defect density as a function of excess carrier density during degradation for three different samples with the same net doping after $1 \times 10^5$ s and $1 \times 10^6$ of illumination. The lines are guides to the eye.

The excess carrier density during degradation was determined as described previously. Even if the degradation is not fully completed after these times, this graph suggests that the defect density increases with the minority hole concentration injected during degradation.

5.2.6 Discussion

Based on our experimental measurements, it is possible that either the defect generation rate is affected by the excess carrier density during BO generation, and/or the final defect density itself is affected by the excess carrier density during illumination. If we assume that only the generation rate is affected by the excess carrier density during illumination, then our observation could be explained within Voronkov’s model where the BO defect needs two excess holes to form thus $R_{gen} \alpha \Delta p^2$. However Figure 5.7 strongly suggests that not only the generation rate is dependent on the excess carrier density, but also the final defect density. If that is the case, this would mean that the defect density is not determined during ingot cooling but is determined at room temperature by the Fermi or quasi-Fermi level for holes. This is difficult to reconcile with Voronkov’s model in which the defect density should not be affected by the ex-
cess hole density during illumination. A further apparent discrepancy with the model is that the defect density seems to be independent of the net doping. This can not be explained by Voronkov’s model, where the defect density in n-type compensated silicon should be inversely proportional to the net doping [127]. Another potential explanation is that we are not observing the slow forming defect described by the Voronkov’s model but we are measuring the equivalent of the fast forming defect in n-type compensated silicon. This is supported by the fact that the defect density of the fast forming defect in p-type silicon has previously been shown to increase with the injected carrier density [122]. This could mean that the BO defect formation in compensated n-type silicon could be due to the charging of a latent B$_2$O$_2$ defect followed by a thermally activated structural change, similar to the fast forming center in p-type silicon [122].

5.3 Recombination activity of the BO defect in compensated n-type silicon

5.3.1 Review of the recombination activity of the BO defect in silicon

5.3.1.1 Recombination activity of the slow forming BO defect in p-type silicon

Schmidt and Cuevas showed that the recombination of the slow forming BO defect in p-type silicon could be modeled by the combination of a deep-defect ($E_C-E_T = 0.45$ eV) and a shallow-defect ($E_C-E_T = 0.15$ eV or $E_T-E_V = 0.15$ eV) [134]. Later Rein and Glunz, determined precisely the energy level of the deep-defect to be $E_C-E_T = 0.41$ eV [132]. The deep level ($E_C-E_T = 0.41$eV) was found to have a capture cross section ratio $\sigma_n/\sigma_p=9.3$ and the shallow level was found to have a capture cross section ratio $\sigma_n/\sigma_p<<1$ or $\sigma_n/\sigma_p>>1$ [135] depending on whether it is near the conduction or the valence bands. Figure 5.8 illustrates the two energy levels of the slow forming defect in p-type silicon.
5.3 Recombination activity of the BO defect

5.3.1.2 Recombination activity of the fast forming BO defect in p-type silicon

Bothe et al. shows the fast forming BO defect in p-type silicon could be modeled by a deep level \( (E_C - E_T = 0.35 - 0.85 \text{eV}) \) with a capture cross section ratio \( \sigma_n / \sigma_p = 100 \) [122]. Figure 5.8 illustrates the position of the fast forming defect energy level.

5.3.1.3 Recombination activity of the BO defect in n-type silicon

Bothe et al. [135] showed that the SRH lifetime of B-doped silicon compensated with thermal donors could be modeled with a mid-gap energy level \( (E_C - E_T = 0.5 \text{eV}) \) with a capture cross section ratio \( \sigma_n / \sigma_p = 10 \) [135]. The same parameters were used for the p-type and n-type sample. However, these results do not allow us to state with certainty that the recombination active defect in boron-phosphorus compensated n-type silicon will also be the same as in p-type silicon.

5.3.2 Recombination of the defect in boron-phosphorus compensated n-type silicon

When using a consistent single mid-gap level as Bothe et al. [135] we cannot fit the injection dependent SRH lifetime in all of our samples of different net doping. On
Figure 5.9: Measured injection level dependence of the SRH lifetime for a compensated n-type silicon sample ($n_0 = 2.8 \times 10^{16} \text{cm}^{-3}$). The lines are fits using the SRH equation. The dotted line represents the effect of the deep level, while the dashed line represents the effect of the shallow level. The solid line represents their combined impact.

The contrary, we required a deep and a shallow defect to produce a good agreement between measurements and SRH simulations across all the net doping values measured. Figure 5.9 shows the measured injection level dependence of the SRH lifetime for a compensated n-type sample ($n_0 = 2.8 \times 10^{16} \text{cm}^{-3}$) after defect activation. The theoretical fit suggests that the recombination activity of the BO defect in compensated n-type silicon is dominated at low injection by a shallow defect ($E_C-E_T = 0.15 \text{ eV}$) with a capture cross section ratio $\sigma_n/\sigma_p=0.006$. At higher injection a deep level ($E_C-E_T = 0.33-0.87 \text{ eV}$) with a capture cross section ratio of 10 or higher dominates. Although Bothe et al. simulated the injection dependence of the SRH lifetime with only one defect it is conceivable that in their case the deep defect dominates leading to a very small injection dependence of the SRH lifetime. Indeed their net doping is relatively smaller ($n_0=7.6 \times 10^{14} \text{cm}^{-3}$) meaning that the Fermi level is now further away from the shallow defect.

In order to test this assumption as well as validate our simulation we simulated the data of Bothe et al. with the same SRH parameters as in our samples (same energy
5.3 Recombination activity of the BO defect

Figure 5.10: Injection level dependence of the SRH lifetime from Bothe et al. The lines are fits using the SRH equation. The dotted line represents the effect of the deep level, while the dashed line represents the effect of the shallow level. The solid line represents their combined impact.

To further confirm the influence of the Fermi level on the activity of the shallow level, we modeled samples with different net doping. Figure 5.11 shows the measured injection level dependence of the SRH lifetime for 3 different samples ($n_0 = 5.7 \times 10^{15} \text{cm}^{-3}$, $9.9 \times 10^{15} \text{cm}^{-3}$, $2.8 \times 10^{16} \text{cm}^{-3}$). We used the same SRH parameters as above. Note that the ratio of deep to shallow levels was kept the same in each case. As the doping changes the shape of the injection dependent SRH lifetime curve changes, which is characteristic of a shallow defect. The simultaneous good fit obtained for different samples gives added credibility to the dominance of the shallow defect described above in compensated n-type silicon. Note that the slight error in the fit with the lower net doping could be due to an error in the doping measurement. Indeed only a small overestimation of the net doping can lead to a significant change in the
Figure 5.11: Measured injection level dependence of the SRH lifetime for 3 different samples ($n_0 = 5.7 \times 10^{15}\text{cm}^{-3}$, $9.9 \times 10^{15}\text{cm}^{-3}$, $2.8 \times 10^{16}\text{cm}^{-3}$). The lines are fits using the SRH equation with a deep and shallow level.

shape of the curve.

### 5.3.3 Correlation between energy level and capture cross section ratio in p-type and n-type silicon

<table>
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<th>Type</th>
<th>Defect</th>
<th>Level</th>
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<th>$\sigma_n/\sigma_p$</th>
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<td>9.3 [132]</td>
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<tr>
<td></td>
<td>Fast forming</td>
<td>Shallow</td>
<td>0.15 or 0.97 [134]</td>
<td>$&gt;&gt; 1$ or $&lt;&lt; 1$ [134]</td>
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<td></td>
<td>Shallow</td>
<td>0.15*</td>
<td>0.06*</td>
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</tr>
</tbody>
</table>

Table 5.1: Energy level in p-type silicon from the literature and in n-type compensated silicon from this study*

Table 5.1 shows the fitting parameters used in our SRH simulation and the one used in p-type silicon for the fast and slow forming defect. It is interesting to note that using a capture cross section ratio of 10 (characteristic of the slow forming defect) or of 100 (fast forming defect in p-type silicon) for the deep-defect, does not change the result significantly. Thus the SRH simulation alone does not allow us to determine
whether the BO defect in p-type silicon (slow or fast) is similar to the BO defect in compensated n-type silicon or not.

### 5.3.4 Single level of the BO defect in compensated n-type silicon

![Graph showing SRH lifetime dependence](image)

Figure 5.12: Measured injection level dependence of the SRH lifetime after 3 lengths of time under illumination in a compensated sample doped at $n_0 = 5.8 \times 10^{16} \text{cm}^{-3}$. The lines are fits using the SRH equation with a deep and shallow level.

As seen above the degradation in compensated n-type silicon was not found to conform to a fast initial decay followed by a slow decay, but rather to a single slow decay. Figure 5.12 shows the SRH lifetime after three lengths of time under illumination. Again we used the exact same SRH parameters as above. As the BO defect is generated the whole SRH lifetime curve is translated downward. If a fast and slow forming defect (with different energy levels) were to form in these samples, one would expect the shape of the injection dependent SRH lifetime to change with time. However the fact the shape of the curve doesn’t alter confirms the previous section that only a single defect (with a deep and a shallow level) forms in compensated n-type silicon.
5.3.5 Deep level transient spectroscopy

Lifetime measurements alone only allows for the determination of the capture cross section ratio and the relative defect density to be measured. In order to measure the actual magnitude of the capture cross sections and the defect density, one needs to perform Deep Level Transient Spectroscopy (DLTS) measurements [136]. The knowledge of the hole capture cross section and the defect energy level would allow one to quantitatively measure the boron oxygen concentration in silicon and better understand its recombination characteristics. Such information would also allow a better modeling of the defect and its implication at the solar cell level. Finally it could also allow one to better determine ways to mitigate the defect. Therefore knowledge of the capture cross section and energy level of the BO defect is a vital piece of information. However, there is no published results of such a measurement in p-type silicon concerning the BO defect. The DLTS technique on Schottky diodes injects majority carriers and therefore only probes the lower half of the band-gap in p-type silicon. Table 5.1 shows that the energy level detected by carrier lifetime measurements (deep or shallow) is in the upper half of the band gap. Therefore by using the DLTS in n-type silicon, one can probe the upper half of the band gap and potentially detect the deep and shallow levels of the BO defect. In the following section we attempt to find such a defect in compensated n-type silicon using DLTS.

5.3.5.1 Experimental methods

In order to achieve a good measurement high quality Schottky diodes are needed with low leakage and high ideality factor. The samples were first etched in order to obtain shiny surfaces. Then a titanium/palladium/silver (Ti/Pd/Ag) stack was evaporated at the back in order to provide an ohmic contact. Ti possess a relatively low barrier height $\Phi_{Bn}=0.6\text{V}$ and therefore creates a good ohmic contact to n-type silicon. The ohmic behaviour of the back surface contact was further measured by the linear behaviour of the current-voltage measurement. The samples were then light soaked for more than two weeks. Photoresist was then spun on and circular features were created through photolithography. Palladium was then evaporated and subsequently
§5.3  
Recombination activity of the BO defect

Figure 5.13: $I/(1-\exp(-qV/kT))$ characteristic of the Schottky diodes on compensated n-type silicon showing an ideality of $n=1.2$ in forward and reverse bias.

Palladium possesses a high barrier height $\Phi_{Bn} = 0.8$ and therefore makes good Schottky contact to n-type silicon. Figure 5.13 shows the $I/(1-\exp(-qV/kT))$ characteristic of the schottky diodes showing an ideality of $n=1.2$ in forward and reverse bias.

5.3.5.2 Results

Figure 5.14 shows the DLTS spectra from a 20Ω.cm compensated n-type silicon samples. No distinctive peak can be found showing that if BO defects are present they are in too small quantities to be detected by this technique. The sensitivity of the technique is about $10^{-5}$ times the net doping. We measured samples with several different net doping values, the lower doping being $n_0 = 7 \times 10^{14} cm^{-3}$, this would mean that the BO defect density is lower than $1 \times 10^{10} cm^{-3}$ in our samples. However it is possible that other mechanisms prevents the detection of this defect. For example it is conceivable that the BO defect acts as a very fast trap and therefore empties before the fall of the forward current pulse [136]. More work is needed in order to further characterize the BO defect using DLTS.
Figure 5.14: DLTS spectra from a 20Ω.cm compensated n-type silicon sample. The sample was light soaked for more than two weeks before deposition of the Schottky diodes.

5.4 Mitigating the BO defect in compensated n-type silicon

The results above show that the defect density appears to be independent of the net doping, and perhaps also the boron concentration (although this is less clear due to the much weaker variation in the boron concentration in our samples). This would mean that, unlike p-type silicon, lower defect densities may not be readily obtained by reducing the net doping in n-type compensated silicon. Therefore alternative methods of mitigating the BO defect in compensated n-type silicon are necessary.

5.4.1 Review of the boron-oxygen mitigation in silicon

5.4.1.1 Permanent de-activation

Herguth et al. have shown that by simultaneous annealing and illumination, one can permanently deactivate the BO defect in p-type silicon [137; 138]. However, Lim et al. have recently shown that this permanent deactivation is not stable in compensated n-type silicon [139]. Therefore alternative ways to mitigate the BO defect are needed in order to make high efficiency n-type solar cells using compensated silicon.
5.4.1.2 High temperature annealing

In p-type silicon, Bothe et al. [135] and Glunz et al. [140] have shown that the defect density can be reduced by a high temperature thermal process (>700°C) due to interstitial oxygen clustering. Bothe et al. [135] also demonstrated a reduction of the defect density by thermal donor creation at low temperature (at 450°C dimers transform to longer oxygen chains). However the effect of intermediate temperature annealing (500°C to 700°C) remains unknown.

5.4.2 Principles

As seen above, in compensated n-type silicon, one can not reduce the BO defect through a reduction of the net doping or permanent de-activation. Murin et al. [121] have demonstrated that in the 500°C - 700°C temperature range the oxygen dimer concentration is reduced through dissociation (without affecting the interstitial oxygen concentrations). Therefore, controlling the oxygen dimer concentration could be a useful approach to reducing the defect density. We have performed an experiment to assess this possible way of controlling the defect density.

5.4.3 Experimental methods

In order to assess the influence of thermal treatment on the defect density, a batch of samples, all with similar net doping \( n_0 = 3 \times 10^{15} \text{cm}^{-3} \), were annealed for one hour at different temperatures from 500°C to 700°C in a quartz furnace tube under nitrogen flow. All samples were then RCA cleaned and coated at 450°C with plasma-enhanced chemical vapour-deposited silicon nitride and annealed at 200°C for 100 hours in order to fully deactivate the defect [129].

5.4.4 Results

Figure 5.15(a) shows the evolution of the defect density during light-induced-degradation for three samples with different annealing conditions. The graph shows that the defect generation saturates at lower defect densities for samples annealed at higher temperature. To further confirm this, figure 5.15(b) shows the annealing
Boron-oxygen related carrier-induced-degradation

Figure 5.15: (a) Evolution of the defect density during light-induced degradation at 30°C for three samples with different annealing conditions. (b) Effective defect density as a function of the annealing temperature for a 1 hour anneal. The solid line is a fit using the Arrhenius law.

temperature dependence of the effective defect density \( N^*_t \) after a month of illumination \((2.7 \times 10^8)\) s. All of the samples had the same net doping \((5.7 \times 10^{15} \text{cm}^{-3})\) and the same interstitial oxygen concentration. The 400°C corresponds to samples which were not annealed but coated with SiN. Annealing between 500°C to 700°C reduces the effective defect density. Note that the interstitial oxygen concentration measured by FTIR before and after annealing was not found to decrease significantly (at 700°C where the highest reduction in interstitial oxygen concentration is expected the oxygen concentration was found to decrease from \([O_i]_{\text{initial}} 8.8 \times 10^{17} \text{cm}^{-3}\) to \([O_i]_{\text{annealed}} 8.5 \times 10^{17} \text{cm}^{-3}\)). It is useful to remember that the interstitial oxygen concentration is several orders of magnitude higher than the dimer concentration \([141]\) and is therefore not expected to change significantly after dimer dissociation.

Analysing Figure 5.15 using an Arrhenius law, we determine an activation energy of \( E_A = 0.14 \text{eV} \) and within the range 0.1 to 0.3eV. Using low temperature FTIR Murin et al. found a dimer binding energy \( E_b = 0.3 \text{ eV} \). There is a large uncertainty in our determination of the activation energy. Therefore it is hard to conclude whether the defect reduction is due partly to the dimer dissociation or if other mechanisms are
dominant. This could be partially due to the fact that the samples are not completely
degraded, even after a month of illumination. Nevertheless, the results demonstrate
that annealing in the 500°C - 700°C range leads to lower defect densities, a conclusion
which should also be valid for p-type silicon.

5.4.5 Discussion

As seen above, the fact that there is a reduction of the BO effective defect density
after annealing in the 500°C - 700°C range could be partially due to dissociation of
the oxygen dimers. This would lead to fewer dimers available to bind with the boron
atoms, and thus a lower defect density. In practice this confirms that any high tem-
perature step will permanently reduce the BO defect density. As mentioned above, it
has previously been demonstrated that a diffusion step (700°C - 1050°C) can signifi-
cantly reduce the defect density [140; 123]. In such thermal processes, both interstitial
oxygen clustering and oxygen dimer dissociation are likely to play a role in the re-
duction of the available oxygen dimer concentration. Therefore any further thermal
process at lower temperature (such as a firing step at 700°C) may increase the defect
density again, due to partial dimer re-pairing, although it should still remain lower
than the value obtained with no thermal processing. Within Voronkov’s model there
is also the possibility that annealing in the temperature range of 500°C-700°C affects
the interstitial boron clusters, which play a key role in determining the defect density.

5.5 Conclusion

In summary, our results indicate that the net defect density during defect formation
does not depend on the net doping in compensated n-type silicon. Moreover, either
the generation rate and/or the final defect density appear to depend on the excess
carrier density during illumination. If the latter is true, it could mean that the defect
density is not fixed during ingot cooling as proposed in recent models [119; 127] but
rather fixed at room temperature by the Fermi level (in p-type) or quasi-Fermi level
(in n-type) for holes. We showed that the effective defect density more than tripled
when the carrier generation rate is increased by a factor of 100. This translates into a
twofold increase of the implied $V_{OC}$ reduction leading to final $V_{OC}$ of 586mV (High light intensity) instead of 604mV (Low light intensity). The strong implied $V_{OC}$ reduction may limit the applicability of this material to high efficiency solar cells. However further experiments are needed to confirm and more precisely quantify the relationship between defect density, defect generation rate and excess carrier density during illumination.

Our results also suggest that recombination via the BO defect at low injection is dominated by a shallow defect ($E_C-E_T = 0.15$ eV) with a capture cross section ratio $\sigma_n/\sigma_p = 0.006$. At high injection the lifetime is limited by a deep defect similar to the ones in p-type silicon ($E_C-E_T = 0.33-0.87$ eV). Additionally we are unable to measure the BO defect density using DLTS, suggesting that the BO defect if present in our samples is in concentrations lower than $1 \times 10^{10} cm^{-3}$. However further experiments are needed to confirm these early results.

Finally, we also demonstrate that annealing between 500 and 700°C effectively reduces the BO defect concentration, with dimer dissociation being a possible explanation. Combined with previous work showing defect reductions after higher temperature anneals, this shows that, in practise, the defect density can be permanently reduced by almost any high temperature step [135; 140].
Conclusion and Further Work

In this thesis, the impact of compensation on the electrical properties of silicon for solar cells has been determined both theoretically and experimentally. We found that compensation can be influential both when performing processes and in the finished solar cells. Reduction of the carrier lifetime and mobility have been predicted and measured in compensated p- and n-type silicon. One outcome of this thesis is a better understanding of the relationship between dopant density and resistivity. The net doping is indeed the most relevant quantity for solar cells optimization and the results in this thesis allow for a better assessment of the resistivity from the net doping. Additionally, this thesis allows one to know that one cannot mitigate light-induced-degradation in compensated n-type silicon through a reduction in the net doping as can be done in p-type silicon.

Inversion layer

Through the use of SIMS, hot probe measurements, and numerical simulations, we reveal the formation of a surface n-type layer after thermal oxidation in highly compensated p-type silicon. This n-layer is shown to interfere with characterization techniques that require a thermal oxidation such as CV measurements on MOS structures. This prevents the determination of the bulk doping density or the density of interface defects from such CV measurements. It is thus preferable to use ECV to obtain bulk doping densities, since the requirement for an oxidation is avoided.

This oxidation induced n-layer could potentially create significant problems in heavily-doped and highly-compensated p-type silicon solar cells involving thermal oxidation for surface passivation. The relatively low doping of the resulting n-layer on our samples means that it is unlikely to be useful as an emitter in a solar cell device. Nevertheless it could potentially act as a non-contacted floating junction, repelling
minority carriers from the surface, and thus decreasing surface recombination.

**Compensation impact on the carrier lifetime and mobility**

We confirm that the lifetime is essentially dependent of the net doping. In certain cases and in particular n-type silicon, metastable defects such as the boron-oxygen defect will reduce the carrier lifetime. Chromium-boron pairs are likely to form in lowly doped n-type silicon, however further work is needed to confirm this experimentally.

Mobility reduction due to compensation has been observed before. Several mechanisms such as reduced screening, potential fluctuation scattering, space-charge-region scattering were suggested as responsible for the observed mobility reduction. Through a thorough theoretical and experimental investigation, we show that an additional mechanism, namely enhanced minority impurity scattering can also explain such a behaviour in compensated silicon. The discrepancy between measured and modelled mobility can also be related to a failure of common mobility models to take into account the large scattering cross section of unscreened ionized impurities in compensated silicon. In order to allow for a better modelling of the carrier mobility in compensated silicon more data in the heavily doped highly compensated regime are needed. Additionally more data of the mobility in lowly doped, highly compensated silicon at low temperature are needed in order to better understand the effects of screening and minority impurity scattering. Indeed at low temperature lattice scattering does not dominate and allow for more precise determination of the influence of ionized impurities on the mobility.

We have shown that both the minority and majority conductivity mobilities are strongly affected by dopant compensation in silicon. In particular, minority carrier mobilities are more affected than majority carrier mobilities. For similar net doping, the majority hole mobility is reduced by around 20% in the samples studied here, while the minority electron mobility is reduced by around 40%. This reduction in carrier mobility would, in isolation, have a negative impact on the solar cell efficiency, with minority carrier diffusion lengths reduced by around 22% due to compensation. For high efficiency devices, simulations confirms that the impact of the mobility re-
duction is only significant when combined with low minority carrier lifetimes.

Additionally, we have found the Hall factor at room temperatures to be similar in compensated and non-compensated silicon, with a value of approximately 0.71 in p-type silicon and 1.1 in n-type silicon.

**Compensation impact on the boron-Oxygen defect**

The net defect density is shown to be independent of the net doping in compensated n-type silicon. Moreover, either the generation rate and/or the final defect density appear to depend on the excess carrier density during illumination which is hard to reconcile with recent boron-oxygen defect models.

The strong efficiency and implied $V_{OC}$ reduction may limit the applicability of this material to high efficiency solar cells. However we suggest a possible way to mitigate the boron-oxygen defect and demonstrate that annealing between 500 and 700°C effectively reduces the boron-oxygen defect concentration, with dimer dissociation being a possible explanation. Finding an efficient way of mitigating the boron-oxygen defect in compensated n-type silicon would make a strong case for high efficiency n-type solar cells using UMG silicon. Therefore further studies of the boron-oxygen defect mitigation are needed.

Experimental results suggest that recombination via the BO defect at low injection is dominated by a shallow defect ($E_C-E_T = 0.15$ eV) with a capture cross section ratio $\sigma_n/\sigma_p = 0.006$. At high injection the lifetime is limited by a deep defect similar to the ones in p-type silicon ($E_C-E_T = 0.33-0.87$ eV). Additionally we are unable to measure the boron-oxygen defect density using DLTS, suggesting that the boron-oxygen defect if present in our samples is in concentrations lower than $1 \times 10^{10} cm^{-3}$. However further experiments are needed to confirm these early results.
Conclusion and Further Work
## List of symbols

### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<td>Scattering cross section between attractive particles</td>
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<tr>
<td>$\Phi_{Bn}$</td>
<td>Barrier height</td>
<td>V</td>
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List of symbols
List of Publications

This thesis is based on the following publications:

Journal papers


Conference papers


Other publications by the author:


3. Tan, J.; Macdonald, D.; Rougieux, F. and Cuevas, A. Accurate measurement of the formation rate of iron-boron pairs in silicon Semiconductor Science and Technology, 2011, 26, 055019


Other publications by the author:
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[22] M. Forster, E. Fourmond, R. Einhaus, H. Lauvray, J. Kraiem, and M. Lemiti, “Ga co-doping in cz-grown silicon ingots to overcome limitations of b and p compensated silicon feedstock for pv applications,” physica status solidi (c), vol. 8,


1962.


[94] F. Rougieux, D. Macdonald, and A. Cuevas, “Transport properties of p-type com-


[129] B. Lim, F. Rougieux, D. Macdonald, K. Bothe, and J. Schmidt, “Generation and annihilation of boron–oxygen-related recombination centers in compensated p-


2008.


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Fiacre Rougieux was born in France in 1985. He received his MEng from the National Institute of Applied Science, INSA, Rennes, France and his certificate in Engineering from the Ecole Polytechnique de Montreal, Montreal, Canada. His studies have been focused on materials science, nanotechnology and semiconductor physics. He started his PhD at the Australian National University (ANU), Canberra, Australia, in 2009, in the field of photovoltaics and semiconductor materials. His research interests includes solar grade silicon, solar cells characterization and silicon defects impact on solar cells.