Identification and Mitigation of Performance-Limiting Defects in Epitaxially Grown Kerfless Silicon for Solar Cells

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering at the

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Submitted to the Department of Mechanical Engineering on May 22, 2014 in Partial Fulfillment of the Requirements for the degree of Doctor of Philosophy in Mechanical Engineering

ABSTRACT

Reducing material use is a major driver for cost reduction of crystalline silicon photovoltaic modules. The dominant wafer fabrication process employed in the industry today, ingot casting & sawing, wastes approximately half of the input silicon feedstock due to sawdust (kerf) and ingot tailings. Alternative "kerfless" wafer-fabrication technologies avoid ingot casting and sawing, and can reduce the amount of silicon feedstock used by over 5×. But for kerfless silicon to be cost effective, wafers must be of high electrical quality, as the power conversion efficiency of a photovoltaic module is the strongest determinant of manufacturing cost. Epitaxially grown kerfless silicon has the potential to both significantly reduce silicon waste, and provide sufficient electrical quality to support high-efficiency photovoltaic modules because of its single-crystal structure and low structural defect density.

The goals of this research effort are to identify the root cause of underperformance of epitaxial wafers, to develop defect-mitigation strategies, and to translate these to electronic performance improvements. Low carrier lifetimes, a measure for electrical performance, of < 1 μs were observed in as-grown epitaxial material. Injection level dependent lifetime, bulk mass spectrometry (ICP-MS), deep level transient spectrometry (DLTS), and micro x-ray fluorescence (μ-XRF) measurements were completed to identify underlying performance-limiting defects. The comparison of the defect concentrations obtained in the above measurements to Shockley-Read-Hall (SRH) recombination modeling indicates that a getterable impurity contaminant is the primary performance limiting defect in p-type as-grown material.
The gettering response of p-type epitaxial material is assessed for two generations of wafer growth equipment. In the first generation of material, gettered lifetimes were < 20 μs at an injection level of $10^{15}$ cm$^{-3}$. While a significant improvement over as-grown performance, this performance level is inadequate for high-efficiency photovoltaics. A second generation of material was grown in an upgraded environment with improved impurity management and greater automation. The effective lifetime of the second generation of material improved over $10^\times$. With the application of standard and extended phosphorus diffusion gettering processes, effective lifetimes of over 300 μs and estimated bulk lifetimes over 800 μs are achieved in < 100 μm thick p-type epitaxial wafers at an injection level of $10^{15}$ cm$^{-3}$ with highly effective Al$_2$O$_3$ surface passivation. Very low concentrations of interstitial iron, a dominant defect in p-type c-Si, were achieved after standard $(2.5 \pm 0.76) \times 10^{10}$ cm$^{-3}$ and extended $(3.2 \pm 7.4) \times 10^9$ cm$^{-3}$ gettering processes. With bulk mass spectrometry and SRH recombination modeling, the source for the lifetime change between generations is identified as a reduction in contamination of difficult to getter impurities including Mo and V. Other potential performance limiting defects, including interstitial iron contamination and structural defect density, are not observed to change between generations.

Both the excellent gettering response and low as-grown lifetime of the material is attributed to the rapid cooling and low density of heterogeneous nucleation sites in as-grown material. This leads to a large concentration of point-defects, a more recombination active configuration than precipitates, in as-grown material. Controlled pre-gettering annealing experiments of as-grown material showed that material performance after gettering can be reduced with pre-gettering annealing.

Similarly, as-grown and gettered material was assessed for n-type epitaxial wafers. As-grown lifetime is again low, < 1 μs, but improves to over 800 μs (effective) at an injection level of $10^{15}$ cm$^{-3}$. In the as-grown state, a getterable impurity is indicated to limit lifetime. The effective lifetime of over 800 μs at an injection level of $10^{15}$ cm$^{-3}$ of the n-type material results in a calculated surface passivation effectiveness that matches the best results obtained with Al$_2$O$_3$. This indicates that no unintended contaminant is responsible for the performance of the wafer.

In conclusion, very high effective lifetimes, eclipsing values achieved with historic kerfless silicon growth technologies, are demonstrated with epitaxial kerfless silicon for solar cells after gettering. The achieved lifetimes are capable of supporting high-efficiency device architecture. Using defect science, the underlying causes for underperformance of as-grown material and early generations of growth are indicated.

Thesis Supervisor: Tonio Buonassisi

Assistant Professor of Mechanical Engineering
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I have started to get a clearer picture of the privileges I have enjoyed as a child, student, company employee, and student (again). This is the case on both international and local levels. I have spent a decent amount of time stressed out while I have been at MIT. A lot of this is because I am a big procrastinator and easily get excited about new things. In moments of particularly high pressure, I would find myself desiring an “easier” situation. There was a hefty dose of elitism in these thoughts, but I have started to appreciate how lucky I am in the framework of Maslow’s Hierarchy of Needs. In short, you can’t work on long-term goals like developing renewable energy technologies, without having a solid foundation that provides food, water, sanitation, safety, etc. It indeed is not “easy” to be in a situation where these fundamental needs are the primary focus. I think it is fair to say that being a graduate student is in the “long-term” category near the top of the pyramid. It is a privilege to have an opportunity to work on such endeavors. Therefore, there are quite a lot of people (and environmental factors) that have played a pivotal role in enabling me to complete this thesis. The group is expansive, ranging from my elementary school teachers to anonymous (to me) and courageous public servants, as well as family and friends. Some people are listed below.

A few things have changed in my life since I wrote the acknowledgements in my Master’s Thesis. For one, Ellen, who I acknowledged in that document, will be marrying me in a few days. I think that is a decent prize for finishing my thesis 😊. Otherwise, my non-academic acknowledgements are the same here: God, Ellen, Mom, Dad, and Joe.

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1.1 Benefits of Photovoltaic Deployment

Solar photovoltaics (PV) are a low-carbon renewable electricity generation technology that harness the power of sunlight with little interaction with the local environment. The amount of capturable power from the sun is abundant, and far exceeds human energy demands by a factor of well over 1,000×. Additionally, while the intensity of sunlight varies over the world, it is less geographically discriminatory than traditional fossil-fuel energy sources.

The deployment of PV technology can help address the imperative challenges facing society today of climate-change and energy supply. Among these challenges, are the 1.3 billion people throughout the world who do not currently have access to reliable electricity and the benefits it provides. The relatively transportable form-factor of PV modules and low maintenance requirements are potentially advantageous attributes for the electrification of this overwhelming demographic.

1.2 Barriers to Photovoltaic Deployment

In spite of the advantages of PV technology deployment, the share of electricity produced by PV is small both globally and in the U.S. Technical factors related to the intermittency of the
solar resource and grid integration provide barriers to PV deployment. However, the price of electricity produced from PV technology, although falling at a rapid pace,\textsuperscript{14, 15} provides a significant barrier to the widespread deployment of PV technology. Two particular market failures contribute to this situation: the non-monetization of externalities (\textit{i.e.}, carbon emissions) of traditional electricity generation technologies,\textsuperscript{16} and the fact that innovators do not capture all of the value they create with an new technology (spillover).\textsuperscript{16}

Incentives are designed to counteract these barriers and include funding for research and development (technology push) and subsidizing technology that may not be financially competitive on its own (demand pull).\textsuperscript{16, 17} Deployment subsidies aim to capture the value of incremental learning and economies of scale.\textsuperscript{14, 18} However, inappropriate subsidization of an inferior technology can lock-in its use and provide significant barriers to the development of other superior technology.\textsuperscript{16} Technology push instruments, including R\&D funding, is an alternative approach to encourage cost reductions through technology development. R\&D funding, although more volatile than demand pull instruments\textsuperscript{17} may reduce the total cost of achieving a policy goal\textsuperscript{19} and provide an improved political reception due to the positive spillovers created R\&D.\textsuperscript{16} However, great effort may be employed to avoid “picking winners” and crowding-out a superior technologies with R\&D funding.\textsuperscript{16, 20}

A blended approach that includes both demand pull and technology push instruments is recommended to combat the distinct market failures of externalities and spillover.\textsuperscript{16} However, the blend must be optimized to avoid spending too much money on technologies that cannot yet benefit from scale, or are inferior to alternatives.\textsuperscript{21}

The U.S. Department of Energy supports R\&D for a wide variety of PV technologies with the SunShot program.\textsuperscript{22} The program targets subsidy-free cost-competitive electricity generation
($/kWh) with PV technology by 2020.\textsuperscript{22} The installed price goals for PV technology are $1.00/W for utility-scale customers and $1.50/W for residential customers (in 2010 US$).\textsuperscript{22} The prices of PV modules themselves are targeted to reach $0.50/W to achieve the above system price goals, with the balance of the price distributed amongst other system components. Significant cost reductions are required for PV module manufacturing to sustainably achieve the $0.50/W module price goal.

1.3 Technology Introduction

A PV system consists of multiple subcomponents. PV modules are installed on a mounting structure and wired together. This circuit is connected to a power inverter that allows the PV system to power the electrical grid when PV production is high, and the consumption of power when PV production is low. The PV module and inverter represent distinct subcomponents of the system, but significant costs are present in the other components of the system. This includes mounting structure and wires, but also labor and overhead costs from installation and permitting. These additional costs are defined as the balance of system (BOS) and currently represent a dominant share of the price of a residential PV system.\textsuperscript{23} The PV module is an assembly of multiple PV cells encased in a weather-tight enclosure. PV devices can be produced with multiple materials, however, crystalline silicon (c-Si) holds a dominant position with over 85% market share.\textsuperscript{24}
1.4 PV Innovation Opportunities

Profit is equal to the selling price of a product minus the cost required to produce it (Figure 1.1, a).

A manufacturer can increase profit by either increasing prices (Figure 1.1, b) or decreasing costs (Figure 1.1, c). However, most manufacturers cannot increase prices freely, as they operate in a competitive marketplace with various alternatives. Therefore, a product should create additional value for a consumer to justify a price increase. Reducing the cost required to manufacture a product is another strategy to increase profit. However, some, all, or none of manufacturing cost reductions may be passed on to the consumer through a change in product price depending on the state of the industry.

Innovations in photovoltaic technologies may provide a price premium or reduce cost. An innovative PV module architecture that increases reliability for example, may allow the manufacturer to charge a price premium. The specific amount of this premium could be determined by understanding how much value the innovation creates for the customer (i.e., lower maintenance costs). On the other hand, an innovative technique for reducing the amount of silver paste needed to manufacture a PV module with the same power output represents an approach to reduce costs.
Profit is equal to price minus the cost to make a product (a). While profit can be increased by either increasing prices (b) or reducing costs (c), some promising innovations provide the capability to congruently reduce manufacturing costs and command a price premium.2

The most promising innovations however, may provide both a price premium and cost reduction at the same time – a “win-win” opportunity for a manufacturer (Figure 1.1, b and c together). Innovations are available within the dominant crystalline silicon material system that accomplish this objective.28-30 Increases in the power conversion efficiency of a module provide this opportunity. Increasing efficiency reduces the amount of labor and land needed for installation for a system,23,31 which creates value for customers and enables a price premium to be charged. At the same time, increasing efficiency without impacting other factors reduces manufacturing costs by decreasing the amount of materials (wafers, glass, etc.) needed to manufacture a module.29,32
1.4.1 Opportunity Assessment with Technical Cost Models

The magnitude of an innovation opportunity can be assessed with a technical cost model. The model includes a technology-driven calculation of the cost to manufacture a PV module coupled to a financial calculation that determines the minimum price that could be charged while maintaining financial sustainability. As shown in Figure 1.2, the cost calculation includes accounting for the direct materials, direct labor, and manufacturing overhead that is required to produce a PV module. The required levels of these resources are calculated considering technical (e.g., geometry and throughput), manufacturing (e.g., yield and uptime), and financial (e.g., depreciation) parameters. The minimum sustainable price (MSP), defining long-term financial sustainable pricing, is then calculated using a discounted cash flow model (Figure 1.2). A technical cost model can therefore be used to calculate the potential financial impact of innovations that either aim to provide an incremental improvement or disrupt incumbent technologies. It is emphasized though, that analyses should note that market prices change over time and serve as a moving target. This is especially the case for disruptive technologies.

Useful resources for developing technical cost models are provided in Appendix A.
A technical cost model is employed to both calculate the cost of manufacturing a PV module and the minimum price that can be charged for the module while providing long-term financial sustainability.\textsuperscript{30,32}

\subsection*{1.4.2 Minimum Sustainable Price Sensitivity Analysis}

Opportunities to reduce the minimum sustainable price were assessed with a technical cost model. Figure 1.3 shows the sensitivity and maximum potential savings of various innovation areas on the MSP of a standard mc-Si PV module.\textsuperscript{29,32} Four groups of influence are shown. The factors shown in red have the largest influence, while the factors shown in blue have an intermediate influence and the factors shown in green have less influence. Financial factors, shown in yellow, also provide a useful price reduction opportunity. Power conversion efficiency provides the highest potential to reduce MSP, as all area-dependent manufacturing costs scale with efficiency.\textsuperscript{29,32} Furthermore, efficiency still provides a significant absolute price reduction opportunity, as module efficiencies are still well below theoretical limits.\textsuperscript{33} The manufacturing parameters of yield and uptime also provide an interesting relationship in the analysis. While little room for improvement is available in these areas because they are already quite high, costs
increases can occur quickly through a reduction in either of these parameters. Silicon feedstock is highlighted as the most expensive material cost for c-Si PV manufacturing and provides a valuable cost reduction opportunity. Lastly, among the most influential factors, the capital cost, or cost required to establish a manufacturing facility, also provides a valuable cost reduction opportunity. Reductions in silicon feedstock use and capital cost however, must not come at the expense of module efficiency.\textsuperscript{34}

![Price Sensitivity Map for Standard mc-Si PV Manufacturing](image)

**Figure 1.3: Price Sensitivity Map for Standard mc-Si PV Manufacturing**

Price sensitivity and maximum absolute savings available for various innovation areas. Better innovation opportunities have both a high sensitivity and maximum absolute savings available (upper right). Efficiency provides the strongest influence to reduce price, while other factors play a less significant role. Figure reprinted from.\textsuperscript{32}

While module efficiency provides a large impact on module prices, it also has a significant influence on installed systems, as many system costs scale with area ($/m^2$).\textsuperscript{23, 31, 35} Figure 1.4 shows the price for a generic PV module (blue curve) and PV systems (green and red curves) as
a function of efficiency assuming that the c-Si wafer is free. This method allows a minimum viable efficiency to be calculated for disruptive technologies by comparing the module price of an incumbent mc-Si module while assuming that all PV technologies have comparable costs of cell fabrication and module manufacturing. While considering only the module, a minimum viable efficiency of 9% is required to compete with incumbent silicon technology. However, the minimum viable efficiency climbs to >11% as the entire PV system is considered, and increases as the price of the balance of systems (BOS) increase for a PV system. This relationship provides the opportunity to charge a price premium for a high-efficiency module, and provides a significant barrier to entry for low-efficiency PV technologies.

![Figure 1.4: Impact of Module Efficiency on Module and System Prices](image)

Increasing module efficiency reduces system prices. While efficiency provides a significant opportunity, it also represents a significant hurdle for low-efficiency technologies.
1.4.3 Enabling Local Manufacturing

Technical cost models were also employed to investigate the prospects of cost-competitive local manufacturing of PV modules. Recently, the scale of PV manufacturing in China has accelerated drastically and has coincided with significant decreases in the market share of U.S.-based manufacturers. In a collaborative effort between the National Renewable Energy Lab (NREL) and MIT, these trends were studied by taking the perspective of a multi-national company selecting a new manufacturing location in the U.S. or China. It was determined that historical MSP advantages in China were not because of inherent factors such as labor, but rather, scale and supply chain development. Therefore, the MSP of PV manufacturing from both locations could be equalized. Furthermore, innovation is a potential key ingredient to provide minimum sustainable price parity by enabling large-scale subsidy-free deployment to erase the scale difference that currently persists between locations. Figure 1.5 shows the historical (1H 2012) disparity of MSP between the manufacturing locations and the impact that targeted advance technology and scale-up have on reaching near-parity MSP. Indeed, the industry climate for c-Si PV is challenging, but a focus on long-term scenarios provides technological guidance and commercial enthusiasm.
1.5 Material Requirements for High-Efficiency Cells

Increasing module efficiency provides the strongest influence on module prices. High-electrical quality substrate materials are required to support high-efficiency PV cells, and are therefore of interest for cost-effective PV material development. Following Coletti, Figure 1.6 shows the impact of substrate electrical quality, measured as the carrier lifetime of the material (detailed in section 3.1), on cell efficiency. The figure was created with a PC1D simulation for standard and advanced cell architectures described in reference. Advanced cell
architectures require a higher electrical lifetime to reach maximum performance than a standard cell architecture.

![Diagram showing cell efficiency vs. bulk defect lifetime]

**Figure 1.6: Lifetime Requirements of High-Efficiency Cells**

The electrical quality requirements of a substrate material increase with cell efficiency. High bulk lifetimes >1,000 μs are required for maximum output with an advanced high-efficiency cell architecture. Simulation inputs from.\(^{34}\)

### 1.5.1 Impact of Miniscule Defect Concentrations in Determining Lifetime

Extremely minute concentrations of defects provide the capability to significantly reduce lifetime in silicon.\(^{38}\) In the case of iron contamination in p-type wafers, an interstitial defect concentration of \(10^{10}\) atom/cm\(^3\) is required for a lifetime of approximately 1,000 μs, an adequate level for maximum performance in Figure 1.6.\(^{38,39}\) If 1% of the iron is found as interstitials, then the \(10^{10}\) atom/cm\(^3\) interstitial concentration allows a maximum total iron concentration of \(10^{12}\) atom/cm\(^3\). While \(10^{12}\) atoms/cm\(^3\) appears at first glance to be a large concentration of allowable contamination, it represents a relative concentration of 1 iron atom per \(5\times10^{10}\) atoms contained in the silicon lattice, almost a one part-per-trillion concentration. The regulatory limits on drinking
water in the U.S. are quite lax in comparison. Arsenic is limited to a concentration of 1 part per $10^8$ and cadmium is limited to 1 part per $2 \times 10^8$. These limits are over 250 times higher than the allowable levels for iron in silicon. Our bodies are more tolerant to these toxic chemicals, than silicon is to impurity contamination.

In conclusion, targeting areas for innovation using the framework presented above provides a mechanism to increase the impact of research and development efforts. It is found that power conversion efficiency provides the strongest influence on module prices, but requires high-electrical quality substrate wafers. Extremely small concentrations of defects are capable of reducing electrical quality of substrate wafers to unacceptable levels.

1.6 Thesis Overview

The identification and mitigation of defects that limit the electrical performance in kerfless crystalline silicon for solar cells is the topic of this thesis. In Chapter 2, historical kerfless wafer growth methods are reviewed, and epitaxially grown kerfless silicon is introduced. In Chapter 3, a review of lifetime-limiting defects in c-Si solar cell material is presented. After the review of lifetime-limiting defects, lifetime measurements are detailed in Chapter 4. Chapter 5 and 6 detail the ALD Al$_2$O$_3$ surface passivation employed for lifetime measurements, and phosphorus diffusion gettering respectively. In Chapter 7, the as-grown performance limits of $p$-type material are presented, followed by the gettering response of $p$-type material in Chapter 8. Both the as-grown performance and gettering response of $n$-type material is presented in Chapter 9. Lastly, the thesis concludes with generalizable conclusions in Chapter 10.
2.1 Standard c-Si PV Module Manufacturing

The standard manufacturing process for c-Si PV includes distinct stages for wafer, cell, and module production. Wafers are fabricated in the dominant manufacturing process by crystallizing large ingots (up to 1000 kg) and subsequently sawing the ingots into individual wafers that are commonly 156×156 mm² with a thickness of 180 µm and p-type doping (boron). Approximately 50% of the ingot is wasted during this process because of unfit material (impurities or geometry) and sawdust (kerf) from cutting. Standard cells are then fabricated from the wafers with the following process. Wafers are first textured to improve light absorption, and then a n+ region is diffused using a phosphorous dopant to form the p-n junction. An antireflective coating is then deposited on the cell to reduce optical reflection and reduce the electrical activity of the surface. Metal contacts consisting of fine silver fingers on the sun facing side of the cell, and aluminum over the full area of the rear of the cell, are then printed and fired to provide electrical contact. After fabrication is completed, the cells are sorted into groups with similar electrical behavior. Modules are constructed with the following process. First, groups of cells are soldered together with flat wire (tabs) and laminated between two sheets of encapsulant to provide isolation for moisture. The encapsulant-cell laminate is placed between glass and a...
backsheet, and then surrounded with an aluminum frame for form a PV module. Lastly, a junction box with quick-connect wiring and electrical protection is placed on the rear of the module.

2.2 Kerfless Silicon Technologies

Given the substantial silicon loss of approximately 50% from traditional ingot crystallization methods due to cropping and wafer sawing loss (kerf),\(^4\) and the significant sensitivity of module prices to silicon feedstock costs (Figure 1.3),\(^2\) many alternative technologies have been pursued for silicon wafer fabrication.\(^2\) An excellent review of these technologies was completed by Ciszek,\(^4\) with a more recent review by Hahn et al.\(^4\) These technologies can broadly be classified as “kerfless” silicon wafer production techniques, as the cutting loss from traditional wafer sawing is avoided. Early techniques focused on the vertical pulling of wafers from a silicon melt, shown in (Figure 2.1, a), and included: dendritic web (single crystal), edge-defined film-fed growth (EFG), and then String Ribbon.\(^2\) However, increased rates of growth (m\(^2\)/hr) can be achieved with horizontally grown ribbons (Figure 2.1, b), as a larger surface area is available on the side, rather than end, of a wafer for heat transfer during solidification.\(^4\) Techniques with this solidification geometry include ribbon growth on substrate (RGS)\(^4\) and the recently developed direct wafer by 1366 Technologies.\(^4\)

Other techniques allow for the kerfless exfoliation of wafers from larger substrates to replace wire-sawing (Figure 2.1, c).\(^2\) In some techniques a region of subsurface damage is created through ion implantation to enable the exfoliation of thin wafers without kerf loss.\(^5\) Other techniques rely on mechanical stress through the thermal mismatch between the substrate and a deposited layer for exfoliation.\(^5\)
Multiple techniques have been pursued to grow silicon crystals directly in the shape of a wafer to avoid the cutting loss of wire sawing. Vertical growth from the melt (a) proceeded horizontal growth from the melt (b). Exfoliation techniques (c), while not a kerfless growth technology, avoid sawing during the separation of a larger silicon substrate into thinner wafers. In epitaxial growth (d), the silicon melt is avoided and the wafer is grown directly from a gaseous silicon source.

An alternative approach of growing wafers directly from a gaseous silicon source via epitaxy avoids the silicon melt (Figure 2.1, d). Free-standing epitaxial wafers can be produced with a layer transfer process (LTP) on a reusable substrate, which is the only component of the process.
that requires polysilicon production. Epitaxial wafers for solar cells are produced at a lower throughput of \(~0.1\ \text{m}^2/\text{hr}\) for one \(156 \times 156\ \text{mm}^2\) substrate in comparison to \(~1\ \text{m}^2/\text{hr}\) for one \(156\ \text{mm}\) wide vertical ribbon. However, advantages including the ability to tune doping throughout the thickness of the wafer and a low average dislocation density <10\(^4\) \text{cm}^{-2}\. The low dislocation density is a significant advantage for these materials, as the structural defects and impurities contained in other technologies impair performance. Record efficiencies for EFG and String Ribbon materials are 18.2% and 17.8% respectively. Although fabricated with a different cell architecture than those used on kerfless silicon in the past, the currently published record cell efficiency for epitaxial silicon is 20.6%. Given that module efficiency is the strongest determinant of manufacturing cost (Figure 1.3), a performance advantage can provide a significant monetary incentive.

### 2.3 Kerfless Epitaxy Manufacturing

Epitaxial growth on a reusable substrate with a porous silicon release layer was first demonstrated with the Canon ELTRAN (epitaxial layer transfer) process. The process begins with anodic etching of highly-doped substrate wafer in an aqueous hydrofluoric acid solution to form a porous silicon layer with a depth of 1 – 2 \(\mu\text{m}\) (Figure 2.2, a and b). The porous layer is then annealed at a high-temperature (> 1,000 °C) in a hydrogen atmosphere to close the pore structure at the substrate surface and form a <100> oriented single-crystal crust that is approximately 20 nm thick and serves as a template future deposition (Figure 2.2, c). The surface of the substrate provides a sink for vacancies, which dissolves vacancies near the sample surface and forms a single-crystal pore-free region. The uniformity of the single-crystal crust is an important factor in determining the structural quality, defined as the density of stacking faults,
of the resulting deposition.\textsuperscript{56} The surface roughness of the resulting crust at two length scales is a strong function of annealing duration.\textsuperscript{64} Large-scale micrometric roughness increases with annealing duration, while small-scale nanometric roughness is observed to decrease.\textsuperscript{64} The micrometric roughness has a significant impact on cell performance, thus shorter annealing times are suggested.\textsuperscript{64} Furthermore, the thickness of porous region also impacts the structural defect density, with thinner regions preferred.\textsuperscript{57} The pore size distribution begins with a lognormal shape but progresses to a bimodal distribution as large pores within the porous bulk grow at the expense of smaller pores.\textsuperscript{62}

![Figure 2.2: Schematic of Epitaxial Wafer Preparation](image)

A porous silicon layer formed in a single-crystal substrate wafer (a) with anodic etching (b). High-temperature annealing in a hydrogen atmosphere is then used to form a single-crystal crust (c) that serves as a template for epitaxial growth (d). The lamination is then exfoliated (e) providing an epitaxial wafer and reusable substrate that can begin the process again after surface preparation.
High-temperature (> 1,100 °C) chemical vapor deposition (CVD) is then used to deposit the silicon layer with an average growth rate over 4 μm/min (Figure 2.2, d).\textsuperscript{52, 53} Trichlorosilane (SiHCl\textsubscript{3}) is used for the silicon source and reacted with a doping gas, BH\textsubscript{2} in the case of \textit{p}-type material and PH\textsubscript{3} in the case of \textit{n}-type material.\textsuperscript{52} The doping of the wafer can be changed throughout the growth process, creating layers of different doping types.\textsuperscript{55} Impurities within the substrate are discouraged from diffusing into the growing wafer because of the high doping of the substrate wafer, with a higher solubility for impurities.\textsuperscript{65} Additionally, the porous layer acts as an effective diffusion barrier.\textsuperscript{66} Increased growth temperatures are observed to increase growth rates while also reducing the density of stacking faults in the resulting epitaxy.\textsuperscript{52}

After growth, the wafers can proceed to front-side processing while still attached to the substrate wafer. The wafers are then mechanically exfoliated from the substrate, allowing the substrate to be reused after subsequent preparation for additional growth cycles (Figure 2.2, e). A resulting single-crystal epitaxial wafer is shown in Figure 2.3. Over 50 reuse cycles have been demonstrated with this technology.\textsuperscript{53}

The resulting epitaxially grown wafers are single-crystalline and flexible when deposited at thicknesses < 100 μm. Photo credit.\textsuperscript{67}
3.1 Intrinsic Lifetime Limits

As shown in Figure 1.6, a key figure of merit for high-efficiency solar cell materials is a high bulk carrier lifetime. The bulk lifetime is limited by both unavoidable mechanisms and unintentional defects and is defined in equation (3.1) below.

The performance impact of defects, \( \tau_{\text{defects}} \), may be mitigated through engineering. However, the bulk lifetime of the doped silicon material is limited to a maximum value by intrinsic material limits, \( \tau_{\text{intrinsic}} \), due to Auger and radiative recombination. Depending on the doping of the material and the cell architecture, these intrinsic lifetime limits could be a limiting factor of solar cell performance. Figure 3.1 shows the intrinsic lifetime limits as a function of doping and injection level for both \( p \)- and \( n \)-type silicon based on the model of Richter et al. With improved solar cell efficiency and reduced wafer thicknesses, injection levels of current cells are expected to increase in the future, potentially above \( 10^{15} \text{ cm}^{-3} \). At this injection level, the intrinsic lifetime of a material is observed to fall with increased doping concentration (Figure 3.1).

\[
\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{intrinsic}}} + \frac{1}{\tau_{\text{defects}}} \quad (3.1)
\]
The intrinsic lifetime limit of a material is unavoidable and reduces with increased doping concentration and injection level.\textsuperscript{69, 71}

### 3.2 Lifetime Limits from Avoidable Defects

In order to maximize $\tau_{\text{bulk}}$, the lifetime impact of defects must be minimized. Equation (3.1) defines the combined impact of individual defects, such as contamination from transition metal impurities or structural defects. The defect lifetime is a harmonic sum of all potential terms (3.2).

$$\frac{1}{\tau_{\text{defects}}} = \frac{1}{\tau_{\text{defect}_1}} + \frac{1}{\tau_{\text{defect}_2}} + \frac{1}{\tau_{\text{defect}_3}} + \ldots = \sum \frac{1}{\tau_{\text{defect}_i}}$$  \hspace{1cm} (3.2)

#### 3.2.1 Shockley-Read-Hall Recombination Model

The recombination of specific defects can be assessed with the Shockley-Read-Hall\textsuperscript{72, 73} model for non-interacting defects under the assumption that no trapping occurs ($\Delta n = \Delta p$).\textsuperscript{52, 74}
The capture rates for electrons, $\tau_{no}$, and holes, $\tau_{po}$, [s] of a particular defect are described by equations (3.3) and (3.4) respectively. $N_t$ is the density of the defect (trap) states [cm$^{-3}$], $v_{th}$ is the thermal velocity of electrons and holes [cm/s] defined in equation (3.4), and $\sigma_n$ and $\sigma_p$ are the capture cross-sections for electrons and holes respectively for the trap state [cm$^2$]. $T$ is temperature [K].

$$\tau_{no} = \frac{1}{N_t v_{th} \sigma_n}$$  \hspace{1cm} (3.3)

$$\tau_{po} = \frac{1}{N_t v_{th} \sigma_p}$$  \hspace{1cm} (3.4)

$$v_{th} = 1.1 \times 10^7 \left( \frac{T}{300} \right)^{0.5}$$  \hspace{1cm} (3.5)

The injection level dependent lifetime of a particular defect is then provided by equation (3.6) as a function of the capture rates. Here, $\Delta n$ is the excess carrier concentration, or injection level [cm$^{-3}$], $n_o$ is the equilibrium electron concentration [cm$^{-3}$], and $p_o$ is the equilibrium hole concentration [cm$^{-3}$]. The factors $n_1$ and $p_1$ are calculated using equations (3.7) and (3.8) respectively, and depend on the energy levels [eV] of the conduction band $E_c$, the valence band $E_v$, and the trap $E_t$, as well as the effective density of states [cm$^{-3}$] in the conduction, $N_c$, and valence, $N_v$, bands defined in equations (3.9) and (3.10). Lastly in equations (3.7) and (3.8), $k$ is the Boltzmann constant.

$$\tau_{\text{defect \_SRH}} = \tau_{po} \left( n_o + n_1 + \Delta n \right) + \tau_{no} \left( p_o + p_1 + \Delta n \right) \frac{1}{n_o + p_o + \Delta n}$$  \hspace{1cm} (3.6)

$$n_1 = N_c \exp \left( \frac{E_t - E_c}{kT} \right)$$  \hspace{1cm} (3.7)

$$p_1 = N_v \exp \left( \frac{E_v - E_t}{kT} \right)$$  \hspace{1cm} (3.8)
\[ N_c = 2.86 \times 10^{19} \left( \frac{T}{300} \right)^{1.58} \]  \hspace{1cm} (3.9)

\[ N_v = 3.10 \times 10^{19} \left( \frac{T}{300} \right)^{1.85} \]  \hspace{1cm} (3.10)

### 3.2.2 Impurity Point Defects

The lifetime impact and tolerable contamination levels of specific defect types can be assessed with the SRH recombination model in Equation (3.6) using measured parameters of defect capture cross-sections and energy levels. QSS-Model, created by A. Cuevas, is a useful tool to complete these calculations.\(^\text{38}\) Figure 3.2 shows the lifetime impact of impurity point defects in \(p\)-type (a, left) and \(n\)-type (b, right) silicon for silicon at a fixed injection level of \(\Delta n = 10^{15} \text{ cm}^{-3}\).\(^\text{38}\) Very small threshold concentrations (<10\(^{10} \text{ cm}^{-3}\)) of most impurity point defects are required to enable the ms lifetimes required for maximum solar cell efficiency (Figure 1.6). In general, the impact of impurity point defects are less pronounced in \(n\)-type silicon than \(p\)-type silicon. The calculations summarized in Figure 3.2
Impurity point defect lifetimes from SRH model\textsuperscript{38} at a constant injection level of $\Delta n = 10^{15}$ cm\textsuperscript{-3} and doping concentrations of $N_A = 10^{16}$ for p-type (a) and $N_D = 3\times10^{15}$ for n-type (b) silicon. Very small concentrations of point defects on the order of $10^{10}$ cm\textsuperscript{-3} are required for high-lifetime material. The lifetime impact of impurity point defects is generally lower in n-type silicon than p-type silicon.

While Figure 3.2 provides a useful comparison of point defects, within a solar cell, the injection level is dependent on the lifetime of the material following Equation (3.11). Here $G_{\text{av}}$ is the average uniform generation rate throughout the thickness of the wafer, and is dependent on illumination intensity. QSS-Model was used to simulate the impact of impurity point defects on bulk lifetime in a solar cell at the maximum power point (MPP) under 1 Sun illumination.\textsuperscript{38} The bulk lifetime of the material, $\tau_{\text{bulk}}$, is taken as the harmonic sum (Equation (3.1)) of $\tau_{\text{SRH}}$ for each impurity type, and the intrinsic lifetime of the material provided by the simplified formulation in Equations (3.12) and (3.12) for p-type and n-type silicon respectively.\textsuperscript{77} A cell thickness of 100 $\mu$m was employed with a low saturation current density of $J_0 = 10^{-15}$ (A/cm\textsuperscript{2}). Following this formulation, Figure 3.3 shows the lifetime impact of impurity point defects in p-type (a, top) and

---

Figure 3.2: SRH Point Defect Lifetimes at Fixed Injection Level

Impurity point defect lifetimes from SRH model\textsuperscript{38} at a constant injection level of $\Delta n = 10^{15}$ cm\textsuperscript{-3} and doping concentrations of $N_A = 10^{16}$ for p-type (a) and $N_D = 3\times10^{15}$ for n-type (b) silicon. Very small concentrations of point defects on the order of $10^{10}$ cm\textsuperscript{-3} are required for high-lifetime material. The lifetime impact of impurity point defects is generally lower in n-type silicon than p-type silicon.
n-type (b, bottom) silicon for a solar cell at 1 sun at the maximum power point. A non-linear relationship between bulk lifetime and defect concentration is observed as low bulk lifetimes also decrease injection level. At low defect concentrations, the bulk lifetime is limited by intrinsic limits at relatively high injection, $\Delta n \approx 1.6 \times 10^{15}$ cm$^{-3}$ at the MPP. At high defect concentrations, the SRH lifetime dominates. Calculations at the MPP also provide an estimate of cell efficiency as a function of point-defect concentration (Figure 3.4).\textsuperscript{38} While some impurity species are more detrimental than others, a maximum point-defect concentration of $10^{10}$ cm$^{-3}$ is advised for maximum performance. These curves provide a similar behavior to experimentally determined impurity sensitivities by the work of Davis et al.\textsuperscript{75}

$$\Delta n = G_{AV} \tau_{\text{bulk}}$$ \hspace{1cm} (3.11)

$$\frac{1}{\tau_{\text{intrinsic}}} = (\Delta n + N_A) \left(6 \times 10^{-25} N_A^{0.65} + 3 \times 10^{-27} \Delta n^{0.8} + 9.5 \times 10^{-15}\right)$$ \hspace{1cm} (3.12)

$$\frac{1}{\tau_{\text{intrinsic}}} = (\Delta n + N_D) \left(1.8 \times 10^{-24} N_D^{0.65} + 3 \times 10^{-27} \Delta n^{0.8} + 9.5 \times 10^{-15}\right)$$ \hspace{1cm} (3.13)
Figure 3.3: SRH and Intrinsic Lifetime at 1 Sun at the Maximum Power Point

Bulk lifetime from SRH point defect model and intrinsic limits at 1 sun illumination for a 100 µm solar cell with excellent surface passivation ($J_0=10^{15}$ A/cm²). Doping concentrations are $N_A=10^{16}$ for $p$-type (a) and $N_D=3\times10^{15}$ for $n$-type (b) silicon. At low defect concentrations, the bulk lifetime is limited by intrinsic limits. At high defect concentrations, the SRH lifetime dominates. The lifetime impact of impurity point defects is generally lower in $n$-type silicon than $p$-type silicon.
Figure 3.4: Simulated Cell Efficiency and Point-Defect Concentration

SRH point-defects reduce simulated cell efficiency\textsuperscript{38} at 1 sun illumination for a 100 μm solar cell with excellent surface passivation ($J_0 = 10^{-15}$ A/cm\textsuperscript{2}). Doping concentrations are $N_A = 10^{16}$ for p-type (a) and $N_D = 3 \times 10^{15}$ for n-type (b) silicon.

The efficiency impact of impurity point defects is generally lower in n-type silicon than p-type silicon. Tolerable point-defect concentrations to avoid performance loss are on the order of $10^{10}$ cm\textsuperscript{-3}.

### 3.2.3 Structural Defects

Structural defects such as grain boundaries and dislocations also provide a potential limit on bulk lifetime. Dislocations are recombination active if decorated by impurity species.\textsuperscript{78, 79} Furthermore, dislocations effectively trap impurity species and make them difficult to remove.
during processing.\textsuperscript{80, 81} The lifetime impact of dislocations are dependent on the baseline lifetime of the material in non-defective regions and the recombination strength of the dislocation.\textsuperscript{82} Figure 3.5 shows the lifetime impact of structural defects following the model by Donolato,\textsuperscript{82} with parameters from Choi \textit{et al.}\textsuperscript{83} Material with a higher baseline lifetime in defect-free regions is more sensitive to dislocations. Increased recombination strength of dislocations is also observed to increase lifetime impact. A simpler correlation shows a reduction in the performance of a solar cell with increased area-coverage of dislocated regions.\textsuperscript{84} Because of the inherently low structural defect densities in epitaxially grown material (Section 2.2), structural defects are expected to play a relatively small role in recombination within epitaxial material.
Increasing recombination strength increases impact of dislocations

Figure 3.5: Lifetime Impact of Structural Defects

Following the Donolato model\textsuperscript{82} with input from Choi \textit{et al.}\textsuperscript{83} structural defects reduce lifetime. Material with a higher baseline lifetime is more sensitive to the presence of dislocations. Dislocations with a higher recombination activity are more potent at reducing lifetime.
4.1 Surface Lifetime Limits

The bulk lifetime of the substrate wafer determines ultimate device efficiency as shown in Figure 1.6, but is not directly measured. The effective, $\tau_{\text{eff}}$ (measured), carrier lifetime is a function of both the bulk lifetime, $\tau_{\text{bulk}}$, and the surface limited lifetime of the wafer, $\tau_{\text{surface}}$ in Equation (3.1). The value of $\tau_{\text{eff}}$ is not necessarily dependent on the quality of the bulk material under study, $\tau_{\text{bulk}}$, but rather on the effectiveness of surface passivation, $\tau_{\text{surface}}$. The effectiveness of surface passivation is computed with the surface recombination velocity (SRV). A favorable SRV is low, which results in a high $\tau_{\text{surface}}$ and makes $\tau_{\text{eff}}$ and $\tau_{\text{bulk}}$ approximately equal in equation (4.1). The impact of SRV on the equivalence of $\tau_{\text{eff}}$ and $\tau_{\text{bulk}}$ in $p$-type silicon ($N_A = 10^{16}$ cm$^{-3}$, thickness = 100 µm) is shown in (Figure 4.1). For thin high $\tau_{\text{bulk}}$ materials, good surface passivation ($<10$ cm/s) is required to measure a high $\tau_{\text{eff}}$ and to be sensitive to changes in $\tau_{\text{bulk}}$. Additionally, a high $\tau_{\text{intrinsic}}$ material is required to measure a high $\tau_{\text{eff}}$ and to be sensitive to changes in the lifetime due to defects in the material.
Figure 4.1: Bulk Lifetime vs. Measured Effective Lifetime

The effectiveness of surface recombination is characterized as the surface recombination velocity. Effective surface passivation is required for the measurement of high effective lifetimes on thin, high bulk-lifetime materials. A low surface recombination velocity increases the sensitivity of measurements to bulk lifetime.

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surface}}} \tag{4.1}
\]

4.2 Injection Level Dependent Lifetime Measurements

The effective lifetime, \( \tau_{\text{eff}} \), of a material is measured with a Sinton WCT-120 tool as a function of injection level.\(^6\) The measurement subjects a sample to a brief pulse from an exponentially decaying flash lamp, and then measures electrical activity in the wafer. Multiple
measurement modes including Quasi Steady State Photo Conductance (QSSPC) and transient photo conductance decay mode are available. In QSS mode, the wafer response is assessed while under quasi steady-state illuminated by a slowly-decaying flash. In transient mode, the wafer response is assessed after a rapidly-decaying illumination source has decayed. A third measurement mode, generalized, combines the lifetime measured through both the QSS and transient modes and is given by equation (4.2) from Ref. 68 The effective lifetime, $\tau_{\text{eff}}$ is given as a function the injection level, $\Delta n$, generation rate, $G$, and the time derivative of the injection level. In QSS mode, the time derivative of the injection level is set to zero, $d\Delta n/dt = 0$, while in transient mode, the generation rate is set to zero, $G = 0$.

$$\frac{1}{\tau_{\text{eff}}} = \frac{\Delta n}{G - \frac{d\Delta n}{dt}}$$  \hspace{1cm} (4.2)

Examples of injection level dependent measurements from the Sinton WCT-120 are shown in Figure 4.2. The injection level dependence of the data is significant, as the behavior of multiple defect types varies with injection level.

4.2.1 Measurement Noise

Data from measurements on samples with a high lifetime often includes significant noise. A small amount of noise in the input photovoltage signal propagates through Equation (4.2). 68 The averaging of 50 measurements is observed to satisfactorily reduce noise in the calculated material lifetime (Figure 4.2), though even 10 measurements provides a noticeable reduction in noise. With some samples however, it has been observed that illumination from the Sinton-WCT 120 flash lamp impacts the measured lifetime. The observation of lifetime improvement with flashing using float zone substrates suggest that this phenomena is due to instability in the Al$_2$O$_3$. 

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passivating layer itself. While this phenomenon is not completely understood, it is suggested that only the necessary number of measurements are employed for adequate averaging of the final result.

![Figure 4.2: Reduction of Measurement Noise with Averaging](image)

Averaging multiple measurements effectively reduces noise in a Sinton WCT-120 measurement. Because of suspected interactions with the passivating layer however, utilizing only the minimum number of measurements required to reduce noise is suggested.

Modifying the default time derivative routine within the Sinton WCT-120 software was also observed to effectively reduce measurement noise (Figure 4.3). The default Sinton WCT-120 settings \( \frac{d\Delta n}{dt} \) calculation utilizes five points (2 leading, 2 trailing) using a linear regression with the included data points. Increasing the data range too nine points provided a significant reduction in noise, while decreasing the number of points to three provided an increase in noise (Figure 4.3). Other alternative “Noise-robust” differentiators from ref\(^{86}\) did not provide an
effective increase in performance, though it is unclear if the linear differentiation method used by the Sinton WCT-120 excessively dampens the result in comparison to more sophisticated methods.

![Figure 4.3: Number of Points for Time Derivative Noise Comparison](image)

Increasing the number of points considered for the time derivative from the default number of 5 effectively reduces noise in the lifetime data.

### 4.2.2 Impact of Room Illumination

Room illumination was investigated as a potential noise source in the Sinton WCT-120 system. While turning lights off in the laboratory for measurements were not observed to impact noise, a bias in lifetime results at low injection levels was exposed (Figure 4.4). With samples exposed to room illumination, a bias towards higher injection levels is introduced under room lighting. This bias is significant enough to improve lifetime by approximately 100 μs in high lifetime material (Figure 4.4). It is suggested that lifetime measurements should be conducted when samples are not exposed to room illumination.
Room lighting was not observed to increase noise in the measurement. However, a pronounced impact on low injection level lifetime is observed, as the room lighting has increased the background injection level of the material.

### 4.2.3 Impact of Flash Lamp Head Height

The impact of changing the head height of the tool was also investigated with the high-lifetime Al₂O₃ passivated float zone sample and an as-diffused single crystal silicon sample. Fifty measurements were averaged for the float zone sample with transient analysis and a 1/64 flash. Generalized analysis with a slowly-decaying 1/1 flash was used for the as-diffused sample with averaging of three measurements. In neither case did the head height provide a significant variation in measured lifetime. Similarly, the inclusion of the IR band pass filter was not observed to significantly impact measured lifetime with these samples. However, in the case of a sample with a more severe surface limited lifetime, this trend may not be observed.
4.2.4 Minimum Sample Thickness

In order to maintain the assumptions of uniform carrier density in the QSSPC measurement, a minimum sample thickness of twice the diffusion length of the material is enforced during measurements. This condition arises with low lifetime material. Because the calculated lifetime is a function of the sample thickness, a solver was implemented to converge on a calculated lifetime and sample thickness that satisfies this constraint. The diffusion length was calculated following equation (4.3) below, with \( \mathcal{L}_D \) as the diffusion length in cm, \( D \) as the minority carrier diffusivity in \( \text{cm}^2/\text{s} \) and \( \tau \) as the carrier lifetime in seconds. The minority carrier diffusivity is a function of doping for both \( p \)-type and \( n \)-type materials.

\[
\mathcal{L}_D = \sqrt{D \tau}
\]  

(4.3)

4.2.5 Reference Cell Aperture

In addition to the diffusion length limitation, low lifetime material may require additional illumination to reach an injection level of \( 10^{15} \text{ cm}^{-3} \). This can be accomplished by lowering the flash lamp to a height of < 200mm above the sample. At this flash lamp height, the reference cell signal will violate its saturation limit of 0.6 Volts. The reference cell signal however, can be attenuated with an aperture supplied by Sinton Instruments following the procedure in Table 4.1.
### Table 4.1: Reference Cell Aperture Procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acquire data with a moderate lifetime sample with a low sample head height without an aperture over the reference cell. Note the lifetime at an injection level that is not impacted by the saturation of the reference cell.</td>
</tr>
<tr>
<td>2</td>
<td>Tape the aperture plate over the reference cell. The 2nd largest aperture has proven appropriate for low flash lamp measurements in the past.</td>
</tr>
<tr>
<td>3</td>
<td>Acquire data again. The reference cell data acquisition ranges will likely need to be zoomed.</td>
</tr>
<tr>
<td>4</td>
<td>Use the goal seek function to modify the reference cell value ([V/\text{sun}]) until the lifetime before and after the aperture match. Note the revised reference cell value for future measurements in this condition. However, begin new measurements without the aperture with a different baseline spreadsheet to preserve the original reference cell value.</td>
</tr>
<tr>
<td>5</td>
<td>Lower the flash lamp as needed to reach the injection level of interest. The diffusion length solver discussed above should be used for an accurate calculation of injection level with low-lifetime samples.</td>
</tr>
</tbody>
</table>

### 4.2.6 Optical Constant

In QSS and Generalized measurement modes, the lifetime calculation requires an optical constant to factor in the amount of incident light from the flash lamp that is absorbed by the sample. A PC1D simulation, provided by Sinton Instruments, was utilized to solve for the optical constant for both bare samples and those passivated by aluminum oxide with and without surface texture (Figure 4.5). The refractive index and extinction aluminum oxide were provided by ref, with the reflection calculated by QSS-Model.
4.2.7 WCT-120 Lifetime Comparison

The Sinton WCT-120 tool in the MIT PV Lab was used to measure a standard set of wafers used in a round-robin study of Sinton WCT-120 lifetime testers deployed throughout the world, though not included in the linked reference. The tool used within this thesis fell within the distribution of the deployed systems.

4.3 \(\mu\)-PCD Lifetime Mapping

Lifetime measurements provided by the QSSPC tool provides information about the variation of lifetime with injection level. This is especially important for identifying the nature and concentration of recombination active defects such as iron (Section: 4.4). However, spatial data indicating the variation of lifetime over the surface of a sample is not provided with this measurement method. Microwave-induced photoconductive decay (\(\mu\)-PCD, Semilab WT-2000)
is used to provide spatial lifetime measurements over the surface of the sample. A 904 nm laser, which corresponds to a absorption depth of approximately 30 μm in silicon, is used to excite carriers in the sample.\textsuperscript{95} A detector is used to sense the microwave reflectivity which depends on the conductivity of sample.\textsuperscript{95} The transient decay of the conductivity signal after a 200 ns laser pulse is used to calculate the lifetime. The excitation area of the laser is approximately 1 mm\textsuperscript{2}. However, the X-Y stage that supports the sample can be moved with a resolution as low as 62.5 μm. Figure 4.6 shows lifetime maps for a float zone silicon sample passivated with Al\textsubscript{2}O\textsubscript{3} with a resolution of a) 62.5 μm and b) 1 mm. Although the method oversamples at resolutions less than 1 mm, useful definition is observed in the maps.

The injection level of the measurement has been investigated with this measurement technique without a bias lamp.\textsuperscript{96}, \textsuperscript{97} However, the actual injection level and lifetime of the measurement still contains significant uncertainty.\textsuperscript{98} However, although more qualitative in nature, μ-PCD measurements are valuable for identifying the distribution of recombination active defects and potential evidence of contamination sources. As explained in (Section: 4.4), μ-PCD can also be used for the analysis of meta-stable defects such as Fe\textsubscript{i}-B\textsubscript{s} pairs, though the unknown injection level of the measurements limits its application herein to a qualitative analysis.
4.4 Interstitial Iron Measurement

Iron contamination substantially reduces the lifetime of \( p \)-type silicon material\(^{75, 99} \) and is common in manufacturing environments. Given the large electrical impact of the impurity, low concentrations of contamination can be accurately measured via lifetime spectroscopy.\(^{100, 101} \) Iron forms metastable defects with boron dopants in \( p \)-type silicon that have different levels of electrical activity than isolated interstitial iron.\(^{88, 101} \) In the equilibrium state in \( p \)-type silicon, positively charged interstitial iron pairs with negatively charged substitutional boron forming \( \text{Fe}_i \)-\( \text{B}_s \) pairs.\(^{102} \) However, these pairs can be dissociated through suitable illumination or high-temperature annealing.\(^{88} \) Via injection level dependent lifetime measurements with \( \text{Fe}_i \)-\( \text{B}_s \), paired and dissociated (Figure 4.7), the iron point defect concentration is calculated with equation (4.4).\(^{101} \) In the equation, \([\text{Fe}_i] \text{ [atom/cm}^3\text{]}\) is the iron point defect concentration, \( C \text{ [\mu s cm}^{-3}\text{]}\) is the...
pre-factor, $\tau_{Fei} [\mu s]$ is the carrier lifetime with iron interstitially distributed after the dissociation of iron-boron pairs, and $\tau_{Fei- Bs} [\mu s]$ is the carrier lifetime with iron paired with boron.$^{101}$

\[
[Fe_i] = C \left( \frac{1}{\tau_{Fei}} - \frac{1}{\tau_{Fei- Bs}} \right)
\]  

(4.4)

Figure 4.7: Injection Level Dependent Lifetime of Metastable Iron Defect

Iron has different levels of electrical activity in $p$-type silicon depending on its pairing with boron dopants. The concentration of interstitial iron can be measured through lifetime measurements with interstitial iron paired with boron, $Fe_i - Bs$, and when pairs are dissociated, $Fe_i$.

4.4.1 Pre-factor

The value of the pre-factor varies as a function of the base doping of the wafer, carrier capture cross-sections, and the injection level of the lifetime measurements in equation (4.4). The pre-factor is shown in Figure 4.8 as a function of doping level and injection level with capture cross sections taken as $\sigma_n = 5.0 \times 10^{-15}$ cm$^2$ and $\sigma_p = 3.0 \times 10^{-15}$ cm$^2$ for $Fe_i - Bs$ pairs and $\sigma_n = 1.3 \times 10^{-14}$ cm$^2$.
cm² and \( \sigma_p = 7.0 \times 10^{-17} \text{ cm}^2 \) for Fe_i. Defect energy levels are \( E_C - E_t = 0.744 \text{ eV} \) for Fe_i and \( E_C - E_t = 0.26 \text{ eV} \) for Fe_i-B_s pairs. A crossover point is observed in the injection level dependent lifetime data of an iron-contaminated sample in Figure 4.7. Above this point, dissociated Fe_i provides higher lifetime than Fe_i-B_s pairs. Below the crossover point, Fe_i-B_s pairs provide higher lifetime than dissociated Fe_i. The injection level of the crossover point can be predicted with a Shockley-Read-Hall (SRH) recombination model. Fe_i is a deeper level than Fe_i-B_s and has a lower electron (minority carrier in p-type silicon) lifetime coefficient that dominates in low-injection conditions. However, at high injection conditions, the impact of both minority and majority carrier recombination is pronounced. Fe_i-B_s pairs have a lower majority carrier lifetime coefficient than Fe_i that overcomes the minority carrier advantage of Fe_i at high-injection conditions. The crossover point is observed in the calculation of the pre-factor (Figure 4.8). Within a narrow injection level regime around the crossover point, the relationship between the pairing of iron point and lifetime becomes erratic (Figure 4.8). To avoid this regime, measurements are completed at a minimum injection level of approximately \( 0.1 \times N_A \), the boron doping concentration. Error bounds for the [Fe_i] calculation are determined assuming a lifetime measurement error of 1.5% for repeated measurements of lifetime on a single Sinton lifetime tester and random propagation through Equation (4.4).
The pre-factor for the iron point defect concentration is a function of wafer doping and the injection level of the measurement. An inflection point is observed in the injection level dependence of the pre-factor. To avoid the crossover point, measurements should be conducted at a minimum injection level of approximately $0.1 \times N_A$.

### 4.4.2 Fe$_1$-B$_s$ Dissociation

Fe$_1$-B$_s$ pairs are dissociated through adequate illumination or thermal annealing. Previous studies have used 2 min of illumination at approximately 2 suns (200 mW/cm$^2$), 5 min of illumination at approximately 1 sun (100 mW/cm$^2$), approximately 20 flashes by a high-intensity flash (Hensel EHT 3000 in Semilab WT2000, estimated 500 suns for 10 ms) or annealing at $> 200$ $^\circ$C. The equilibrium concentration of Fe$_1$-B$_s$ pairs are given as a function of temperature, $T$ in K, and doping, $N_A$ in cm$^{-3}$, in Equation (4.5). Figure 4.9, a shows...
the required temperature to dissociated 99%, 90%, and 70% of Fe<sub>i</sub>-B<sub>s</sub> pairs as a function of doping. High temperatures are required to dissociate 99% of Fe<sub>i</sub>-B<sub>s</sub> pairs.

\[
\frac{[Fe_iB_s]}{[Fe_i]} = 10^{-23} N_A \exp \left( \frac{0.65}{kT} \right)
\]

(4.5)

The initial rate of Fe<sub>i</sub>-B<sub>s</sub> pair dissociation, \( \Gamma_d \) [1/s] under illumination follows Equation (4.6).\textsuperscript{111,112} \( G_{av} \) is the average (uniform) generation rate in cm\(^{-3}\)s\(^{-1}\) in the sample and [Fe<sub>i</sub>-B<sub>s</sub>] is the concentration of recombination centers in cm\(^{-3}\). Figure 4.9, b shows the time required for dissociation at four generation rates,\textsuperscript{111,112} and the approximate illumination intensities in suns as estimated with a wafer thickness of 100 \( \mu \)m with 20nm of Al\(_2\)O\(_3\).\textsuperscript{38} Heavily contaminated samples require substantial illumination times > 1hr to dissociate Fe<sub>i</sub>-B<sub>s</sub> pairs. Because of this dependence, thermal dissociation is suggested for Fe<sub>i</sub>-B<sub>s</sub> pair dissociation of heavily contaminated samples. However, an initial dissociation of 90% may significantly reduce the required thermal input.

\[
\Gamma_d = 5 \times 10^{-15} \frac{G_{av}^2}{[Fe_iB_s]^2}
\]

(4.6)
To avoid dissociation, a maximum integrated absorbed energy of 0.01 J/cm² is specified. The integrated absorbed energy is estimated at $7 \times 10^{-4}$ J/cm² and 0.02 J/cm² for a Sinton WCT-120 flash lamp in 1/64 and 1/1 modes respectively. Therefore, the 1/1 flash mode is expected to dissociate Fe₇-B₅ pairs. However, experience has shown that the 1/64 flash mode is also capable of modifying the distribution of iron within a sample, requiring minimum measurements for lifetime in the associated state.

### 4.4.3 Fe₇-B₅ Association Time

The time required for the association of Fe₇-B₅ pairs is a function of the boron doping concentration and ambient temperature. The time constant for association is provided by Equation (4.7), based on the recently updated work for Tan et al. The time required for 99.3% association (5 time constants) of Fe₇-B₅ pairs for the three doping levels shown in Figure...
4.8, $\left(5 \times 10^{15} \text{ cm}^{-3}, 1 \times 10^{16} \text{ cm}^{-3}, \text{ and } 5 \times 10^{16} \text{ cm}^{-3}\right)$ are shown in Figure 4.10 as a function of temperature.\textsuperscript{87, 113} It is recommended that associated measurements are conducted at the minimum time required to form Fe\textsubscript{r}-B\textsubscript{s} pairs to avoid convolution with other metastable defects that may have a different time constant for association, such as chromium.\textsuperscript{88}

$$\Gamma_{\text{assoc}} = 5.7 \times 10^5 \frac{T}{N_A} \exp\left(\frac{0.66}{kT}\right)$$

(4.7)

**Figure 4.10: Fe\textsubscript{r}-B\textsubscript{s} Pair Defect Association Time**

The time required for the association (5 time constants, 99.3 % formation) of the Fe\textsubscript{r}-B\textsubscript{s} pair is a strong function of boron doping concentration and temperature.\textsuperscript{87, 113}

### 4.4.4 Measurement Process

The [Fe\textsubscript{r}] measurement process is shown in Figure 4.11. The sample is first flashed 15-20 times with the flash lamp within the Semilab WT2000. Then, within 30 seconds of the final flash, injection level dependent lifetime measurements are completed with the Sinton WCT-120.
In the case of low-lifetime samples, single generalized measurements are completed in increments of 30 seconds until approximately 150 seconds have elapsed since the final flash. In the case of high-lifetime samples that require significant averaging of transient measurements to minimize noise (Section 4.2.1), a single measurement with many averages may be taken. The sample is then stored in a dark enclosure for an adequate time for Fe\textsubscript{i}-B\textsubscript{s} pair association. Lifetime is then re-measured with the Sinton WCT-120. Here a single measurement is completed in low-lifetime samples, and a reduced number of measurements are utilized for high-lifetime samples, as the Sinton WCT-120 measurement flash lamp has been observed to modify the sample lifetime, potentially through an interaction with Fe\textsubscript{i}-B\textsubscript{s} pairs. A \( \mu \)-PCD measurement is then completed on the associated state sample, followed by another 15-20 flashes to re-dissociate Fe\textsubscript{i}-B\textsubscript{s} pairs and a \( \mu \)-PCD measurement in the dissociated state.

Figure 4.11: Iron Boron Pair Dissociation Experimental Schematic
SURFACE PASSIVATION

Bare silicon surfaces provide an effective recombination pathway with a recombination rate $U_s$, in cm$^{-2}$s$^{-1}$, following the SRH recombination model defined in Equation (5.1).

The recombination rate may be reduced through a reduction in the interface defect density $D_{it}$, in cm$^{-2}$, or the concentration of carriers at the surface ($n_s$ and $p_s$). The surface recombination velocity $S$, in cm/s, is then defined following Equation (5.2), and allows the surface limited lifetime to be calculated following Equation (5.3). This expression assumes both sides of the sample are identically passivated, which has an error of less than 5% over a large range of surface recombination velocities.

The expression however is most accurate when the surface lifetime is dominated by either the effectiveness of passivation at the surface or carrier transport to the surfaces ($SW/D << 1$ or $SW/D >> 10$).

$$U_s = \frac{(n_s p_s - n_i^2) \nu_{th} D_{it}}{n_s + n_i + p_s + p_i}$$  \hspace{1cm} (5.1)

$$S = \frac{U_s}{\Delta n_s}$$  \hspace{1cm} (5.2)

$$\tau_{surface} = \frac{W}{2S} + \frac{1}{D} \left( \frac{W}{\pi} \right)^2$$  \hspace{1cm} (5.3)
In addition to the surface recombination velocity, the sample thickness $W$ in cm, and $D$ the minority carrier diffusivity in cm$^2$/s significantly influence surface lifetime limits of a sample. Therefore the effect of surface recombination becomes critical for thin samples. As discussed in Section 4.1, excellent surface passivation is required to obtain high effective lifetime and to be sensitive to changes in bulk lifetime. Figure 5.1 shows the surface limited lifetime as a function of sample thickness and the surface recombination velocity (SRV) for a silicon wafer. Relatively small changes in SRV and sample thickness have a large impact on the resulting effective lifetimes. A SRV < 10 cm/s is required to measure lifetimes up to 1,000 μs on a 200 μm thick wafer, while a SRV < 5 cm/s is required for a 100 μm thick wafer.

![Figure 5.1: Surface-Limited Lifetime](image)

The lifetime limitation of a silicon wafer surface is defined by wafer thickness and the surface recombination velocity of the passivating layer. Excellent surface passivation is required to measure effective lifetimes >1,000 μs with 100 μm thick wafers.  

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85
5.1 ALD Aluminum Oxide

Aluminum oxide (Al\(_2\)O\(_3\)) deposited by atomic layer deposition (ALD) was utilized as a passivation layer for lifetime measurements. Extensive literature is available on Al\(_2\)O\(_3\) passivation, and is summarized in Ref.\(^90\) Al\(_2\)O\(_3\) reduces the electrical activity of sample surfaces by repelling charges with a field-effect and reducing the density of interface states.\(^90\) The fixed negative charge in an Al\(_2\)O\(_3\) layer effectively repels the minority carrier electrons in \(p\)-type silicon by forming an accumulation region.\(^90\) In \(n\)-type silicon, the fixed negative charge forms an inversion condition near the sample surface.\(^90\) Very good SRV values \(< 5\) cm/s have been achieved with Al\(_2\)O\(_3\).\(^90\) The processes utilized are detailed in Appendix D.

A thermal ALD system (Cambridge Nanotech Savannah 200) was used at a temperature of 200 °C with water as a precursor to deposit that passivating layer. An ALD reaction includes the formation of single monolayers on the wafer surface, and allows for the alternation of species. This regime however, requires adequate purging after injection of a precursor gas into the reaction chamber to allow excess precursors vent. Figure 5.2 shows the pressure inside the ALD reaction chamber after injection of water and the aluminum precursor at a temperature of 200 °C. A 9 second of purge duration for both water and the aluminum precursor were determined as adequate for the reaction chamber to obtain roughly base pressure and avoid a less uniform CVD deposition mode.\(^90\)
The standard operating procedure for passivation is detailed in Appendix D. If samples are diffused before passivation, the emitters are removed following the procedure in Appendix C. Samples are first chemically cleaned with RCA process that does not include a final HF dip to preserve the oxide that results from the RCA2 step. Samples are placed atop chips of single crystal silicon within the reaction chamber to enable deposition on both sides of the samples. After roughly positioning the chips to support the wafers with a minimum of sample contact, 5 nm of Al₂O₃ is deposited in an attempt to isolate the samples of interest from any contamination that is present in the reaction chamber of the shared-use tool. After the deposition of the capping layer and sample loading, 20 nm of Al₂O₃ is deposited on the samples over 170 cycles. The samples are then annealed at approximately 350 °C in a N₂ atmosphere.

The electrical characteristics of the passivation layer are assessed with a contactless voltage-capacitance (V-Q) measurement technique (Semilab WT2000). During the measurement,
charge (Q) is deposited on the sample surface while the surface potential (V) is monitored with a Kelvin Probe. The fixed negative charge density (Q\text{total}) in the film is then assessed as the amount of deposited charge that provides a surface potential of zero. The density of interface states (D_{it}) is then calculated by comparing the actual V–Q measurement curve to an idealized measurement with \( D_{it} = 0 \). An Al₂O₃ passivation film deposited and measured using the above procedures yielded a fixed negative charge density of \( Q_{\text{total}} = -1.15 \times 10^{12} \text{ cm}^{-2} \) and density of interface defects of \( D_{it} = 1.65 \times 10^{11} \text{ eV}^{-1} \text{cm}^{-2} \). These values fall within the range of the expected properties of Al₂O₃ passivation.

5.2 Measuring Passivation Effectiveness

The effectiveness of the passivating layer can be assessed by comparing the measured effective lifetime (\( \tau_{\text{eff}} \)) of the wafers to the maximum intrinsic lifetime given by the model of Richter et al. This is completed by assuming the bulk lifetime (\( \tau_{\text{bulk}} \)) of the material in Equation (4.1) is equal to the intrinsic limit (\( \tau_{\text{intrinsic}} \)). Because of this assumption, the use of high-purity float zone (FZ) silicon is preferred for this calculation. Equation (5.4) provides the surface limited lifetime (\( \tau_{\text{surface}} \)) as a function of these parameters. Additionally, because the doping or surface roughness of the sample may impact the effectiveness of surface passivation, the control sample should match the composition of the samples of interest. Following (5.3), the resulting surface recombination velocity is given by Equation (5.5).

\[
\tau_{\text{surface}} = \frac{-\tau_{\text{eff}} \cdot \tau_{\text{intrinsic}}}{\tau_{\text{eff}} - \tau_{\text{intrinsic}}} 
\]

\[
S = \frac{D \pi^2 W}{2D \pi^2 \tau_{\text{surface}} - 2W^2} 
\]
This calculation can be completed with an injection level dependence. Figure 5.3 shows the effective and intrinsic lifetimes for a 3 Ωcm, p-type, 253 μm thick, FZ control wafer after Al₂O₃ passivation with the calculated surface recombination velocity. As in Figure 3.1, the intrinsic lifetime falls at high injection levels. The resulting surface recombination velocity, as calculated by Equation (5.5), is also a function of injection level. However, for the purposes of analysis, a constant surface recombination velocity is applied from the lower injection level regime. In an alternative method to that presented herein, the surface recombination velocity can also be calculated at multiple sample thicknesses. Ongoing work in Al₂O₃ passivation includes characterizing the stability of passivated samples.

![Figure 5.3: Lifetime and SRV of Float Zone Control Wafer](image)

The effective lifetime of a float zone control wafer (blue) is compared to its intrinsic performance limit (red) to calculate the surface recombination velocity of the passivating layer (green). The surface recombination velocity is observed to increase at high injection levels.
5.3 Corona Charge of Surface Passivation

Depositing additional negative charge on the sample surface can be used to increase the effectiveness of the field-effect passivation already provided by the fixed negative charge of the A12O3 layer. Corona charge was deposited on samples using a small diameter wire placed over the surface of the sample at a voltage of 10 kV (Semilab WT-2000). The fixed charge of an A12O3 passivation layer is generally on the order of −1 × 10^{12} to −5 × 10^{12} cm^{-2} (approximately −160 nC/cm^{2} to −800 nC/cm^{2}) and was Q_{total} = −1.15 × 10^{12} cm^{-2} on a A12O3 film deposited with available equipment and procedures. Figure 5.4 shows an improvement in measured effective lifetime and a reduction in the calculated surface recombination velocity with the deposition of additional negative corona charge. The resulting surface recombination velocity of < 3 cm/s is exceptional. However, it is noted that excessive corona charge can cause damage to the passivation layer. The range assessed herein did not appear to degrade passivation quality.

![Figure 5.4: Lifetime Improvement with Corona Charging of n-type Samples](image)

The effective lifetime at an injection level of 10^{15} cm^{-3} of a n-type sample increased and the calculated upper bound surface recombination velocity decreased with the deposition of corona charge. The SRV upper bound was calculated assuming a bulk lifetime equal to the Richer et al limit.69
6.1 Internal vs. External Gettering

Impurity gettering consists of the transport of harmful impurity species (Figure 3.3) from detrimental wafer areas to more benign locations. A gettering process can move impurity species towards a surface for potential removal with an external gettering process, or towards pre-determined locations within the bulk of the wafer through an internal gettering process. Internal gettering processes, such as to intentional silicon-oxide precipitates, are not traditionally used in PV manufacturing as the entire wafer is electrically active. Phosphorus diffusion gettering (PDG) is a commonly employed external gettering technique for PV manufacturing that simultaneously getters impurities and forms the $p$-$n$ junction for $p$-type solar cells. The gettering process consists of three primarily steps. First, an impurity species is unlocked from its detrimental location through an increase of diffusivity and solubility with temperature. The impurity then diffuses to the heavily phosphorus doped $n^+$ region driven by a difference in solubility and is captured in the heavily doped gettering layer. The relationships between the driving force for gettering, the diffusivity of impurities and their rate of dissolution are strong functions of temperature.
6.2 Phosphorous Diffusion Gettering

The progression of a gettering process is shown schematically in Figure 6.1.\textsuperscript{119,120} First, in an as grown wafer, impurity contamination is distributed between precipitate and interstitial locations. Then, during high-temperature phosphorus diffusion, the heavily doped $n^+$ emitter region begins to form and precipitated impurities dissolve. Some interstitial contamination begins to be gettered to the emitter. During cool-down, the driving force for gettering increases, as the solubility difference between the emitter and bulk rises, while the diffusivity of interstitial contamination falls. Also during cool-down, some interstitial contamination forms precipitates through a relaxation gettering process.\textsuperscript{39}
Evolution of Metal Impurities

As-grown material contains impurities that are distributed as interstitial defects and precipitates. During phosphorus diffusion gettering, interstitial impurities diffuse towards a heavily doped $n^+$ gettering layer while precipitates dissolve. During cool-down, the driving force for gettering increases while interstitial defects precipitate.

A standard, high-throughput, gettering process includes a single high-temperature diffusion step and exponential cooling to room temperature from the plateau step (Figure 6.2, Red). For some materials, this process is sufficient to reduce interstitial contamination levels below performance-limiting thresholds. Further reductions in interstitial contamination can be realized through extended processes to lower temperatures. Given the stronger driving force for impurity segregation and precipitation at low-temperatures, a slow cooling rate ($2 - 4 \, ^\circ\text{C/min}$) from the gettering plateau temperature effectively reduces the final impurity concentration (Figure 6.2, Green). A low temperature anneal (LTA), (Figure 6.2, Blue) further capitalizes on the increased driving force at reduced temperatures, by annealing material at approximately $550 - 68$
600 °C, and has proven effective at substantially reducing gettered interstitial iron contamination.\textsuperscript{34, 122, 123}

![Diagram showing Gettering Time-Temperature Profiles](image)

Figure 6.2: Gettering Time-Temperature Profiles

A standard high-throughput gettering process, shown in red, includes unloading material directly at the plateau temperature. Significant reductions in the final interstitial contamination after gettering however, can be realized through the application of a slow cool, shown in green, or a low temperature anneal, shown in red.

The application of the slow cool or LTA processes do not significantly influence the doping profile of phosphorus in the wafer. The model of Bentzen \textit{et al.}\textsuperscript{124} was applied to simulate the doping profile following Fick's law in Equation (6.1). \(D(C)\) is the concentration dependent diffusivity of phosphorus in cm\(^2\)/s, and is defined in Equation (6.2).\textsuperscript{124} Following ref\textsuperscript{124} the first term of Equation (6.2) defines the diffusivity of phosphorus in silicon through an interstitial mechanism, while the second term defines the diffusitivity of phosphorus through a vacancy mechanism. At low P concentrations, the interstitial mechanism dominates, while at high P
concentrations, the vacancy mechanism dominates.\textsuperscript{124} The corrected value of $D_0 = 5.8 \times 10^{-5}$ cm$^2$/s for interstitial diffusion is applied within this model,\textsuperscript{124} as identified by the author.\textsuperscript{125} Figure 6.3 shows the simulated doping profiles obtained with standard (red), and both slow cooling and LTA (both represented by blue) gettering processes. The addition of either a slow cool or LTA does not appreciably change the doping profile of the $n^+$ region.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(C) \frac{\partial C}{\partial x} \right)$$  \hspace{1cm} (6.1)

$$D(C) = \frac{D_{pi}^{eff} D_l^{eff}}{D_{pi}^{eff} + D_l^{eff}} + D_{PV}^{eff}$$  \hspace{1cm} (6.2)

Figure 6.3: Calculated Phosphorus Diffusion Doping Profiles

Phosphorus doping profiles calculated using the model of Bentzen et al.\textsuperscript{124,125} Standard gettering is shown in red. Because of the low-temperatures employed, the doping profile of phosphorus does not change appreciably with the addition of a low temperature anneal after slow cooling (both represented in blue).
6.3 Getterability of Impurities

Not all impurities can be effectively removed during gettering.\textsuperscript{80, 126} Molybdenum for example, with its low diffusivity,\textsuperscript{118} has not been observed to effectively getter even after extended treatments.\textsuperscript{80, 127} An impurity must have a sufficient diffusivity to move to the benign area to be effectively gettered.\textsuperscript{39} Figure 6.4 a shows the diffusivity (a) and solubility (b) of common impurities as a function of inverse temperature.\textsuperscript{118, 128, 129} Generally, slowly diffusing species have lower solubilities. The resulting diffusion length for these impurity species are shown for a 25 minute 845 °C process in Figure 6.4, c. A wafer is on the order of 10^2 μm thick, suggesting that only species that diffuse at a rate of magnesium or faster are readily getterable at standard temperatures. Furthermore, substitutional diffusors may also be non-getterable because of their low diffusivities.\textsuperscript{126} The solubility of a species at the gettering temperature (Figure 6.4) defines an upper limit for the level of interstitial contamination expected after gettering. Unfortunately, some non-getterable impurities also have a large lifetime impact (Figure 3.2), indicating that some impurities must be effectively controlled during growth for high lifetime material.\textsuperscript{130}
The diffusivity (a) and solubility (b) of metal impurities varies strongly with species and is a strong function of temperature. During a 25 minute gettering process at 845 °C, some species have an inadequate diffusivity to be effectively gettered (c). The solubility of a species at the gettering temperature of 845 °C helps indicate the upper limit for interstitial contamination after gettering (d).

6.4 Furnace Maintenance

The level of doping achieved during diffusion was observed to decrease over the course of multiple experiments with the furnace used (Tystar Tytan 3800) within this thesis. Multiple
sources of this process shift were investigated and included 1) an inadequate seal on the furnace tube to provide slight positive pressure, 2) an improper calibration of the thermocouples used to maintain the furnace temperature, 3) an expired liquid POCl₃ source, 4) buildup of residue within the furnace tube (Figure 6.5, a), and 5) buildup of liquid droplets within the tubing used to connect the POCl₃ source to the furnace tube (Figure 6.5, b). After repairing or checking items 1-4 with the furnace manufacturer, the liquid droplets within the tubing were removed (Figure 6.5, b). The liquid was expected to have migrated into the tubes through the inadequate refrigeration of the POCl₃ source and condensation of the warm gas on cooler tubing walls due to the lack of thermal grease within a thermocouple well. In addition to the repairs above, a reduced level of insulation was installed in the furnace tube to increase the tube exit temperature to reduce residue build-up (Figure 6.5, a), and new procedures for furnace programing were implemented to reduce challenges in the future (detailed in Appendix B). After these changes, the doping levels provided by the furnace were observed to increase.
Figure 6.5: POCl₃ Furnace Contamination before Cleaning

Deposits of P₂O₅ powdered solids were observed within the furnace tube (a). Liquid deposits were also observed in the gas tubing that connects the POCl₃ source to the furnace tube (b).
Chapter 7

Defect Identification in As-Grown Epitaxial Wafers

7.1 As-Grown Lifetime and Interstitial Iron Concentration

The as-grown lifetime of p-type epitaxial material was measured after Al₂O₃ passivation (Section 5.1). A very low effective lifetime < 1μs was observed for as-grown p-type material at an injection level of 10¹⁵ cm⁻³ (Figure 7.1). This result is far below expectation, given the low structural defect density of the material. An interstitial iron concentration ([Feᵢ]) of (4.5 ± 77) x 10¹¹ cm⁻³ was measured via injection level dependent lifetime spectroscopy after 20 flashes from a Semilab WT2000 flash lamp (Hensel EHT 3000, Section 4.4). A Feᵢ concentration of 4.5 x 10¹¹ cm⁻³ is relatively low, and well below the concentration required to degrade lifetime to < 1 μs. SRH modeling³⁸ indicates a defect lifetime of τₜₜ₋₆₆ = 56 μs for this concentration, far above the observed lifetime. However, the significant uncertainty of the measurement indicates that this measurement is near its detection limit. Furthermore, the low lifetime of the material suggests the presence of a substantial concentration of [Feᵢ], which requires substantial energy input for the dissociation of Feᵢ-Bₓ pairs which may not have been achieved with flash-lamp illumination (Figure 4.9). Therefore, additional measurements were completed to elucidate the root-cause of the low lifetime in as-grown material.
The effective as-grown lifetime of p-type material is less than 1 μs. The Fe concentration of $4.5 \times 10^{11}$ cm$^{-3}$ determined by lifetime spectroscopy is inadequate to reduce lifetime to $< 1$ μs.

### 7.2 Bulk Mass Spectrometry

Injection level dependent lifetime measurements are sensitive to defects distributed interstitially in the bulk of the wafer. A majority of metal contamination however, is usually distributed in precipitates. Inductively coupled plasma mass spectrometry (ICP-MS, Fraunhofer Center of Silicon Photovoltaics) was completed to measure the total concentration (interstitial + precipitate) of various species: Fe, Cr, Cu, Ni, Ti, Zn, W, Mo, V, Co, Mg, Al, Mn, Zr, Ag, Sn, Au, Nb, P, and B. Four samples were provided for measurements: Gen I epi, Gen II epi, a float zone control wafer directly from the box with saw damage, and a float zone control wafer that was laser-cut following the sample preparation procedure used for the epitaxial samples. In all cases but Gen I material, $> 2$ g of material was provided to allow for two measurements with ICP-MS. Very-high concentrations of many contaminants were measured in both the epi samples and
float zone controls. This casts doubt on the absolute concentrations of detected impurities, but still allows for relative comparisons. Significant relative concentrations of Zn, Fe, Ti, Al, and Mg are observed in the material. Zn, Fe, and Ti are significant lifetime limiting defects in p-type silicon (Figure 3.2).  

7.3 Synchrotron micro x-ray fluorescence

ICP-MS measurements provide the total concentrations of impurities. However, the distribution of impurities in addition to their total concentration provide valuable information about the nature of defects. Micro x-ray fluorescence (μ-XRF) measurements were completed by colleagues at beam line 2ID-D at the advanced photon source (APS) synchrotron on structural defect etched material. μ-XRF is sensitive to precipitates composed of impurities with a K x-ray absorption edge <10 keV. Of the species measured with ICP-MS, this excludes detection of the heavier elements of W, Mo, Zr, Ag, Sn, Au, and Nb. Precipitates of Ti, Fe, Cr, Cu, and Zn are observed in as-grown p-type material (Figure 7.2). Of these species, Zn, Fe, and Ti were observed in high total concentrations from bulk mass spectrometry and corroborate these results. However, these results do not indicate absolute concentration as the solubility of these species differs over five orders of magnitude (Figure 6.4, b) and an insignificant sample area was analyzed with the tool. The highest precipitate concentration observed [μg/cm²] is Ti, which also has the lowest solubility of the species measured (Figure 6.4).

The size of iron precipitates is measured from the μ-XRF data assuming spherical precipitates assuming a volumetric density of precipitated iron of $C_{Fe} = 2.6 \times 10^{22}$ cm⁻³. The maximum iron precipitate radius of approximately 16 nm is consistent with the observed range of iron precipitate radii found in as-grown mc-Si materials. An increased density of small precipitates may be present in the epitaxial material however, as the minimum precipitate radius observable
with the technique is approximately 8 nm.\textsuperscript{138} The radius of the peak Ti precipitate was assessed using the same method as applied for Fe.\textsuperscript{134-136} The volumetric density of Ti precipitates were calculated by adjusting $C_{\text{Fe}}$ based on the volume of single Ti and Fe atoms using their respective atomic radii.\textsuperscript{139} The resulting $C_{\text{Ti}} = 1.8 \times 10^{22}$ cm$^{-3}$, and maximum precipitate radius is approximately 58 nm. While significantly larger than the observed size of Fe precipitates, this value falls below the size of foreign inclusions.\textsuperscript{136}
Figure 7.2: Synchrotron X-Ray Florescence Analysis of As-Grown p-type Material

Impurity precipitates of Ti, Fe, Cr, Cu, and Zn are observed in as-grown p-type material.
7.4 Oxygen

Oxygen forms a recombination active defect in boron doped $p$-type silicon that is metastable with illumination.\textsuperscript{79} Oxygen in epitaxial silicon may diffuse from the substrate, or from inadequate removal of the SiO$_2$ before initiating deposition.\textsuperscript{140-142} However, the oxygen concentration in epitaxial silicon is low ($< 10^{17}$ cm$^{-3}$) in the literature.\textsuperscript{140-142} This is below normal values for Czochralski (CZ) single-crystal silicon,\textsuperscript{143} and is not sufficient to degrade lifetime to the observed as-grown level.\textsuperscript{144}

7.5 Response to Gettering and High-Temperature Annealing

Useful conclusions about the nature of as-grown lifetime-limiting defects can be drawn from assessing the gettered performance of the material. As detailed in the next chapter, lifetime improves by $>>100\times$ after gettering. This indicates that a getterable defects limit as-grown performance. A comparison with the diffusivities of point defect impurities (Figure 6.4) suggests that V, Ti, Mo, or W cannot be responsible for the poor as-grown performance as these species should not respond to gettering.

Conversely, of the initially considered impurities limiting as-grown lifetime, the effectiveness of gettering Pt, Fe, Cr, and Ag is demonstrated.\textsuperscript{80, 118, 126} The gettering response for Zn, however, is less well known.\textsuperscript{126} Zn diffuses by a kick-out mechanism,\textsuperscript{118} and may be influenced by the density of structural defects.\textsuperscript{145} Pt and Au however, have similar diffusion mechanisms and solubilities as Zn and are also gettered by phosphorus diffusion.\textsuperscript{118, 145, 146}
7.6 Deep Level Transient Spectrometry

Deep level transient spectrometry (DLTS, V.P. Markevich and A.R. Peaker, University of Manchester) measurements and analysis were completed on as-grown p-type material to identify the species and concentrations of electrically active majority carrier traps in the lower half of the bandgap. 1 mm diameter Al+Ti Schottky diodes were used on p-type material with an Au rear contact. Figure 7.3 shows the DLTS spectra of as-grown material at two probing regions (depths, W in μm) at a rate window of 80 s⁻¹. Two peaks are observed in Figure 7.3. Two levels within the bulk of the sample are observed at $E_v + 0.09$ eV and $E_v + 0.32$ eV.

![DLTS Spectra for As-grown p-type Material](image)

**Figure 7.3: DLTS Spectra for As-grown p-type Material**

The DLTS spectra for as-grown p-type material shows two distinct peaks at two probing regions (W) in the sample. The peaks correspond to energy levels of $E_v + 0.09$ eV and $E_v + 0.32$ eV. Figure printed with permission from V.P. Markevich and A.R. Peaker.
The $E_v+0.09$ eV trap is observed at a concentration of approximately $3.5 \times 10^{13}$ cm$^{-3}$ in the sample bulk, while the $E_v+0.32$ eV trap is observed at a concentration of approximately $4.5 \times 10^{13}$ cm$^{-3}$. Both the $E_v+0.09$ eV and $E_v+0.32$ eV traps lie within literature values for the double donor and single donor states of Pt in Si.\textsuperscript{118} Pt is sometimes used as an electrode material in anodic etching of porous silicon, and has been observed in large concentrations after porous silicon formation in the literature\textsuperscript{147}.

The $E_v+0.09$ eV trap is also near to the expected position of the shallow donor state of Fe\textsubscript{i}-B\textsubscript{s}.\textsuperscript{103} This confounds the carrier lifetime spectroscopy measurement of $[\text{Fe}] = (4.5 \pm 77) \times 10^{11}$ cm$^{-3}$. However, the large uncertainty of the $[\text{Fe}]$ measurement with carrier lifetime spectroscopy indicates that the measurement is near detection limits for the very low lifetime of the sample considered.

The $E_v+0.32$ eV trap is also near the expected donor trap level of Ag in ref\textsuperscript{148} however literature values generally fall between $E_v+0.34$ eV and $E_v+0.40$ eV.\textsuperscript{149} Ag is observed in significant concentrations in the ICP-MS analysis and is an interstitial diffusor that responds to phosphorus diffusion gettering.\textsuperscript{126} The $E_v+0.32$ eV trap is also near literature values for the donor levels of Mo and W, however, the high lifetime of the material after gettering excludes the possibility of $4.5 \times 10^{13}$ cm$^{-3}$ contamination from either of these impurity species given their poor gettering response (Figure 6.4).

### 7.7 As-Grown Performance Limit Assignment

Injection level dependent lifetime, bulk mass spectrometry, micro x-ray fluorescence, and deep level transient spectrometry measurements were completed to identify the underlying performance-limiting defect. The comparison of the defect concentrations obtained in the above
measurements and the gettering response of the material indicates that Pt, Fe, Cr, Zn, and Ag contamination may limit as-grown lifetime. Fe, Cr, Zn, and Ag contamination was measured in significant bulk concentrations via mass spectrometry and observed to form precipitates via micro x-ray fluorescence. Ag and Pt are undetectable with 10 keV x-ray, while Pt was also not measured with bulk mass spectrometry. DLTS analysis indicates Pt as the primary electrically active defect. It is a known impurity species in some porous silicon and responds positively to gettering. Electrically active contamination with concentrations of $3.5 \times 10^{13}$ cm$^{-3}$ to $4.5 \times 10^{13}$ cm$^{-3}$ is sufficient to reduce lifetime to the observed levels in as-grown material (Figure 3.2).

### 7.8 Defect Distribution in As-Grown Epitaxial Wafers

Attributes of epitaxial wafer growth encourage a high density of as-grown interstitial contamination, which limits as-grown lifetimes but improves gettering response (Chapter 8). With iron for example, in traditional ingot silicon only 0.1% to 10% of the total contamination is found as interstitial point-defects in an as-grown wafer. This encourages higher as-grown lifetimes as the vast majority of contamination is maintained in the more benign precipitated form. The rapid cooling of an epitaxial wafer from growth temperatures at 60 °C/min, in comparison to ingot materials at a much slower 2-3 °C/min, provides less time for interstitial impurities to find favorable precipitation locations. Furthermore, the rate of precipitation of iron is observed to increase with the density of structural defects and oxygen precipitates. In epitaxial material however, a low density and size of oxygen precipitates are observed in the literature. Figure 7.4 indicates this phenomenon with a schematic for the evolution of point defects during cooling in both epitaxial (a) and traditional mc-Si (b) growth. During growth point-defects are distributed amongst structural defects. As wafer cooling begins, the solubility
of point-defects falls, and precipitation begins at favorable nucleation locations. Although both materials may have a similar concentration of total contamination, the increased time available for precipitate nucleation and growth, and the increased density of favorable nucleation locations result in a reduced point-defect concentration after cooling. A reduced proportional concentration of interstitial contamination leads to better as-grown lifetimes.

**Figure 7.4: Evolution of Impurities during Wafer Growth**

Material during growth contains impurities that are distributed as interstitial defects. During wafer cooling, precipitation occurs at heterogeneous nucleation sites. Epitaxial material (a) has a lower density of favorable sites and is cooled more quickly than mc-Si (b), leading to a higher proportion of total contamination found as point defects. The time axis is not to scale.
The effect of the cooling rate on the final point-defect concentration is modeled for Fe with Ham's law\textsuperscript{154} in Equation (7.1) as modified by Hieslmair et al\textsuperscript{135} for numerical computation. The time constant for precipitation, $\Gamma_{\text{precipitation}}$ [s], (Equation (7.2)) is observed to increase with decreasing diffusivity, $D_i$ [cm$^2$/s] (Equation (7.3)) from Istratov et al\textsuperscript{103} precipitation site density, $n$ [cm$^{-3}$],\textsuperscript{153,155} and the precipitate radius $r_i$ [cm]. The solubility of interstitial iron, and the driving force for precipitation, is shown in Equation (7.4) from Istratov et al\textsuperscript{103}. The second order effect of the changing precipitate radius is considered in Equation (7.5), with $c_p = 2.6 \times 10^{22}$ cm$^{-3}$, the density of iron in $\beta$-FeSi$_2$ precipitates.\textsuperscript{135,156} Figure 7.5 shows the simulated $[\text{Fe}_i]$ for an epitaxial (a) and mc-Si (b) material with an initial iron concentration of $3.5 \times 10^{13}$ cm$^{-3}$ during cooling from growth with $n = 10^8$ cm$^{-3}$ following ref\textsuperscript{157} and initial precipitate radii of $r_o = 1.5 \times 10^{-6}$ cm for mc-Si and epi fit to the final as-grown radii from synchrotron $\mu$-XRF measurements.\textsuperscript{137} In epi, the final interstitial iron concentration of $[\text{Fe}_i] = 2.7 \times 10^{13}$ cm$^{-3}$ corresponds to 77% of the total iron found as Fe$_i$ in the as-grown material. This is far higher than the final concentration of interstitial iron found in the mc-Si material, $[\text{Fe}_i] = 1.6 \times 10^{11}$ cm$^{-3}$, which corresponds to a interstitial proportion of 0.5% that aligns with experimental observations in as-grown mc-Si material.\textsuperscript{150}

\begin{equation}
[\text{Fe}_i]_{t+\Delta t} = (S - [\text{Fe}_i]_t) \left( 1 - \exp \left( \frac{-\Delta t}{\Gamma_{\text{precipitation}}} \right) \right) \tag{7.1}
\end{equation}

\begin{equation}
\Gamma_{\text{precipitation}} = \frac{1}{4\pi D_i nr_i} \tag{7.2}
\end{equation}

\begin{equation}
D_i = 1.0 \times 10^{-3} \exp \left( \frac{-0.67}{k_B T} \right) \tag{7.3}
\end{equation}

\begin{equation}
S = 8.4 \times 10^{25} \exp \left( \frac{-2.86}{k_B T} \right) \tag{7.4}
\end{equation}
Because of the rapid cooling of the epitaxial material, a low density of precipitate iron is expected in as-grown material.\textsuperscript{153} This however, suggests that external gettering should be very effective in the material as shown in Hieslmair \textit{et al}\textsuperscript{153} and Hofstetter \textit{et al},\textsuperscript{158} as the impurity species are not strongly bound. Indeed, excellent gettering response is observed (Section 8.2).
Based on the work of Ham,$^{154}$ Hieslmair et al,$^{135}$ and Haarahiltunen et al,$^{157}$ the proportion of total iron contamination that is found as interstitial point defects in as-grown epitaxial material (a, 77%) is much higher than as-grown mc-Si material (b, 0.5%). This depresses as-grown lifetimes in epi, but provides a strong gettering response.$^{153}$ As observed in (b), epi is cooled much more quickly after growth.

With the same model,$^{135,154}$ the as-grown iron distribution in epi is calculated as a function of wafer cooling rate in Figure 7.6. The current cooling rate of 60 °C/min provides an as-grown proportion of Fe$_i$ of 77%. Decreasing the wafer cooling rate to 1 °C/min is predicted to reduce the as-grown Fe$_i$ proportion to < 0.1%, however such a modification would significantly reduce the throughput of wafer growth by adding approximately 490 minutes to the growth cycle-time. Further increases in cooling rate, however, may provide an appreciable increase in throughput.
without significantly increasing the as-grown Fe\textsubscript{i} proportion. Given the observation that the material is gettered effectively because of its low density of heterogeneous nucleation sites and high proportion of as-grown Fe\textsubscript{i} (Section 8.3), rapid wafer cooling during growth is a viable mechanism to increase performance of gettered material.

Figure 7.6: As-Grown Iron Distribution as a Function of the Wafer Cooling Rate
The as-grown distribution of iron is calculated as a function of wafer cooling rate for epitaxial material using the model of Ham\textsuperscript{154} and Hieslmair et al.\textsuperscript{135} The as-grown proportion of Fe\textsubscript{i} can be reduced through slowing the cooling step from the growth temperature. However, this would negatively impact growth throughput and economics, and may also reduce the gettered performance of the material.

### 7.9 Contamination Source
As-grown contamination with Pt, Fe, Cr, Zn, and Ag are suggested by ICP-MS, synchrotron \(\mu\)-XRF, and DLTS. Fe and Cr are found in large concentrations (atomic percent) in stainless steel, while Fe and Zn are found in large concentrations in galvanized steels. Ag is used in cell metallization, while Pt can be used as an electrode in porous silicon etching.
In traditional ingot crystallization, or kerfless techniques that utilize a growth from melt, the strong segregation coefficient ($k_{eff}$, $10^{-8}$ to $10^{-5}$, meaning $10^{-8}$ to $10^{-5}$ of the impurities within a melt are incorporated during solidification) of many metals impurities between the solidifying crystal and the adjacent melt provides a significant driving force for contamination reduction. While the epitaxial process benefits from never being in direct contact with a crucible wall, it does not benefit from this strong segregation to a melt during growth. Therefore, unintended contamination of process gases and equipment may have a more detrimental impact than in traditional growth from melt growth techniques.
GETTERING RESPONSE

8.1 Material

As-grown $p$-type (boron doped) epitaxial wafers were provided with a thickness of $<110$ μm and crystal orientation of $<100>$ from two generations of furnace growth equipment, herein referred to as Gen I and Gen II. The second generation of growth includes improved impurity management and greater automation. Doping concentrations were determined as $0.50 \ \Omega$-cm for Gen I material and $1.79 \ \Omega$-cm for Gen II material using a four point probe (Cascade Microtech probe, Keithley 4200). Average sample thickness was determined from separate measurements of sample area with a flatbed scanner at 1200 dpi (Epson Perfection V700) and sample mass (Ohaus Discovery). As-grown samples were exfoliated manually from their growth substrates and laser-cut into approximately $4 \times 4 \ cm^2$ samples. Residual porous silicon was cleaned from the sample with a chemical polishing etch (CP4).

8.2 Lifetime Improvement with Gettering

The as-grown lifetime of the $p$-type material is inadequate for high-efficiency solar cell operation. Phosphorus diffusion gettering was employed to increase lifetime to level that could enable cell efficiencies $> 20\%$. 

8.2.1 Phosphorus Diffusion Time Temperature Profiles

Two processes were employed to reduce the concentration of electrically active point defects.\(^{160}\) First, a high-throughput standard process consisting of furnace loading at 800 °C followed by a 25 minute plateau at 845 °C and furnace unloading immediately at 845 °C was applied. The plateau stage consists of three stages of gas flow. First, the PSG is formed during \(\text{POCl}_3\) deposition. Then two steps consisting of a nitrogen purge and oxidation are completed. A second extended process consisting of a low temperature anneal (LTA) was employed to test for the continued presence of \([\text{Fe}]\) and available gains from additional optimization of the standard process.\(^{160}\) Low temperature anneals have been demonstrated to effectively reduce the concentration of \([\text{Fe}]\) contamination.\(^{122, 123}\) Based on the work of Rinio et al.,\(^{122, 123}\) a 2 hr LTA at 575 °C was employed after free cooling at approximately 2.6 °C/min from the plateau temperature. A nitrogen ambient surrounds the sample during the cooling and LTA steps. After gettering, emitter sheet resistances of \(75^{+11/-20} \Omega/\text{sq}\) and \(77^{+10/-11} \Omega/\text{sq}\) were measured on the front and back of single samples from the standard and extended gettering processes respectively using a four point probe.

8.2.2 Lifetime and Iron Contamination after Gettering

After standard phosphorus diffusion gettering of Gen I material, lifetime improved to \(12 \pm 1.2 \mu\text{s}\) at an injection level of \(10^{15} \text{ cm}^{-3}\) on a 52 \(\mu\text{m}\) thick sample, and a \([\text{Fe}]\) of \((4.9 \pm 23.9) \times 10^{10} \text{ cm}^{-3}\). The extended process resulted in a reduced effective lifetime of \(9 \pm 0.9 \mu\text{s}\) and a \([\text{Fe}]\) of \((2.9 \pm 31.6) \times 10^{10} \text{ cm}^{-3}\) on a 57 \(\mu\text{m}\) sample. The change in \([\text{Fe}]\) between processes is within the margin of error. The lifetime of the upgraded Gen II material increased markedly with the application of phosphorus diffusion gettering. The standard process resulted in a reduced effective lifetime of
342 ± 34 μs and a [Fe_i] of (2.5 ± 0.76)x10^{10} cm^{-3} on a 95 μm sample. The extended process resulted in an effective lifetime of 313 ± 31 μs and a [Fe_i] of (3.2 ± 7.4)x10^{9} cm^{-3} on an 80 μm sample.

Table 8.1 summarizes the gettered lifetime results obtained on p-type material. The implied open circuit voltage ($V_{oc}$) are shown as well as the estimated bulk lifetime for the material. The estimated bulk lifetime was calculated using a SRV of 8.1 cm/s calculated by comparing the effective lifetime of a float zone control sample to intrinsic limits (Figure 5.3). The [Fe_i] estimates herein have been updated from those displayed in ref. because of a modification to the dissociated and associated fractions of [Fe_i]/[Fe_i-B_3] following Tan et al., a more accurate estimate of ambient temperature during re-association, and a larger uncertainty (5%) in lifetime for error bound calculations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective lifetime at $10^{15}$ cm$^{-3}$ [μs]</th>
<th>Sample Thickness [μm]</th>
<th>Est. Bulk lifetime at $10^{15}$ cm$^{-3}$ [μs]</th>
<th>Implied $V_{oc}$ at 1 sun [mV]</th>
<th>Interstitial iron concentration [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen I, Standard</td>
<td>12 ± 1.2</td>
<td>52</td>
<td>13 ± 1.3</td>
<td>647</td>
<td>$(4.9 ± 23.9)x10^{10}$</td>
</tr>
<tr>
<td>Gen I, Extended</td>
<td>9 ± 0.9</td>
<td>57</td>
<td>9 ± 0.9</td>
<td>628</td>
<td>$(2.9 ± 31.6)x10^{10}$</td>
</tr>
<tr>
<td>Gen II, Standard</td>
<td>342 ± 34</td>
<td>95</td>
<td>851 ± 85</td>
<td>710</td>
<td>$(2.5 ± 0.76)x10^{10}$</td>
</tr>
<tr>
<td>Gen II, Extended</td>
<td>313 ± 31</td>
<td>80</td>
<td>830 ± 83</td>
<td>713</td>
<td>$(3.2 ± 7.4)x10^{9}$</td>
</tr>
</tbody>
</table>

After correcting for surface recombination, estimated bulk lifetimes > 800 μs are achieved with Gen II material at $\Delta n = 10^{15}$ cm$^{-3}$. This lifetime is sufficient to support advanced cell
architectures with efficiencies much greater than 20% and represents extremely high electrical quality for a kerfless silicon substrate. Injection level dependent lifetime of Gen II material with Fe\textsubscript{i} dissociated and Fe\textsubscript{i}-B\textsubscript{3} pairs is shown in Figure 8.1. The effective lifetime (a) of the standard gettering material outperforms the extended gettering process. However, after correcting for differences of surface limited lifetimes due to different sample thicknesses, the estimated bulk lifetimes (b) are approximately equivalent. The strong signature of interstitial iron is observed in the standard gettering sample with an expected crossover point near \( \Delta n = 10^{14} \text{ cm}^{-3} \) and a large response at high injection levels. Within a limited range of injection levels, estimated bulk lifetimes over 1,000 \( \mu \text{s} \) are observed. The injection level for 1-Sun operation with a 50 \( \mu \text{m} \) thick cell is also indicated with the black diamond in the estimated bulk lifetime (Figure 8.1 (b)).
Effective lifetimes of $> 300 \, \mu s$ are observed for Gen II wafers after gettering at $\Delta n = 10^{15} \, \text{cm}^{-3}$ (a). The change in lifetime with Fe$_i$-B$_x$ pairs dissociated and associated, and the observation of a crossover point, indicates the presence of interstitial iron in the standard gettering sample. The estimated bulk lifetimes are shown in (b) with an estimated SRV of 8.1 cm/s. The lifetime impact of Fe$_i$-B$_x$ pairs is pronounced. The injection level corresponding to 1-Sun operation with a 50 $\mu m$ cell is indicated in (b) with a black diamond.

After gettering, estimated lifetimes were compared to their theoretical limits, or “entitlement”, to determine if lifetime is limited by interstitial iron. Figure 8.2 shows the estimated bulk lifetimes of Gen II material and their concentration of Fe$_i$ contamination.
compared to the limiting lifetime due to unavoidable intrinsic mechanisms by the Richter et al model\textsuperscript{69} and Fe\textsubscript{i} due to SRH modeling at $\Delta n = 10^{15}$ cm$^{-3}$.\textsuperscript{38} With both Gen I and Gen II material, the estimated bulk lifetime does not appear to be limited by interstitial iron because a) the extended gettering processes which provided reduced [Fe\textsubscript{i}] did not improve lifetime, and b) bulk lifetime does not appear to be a function of the Fe\textsubscript{i} limited lifetime. DLTS was again performed on Gen II material after extended gettering. While numerous peaks were observed in as-grown material, no detectable peaks are observed after standard (Figure 8.3), and extended (not shown) gettering.

![Figure 8.2: Performance Limits of Interstitial Iron](image)

Estimated bulk lifetimes assuming a SRV = 8.1 cm/s and interstitial iron concentration compared to theoretical limits at $\Delta n = 10^{15}$ cm$^{-3}$. The lack of a relationship between the theoretical Fe\textsubscript{i} limited lifetime with the estimated bulk lifetime, and the ineffectiveness of the extended gettering process at increases lifetime indicate that the gettered material is not limited by Fe\textsubscript{i}. Figure reprinted from ref.\textsuperscript{34} with updated data.
0.12 - As-grown (low T, high [Fe] region)

W from 1.30 pm to 1.57 pm (@ RT)

0.10 - Get (low r, high [Fe] region)

W from 1.74 pm to 2.02 pm (@ RT)

0.08

0.06

0.04

0.02

0.00

-0.02

-0.04

-0.06

-0.08

-0.10

-0.12

Temperature (K)

\[ \Delta C \ (pF) \]

\[ E_v + 0.09 \ eV \]

\[ E_v + 0.32 \ eV \]

Standard gettering eliminates detectable traps in p-type material

Figure 8.3: DLTS Spectra of As-Grown and Gettered Gen II p-type Material

Various DLTS peaks are observed in the as-grown material (red). After standard gettering, no detectable peaks are observed (blue). Figure printed with permission from V.P. Markevich and A.R. Peaker.

8.3 Impact of Impurity Distribution on Gettering Response

As indicated in Section 7.8, the growth conditions of epitaxial material lead to a large proportion of total contamination residing as interstitial species. This limits as-grown lifetime, but enables excellent gettering response. Figure 8.4 shows the respective evolution of impurities during gettering of epitaxial (a) and mc-Si (b) materials following Figure 7.4. In epitaxial material, a large proportion of impurities in the as-grown state are distributed as interstitial point-defects. These point-defects respond positively to external gettering, as they are not bound on precipitates that resist the movement of the impurity species to the gettering layer (Figure 8.4, a). Conversely, in mc-Si materials a large concentration of precipitates reduces gettering effectiveness (Figure 8.4, b). Heterogeneous nucleation sites, such as dislocations, prove difficult
to getter$^{80, 81}$ as the resulting strain field around the dislocation resists the driving force for gettering.

**Metal Impurity Evolution During Gettering**

*a) Epitaxial Wafer*

As-Grown Wafer  
During High-T Diffusion  
During Cool-down

*b) mc-Si*

As-Grown Wafer  
During High-T Diffusion  
During Cool-down

**Figure 8.4: Schematic Gettering Comparison of Epi and mc-Si Materials**

As-grown material contains impurities that are distributed as interstitial point-defects and precipitates. Because of the difficulty of gettering impurities from heterogeneous nucleation points such as dislocations,$^{80, 81}$ the bulk of epitaxial material (a) is more easily gettered of deleterious impurities than mc-Si (b) material.

Controlled pre-anneals of epitaxial material to increase the proportion of precipitated iron on the onset of gettering were completed following the work of Henley *et al*,$^{161}$ Haarahiltunen *et al*,$^{162}$ and Hieslmair *et al*.$^{153}$ As-grown material was annealed in a nitrogen ambient at 500 °C for 30 min, 90 min, and 1,260 min. Based on ref$^{161}$ and ref$^{162}$ a 90 minute anneal is expected to
effectively increase the precipitated iron concentration. After annealing, the as-grown lifetime of all wafers persisted at values < 1 µs. However, after standard gettering, a significant dependency on pre-annealing duration and lifetime is observed (Figure 8.5, a). Effective lifetimes after Fe-B dissociation at an injection level of 10^{15} \text{ cm}^{-3} are 115 \pm 12 \mu s with the no pre-annealing control sample, 56 \pm 5.6 \mu s with the 30 minute pre-annal sample, and only 35 \pm 3.5 \mu s with the 90 minute pre-anneal sample. Corresponding increases in [Fe], summarized in Table 8.2, after gettering are observed with increasing pre-annealing time and reduced lifetime (Figure 8.5, b). As precipitated impurities at heterogeneous nucleation sites prove difficult to getter, the observed trend in post-gettering lifetime suggests that the gettering response of epitaxial material should be high due to its favorable as-grown distribution of more readily-gettered point-defects.

Also included in Table 8.2, are the results of the sample annealed for 1,260 minutes. With this sample however, the lifetime after gettering improved significantly to 199 \pm 20 \mu s after gettering. Although the wafer was not intentionally doped, the extended duration at an elevated temperature in the POCl₃ furnace may have provided the wafer with effective external gettering due to residual phosphorus in the furnace. Other experiments, at higher temperatures but much shorter durations, have indicated the ability of residual phosphorus to diffuse into wafers during annealing treatments.

<table>
<thead>
<tr>
<th>Pre-Annealing Duration [min]</th>
<th>Effective lifetime at (10^{15} \text{ cm}^{-3} \text{[µs]})</th>
<th>Interstitial iron concentration [\text{cm}^{-3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>115 \pm 12</td>
<td>((8.6 \pm 2.3) \times 10^{10})</td>
</tr>
<tr>
<td>30</td>
<td>56 \pm 5.6</td>
<td>((4.3 \pm 0.56) \times 10^{11})</td>
</tr>
<tr>
<td>90</td>
<td>35 \pm 3.5</td>
<td>((8.5 \pm 1.0) \times 10^{11})</td>
</tr>
<tr>
<td>1,260</td>
<td>199 \pm 20</td>
<td>((1.1 \pm 1.2) \times 10^{10})</td>
</tr>
</tbody>
</table>
Figure 8.5: Impact of Pre-Annealing on Gettered Lifetime

Increased duration of pre-annealing at 500 °C in a nitrogen atmosphere is observed to reduce lifetime (a,b) and increase the concentration of Fe after gettering (b). In b, 10% absolute error is shown for the QSSPC lifetime data, while error in [Fe] is calculated assuming random propagation of errors through the [Fe] calculation with a QSSPC lifetime repeatability of 5%.\textsuperscript{94}

To further identify the cause for lifetime improvement with gettering, epitaxial samples were also annealed with the same time temperature profile used by the standard gettering process at 845 °C, but without the flow of POCl\textsubscript{3} gas. A sheet resistance of 183\textsuperscript{+38/-37} Ω/sq was provided by the process, indicating that a small amount of residual phosphorus was present in the tube, providing a small effect of external gettering. Lifetimes after the high temperature anneal remained low at < 1 μs (Figure 8.6), suggesting that an impurity species that responds to external
gettering with a phosphorus source is responsible for the as-grown lifetime limit. The result also indicates that external gettering dominates the lifetime improvement observed during gettering. A Fe concentration of $(7.8 \pm 46) \times 10^{11}$ cm$^{-3}$ was measured on the no POCl$_3$ control sample. This is within the error of the Fe concentration of $(4.5 \pm 77) \times 10^{11}$ cm$^{-3}$ measured on as-grown material, but as with the as-grown sample, an inadequate concentration to warrant the $< 1$ ms lifetime of the material.

![Figure 8.6: Lifetime in p-type Material after High Temperature Anneal without POCl$_3$](image)

The lifetime of material did not appreciably improve from the as-grown state (blue) after completing a high temperature anneal (red) following the time-temperature profile of a gettering process but with phosphorous doping. The lack of a response indicates that external gettering plays a dominant role in the gettering response of the material.

### 8.4 Root Cause of Lifetime Change between Generations

Determining the root cause for the large change in effective lifetimes between generations of wafer growth validates the effectiveness of system changes. It also can elucidate the persisting
causes for the discrepancies between the achieved lifetimes of Gen II material in comparison to the theoretical entitlement (Figure 8.2). The bulk lifetime of the material is defined by Equation (8.1). The bulk, intrinsic, and Fe limited lifetimes of Gen I and Gen II material after standard gettering are summarized in Table 8.3, allowing the lifetime of the unaccounted for defect(s), \( \tau_{\text{defect}} \), that is responsible for the underperformance of the both materials to be determined. The materials have a different intrinsic lifetime due to a change in doping concentration. The resulting \( \tau_{\text{defect}} \) is 13 \( \mu \)s for Gen I material, and \( \tau_{\text{defect}} \) is 1,120 \( \mu \)s for Gen II material. In both materials, the estimated bulk lifetime is dominated by the impact of \( \tau_{\text{defect}} \). \( \tau_{\text{defect}} \) for Gen II material is 100 times higher than \( \tau_{\text{defect}} \) of the Gen I material.

\[
\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{intrinsic}}} + \frac{1}{\tau_{\text{Fei}}} + \frac{1}{\tau_{\text{defect}}} \quad (8.1)
\]

\[
\frac{1}{\tau_{\text{defect}}} = \frac{1}{\tau_{\text{structural}}} + \frac{1}{\tau_{\text{slow impurity}}} + \frac{1}{\tau_{\text{other}}} \quad (8.2)
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_{\text{bulk}} ) at ( 10^{15} \text{ cm}^{-3} ) [( \mu )s]</th>
<th>( \tau_{\text{intrinsic}} ) at ( 10^{15} \text{ cm}^{-3} ) [( \mu )s]</th>
<th>( \tau_{\text{Fei}} ) at ( 10^{15} \text{ cm}^{-3} ) [( \mu )s]</th>
<th>Resulting ( \tau_{\text{defect}} ) at ( 10^{15} \text{ cm}^{-3} ) [( \mu )s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen I, Std</td>
<td>13</td>
<td>1,030</td>
<td>885</td>
<td>13</td>
</tr>
<tr>
<td>Gen II, Std</td>
<td>851</td>
<td>8,990</td>
<td>5,750</td>
<td>1,120</td>
</tr>
</tbody>
</table>

The root cause of \( \tau_{\text{defect}} \) may be caused by decorated structural defects, contamination from slowly-diffusing difficult to getterable impurities, or another defect type (Equation (8.2)). Structural defects are one possibility. Epitaxial kerfless grown on a porous release layer has average structural defect densities of \( \leq 10^4 \text{ cm}^{-2} \). Structural defects were revealed with a Sopori etch\(^{132}\) and analyzed over a 1 cm\(^2\) and 4 cm\(^2\) portion of a Gen I and Gen II sample respectively with optical microscopy (Nikon Eclipse LV100, NIS-Elements software). In line
with previous measurements, an average structural defect density of approximately $10^4 \text{ cm}^{-2}$ was observed for both generations of material. Similarly, the percent wafer surface covered by high structural defect density ($>10^5 \text{ cm}^{-2}$) is low ($<5\%$) and comparable between generations.\textsuperscript{160} The low area coverage of defective regions, a predictor of performance loss,\textsuperscript{84,163} in epitaxial kerfless silicon compares favorably to standard ingot multicrystalline material (Figure 8.7). Given the similarity of the structural defect distribution between epitaxial generations, structural defects are concluded to not be the root cause of performance difference between generations.

![Figure 8.7: Comparison of Structural Defects in Std. mc-Si and Epi Silicon](image)

Epitaxial kerfless silicon (b, right) has a lower area coverage of structurally defective regions than standard multicrystalline material (a, left).\textsuperscript{84,163}

Difficult to getter impurities are another potential source of performance loss. Bulk mass spectrometry indicates significant concentrations of impurities (Ti, Mo, V) that may prove difficult to getter and are recombination active (Figure 6.4). Additionally, significant reductions are observed in the concentration of Mo (82\% reduction to detection limit) and V (59\% 102
reduction) in Gen II relative to Gen I material (Figure 8.8). Decreased concentrations of Cr and Nb are also observed in Gen II material. However, the impact of Cr is considered negligible because Cr has similar gettering characteristics as Fe_{i},^{126} and such effective Fe_{i} extraction was observed in both Gen I and Gen II materials.

![Figure 8.8: Reduction in Impurity Contamination in Gen II Material](image)

Gen II material exhibits a reduced concentration of Mo, V, Cr, and Nb contamination relative to Gen I material. Comparison with SRH recombination modeling indicates good agreement between measured concentration reductions in Mo and V and the lifetime improvement in Gen II material.

Figure 8.9 shows the estimated bulk lifetime (SRV = 8.1 cm/s) of Gen I material after standard gettering compared to the SRH^{38} and intrinsic^{69} lifetimes for the know level of Fe_{i} contamination from lifetime spectroscopy and Mo (1.2×10^{13} cm^{-3}) and V (1.5×10^{13} cm^{-3}) contamination from bulk mass spectrometry. Literature suggests that the interstitial, electively active, concentrations of Mo are equal to 15% to 100% of the total Mo concentration.^{164, 165} A good fit is observed between the estimated bulk lifetime (red circles) and modeled lifetime with an assumed 40% of Mo and V (widely-dashed black line) residing as an interstitial species.
(Figure 8.9). A poor fit is obtained if 100% of Mo and V are electrically active (tightly-dashed grey line), suggesting some precipitation has occurred. At high injection levels, the modeled curve for a 40% interstitial fraction deviates from the acquired data. This deviation can largely be attributed to increased uncertainty of the effectiveness at high injection levels. As seen in Figure 5.3, the SRV of the passivation increases rapidly at high injection levels. When this is accounted for, a better fit is obtained. These results indicate that a reduction in the concentration of Mo and V during growth is the root cause of the lifetime improvement observed in Gen II material. The high concentrations of these difficult to getter impurities observed in Gen I material would not support the > 1 ms estimated bulk lifetimes observed in Gen II material.

![Image](image_url)

**Figure 8.9: SRH Modelling of Gen I Material after Gettering**

A good fit is observed between the estimated bulk lifetime (red circles) and the modeled SRH and intrinsic lifetimes of the material with contamination from Fe, Mo, and V with 40% of the Mo and V contamination is electrically active (black line). The lifetime of the material excludes the possibility of 100% electrical activity of the Mo and V contamination (grey line). 10% absolute error is shown for the QSSPC lifetime data following Blum et al.94
n-type wafer doping provides numerous advantages for high-lifetime silicon substrates, and is employed the highest efficiency commercial cells available.\textsuperscript{166} n-type silicon has an overall lower sensitivity to metallic impurities, especially Fe\textsubscript{i}, (Figure 3.2). Additionally, metastable defects with boron are eliminated through the absence of boron doping including: oxygen-boron, iron-boron, and chromium-boron. However, it is noted that a lifetime of approximately 3 \texttimes p-type material is required for n-type material for roughly equivalent carrier diffusion lengths, the spatial embodiment of lifetime.\textsuperscript{106} This discrepancy arises because of lower carrier diffusivity in n-type vs. p-type silicon. As with p-type material above, lifetime and spectroscopy measurements are employed to identify defects in n-type material.

9.1 As-Grown Lifetime and Defect Identification

The as-grown lifetime of n-type matches the behavior of p-type material at < 1 \, \mu s. Figure 9.1 shows the injection level dependent lifetime for as-grown n-type material. As with the p-type material, the root cause for the poor lifetime of as-grown n-type material is assessed. However, a reduced subset of tools are employed, though general trends from ICP-MS measurements may still apply with the n-type material.
As with \( p \)-type material, the as-grown performance of \( n \)-type material is less than 1 \( \mu \)s. A stronger injection level dependence of lifetime is observed in \( n \)-type in comparison to \( p \)-type material.

DLTS measurements and analysis were also completed (V.P. Markevich and A.R. Peaker, University of Manchester) on as-grown \( n \)-type material to identify the species and concentrations of electrically active majority carrier traps in the upper half of the bandgap. 1 mm diameter Au Schottky diodes were deposited on the sample with an Al rear contact. One strongly distinct trap is observed. Figure 9.2 shows the DLTS spectra of as-grown material at two probing regions at a rate window of 80 s\(^{-1}\).
The DLTS spectra for as-grown $n$-type material shows a distinct peak at $E_c - 0.23$ eV at two probing regions (W) in the sample. Figure printed with permission from V.P. Markevich and A.R. Peaker.

An Arrhenius analysis identified the observed trap in $n$-type material at an energy level $E_c - 0.23$ eV after correcting for an electric field dependence of the trap with Laplace DLTS analysis. The $E_c - 0.23$ eV trap is measured at a bulk concentration of $3.0 \times 10^{13}$ cm$^{-3}$, and lies near the level of Pt in Si.\textsuperscript{118} The potential observation of Pt in $n$-type material suggests a common impurity source for the contamination observed in $p$-type material (Section 7.6). The $E_c - 0.23$ eV defect also lies near expected values for Cr.\textsuperscript{148, 167} The minor peaks observed in the spectra are attributed to impurity complexes with hydrogen.

These results coupled with previous $p$-type ICP-MS measurements, gettering lifetime response, gettered $\mu$-XRF, and SRH modeling indicate that Pt, Cr, Fe, Zn, and V may limit as-grown performance. Pt is most strongly suggested from DLTS measurements. Point-defect contamination at a concentration of $3.5 \times 10^{13}$ cm$^{-3}$ is adequate to reduce lifetime to $< 1$ $\mu$s in $n$-
type material (Figure 3.2). As with p-type material, the excellent response of the material during phosphorus diffusion suggests that the deep-level defect unidentified in DLTS measurements is a getterable species.

9.2 Lifetime Improvement with Gettering

Similar gettering methods to those employed for p-type material were expected to improve the lifetime of n-type material. Phosphorous diffusion gettering is effective at gettering n-type material by forming a heavily doped n+ region. Standard and extended gettering processes were again employed on the n-type material. Al₂O₃ is also used again on n-type material for surface passivation. Al₂O₃ effectively passivates n-type silicon through a reduction of the interface defect density and the formation of an inversion layer with large amount of fixed negative charge in the film. This mechanism provides excellent results, however, over a limited range of sheet resistances (emitter, 100-200 Ohm/sq) Al₂O₃ is not effective at passivating n-type material. As in p-type material, gettering removes detectable traps from DLTS (detection limit approximately 3×10¹¹ cm⁻³) in n-type material (Figure 9.3).
Figure 9.3: DLTS Spectra after Standard Gettering of $n$-type Material

As in $p$-type material, phosphorus diffusion gettering removes detectable traps from DLTS in $n$-type material (detection limit approximately $3 \times 10^{11}$ cm$^{-3}$). Figure printed with permission from V.P. Markevich and A.R. Peaker.

Figure 9.4 shows the injection level dependent lifetime of a 120 μm thick $n$-type silicon sample after gettering. The effective lifetime is $878 \pm 88$ μs at an injection level of $\Delta n = 10^{15}$ cm$^{-3}$. This lifetime provides a minority carrier diffusion length on the same order as the > 300 μs $p$-type results. Additionally, it should also be capable of supporting cell efficiencies well over 20%. The intrinsic lifetime limit is shown for comparison in Figure 9.4, and used to calculate a SRV assuming that the bulk wafer performance is equal to the intrinsic limit. In this case, additional corona charge was used to increase the strength of the inversion layer (Figure 5.4). The resulting SRV of < 3 cm/s is exceptional and among the best results obtained with Al$_2$O$_3$ passivation.
Figure 9.4: Injection Level Dependent Lifetime of Gettered n-type Material

Effective lifetimes > 850 µs are obtained with n-type material after gettering.

Exceptional surface passivation is provided by corona-charged Al₂O₃ with a resulting SRV < 3 cm/s.

9.2.1 Comparison to Intrinsic Limits

The exceptional results for surface recombination (SRV < 3 cm/s) indicate that the observed lifetime is a strong function of bulk performance, as better passivation performance relative to that achieved cannot be expected. In this case, the SRV calculation indicates that the actual bulk lifetime of the material is equal to the intrinsic limit. Therefore, no unintended contaminant dictates the material lifetime. As shown in Figure 9.5, a decrease in the doping concentration of this material could increase the achievable lifetime to > 10 ms over its current level (red dotted line) based on the Richter et al model for intrinsic lifetime.⁶⁹
The intrinsic lifetime of material is a strong function of doping concentration. The material shown in Figure 9.4 (red dotted line) has a high doping concentration that limits its performance due to unavoidable intrinsic mechanisms. The lifetime of the material could therefore be increased significantly with a change in doping concentration.

9.2.2 μ-XRF Measurement of Gettered n-type Material

As with as-grown p-type material, μ-XRF measurements were completed on gettered n-type material by colleagues at beam line 2ID-D at the APS synchrotron. Impurity precipitates of Cr, Zn, and Fe were again observed (Figure 9.6). Additional precipitates of Co and Ni were also observed. The precipitates observed in n-type material are larger than those observed in p-type material. The size of precipitates were again measured from the μ-XRF data assuming spherical precipitates following references. An iron precipitate radii of approximately 13 nm is similar to the observed size in p-type material. Other impurity species were found in larger precipitates. The density of Cr and Zn precipitates [atoms/cm³] were determined by adjusting the density of iron precipitates based on the volume of a single impurity atom using the atomic
radius. The resulting densities are $C_{Fe_p} = 2.6 \times 10^{22} \text{ cm}^{-3}$, $C_{Cr_p} = 2.1 \times 10^{22} \text{ cm}^{-3}$, and $C_{Zn_p} = 3.4 \times 10^{22} \text{ cm}^{-3}$, and precipitate radii of 38 nm for Cr and 26 nm for Zn. These radii fall below the size of foreign inclusions. As mentioned above, stainless steel has large concentrations (atomic percent) of Fe and Cr, while galvanized steel has large concentrations of Fe and Zn. The presence of precipitates after gettering suggests that further high-temperature processing could reduce lifetime through the dissolution of existing precipitates.
Cr, Zn, Co, Fe, and Ni precipitates are observed in $n$-type material after gettering.

The size of the Fe precipitate is comparable to the as-grown $p$-type material.
10

CONCLUSIONS

10.1 Conclusions

Significant innovation is required to reach the module price goal of $0.50/W by 2020 put forth by the U.S. DOE SunShot program. Epitaxially grown kerfless silicon could play an important role in achieving this target by reducing silicon utilization while enabling high-efficiency devices. Herein, screening criteria for high-impact research projects was presented, and then used to explore the benefits of epitaxially grown kerfless silicon in comparison to historic kerfless growth techniques. Then, the identification of lifetime-limiting defects in as-grown p-type epitaxial material, and the mitigation of those defects through improvements to both growth and processing were presented. Lastly, lifetime-limiting defects were identified in n-type material, and gettering response was assessed.

Conclusions include:

Cost Modeling Elucidates Fruitful Innovation Areas

Power conversion efficiency is the strongest influencer of manufacturing cost. Opportunities to reduce cost through material or process substitution, such as kerfless wafers, must be weighed against any detrimental effects on cell efficiency. A “cheap and dirty” strategy won’t necessarily be cheap, especially if the costs of the entire PV system are not considered.

Excellent Surface Passivation is Required to Study High-Lifetime Material
Excellent surface passivation (< 5 cm/s) is needed to measure high effective lifetimes (> 1 ms) on 100 μm thick high-quality materials such as epitaxial kerfless silicon. Al₂O₃ deposited by thermal ALD provided such passivation. However, even with excellent SRV values of 3 cm/s, many hundreds of μs of effective lifetime are lost to surface recombination with thin wafers.

As-Grown Epitaxial Material Suffers from Unique Performance Limits

Poor lifetime was observed in as-grown material. The root cause was identified as contamination by impurities with a strong response to gettering. Rapid cooling discourages precipitation of impurity species, and leaves a larger proportion of the total impurity contamination in an electrically active form. However, excellent gettering response is observed due to the high interstitial proportion in as-grown material.

Improving As-grown Material is an Effective Method to Increase Gettered Lifetime

All impurities are not easily getterable. Therefore, there is a limit to the lifetime improvement that can be realized during processing, so steps should be taken to minimize contamination during growth. The lifetime improvement in Gen II material is due to a reduction in ungetterable impurities present in Gen I material. Because epitaxial silicon does not benefit from solid to liquid impurity segregation during growth, extra care must be employed to limit contamination.

Epitaxially Grown Kerfless Silicon can Support High-Efficiency Devices

Effective lifetimes > 300 μs and > 800 μs were achieved with p-type and n-type material respectively at injection levels of 10¹⁵ cm⁻³ after gettering. Estimated bulk lifetime for both materials approached or exceeded 1 ms. This lifetime is sufficient to support cell efficiencies well greater than 20%, and shows that a material use saving technology can provide an efficiency increase.
REFERENCES

17. G. F. Nemet and E. Baker, *Demand Subsidies vs. R&D: Comparing the Uncertain Impacts of Policy on a Pre-Commercial Low-Carbon Energy Technology*, La Follette...


25. I acknowledge Sriram Krishnan for the Cost / Price innovation opportunity framework.


67. Photo Credit: Jasmin Hofstetter.


71. Model prepared by Tonio Buonassisi.
105. Daniel Macdonald provided the [Fe] and C calculation spreadsheet used in this work.


113. David Fenning provided the calculation spreadsheet for Fei-B association time used in this work.


COST MODELING RESOURCES

High-Level Perspectives


Prof. Varun Rai at UT Austin http://www.estresearch.com/

Ryan Wiser at LBNL http://eetd.lbl.gov/people/ryan-wiser

Innovation and Cost Modeling

NREL/MIT U.S. China Study http://pubs.rsc.org/en/content/articlelanding/2013/ee/c3ee40701b


SEMI Cost of Ownership Standard http://www.pvgroup.org/node/3201

SEMI PV Innovation Roadmap http://itrpv.net/Reports/Downloads/

MIT Modeling Efforts http://pv.mit.edu/TMA/

Photon International equipment surveys, and Photovoltaics international magazine

Green Tech Media Research Webinars (released with new reports, give plenty of information)

Installed / System Economics


System Advisor Model (Cost of Electricity) https://sam.nrel.gov/
Appendix

GETTERING STANDARD OPERATING PROCEDURE

Recipes

As part of the changes made during the maintenance of the POCI₃ furnace in 2013, there are two new standard recipes. They have variable inputs for the temperatures and durations of certain steps, and should provide us with the flexibility we need without having to make a new recipe for most cases. Because of the variables, good bookkeeping is essential to record what inputs were made when the recipe was used. Both load at 700 °C, a more gentle temperature for both the furnace and operator, and consist of a few other enhancements for reliability and maintenance. They also have two-stage diffusions, were a high flow period is meant to saturate the tube with POCI₃ and a low flow period is meant to reduce turbulence and improve uniformity.

The first recipe is STD1STEP.002. It includes one fixed temperature diffusion, and allows for ramping down to an unload temperature. The next is STD2STEP.002. As you can imagine, this provides two fixed temperature diffusions, i.e. LTA. The directions below to run the recipes do not substitute for training by the tool owner.

Loading and running STD1STEP.002 and STD2STEP.002

Select recipe load on the POCI₃ furnace computer and select the new recipe (always loading the recipe fresh will allow you to confirm the recipe parameters). When the recipes load, they will prompt you for the value of the variables within the program. If you make an error, re-load the program. Figure B.1 shows a schematic of the input variables described below.
Figure B.1: Schematic of Standard Recipe Time Temperature Profile Variables

1. Loading STD1STEP.002

   a. PTMP - plateau temperature. You must enter XXX.X i.e. 845.0 for each of the 3 zones. Each zone should match. The minimum is temperature is 750 °C and the max is 1110 °C (for the new baffle set) for this step or the run will be aborted.

   b. STME - extra soak time in addition to the baseline 6 minutes used in program. Do not put 0 for short times, put 00.00.01. A time of 0 will mean the step will not end. Refer to POCl₃ application guide for sheet resistance targets for the plateau temperature and time that are specified. The total plateau time for the baseline process is 25 minutes.

   c. UTMP - unload temperature. The furnace will ramp to this temperature before unloading. The stabilization counter is 1 minute, so if you are unloading at you
plateau temperature, then it will add 1 minute. The run will be aborted if the
temperature is greater than 850 °C after stabilization.

2. Running STD1STEP.002
   a. Turn on the furnace cooling fans.
   b. To run, select the “Run” button. This will ramp the furnace up to the load
temperature to avoid having to use “Recipe Modify”.
   c. Start and complete RCA cleaning while the furnace is heating up.
   d. Once stable at 700 °C, select the Event button to open the furnace door.
   e. Acknowledge the alarm and load samples when the door has opened fully.
   f. Select Event again to close the furnace door. The recipe will automatically begin.
   g. Once stable at the unload temperature, an alarm will sound. Acknowledge the
      alarm and use the event button to open the door.
   h. Unload samples by putting wafer boat on the piece of glass under the furnace tube
to cool.
   i. Select Event again to close the furnace door. The furnace will automatically go
      back to idle.
   j. After the furnace is cool, turn off the cooling fans.

3. Loading STD2STEP.002
   a. Set the first 3 variables as directed for STD1STEP.002 above.
   b. This recipe adds another variable ATMP – annealing temperature. The recipe
      will ramp to the second plateau defined by ATMP as quickly as it can from the
      plateau step. You can again specify an unload temperature.
   c. This recipe also adds another variable ATME – annealing time. Set the length of
      the annealing plateau. Again, do not put 0 for short times, put 00.00.01. A time of
      0 will mean the step will not end. Refer to POCl₃ application guide for sheet
      resistance targets for the plateau temperature and time that are specified.

4. Running STD2STEP.002
   a. Follow the process for STD1STEP.002 above.
Custom Recipes

Please follow/modify to the following guidelines if your experiment allows:

1. Do not load at a temperature higher than 700 °C. Remember that the experimental evidence has shown that the load temperature does not affect results (but it probably does effect the lifetime of the furnace).

2. When opening the furnace door, keep the set temperatures 100 – 200 °C below the load temperature to avoid having the heating elements stressing to keep the tube hot with the door open.

3. When the furnace is hot (> 700 °C), please don’t run the loader faster than 15 ipm. It was hard to pin down what an appropriate value for this is from Henry. But again if you experiment can handle it, and the faster speed was to avoid waiting, then I think reducing the boat speed will reduce furnace stress.

4. Do not unload over 850 °C. Henry is already uncomfortable with 800 °C, so I don’t think we should push too hard hear unless really warranted.

Chemical Cleaning of Sample for Gettering with RCA

Multiple chemical cleaning procedures are available to use before gettering. RCA cleaning is likely the most conservative process.

1. Start heating the furnace up to the load temperature as described above. If necessary remove saw damage or other wafer defects with a CP4 etch described in the next appendix.

2. Pre-rinse all beakers and the thermometer

3. Fill beakers
   a. HF Dip (approximately 3% by volume in DI)
   b. RCA1 (350 ml DI, 70 ml ammonium hydroxide, 70 ml hydrogen peroxide)
   c. RCA2 (350 ml DI, 70 ml hydrochloric acid, 70 ml hydrogen peroxide)
4. Heat RCA beakers to 70 °C on hotplates (I usually set the hotplates to about 250 °C until the temperature reads approximately 60 °C, and then back down the temperature to around 70 °C)

5. Process
   a. Initial DI rinse one time to remove dust from sample
   b. Initial HF Dip (To remove initial oxide)
   c. DI Rinse three times in plastic DI beaker
   d. RCA1 70 °C, 10 minutesDI Rinse three times in DI (1) beaker
   e. HF Dip
   f. DI Rinse three times in DI (1) beaker
   g. RCA2 70 °C, 10 minutes (during this, make a fresh HF bath)
   h. DI Rinse three times in DI (2) beaker
   i. Final HF Dip (To remove RCA2 contaminants and prepare for gettering)
   j. DI Rinse three times in DI (2) beaker
   k. Blow dry samples with N2 gun
   l. Unload sample boat with dedicated “after RCA” tweezers into POCl₃ furnace wafer boat. (It is preferred to have a buddy do this and start the gettering process to reduce the duration elapsed between the final HF dip and loading the samples into the furnace).

6. Start the furnace program (or have a buddy do it) as described above.

7. Properly dispose of waste, rinse all beakers 3x, and store them in cabinet

**After Gettering**

1. Let wafers cool.

2. I think it is always worth completing a lifetime test on the WCT-120, and rough lifetime map with the Semilab WT-2000 after gettering. The data may prove useful in the future.

3. If the wafers are p-type, measuring sheet resistance using the Keithley 4200 and the four point probe may also prove valuable.
Emitter removal & Wafer Thinning with CP4

CP4 etches (removes) silicon while smoothing a sample. Emitters should be removed before passivation and lifetime measurements with both \textit{p}-type and \textit{n}-type samples. The initial process was provided by Dr. Jasmin Hofstetter.

1. Pre-rinse all beakers and the thermometer
2. Fill beakers
   a. HF Dip (approximately 3\% by volume in DI)
   b. CP4 (540 ml nitric Acid, 180 ml acetic acid, 72 ml hydrofluoric acid)
   c. KOH 30\% (in solvents hood, the KOH is pre-mixed and contained in a re-sealable white frosted bottle under the solvents hood. It is labeled KOH 30\%)
3. Process
   a. DI Rinse once in plastic DI beaker to remove dust
   b. CP4 (duration depends on number of samples and target removal. I use 2 minutes to remove emitters, and 4 minutes to remove \sim 15 \text{ um total from a wafer})
   c. DI Rinse three times in plastic DI beaker
   d. HF Dip
   e. DI Rinse three times in plastic DI beaker
   f. KOH 30\%, 10 minutes (this steps remove some left over contamination from the CP4 etch)
   g. DI Rinse three times in plastic DI beaker
   h. HF Dip
   i. DI Rinse three times in plastic DI beaker
j. Unload samples (If a RCA clean is followed by this, Restarting with another HF dip is conservative. Before whatever final HF dip is employed (After RCA2 for POCl3 or after RCA1 for ALD), it is advised to make a fresh mixture of HF to reduce contamination).

4. Properly dispose of waste, rinse all beakers 3x, and store them in cabinet.
Appendix

D

ATOMIC LAYER DEPOSITION
STANDARD OPERATING PROCEDURE

The initial chemical cleaning and ALD processes were provided by Dr. Jasmin Hofstetter and Dr. David Fenning.

Chemical Cleaning for ALD Aluminum Oxide

1. Pre-rinse all beakers and the thermometer
2. Fill beakers
   a. HF Dip (approximately 3% by volume in DI)
   b. RCA1 (350 ml DI, 70 ml ammonium hydroxide, 70 ml hydrogen peroxide)
   c. RCA2 (350 ml DI, 70 ml hydrochloric acid, 70 ml hydrogen peroxide)
3. Heat RCA beakers to 70 °C on hotplates (I usually set the hotplates to about 250 °C until the temperature reads approximately 60 °C, and then back down the temperature to around 70 °C)
4. Process
   a. Initial DI rinse one time to remove dust from sample
   b. Initial HF Dip (To remove initial oxide)
   c. DI Rinse three times in plastic DI beaker
   d. RCA1 70 °C, 10 minutes (during this, make a fresh HF bath)
   e. DI Rinse three times in DI (1) beaker
   f. HF Dip
   g. DI Rinse three times in DI (1) beaker
   h. RCA2 70 °C, 10 minutes (during this, begin heating the DI post beaker on the hotplate that held the RCA1 beaker)
i. DI Rinse three times in DI (2) beaker
j. Blow dry samples with N2 gun
k. Unload sample boat with dedicated “after RCA” tweezers into dedicated “after RCA” sample box

5. Properly dispose of waste, rinse all beakers 3x, and store them in cabinet

**ALD deposition at Harvard CNS**

1. Log into CNS system
2. If the chamber is very “flaky” vacuum the chamber with the vacuum stored next to the sputtering tool on the floor. Remove the plastic fitting on the end of the hose, to avoid melting the plastic in the chamber.
3. Set inner and outer ring temperatures to 200 °C
4. Load program “AL2O3_5nm_200C_Season” in software
5. Place Si chips in chamber in rough pattern for propping up samples with ceramic tweezers
6. Run program
7. Load program “AL2O3_20nm_200C_Deposit” in software
8. Load wafers in chamber with ceramic tweezers while attempting to cover as little of the chips as possible
9. Run program
10. Unload wafers into dedicated after ALD sample box
11. Unload chips into chip box
12. Reset furnace temperatures to default
13. Log out of CNS System

**ALD annealing**

1. Ensure the correct tube in placed in the furnace. The new tube, goes with the new pushrod stored in the glass containment tube, and the new wafer boat stored in the plastic box. Ultra high purity nitrogen (UHP300) should be used for the gas.
2. Set furnace to 350 °C
3. Set N₂ flow rate to 5 SCFM
4. Uncover tube end
5. Remove boat from box on cooling plate while not touching the boat
6. Load samples in boat within furnace enclosure
7. When temperature has stabilized, load sample boat into end of furnace with push rod located below furnace
8. Run for 10 to 30 minutes
9. Pull boat into cool in end of furnace gently (It takes me ~ 1min) and leave for 5 minutes until cool
10. Unload samples into general sample box within furnace enclosure
11. Place sample boat on cooling plate back within box
12. Turn off furnace
13. When temperature reaches approximately 200 °C, turn off N₂ flow and place clean wipe over the end of the furnace
14. Leave furnace enclosure doors closed when not in use, and leave air filter running