Electrical Impact Assessment of Dislocations in Silicon Materials 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

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ABSTRACT

Cast multicrystalline silicon (mc-Si) makes up about 60% of the global photovoltaics market production, and is favored due to its lower areal and capex costs relative to monocrystalline silicon. This method, however, produces material with a higher density of defects (e.g., dislocations, grain boundaries, metal impurities) than more expensive single-crystalline growth methods.

A higher density of defects, particularly dislocations, results in a greater density of charge-carrier recombination centers, which reduce a solar cell’s efficiency. Interestingly, the recombination activity of individual dislocations and dislocation clusters can vary by orders of magnitude, even within the same device and a separation of only by millimeters of distance.

In this thesis, I combine a surface-analysis approach with bulk characterization techniques to explore the underlying root cause of variations in recombination activity between different dislocation clusters. I propose and validate an optical inspection routine based on dislocations’ surface characteristics to predict their recombination activity, and extend this methodology to novel growth processes. Lastly, I explore a spatial dispersion metric to assess its potential as a descriptor for the electrical recombination activity of clusters in silicon.

This work provides tools to crystal growers and solar cell manufacturers that facilitate the evaluation of electrical performance at early stages of the cell processing, enabling them to reduce the time required for cycles of learning to improve crystal growth processes.

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The use of fossil fuels, such as oil and coal, to supply humans’ energy needs, has had negative influence on the global climate and challenges us to re-think how to supply our energy demands in a sustainable, responsible, and environmentally-benign way. The use of solar energy as a renewable source has a clear potential to meet projected human demand of energy in years to come \(^1\). This renewable energy, besides reducing the negative impact on global climate change, it also represents a secure and virtually unlimited energy supply, and constitutes a transformation toward energy independence for countries \(^2\).

Solar technologies can either transform heat into electricity, or light into electricity. The latter, termed solar photovoltaic (PV), is the focus on this thesis. PV technology has been doubling every two years since 2002, increasing at a pace close to 48% each year \(^3\), and is expected to continue growing at an accelerated pace.

Although PV devices have been created from different absorber materials, silicon dominates the world’s production capacity, with close to 90% \(^4\). Si-based PV modules have been progressively attaining higher efficiencies, lower technical risk, and lower degradation rates, which have been translating into an even more grid-competitive levelized cost of electricity (LCOE), placing this technology closer to subsidy-free scale adoption in many markets \(^5,6\).
1.2 Crystalline Silicon Photovoltaics

Silicon is the dominant feedstock material among the different sources used for PV absorbers. This material dominance derives mainly from an abundance of knowledge transfer from the microelectronics industry into the PV industry; namely knowledge of Si crystal growth and processing of high-purity, low-defect-density Si wafers.

Low manufacturing costs and PV module prices, paired with high performance and reliability, are fundamental requirements for market expansion and consumer adoption. To meet these requirements, extensive research has been focused toward developing growth methods with high throughput, yield, and efficiency, while at a fraction of the cost of the microelectronics industry’s single crystal methods.

Although a number of alternative crystallization methods have accomplished some of the sought features, they come at the expense of creating defects that limit cell performance. These growth-related defects not only affect cell efficiency (which is the most important technical variable affecting module price), but also reduce manufacturing yield (the second most important technical variable affecting module price).

Given the importance of producing high-efficiency PV modules to reduce costs, efforts have been geared towards identifying the processing steps along the value chain that introduce the higher amount of efficiency losses. Among these steps, the crystal-growth stage is identified as a critical step.

One of the most common materials grown is cast multicrystalline silicon (mc-Si), which makes up about 60% of the global photovoltaics market production, and is favored due to its lower cost structure relative to monocrystalline silicon. This method, however, produces material with a higher density of defects (e.g., dislocations, grain boundaries, metal impurities) than other more expensive growth methods.

A higher density of defects, particularly dislocations, results in a greater number of centers for charge-carrier recombination, which reduce a solar cell’s efficiency. Interestingly, the recombination activity of individual dislocations and dislocation clusters can vary by orders of magnitude, even within the same device and a separation of only by millimeters of distance. This thesis work is aimed at understanding the root cause of variations in recombination activity of these defects.
1.3 Thesis Outline

This thesis starts with an overview of dislocations, their impact on mechanical and electrical properties of a bulk material, and their interaction with metal impurities in Chapter 2.

Chapter 3 describes phosphorus diffusion gettering, a process used in PV-device manufacturing lines to form the $pn$-junction and reduce metal impurity concentrations in as-grown silicon. A description of thermal annealing and its impact in changing dislocation density of the material is presented.

Chapter 4 presents an overview of the main methods and techniques used in this thesis to assess the electrical impact of dislocations in different materials.

Chapter 5 describes the dislocation density reduction in a Si-based material after subjecting it to thermal annealing. Challenges and limitations are discussed.

Chapter 6 introduces a proxy to determine the relative recombination activity of dislocation clusters by identifying the variation of dislocation etch-pit geometry. Correlations between the surface and bulk properties are studied and discussed.

Chapter 7 introduces a new material (HPMC-Si), which is compared systematically to mc-Si. The impact in electrical performance of dislocations after phosphorus diffusion gettering is evaluated. The proxy proposed in Chapter 6 is tested in HPMC-Si.

Chapter 8 discusses the Morisita Index methodology to measure the spatial patterns distribution of dislocation etch pits, and its relation to the recombination activities of dislocation clusters.
2.1 Abstract

The goal of this chapter is to discuss the origin of dislocations in silicon, their impact in solar cell performance, and the models describing the recombination activity of these defects, while pointing the outstanding questions this thesis will address in following chapters.

2.2 Fundamentals of Dislocations

2.2.1 Nucleation and Dynamics

A dislocation is a one-dimensional structural defect in a crystalline solid that reduces elastic strain energy, and represents a localized, large-amplitude, and irreversible deformation, which leads to inelastic or plastic shear. The presence of a dislocation indicates that the material has experienced plastic deformation, which can result when applied (e.g., thermal or mechanical) stress exceeds the yield point of the material. Because dislocations are detrimental for solar-cell device performance, understanding nucleation, multiplication, and annihilation behaviors of dislocations can lead to improved crystal growth parameters that can eventually minimize the concentration of this defect.

The onset of plasticity in a material is marked by the nucleation of dislocations. The plastic regime is highly dependent on applied stress, strain rate, and temperature. Stress can be applied either directly or indirectly. A direct method can be subjecting a body to mechanical loads. An indirect method can be changing the material’s temperature, leading to thermal
gradients and inhomogeneous lattice strain. Depending on the dopant density and strain rate, dislocations can nucleate at temperatures as low as 530–660°C in silicon, termed the brittle-to-ductile transition\textsuperscript{16-19}.

The distance displaced in the crystal lattice by a dislocation is measured in terms of the Burgers vector, $b$, which represents the magnitude and direction of the crystal distortion. The Burgers vector connects two points within the lattice in by the shortest translation vectors\textsuperscript{20}.

Dislocations can be broadly categorized into edge, screw, and mixed, based on the way the Burgers vector is enclosed. For edge dislocations, the Burgers vector is normal to the line of the dislocation, while for screw dislocations the Burgers vector is parallel to the dislocation line as seen in Figure 2.1. Mixed dislocations contain both edge and screw components.

The dislocation line starts and ends at a free surface; although the line direction may vary as dislocations propagate through the bulk, the Burgers vector remains constant.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.1.png}
\caption{Figure 2.1. Representation of a crystal lattice with an edge-type dislocation and its line direction, and a screw-type dislocation with its corresponding line direction. A mixed dislocation (not shown) happens in the transition from edge to screw dislocation. Dislocations are contained in a slip plane. The Burgers vectors, $b$, for both edge and screw dislocations, are represented by a red arrow. Figure adapted from Ref. \textsuperscript{21}}
\end{figure}

Once nucleated, dislocations can “glide,” i.e., move along certain crystallographic planes. The preferential gliding directions will depend on the crystal structure of the system, and tend to be parallel to planes with the highest density of atoms, so-called close-packed planes. These
close-packed planes result in the lowest required energy to move a plane of atoms past another. The movement of many dislocations is called slip. In silicon, the slip systems correspond to the \{111\} plane family. Within these \{111\} planes, dislocations can point along the \langle110\rangle directions, with a Burgers vector of \((a/2)\), where \(a\) is the lattice constant\(^2\).

Figure 2.2 shows a face-centered cubic unit cell with a (111) plane and different directions for slip to occur. A total of 12 different slip configurations exist and can be activated in Si.

![Figure 2.2. Example of slip configuration for silicon, with (111) plane view shown in red, and three \langle110\rangle directions.](image)

The conditions aforementioned are valid for “edge” dislocations in face-centered and diamond cubic lattices, and variations for dislocation mobility and dissociation modes depending on the dislocation character have been extensively studied\(^{20,23-26}\).

Dislocation dynamics are governed by different variables, such as temperature, stress, and other material characteristics. From Refs.\(^{16,27}\), dislocation velocity in silicon can be described by

\[
v = B_o \left( \frac{\tau}{\tau_o} \right)^m \exp \left( \frac{-Q}{kT} \right),
\]

where \(B_o\) is a constant related to dislocation velocity in the material, \(\tau\) is the shear stress resolved in a slip plane, \(\tau_o\) is the standard stress for dimensional correctness, \(m\) is the stress exponent with
values between 1 and 2, $Q$ is the activation energy for different dislocation types (e.g., screw, edge), $k$ is the Boltzmann constant, and $T$ is temperature. As evidenced, temperature strongly influences dislocation velocity due to its presence in the exponential.

Deviations from Equation 2.1 occur as one enters a regime with higher temperatures (>1000 °C) and higher stress (>40 MPa)\(^2\). In this regime, another mechanism for dislocation mobility exists, termed “climb”, which allows dislocations to move out of their glide planes. Climb is assisted by the diffusion of vacancies to segments of a dislocation, or by the creation of self-interstitials which can then diffuse away\(^2\).

### 2.2.2 Dislocation Properties

Dislocations distort the lattice locally, resulting in strain fields. Depending on the type of dislocation, the associated strain field will be different\(^2\). In the case of screw dislocations, the stress contains an out-of-plane shear component ($xz$-plane, $yz$-plane), as shown in Equations 2.2, and 2.3,

\[
\sigma_{xc} = -\frac{\mu b}{2\pi} \frac{y}{x^2 + y^2}, \tag{2.2}
\]

\[
\sigma_{yc} = \frac{\mu b}{2\pi} \frac{x}{x^2 + y^2}, \tag{2.3}
\]

where $\mu$ is the shear modulus, $b$ is Burgers vector, and $x$ and $y$ are positional values in Cartesian coordinates.

As for edge dislocations, the out-of-plane shear stress components are null, and only in-plane normal components ($x$-axis, $y$-axis), in-plane shear components ($xy$-plane), and out-of-plane normal components ($z$-axis) exist. The other stress tensor components are shown in Equations 2.4 (normal stress in $x$-axis), 2.5 (normal stress in $y$-axis), 2.6 (plane shear $xy$-plane), and 2.7 (plane stress),

\[
\sigma_{xx} = -\frac{\mu b}{2\pi(1 - \nu)} \frac{3x^2 + y^2}{(x^2 + y^2)^2}, \tag{2.4}
\]
\[ \sigma_{yy} = \frac{\mu b}{2\pi(1-\nu)} y \frac{x^2 - y^2}{(x^2 + y^2)^2} , \]  
(2.5)

\[ \sigma_{xy} = \sigma_{yx} = \frac{\mu b}{2\pi(1-\nu)} x \frac{x^2 - y^2}{(x^2 + y^2)^2} , \]  
(2.6)

\[ \sigma_{zz} = \nu(\sigma_{xx} + \sigma_{yy}) . \]  
(2.7)

The strain fields in a mixed-type dislocation are a weighted superposition of both screw and edge dislocation strain fields \(^{29,30}\).

Some of the most relevant distinctions between screw and edge dislocations in terms of their stress fields are summarized in \(^{30}\) and shown in Table 2.1.

**Table 2.1. Differences in elastic strain fields between screw and edge dislocations.**

<table>
<thead>
<tr>
<th>Screw Dislocations</th>
<th>Edge Dislocations</th>
</tr>
</thead>
<tbody>
<tr>
<td>No hydrostatic component</td>
<td>Hydrostatic component</td>
</tr>
<tr>
<td>Stress field proportional to (b)</td>
<td>Stress field proportional to (b)</td>
</tr>
<tr>
<td>Stress field proportional to (\mu)</td>
<td>Stress field proportional to (\mu)</td>
</tr>
<tr>
<td>No (p\Delta V) interaction w/ point defects</td>
<td>Strong (p\Delta V) interaction w/ point defects</td>
</tr>
<tr>
<td>-</td>
<td>Compressive/tensile on different sides of half plane</td>
</tr>
</tbody>
</table>

In terms of the dynamic properties described before, non-screw dislocations in Si have been shown to attain a higher velocity (described by Eq. 2.1) than screw dislocations \(^{16}\).

A material that contains dislocations is not in its lowest energy state, as energy is stored in the form of strain energy surrounding the dislocations, evidenced by the stress states described in Equations 2.1–2.7.
2.2.3 Dislocations in Multicrystalline Silicon (mc-Si)

Dislocations in ingot cast multicrystalline silicon (mc-Si) have attracted attention of researchers because of the adverse electrical impacts on solar cell devices. As detailed in Ref. 14, among the typical methods to grow ingot cast mc-Si is the heat extraction method (HEM). In this method the crucible is first filled with silicon, then silicon is molten, and afterwards it is slowly solidified through a controlled temperature decrease. A variation for this method called direct solidification (DS) which ensures columnar growth by maintaining a flat solid-liquid interface. HEM is schematically shown in Figure 2.3.

Figure 2.3. Schematic representation of an ingot casting heat extraction method, used to grow multicrystalline silicon. Figure adapted from Ref. 14

To prevent ingots from cracking and the feedstock material from sticking to the crucible, the walls of the crucible are usually coated with a Si₃N₄ layer. Feedstock is melted in a high-purity gas atmosphere, and thermal gradients carefully controlled during growth and cool down.

In this process, dislocations arise through thermo-mechanical stress that occurs during growth and cooling. Stress can occur if the solid-liquid (or melt) interface is not kept planar, potentially triggering dislocation nucleation. In other words, the uneven cooling conditions can alter the stability of the interface, building up thermal stresses and leading to viscoplastic deformation during all stages of growth: crystallization, solidification, and cool down.

The nucleation of dislocations is a cascading effect; once nucleation occurs, dislocations tend to progressively multiply and increase in density as a function of ingot height. The onset of dislocations can also be traced to different sources, besides the one aforementioned, as
detailed in Refs. 20, 29, 40-44. These sources can be stress-concentrating interfaces at grain boundaries, at the liquid/solid interface with the crucible, or at the liquid/solid interface with the initial feedstock seeding. In addition, second-phase particles incorporated during growth can also induce distortion in the silicon lattice due to mismatch in coefficients of thermal expansion.

The multiplication mechanisms can be either by Frank-Read sources 20, or multiple cross glide 20, and lead to dislocation densities that can range typically in this material from $10^4 \text{ cm}^{-2}$ to well above $10^6 \text{ cm}^{-2}$ 14.

When dislocations multiply, they can also start intersecting one another, occasionally forming immobile (sessile) sections that pin sections of dislocations, and thus lead to entanglements 20.

Plastic deformation dynamic models that describe the nucleation and multiplication of dislocations have been formulated by Alexander-Haasen 46, and K. Sumino 16, 17. These models have been further adapted to thermo-mechanical loading conditions existing in cast-based silicon growth, to understand the dynamic behavior of dislocations during ingot casting of multicrystalline silicon 39.

Increased knowledge on dislocation dynamics in silicon have led to further growth refinements being proposed and established; both at the simulation and at the experimental level. For example, modeling of temperature inhomogeneities after solidification — during the cooling stage — has shown how dislocation densities can rapidly increase 39, 47. Modeling of liquid-solid interfaces 48, 49 and thermo-mechanical stresses 37, 50-52 during growth have provided information to optimize time-temperature profiles. These studies aim to decrease dislocation density and process variability.

Interestingly, dislocation densities have been shown to vary from ingot to ingot. This has been attributed mostly to the initial nucleation conditions 45. Therefore, besides only controlling the time-temperature profiles previously described, alternative approaches have been proposed wherein nucleation conditions, both in the crucible and in the seeding, are modified to obtain lower dislocation density in silicon materials.

### 2.2.4 Dislocations in High-Performance Multicrystalline Silicon (mc-Si) materials

Modification of the crystallization nucleation process during ingot growth can either increase or reduce dislocation density. One approach to crystal nucleation control has been to
form faceted dendrite crystals by undercooling during the initial stage of crystal growth, and then using these dendrites as templates to grow the remaining crystal. This method reduces the nucleation of small-angle grain boundaries by creating highly twinned grains with relatively large sizes. However, dislocations tend to appear in the upper portions of these seeded ingots, and difficulties to precisely control undercooling have prevented widespread adoption in industry.

A related growth method, which also relies on controlling crystal nucleation, is known as “high-performance mc-Si” (HPMC-Si). This method consists of seeding growth with a high density of small grains that are randomly oriented. The small grains can either be formed by intermediate undercooling or by crushing polysilicon feedstock materials. In addition to resulting in lower dislocation densities than standard mc-Si, HPMC-Si crystal nucleation is easier to control than dendrite seeding, making it more attractive for industrial crystal growers.

Different approaches can render the same HPMC-Si type of material. To homogenize definitions, Ciftja and Stokkan describe HPMC-Si, as materials that have (a) smaller grain size than mc-Si, (b) higher random-angle grain boundary density, and lower amount of twin-boundaries, (c) dislocation clusters that do not grow uncontrollably (in the case of standard mc-Si), and that result in (d) increased solar cell efficiency with the same processing conditions as mc-Si.

Similarly, kerfless techniques have been developed, attaining similar characteristics as HPMC-Si (i.e., lower dislocation density, smaller grain size, increased efficiency) and could be potentially considered a type of HPMC-Si, as well.

Dislocation density in HPMC-Si has been reported to be low, but localized dislocation clusters can still be found. These clusters are reported to grow intra-granularly, and then disappear again as a function of height. The termination of dislocation clusters in HPMC-Si has been proposed by Stokkan et al. to occur at random-angle grain boundaries throughout the ingot, mainly due to these grain boundaries being amorphous-like, allowing them to behave as free surfaces, or sinks. A detailed assessment of their electrical impact, however, is still lacking, and is presented in this thesis work in Chapter 7.
2.3 Dislocation Recombination Activity

2.3.1 Interaction of Dislocations with Impurities

As described in Section 2.1.2, edge dislocations experience a pressure-volume interaction ($p\Delta V$) with point defects. The total strain energy, arising from the stress components detailed in Equations 2.1–2.7, can be further broken down into:

$$E_{\text{total}} = E_{\text{core}} + E_{\text{elastic}},$$

where $E_{\text{core}}$ represents the energy associated with the core of the dislocation, and $E_{\text{elastic}}$ is the energy associated with the strain field surrounding the core, or long-range elastic field. Equation 2.8 is commonly used to understand whether dislocation lines will minimize their energy by dissociating $^{20}$, but it also points towards an important distinction at a dislocation, which is the partition of it into two critical segments: a core region, and the area outside of it, or screening radius $^{63}$.

To understand the importance of lattice strain and its association with impurity point defects, we refer to Figure 2.4. Figure 2.4(a) shows a schematic representation of an edge dislocation and its core region. In Figure 2.4(b) we observe the same core region, however now interacting with a limited and relatively low concentration of point defects present in the volume matrix. Figure 2.4(c) represents the same dislocation as in Figure 2.4(b), but interacting with a higher concentration of point defects, saturating the core (with higher probability of precipitation) and forming an impurity cloud in the surrounding strain field $^{64}$. Figure 2.4(d) shows the diffusion potentials for an interstitial atom within the strain field of the same edge dislocation. The forces acting on interstitial atoms are shown in dashed lines. These forces are the drivers for impurities to diffuse toward and aggregate at the dislocation, as shown in Figures 2.4(b) and 2.4(c) $^{65}$.

It is worth noting that there are further interactions between point defects and dislocations: chemical binding of impurities to the dislocation core, and impurities diffusing via intrinsic point defects that equilibrate near the dislocated region $^{25,66}$. These mechanisms generally increase the interaction between dislocations and impurities.
When very high concentrations of impurities accumulate at dislocations and form second-phase particles, "pinning" of dislocation motion can occur\textsuperscript{20, 29, 67}, which, as will be discussed in Chapter 5, might be undesirable if motion and annihilation of dislocations is sought.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_4.png}
\caption{Schematic representation of interaction between dislocation and impurity point defects. (a) Clean dislocation without interacting with point defects, (b) Dislocation core decorated by a low density of impurities. (c) Dislocation core strongly decorated by impurities; impurity cloud formed by impurity point defects accumulating in the dislocation strain field. (d) Motion of interstitial atoms in the strain field of the edge dislocation, with arrows indicating the strain-induced impurity flux. Adapted from Refs. \textsuperscript{64, 65}.}
\end{figure}

When strain fields drive a local influx of impurities toward the dislocation core, the solid solubility of metal impurities can be exceeded locally upon cooling (from either crystal growth, or processing). Thus, dislocations serve as "heterogeneous" nucleation sites for precipitation\textsuperscript{25}. For impurity point defects to precipitate into second-phase particles, the impurity point defect species must be supersaturated yet have sufficiently high diffusivity and solubility to diffuse to and aggregate at the dislocation core. Thus, sufficiently slow cooling rates must be enforced\textsuperscript{68}. 

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Studies comparing different types of dislocations in Si and their interaction with metal impurities (e.g., Cu) report that perfect edge dislocations tend to serve as more favorable heterogeneous precipitate nucleation sites than other dislocation types.

In “perfect” single crystals, impurities precipitate “homogeneously”; because of the absence of heterogeneous nucleation sites, a higher driving force (degree of supersaturation) is generally required for precipitation to occur. Many impurities, including copper, form punched out dislocations upon precipitation, because the density of silicon atoms in Cu$_3$Si is lower than the silicon lattice.

Not only is it more favorable for metal impurities to segregate preferentially at dislocations and locally exceed their solid solubility around them due to strain fields and chemical binding, but conditions are also favorable for enhanced diffusion. An edge-type dislocation tends to diffuse species faster through it than a screw dislocation, a dissociated dislocation, and the non-distorted crystal lattice. This effect is named dislocation pipe diffusion.

Dislocation pipe diffusion is accelerated at the core (close to two interatomic distances), given the structural variation. As Balluffi et al. describe, the “atomic environment for jumping” becomes freer as one progressively introduces defects (e.g., dislocations and plane defects), and the activation energy for diffusion processes are significantly reduced, in comparison to a perfect crystal lattice.

Figure 2.5 describes the effect of a dislocation in terms of diffusivity from the surface to the bulk (or vice versa). Diffusion at the crystal through the surface source is dominant at the surface. At depths within the sample, beyond the range at which atoms can be delivered by crystal diffusion alone, the dislocation pipe diffusion mechanism governs the diffusion of species.
Figure 2.5. Diffusion for self-diffusion into a dislocated crystal from a source at the surface. Reproduced from Ref. 65

The detriment of dislocation pipe diffusion will become more relevant, as we understand the interaction between point defects and dislocations and the recombination mechanisms in the next sections.

2.3.2 Defects Impacting Carrier Lifetime

2.3.2.1 Recombination Mechanisms

The role of metal impurities in reducing solar cell efficiency has been a topic of extensive studies. To understand their impact, it is important to first define charge carrier lifetime, and its role, relevance, and relation to efficiency.

Different mechanisms can limit the performance of a device by inducing recombination of the generated electron-hole pairs created under operating illuminated conditions of the final cell device. These principal mechanisms are Radiative (band-to-band) recombination, Auger recombination, and Defect-Assisted or Shockley-Read-Hall (SRH) recombination, as seen in Figure 2.6.
In $p$-type Si, the minority-carrier recombination rate at low injection is expressed as,

$$U = \frac{1}{\tau_n} (n - n_0),$$

(2.8)

where $n$ is the electron concentration, $n_0$ is the equilibrium electron concentration, and $\tau_n$ is the minority carrier (or electron) lifetime. The lifetime can be further broken down into its different recombination mechanisms detailed in Figure 2.6, leading to Equation 2.9,

$$\frac{1}{\tau_{\text{eff}(n,p)}} = \frac{1}{\tau_{\text{Radiative}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}}. $$

(2.9)

The recombination mechanism associated with dislocations and impurities is the Defect/Trap-assisted, or SRH mechanism. In SRH, the electron is trapped by an defect energy level in the defect-induced forbidden region. These regions tend to be attributed to impurities, or dislocations decorated with impurities. The hole then moves to the forbidden region where the defect level has trapped the electron, and both recombine $^{77, 78}$.
The detailed equation describing the SRH recombination mechanism as a function of injection level is described by Equation 2.10,

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

(2.10)

where \( \tau_{p0} \) is a defect’s capture rate for holes, \( \tau_{n0} \) is a defect’s capture rate for electrons, \( p_0 \) is the equilibrium hole concentration, \( n_0 \) is the equilibrium electron concentration, \( \Delta n \) is the excess carrier concentration, and \( n_1 \) and \( p_1 \) are factors that vary with temperature, energy levels and density of states on the conduction band, valence band, and trap.\textsuperscript{79, 80}

A closer inspection of Equation 2.11 shows that \( \tau_{p0} \) and \( \tau_{n0} \), the fundamental electron and hole lifetimes, and which can be generalized as \( \tau_0 \) for both \( n- \) and \( p-\)type material

\[
\tau_{0(n,p)} = \frac{1}{\sigma_{(n,p)}v_{th}N},
\]

(2.11)

are a function of the capture cross-section, \( \sigma_{(n,p)} \), which is related to the “size” of the defect to the charge carrier; carrier thermal velocity, \( v_{th} \); and recombination center density, \( N \). If (i) a trap is found to be large target to carriers, (ii) the carrier’s velocity is high, or (iii) the recombination center density \( N \) is high, then \( \tau_{p,n,0} \) will be low, and by consequence, \( \tau_{SRH} \) will also decrease (neglecting trapping effects). The exact relation varies with temperature and injection levels, however the importance of recombination centers \((N, \sigma)\) persists.

An additional mechanism that reduces the effective lifetime in Si is that of surface recombination. As shown in Equation 2.12, the effect of surface recombination (through surface dangling bonds) can act as centers for carrier recombination, and is common to experimentally passivate the surfaces to neglect this term and solve for the remaining constituents of SRH recombination equation,
\[
\frac{1}{\tau_{\text{eff}(n,p)}} = \left( \frac{1}{\tau_{\text{Radiative}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}} \right) + \frac{1}{\tau_{\text{Surface}}}. \tag{2.12}
\]

Another metric related to lifetime—defined as the time associated with the persistence of a charge carrier before it recombines—is the diffusion length, which is the average length the carrier can travel before recombining. A relation between these two metrics is defined in Equation 2.13,

\[ L = \sqrt{D \cdot \tau} \tag{2.13} \]

where \( L \) is the diffusion length, \( D \) is the diffusion constant for minority carriers, and \( \tau \) is the lifetime previously calculated. By comparing the characteristic length where the carrier is being generated and the length to the \( pn \)-junction, we can assess the feasibility of charge collection for current extraction in operating solar cell devices.

### 2.3.2.1 Impact of Point Defects

As previously mentioned, the defect-induced regions that introduce energy states for SRH recombination are a function of the recombination centers density \( N \), and on the capture-cross section, \( \sigma \), the latter being specific to each impurity.

From the perspective of energy levels, impurities are known to introduce deep energy levels in silicon’s bandgap, based on their varying capture cross sections\(^{81}\).

The incorporation of transition metal point defects (\( e.g., Ni, Ti, Fe, Cr \)) negatively impacts lifetime and ultimately reduces solar cell device efficiency, as reported for different solar cell architectures and a wide point defect concentration range in Ref.\(^{82}\).

Other elements can also be incorporated during growth, such as carbon, nitrogen, and oxygen, nucleating SiC, Si\(_3\)N\(_4\), and SiO\(_2\) precipitates, respectively\(^{83-85}\). However, in the case of as-grown mc-Si, it has been reported that the electron lifetime is mainly limited by interstitial iron (Fe\(_i\))\(^{86}\). Studies have indicated a frequent presence of nano-precipitates from transitional metals, similarly impact carrier lifetime in mc-Si\(^{87,88}\).

Methods to prevent the incorporation of defects into the growth environment include increased control on the crucible and crucible lining quality, and gases\(^{89-91}\). In addition, other
processes can reduce the impact of already nucleated structural defects. These processes are hydrogen passivation and external gettering mechanisms (e.g., phosphorus gettering)\textsuperscript{92-96}. Chapter 4 will further describe the latter.

2.3.2.2 Point Defects and Dislocations

Clean dislocations, as schematically represented in Figure 2.2(a), have been shown to only introduce shallow levels in the bandgap, and it is only upon their interaction with metal point defects that they act as centers for carrier recombination by introducing deep energy levels\textsuperscript{34, 97}. The recombination of carriers at dislocation bands is amplified by small concentrations of impurity atoms due to overlap between wave functions of impurity atoms at the core, and dislocation bands positioning\textsuperscript{98}. Similarly, a deep energy level of the impurities and the relative large capture-cross section, all are fundamentally linked and responsible for the detriment.

Recombination activity has been determined to be sensitive to metallic decoration\textsuperscript{99-101}. Kveder \textit{et al.}\textsuperscript{102} and Kittler \textit{et al.}\textsuperscript{103} have experimentally demonstrated this effect through electron-beam-induced current (EBIC) measurements, where a higher amount of contrast – indicative of electrical recombination –, and its temperature dependence, correlated strongly with the amount of metal contamination introduced at the crystal defects. Experimental results showed that dislocations decorated with metal silicide precipitates had the highest recombination activity detected throughout a broad range of temperatures\textsuperscript{98}.

2.4 Modeling Dislocation Recombination Activity

To fully understand and quantify the impact of dislocations and their detrimental interaction with impurities, different models have been proposed. For the experimental portion of this thesis, we employ one of the most well-known models, proposed by Donolato, and used to describe the recombination activity of dislocations\textsuperscript{104}. The most significant equations are detailed below, however for exhaustive details on his mathematical approach and simplifications, the reader is referred to Ref.\textsuperscript{104}.

In essence, Donolato’s model predicts the influence of an array of straight dislocations on the effective diffusion length.
Donolato's recombination model introduces the normalized recombination strength of a dislocation cluster, $\Gamma$, as a parameter to relate the dislocation-limited lifetime, $\tau_d$, and dislocation density, $\rho_d$, in a semiconductor material.

This model starts by considering an individual dislocation as a cylinder with a radius, $\varepsilon$, and a carrier recombination velocity, $v_s$, occurring at the line, as shown in Equation 2.14,

$$\gamma_d = 2\pi \varepsilon v_s.$$  \hspace{1cm} (2.14)

The dislocation recombination strength, $\gamma_d$, is assumed to be constant and independent of carrier density. This parameter can be understood as the ratio between the incoming flux of minority carriers per unit length, and the excess carrier density, with units of cm$^{-2}$/s. By dividing the recombination strength, $\gamma_d$, by a diffusion coefficient at the dislocation, $D$, as expressed in Equation 2.15, the normalized recombination strength of a dislocation cluster, $\Gamma$, is obtained,

$$\Gamma = \frac{\gamma_d}{D}.$$  \hspace{1cm} (2.15)

The dislocation-limited lifetime can be approximated as shown in Equation 2.16,

$$\tau_d = \frac{1}{2\pi \rho_d D} \left[ - \ln \left( \varepsilon \frac{\rho_d^2}{\pi} \right) \frac{1}{2} \frac{1}{2} \ln(\pi) - C + \frac{1}{2} \right] + \frac{1}{2\pi \varepsilon v_s \rho_d} ,$$  \hspace{1cm} (2.16)

where $C$ is Euler's constant, and $\rho_d$ is dislocation density.

The effective lifetime can be separated into the lifetime component arising from the dislocation, and the lifetime from a dislocation-free bulk, as expressed in Equation 2.17,

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_0} + \frac{1}{\tau_d}.$$  \hspace{1cm} (2.17)

An effective diffusion length can be obtained, as shown in Equation 2.18, with parameters arising from the dislocation-free bulk and the influence of the dislocations present in the material,
\[ L_e \cong \left( \frac{1}{L_0^2} + \frac{\rho_d (\gamma D)}{1 + \left( \frac{\gamma D}{2 \pi D} \right) \left[ -\ln \left( \frac{\pi}{a} \right) - C + \frac{1}{2} \right]} \right)^{\frac{1}{2}}, \]  

(2.18)

where \( L_0 \) corresponds to the diffusion length of the dislocation-free bulk material, \( C \) is Euler’s constant, \( a \) is the unit radius containing a dislocation (equivalent to the inverse square root of \( \rho_d \)).

A representation of the resulting constructed plots based on this model, and used in the experimental section of this thesis, are shown in Figure 2.8. Two curves constructed through Equation 2.17, for similar parameters except \( \Gamma \), which changed from 0.01 to 0.1 to highlight the impact in effective bulk lifetime. An important remark is that at a given dislocation density, a wide variation in charge carrier lifetime can be obtained depending on the normalized recombination strength. In the particular example of Figure 2.8, at a dislocation density of \( 1 \times 10^6 \), the effective bulk lifetime can be either \( \approx 10 \) \( \mu s \) for \( \Gamma = 0.1 \), or \( \approx 50 \) \( \mu s \) for \( \Gamma = 0.01 \).

---

**Figure 2.7.** Effective bulk lifetime vs. dislocation density curves constructed with inputs from Donolato’s dislocation recombination model \(^{164}\). The two curves are strongly influenced by their normalized recombination strength, \( \Gamma \), as shown in the red (\( \Gamma = 0.01 \)) and green (\( \Gamma = 0.1 \)) lines. For a dislocation density of \( 1 \times 10^6 \), \( \tau_{\text{eff}} \) can be either \( \approx 10 \) \( \mu s \), or \( \approx 50 \) \( \mu s \), *ceteris paribus*. 

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Experimentally, studies have reported values for $I$ can vary by more than an order of magnitude in $p$-type multicrystalline silicon, even for dislocation clusters in the same wafer separated by only millimeters of distance $^{10,105}$. A detailed analysis explaining the reason for this phenomenon through extensive characterization techniques is presented in Chapter 6 of this thesis work.

### 2.5 Modeling Spatial Impact of Defect Clusters on Solar Cell Devices

Figure 2.9 shows schematic cross-sectional view of a solar cell with a dislocation line going through the different critical sections being affected. It is known that in a solar cell device, both the short-circuit current, $J_{sc}$ $^{106}$, and the open-voltage circuit, $V_{oc}$, are severely affected by the presence of dislocations $^{35,107}$. This effect can be exacerbated upon the presence of metal impurities along dislocation lines through the device thickness.

![Figure 2.8. Schematic representation of dislocation line in the context of a finished device and the regions it affects. Adapted from $^{108}$](image)

Through an equivalent circuit model, Sopori modeled the characteristics of a non-uniform junction device, covered by defects-saturated areas $^{108}$. In his work, Sopori highlighted the relevance of dislocations spatial distribution by means of dividing a large-area cell into an array of diodes, each one assuming a given distribution of defects, and connected to other diodes (representing other cell areas) through resistors, which represent the sheet resistivity of the $pn$-junction and the metallization pattern in a cell. By switching the current being transmitted through the different elements in the diode arrays, he modeled the effect of spatially dispersing, or clustering, dislocations in solar cell efficiency.
The main point demonstrated through the equivalent-circuit model was that dislocations that were spatially clustered are more detrimental for the electrical performance of a solar cell than the same number of dislocations that were homogeneously distributed in an equivalent area.

While this work provides a useful insight into the optimal arrangement of dislocations, a crystal grower would try to arrange a given dislocation density (in the absence of a process that eradicates them, discussed in Chapter 5 of this thesis), no equivalent metric to measure or report degree of clustering exists in the experimental community. To address this metric void, a spatial distribution method is proposed and discussed in Chapter 8.
3.1 Abstract

The purpose of this chapter is to illustrate two processes: one that is heavily used in industry and one that can be, and both ultimately having an impact in either the structure of the dislocations, or their recombination activity behavior. These processes are (i) phosphorus diffusion gettering (PDG), and (ii) high-temperature annealing. PDG is geared towards increasing the material quality by increasing charge carrier lifetimes, via a reduction of the impurity concentration in the bulk. High-temperature annealing is considered a supplemental technique to achieve lower dislocation densities in the bulk.

3.2 Phosphorus Diffusion Gettering

As illustrated in Chapter 2, point defects, dislocations, and their interaction can significantly suppress carrier lifetimes in bulk silicon. To remove unwanted impurities in the bulk material and into the emitter, where the metals are less detrimental than in the bulk due to the dominance of Auger recombination and a reduced recombination activity by a high Fermi level, a gettering process is performed.

PDG is a segregation gettering mechanism, which unlike a relaxation gettering mechanism where metal points tend to precipitate once the solid-solubility is exceeded at a given temperature. This mechanism relies on the impurity’s higher solubility in the deposited phosphorus layer, than on the silicon bulk material. This solubility gradient constitutes the driving force for impurities to diffuse to the P-layer and out of the bulk material.
The PDG process is two-pronged: not only does it transport metal impurities out of the bulk material, but it does so by depositing and in-diffusing P into a p-type base to form a pn-junction, which is required for creating a solar cell device.

Although PDG is a segregation gettering mechanism, relaxation gettering can simultaneously occur by the presence of second-phase particles and structural and extended defects that reduce the energy barrier for metal impurities to precipitate out.

The gettering process can be broken down into three broad different sections, as seen in Figure 3.1: (i) Ingot cast growth and cool down [as-grown stage]; (ii) PDG, and (iii) Cool down.

![Figure 3.1. Schematic representing as-grown and PDG evolution of dissolved and precipitated metals in a material. First step (blue region) corresponds to growth and cool down of the material, for which preferential precipitation occurs at a crystal defect (e.g., dislocation). Metal atoms can be found interstitially in the bulk, too. During PDG (red region), high temperatures dissolves a precipitate volume portion into metal atoms, and the segregation coefficient of P on Si drives these atoms to the P-layer being in-diffused. Lastly (green region), as the temperature decreases, the segregation coefficient from the P-layer is much stronger for individual atoms to diffuse to it.](image)
Figure 3.1 denotes three sections and visually emphasizes the impact that a structural defect (e.g., dislocation) can have on the initial as-grown metal impurities, and the evolution after different steps within the PDG process. This schematic, which includes a structural defect, is a generalization and the detailed behavior depends on the type of structural defect $^{110, 111}$.

The wafer is grown (blue region in Figure 3.1) through a time-temperature profile that renders a crystal with a specific metal and structural defect density. Metal defects, for example Fe, can be found both in precipitated form and interstitially dissolved in the bulk, with the proportion being determined by the cooling profile $^{112}$. Through the PDG process (red region of Figure 3.1), precipitates shrink, and can sometimes fully dissolve because of the relative high temperatures. The reduction of precipitated and interstitial iron concentration after PDG will vary depending the precipitate as-grown size distribution, and the time-temperature profiles employed during PDG $^{113-115}$. Dislocations can also serve as heterogeneous sites for re-precipitation upon cool-down (green region of Figure 3.1). This re-precipitation can be further exacerbated if precipitates are present at the dislocation, because metal precipitates are known to act as sinks for dissolved impurity atoms, internally gettering them $^{116}$. In general, due to their interaction with metallic impurities, dislocations tend to perform worse than dislocation-free regions upon PDG $^{117, 118}$.

Experimental work to determine what kinds of dislocation clusters are more susceptible to perform worse (i.e., have a higher electrical recombination activity) after a PDG process is a topic discussed in detail in Chapters 6 and 7, with experimental evidence shown for two different materials.

Understanding the thermodynamic and kinetic fundamentals of point defects and their interactions in binary systems has been a topic of extensive study $^{95, 96, 114, 119}$, and not one discussed in detail in this thesis. An extensive review of different PDG models and the physics behind the process can be found in Refs $^{116, 120-122}$.

### 3.3 High Temperature Annealing

#### 3.3.1 Dislocation mobility and annihilation

It is well known that dislocations’ mobility increases as a function of temperature, dopant concentration, and strain rate $^{18}$. As mentioned in Chapter 2, climb allows dislocations to move out of their gliding plane upon high temperatures $^{20}$. These temperatures are usually above
1000°C. Both high temperatures and stress drive dislocation movement by overcoming an activation energy. In conjunction, higher temperatures, lower activation energy, and a proper amount of stresses, among other variables may enhance dislocation velocity (as shown in Equation 2.1) and intensify recovery.

Recovery refers to a stage of an annealing process in which a material restores its mechanical properties and in which dislocations tend to move, re-arrange, and in some instances annihilate \(^{123, 124}\). Recovery is a sequential event that leads into recrystallization, and can be considered a competing mechanism with recrystallization as it utilizes the same stored energy in the material arising from both dislocations and locked-in stress \(^{125}\).

Dislocation reduction can be achieved via an out-diffusion to the surface mechanism, or to pairwise-annihilation, which represents an increase in the probability of dislocations from opposite Burgers vectors sign encountering and canceling each other. As detailed in Ref. \(^{124}\), the reduction if attributed to solely pairwise-annihilation, it can be broadly estimated by Equation 3.1,

\[
\frac{\sqrt{N}}{\sqrt{N_0}} \approx \left[ 1 + \frac{t}{A \exp \left( \frac{B}{k_B T} \right)} \right]^{-1}, \tag{3.1}
\]

where \(N\) is the final dislocation density, \(N_0\) is the initial dislocation density, \(k_B\) is the Boltzmann’s constant, \(T\) is the temperature, \(t\) is the annealing time, \(A\) and \(B\) are constants related to the material being annealed.

Stress, either mechanically applied \(^{126}\) or induced by thermal variations \(^{127}\), is considered to be strong driver in achieving dislocation density reduction. For the scope of this work we focus on isothermal annealing in Chapter 5, without the introduction of additional stress to the already pre-existing residual stress in the as-grown sample.

### 3.3.2 Isothermal Annealing

For the instances were dislocations cannot be eliminated during growth, a method to reduce dislocation density has been proposed by Hartman et al. \(^{128}\). Such work consisted in subjecting Si string ribbon wafers to temperatures up to 1366°C for a period length of 6 h, achieving a dislocation density reduction of >95% in some instances.
The structural characteristics as grain orientations, grain size, grain boundary types, and overall residual stress, differ between Si materials \(^{127, 129-132}\). All of these characteristics are thought to play a significant role in reducing dislocation density reduction \(^{126, 127, 131}\). Therefore, the applicability of this technique might be restricted to certain materials under specific conditions.

An expansion of this technique to a new material is discussed in Chapter 5 with a specific focus on the limitations and efficacy of isothermal annealing in reducing dislocation densities.
4.1 Abstract

The principal structural and electrical characterization techniques used in this thesis work are detailed in this chapter. The “Electrical Characterization” section comprises techniques used to determine the charge carrier lifetime, charge carrier diffusion length, dislocation recombination strength, and presence of impurities serving as recombination centers for carriers. The “Structural Characterization” section details the techniques used for detecting and imaging dislocations and grain orientations in which dislocations are observed. The stress characterization subsection briefly reviews an optical method to spatially resolve strain distribution in silicon. Lastly, a review of the geometrical and spatial characterization techniques used to describe both the dislocation etch pit shapes and their spatial distribution, respectively, is presented. The techniques described in this chapter are restricted in scope to characterize silicon materials at the wafer stage, and not in a finished solar cell device.

4.2 Electrical Characterization

4.2.1 Surface Passivation

As shown in Equation 2.12 from Chapter 2, the effective carrier lifetime is influenced by recombination at the surface. To reduce this influence and determine the true bulk carrier lifetime, sample surfaces are passivated.

Surface passivation is performed by depositing aluminum oxide (Al₂O₃) via atomic layer deposition (ALD). ALD-deposited Al₂O₃ has three advantages: (i) it produces very uniform and
conformal depositions that accommodate high aspect-ratio features and large areas; (ii) the mechanism for passivation is a field effect which reduces the recombination of carriers by reducing the density of a type of charge carriers via an electric field at the surface; (iii) reduces the density of defect states at the surface by introducing hydrogen and chemically bonding with dangling bonds at the surface\textsuperscript{133,134}.

4.2.2 Lifetime Measurements

4.2.2.1 Photoluminescence Imaging

Photoluminescence Imaging (PLI) is a spatially resolved technique based upon the luminescence produced by radiative (band-to-band) recombination of charge carriers in Si upon external illumination.

Although radiative recombination is low compared to SRH-induced recombination, the PL signal has been shown to be sensitive enough for mapping diffusion lengths in the vicinity of defects, solar cell performance (including shunt location detection), and iron interstitial concentrations\textsuperscript{135-138}.

In our current setup, a fiber-coupled diode laser with a wavelength of 808 nm excites carriers in the Si sample, and a Si-charge-couple device (Si-CCD) camera captures the energy emitted through radiative recombination.

In addition, [Fe\textsubscript{i}] maps can be acquired by manipulating the defect state so that it forms a complex under certain illumination conditions dissociating FeB pairs, associates FeB pairs under other conditions, and comparing images under different states controlling for the complex changes. In other words, the recombination properties (\textit{i.e.}, lifetime) change with variations in the chemical state (\textit{i.e.}, FeB changes into Fe\textsubscript{i}), and by comparing image changes before and after FeB pair dissociation, a spatially-resolved [Fe\textsubscript{i}] map can be obtained\textsuperscript{135,139}.

4.2.2.2 Quasi-Steady-State Photoconductance

The quasi-steady-state photoconductance (QSSPC) technique is a steady-state measurement that is based on Equation 4.1,
\[
\tau = \frac{\Delta n}{G - \frac{d\Delta n}{dt}},
\]

(4.1)

which, under steady or quasi-steady-state conditions, can be simplified to Equation 4.2,

\[
\tau_{QSS} = \frac{\Delta n}{G},
\]

(4.2)

where \(\tau_{QSS}\) is the measured lifetime measured, \(\Delta n\) is the excess carrier density, and \(G\) is the generation rate produced by illuminating the sample. This technique relates the changes in the material's conductance to changes in charge carrier lifetime as a function of excess carrier density, or injection level. One can then know the effective carrier lifetime of a sample, in a non-spatially resolved way through this method, by assuming a uniform photogenerated excess carrier density throughout the bulk.

The steps to measure carrier lifetime, are detailed in Ref. 140. First, a sample is subject to a decaying pulse of light, where the flash decay constant is smaller than the expected carrier lifetime to allow a virtual steady state, balancing both recombination and generation. The light intensity and the conductivity are then measured with a calibrated reference cell and a calibrated inductively-coupled RF coil, respectively, as a function of time. The excess carrier densities, \(\Delta n\), for each of the steady states measured are obtained by fitting conductivity results to carrier mobility models, which are functions of doping concentration, and injection levels. The measured light intensity is converted to \(G\), and \(\tau\) is obtained. It is important to mention that these measurements are average values over region with less than 4.0 cm in diameter.

### 4.2.2.3 Microwave Photoconductance Decay

In the case of microwave photoconductance decay (\(\mu\)-PCD), the photoconductance values are obtained by detecting reflectivity changes of microwaves that are directed towards the sample's surface. To better estimate lifetime values, this technique is best suited for low-injection samples given the nonlinearities of the reflectivity at high injection levels 80. The ability to spatially resolve and obtain lifetime maps makes this a very attractive method when wafers operate in a relatively low injection regime.
In our setup, carriers in a circular area of the sample with 250 μm diameter are excited with a 200 ns laser pulse, exciting carriers in the bulk. The decaying lifetime is measured by microwave reflectance at that particular spot and has a rapid cut-off time for acquisition. To create a map, this process is repeated continuously until the entire region of interest has been analyzed.

4.2.2.4 μ-X-Ray Fluorescence

The X-ray fluorescence microscopy (μ-XRF) technique consists of subjecting a sample to high energy X-ray radiation. The electrons located in the inner atomic shell of the material are promoted into higher energy states, and simultaneously inducing the decay of an outer atomic shell electron which emits excess energy by photoemission. For our studies, the fluorescence signal of different metal impurities is probed in silicon to determine chemical composition and the influence of different metals on recombination activity\textsuperscript{141-145}. Though not a lifetime technique per se, this technique can provide insights into the interaction mechanisms between defects and poor carrier lifetime performance by analyzing the relationship between metal impurities and structural defects.

For this work, synchrotron-based μ-XRF measurements were conducted at Beamline 2-ID-D of the Advanced Photon Source at Argonne National Laboratory. A 10 keV X-ray energy is used to scan regions of interest.

4.3 Structural Characterization

4.3.1 Etching Solution and Dislocation Etch Pit Counting Algorithm

Subjecting a Si sample to a chemical solution process can chemically-reveal dislocations as etch pits on the surface\textsuperscript{146-148}. There are two mechanisms that can describe the enhanced dissolution rate at the location of a dislocation etch pit: (i) strain field caused by extended defects, and (ii) the surface potential difference at the defect site compared to the surface potential in a continuous defect-free region\textsuperscript{149}.

The common etchants used in the PVLab to delineate crystal defects, in particular dislocations, consist of a mixture of HF:HNO\textsubscript{3}:CH\textsubscript{3}COOH, in a common mixture as proposed by
The Si surface in contact with the etchant solution is firstly oxidized, due to HNO$_3$ reaction, and the HF reacts with the oxidized region, consuming the oxidized material \cite{151}. CH$_3$COOH acts as a buffer substance to help control the etching rate.

Dislocations are chemically revealed as etch pits on the surface, with approximately 5 \mu m diameter after a 40 s dip in the chemical solution. The etch pit counting algorithm used herein was developed at the PVLab, and is available online \cite{152}.

4.3.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a powerful technique that provides high-resolution observation of defects at a theoretical resolution of to \sim 1.9 \AA \cite{153}.

A high-energy, coherent beam of electrons is transmitted through a thinned specimen; some electrons interact with crystalline specimens and are diffracted by a certain angle. The transmitted and diffracted electrons are then either imaged onto a screen by a set of objective lenses or collimated to produce a set of discrete sub-beam rays. These rays then project as points in the back focal plane of the lens; both the projected pattern and the individual rays contain information on the various sections of the specimen.

There are different types of contrast that can be analyzed via TEM: mass-thickness contrast, phase contrast, scanning TEM (high resolution of thickness and elemental contrast), and diffraction contrast.

For crystalline materials, the coherent scattering based on Bragg diffraction depends on the crystal’s structure and orientation, therefore distortions in the lattice lead to diffraction contrast. Diffraction contrast is commonly used for imaging defects and phases, and is obtained by the interference between the diffracted and transmitted beams due to the existence of local crystallographic changes in the specimen \cite{154}. In the case of dislocations, due to their half-plane-insertion nature, they tend to bend planes in their near vicinity, and if these planes are bent into a different diffracting orientation from the bulk, a separate set of locally diffracted beams will be created and interact with the bulk transmission/diffraction image, leading to a significant image contrast \cite{20}.

An extensive literature body exists on TEM, and the reader is referred to other references for an exhaustive and rigorous description of this technique \cite{155-157}. 

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4.3.3 Electron Backscatter Diffraction

Electron backscatter diffraction (EBSD) technique is conducted in a scanning electron microscope (SEM). The images obtained through SEM are a result of multiple scattering processes, involving both elastic (energy-preserving) and inelastic scattering (non energy-preserving). Among the most important electron signals detected, one finds secondary electrons, Auger electrons, and backscattered electrons.

Backscattered electrons are generated by scattering events within the sample, and typically have energies larger than 50 eV. The higher the beam energy, the deeper the interaction volume probed through SEM, although the amount of backscattered electrons is approximately energy independent. Also, the number of backscattered electrons is a function of the atomic number; giving a high atomic contrast at low atomic numbers, and vice versa.

The diffraction patterns observed through analysis of the backscattered electrons are known as Kikuchi bands, and include information about both the separation between planes of atoms and the orientation of the lattice plane that gives rise to the observed diffraction bands; these signals together indicate a unique crystallographic orientation relative to the specimen’s surface normal.

The Kikuchi bands are projected onto a phosphor screen, which is connected to a CCD camera that captures the projected pattern, and through computer algorithms, subtracts background noise, indexes the observed diffraction pattern, analyses and fits the orientation that minimizes the error for a given orientation. From this procedure, grain orientation is computed, and grain size, grain boundary types, and plane traces can be calculated. The latter is commonly used to determine the crystallographic directions in which slip activity occurs in a system. In the case of Si, it is known from Chapter 2 it is known that this occurs on the {111} planes.

For this work the mounted sample is tilted at 70° to the horizontal. The detector is placed at a 20° position from the horizontal axis, creating a 90° with the sample surface, increasing the fraction of scattered electrons into the detector. A 20 kV electron beam, in high-current mode is used with spatial step sizes ranging between 1 and 10 μm. Samples are mechanically or chemically polished to minimize spurious diffraction.
4.4 Stress Characterization

4.4.1 Infrared Birefringence Imaging

Infrared birefringence imaging (IBI) is a technique based on the photoelastic effect. This experimental method determines the stress distribution in Si by analyzing the induced birefringence phenomenon via polarized light \(^{160, 161}\). Birefringence is an optical material property where the speed of light oriented along one axis is higher than the speed of light along another axis. Upon the emergence of these rays, they are found to be out of phase (\(\delta\)) and their different propagation velocities produces variations in the light vector, which can then be analyzed with a set of polarizers and a camera \(^{162, 163}\).

With this technique phase differences in light vectors (termed “retardation”; units of distance [nm]) propagating through silicon are measured and correlated with the direction and magnitude of principal stresses \(^{164, 165}\).

In this experimental work, the tool described and employed in Ref. \(^{129}\) is used. In essence, an 1100 nm optical band pass filter is used to reduce white light to monochromatic light. At this wavelength, Si is virtually transparent, and transmission imaging can be done to spatially resolve not only the stress distribution within the bulk, but also to detect non-Si particles in the bulk that absorb the monochromatic light.

4.5 Geometrical Characterization

4.5.1 Eccentricity

The variation in eccentricity values is utilized as a metric to quantify the shape of individual dislocation etch pits, and as agglomerate, the degree of disorder within a dislocation cluster.

The eccentricity, which is the ratio of the distance between the foci of the ellipse and its major length, is described in Equation 4.3 where \(a\) is the ellipse major length, and \(b\) is the ellipse minor length

\[
e = \frac{2}{a} \sqrt{\frac{a^2}{2} - \left(\frac{b}{2}\right)^2}.
\]
Through the eccentricity measurement, we fit the major and minor axes of an ellipse that would most accurately contour a dislocation etch-pit perimeter and extract the eccentricity for each etch pit, varying between 0 (perfect circle) and 1 (elongated ellipse).

In this thesis, the MATLAB algorithm capabilities from the dislocation etch pit counting method are expanded to also calculate the eccentricity of the individual dislocation etch pits measured.

4.6 Spatial Characterization

The relevance of dislocations' spatial distribution has been elucidated by Sopori through his circuit-network model \(^{108}\). Sopori describes how clustered dislocations are more detrimental for the electrical performance than the same number of dislocations found spread in an equivalent area.

A common practice in the community is to report the sample’s dislocation density. The sole descriptor of dislocation density, however, can be considered insufficient, as it does not provide further information on the electrical performance of any particular cluster.

Moreover, no formalism has been presented in the community—to the author’s knowledge—, to further describe the spatial distribution of dislocations, or degree of clustering. The absence of descriptor exists despite the fact that theoretical studies have predicted detrimental effects from clustering. Hence, an indicator of the spatial characteristics (e.g., dispersion) of defects would allow for a more thorough description of dislocation density, and a deeper understanding of the impact on electrical performance.

Though the spatial statistics field is broad, the author explores a method, the Morisita Index, which can arguably be considered simpler than other existing methods, to demonstrate the viability of the spatial pattern analysis as (i) an additional descriptor for reported dislocation densities, and (ii) predictor of the electrical recombination activity of dislocation clusters in silicon wafers.

4.6.1 Morisita Index

Morisita index of spatial aggregation is a diagnostic testing for independence, or dependence, between spatially distributed points \(^{166}\). To compute this index, the entire spatial
domain is broken down into subsets, or quadrats, and the Index based on quadrat counts is then acquired with a value obtained depending on the data points falling into each, as computed following Equation 4.4,

\[ I_\delta = Q \frac{\sum_{i=1}^{Q} n_i(n_i - 1)}{N(N - 1)} \]  \hspace{1cm} (4.4)

In this equation \( Q \) corresponds to the total number of quadrats, \( n_i \) defines the number of points counted in quadrat \( i \), and \( N \) corresponds to the total number of points. The quadrat distance corresponds to the diagonal that cuts through the middle of the quadrat. Also, the shape of the quadrats could be square or rectangular, and adjusted in the \( Q \) term by a geometrical relation, where the grid length and the angle of the diagonal are trigonometrically related.\(^{167,168}\)

This index—a normalized measure of the dispersion of a probability distribution—indicates the likelihood of two sampled points being from the same quadrant in comparison to a randomly distributed Poisson distribution process.\(^{169}\)

The Poisson distribution is stated in Equation 4.5,

\[ I_{\text{Poisson}} = \frac{\sum_{i=1}^{Q} n_i^2 - \frac{N^2}{Q}}{\frac{N}{Q}} \]  \hspace{1cm} (4.5)

In this case, the Poisson distribution is one of many distributions known for having a mean-to-variance distribution of value 1.0.\(^{170}\) The departure from a Poisson distribution results in values non-equal to zero, giving the Morisita Index its range below and above values of 1.0.

From the Morisita index methodology, a value of \( I_\delta = 1.0 \) is given for randomly distributed point patterns; \( I_\delta > 1.0 \) corresponds to clustered patterns; and \( I_\delta < 1.0 \) denotes a dispersed, or regular pattern. A visual representation of different scales of dependence in the point pattern data is given in Figure 4.1, where the point pattern distribution is shown for three cases: (1) regular, or sparse distribution, (2) random, and (3) clustered pattern.\(^{171}\) The Morisita Index plot is directly below each of the point distribution patterns. The intensity of clustering can be therefore interpreted from the plotted \( I_\delta \) values on each distribution, and quadrat distances, or size.
Figure 4.1. Figure representing three spatial point patterns: Regular, Random, and Clustered, corresponding to Morisita Indices below a value of 1, 1, and above 1. Figure adapted from Ref. 171
5.1 Abstract

In an attempt to reduce dislocation density, this chapter presents the results obtained from subjecting different Si materials to high-temperature annealing processes. Herein, an annealing process, previously tested in conventional mc-Si to reduce dislocation clusters that remain after crystal growth, is employed. A sample is subjected to a 1390 °C annealing process for 24 h and its dislocation density reduction is evaluated. We conclude that despite achieving significant average dislocation density reductions, if inclusions are present in the sample, these may limit the thermal annealing efficacy by nucleating new dislocations due to a mismatch in coefficients of thermal expansion between the second-phase particles and the Si volume.

5.2 Introduction

Techniques to reduce dislocation density after growth have been previously developed and successfully tested on conventional cast-based multicrystalline silicon (mc-Si) \textsuperscript{127}, and kerfless Si ribbon \textsuperscript{128, 130}. Here, we analyze the impact of this high temperature annealing

technique on reducing dislocation density in a material termed kerfless high performance multicrystalline silicon (kHPMC-Si). We explore the stress state evolution after annealing and determine the presence of second-phase particles as potential barriers to successfully implement this technique for dislocation density reduction.

5.3 Experimental Methods

A p-type Si wafer, grown by a kHPMC-Si (small-grain, low dislocation density) method, was laser cut into 2×2 cm² and 200 μm thick sample. The growth method employed herein (from 2012) is similar to that of crystallization on dipped substrate (CDS) from Refs. 61, 172 in 2008.

The sample was mechanically polished to achieve a flat homogeneous surface and ensure a clear dislocation etch-pit reveal. Chemical etching in a Sopori solution 150 was performed for 45 seconds, to avoid potentially carcinogenic chromate-based solutions. Previous work has shown comparable results between Sopori and chromate-based solutions for our annealed samples 127, suggesting that the mechanism described by Reimann 173 is not “masking” dislocations in our sample; furthermore, some dislocations can be seen after etching. Dislocations intersecting the surface are revealed as etch pits and maps are acquired with a Nikon LV 100 light optical microscope, at a pixel resolution of 1.46 μm.

Grain orientations and grain boundaries (GBs) information is acquired through an electron backscatter diffraction (EBSD) technique using a Supra 55VP scanning electron microscope, utilized to understand the potential role of GBs in annealing efficacy. In this study, EBSD is simply used to determine grain-boundary location.

Infrared birefringence imaging (IBI) is used to spatially-resolve the stress distribution both in the as-grown state, and after annealing. This method, described in detail in Ref. 164, detects phase differences in light vectors (termed “retardation”; units of distance [nm]) propagating through silicon, and correlates them with the direction and magnitude of principal stresses. A 1100 nm optical band pass filter is used to convert white light into monochromatic light. At this wavelength, Si is virtually transparent, and transmission imaging can be done to detect non-Si particles in the bulk that absorb the monochromatic light.

In addition, a Si string ribbon sample undergoing a similar annealing process was imaged via IBI to visualize the evolution of dislocation bands, addressing previous concerns on the validity of Sopori-etching annealed samples, reported by Ref. 173.
The sample's as-grown state is characterized with the techniques aforementioned, then annealed at 1390°C in a N₂ environment for 24 h to induce a dislocation density reduction. Subsequently, the sample is subjected to the same characterization process for a comparative analysis between pre- and post-annealing states.

5.4 Results and Discussion

It has been previously reported that the presence of frozen-in stress, or residual stress, enhances dislocation density reduction. The reduction in retardation ([Δλ]) levels, as shown in Figure 5.1, corresponds to a reduction in stress levels within the sample. The residual strain energy in this case is thought to be enhancing mobility of dislocations, which in turn, promotes dislocation-pair annihilation.

![IBI before and after annealing](image)

Figure 5.1. IBI before and after annealing at 1390 °C for 24 h. Residual stress is observed to be high (orange/yellow values) before annealing, and low (blue/white values) after annealing.

The dislocation density reduction, suspected through IBI stress analysis, is evidenced upon etch pit density analysis. Overall, a ~40% dislocation density reduction is achieved. A section of the sample showing unusually high dislocation density is shown in Figure 5.2, with two dislocation clusters denoted by red and green arrows. The red arrow in Figure 5.2(a) points toward the location of a cluster that remains with a high amount of dislocations after the annealing procedure, as evidenced when comparing to the same arrow in Figure 5.2(b). The green arrow in Fig. 5.2(a) denotes a region where dislocation density is high in the as-grown
state, but is significantly reduced upon annealing, when compared to the cluster from the red arrow, as seen in Fig. 5.2(b). These results lead to a classification of two categories of clusters upon annealing: (i) persistent, and (ii) non-persistent dislocation clusters.

![Figure 5.2](image)

Figure 5.2. Microscope images (a) before and (b) after annealing at 1390 °C for 24 h. arrow indicates dislocation cluster with significant dislocation density reduction upon gettering. The red arrow indicates a region that remains with an abundance of dislocations even after annealing, and the green arrow points towards a dislocation cluster that was significantly reduced after annealing. Bubbles adhering to the surface upon etching can cause faint circular contours, as observed in regions of Fig. 5.2(b).

Focusing on the persistent dislocation clusters upon annealing, a region with two nearby clusters, as shown in Fig. 5.3(a), was selected. The area covered by the etch pits is enclosed in a yellow-dashed oval, and serves as guideline to reference their position in subsequent measurements.

We employed EBSD to determine if these dislocation clusters were re-appearing due to stress-concentrating points at GBs, or mismatch between slip planes on different grains\(^\text{174}\). EBSD is shown in Figure 5.3(b). Interestingly, the location of these dislocation clusters does not entirely match with the exact location of grain boundaries, discarding the effect of dislocation nucleation due to GB effects.
To test the presence of second-phase particles as potential responsible of this type of dislocations, infrared transmission imaging was performed, as shown in Figure 5.3(c). In here, two particles, shown as dark (monochromatic light-absorbing) spots, are shown within the confines of the yellow ovals. Few other dark spots are seen elsewhere. To determine the difference between surface irregularities caused by mechanical polishing that could distort light transmission, and inclusions that could be present, IBI analysis was performed, as shown in Figure 5.3(d).

![Figure 5.3. (a) Microscope image with two dislocation etch pit clusters circled in yellow. (b) Electron backscatter diffraction image with color-coded grain orientations and location of the dislocation etch clusters labeled in dashed-yellow contour lines. (c) Infrared transmission image of the same analyzed region with two light-absorbing particles in the interior of the regions of interest. (d) Infrared birefringence image showing high retardation values (corresponding to high stress intensity) arising from the light-absorbing particles in the interior of the dislocation etch pit clusters.](image)

A highly concentrated stress pattern is observed to emanate from the two dark spots matching the dislocation cluster regions. This analysis was expanded to nine more persistent dislocation clusters, with consistent results as those shown in Figure 5.3.

These experiments point toward the existence of infrared-light-absorbing second-phase particles in the Si matrix with a different coefficient of thermal expansion (CTE) than Si. Differences in CTE of an inclusion in a matrix of different material have been reported to lead to high stress concentrating regions and nucleate dislocations. Based on the authors’ experience of previous work, the suspected particle is hypothesized to be SiC. Misfit strains, caused by different CTEs between materials, as shown in Table 1, can be high enough to generate dislocations due to thermal contraction differences at the SiC-Si interface upon cooling. The local stress values upon cooling are thought to far exceed those required for dislocation
motion (which increase annihilation probability) \textsuperscript{127}, and instead lead to the nucleation of dislocations \textsuperscript{127,175,176}.

Table 5.1. Thermal and Mechanical Properties of Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of Thermal Expansion*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$3.61-3.84 \times 10^{-6} \degree C$ \textsuperscript{22}</td>
</tr>
<tr>
<td>SiC</td>
<td>$4.57-4.74 \times 10^{-6} \degree C$ \textsuperscript{177}</td>
</tr>
</tbody>
</table>

*Ranges of CTE values tabulated correspond to the brittle-to-ductile temperature transition range for Si (500–600 °C).

Concerns were raised in Ref. \textsuperscript{173} regarding the validity on etching annealed samples and revealing true dislocation density. The concerns are based on a hypothesized improper etching solution adaptation for samples with varying resistivity. To test this hypothesis, a Si string ribbon sample was annealed for 6 h at 1360°C, and IBI was performed before and after annealing. The results shown in Figure 5.4 denote a clear decrease in the signal arising from the dislocation bands, shown as diagonal lines inside the red rectangles.
Figure 5.4. IBI of a string ribbon Si sample before and after being subjected to a 6 h, 1360°C anneal. The bands corresponding to dislocations are enclosed in the red rectangle. A disappearance of the bands is visible by means of IBI, in contrast to the reported claims in Ref. 173

5.5 Conclusions

While overall dislocation density in kHPMC-Si is low, some dislocation-rich clusters remain. Herein, we explore the efficacy of high-temperature annealing to reduce these residual dislocations. While annealing appears to be successful overall, in local areas, second-phase particles (inclusions) are suspected to be reducing the efficacy of high-temperature dislocation-density reduction. The difference in coefficient of thermal expansions between the matrix (Si) and an inclusion (e.g., SiC) is likely exceeding locally the yield point of Si upon cooling and creating the punch out-like type of dislocations observed. A stringent control upon crystal growth could be implemented to either (i) reduce completely the presence of dislocation clusters, or (ii) reduce the concentration of second-phase particles that appear to cause dislocation nucleation upon cooling.
Moreover, the validity of Sopori etching for samples annealed at high temperature is validated by means of IBI, which shows the reduction of dislocations after subjecting a sample to an annealing process, indirectly demonstrating a dislocation density reduction.\textsuperscript{128, 130}
6.1 Abstract

In conventional cast-based mc-Si materials, dislocations and dislocation clusters are still abounding. Although post-growth treatments have been proposed to reduce dislocation density, they have limited efficacy, as it has been demonstrated in Chapter 5. A deeper understanding of the electrical impact of dislocation clusters and methods for characterizing them in a facile manner are approaches aimed at mitigating their impact, and that serve as tools for crystal growers to improve their growth conditions.

These dislocation clusters found in mc-Si have shown to have recombination strength values, $\Gamma$ (described in Chapter 2), that vary by up to two orders of magnitude, even within the same wafer.

In the work presented in this chapter, we combine a surface-analysis approach with bulk characterization techniques to explore the underlying root cause of variations in recombination strength among different clusters. We observe that dislocation clusters with higher recombination strength consist of dislocations with a larger variation of line vector, correlated with a higher
degree of variation in dislocation etch-pit shapes (ellipticities). Conversely, dislocation clusters exhibiting the lowest recombination strength contain mostly dislocations with identical line vectors, resulting in very similar etch-pit shapes. The disorder of dislocation line vector in high-recombination clusters appears to be correlated with impurity decoration, possibly the cause of the enhanced recombination activity. Based on our observations, we conclude that the relative recombination activity of different dislocation clusters in the device may be predicted via an optical inspection of the distribution and shape variation of dislocation etch pits in the as-grown wafer.

6.2 Introduction

The current procedure to study the recombination strength of dislocation clusters consists of processing a wafer into a cell, measuring spatially resolved current collection probability, then stripping the metal contacts to then evaluate the wafer microstructure \(^{178}\). This experimental procedure can be time intensive, complicating the accumulation of large amounts of data. In this work, we propose a method to quickly predict the relative recombination activity of a given dislocation cluster in the solar cell from inspection of the as-grown wafer.

It has been observed by Rinio et al. that values for \( \Gamma \) can vary by an order of magnitude in \( p \)-type multicrystalline silicon, even for dislocation clusters in the same wafer separated by only millimeters of distance \(^{10, 178}\). Rinio \(^{10}\) and Lawerenz \(^{179}\) attributed such differences to the presence of oxide precipitates at high-\( \Gamma \) dislocation clusters, and their absence in low-\( \Gamma \) dislocation clusters. Bertoni et al. observed high-\( \Gamma \) regions to contain dislocations with high metal-impurity decoration detected by nano-X-Ray Fluorescence \(^{180}\). These results are consistent with observations of intentionally contaminated dislocations in Si, in which the recombination activity of dislocations is found to be strongly dependent on metal decoration \(^{100-102}\).

The preponderance of evidence suggests that some dislocation clusters tend to interact more strongly with impurities, which enables precipitates to form more readily, presumably resulting in higher \( \Gamma \) values. During subsequent high-temperature processing steps (e.g., phosphorous diffusion), metal silicide precipitates partially dissolve \(^{114}\) and release metal point defects that may decorate nearby structural defects, increasing their recombination activity \(^{181}\).

We hypothesize that the degree of disorder of the dislocation microstructure is correlated with the density of heterogeneous nucleation sites for impurity precipitation, and hence,
dislocation recombination activity. Furthermore, after an anisotropic wet chemical etch to reveal
dislocations as etch pits, we hypothesize that the degree of shape variation of the etch pits may
serve as a proxy for the degree of disorder of dislocations microstructure.

These hypotheses are informed by previous studies. A correlation between the shape of
the dislocation etch pits on the surface and the bulk dislocation line direction has been inferred
previously by Sopori \textsuperscript{182} and demonstrated experimentally by Rau \textsuperscript{183} and Takahashi \textsuperscript{184}. From
these studies, we infer that a group of dislocation etch pits with similar ellipticity and orientation
will likely exhibit an ordered structure beneath the wafer surface and hence a low density of
heterogeneous nucleation sites (Figure 6.1a). Conversely, groups of etch pits with varying
ellipticity suggest widely varying dislocation line vectors beneath the wafer surface, increasing
the likelihood of dislocation tangles. Kinks, jogs, and other discontinuities of the dislocation line
vector likely represent energetically favorable heterogeneous nucleation sites (Figure 6.1b).

Figure 6.1. Schematic representation of chemically-revealed dislocation etch pits, and their presumed line
directions inferred from surface characteristics. Herein, ‘Ordered’ arrangement refers to etch pits with
consistent eccentricity, and ‘Disordered’ refers to the combination of different etch pit shapes with no
discernible arrangement. Line propagation through the bulk, as represented in the ‘Disordered’ case, denotes
entanglement and line curvature variations, whereas ‘Ordered’ illustrates continuous line vectors.

In essence, the model we propose for dislocations bears resemblance to the grain boundary (GB) recombination-activity model proposed by Chen \textit{et al.} \textsuperscript{111} seen in Figure 6.2: An
increasing disorder within the extended defect microstructure results in an increasing interaction probability with impurities, and hence increasing recombination activity. In a manner analogous to Chen’s GB microstructure assessment via EBSD and EBIC, we propose a surface method to rapidly quantify the degree of dislocation disorder from dislocation etch-pit images: the variation of etch-pit ellipticity.

![Figure 6.2. GBs contrast in EBIC as a function of CSL Σ-value and contamination level. Reproduced from Ref. 111.](image)

**6.3 Experimental Methods**

**6.3.1 Dislocation-Cluster Selection and Electrical Characterization**

A p-type mc-Si wafer (5×5 cm², 200 μm thick) from a directionally solidified boron-doped ingot (~1 Ω-cm) was saw-damage etched and processed into a solar cell by applying a 30 min phosphorous diffusion step at 860°C, followed by the deposition of a 150 nm magnesium fluoride layer as anti-reflection-coating (ARC), and finalized with screen printing of aluminum contacts, as partly described in Ref. 185. For electrical characterization, a spatially resolved light beam induced current (LBIC) map was measured using a 832 nm excitation wavelength at an approximate injection of one sun, as described in Ref. 10. The LBIC map was converted into an internal quantum efficiency (IQE) map with a pixel resolution of 12.5 μm.
The sample was chemically-mechanically polished and etched with a Secco solution \(^{146}\) for 1 min, revealing dislocations intersecting the sample surface as etch pits with a maximum diameter of 5.5 \(\mu m\).

Images of the defect-etched sample surface were taken with a LV100 Nikon optical microscope at a pixel resolution of 0.74 \(\mu m\), and individual images were automatically stitched into a mosaic image using NIST-Elements AR 3.2 imaging software. The resulting mosaic image was processed by a MATLAB algorithm, available online \(^{152}\), to calculate the etch-pit density, as described in Ref. \(^{132}\).

To quantify the electrical recombination strength of dislocation clusters, Donolato’s model for minority carrier diffusion length as a function of the dislocation density was extended by a PC1D model \(^{186}\). This extension included IQE as a function of the minority carrier diffusion length \(L\), and used \(\Gamma\) as a fitting parameter to determine \(L\). By correlating IQE and dislocation density \(\rho\) maps, we obtain a scatterplot of IQE(\(\rho\)), and fit these data to determine the \(\Gamma\) value of the dislocation cluster, as previously demonstrated in Refs. \(^{10,179}\).

Five different dislocation clusters were selected and analyzed for this study, denoted as A, B, C, D, and E, and exhibiting up to two orders of magnitude difference in \(\Gamma\) values.

### 6.3.2 Dislocation-Cluster Selection and Electrical Characterization

Additional optical-microscope scans of the five dislocation clusters were performed at higher magnification, resulting in a pixel resolution of 0.15 \(\mu m\). We expanded the MATLAB algorithm capabilities from Ref. \(^{132}\) to analyze the geometry of the etch pits which can be approximated by circular or elliptical shapes, as detailed in Chapter 3.

### 6.3.3 Metal-Decoration Analysis

Synchrotron-based micro X-Ray Fluorescence (\(\mu\)-XRF) measurements were conducted at Beamline 2-ID-D of the Advanced Photon Source at Argonne National Laboratory, with the characteristics described in Chapter 3.

### 6.3.4 Dislocation Microstructure Analysis

The grain orientations of the multiple selected regions were analyzed by EBSD in a ZEISS Supra-55 VP scanning electron microscope (SEM) operating at 20 kV, with 10 \(\mu m\) step
size. A TSL OIM Analysis Software package was used to record EBSD measurements and determine the plane traces of interest along the different detected grain orientations.

Microstructure characteristics of dislocations in the bulk were analyzed by a JEOL-2100 and 2010 Transmission Electron Microscope (TEM), operating at 200 kV. Prior to this step, the sample was ground down to ~100 μm thickness with SiC paper, a 3 mm diameter disk containing the regions of interest was laser-cut from the sample, and dimpled to ~20 μm thickness. The center of the disk was then thinned by a low angle argon ion milling technique using a Gatan Precision Ion Polishing system. Planar samples were prepared by this method, rendering a suitable approach for a general dislocation line analysis in the selected dislocation clusters. Final specimens were ~80–110 nm thick, suitable for low-resolution analysis of dislocation lines.

6.4 Results

Figure 6.3a shows the IQE map of the sample region containing the five dislocation clusters, with color-coded current-collection efficiencies. The optical microscope image of the same region on the defect-etched sample is shown in Figure 6.3b and the five dislocation clusters are delineated and labeled as A–E.

Measured IQE values as a function of the dislocation density are plotted in Figure 6.3c, where the respective Donolato fits are also shown. The recombination strength values, $\Gamma$, of the five dislocation clusters are determined to be $\Gamma_A = 4.6 \times 10^{-4}$, $\Gamma_B = 1.0 \times 10^{-3}$, $\Gamma_C = 1.8 \times 10^{-3}$, $\Gamma_D = 8.79 \times 10^{-3}$, and $\Gamma_E = 2.43 \times 10^{-2}$. These $\Gamma$ values span almost two orders of magnitude, even though the corresponding dislocation clusters are less than 3 mm apart, consistent with results of high variation of $\Gamma$ values over a small distance previously reported by Rinio et al. 178.
Figure 6.3. (a) Internal Quantum Efficiency (IQE) map from LBIC measurement. (b) Dislocation etch pit map of mc-Si sample containing five dislocation clusters. (c) Correlation of IQE values and dislocation density for each of the dislocation clusters. Plotted lines for all dislocation clusters were calculated using the extended Donolato theory for $\Gamma$ values from Refs. 10, 104.
As an example, a representative selection of etch pits from clusters A and E, which have the lowest and highest normalized recombination strength, respectively, and the fitted ellipses with their corresponding eccentricity value are shown in Figure 6.4.

![Figure 6.4](image)

**Figure 6.4.** Selected dislocation etch pit regions from Clusters A and E, with fitted elliptical shape, and their corresponding eccentricity values. Fitted eccentricity values range from 0 for a perfect circle, to nearly 1 for an elongated ellipse.

The frequency distribution for eccentricity at each dislocation cluster is shown in Figure 6.5. These histograms show the total fraction of dislocations measured at a given eccentricity value.

![Figure 6.5](image)

**Figure 6.5.** Frequency distribution of eccentricity values corresponding to clusters A through E.

The variation of eccentricity values at each dislocation cluster is plotted in Figure 6.6 as a function of the recombination strength of the respective cluster. The variation of eccentricity values is defined as the ranges found in 90% of the analyzed etch pits. The data show a trend of increasing variation in eccentricity values with increasing recombination strength.
Each value in Figure 6.6 is color-coded in accordance to the orientation of the grain in which the dislocation cluster is located, as highlighted in the inverse pole figure. Neglecting small deviations, cluster A is located in a grain with (212) orientation, B, D, and E in a grain with (112) orientation, and C in a grain with (101) orientation. Remarkably, regions B, D, and E all lie within the same grain but show a very different variation in eccentricity, therefore, excluding the possibility of anisotropic etching effects\textsuperscript{146,150}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.6.png}
\caption{Variation in eccentricity values within each dislocation cluster as a function of its recombination activity. The variation in eccentricity value is defined as the range, or the difference between the maximum and the minimum eccentricity values lying within 5\textsuperscript{th} and 95\textsuperscript{th} percentile of the data. The color of each data point indicates the crystal orientation of the grain in which the dislocation cluster is located, obtained from EBSD data, as shown in the Si inverse pole figure.}
\end{figure}

Areas containing a total of 28, 24, and 29 etch pits from clusters A, C, and E, respectively, were surveyed by \(\mu\text{-}XRF\) to investigate the presence of metal decoration. Representative \(\mu\text{-}XRF\) maps are shown in Figure 6.7. \(\mu\text{-}XRF\) maps of different elements were measured but only the Si and Cu maps are shown. Dark regions in the silicon maps correspond to dislocation etch pits, while dark pixels in the copper channel represent a higher count rate of Cu Ka radiation, indicating the presence of Cu-rich particles. Small magnified maps within clusters C and E reveal copper-rich particles with a Cu area density up to 0.026 \(\mu\text{g/cm}^2\) and 0.071
μg/cm², respectively. No XRF signal above the noise floor of 0.0088 μg/cm² was detected for Cu in the μ-XRF maps in cluster A.

![Si XRF signal](image1) ![Cu XRF signal](image2)

Figure 6.7. μ-XRF maps of selected etch pits from clusters A, C, and E. Dark regions in the silicon channel correspond to dislocation etch pits. The copper channel in cluster A shows no fluorescence signal above the noise floor. Clusters C and E show several pixels of high Cu concentration detected in the vicinity of etch pits.

A statistical summary of μ-XRF results is shown in Table 6.1. In cluster A, a total area of 557 μm² was mapped, containing 28 etch pits, where no metal-rich particles were detected. In cluster C, a total area of 817 μm² was mapped, containing 24 etch pits, and 13 Cu-rich particles were found. Similarly, a total area of 539 μm² was mapped in cluster E, containing 29 etch pits and 6 Cu-rich particles were detected. These Cu-rich particles are assumed to be copper silicide precipitates, Cu₃Si, as observed and identified at grain boundaries and dislocations in mc-Si in previous studies.¹⁸⁷
Table 6.1. Total area mapped by μ-XRF in clusters A, C, and E, total number of etch pits observed, and number of Cu-rich particles detected in the vicinity of etch pits.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Total Area Mapped by μ-XRF (μm²)</th>
<th>Number of Etch Pits Observed</th>
<th>Number of Cu-rich Particles Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>557</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>817</td>
<td>24</td>
<td>13</td>
</tr>
<tr>
<td>E</td>
<td>539</td>
<td>29</td>
<td>6</td>
</tr>
</tbody>
</table>

Clusters A and E, with the lowest and highest $\Gamma$ values, respectively, were studied using TEM to determine the general bulk characteristics of dislocation lines. Dislocations from Cluster A (Figure 6.8a) are consistently observed in TEM as short straight line segments, indicating an inclination at a large angle to the surface, and with alternating contrast (Figs. 6.8 b–d). The dislocations are mostly similar throughout the region, and no precipitates were observed. Dislocations from Cluster E (Figure 6.8e), on the other hand, show different geometrical features: they vary in length, direction, entanglement, and degree of curvature as shown in Figs. 6.8f–h. These dislocations appear in a variety of planes, some of which are considered to be near surface planes, given the dislocation length and propagation. Measurements of dislocation character were not performed.
Figure 6.8. Micrographs of dislocation etch pits from cluster A are shown in a). (b–d) Representative TEM images of dislocations found in cluster A. (e) Micrographs of dislocation etch pits from cluster E. (f–h) Representative TEM images of dislocations in cluster E. Variation in line direction, curvature, length, and dislocation interaction is evident in cluster E. Plane traces for the \{111\} system are outlined in the micrographs. Dislocations in A tend to align perpendicular to a (111) gliding plane, as shown by the red-dashed line creating a 90° angle with one of the \{111\} plane traces. Dislocations from E do not have a particular arrangement.

From Figure 6.4, and Figure 6.9, a further correlation can be proposed between the etch pit geometry on the surface, and the line propagation through the bulk. To relate the surface geometry with a potential line direction, the eccentricity values shown in Figure 6.4 were converted to angles between the surface normal, \(n\), and the dislocation tangent line vector, \(t\). The angles, obtained by establishing the eccentricity value of 0.5 as the equivalent of a projected line at 45° from the surface normal, were then used in a cosine function to project a unit dislocation line at each of the eccentricity values.

Akin to Figure 6.6, the variation of projected line direction values at each dislocation cluster (eccentricity-to-line) is plotted in Figure 6.9 as a function of the recombination strength of the respective cluster.
Figure 6.9. Variation in line projection values within each dislocation cluster as a function of its recombination activity. The variation in eccentricity value is defined as the range, or the difference between the maximum and the minimum eccentricity values lying within 5th and 95th percentile of the data. The color of each data point indicates the crystal orientation of the grain in which the dislocation cluster is located, obtained from EBSD data, as shown in the Si inverse pole figure.

6.5 Discussion

Our results suggest that the variation in eccentricity values of dislocation etch pits at the surface can be used as a proxy to determine the degree of “order” or “disorder” of dislocation lines in the bulk. We observe that dislocation clusters containing surface etch pits with a wide range of eccentricity values show a larger recombination strength than clusters in which most etch pits have similar shapes. Consequently, the variation of eccentricity values of surface etch pits within a dislocation cluster can be used as a proxy to determine the recombination activity of the cluster.

The dislocation clusters compared herein are less than two millimeters apart, but their recombination strengths vary by up to two orders of magnitude. This variation is likely due to a difference in metal impurity decoration of the different clusters, as previously proposed and supported by our μ-XRF results. At high temperature during crystal growth, metal impurities are assumed to be homogeneously distributed throughout the wafer, thus metal concentrations
within the proximity of dislocation clusters were similar prior to the onset of metal silicide precipitation. However, we hypothesize that the varying degree of disorder in dislocation line segments observed by TEM might have caused variations in nucleation energy barrier, resulting in the observed difference in metal decoration among different clusters, as detected by µ-XRF. The preferential precipitation at the disordered dislocation arrangement, corresponding to a high degree of dislocation interaction and varying curvature of line segments, is similar to the observation by Shen et al. in single-crystal Si, where the precipitation behavior of metallic impurities at dislocations was observed to vary as a function of dislocation type, and degree of dislocation-line segmentation $^{69,188}$.

The difference in dislocation microstructure observed may be attributed, at least in part, to a high-temperature recovery process. Dislocations in low-$\Gamma$ clusters appear to have attained a low-energy configuration through a process known as polygonization $^{189,190}$. At this stage of the recovery process, the compressive stress field of one dislocation aligns with the tensile stress field of its neighbor, thus reducing total strain energy of the system $^{191}$. Reduced strain likely increases the precipitate nucleation energy barrier. Figure 6.8 shows optical micrographs of dislocation clusters A and E, having the lowest and highest $\Gamma$ values, respectively, with the traces of the $\{111\}$ planes outlined. In cluster A, the etch pits are aligned in a direction (red-dashed line) perpendicular to a $(111)$ plane trace, showing evidence of polygonization $^{192}$. In cluster E, however, there is a random distribution of etch pit orientation with no preferential alignment perpendicular to a $(111)$ plane trace.

The plane trace analysis suggests that: 1) cluster E is not in a low-energy configuration state, and 2) dislocations from clusters A and E may have reached their final state at different phases of ingot growth. Some researchers believe that lower $\Gamma$ dislocations may have formed at the melt-solid interface and underwent significant polygonization owing to higher temperatures at the solidification front. Higher $\Gamma$ dislocations may have formed upon cool down, where dislocation motion is limited, resulting in a more disordered microstructure, with a different type of interaction between dislocations and by consequence, potentially a larger interaction with impurity point defects $^{42,193}$. These speculations require further experimental investigation.

Furthermore, the tangent vector $t$, as it reaches the free surface with normal $n$, provides an insight into the line propagation into the bulk by surface inspection of the etch pit. In accordance to the assumption from the surface etch pit geometry, if the line direction is assumed
to be related too, a wide spread in line direction corresponds to higher recombination activity at the dislocation cluster.

As a critical remark to results from our sub-surface analysis, in the μ-XRF measurements, fewer metal precipitates were detected in the vicinity of ech pits in cluster E, which shows the highest recombination activity, as compared to cluster C, which shows one order of magnitude lower recombination activity. The reason for this inconsistency is undetermined. However, low statistics are inherent to high-resolution and low-throughput techniques as TEM and μ-XRF. The difference in total mapped area, and the random selection of a low-statistical population can play a factor in the measured density distribution. Additionally, a higher density of nucleation sites with a lower nucleation energy barrier in cluster E may have enabled the formation of a higher density of smaller precipitates too small to be detected by μ-XRF. We acknowledge the possibility that more of these precipitates may have dissolved into the bulk during gettering. The most remarkable fact, however, is that none of the surveyed etch-pits in cluster A showed evidence of metal precipitate decoration above detection limits.

Regarding the surface analysis, it should be noted that some limitations exist in the automated etch-pit analysis, including the imprecise fitting of ellipses to irregular etch pit shapes (e.g., “tear-drop” features) and the deviations from zero-values for seemingly perfect circular etch pits. However, the simplified approach used herein has the advantage of being readily accessible, while still capturing the essential shape variations of dislocation etch pits that enable the observed trends in Figure 6.5.

6.6 Conclusions

We present a proxy to determine the relative recombination activity of a dislocation cluster by means of identifying the variation of dislocation etch-pit geometry. This proxy is based on the observed correlation between the variation of etch-pit eccentricity and the degree of order/disorder of dislocation line vectors through the bulk. Dislocation clusters with higher degree of disorder exhibit a higher probability of metal decoration and consistently, a larger detrimental impact on material performance.

This framework for predicting dislocation recombination activity based on a proxy for microstructural disorder bears resemblance to frameworks for grain boundaries, where impurity decoration is shown to be enhanced at grain boundaries with a higher degree of disorder at the
boundary interface (i.e., higher Σ values in the Coincident Site Lattice model)\textsuperscript{110,111}

A plane trace analysis suggests that ordered dislocation clusters with low recombination activity undergo polygonization, and that their evolution during crystal growth is likely different from randomly arranged dislocations in clusters with high recombination activity.

The etch-pit shape variation within a dislocation cluster appears to be a facile and fair predictor of its recombination strength, suggesting that a qualitative assessment of its impact on material performance may be possible on a bare wafer. Consequently, the surface inspection of etch pits can provide an easy path to infer solar cell performance, and has the potential of evolving into an early-stage predictive method of electrical impact, shortening the feedback loop for industry’s crystal-growth process control.
7.1 Abstract

As observed in Chapter 6, a surface-analysis approach with bulk characterization techniques were used to explore and explain the underlying root cause of variations in recombination strength among different clusters in mc-Si. However, alternative techniques to cast-based mc-Si that are able produce high quality materials at high throughput and low cost have been the subject of tremendous research efforts. In part, given the intensified competitive environment in the PV industry, where companies are pressed to reduce their cost structure to remain profitable, while increasing their devices efficiency. The validity of the proposed technique in Chapter 6 on emerging materials remains an open question.

High-Performance Multicrystalline Silicon (HPMC-Si) constitutes an attractive alternative to supplant conventional cast-based growth methods, given its different crystallographic structure (i.e., lower amount of dense dislocation clusters) as mc-Si and equivalent infrastructure and cost.

Though the dislocation density is in general lower, there is still the presence of dislocation clusters that may or may not be homogeneously adversely affecting the potential device performances.

To understand the lifetime response of this material upon P-gettering is herein performed, and compared to mc-Si. This response is majorly attributed to the difference in dislocation clusters. We observe that the electrical performance upon P-gettering is inhomogeneous in both mc-Si and HPMC-Si. A higher density of dislocation clusters in mc-Si leads to higher inhomogeneity and a poorer P-gettering response. Also, the recombination-active dislocations in HPMC-Si are found to be decorated with metal impurities, akin to results found for recombination-active dislocations in mc-Si (Chapter 6).

The contribution from Chapter 6 in mc-Si is expanded to HPMC-Si, and the recombination activity of non-dense dislocation clusters is assessed by the eccentricity variation methodology, despite the differing crystallographic structures between mc-Si and HPMC-Si, the latter having higher number of grains, grain boundaries, and a lower dense dislocation clusters.

### 7.2 Introduction

As competition in the PV industry intensifies, companies are pressed to reduce their cost structure to remain profitable. Within the cost components of a module, wafers roughly comprise ~30–40% of the total cost. In addition to reduce costs, a simultaneous importance is placed on increasing module efficiency, as this variable has been shown to be the main driver for module price. Efforts in industry have therefore focused on growing low-cost wafers with sufficient quality for processing into high-efficiency devices.

To increase silicon quality (i.e. potential for high bulk lifetimes) while reducing or maintaining a low-cost growth scheme, different methods that can reduce crystal defects during growth have been developed. Effort has been in great part focused on suppressing dislocations, as they are among the most detrimental defects in cast-based multicrystalline silicon (mc-Si). As discussed in Chapter 2, a lower initial dislocation density would reduce the amount of energetically-favorable sites for metal precipitation.

Recent works have detailed the growth method and structural characteristics of an emerging material referred to as high-performance multicrystalline silicon (HPMC-Si), which has higher quality than mc-Si. In contrast to mc-Si, HPMC-Si is known for a lower average
grain size and a lower dislocation cluster density due to controlled grain-growth kinetics that render favorable grain boundary (GB) types for a low density of dislocation clusters\textsuperscript{198, 199}. However, the presence of dense dislocation clusters in HPMC-Si can still be observed.

Because defects, in particular dislocations, can result in an inhomogeneous electrical response upon phosphorous gettering (P-gettering), it is unclear how HPMC-Si responds to P-gettering and how this response compares to P-gettered mc-Si, grown under similar conditions. Understanding this response is essential to maximizing the wafer and cell performance.

Herein, we study both mc-Si and HPMC-Si materials grown under identical growth conditions (e.g., crucible, crucible lining materials, feedstock, and gas). Samples are selected for processing and analysis at equal ingot heights in order to elucidate the differences between their dislocation densities and electrical performances upon P-gettering. We compare and quantify the lifetime improvements of both materials after processing. We correlate local differences in regions of low performance with structural and elemental origins (e.g., dislocations and impurities) to assess the root cause(s) of performance differences between mc-Si and HPMC-Si. We also test and validate a methodology in HPMC-Si, proposed in mc-Si material in Chapter 6, which can help determine the relative electrical recombination activity of dislocation clusters in a rapid manner.

7.3 Experimental Methods

7.3.1 Material Growth

To enable comparison on the basis of material properties, HPMC-Si and mc-Si ingots were prepared using the same hyper pure poly silicon feedstock, growth furnace, crucible, and crucible lining material. Two $p$-type 12kg pilot-scale ingots, a seed-assisted HPMC-Si ingot and a conventional mc-Si reference ingot, are grown in a Crystalox DS 250 directional solidification furnace. The crucible used for both materials is a Fused Silica Solar Crucible from Vesuvius, coated with Si$_3$N$_4$ from UBE America.

The mc-Si ingot is grown from polysilicon chips, with a final ingot diameter of 250 mm and height of 105 mm. The time-temperature profile resembles those typically used in industrial settings for large-scale growth. Melting is performed over a time span of 420 min at a plateau temperature on the susceptor of 1808 K. The cooling process is split into two parts; the first part
cools down at a rate of 0.75 K/min for 70 min, while the second part cools at a rate of 0.1 K/min for 400 min, until complete solidification is achieved.

The section of HPMC-Si ingot studied herein is grown also from polysilicon chips, and similar feedstock in the same crucible as the mc-Si ingot. The time-temperature profile differs from that of the mc-Si ingot in that the melting step is shortened in order to not fully melt the seeds. Melting is performed at the same susceptor temperature of 1808 K but over a total time span of 170 min, with a split-cooling rate of 0.75 K/min the first 80 min and a cooling rate of 0.1 K/min for the remaining 360 min. This resulted in a remaining seed height of approximately 40 mm after solidification. The final ingot was cut into nine 50 × 50 × 105 mm³ blocks whereas the three blocks in the central row was wafered by a slurry-based wire-saw.

Sample wafers are extracted and laser cut (50 mm × 50 mm × 200 µm) from the same solidified fraction height (f=0.75) from both mc-Si and HPMC-Si grown bricks, with measured resistivity values of 0.97 Ω·cm and 0.92 Ω·cm, respectively.

### 7.3.2 Minority Carrier Lifetime Analysis

To conduct minority-carrier lifetime analysis, samples are first saw-damage etched in a HNO₃:CH₃COOH:HF volumetric ratio mixture of 36:12:5 for five minutes, which removes approximately 20 µm off from the wafer (Note that handling HF requires proper personal protection equipment). Samples are then cleaned in a RCA solution to eliminate organic and metal contaminants prior to surface passivation. Surface passivation is performed by first depositing 20 nm of Al₂O₃ via atomic layer deposition in a Cambridge NanoTech Savannah 200 tool at a temperature of 200 °C, then subsequently annealing the samples at 350 °C for ten minutes in a N₂ environment.

Lifetime is mapped a Semilab WT-2000 microwave-photoconductance decay (μ-PCD) tool with a pixel resolution of 250 µm, both for the as-grown and after processing states. Normalized “lifetime improvement” maps, herein termed ratio maps, are processed by matching spatial coordinates between the as-grown and P-gettered lifetime maps, and dividing their pixel (lifetime) values.

Photoluminescence imaging (PLI) maps, with a pixel resolution of approximately 50 µm, are acquired by illuminating passivated samples with a 25 W, 808 nm, fiber-coupled diode laser,
and captured with a PIXIS 1024BR Si CCD camera with an InP wafer and a Schott RG1000 long-pass filter to improve sensitivity.

Interstitial iron concentration (Fe$_i$) is calculated by measuring lifetime after dissociating iron-boron (Fe$_i$-B$_s$) pairs, and then allowing for re-association for 150 min in the dark, then measuring lifetime again by quasi steady state photoconductance (QSSPC) (Sinton WCT-120). The calculation and experimental parameters used herein are detailed in Ref. 196. Noise analysis for the Fe$_i$-B$_s$ measurement technique is described for Cr$_i$-B$_s$ in Ref 200.

Qualitative, spatially-resolved Fe$_i$ maps are acquired with the PLI experimental setup (laser and camera). The maps are acquired after dissociating Fe$_i$-B$_s$ pairs with the diode laser and allowing for pair re-association.

The impact of grain size upon P-gettering and its combined effect with intragranular dislocation clusters is assessed by performing line scans between GBs on a normalized-PLI-counts map of the HPMC-Si P-gettered sample, with normalized values ranging from 0 to 1, and a pixel resolution of approximately 50 μm.

7.3.3 Phosphorous Diffusion Gettering

Wafers were cleaned prior to gettering using an RCA clean. Phosphorous gettering is performed in a Tystar Tytan 2800 POCl$_3$ furnace, using a time-temperature profile that consists of loading the sample at 700 °C, ramping up to 845 °C, and held for 30 minutes before cooling down and unloading at 750 °C.

After phosphorous gettering, the samples are etched again in a HNO$_3$:CH$_3$COOH:HF solution (volumetric ratio mixture of 36:12:5) for two minutes to remove the formed emitter, cleaned in RCA, and surface-passivated with Al$_2$O$_3$ for characterization of the materials’ lifetime-performance response to the P-gettering process, with the same lifetime analysis procedure detailed before.

7.3.4 Defect Elucidation and Eccentricity Characterization

Samples are etched with a Sopori solution (HNO$_3$:CH$_3$COOH:HF solution with volumetric ratio mixture of 36:15:1) for 45 seconds to reveal dislocations intersecting the sample surface as etch pits, averaging 6 μm in diameter. Dislocation etch pits are imaged with a Nikon LV 100 optical microscope at a pixel resolution of 1.46 μm.
To quantify the degree of disorder of dislocation clusters, which indicates relative recombination activity in mc-Si dislocations, two regions on the HPMC-Si samples were analyzed at a higher pixel resolution of 0.15 μm. From the existing dislocation etch pits on these regions, eccentricity values of the etch pits were computed by fitting the pit major and minor axes, as detailed in the previous chapter, and in Ref. 201.

7.3.5 Metal-decoration analysis

To identify the presence of metals decorating dislocation clusters, synchrotron-based micro X-Ray Fluorescence (μ-XRF) measurements are performed at Beamline 2-ID-D at the Advanced Photon Source at Argonne National Laboratory with 10 keV X-ray energy and a 200 nm full-width at half-maximum beam spot size. The selected dislocation etch pits from two different dislocation clusters are scanned via a flyscan method, with a 220 nm step size and a 750–900 ms dwell time per pixel.
7.4 Results

Figure 7.1. μ-PCD lifetime images: before P-gettering, after P-gettering, and a ratio of P-gettered/as-grown are shown in (a) and (b) for mc-Si and HPMC-Si, respectively. Red colors in the ratio images (values below 1) denote a decrease in lifetime performance, and gray scale (values above 1) denotes a range of lifetime improvement. A scatter plot of P-gettered lifetime vs. as-grown lifetime is shown in (c) for mc-Si, and in (d) HPMC-Si, where the data plotted is the same in both graphs, but the colors emphasize the material being analyzed. In these plots, slopes with different intensity ratio improvements are shown as 1:1, 1.5:1, and 2:1. Median values for every 5 μs intervals in the as-grown lifetime are shown as yellow triangles for mc-Si, and blue squares for HPMC-Si.

Figure 7.1(a) shows the change in mc-Si minority carrier lifetime performance after P-gettering. The first two μ-PCD maps show the as-grown and P-gettered lifetime values, normalized to the same color bar, corresponding to lifetime values up to 100 μs. The third image shows the ratio between P-gettered and as-grown maps. Lifetime values that did not change after P-gettering have a numerical value of 1.0. Areas that perform worse after the gettering process are shown in red, and lighter shades of gray color indicate greater lifetime improvement after P-gettering. These lifetime maps are acquired in a low-injection regime (<1e14 cm⁻³), as confirmed by QSSPC lifetime measurements.
The lifetime values from both mc-Si as-grown and P-gettered lifetime maps are plotted on the x- and y-axis, respectively, of Figure 7.1(c). The lifetime performance evolution of the mc-Si sample from as-grown and after P-gettering is represented in orange circles. The median lifetime values are binned in 5 μs intervals and shown as yellow triangles. Lifetime performance evolution of HPMC-Si is also shown in gray circles in the background, with their median lifetime values acquired in 5 μs intervals and shown as white squares.

Shown in the same scatter plot are three lines with different slopes denoting: no difference in lifetime between the as-grown and P-gettered state (“1:1”), 50% lifetime improvement by P-gettering (“1.5:1”), and 100% improvement after P-gettering (“2:1”). Two arrows show the tendency of lifetime performance after gettering, with directions towards “Better” (above 1:1 slope line), or “Worse” (below 1:1 slope line) regions. The majority of median values for mc-Si lie below the 1:1 dashed line, indicating a decrease in lifetime after P-gettering. Only values between ~50 μs and ~60 μs in the as-grown state improved.

Figure 7.1(b) shows two μ-PCD lifetime maps of the as-grown and P-gettered HPMC-Si sample, with the third image corresponding to a ratio between P-gettered and as-grown maps. Color-code and values represent the same performance changes as in Figure 1(a). Lifetime values are normalized to the same color bar, corresponding to lifetime values up to 250 μs.

In Figure 7.1(d), the lifetime values from both HPMC-Si as-grown and P-gettered lifetime maps are plotted on the x- and y-axis, respectively. The lifetime performance evolution of the HPMC-SI sample, as-grown and after P-gettering, is represented in green circles, with median lifetime values binned in 5 μs intervals shown as blue squares. Lifetime performance evolution of mc-Si (shown in orange color in Figure 7.1(c)) is also plotted in gray circles in the background, with respective median lifetime values shown as white triangles.

Lines with different improvement intensity slopes are also shown. The majority of median values for HPMC-Si lie above the 1:1 dashed line, and in some instances, close to 2:1. An increased performance is observed in low as-grown lifetime regions (~0–50 μs), and in higher as-grown lifetime regions (~60–100 μs).

Ratio maps for both mc-Si (Figure 7.2a) and HPMC-Si (Figure 7.2c) are shown with corresponding Fei maps in Figure 7.2b and 7.2d, respectively. Both ratio maps, and Fei maps (acquired after P-gettering) have a yellow-dashed line enclosing a representative region of interest.
Dislocation etch pit maps from the yellow regions in the mc-Si and HPMC-Si samples are shown in Figures 7.2e and 7.2f, respectively. A greater amount of dense dislocation etch pit clusters are observed in mc-Si as compared to the HPMC-Si sample. The red (underperforming) areas correspond to regions with dense dislocation clusters in both samples.

Likewise, the underperforming (red) areas corresponding to high dislocation cluster areas in the enclosed regions also match qualitatively with the relative high Fei values shown in the Fei maps. Quantitative Fe-boron (Fe-B) pair dissociation measurements indicate an as-grown Fei concentration of $1.14 \times 10^{11}$ cm$^{-3}$ in an adjacent HPMC-Si sample. After a standard P-gettering process, the Fei concentration is reduced by 95% to $5.44 \times 10^9$ cm$^{-3}$. The as-grown Fei concentration in the mc-Si sample is reduced from $1.34 \times 10^{11}$ cm$^{-3}$ to $1.14 \times 10^{10}$ cm$^{-3}$ upon P-gettering.

![Figure 7.2. Ratio image of (a) mc-Si and (c) HPMC-Si. Qualitative Fei maps for the same samples are shown in (b), and (d), respectively. Microscope images after chemically etching of the yellow-dashed regions are shown for (e) mc-Si and (f) HPMC-Si, where dislocation etch pits are shown as dark spots. These dislocation etch pit maps are acquired from representative performing regions within each sample.](image-url)
A photoluminescence (PL) image of a HPMC-Si region is shown in Figure 7.3(a). Dark regions represent low counts and low lifetime, while bright regions indicate higher counts and relative higher lifetime.

The PL image corresponds to a region of the HPMC-Si sample that contains dislocation etch pits, as observed in Figure 7.3(b). Dislocations populations 5.6 mm apart are selected from regions with high PL counts (white square on the left) and low PL counts (white square on the right).

The areas enclosed in the white squares are surveyed for etch pit eccentricity analysis. Optical micrographs of the two surveyed areas are shown in Figure 7.3(c), where the high PL counts region corresponds to the dislocation etch pits shown on the left, and the low PL counts region corresponds to the dislocation etch pits shown on the right.

Frequency histograms of etch pit eccentricity for each of the dislocation populations are shown in Figure 7.3(d). These histograms demonstrate the total fraction of dislocation etch pits measured with a given eccentricity value, ranging from 0 (perfect circle) to 1 (elongated ellipse). The distribution for the population labeled “Low Recombination” (high counts) is narrower than the distribution for the population labeled “High Recombination” (low counts) in Figure 7.3(d).
Figure 7.3. (a) PLI of a HPMC-Si region with low PL counts regions (low lifetime) shown in dark color, and high PL counts regions (high lifetime) shown in bright color. (b) Dislocation etch pit map of the PLI from (a), where two dislocations populations (c), one from a low recombination activity region (left) and one from a high recombination activity region (right) are selected. The etch pit eccentricity analysis, for (c) is shown in (d).

Regions around the enclosed area in white in Figure 7.3(b) are further surveyed with μ-XRF analysis to determine the presence of metal decoration. A total surface area of 912 \( \mu \text{m}^2 \) and...
a total surface area of 606 \( \mu \text{m}^2 \) are scanned from the high- and low-recombination activity regions, respectively. The \( \mu \)-XRF map from the high-recombination activity region is shown in Figure 7.4. Different elements are measured; however, given the relatively high detection of Fe fluorescence compared to other elements and its known detrimental impact on solar cells performance, only Si and Fe maps are shown. Dark regions in the Si channel are dislocation etch pits, and dark regions in the Fe channel correspond to a higher count rate of FeK\( \alpha \) radiation, indicating the presence of Fe-rich particles. A magnified map within the recombination-active region reveals the presence of Fe-rich particles with an area density of up to 0.037 \( \mu \text{g/cm}^2 \). There is no signal above the noise floor of 0.010 \( \mu \text{g/cm}^2 \) detected in the Fe channel for the five recombination-inactive dislocation etch pits surveyed (not shown).

![Si XRF signal](image1)  ![Fe XRF signal](image2)

Figure 7.4. \( \mu \)-XRF map from the high recombination activity region selected in Figure 3(b). X-ray metal point defect analysis shows the presence of Fe precipitates in the vicinity of dislocations from the recombination active cluster. No metal impurity precipitates are found in the surveyed recombination-inactive dislocation etch pits.

To determine the combined effect of intragranular dense dislocation clusters with GBs – the latter being present in high density in HPMC-Si--, a minority carrier lifetime analysis is performed in the P-gettered HPMC-Si sample across different grains, with and without dense dislocation clusters.

A PL image of the HPMC-Si P-gettered sample is shown in Figure 7.5(a). Dark regions represent low PL counts and relate to low carrier lifetimes, while bright regions indicate high counts and relative higher carrier lifetimes. The maximum normalized PLI count was acquired at the center of 65 different grains, indicating their relative intragranular carrier lifetime, and plotted on the y-axis of Figure 7.5(b). On the x-axis, the distance measured between GBs through...
their minor axes (conservative proxy for grain size) is plotted. The open circles correspond to grains without dense intragranular dislocation clusters.

![Image](image_url)

**Figure 7.5.** (a) A PL image of P-gettered HPMC-Si, where dark and bright color represents low and high normalized PL counts, respectively. (b) Maximum normalized PL counts computed for 65 grains without dense intragranular dislocation clusters (open circles), and with dense intragranular dislocation clusters (red rhomboids).

### 7.5 Discussion

The most striking electronic-quality difference between HPMC-Si and mc-Si is the response to P-gettering. A remarkable improvement in lifetime is observed after gettering of HPMC-Si, much larger than mc-Si, as quantified in Figure 7.1. For HPMC-Si, 75% of the analyzed wafer area in Figure 7.1 improved after gettering, with the “improvement ratio” (defined as final vs. initial lifetime) generally increasing with as-grown lifetime. In contrast, for
mc-Si, only 49% of the lifetime values improved upon gettering, or fell above the 1:1 ratio line as seen in Figure 7.1c.

To assess the root cause of the difference of performance improvement with gettering, microanalytical techniques were employed. Our results show that HPMC-Si and mc-Si share several similarities in underlying lifetime-limiting defect types, yet the relative concentrations and distributions are different. HPMC-Si appears to contain far fewer dislocations than mc-Si \(^{58}\), \(^{199}\); those remaining dislocations in HPMC-Si nevertheless follow similar physics to mc-Si. Furthermore, the grain boundaries of HPMC-Si are recombination active, and the recombination activity thereof must be reduced (e.g., through gettering and passivation) to enable high-performance devices.

Regions of high dislocation density (Figures 7.2e, 7.2f) appear to correspond to red-colored areas in Figures 7.2a, 7.2c, i.e., areas that degraded in lifetime after gettering. We note that the selection of mc-Si and HPMC-Si samples at the same solidification height \((f=0.75)\) ensures consistency in height-dependent variables, such as structural-defect propagation, metal point defects in-diffusion, and dopants segregation. Therefore, we conclude that differences in gettering response of our HPMC-Si and mc-Si grown under similar conditions can be attributed chiefly to differences in area fraction of high dislocation density.

Although HPMC-Si contained far fewer dislocation-rich regions (and hence, fewer red regions in Figure 7.2c, our results indicate room for further improvement by reducing dislocation clusters. In HPMC-Si, as in mc-Si, the recombination activity of dislocations can be inhomogeneous, warranting a detailed assessment on the impact of such dislocation clusters for further crystal growth and cell processing improvements. For the etch pit geometry analysis, the two dislocation etch pit populations from HPMC-Si selected are less than 6 mm apart and show a significantly different PL contrast, indicating a difference in electrical recombination activity. We verify a characterization method developed for mc-Si in which the eccentricity variation of the dislocation etch pits can also be used to determine relative recombination activity of a dislocation cluster in HPMC-Si \(^{201}\). When the distribution of the etch pits’ eccentricity is spread, or disordered, as shown in Figure 7.3c, a tendency for favorable precipitation in such dislocations is shown to occur. The influence of GB character in nucleating disordered types of dislocations, and hence impacting the recombination activity is not analyzed herein.

It should be noted that the eccentricity proxy is more effective to study populations of dislocations that are not densely clustered because dense dislocation clusters tend to have a
significant amount of etch pits overlapping each other, inhibiting an accurate assessment of the
degree of eccentricity. Dense dislocation clusters, as observed from the plain dark regions in
Figure 7.2e and 7.2f, tend to have an ineffective, and sometimes detrimental, gettering response.
These results suggest that further engineering of thermal profiles during growth or seeding
optimization should be pursued to reduce the concentration of dense dislocation clusters in
HPMC-Si.

Similar as-grown Fe\textsubscript{i} concentrations are measured on both HPMC-Si and mc-Si, but their
Fe\textsubscript{i} concentration after P-gettering is very different. In the case of HPMC-Si, the lower Fe\textsubscript{i}
concentration measured upon P-gettering matches an increased effective lifetime in comparison
to mc-Si, as evidenced in Figure 7.1. mc-Si’s poor gettering response, compared to HPMC-Si,
could be attributed to dense dislocation clusters and the presence of higher point-defect
concentrations on the cluster areas, observed in Figure 7.2b and quantified by QSSPC Fe\textsubscript{i}
measurements. The relative high point-defect concentrations at the dense dislocation clusters
suggest the presence of precipitated metals at intragranular dislocations.

An important remark is that although we have measured a low Fe\textsubscript{i} concentration after P-
gettering, the intragranular lifetime values of grains without dense dislocation clusters are not
correspondingly high. Attributing the difference to the BO defect complex seems unlikely,
because after conducting a BO complex analysis as reported in Ref.\textsuperscript{139}, we only observe a
minimal influence of this defect in lifetime. One possible explanation for the carrier lifetime
discrepancy is that most of the Fe is found in precipitated form at sparse dislocations and cause
the additional carrier recombination. Another possibility that the authors do not disregard is that
other metal point defects, especially non-getterable slow diffusers, might be present, being
responsible for the gap between the observed lifetime values and what is expected based on
Shockley-Read Hall theory.

Through our \textmu-XRF measurements we conclude, at minimum, that metals are present at
the high-recombination active cluster. Though no metals were detected at the five etch pits
analyzed in the recombination-inactive cluster, there is insufficient statistics to render judgment
on the absolute absence of metals at other recombination-inactive etch pit clusters. Our results,
however, are consistent with previous observations where recombination-inactive dislocations do
not tend to coincide with metal-rich precipitates\textsuperscript{180, 201}. We therefore posit that the mechanism
for preferential metal decoration at energetically favorable heterogeneous nucleation sites
(disordered dislocation etch pits) in HPMC-Si is akin to that reported in conventionally grown mc-Si.

Although the degraded HPMC-Si response to P-gettering (i.e., red areas in ratio map) can be mainly attributed to the presence of dense dislocation clusters, the overall inhomogeneous improvement upon P-gettering may be due to the GBs found in this material, as they can also serve as favorable metal segregation and precipitation sites.

To demonstrate that GBs coupled with intragranular dislocations reduce the efficacy of HPMC-Si’s P-gettering response, we analyze the length between GBs (as proxies for grain size) and study the GBs’ impact on minority carrier lifetime upon P-gettering, both with and without the presence of dense dislocation clusters.

We hypothesize that grain size governs maximum intragranular lifetime due to diffusion of carriers from the intragranular regions to the nearby GBs. During P-gettering, precipitates found in GBs can dissolve and impurities segregate to the P-diffused layer due to a solubility difference between the bulk and the phosphorous sink layer. Although this process significantly reduces the volume of metal precipitates at the GBs, it usually does not lead to complete dissolution and gettering, resulting in higher concentration of metal point defects closer to the GBs, as shown in the Fe map from Figure 7.2d.

The impact of grain size is plotted in Figure 7.5b, where one can see that the larger the grain size, the higher the carrier lifetime achieved. The open circles in Figure 7.5a show a consistent trend between the measured maximum PL counts after P-gettering, and distance between GBs. The tight distribution of the open circles around the fit line suggests that the recombination activity of GBs, and their intragranular impact, is similar for all of the measured grains, as reported in Ref. However, when selecting grains that contain dense dislocation clusters, the maximum PL counts computed is significantly depressed, as shown by the red rhomboids in Figure 7.5b. Grains with dense dislocation clusters tend to have the lowest measured PL counts for a given grain size, when compared to dislocation-free grains. Interestingly, the dense dislocation clusters were mostly found at small grain sizes, and in few quantities, as shown in Figure 7.2f and illustrated in Figure 7.5b.

Besides containing fewer dense dislocation clusters than mc-Si (though highly detrimental, as shown in this contribution), HPMC-Si is also known for having small grains, and therefore, higher GB density, especially random angle GBs. The high PL contrast seen at the GBs in Figure 7.5a shows that GBs play a significant role in driving the minority carrier
lifetimes down. To mitigate this effect, a hydrogen in-diffusion process is commonly used in industry, in which the majority of GBs tend to be passivated prior to the wafer being finalized into a solar cell device. Further studies on the passivation of GBs and dislocation clusters in HPMC-Si can lead towards improved crystal growth conditions, as well as tailored processing steps (e.g., P-gettering and hydrogenation) to enable high-efficiency devices from this material.

7.6 Conclusions

A systematic comparative study of the impact of structural defects, namely dislocations, was performed between HPMC-Si and mc-Si, and their response to P-gettering. Care was taken to ensure similar growth environments and feedstock quality. We observe that HPMC-Si achieves a better gettering response than mc-Si because of a significant lower concentration of dense dislocation clusters.

The electrical performance improvement upon P-gettering was quantified in both mc-Si and HPMC-Si. The presence of dense dislocation clusters, albeit found in much lower density in HPMC-Si than in mc-Si, was observed to be responsible for detrimental lifetime response upon P-gettering on both materials. A higher density of dislocation clusters in mc-Si leads to higher inhomogeneity and a poorer P-gettering response. A higher Fe concentration is observed at these dense dislocation clusters, likely being the result of a high density of metal precipitates dissolving into interstitial metal points, and causing the underperformance in those regions.

Although the concentrations of defects in mc-Si and HPMC-Si are different, the physics governing their recombination activity is similar, offering a path for further improvements in HPMC-Si. As in mc-Si, the recombination activity of dislocation clusters in HPMC-Si was found to be inhomogeneous. We tested and validated a proxy to measure the relative recombination activity of non-dense dislocation clusters in this new industrial material and found that the degree of disorder of the dislocation etch pits can be correlated to the electrical performance of a dislocation cluster.

Our results indicate that although GBs influence the intragranular gettering efficacy, the detrimental effect is exacerbated in the presence of both GBs and intragranular dislocations. In other words, the combined presence of favorable precipitation sites (e.g., GBs and dislocations) impacts significantly the electrical performance at different grain sizes in HPMC-Si.
Furthermore, GB recombination in HPMC-Si must be reduced to minimize the efficiency gap between multi and mono. Advanced gettering and passivation, coupled to as-grown impurity control during crystallization, offers a pathway to achieve this objective.
CHAPTER 8

SPATIAL POINT PATTERN ANALYSIS: AN ALTERNATIVE APPROACH TO ASSESS DISLOCATIONS' ELECTRICAL RECOMBINATION ACTIVITY

8.1 Abstract

Chapter 6 and 7 demonstrated the suitability of a proposed proxy to assess the electrical recombination activity of dislocation clusters, both in mc-Si and HPMC-Si, respectively. An interesting observation was that not only the variation in etch pit eccentricity shown at the surface was changing between clusters, but also the spatial distribution of the dislocations within each of the clusters.

In this chapter, the analysis of dislocation etch pits' spatial dispersion is studied to assess its potential as a descriptor for the electrical recombination activity of clusters in silicon.

The Morisita index is used as a clustering descriptor on the same five different dislocation etch pit clusters from chapter 6; all with varying degrees of recombination activity. We observe that the lowest-Γ cluster tends to have a dispersed distribution, whereas the highest-Γ cluster is agglomerated, by the spatial descriptor detailed in Chapter 3. Clusters that fall in between tend to fall in a randomly distributed category.

8.2 Introduction

As described in Chapter 2 the importance of dislocations' spatial distribution has been modeled by Sopori through his circuit-network model. In his work, Sopori described how the
clustered dislocations were more electrically detrimental for the device performance, than if the same number of dislocations were spread over the same area.

Studies have lumped the total amount of defects, and assigned a “total area fraction”, based on this lumped number. This fraction value, however, is non-spatially resolved, and does not allow for a distinction between the possible types of dislocation clusters that could—or could not—be electrically detrimental, as shown in Chapters 6 and 7.

The existence of a metric to quantify the distribution of dislocations could allow for a deeper understanding of dislocation behavior, while adding depth to reported density values. Though the eccentricity variation proxy presented in Chapters 6 and 7 of this thesis constitutes a rapid evaluation method, a potential to further increase the assessment speed (obviating the high-magnification scanning required to determine the etch pit geometry), while remaining a facile method, could benefit the crystal growth community.

After observing the spatial differences observed between the different clusters analyzed in Chapter 6, and relying on the exhaustive characterization performed on such defect populations, we turn to a spatial point pattern analysis to further investigate a method to describe these same clusters.

Applied spatial statistics is an emerging field that has gained much attention in different areas, such as public health, where the spread of diseases can be evaluated and attributed to spatial phenomena; geography, where the risk of landslide hazards by earthquakes can be spatially assessed; government policy, where the socioeconomic distribution of population can lead to better allocation and execution of social programs, among others.

In the solar industry, spatial pattern analysis has begun to be employed. That is the case with studies on the geospatial pattern of diffusion and adoption of residential solar PV systems on rooftops. Yet, spatial patterns to identify the electrical performance impact of defects at the wafer level, has yet to gain attention.

Though the spatial statistics field is broad, the author explores one method, the Morisita Index (described in Chapter 3), which can arguably be considered simpler than other existing spatial-evaluating methods, to demonstrate the viability of the spatial pattern analysis as: (i) an additional descriptor for reported dislocation densities, and (ii) predictor of the electrical recombination activity of dislocation clusters in silicon wafers.
8.3 Materials and Methods

8.3.1 Multicrystalline Silicon Sample

The p-type mc-Si wafer which was described in Chapter 6 which was saw-damage etched, processed into a solar cell, electrically characterized, Secco-etched, and structurally characterized (i.e., dislocation etch pits count and geometry, and through TEM), was used for this study.

Within this sample, the five dislocation clusters previously characterized, labeled as “A”, “B”, “C”, “D”, and “E”, were selected for spatial analysis.

8.3.2 Morisita Index

The principles of the Morisita methodology are described in Chapter 3.

Representative distribution patterns of the etch pits within the entire cluster are selected. Given the initial areal differences between the five dislocation clusters, a consistent region size to homogenize spatial dimensions is proposed. To select a representative area, they must have high enough dislocation densities, such that they lie on sections of the Donolato fit curves that are separated enough from each other, enough to be able to differentiate between their $I$ values. Herein, based on the Donolato fits obtained for the five clusters, a threshold dislocation density of $>5 \times 10^5 \text{ cm}^{-2}$ was selected as requirement for the representative area selection.

The dislocation density is computed through the MATLAB® dislocation counting code used in Chapters 5–7. As part of the algorithm, the etch pit centroids are detected. The position of these centroids are then saved and used to determine the spatial location, both in $x$ and $y$ coordinates, of each dislocation in each cluster. The coordinate system used at each cluster corresponds to that particular cluster being analyzed, and is not considering the relative position of the etch pits in other dislocation clusters.

A rectangle with dimensions of 136 $\mu$m $\times$ 166 $\mu$m is cropped out from all five clusters, defining the representative regions for this study.

To construct Morisita plots in these regions, an initial sense of critical quadrat sizes is required to interpret the results and relate them to experimental attributes. To determine a critical distance threshold (i.e., quadrat), different distances within cluster A are probed. The distances are selected by measuring the linear separation between different rows of polygonized
dislocation lines. An estimated average distance value is then assigned to be the metric to compare all the remaining clusters against with.

The computational analysis is performed in a $R$-software statistical package called *spatstat*, available online. The centroids obtained through the MATLAB® code are then input into $R$’s *spatstat* package to be sectioned into quadrats, and compute the cluster’s Morisita Index for a range of quadrat sizes. Values are automatically tested with a $\chi^2$ statistic to determine if it varied significantly ($p<0.05$) from a random distribution and plotted.

### 8.4 Results

The representative regions selected from cluster A–E are shown in Figure 8.1 As seen in this figure, the recombination strength follows an increase in value with the alphabetical order. Also in Figure 8.1, the processed centroids, as seen in $R$-*spatstat*, are shown below each of the dislocation etch pit maps.

![Figure 8.1](https://via.placeholder.com/150)

**Figure 8.1.** Etch pit maps of the regions extracted for spatial point analysis from clusters A through E, and corresponding to an increasing recombination strength (or “worst efficiency”). The centroid for each dislocation etch pit is represented on the same dimension area below. Two white spots are observed in cluster B, corresponding to dislocations whose centroids could not be decoupled and therefore were cropped out to eliminate spurious values.
The range of dislocation density for this study is highlighted in Figure 8.2. In the selected range, a difference in \( I' \) values can be observed. The dislocation density measured for each cluster was approximately \( 1.4 \times 10^6 \text{ cm}^{-2} \) for cluster A; \( 0.50 \times 10^6 \text{ cm}^{-2} \) for cluster B; \( 0.95 \times 10^6 \text{ cm}^{-2} \) for cluster C; \( 0.84 \times 10^6 \text{ cm}^{-2} \) for cluster D; \( 0.85 \times 10^6 \text{ cm}^{-2} \) for cluster E.

This selection was performed with two criteria in mind: *(i)* Have a representative distribution from the entire cluster in a consistent area, and *(ii)* obtain a similar dislocation density between the existing populations, in as much as possible. Not all clusters have sufficient overlapping regions of density, as evidenced in Figure 8.2, hence the width of the selected range.

![Figure 8.2. Recombination strength values for five dislocation clusters are shown, which were calculated using the extended Donolato theory. The rectangle shown in red highlights the range of dislocation densities found at the different representative areas of this study.](image)

The distance between dislocations that have minimized their strain energy, shown by the polygonized configuration (e.g., parallel rows) in the region from cluster A, varies between 11 \( \mu \text{m} \) and 20 \( \mu \text{m} \), approximately, as seen in Figure 7.3. This range provides an insight into the distance values to consider for the critical quadrat size. Herein, the value of 15 \( \mu \text{m} \) was selected as representative of the average distance separation between dislocation etch pits. This distance therefore corresponds to the threshold quadrat size for analysis.
Figure 8.3. MC-Si Sopori-etched sample with dislocations revealed as dark spots. Distances from three different areas, labeled “Distance 1”, “Distance 2”, and “Distance 3”, with their respective distances of 20.4 μm, 16.6 μm, and 11.4 μm, respectively. These distances serve as distance criteria to determine quadrat distance of interest.

The Morisita index results for the different clusters are shown in Figure 8.4. The quadrat distance is shown in the x-axis, and the Index value on the y-axis. Shown in light red is the critical quadrat distance of 15 μm across all clusters. The value of 1, corresponding to a random distribution, is shown at each cluster with a dashed line.
Figure 8.4. Morisita Index value for the different clusters A through E. The dashed line represents a random pattern, corresponding to a Morisita index value of 1. The quadrat distance of interest (15 μm) is enclosed in a light red rectangle for all the different clusters.
Table 8.1. Average Morisita Index value for clusters A, B, C, D, and E. The index values are taken at a quadrat distance of 100 μm.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Avg. Morisita Index at δ=15 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.85</td>
</tr>
<tr>
<td>B</td>
<td>0.94</td>
</tr>
<tr>
<td>C</td>
<td>1.10</td>
</tr>
<tr>
<td>D</td>
<td>1.06</td>
</tr>
<tr>
<td>E</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 8.1 summarizes the results from Figure 8.4. The average Morisita Index computed at a distance around 15 μm, for the five dislocation clusters “A”, “B”, “C”, “D”, and “E”, were 0.85, 0.94, 1.10, 1.06, and 1.75, respectively.

Interpreting these values, at the scale corresponding to the quadrat size δ of 15 μm, the \( I_δ \) value of 1.75 for cluster E indicates a strong aggregation, or the clustering is 75% greater than it would be if the individuals were distributed randomly. The same logic applies to the rest of the clusters analyzed.

Figure 8.5 is the visual representation of results shown in Table 8.1. The progression is shown starting from a patterned state (cluster A), going through a random distribution (clusters B, C, and D), and finalizing in a clustered pattern (cluster E).
Figure 8.5. Morisita Index values for the different dislocation clusters at a quadrat size of 15 μm.

An important remark, however, is that the values shown in both Table 8.1 and Figure 8.5 are at a quadrat size of 15 μm. The sensitivity of the results is tested at the lower and upper range of the distances shown in Figure 8.3, that is, at quadrat sizes of 10 μm and 20 μm.

Based on the index values shown in Figure 8.4, an average value was obtained for Morisita values in the vicinity of 10 μm, and 20 μm. Results are shown in Figure 8.6.
8.5 Discussion

The characterization of dislocations through a spatial point pattern analysis, through the Morisita Index, demonstrates an interesting trend that is consistent with theoretical studies. The trend shown elucidates a tendency of defect clustering (Morisita $> 1$) to be more detrimental than defects that are found in a random way (Morisita $= 1$) or patterned way (Morisita $< 1$) at the length scales evaluated. Furthermore, evaluating an entire breadth of quadrat sizes, we observe this general trend that goes from patterned to clustered, corresponding to cluster A and E. The general trend is unclear however for the remaining clusters, which might be catalogued as randomly distributed given their wide variation around the value of 1 for neighboring quadrat sizes.

The values of the index can be highly sensitive to the division of the space, especially at small quadrat sizes $^{216, 217}$. Additionally, the variation of distance observed between dislocation
rows can also introduce uncertainty in the established quadrat size. To that effect, Figure 8.6 shows a variation in Morisita index values, depending on the selected critical quadrat size.

The fact that we have previously measured dislocation eccentricity, and that this correlates with the degree of dispersion, could point towards dislocations not only having a high degree of disorder on the surface—and by consequence, high interaction occurring at the bulk—but also, might suggest that the spatial patterns observed for low \( r \) clusters might be due to process that only occur at certain time-temperature regimes which allow them to minimize their energy (\textit{i.e.} polygonize). In other words, the eccentricity, which is the proxy for the angle at which dislocations intersect the surface and interact in the bulk, could be a coupled phenomenon with the spatial distributions of those dislocations and their interactions in the bulk.

In addition, the introduction of Morisita Index can be used in conjunction with reported dislocation density values to provide the community with a sense of how dispersed, or agglomerated, are the dislocations being evaluated. Pending further analysis on a higher cluster population, this analysis shows promise to be used as a proxy for evaluating dislocation clusters’ relative electrical recombination activity.

### 8.6 Conclusions

The Morisita Index spatial point pattern analysis, elucidates a trend corresponding to theoretical studies in which, for a given dislocation density, the spatial clustering of defects tends to be more detrimental than if found dispersed, or in a regular patterned fashion.

The spatial distribution of five different clusters was analyzed. The most remarkable observation found was that the least recombination active, and the most recombination active dislocation etch pits tend to be categorized as regular (or patterned), and clustered, respectively. The remaining etch pit populations tend to have Morisita Index values fluctuating around 1.0, indicative of a random distribution.

This method should be scaled to a larger population set of different samples with different clusters that vary in their recombination activity to corroborate the results herein presented. A study on further dislocation clusters would corroborate the trends herein reported by the author.
An overview of the impact of dislocations in the performance of silicon-based solar cell devices is presented in this thesis.

Dislocations are evaluated at different steps of the cell-forming process: starting the analysis on an as-grown wafer as shown in Chapter 5, to their electrical performance after being subjected to a P-gettering process as shown in Chapter 7, to their impact in a fully processed solar cell device as shown in Chapter 6.

In Chapter 2, the mechanical and electrical properties of dislocations and their interaction with metal impurities were described.

Chapter 3 highlighted two different processes: phosphorus diffusion gettering, and thermal annealing. The main contribution from these processes arises from inducing changes in both dislocations' electrical, and their density, respectively.

Chapter 4 presents an overview of the main methods and techniques used in this thesis to assess the electrical impact of dislocations in different materials.

In Chapter 5, a method to reduce dislocation density is presented. This initial approach is motivated by the detriment of dislocations presented in earlier chapters. A 1390°C anneal for 24 h is shown to achieve ~40 % average dislocation density reduction in a Si-based material. A severe limitation on the annealing efficacy is identified in the form of second-phase particles, which are shown to be present in the bulk and causing recurrent dislocation cluster nucleation upon cool down.

Chapter 6 is motivated by the vast presence of dislocation clusters in mc-Si, and the significant variation in measured recombination activity despite their spatial proximity. To this end, this thesis work introduces a proxy to determine the relative recombination activity of dislocation clusters by identifying the variation of dislocation etch-pit geometry. It is proposed that dislocation clusters with higher degree of disorder exhibit a higher probability of metal
Chapter 7 introduces a new material (HPMC-Si), which is compared systematically against mc-Si. The electrical performance upon P-gettering is found to be more inhomogeneous in mc-Si than in HPMC-Si due to its relative higher amount of dislocation clusters. The lowest lifetime values measured in HPMC-Si correspond to grains with a high density of dislocation clusters. Additionally, the proxy developed in Chapter 6 is successfully expanded to HPMC-Si.

Chapter 8 introduces the Morisita Index methodology to measure the spatial patterns distribution of dislocation etch pits. The spatial distribution of five different clusters is analyzed and evaluated with this methodology, demonstrating that the least recombination active, and the most recombination active dislocation etch pits tend to be categorized as regular (or patterned), and clustered, respectively. Further studies are warranted in a larger population set to validate this methodology in an industrial setting.

As summarized in Figure 9.1, from a crystal-grower’s and cell-manufacturer’s perspective, a simplified approach can be conceived in which, in order to obtain a material that is suitable for the creation of a high-efficiency solar cell device, a high quality material must be used in the initial stage.

This thesis work attempts to analyze the feasibility of reducing dislocation density through thermal annealing as shown in Chapter 5, and evidenced in the first step (red box) in the flowchart. It also points to “modify growth to reduce density of structural defects”, as shown in the red box from the right in the flowchart, and demonstrated by the novel material used in Chapter 7. Novel methods introduced in Chapter 6 and 8 can enable crystal growers and solar cell manufacturers to reduce the time required for cycles of learning and improve their crystal growth processes.
Figure 9.1. Flowchart detailing a simplified approach to manage performance-limiting defects in Si materials. The boxes highlighted in red correspond to the stages where dislocations have a major role in enabling (or impeding) materials to be converted into high-efficiency solar cell devices. Figure from Ref. 82
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