Oxygen Defect Engineering for Solar Cell Applications:

Process Design and Modeling

by

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ABSTRACT

One of the main remaining impurities that lowers efficiencies of silicon solar cells are oxygen ring defects that are incorporated into the material during growth. These defects decrease overall cell efficiencies by around 20% (rel.) resulting in a yield loss of about 1/4\textsuperscript{th} of each monocrystalline silicon ingot.

To control the oxygen defects and put them in the least harmful form possible, a new cell processing step call \textit{tabula rasa} (TR) is explored. TR is a high temperature process for a short duration. In this work, TR is found to be a kinetically-limited process through several oxygen precipitate dissolution experiments from which the activation energy of dissolution is found to be equivalent to the migration enthalpy for oxygen in silicon. With this knowledge, a predictive kinetic model is built which can be used for process optimization.

A multiscale end-to-end model is also developed to determine the effect of rings on cell performance. Using oxygen defect parameter inputs, device modelling, and a spatially resolved two diode mesh, PL images are transformed into current maps and used to determine cell efficiencies for inhomogeneously distributed defects. A reduction in efficiency for cells with ring defects is simulated for several ring defect concentrations and compared to a non-defective cell.

Another strategy for lowering cost and mitigating oxygen ring defects is using thinner silicon absorbers with inherent defect tolerance. Using the multiscale modeling platform described above, thin silicon wafers are compared to typical cells. It is shown that thin cells with ring defects perform with higher efficiencies, with less than half the material used. The thin silicon strategy is compared with the TR process addition, and future work is outlined to further explore these oxygen mitigation options.

Thesis Supervisor: Tonio Buonassisi
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# Table of Contents

Abstract ........................................................................................................................................... 3

Acknowledgements .......................................................................................................................... 4

Figures ............................................................................................................................................... 7

1. Introduction ......................................................................................................................................... 10
   1.1 Why Solar? ..................................................................................................................................... 10

2. Defect engineering ........................................................................................................................... 14
   2.1 Fundamentals of Solar .................................................................................................................. 14
      2.1.1 Semiconductors .................................................................................................................... 14
      2.1.2 Recombination ..................................................................................................................... 15
      2.1.3 PN Junction .......................................................................................................................... 15
      2.1.4 Devices ................................................................................................................................... 17
   2.2 Defects in Silicon ........................................................................................................................... 18
      2.2.1 Material Grades and Growth Methods .................................................................................. 18
      2.2.2 Shockley-Read-Hall Recombination .................................................................................... 20
      2.2.3 Defect Mitigation through process optimization .................................................................. 20
   2.2 Oxygen Defects in Silicon ............................................................................................................. 21
      2.3.1 Oxygen incorporation and ring defect formation................................................................. 21
      2.3.2 Oxygen morphology and recombination in silicon ............................................................ 22
   2.4 Strategies for mitigation ............................................................................................................... 24
      2.4.1 Lessons from the electronics industry[34] ....................................................................... 24
   2.5 Oxygen Characterization ............................................................................................................. 25
      2.5.1 Interstitial oxygen detection ............................................................................................... 25
      2.5.2 Precipitate Oxygen Detection ............................................................................................. 28

3. Tabula Rasa Methods ..................................................................................................................... 29
   3.1 *Tabula Rasa* for Oxygen Mitigation ......................................................................................... 29
   3.2 TR Process Setup ......................................................................................................................... 31
   3.3 TR feasibility on a manufacturing line ......................................................................................... 34

4. Oxygen Dissolution Study .............................................................................................................. 35
   4.1 Motivation for oxygen dissolution study .................................................................................... 35
   4.2 Experimental Methods ................................................................................................................. 35
      4.2.1 Sample Preparation ............................................................................................................... 35
      4.2.2 Experiment ............................................................................................................................ 36
      4.2.3 Characterization .................................................................................................................... 37
      4.2.4 Design of experiments ......................................................................................................... 38
   4.3 Results and Discussion ............................................................................................................... 40
      4.3.1 Oxygen Dissolution ............................................................................................................. 40
Figures

Figure 1: Total PV installed capacity as a function of time.......................................................... 11
Figure 2: (a) Efficiency as a function of years and (b) decline in module cost per watt as more
modules are shipped............................................................... 12
Figure 3: Cartoon representation of band gap separation differences between metals,
semiconductors and insulators. [10].................................................. 15
Figure 4: Operating diagram of a PN Junction, the diode used to make silicon solar cells [11]. 16
Figure 5: IV curve shown with relevant device parameters such as short circuit current (Isc),
voltage (Voc), max power point (MPP), and fill factor (FF) [12].......................... 17
Figure 6: (a) Representative ring defects shown in a photoluminescence image and (b) an ingot
cartoon to show the amount of the ingot affected.................................................. 21
Figure 7 Changes in oxygen morphology and recombination activity of oxygen defects due to
change in temperature............................................................................................ 23
Figure 8: Images of silicon cross sections that have been defect etched............................... 25
Figure 9: Fourier Transform Infrared spectroscopy (FTIR). .................................................. 26
Figure 10: Calibration curve found using ASTM 121-83 standards provided by SunEdison
Semiconductor. ....................................................................................... 27
Figure 11: Different standards used for interstitial oxygen measurement in silicon using FTIR. 27
Figure 11: Sopori defect etching images done with a Nikon LV100 optical microscope........ 28
Figure 13: The TR process at NREL in an oxidation furnace.............................................. 31
Figure 14: The MIT tabula rasa set up............................................................................... 34
Figure 15: Time and temperatures that the sample wafers underwent throughout preparation and
experiment........................................................................................................ 36
Figure 16: The microscope images of two samples underwent Sopori defect etching........... 37
Figure 17: Simulated experimental points based on realistic noise levels........................... 39
Figure 18: Oxygen precipitate dissolution curves plotted as interstitial oxygen content for four
temperatures........................................................................................................ 42
Figure 19: Arrhenius-like temperature dependent dissolution behavior............................. 44
Figure 20: Flow chart for 12E process model with oxygen.................................................. 46
Figure 21: 12E simulation results compared with experiment............................................ 47
Figure 22: A qualitative figure to visualize dissolution of oxygen precipitates of inhomogeneous size distribution................................................................. 48
Figure 23: Schematic of multiscale end-to-end modeling approach. ........................................ 52
Figure 24: J-V curves output from Sentaurus device for unit cells with homogenously distributed oxygen defects. .................................................................................................................... 54
Figure 25: \( J_{01} \) and \( J_{02} \) values fitted to Sentaurus-simulated J-V curves. ......................... 55
Figure 26: (a) Oxygen rings from binary image, and (b) oxygen rings from gradient image. .... 56
Figure 27: Comparison of the current density map made in Griddler at maximum power point. 58
Figure 28: Silicon heterojunction device. .................................................................................. 63
Figure 29: A plot of two devices of different thicknesses while sweeping SRV (cm/s), and effective lifetime. ................................................................................................................................. 64
Figure 30: Simulated vs. experimental J-V curves of thin Cz-Si.................................................. 65
Figure 31: Thick vs. thin cell J-V curves. ..................................................................................... 66
Figure 32: Theoretical efficiency potentials of thick and thin devices with different effective lifetimes.................................................................................................................................. 67
Figure 33: Minority carrier lifetime components of samples with oxygen defects.................... 68
Figure 34: J-V curves for cells of different thickness and defect concentration.......................... 69
Figure 35: Dark saturation current \( (J_{01}) \) plotted for several oxygen defect concentrations..... 70
Figure 36: Cell efficiencies plotted for several cell thicknesses of 50, 100 and 180 \( \mu \)m. ........ 71
TABLES

Table 1 Defect parameters for oxygen precipitates in Cz-Si. .................................................. 53
Table 2: Important parameters for end-to-end oxygen modeling. ........................................... 57
Table 3: Griddler results from current maps representing inhomogeneous ring defects. .......... 57
Table 4: Results from Griddler simulations using cells of different thicknesses. ....................... 70
CHAPTER

1

INTRODUCTION

1.1. Why Solar?

Renewable energy sources represent the future energy landscape necessary for sustainable human growth and development. Continued reliance on fossil fuels is untenable due to dwindling resources requiring more costly and dangerous mining techniques in addition to the catastrophic effects of continued greenhouse gas emissions on climate change. However, to achieve this goal and prevent further increase in greenhouse gas emission, a change in today’s power generation is needed toward renewable energies. Today, one of the most important renewable energy sources is solar power. Solar based energy technologies has the potential to make the shift from fossil fuels to clean and sustainable energy, taking as much as 27% of the electrical market capacity by 2050 [1]. To give perspective on scale, if solar panels covered 500,000 km², an area approximately the size of Spain, the entire world’s electricity needs would be met based on 2030 projections of total energy consumption including all electricity and transportation [2]. Each year more solar panels are installed worldwide, but this scale up needs the help of both political strategies and technical solutions to reach the massive capacity gains needed. As can be seen in Figure 1 [3], if the status quo is maintained at “baseline” the total installed capacity will only reach under 1 TW [4], which is not close to the 2-10 TW of solar needed by 2030 to reach climate targets set out by the Intergovernmental Panel on Climate Change in 2015 [5].

As seen in Figure 1, there are several paths to achieve TW scale photovoltaics (PV) [6] which can be broken into research topics including: (1) increasing efficiencies of solar wafers, cells, and modules (blue line in Fig. 1), (2) lowering the variable costs of solar manufacturing that fluctuate with sales including raw material and energy use (green line in Fig. 1), and (3) lowering the capital expenditure (capex), or fixed cost upfront investment needed to start a new solar manufacturing plant.
Climate targets are shown as gray line and symbols representing preventing more than a 2°C increase in average temperature above pre-industrial levels target as projected by several different sources. The light blue line represents the baseline technology, where no additional manufacturing capability is built, while the other lines (dark blue, green, yellow and red) show different technology innovations and economic schemes that could increase the growth of PV to reach the climate target [3].

To understand how to move forward on any of these individual research topics, an understanding of current state of the art is needed. Solar cell efficiencies have increased dramatically since the 1970s as they first gained a foothold in the terrestrial energy market. Figure 2(a) shows this dramatic increase in efficiencies for all types of solar cell materials as recorded by the National Renewable Energy Laboratory (NREL) [7]. Silicon is not the only material shown, and new materials such as perovskites might still be the answer to cheaper solar than ever before. However, silicon dominates the marketplace with over 90% of sales due to low technical risks, relatively cheap manufacture, and taking advantage of material and knowledge from the electronics industry [8]. Figure 2(b) shows the coinciding decrease in cost of solar materials as...
following a trend, or “learning curve” of drastic price reduction over the same years as the drastic increase in efficiencies and installed capacity [9]. These trends are promising, but continued research is needed to continue down the learning curve at an even greater pace.

Figure 2: (a) Efficiency as a function of years and (b) decline in module cost per watt as more modules are shipped. Crystalline silicon technologies are pictured in blue with the highest recorded efficiency of 25.6% on a heterostructure cell. It should be noted that these efficiencies are not what manufacturers can industrially produce, but rather these are lab results. However, the trend holds true for industry also [5]. Fig. 2(b) shows the decline in module cost per watt as more modules are shipped and installed [7].
Increases in efficiency seen in Figure 2(a) for silicon solar cells have been driven by several research and development areas including defect engineering of harmful metal impurities that cause electrical power losses in solar materials, new device architectures that control electrical losses at interfaces and contacts, new passivation schemes, predictive process optimization tools and more. The dropping costs of silicon solar cells and modules has been driven by some of these innovations but also by market forces, e.g. in the early 2000s the Chinese government began to throw their weight behind the solar industry investing heavily and pulling in experts from all over the world. The result was a 70% drop in solar prices between 2008 and 2011. Coupled with a worldwide economic recession, this has strained the solar manufacturing landscape close to the breaking point [10].

The reality of the solar marketplace and the need for massive expansion in solar installations, creates a research landscape that pinpoints the key areas where research can help industry increase margins through increased efficiency, lower variable cost, and lower capex [3]. The research questions explored in this thesis present an approach towards these research goals by specifically targeting the remaining defects in silicon material that limit efficiency. The development of feasible manufacturing solutions to defect mitigation, and new defect tolerant technologies such as thinner wafers (to reduce capex) are explored. The research directions include:

1) Defect engineering of oxygen impurities which represent a significant yield loss in industry today. Through process development and preliminary optimization, a feasible manufacturing solution is demonstrated to prevent losses in efficiency, and therefore yield, due to oxygen defects. This solution is called the tabula rasa process.

2) Thinner silicon wafers are explored for their inherent defect tolerance. Device modeling shows this as another solution to increase cell efficiencies and even lower material consumption.

Before these research directions can be described in detail, the fundamental concepts behind this work are briefly introduced.
2.1 Fundamentals of Solar

2.1.1 Semiconductors

The elegance of solar as an energy solution is in the creation of electricity, the highest form of energy, directly from the most abundant energy source available on earth, the sun. From this electrical form, solar energy can be converted into virtually every other form of power needed. This is possible because semiconductors have a special material property: the perfectly positioned band gap. The band gap is best described as an absence of available energy states in which a charge carrier can exist, either electron or hole. Every element and compound has a set of energies at which electrons can exist and certain number of electrons per atom to fill those levels. Unfilled energy levels exist in the conduction band, while filled energy levels exist in the valence band. When a photon from sunlight is incident on a semiconductor, the photon can give energy to electrons creating an electron-hole pair. This means that an electron is given the energy required to bridge the gap into the conduction band, leaving a hole in the valence band behind. As seen in Figure 3 [11], in a metal there is no gap between the valence and conduction bands, so electrons can be in any energy state, and in an insulator, the gap is so large, photons or thermal energy cannot provide enough energy that an electron can make it to the conduction band. In semiconductors, once electrons are excited into the conduction band, they must be extracted as current from the material before dropping back into the lower energy state valence band through a process called recombination.
2.1.2 Recombination

There are several mechanisms by which an excited electron can recombine and lose power including surface recombination and bulk recombination mechanisms such as Radiative, Auger, and Shockley-Read-Hall (SRH) recombination. Surface recombination is a loss of electrons at the front or rear surface of the device where the crystal lattice is disrupted and dangling bonds are accessible (not passivated) for recombination. Radiative recombination occurs when an electron recombines with a hole by falling from the conduction to the valence band while emitting a photon of the respective wavelength (energy difference of the states). This is the basic operating principle of light emitting diodes (LEDs), and is the dominant mechanism in direct band gap semiconductors. For indirect band gap semiconductors, e.g. silicon, the shortest distance between valence and conduction band has an offset and thus, radiative recombination can be neglected. Auger recombination is the mechanism by which an electron hole pair recombine, and energy is given to another electron in the conduction band which loses this extra energy through heat, "thermalizing" back to the conduction band. The fourth mechanism, called SRH recombination occurs when an electron can fall back to the valence band due to an energy state introduced into the band gap by an impurity. The SRH recombination mechanism is the dominant one in silicon, and silicon based materials.

2.1.3 PN Junction

Separation and extraction of carriers is necessary and occurs through the formation of a diode, the pn-junction, as shown in Figure 4 [12]. To create a diode, an electrical mismatch must be made.
at the junction between two silicon materials doped with phosphorus or boron. Doping is the process of introducing atoms extrinsic to the material to change the properties of that material. In the case of silicon, a group IV material with four outer electrons, is doped with phosphorus, a group V element with five outer electrons, and therefore an excess of electrons. If silicon is doped with boron, a group III material with three outer electrons, then an excess of holes is available in that material.

If a n-type, phosphorus-doped silicon material with an excess of electrons is brought into contact with a p-type, boron-doped, silicon material with an excess of holes, an electric field necessarily forms at the junction of these materials, shown as a pn-junction in Figure 2.2. The area at the junction is called the depletion region which exhibits the two key transport properties that allow for power extraction: drift and diffusion of electrons or holes, called charge carriers. Diffusion is the physical process by which carriers will move from an area of high concentration to an area of low concentration through random motion. Drift is the movement of carriers due to an electric field imposed on a material giving an impetus for free carriers to move toward the oppositely charged portion of the material. Through the properties of drift and diffusion, the carriers within a material exhibit a directional flow which is the current of the cell equating zero under equilibrium conditions. A built in electrostatic potential difference, or voltage occurs due to this electrical field.

Figure 4: Operating diagram of a PN Junction, the diode used to make silicon solar cells [11].
When photons are incident on the cell under sunlight or when electrical charge is applied in forward bias from a circuit, this throws off the balance of drift and diffusion in the pn-junction, and minority carriers begin to diffuse across the depletion region creating a current through the external circuit. The mathematical relationship of the ideal pn-diode is an exponential shown in Equation 1, demonstrating the characteristic rectifying behavior, where $I$ is current, $q$ is charge, $V$ is voltage, $n$ is ideality factor, $k$ is the Boltzmann constant, and $T$ is the temperature.

$$I = I_L - I_0 \left( \exp \left( \frac{qV}{nkT} \right) - 1 \right)$$

(1)

Most of the important parameters of a solar cell can be taken from an IV curve fit to Equation 1, including maximum current allowed by a device, $I_{sc}$ short circuit current, or the maximum voltage allowed by a device, $V_{oc}$, or open circuit voltage. The shape of the IV curve determines the power output which is calculated as the area under the IV-curve. The more "square" the curve is, the better the power output, and a measure of this is called the fill factor shown in Figure 5 [13]. Using these three parameters, a measure of maximum power and efficiency of cells can be determined.

![Figure 5: IV curve shown with relevant device parameters such as short circuit current ($I_{sc}$), voltage ($V_{oc}$), max power point (MPP), and fill factor (FF) [12].](image)

2.1.4 Devices

Solar cells are not only silicon pn-diodes, but actually a stack of materials including passivating layers, metal contacts, encapsulant, glass, and more. A typical silicon solar cell is around 150-180 μm thick including the $n$- and $p$- type side of the junction with front and rear
passivation layers and metal contacts, front anti-reflection coating, and an encapsulant to protect the device.

The traditional solar cells are $p$-type Al-BSF, standing for aluminum back surface field which has a full sheet of aluminum contacting the rear cell and a highly doped layer at that surface, $p^{++}$, to help prevent minority carriers from recombining. The front surface is also a concern and must be passivated which means a layer of material is deposited on the top of the $n$-type silicon to stop massive amounts of recombination at the dangling bonds at the surface. Traditional front side passivation and contacts are silicon nitride ($\text{SiN}_x$) and three silver busbars as front contacts.

As solar cell efficiencies are pushed higher, new device architectures, passivation stacks, contact configurations, cell size have to be deployed. Notable advancements include passivated emitter and rear contact (PERC) architectures which remove the full aluminum back surface replacing with passivation and targeted silver contact points. Also, the use of aluminum oxide ($\text{AlO}_x$) as a passivation layer is shown to have lower recombination. Another area of research for improving efficiencies while reducing cost is using high performance (hp) mc-Si which in the PERC configuration has been successful at reaching around 22% efficient cells.

Individual solar cells are also not the end product that customers buy, but rather the modules which are made of an array of solar cells electrically connected. There is often a 2-3% efficiency drop in the solar module efficiency as compared to individual cell efficiencies.

From this brief overview looking at the solar cell from the pn-junction all the way to the module, many areas for incrementally pushing toward higher efficiencies, lowering cost, and lowering capital expense are revealed. One area to do this is in defect engineering for manufacturing processes on the material level. These changes would be made to the cell manufacturing line in the form of optimized processes that control the impurities in the material so that they do not become recombination centers.

### 2.2 Defects in Silicon

#### 2.2.1 Material Grades and Growth Methods

The solar marketplace is dominated by silicon which takes up about 90% of the marketshare with the rest being earth abundant thin film materials such as copper indium gallium diselenide (CIGS) or cadmium telluride (CdTe). For silicon materials, there are three primary grades that describe the purity of the material: Metallurgical grade silicon (98-99% pure silicon...
with 1-2% extrinsic impurities), solar grade silicon (SoG, 99.99-99.9999% pure silicon, 4-6 N’s), and electronic grade silicon (99.99999-99.9999999%, 7-9 N’s pure). Using electronic grade material for solar panels would be ideal from an efficiency point of view, but the cost is prohibitive. Thus processing and other techniques have to be employed after the silicon growth process to manage and control impurities and defects of these lower grade materials.

In the silicon solar industry, polysilicon chunks of solar grade material are formed into either monocrystalline or multicrystalline material (mc-Si) [9]. Monocrystalline silicon is grown using the Czochralski (Cz) growth method in which a crystal seed is introduced into the silicon melt made of melted polycrystalline chunks, and then pulled and rotated such that a single crystal of silicon forms in a cylindrical shape. Mc-Si is grown through directional solidification where polysilicon chunks are packed into a crucible, melted down and solidify from crystal seeds from the bottom of the crucible upwards through temperature and pressure control. Both methods of crystal growth exhibit unique challenges: impurity incorporation, manufacturing throughput, and quality of material produced. Traditional mc-Si is lower efficiency due to the crystallographic defects of grain boundaries and dislocations caused during directional solidification in comparison to the single crystal grown through the Cz-Si method. However, mc-Si can be produced at higher throughput and lower cost. Also mc-Si solar cells have been gaining higher efficiencies in the past few years with the newer “high performance” mc-Si and more advanced device architectures.

Both Cz-Si and mc-Si have incorporated impurities which are introduced during the growth process and these impurities must be managed during processing steps in order to achieve high efficiency materials. This can be done through defect engineering which includes characterization of bulk defects and optimization of processes to identify and control these defects. The most common extrinsic defect in SoG-Si is oxygen present at around $1 \times 10^{17}$-$1 \times 10^{18}$ atoms/cm$^3$ in monocrystalline silicon ingots [14]. In addition to oxygen, some of the most harmful defects in silicon are transition metals such as Fe, Cr, Cu, Ni, Ti, etc. that can be present in much lower amounts ($1 \times 10^{10}$-$1 \times 10^{13}$) in the material [15]. These defects can have a detrimental impact on the efficiency of a solar cell, thus engineering solutions are required in order to characterize and develop mitigation strategies to create high efficiency solar cells.
2.2.2 Shockley-Read-Hall Recombination

The aim of defect engineering in solar materials is to prevent recombination of minority carriers, or loss of current, in bulk silicon due to impurity trap states. Defects in silicon allow for Shockley-Read-Hall (SRH) recombination as energy levels within the band gap are introduced where electrons and holes can recombine. Different forms of intrinsic and extrinsic defects exhibit different energy levels for recombination as well as capture cross sections which is a parameter that describes how easily a defect captures a carrier for recombination. Intrinsic defects are those created when the silicon lattice has a vacancy or self-interstitial disrupting the lattice. Extrinsic defects are impurities introduced in the silicon lattice that can be either substitutional (in the place of a silicon atom), or interstitial (in between the normal silicon lattice). Extrinsic defects can be in point defects, also known as interstitial form of one atom, or in precipitates, conglomerates of many atoms that disrupt the crystal lattice. Each defect and defect type has its own parameters that describe how it may effect the electronic properties of a material.

Further, deep level donors and acceptors are the worst impurities as they are far from both conduction and valence band, allowing for the highest recombination activity. In silicon, low concentrations of transition metals (<10^{12} atoms/cm^3 or less) are present, but even in these concentrations these metals can lead to high recombination currents and thus, lead to a drop in efficiency[16]. Oxygen defects, the most abundant have many different forms that cause recombination. More about these defects is found in section 2.3.

2.2.3 Defect Mitigation through process optimization

Using defect modeling, processing can be optimized to control these defects on the manufacturing line. For example, the process used to create pn-junctions of solar cells for p-type materials called phosphorus diffusion gettering (PDG), has been optimized with such kinetic modeling. In this process, the PDG emitter has the property of providing a sink for metal contamination within the bulk. During the diffusion process, the wafer is heated for long enough to mobilize fast diffusing metals in the bulk silicon so that they may diffuse through the wafer. The phosphorus layer deposited on top is energetically preferable for many of these metal atoms to segregate there. This means that during emitter formation, metals that would be recombination active in the bulk are extracted from the bulk material into the emitter. The effectiveness of the “gettering” of iron and other impurities out of the material has been optimized based on the input
material quality, time-temperature profile of the process, and diffusivity and solubility of the impurity in question. This type of modeling has proven effective for the PDG process and mitigation of iron [17]. Using a similar approach to tackle oxygen defect mitigation is a next logical step.

2.3 Oxygen Defects in Silicon

2.3.1 Oxygen incorporation and ring defect formation

Oxygen is the most abundant extrinsic defect present in Cz-Si usually present at 10-20 ppma in as grown material [14]. During crystal growth, the slowly dissolving silica (SiO$_2$) crucible incorporates silicon and oxygen into the melt. Due to the rate of dissolving crucible, evaporation of oxygen at the surface, and rotation of the seed, the amount of incorporated oxygen is not uniform along the ingot. There is generally more oxygen incorporated at the top of the ingot near the seed as it is longest exposed to dissolving crucible [14]. Also, the recombination and diffusion of silicon self-interstitials and vacancies varies along the crystallization front meaning that bulk microdefects (BMD) are also non-uniformly distributed along the ingot height or radially across the ingot width [18]. The resulting BMD and oxygen distributions result in some unique defect behavior involving oxygen, silicon self-interstitials, and vacancies. For example, about 25-30% of the ingot is afflicted with ring defects also sometimes called swirl defects that arise from the interplay of BMD and oxygen shown in Figure 6 [19].

![Figure 6](image)

Figure 6: (a) Representative ring defects shown in a photoluminescence image and (b) an ingot cartoon to show the amount of the ingot affected.

The mechanism of ring defect formation has been studied extensively and it has been shown that the ratio of the rate of crystal growth, V and the axial temperature gradient, G controls
the vacancy mode vs. the interstitial mode of crystal growth. During vacancy mode, ring defects can form if that portion of the ingot has a high concentration of oxygen [18] [20]. Oxygen ring defects reduce conversion efficiencies up to 20% relative, or 4% absolute when a solar cell is made from this defective material [21]. Therefore, around 1/4th to 1/3rd of all Cz-Si is sorted into lower quality material or scrapped representing a loss in yield or efficiency.

In the electronics industry with its high margins, ring defect problems have been resolved as electronics manufacturers can afford to include a high thermal budget and take a loss of material without cutting to deeply into profit margins. However, for the solar industry operating on narrow margins, all material wasted and higher thermal budgets mean more $/W that cannot be afforded. Thus, in order to use this material, we have to characterize what is causing these rings and develop mitigation strategies to avoid them. Mitigation strategies are presented in section 2.4. In order to develop mitigation strategies, it must be understood how oxygen changes morphology and recombination effects.

2.3.2 Oxygen morphology and recombination in silicon

Oxygen has many forms in as-grown material from interstitial to precipitated, and from low recombination to high recombination activity. During cell fabrication, certain process steps introduce the wafer to temperatures that allow the oxygen to change between these different morphologies, and therefore change the material quality in terms of recombination activity [22][23].
Unlike many transition metals which are most harmful in interstitial or point defect form, oxygen, as seen in Figure 7 [24][25] is least harmful in interstitial form. However, oxygen atoms within the silicon lattice can bond together at different temperatures seen during manufacturing to form silicon-oxygen complexes that disrupt the crystal lattice, getter metal impurities, and become recombination-active sites. For example, thermal donors are strings of oxygen atoms between 2-20 atoms in size that are recombination sites called double donors. Double donors are impurities that are ionized twice giving two extra electrons at the standard doping levels used in PV applications. This will shift the materials resistivity down and has a notable effect on minority carrier lifetime indicating a lower efficiency for cells made with thermal donor’s present [26] [27].

Oxygen can also form clusters or precipitates that range in size from dozens to millions of atoms which take on different characteristics in terms of recombination, gettering, and detectability. An oxide precipitate that is unstrained and undetectable without advanced microscopic techniques are called “ninja” particles and are not active gettering sites [28]. For the solar industry these are problematic as they are not easily detected but could become strained and recombination active during processing. Strained oxide precipitates in contrast are detectable, recombination active, and getter metals, and are the worst type of oxygen morphology for solar materials. These precipitates can come in several forms, one of the most common being amorphous oxide platelets [29][30].
Silicon growth methods as well as solar cell manufacturing introduces wafers to times and temperatures at which oxygen can move between these different morphologies [31][32][19]. For example, during growth, the silicon melt is above 1414 °C and while slowly cooling, is exposed to the temperatures best for oxygen precipitate growth leading to oxygen nucleation and some precipitation already present in as-grown material [33]. Furthermore, during silicon heterojunction formation, low temperature process steps occur between 350-550 °C the exact range for thermal donor growth to concentrations between $10^{13} - 10^{15}$ cm$^{-3}$ [26]. The possibility for oxygen to move from low to high recombination activity during growth and processing demonstrates the need for a mitigation strategy that can reliably keep oxygen from forming harmful morphologies in the final cell.

### 2.4 Strategies for mitigation

#### 2.4.1 Lessons from the electronics industry[34]

Oxygen defect mitigation has been studied extensively for over three decades in the electronics industry. During these years it was discovered that oxygen precipitates can act as sinks for metal impurities. In other words, oxygen precipitates grown outside the top layer of the wafer can clean this top layer of the Si wafer used for transistors as the impurities preferentially segregate to the oxygen precipitates. This process called the “Magic Denuded Zone” or MDZ© as seen in Figure 8 [35] is described as a rapid thermal process (RTP) during which Frenkel pairs (one silicon vacancy and one silicon self-interstitial) form and equilibrate [36]. Then with rapid cooling between 40 and 100 K/s, the vacancies do not have time to out-diffuse from the middle of the wafer leaving a grown-in vacancy profile several microns from the surface. Due to this MDZ process, the vacancy concentration and oxygen precipitation concentration can be controlled. After a nucleation and growth process is implemented, the wafer has a pristine top layer, and the oxygen precipitates are perfectly positioned to getter impurities out of the top surface. This erasure of oxygen nucleates in the top layer is what the electronics industry calls a *tabula rasa* process meaning “blank slate.” This comes from the fact that once oxygen nucleation sites have been erased due with the rapid thermal process (RTP), it takes hours of “incubation” time at a lower temperature to reform nucleation sites and precipitates [37].
Figure 8: Images of silicon cross sections that have been defect etched. The images show the Magic Denuded Zone, MDZ© with grown in oxygen precipitates of varying densities dependent on the RTP process temperature below a clean top layer free of oxygen nucleation or precipitation. These images can from a SunEdison data sheet advertising this material process. [32]

2.5 Oxygen Characterization

2.5.1 Interstitial oxygen detection

The standard method of measuring interstitial oxygen content in silicon is Fourier Transform Infrared Spectroscopy (FTIR) [38]. This technique involves absorption of certain wavelengths of a mid-infrared broadband light shined on a sample, and the resulting interferogram is then processed using a Fourier transform algorithm to see the absorption peaks that correspond with certain elements or molecules in the sample. For example, in silicon, the Si-O-Si bond has a specific absorption peak at 1107 cm$^{-1}$ wavenumber as seen in Figure 9.
Figure 9: Fourier Transform Infrared spectroscopy (FTIR).
It was baselined with a FZ wafer with minimal oxygen interstitials (1107 cm\(^{-1}\)). The other peak is for silicon, and this peak is matched between the FZ control and the sample to baseline the spectra.

The absorption peak given in absorbance can be used to calculate a concentration of interstitial oxygen using the Beer-Lambert Law shown in Equation 2.1, with absorption coefficient \(\alpha\), thickness \(t\), and concentration of the impurity, \(N\).

\[
Absorbance = \alpha \times t \times N
\]  
(2.1)

Using calibration standard samples provided by SunEdison semiconductor, ASTM 121-83, and solving Equation 2.1 for absorption coefficient, a calibration curve is created from which the interstitial oxygen content can be calculated (shown in Figure 10). To calculate the height of the absorbance peaks, a float zone (FZ) control spectrum is subtracted from the samples to fix the signal that can be unclear due to phonon absorption from the Si crystal lattice structure. This subtraction takes care of three phonon bands at 1118 cm\(^{-1}\) that can warp the interstitial oxygen peak.
An important distinction to make when measuring interstitial oxygen is what standard is being used. Using the incorrect standard can throw off the measurement by as much as a factor of two. There is no international consensus on which standard is used, so this is a nuance that must be understood when working with oxygen in silicon. For instance, when buying wafers for an academic study from a secondary wafer supplier, they may use a different standard than the company that manufactured the wafer. Calibration factors for the different standards used can be seen in Figure 11 as complied by SEMI © in 2005 [39][40].

```
<table>
<thead>
<tr>
<th>Calibration Factor</th>
<th>Cited in Standard(s) or Publication</th>
<th>Value to Obtain Oxygen Content in ppma</th>
<th>Value to Obtain Oxygen Content in atoms/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;JEIDA Coefficient (Original)&quot;</td>
<td>Cited in Iizuka et al., see Footnote 5</td>
<td>6.06</td>
<td>3.03 × 10¹⁷</td>
</tr>
<tr>
<td>Guo Biao (Old Edition)</td>
<td>Cited in Baghdadi et al., see Footnotes 1 and 2.</td>
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<tr>
<td>IOC-88</td>
<td>SEMI MFI188; DIN 50438, 1994 and 1995; JEITA EM3504; Guo Biao GB/T 1557-1989</td>
<td>6.28</td>
<td>3.14 × 10¹⁷</td>
</tr>
</tbody>
</table>
```

Figure 11: Different standards used for interstitial oxygen measurement in silicon using FTIR.

Figure 10: Calibration curve found using ASTM 121-83 standards provided by SunEdison Semiconductor.

\[
y = 2.225x + 0.8416
\]
2.5.2 Precipitate Oxygen Detection

Oxygen precipitate detection can be achieved with defect etching which reveals stacking faults, dislocations, and extrinsic defects seen with optical microscopy. There are several concerns with this technique for oxygen precipitate detection as it is destructive and targets more than just oxygen precipitates, revealing many types of defects. One such etch, called the Sopori etch was used in this work to find oxygen precipitates as seen in Figure 12 [41]. When using such defect etches, as is done for imaging MDZ in the electronics industry, the material is expected to contain oxygen precipitates at a certain density, so this method is effective in confirming more accurate numbers. If the oxygen content is completely unknown this method is not effective as it reveals defects other than oxygen such as structural defects. Often this method can be confirmed used electron microscopy techniques.

![Sopori defect etching images done with a Nikon LV100 optical microscope.](image)
The image area is 180 µm x 450 µm

Figure 12: Sopori defect etching images done with a Nikon LV100 optical microscope.

The need for a new, accurate techniques for specific oxygen precipitate detection leads to a new method under development in the MIT PVlab. This involves copper “flagging” of oxygen precipitates and detection using micro-X-ray fluorescence (µ-XRF). Preliminary work has been done with CuCl₂ solution contamination and copper drive in anneals at temperatures between 700 – 900 °C and µ-XRF used to map the copper precipitates.
CHAPTER

3

TABULA RASA METHODS

3.1 Tabula Rasa for Oxygen Mitigation

For the solar industry, the ideal scenario would be to use the 9-11 N’s pure top layer of a Magic Denuded Zone (MDZ) wafer as the solar cell material. However, this is unrealistic as the bottom of the wafer full of oxygen precipitates decorated with metals would be wasted material. Also, the thermal budget required would be too expensive for a solar manufacturing line. Instead, to achieve as close to this pristine wafer quality as possible, it has been hoped that one short, high temperature annealing step added to the cell manufacturing line could improve bulk lifetime for the solar industry [42][43][44].

*Tabula rasa* (TR) is proposed as a lone processing step addition to solar cell manufacturing lines, which would erase the thermal history of wafers with respect to oxygen, leaving all oxygen in non-recombination active interstitial form [45]. The process can be envisioned as a tube furnace which wafers would be continuously run through with a relatively quick ramp up to a very high temperature between 1000-1300°C and quick ramp down back to the base temperature of the processing line, presumably room temperature.

*Tabula rasa* in the electronics industry is performed above 950 °C for 1-5 minutes, and will dissolve as-grown precipitates completely. To regrow oxygen precipitates, an incubation period is needed of at least 4 hours at relatively low temperatures (550-650 °C) to create nucleation sites [46]. Because no solar cell processing step can replicate this incubation period, *tabula rasa*, if it succeeds in dissolving all precipitation sites, is a good solution for oxygen mitigation in the solar industry because oxygen precipitates will not regenerate in time to be harmful during processing.
It can be asked why the process has not yet been added to a solar line, and there are several reasons for this. One thing is that a reduction of carbon impurities in the silicon melt has opened up the possibility that oxygen clusters will be small enough to dissolve in a reasonable time. Carbon increases the rate of oxygen precipitate formation during growth, so with less present, the oxygen clusters left in the as-grown wafer have been reduced in size [47]. It has been shown in electronic grade material that *tabula rasa* can dissolve clusters of this size without creating any harmful effects, and it is hoped that the same is true for solar grade materials [48]. Another reason the process has not yet been added is that for many years impurities other than oxygen had a larger impact on efficiency, for example the transition metals mentioned in Chapter 2. Now that industrially-used processes have been optimized to rid the wafers of these defect limitations, oxygen is one of the next impurities that most limits performance.

There are factors that must be considered while designing the TR process. First, oxygen clusters are gettering sites, which means metal impurities can precipitate at oxygen clusters. If a TR process dissolves oxygen precipitates and the metals that decorate them, the metal point defects can cause more harm than the oxygen precipitates were causing. This can be overcome with appropriate gettering, as long as those oxygen-cluster gettering sites are completely dissolved. This leads another factor to consider when designing the TR process, the difficulty in predicting when oxygen precipitates will fully dissolve. The order of processing and TR time/temperature profile can both affect the outcome of the process. Studies have been done by Youssef *et al.* [49] and Jensen *et al.* [50] showing the effect of TR if performed at different times during processing of Cz-Si and a newer material called non-contact crucible Si (NOC-Si). These times include before and after standard PDG, extended PDG and oxidation, also with and without an additional low temperature anneal. Each result is different, with only a few of the experiments fully dissolving the ring defect.

The time and temperature at which TR will be effective in dissolution is dependent on the size and density of precipitates as well as the total amount of oxygen in the wafer. Given these design restraints, to be an industrially viable process, it is preferred to model and optimize the TR process for wafers of known oxygen content and distribution so that the results of the process can be predicted for whatever wafer is input. With such a predictive process model, a TR process can be used that will reliably dissolve oxygen precipitates into interstitial form.
3.2 TR Process Setup

The *tabula rasa* set up at MIT was modeled after the one demonstrated at the National Renewable Energy Laboratory (NREL) by La'Salvia *et al.* [45]. The setup is shown in Figure 13. In the TR setup, wafers are cleaned and placed in a quartz wafer boat within a closed glass “elephant” container with a small circular rod opening. An oxidation quartz tube furnace is used for the process. Wafers are pushed into the center of the quartz tube at a rate of about 0.5 m/min to give a quick ramp up in temperature. The wafers stay at the center of the tube for 1-2 minutes, and are extracted out of the same end of the furnace at the same rate, cooling in ambient after removed from the furnace.

The *tabula rasa* setup was emulated at MIT to study the process and its validity for solar applications. There are several key differences with the MIT setup from the original NREL setup. The MIT set up enables higher temperatures due to the use of a mullite tube that can handle temperatures up to the melting point of silicon as compared to the quartz tubes used at NREL that can only get up to around 1100 °C safely. The additional temperature range enable us to understand the limiting mechanism of TR process as described later in Chapter 4 by testing oxygen dissolution in silicon up to 1300°C.

The new temperature range enabled by the MIT causes several new design details to be considered during process development. First, the wafer holding apparatus must be something other than the quartz boats usually used due to the melting point of quartz. The sample holder changed in form several times, starting with a ceramic holder which can withstand the temperatures, but cracked the tube. The final design was a flat wafer of electronic grade silicon cleaved into a rectangle (see Figure 14 (a)). The surface of this holder is roughened with a diamond scribe so that the samples will have traction on the holder when being pushed into and pulled out of the furnace. The rod used is made of
ceramic with a high temperature paste used to attach a perpendicular ceramic tube to hook the plate end for pulling and pushing into and out of the furnace. The silicon plate was finally decided to be the best option as it will not crack under thermal stress, melt at the temperatures involved, or contaminate the samples. Ideally a silicon plate with some lip to keep any sample from slipping is employed.

A second new consideration due to the additional temperature range is thermal stress of moving parts even if the materials used are rated to that temperature. The furnace tube can be due to thermal stress fractures. One solution to prevent this from happening is using a wafer holder that is very light-weight as anything heavier can create stress as it is dragged along the tube surface. An even more elegant solution is a wafer holder suspended with wheels so that it never touches the tube surface as can be seen in Figure 14. Another thermal stress concern is placing the tube in an unbalanced position. For example, if even several inches extend farther of the furnace in one direction the extra weight at the end of the tube can create cracking. This should be avoided especially on the end that is connected to the gas inflow line as this adds extra weight to that end. Lastly, the high temperature thermal paste used, while rated to TR temperatures, can flake or the components it connects break apart during usage. Avoidance of components that must be joined at these high temperatures is preferable.

A third consideration brought about by the high temperatures is that many materials can outgas or react at these temperatures and special attention should be taken to check each components properties. For example, graphite is often used as a connecting piece in experimental setups. Graphite will vaporize slowly at these high temperatures, coating experimental samples with carbon that can diffuse into the wafers. Carbon is an especially harmful contaminant when studying oxygen as it changes the behavior of oxygen dissolution and precipitation.

The fourth consideration for high temperatures is the gas flow. Nitrogen or oxygen is needed for TR processing. In the MIT setup this is attached using a metal brace and tube cap at the end of one tube tightened with screws with a plastic tube the delivers gas flow. This tube, while not directly in the high temperature furnace, directly contacts the metal plate that is a part of the tube cap. The transfer of heat to the plastic can melt the tube closed restricting gas flow. This happens slowly over several TR runs so the plastic tube needs to be trimmed before each TR process run. Replacement with a better material would be ideal to prevent any melting for future processing endeavors.
Temperature control is also crucial to studying the effects that TR might have on oxygen precipitates, therefore several temperature calibrations were performed. The Lindberg Big Blue single-zone tube furnace has double-end silicon carbide heating elements above and below the furnace chamber with insulation surrounding the tube. The furnace temperature control is a fast response type R-type thermocouple with six feet of compensated thermocouple lead wire. This thermocouple reading is displayed on the furnace control console. To test the readout, an independent S-type thermocouple placed within the tube at each temperature from 1100-1350°C. These temperature readouts are also compared to a disappearing filament optical pyrometer (Spectrodyne DFP 200) read out. The temperature readout from the furnace controller display regularly shows a 10-15°C offset from that read with the pyrometer or thermocouple within the furnace tube. Therefore, for experimental control, before each process, the temperature readouts from both the furnace temperature control and optical pyrometer were noted and the inner temperature was used for process simulations.

A last thing to note about high temperature processing is that ideally the process occurs in a clean room so that contamination is tightly controlled. The MIT setup is not in a clean room but each surface the wafers contact is either clean silicon or a clean wipe, and while at high temperatures when the samples are at danger from contamination diffusion, the wafer is in the tube where inert gas is flowing. Lastly, during cool down outside of the tube, the samples are placed on a silicon plate heat sink that is clean and within a protected chamber to avoid undue contamination.

Other than the higher temperature, an advantage of the MIT TR setup is the speed at which the wafers can be pushed and pulled from the tube is faster. The wafers are pushed into the tube at about 1 m/min and pulled out at around 3m/min in the MIT set up as opposed to 0.5m/min in [45]. The reason that the faster ramp is better is that during the temperature range which the wafers experience in the ramping and cooling steps, oxygen precipitate nucleation and growth occurs (800-1000°C) and also thermal donor formation (550-650°C). Therefore, reducing the time spent at these temperatures is preferable.

Several images are shown in Figure 14 give an idea of the setup. Fig. 14 (a) is the sample holder with samples on top, and Fig. 14 (b) shows the Lindberg furnace heated to 1300°C with the suspended push rod on rolling tracks.
3.3 TR feasibility on a manufacturing line

One consideration that can often be overlooked when trying to improve efficiencies is how feasible a new process will be on a manufacturing line. TR has several advantages, one is that it is a short step so it would not limit throughout on a cell line. Another advantage is that wafers could potential be run through the process on a belt furnace such that they would not have to put in and extracted from the same end of a tube furnace is must be done for PDG processes. Therefore, it could be done in a continuous line rather than in batches which is also good for throughput. Lastly, with a predictive model and nondestructive oxygen testing methods in place, it could be possible to guarantee the elimination of oxygen ring defects.

However, there are some concerns with the process also. First, it would be the highest temperature process on the cell manufacturing line which increases the thermal budget by a significant amount. This is costly both for energy costs but also because each high temperature step opens the wafer up to contamination and diffusion of any extrinsic impurities that may be present. Lastly, a cost benefit analysis would need to be performed to understand how much the efficiency gain would be worth in profit versus how much the thermal budget and new furnace would cost.
OXYGEN DISSOLUTION STUDY

4.1 Motivation for oxygen dissolution study

As described in Chapter 2, oxygen is the most abundant impurity in industry materials today and can have harmful effects on efficiency. *Tabula rasa* (TR) is a process that could mitigate these defects. To explore whether the TR process could reliably improve bulk lifetime, several research questions will be answered: (1) Does TR dissolve all oxygen precipitates? (2) What physical mechanisms limit the dissolution of oxygen precipitates in silicon? (3) Can a model of the TR process be built to predict this dissolution?

The size and density of oxygen precipitates as well as the total oxygen content in a Si wafer determine the time interval and temperature at which TR is effective in oxygen dissolution. Optimization of the TR process is necessary to predict whether complete dissolution of all oxygen clusters occurs. This predictive power ability is essential when integrating the process into a solar cell manufacturing line. The fastest and most economical way to optimize the TR process is to build a dissolution model of oxygen precipitates with input parameters that are easily measured. Therefore, in this chapter, the dissolution of oxygen precipitates through the TR process is investigated through a set of TR experiments at different times and temperatures. These experiments are used to quantify the limiting energy of the TR process, a needed input for the dissolution modeling and subsequent optimization. In addition, observations are made on the limitations of the process to dissolve precipitates of different sizes.

4.2 Experimental Methods

4.2.1 Sample Preparation

Electronic grade *p*-type Cz-Si material was used for this experiment with resistivity of 10 – 12 Ω-cm at 745 μm thickness, double side polished, and 200 mm in diameter. The oxygen content
of the wafers was 13.75 ppma, with negligible other extrinsic defects as reported by the wafer supplier, WRS Materials, Inc. The wafers were cut into pieces of $3.5 \times 3.5\ cm^2$ by laser, and each sample was RCA cleaned (standard wafer cleaning process before high temperature processing) for removal of organic and metal contaminants. The samples were then subjected to a series of high temperature process steps in a quartz tube furnace with $N_2$ atmosphere. These steps are commonly used in the electronics industry to nucleate and grow homogeneously distributed large oxygen precipitates [51]. Figure 15 shows the time-temperature profile, including a nucleation step at 550 °C for 6 hours, precipitate growth steps at 800°C for 4 hours, 925°C for 4 hours, and 1000°C for 16 hours, and lastly ambient cooling to 700°C before being pulled out of the furnace. The samples are then cleaved into smaller pieces of $1 \times 1\ cm^2$, chemically etched with CP4 and HF-dipped to remove any surface damage or oxide left from the high temperature processing.

![Figure 15: Time and temperatures that the sample wafers underwent throughout preparation and experiment.](image)

To make sure that the oxygen atoms in precipitates or in interstitial form were completely known, precipitates were nucleated and grown and, to the right preferential defect etching was done to confirm precipitate density. The two images are from a sample before precipitate growth and after precipitate growth.

### 4.2.2 Experiment

After precipitate growth, samples were put through the TR process at five temperatures between 1100°C and 1290°C, and at six different times between 1 and 30 minutes. The process used a mullite horizontal tube furnace with measured temperatures from a disappearing filament optical pyrometer targeted at the silicon sample holder as the target and thermocouples external to
the tube. Gas flows through the tube, either ultra-high purity nitrogen or oxygen at 5 SCFM. The loading of the wafer boat both into the furnace was about 10 seconds, at about 1m/min, and about 30 seconds unloading at about 3m/min. The samples were left at the end of the furnace for 10 seconds for cooling. The samples were subsequently placed on a large silicon plate that acts as a heat sink directly after the process for cooling. The samples were then HF dipped to remove any oxide formed on the surface. The full process is described in detail in Chapter 3.

4.2.3 Characterization

Defect analysis methods described in Chapter 2, such as FTIR and chemical defect etching were utilized to determine interstitial oxygen content and precipitate density, respectively. FTIR at room temperature in the 400-4000 cm\(^{-1}\) wavenumber range was used to determine interstitial oxygen \([O_i]\) concentration at 1107 cm\(^{-1}\) before precipitate growth, after precipitate growth, and after the TR step. Sopori defect etching revealed imperfections in the lattice [41]. Since Cz-Si has negligible other impurities, these pits are assumed to by oxygen precipitate related. This assumption was corroborated by the microscopic images before and after precipitates are grown, as shown in Figure 16.

![Figure 16: The microscope images of two samples underwent Sopori defect etching.](image)

(a) A sample defect etched before precipitates are grown and (b) the sample after precipitates are grown. The image dimensions are 100 \(\mu\)m \(\times\) 100 \(\mu\)m.

FTIR measurements were calibrated using ASTM standard 121-83 as described in Chapter 2. All oxygen was in interstitial form before growth, therefore the \([O_i]\) measurement for these samples is equivalent the total oxygen content. This assumption was tested by annealing an as-grown
sample for 12 hours at 1250°C to be certain all oxygen was dissolved, and measuring before and after to show an equivalent amount of \([O_i]\). FTIR showed that \([O_i] = 13.75\) ppma, or \(6.88 \times 10^{17}\) atoms/cm\(^3\) before and after annealing. After growth, the peak dropped to 5.35 ppma indicating that 61% of oxygen atoms precipitated during growth. The precipitate density is determined to be \(2.59 \times 10^9\) ppt/cm\(^3\) Through chemical defect etching done for 45 seconds (HF:CH\(_3\)COOH:HNO\(_3\) with a volume ratio of 36:15:2)[41]. Using the radius of silicon dioxide unit cell, \(r = 5.4 \times 10^{-9}\) cm, assuming that these precipitates are all of similar size and spherical, the oxygen precipitates have around \(1 - 2 \times 10^8\) oxygen atoms per precipitate, and a diameter between 55 – 65 nm. After each TR process, \([O_i]\) is measured again to determine how many of these precipitates have dissolved.

### 4.2.4 Design of experiments

Determining what set of experiments should be performed so that conclusions can be made about oxygen distribution before and after the TR process required design of experiments methodology. The large random error in the FTIR tool as well as the difficulty in controlling the experimental environment with regard to contamination and the time-temperature profile made data too messy to extract dissolution time constants or fit an activation energy. Therefore, a systematic method to determine what inputs to change to optimize the result was used to help determine what the best set of experiments would be.

The approach taken was to create dissolution curves representative of the process step as seen in preliminary experimental data using Equation 4.1 and 4.2 and adding noise representative of noise present in the experimental setup, both positive and negative. With these new simulated dissolution curves using actual values extracted from the fitting routine used to analyze the experimental data, several new experimental scenarios were explored. The aim was to find a set of experimental inputs that would minimize the mean square error for the fitting routines.
Figure 17: Simulated experimental points based on realistic noise levels.

(a) Extra times were added as were extra temperatures to determine the difference in error between different experimental sets. A scenario with several data points taken for the same process is shown in (b) with 1, 3, 5, and 30 minute TR steps doubled.

The scenarios tested changed two parameters (1) time and (2) temperature, and also tested (3) repetition of a single experiment. For example, if you began with three TR process steps at 1100°C, 1200°C, and 1300°C and did three times for each temperature 1, 5, and 10 minutes, nine points of
data are collected and are likely too noisy to extract meaningful dissolution time constants. Using the data noise generator, scenarios are tested to see if the result could be more meaningful. For scenario (1) new TR experiments are added with a different time, for scenario (2) new TR experiments are added with a different temperature, or for scenario (3) doubling up experiments at the same time and temperature is tried. Combinations of adding more times and more temperatures and other permutations were also tested.

As can be seen in Figure 17 (a) above, several new temperatures and times were added to this the top figure (nine times, six temperatures) in comparison to the original experiment (six times, five temperatures). Another scenario is shown in Figure 17 (b) that included additional experiments of the same time and temperature so as to do identical experiments.

To determine how well this simulated experiment might perform in comparison to the experiment first attempted, the dissolution time constant is found using the same fitting routine as is used for the experiment and an activation energy is extracted. Then, the error between the fit and the simulated noisy data is found, and the root mean square error (RMSE) calculated. With additional temperatures and additional times, the RMSE unsurprisingly goes down. One convenient thing about using the RMSE is that it is in the same units as the response variable \([52]\), or in this case the dissolution time constant in minutes. Comparing the RMSE for the different experiments can show which set of experiments is likely to give the best fit.

The other constraint on the design of this experiment was that there were only 50 samples available. Trying out different scenarios of time/temperature sets that use only 50 samples resulted in finding the minimum RMSE for the scenario with more doubled experiments and at least 4 temperatures. Therefore, the set of experiments chosen for the experiments described here included five temperatures with six times at each temperature, and then the 3 min, 5 min, 10 min, and 30 min process duplicated for each temperature. That is 10 samples per temperature equaling 50 total samples. The RMSE for the activation energy fit was found to be 0.0727 min as compared to 0.3-0.4 min for the original experimental design.

4.3 Results and Discussion

4.3.1 Oxygen Dissolution

The \([O_i]\) concentration is shown in Figure 18 as a function of annealing time for each TR temperature. Oxygen precipitates dissolve over time and the concentration increases steadily at
each TR temperature. The dissolution time constant $\tau_{\text{diss}}$ was quantified for each temperature by fitting the interstitial oxygen data with Equation 4.1, where $C_s$ is the observed saturation concentration of interstitial oxygen at each TR temperature.

$$[O_i](t) \propto C_s \left[1 - \exp\left(-\frac{t}{\tau_{\text{diss}}}\right)\right]$$  \hspace{1cm} (4.1)

The lowest temperature, shortest time process, 1100°C for 1 minute, is expected to dissolve the least grown-in precipitates and the highest temperature, longest time TR process, 1290°C for 30 minutes, to dissolve the most grown-in oxygen precipitates. The TR process results are represented by the four curves in Figure 18, showing oxygen precipitates dissolving at a steep initial rate with a saturation at a certain concentration, which represents the kinetic limitations of dissolution. None of the TR temperature dissolution curves reach the solid solubility limit of $[O_i]$ in silicon except for the 1145°C curve according to the intrinsic solubility described by $9\times10^{22} \exp\left(-1.52 \text{ eV}/kT\right) \text{cm}^{-3}$ [53]. The 1100°C curve is not shown in Figure 18 because no change in interstitial oxygen concentration was observed at 1100°C. This is because the solid solubility at this temperature is 4.74 ppm, which corresponds to the starting concentration of interstitial oxygen for these samples within the uncertainty of the measurement ($\pm0.5$ ppm). At 1193°C and 1245°C, $[O_i]$ reaches a steady dissolution rate below their solid solubility limits.
Figure 18: Oxygen precipitate dissolution curves plotted as interstitial oxygen content for four temperatures. The dissolution time constant ranged from around 1 to 6 minutes between the temperatures, and none of the temperatures managed to completely dissolve the precipitates to $[O_i] = 13.75$ ppm which is the total oxygen content of the samples. Also shown are samples at each temperature quenched in silicone oil to check that the ramp down did not cause substantial re-precipitation. At right, defect etch images of $90 \times 90 \mu m^2$ area show the decreasing density of oxygen precipitates at each temperature [ppt/cm$^3$]. 85% Confidence intervals calculated from the error in the free parameter, final saturation at the last time step, are shown with the dashed lines. The error bars represent the standard error due to the distribution of measurements taken at each time step. If only one measurement was taken at a time step the error bars are an average of all standard error.

In Figure 18, etch pit images corresponding to a 30-minute TR process are shown to the right of the dissolution curves at each temperature. At each higher temperature the dissolution of a greater percentage of oxygen precipitates is observed. The density of precipitates and the $[O_i]$ content are measured and used to calculate precipitate radius. The radius is found not to vary significantly between temperatures. Precipitates do not fully dissolve for any of the TR experiments, and assuming homogenous size, the precipitate density ranges from around $1 \times 10^8 - 2 \times 10^9$ precipitates/cm$^3$, the interstitial oxygen ranges from $3.7 \times 10^{17} - 6.8 \times 10^{17}$ atoms/cm$^3$, and the precipitate diameters ranging from 45 – 60 nm. The lowest precipitate density and highest
interstitial content are measured after the highest temperature TR process at 1290°C, whereas the lowest TR temperature at 1145°C results in lower interstitial content and higher precipitate density.

These curves indicate that TR will only be effective if the temperature is above that demanded by the oxygen precipitate size, density, and interstitial oxygen solubility demand. In addition, the time it takes to get to even the saturation point is more than 5 minutes. The traditional TR process in the electronics industry is around 1090-1150°C for 1-2 minutes, which would not be sufficient in this case. These samples have oxygen precipitates of a radius of 27-30 nm, which is larger than is normally present in as-grown or even processed solar cells. These curves are not indicative of the temperature required for the typical solar cell. What these curves demonstrate is that for TR to be an effective process, the appropriate time and temperature for complete dissolution of oxygen precipitates must be used which is not necessarily in line with traditional processing. This profile must take into consideration the oxygen content and morphologies within the as-grown wafer.

4.3.2 Activation Energy

The activation energy for dissolution, $E_a$, was found using the fitted dissolution time constants, $\tau_{diss}$, and fitting these to an Arrhenius-type temperature-dependent equation.

$$\frac{1}{\tau_{diss}} \propto \exp \left( \frac{E_a}{k_B T} \right)$$

(4.2)

The limiting physical process in dissolution is indicated by the activation energy. Comparing the activation energy to the migration enthalpy for interstitial oxygen in silicon, can show whether there is an additional physical process limiting the dissolution process. If the migration enthalpy is smaller, then the limiting process is not necessarily kinetics. Instead, the limiting process could be the reaction in which one oxygen atom breaks away from a precipitate called reaction-limited dissolution, as has been shown in iron silicide dissolution[54]. If the activation energy is found to be equal to the migration enthalpy, then the diffusion of an oxygen atom away from a precipitate is the energy-limiting step. In this case, no extra energy is needed to dissolve precipitates greater than the kinetic limitations of diffusion [55]. If the migration enthalpy is larger than the activation energy found, then the dissolution of oxygen precipitates is enhanced lowering the energy needed for oxygen to diffuse away from a precipitate. As can be seen in Figure 19, the activation energy was found to be $2.6 \pm 0.5$ eV which is within the range of the migration enthalpy for $[O_i]$ in silicon which is $2.53 \pm 0.3$ eV [53]. Therefore, the TR process is shown to be kinetically limited for these
samples. The dissolution of oxygen precipitates can be modeled based on the known kinetics and solubility material properties without any extra energy barrier.

![Graph](image)

**Figure 19: Arrehenius-like temperature dependent dissolution behavior**

Activation energy is found to be 2.6 eV as the slope of the line going through the dissolution time constants. The error bars represent 85% confidence in the dissolution time constant fit from Figure 18.

### 4.4 Preliminary Tabula Rasa Modeling

#### 4.4.1 Impurity to Efficiency Calculator

Within the PVlab, a kinetic model that is called the impurity to efficiency (I2E) model was previously developed by several former colleagues [56]. The I2E model was primarily used for modelling iron impurities in silicon. Fick’s Law of diffusion shown in Equation 4.3 is used to describe the diffusion of phosphorus during the PDG process, with $[P]$ as the local phosphorus concentration, $D_P$ as the diffusion of phosphorus via Si vacancies and Si self interstitials. The same diffusion law in concert with a segregation term shown in Equation 4.4 is used for iron kinetics, with $D_{Fe}$ as the diffusion coefficient of iron in silicon, and $\sigma$ as the space dependent segregation coefficient of iron in the phosphorus layer. Dissolution of iron atoms is accounted for through Ham’s Law shown in Equation 4.5 with $C_{eq,Fe}$ as the temperature dependent solid solubility of iron, $N$ as the precipitate density, and $r$ as the radius of an oxygen precipitate. The change in radii of
precipitates during processing is accounted for with Equation 4.6 where $V_{Fe}$ is the volume of a $\beta$-FeSi$_2$ complex.

\[
\frac{\partial [P]}{\partial t} = \frac{\partial}{\partial x} \left( D_P([P]) \frac{\partial [P]}{\partial x} \right) \tag{4.3}
\]

\[
\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left[ D_{Fe} \left( \frac{\partial C_i}{\partial x} - \frac{C_i}{\sigma} \frac{\partial \sigma}{\partial x} \right) \right] \tag{4.4}
\]

\[
\frac{\partial C_i}{\partial t} = 4\pi Nr D_{Fe} (C_{eq,Fe} - C_i) \tag{4.5}
\]

\[
\frac{\partial r}{\partial t} = V_{Fe} D_{Fe} \frac{(C_i - C_{eq,Fe})}{r} \tag{4.6}
\]

These equations with as-grown precipitate density and precipitate radius as fit parameters, are used to calculate final iron distributions. Then these iron distributions are used to calculate final charge carrier lifetimes which can be used to evaluate solar cell performance with PC1D device simulation. The implementation of optimized processes within solar cell manufacturing lines can lead to higher efficiency materials [57], and the emphasis on transition metals for research has waned. But, oxygen still causes considerable yield loss due to lower efficiencies, so application of these tools to oxygen is warranted.

### 4.4.2 I2E with Oxygen

The I2E calculator was modified from its original version to introduce oxygen parameters, taking out phosphorus diffusion, and adding a continuous time profile. The last modification was necessary because the I2E model with discrete time steps could not handle the quick dissolution rates of oxygen precipitates during the tabula rasa process. With the help of Hannu Laine, a visiting Fulbright student, a continuous time vector replaced the old discrete system.
In Figure 21, I2E simulations for each dissolution curve from the experiment are shown with the experimental curves. Each I2E simulation models the dissolution of oxygen until the solubility limit is reached, or all oxygen is dissolved. The experimental results and simulation results match for the 1100°C curve, which shows no dissolution because the solubility limit is around the starting interstitial oxygen concentration. The 1145°C curve shows oxygen precipitates experimentally dissolving to the solubility limit and therefore matching the I2E simulation. The reason the 1145°C experiment reached solubility is that a sufficient number of small precipitates below the critical size existed in the starting material to dissolve and reach the solubility limit. For the 1193°C and 1245°C curves, the experimental curves do not reach solubility and therefore do not match the simulation.
Figure 21: I2E simulation results compared with experiment. Experimental curves (solid) are plotted with simulated curves (dashed) with disagreement (arrows) due to the simulation missing a key physical feature of the oxygen in these samples which is an inhomogeneous size distribution.

This can be explained by noting that the I2E solver does not account for a key physical feature of the experimental samples. It is probable that there is in reality an inhomogeneous size distribution of precipitates going against the previous assumption of homogeneous oxygen precipitate size made in section 4.3.1. When assuming that all precipitates are the same size, they are all of small enough size to dissolve to solubility. In reality, there is likely a size distribution of precipitates that were grown into the samples due to the Ostwald ripening process [58][59]. Therefore, the precipitates below a certain size dissolve and above that size stay in the wafer slowly dissolving for hours to the solubility limit. Figure 4.8 is a qualitative figure for visualizing this dissolution with the critical size. The precipitate size profile is a typical profile for grown oxygen precipitates occurring through the Ostwald ripening process after nucleation [60]. Each dashed line represents the critical radius at each process temperature, 1100°C, 1145°C, 1193°C, and 1245°C. All of the precipitates to the left of the dashed line dissolve during the 30-minute process.
time, and those to the right do not. This explains the reason why none of the precipitates fully dissolve in even the highest temperature, 30-minute step, and why the density of precipitates decreases for each temperature.

![Graph showing precipitate density vs. precipitate size](image)

**Figure 22:** A qualitative figure to visualize dissolution of oxygen precipitates of inhomogeneous size distribution. This is for the 30-minute TR process at different temperatures. The profile of precipitate size is a typical oxygen precipitates size distribution [53]. When compared to the etch pits in Figure 18, it can be seen that the density of etch pits decreases at the higher temperature, but the precipitates never fully dissolve at these times because the critical radius, represented by the dashed lines for each temperature do not allow for further quick dissolution.

The I2E calculator is a limited, but powerful tool when modeling the TR process. It models dissolution of oxygen precipitates to the solubility limit when precipitates are below the critical radius represented by the dashed lines in Figure 22. This means that if the precipitates are all below the size at which they can dissolve completely without reaching the solubility limit at the TR temperature being modeled, then I2E gives an accurate output. In the dissolution curves for the experiment used to extract activation energy, some of the precipitate sizes were much too large for complete dissolution in the TR times.
The next step to implementing a successful I2E oxygen simulation is to implement a Fokker-Planck equation-based precipitation model that has an input precipitate size distribution and handles a variety of densities for each precipitate size. The Fokker-Planck model defines a critical radius size which maximizes the Gibbs free energy, $\Delta G(n)$ [17]. While below the solid solubility of interstitial oxygen in silicon for the process temperature, precipitates smaller than the critical radius will dissolve while precipitates larger will not dissolve fully, best explaining the experimental results from the dissolution study. In the case where all the precipitates are below the critical radius, the I2E simulator without the Fokker-Plank equation is sufficient for modeling TR with the Ham’s law implementation of homogenous precipitate dissolution. For solar materials, the ring defects are oxide nano-precipitates that are small in comparison to the precipitates in the samples used in this study [33]. Therefore, the I2E TR predictive process model would be sufficient for modeling oxygen dissolution in solar materials where all precipitates are below the critical radius.

4.5 Chapter Summary

The *tabula rasa* process is a promising solution to oxygen related yield loss for Cz-Si solar cells due to ring defects. There are legitimate concerns with implementation of the process as outlined in Chapter 3 due to the high thermal budget required and difficulty in predicting the outcome. Predictive process modeling capabilities are key to implementation to justify such a high temperature process step. The work presented in this chapter enables this modeling as TR is shown to be kinetically limited dissolution, and the activation energy is found for dissolution. Using oxygen distributions within the as-grown wafer, time-temperature profiles can now be optimized to put oxygen into the least recombination active form.

The activation energy of oxygen dissolution was determined to be in the same range as the coefficient of diffusion, $\sim 2.6$ eV revealing a kinetic limitation to oxygen precipitate dissolution for this sample set, which saturates before the solid solubility limit. From that saturation point, the precipitates slowly dissolve after an initially quick dissolution rate because the oxygen precipitates are above the critical radius for that temperature. This explains why the only TR process that fully dissolved precipitates with diameters of around 70 nm was the 1290°C process lasting over 5 minutes. For other material, including industrial PV materials, shorter and lesser temperature processes are possible if the material has smaller oxygen precipitates. Knowledge of the size and
density of the oxygen precipitates within the wafer is needed to determine which TR process is appropriate.

The I2E process model that was modified for oxygen dissolution is shown to be effective for certain situations when the precipitates are all below the critical radius so that the precipitates all dissolve to the solubility limit. For the typical size of oxygen precipitates in as-grown wafers, I2E should be sufficient. To generalize the model even further, the addition of inhomogeneous precipitate sizes should be explored through the Fokker-Planck equation.

Another step toward realizing a TR process that can be implemented in industry is efficient and thorough characterization of the as-grown oxygen to be fed into the model. Currently interstitial oxygen is easily measured with FTIR, but oxygen precipitate characterization is challenging without a previously known total oxygen content and precipitate density. Work is ongoing using techniques such as micro-X-ray fluorescence (as described in Chapter 2), electron beam induced current, transmission infrared microscopy, and transmission electron microscopy to determine a process for oxygen precipitate characterization.
5.1 Introduction

The ideal TR process model would include the ability to predict the efficiency of a solar cell after the Si wafer with the ring defects are treated by different TR processes. One way to accomplish this is through a multiscale end-to-end modeling approach shown in Figure 23. Developing such a model allows exploration of these research questions: (1) How much do swirl defects limit performance? (2) What is the performance gain when swirl defects change due to processing? (3) What are the best device architectures for handling swirl defects?

5.2 Methodology

To begin to answer these questions several experimental techniques and modeling packages are used together as is outlined in Figure 5.1. The modeling starts at the nanoscale with defect parameters including defect energy level and capture cross sections gained from temperature- and injection-dependent lifetime spectroscopy (TIDLS). Another parameter needed is the concentration of defects which unfortunately cannot be determined through TIDLS, so a range of defect concentrations are simulated using a 2D device model in Sentaurus © TCAD [61]. Using the output $J-V$ curves from the Sentaurus simulations, a two diode model [62] is fit, extracting $J_{01}$ and $J_{02}$ for each defect concentration. These $J_{01}$ and $J_{02}$ values can be used in a finite-element model (FEM) where the nodes are described by the two-diode model in Equation 5.1. The FEM model used is called Griddler 2.5 PRO © [63] created at the Solar Energy Research Institute of Singapore (SERIS) by Johnson Wong.
Figure 23: Schematic of multiscale end-to-end modeling approach.

This modeling package is used to determine efficiency potentials for solar cells with oxygen rings before and after *tabula rasa* processing (images from [19][84]).

The defective vs. non-defective areas of the mesh input into Griddler are determined through a PL image of the cell. The contrast from the PL image is matched with the simulated contrast of radiative recombination rate from the Sentaurus simulations. This approach is similar to the work done for inhomogeneous structural defects modeling done in [64]. Two different methods are attempted, one with a binary image, and the other image with a gradient. The binary image shown on the left in Figure 26 has a threshold value of 55%, below which everything is assigned “non-defective” $J_{01}$ and $J_{02}$ values and above which everything is assigned “defective” $J_{01}$ and $J_{02}$ values. The gradient image shown on the right in Figure 26 is broken into the contrast percentage groups that are assigned graded $J_{01}$ and $J_{02}$ values based on linear interpolation from the values simulated in Sentaurus and fit with the 2-diode model. In this way each pixel can be assigned a $J-V$ curve closer to its actual contrast, capturing more of the gray area between different PL pixel values rather than only assigned “dark” as defective, and “light” as non-defective. More detail about the image processing can be found in Section 5.5.
With this input current based image, Griddler can encapsulate the effects on inhomogeneous effects that Sentaurus cannot. From the device performance parameters.

5.3 Determining input parameters

Temperature- and injection-dependent lifetime spectroscopy can be used to identify defect parameters for lifetime limiting defects, so it is an ideal method for determining the parameters that cause the ring defects shown in many Cz-Si PL images. In work done at Fraunhofer Institute for Solar Energy Systems, this technique was applied to ring defects in Cz-Si material [19] with two defects identified for the Cz-Si material in good agreement with SRH defect parameters found for oxide precipitates by Murphy et al. [65]. The parameters found are energy level of the trap within the bandgap, $E_t$, as well as the capture cross-section ratio called $Q$ (or $k$ in other literature), which is defined as the ratio of capture cross-sections of electrons and holes ($Q = \frac{\sigma_e}{\sigma_h}$). In Table 1 below, these parameters are listed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c-E_t,[\text{eV}]$</td>
<td>0.07</td>
<td>Schon, Youssef [19]</td>
</tr>
<tr>
<td>$Q_a,[-]$</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>$E_i - E_v,[\text{eV}]$</td>
<td>0.24</td>
<td>Schon, Youssef [19]</td>
</tr>
<tr>
<td>$Q_b,[-]$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$E_t-E_c,[\text{eV}]$</td>
<td>0.22</td>
<td>Murphy [65]</td>
</tr>
<tr>
<td>$Q_1,[-]$</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>$E_c-E_t,[\text{eV}]$</td>
<td>0.08</td>
<td>Murphy [65]</td>
</tr>
<tr>
<td>$Q_2,[-]$</td>
<td>0.000833333</td>
<td></td>
</tr>
</tbody>
</table>

A missing component is the concentration of defects within the rings as both $E_t$ and $Q$ are found independently of concentration. Finding the absolute densities of defects is not possible from only lifetime measurements, but the product of defect concentration times the recombination centers capture cross section (i.e., $N_t\sigma_n$ for p-type samples, and $N_t\sigma_p$ for n-type samples) can be found. Plotting this against the density of strained oxide precipitates, Murphy et al. provides a rough map of how oxide precipitate concentration, both strained and unstrained, relates to defect concentration with a given capture cross section [65]. While this method works for homogenously...
distributed oxygen defects, for the ring defects in particular, the number of oxygen precipitates within the rings is unknown, so this method of determining the relationship of defect concentration to oxide precipitate concentration will not work. The direct determination of the defect concentration is a good next step for this work, but for this study, a range of concentrations were varied to see its impact on the efficiency of solar cells.

5.4 Device modeling with oxygen defects

The 2-D TCAD model used was created to model PERC cells with parameters given in [66]. Both defect 1 and defect 2 are added to the model using $E_t$, $\alpha_n$, $\alpha_p$, and $N_t$. A $J$-$V$ curve is extracted for each $N_t$, but these simulations only took into account a homogeneously distributed defect in a unit cell. The point at which the defects no longer impact performance is found at around $1 \times 10^9$ precipitates/cm$^3$ as this $J$-$V$ curve and the one with no defects are equivalent as shown in Figure 24.

![Figure 24: $J$-$V$ curves output from Sentaurus device for unit cells with homogenously distributed oxygen defects. There are curves for different concentrations, and a $J$-$V$ curve for a Cz-Si cell with no defects.](image)

Using a two-diode fit seen in Equation 5.1, $J_{01}$ and $J_{02}$ were extracted for different concentrations of oxygen defects.

$$J = J_L - J_{01} \left\{ \exp \left[ \frac{q(V + J R_S)}{kT} \right] - 1 \right\} - J_{02} \left\{ \exp \left[ \frac{q(V + J R_S)}{2kT} \right] - 1 \right\} - \frac{V + J R_S}{R_{shunt}} \quad (5.1)$$
where $J_L$ is the photocurrent, $J_{01}$ and $J_{02}$ are dark saturation currents for diode 1 and 2, $q$ is the absolute value of electron charge, $V$ is the voltage, $J$ is the current, $R_S$ is series resistance, $k$ is Boltzmann’s constant, $T$ is absolute temperature in Kelvin, $R_{\text{shunt}}$ is shunt resistance [67].

The $J_{01}$ and $J_{02}$ results of the two-diode fitting are shown in Figure 25. These diode fittings were done by Liu Zhe, a postdoctoral researcher at the MIT PVlab. Linear interpolation between each point was used to determine the $J_{01}$ and $J_{02}$ values assigned to different PL contrast values based on simulated recombination contrast in the next section.

![Graph](image)

**Figure 25:** $J_{01}$ and $J_{02}$ values fitted to Sentaurus-simulated $J$-$V$ curves. This was done using a freely available two-diode fitting program [62].

### 5.5 Simulation of oxygen rings in Griddler

The next step is to take these $J_{01}$ and $J_{02}$ values and assign them to the pixels of a PL image according to the pixel contrast. Two approaches were taken including a binary $J_0$ map and a graded $J_0$ map. For the binary $J_0$ map, white pixels are assigned to any PL pixel of 55% contrast and below, and black pixels to the others. The 55% is chosen because it captures the majority of the ring-effected area. The image shown in Figure 26(b) is the binary $J_0$ map that was uploaded into Griddler. The white pixels represent the defective areas and are assigned the defective $J$-$V$ curve of $N_i = 1 \times 10^{11}$, $1 \times 10^{12}$ and $1 \times 10^{13}$ precipitates/cm$^3$ from Figure 24, and the black pixels represent the non-defective $J$-$V$ curve.
Figure 26: (a) Oxygen rings from binary image, and (b) oxygen rings from gradient image.

The gradient $J_0$ map shown in Figure 26(b) was accomplished by matching simulated radiative recombination ($R_{\text{rad}}$) for different concentrations of defects to percent difference in PL contrast and assigning each pixel a representative $J_0$ similar to the simulations done in [68]. To help elucidate this method, Table 5.2 shows the $R_{\text{rad}}$ contrast from Sentaurus simulations and how they match onto PL contrast. The current maps shown in Figure 26 are normalized to the average current value of all the pixels represented and are inputs for Griddler 2.5 PRO© software, a finite element solver with a built-in database of parameters for solar cells. After the TR process, the rings have been shown to mostly dissolve, and therefore a uniform non-defective $J_{01}$ and $J_{02}$ are put into Griddler to represent the post TR cell. Results from the Griddler simulations with rings and without, are summarized in Table 5.3.
Table 2: Important parameters for end-to-end oxygen modeling.

These include $R_{rad}$ in the last column which is used to interpolate $J_{01}$ and $J_{02}$ for $R_{rad}$ from 0% – 100% with a step of 10%. The contrast between PL pixels is then matched to the ranges covered by $R_{rad}$, so that these interpolated $J_{01}$ and $J_{02}$ values can be assigned to the PL image. As was shown in Figure 24, oxygen defect concentrations below $1 \times 10^9$ no longer greatly impacts parameters and therefore they are labeled equivalently in row 1 below.

<table>
<thead>
<tr>
<th>Oxygen Defect Concentration [cm$^{-3}$]</th>
<th>$J_{01}$ [fA/cm$^2$]</th>
<th>$J_{02}$ [nA/cm$^2$]</th>
<th>$\eta$ (%)</th>
<th>Radiative recombination at MPP [cm$^{-3}$]</th>
<th>Radiative recombination, $R_{rad}$ Contrast (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input into Sentaurus Device</td>
<td>Input $J-V$ curve from Sentaurus, output $J_{01}$ and $J_{02}$ from 2-diode fit</td>
<td>Output from Sentaurus Device</td>
<td>Ratio between each simulated concentration to non-defective area and</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00E+00 ≈ 1.00E+09</td>
<td>163</td>
<td>3.66</td>
<td>22.79</td>
<td>4.00E+20</td>
<td>100.00</td>
</tr>
<tr>
<td>1.00E+10</td>
<td>187</td>
<td>14.2</td>
<td>21.93</td>
<td>2.75E+20</td>
<td>68.82</td>
</tr>
<tr>
<td>1.00E+11</td>
<td>941</td>
<td>14.7</td>
<td>18.86</td>
<td>4.82E+19</td>
<td>12.05</td>
</tr>
<tr>
<td>1.00E+12</td>
<td>8970</td>
<td>5.69</td>
<td>15.14</td>
<td>9.59E+18</td>
<td>2.40</td>
</tr>
<tr>
<td>1.00E+13</td>
<td>32500</td>
<td>12.4</td>
<td>11.83</td>
<td>1.75E+18</td>
<td>0.44</td>
</tr>
<tr>
<td>1.00E+14</td>
<td>112000</td>
<td>50.3</td>
<td>8.34</td>
<td>5.19E+17</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 3: Griddler results from input current map values representing inhomogeneous ring defects.

There is a 0.55% (abs.), 2.72 (rel.) difference between the graded ring defect cell and non-defective cell, and up to a 2.64% (abs.), 13.08% (rel.) change if the rings have defect concentrations as high as $1 \times 10^9$ defects/cm$^3$.

<table>
<thead>
<tr>
<th></th>
<th>binary</th>
<th>gradient</th>
<th>no defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_t = 1 \times 10^{11}$ [cm$^{-3}$]</td>
<td>632</td>
<td>611</td>
<td>590</td>
</tr>
<tr>
<td>$N_t = 1 \times 10^{12}$ [cm$^{-3}$]</td>
<td>40.43</td>
<td>40.43</td>
<td>40.43</td>
</tr>
<tr>
<td>$N_t = 1 \times 10^{13}$ [cm$^{-3}$]</td>
<td>77.62</td>
<td>75.51</td>
<td>73.52</td>
</tr>
<tr>
<td>$N_t = 0$ [cm$^{-3}$]</td>
<td>19.85</td>
<td>18.64</td>
<td>17.55</td>
</tr>
<tr>
<td>$V_{oc}$ [mV]</td>
<td>520</td>
<td>491</td>
<td>464</td>
</tr>
<tr>
<td>$J_{sc}$ [mA/cm$^2$]</td>
<td>38.14</td>
<td>37.98</td>
<td>37.78</td>
</tr>
<tr>
<td>$V_{mp}$ [mV]</td>
<td>average $J_{01}$ [fA/cm$^2$]</td>
<td>398</td>
<td>3245</td>
</tr>
<tr>
<td>$J_{mp}$ [mA/cm$^2$]</td>
<td>average $J_{02}$ [nA/cm$^2$]</td>
<td>7.5</td>
<td>4.4</td>
</tr>
<tr>
<td>$J_{01}$, within rings [fA/cm$^2$]</td>
<td>941</td>
<td>8970</td>
<td>32500</td>
</tr>
<tr>
<td>$J_{02}$, within rings [nA/cm$^2$]</td>
<td>14.6</td>
<td>5.7</td>
<td>12.4</td>
</tr>
<tr>
<td>$J_{01}$, outside rings [fA/cm$^2$]</td>
<td>163</td>
<td>163</td>
<td>163</td>
</tr>
<tr>
<td>$J_{02}$, outside rings [nA/cm$^2$]</td>
<td>3.7</td>
<td>3.7</td>
<td>3.7</td>
</tr>
</tbody>
</table>
The impact of the rings on performance can be visualized in the maps of current density at maximum power point in Figure 27. The ring defect is shown to impact performance in every case as described in Table 5.3. The gradient image distributes the affected ring area more uniformly than the binary images.

Figure 27(a) is the non-defective cell performing at an efficiency of 20.19%, in 27(b) the gradient $J_{01}$ and $J_{02}$ maps are used with a final efficiency of 19.64%, in 27(c) is the binary image with $N_i = 1 \times 10^{11}$ cm$^{-3}$ gives an efficiency of 19.85%, and lastly 27(d) is the binary image with $N_i = 1 \times 10^{11}$ cm$^{-3}$ and an efficiency of 18.64%. These figures and the values they represent can be used in a comparative study to determine a trend of cell performance impact with oxygen defect concentration for both binary and gradient image processing, answering some open question.

![Current Density at MPP (A/cm²)](image)

**Figure 27: Comparison of the current density map made in Griddler at maximum power point.**

Simulated for a cell (a) without rings and (b) with rings as modelled with gradient $J_0$ maps. Then, a binary image is used with a concentration of around (c) $1 \times 10^{11}$ cm$^{-3}$, and (d) $1 \times 10^{12}$ cm$^{-3}$ oxygen precipitates assumed in the rings.
5.6 Discussion & Preliminary Conclusions

This modelling is still in the preliminary stages, but several conclusions have been ascertained so far. The modelling confirms that oxygen rings can impact device performance by a significant amount, affecting up to 35% of the area of a solar cell after processing for this example. The impact on device performance for this particular cell is around 0.3% (abs.), 1.7% (rel.) when using binary $J_0$ map with $1 \times 10^{11}$ cm$^{-3}$, and when using the gradient $J_0$ map, the impact is around 0.6% (abs.), 2.7% (rel.). For the gradient $J_0$ map, the recombination contrast matching the PL contrast within the ring defects matches defect concentrations between $1 \times 10^{10}$ cm$^{-3}$ – $1 \times 10^{11}$ cm$^{-3}$ making the cell defects likely in this range of concentration. This finding indicates that an average of around 450 fA/cm$^2$ are added to $J_0$ and 3 nA/cm$^2$ added to $J_{02}$ for areas inside ring defects.

The modeling with binary $J_0$ maps gives a less accurate representation of the rings impact, as shown with the $1 \times 10^{11}$ cm$^{-3}$ simulation shown in Table 5.3, which shows a 19.85% efficiency which is greater than the gradient image efficiency of 19.64% even though the gradient image has the majority of defects represented below the $1 \times 10^{11}$ cm$^{-3}$ mark. Due to the encompassment of the full range of defect values, the gradient $J_0$ map captures more of the rings impact. Therefore, it is thought that the gradient $J_0$ map is a better method going forward. The usefulness of the binary image is in allowing for specific designation of how many defects are inside the rings demonstrating how the performance might be impacted by different concentrations of defects. For example, the highest defect concentration used is $1 \times 10^{13}$ cm$^{-3}$, which has a 2.64% (abs.), 13.08% (rel.) drop in efficiency as compared to $1 \times 10^{11}$ cm$^{-3}$ which has a 0.3% (abs.), 1.7% (rel.) drop.

Taking defect rings of different shapes or distribution and using the binary maps, it can be shown how much different defect concentrations in the rings can impact the final cell performance.

This multiscale end-to-end modeling framework starting from the nanoscale with oxygen defect parameters extends to macroscale with full-size solar cells (i.e. the area of 156mm×156mm). This framework, once verified experimentally, will have the ability to optimize the solar cell design for ring defects that can occur in Cz-Si. By including both Sentaurus Device and Griddler modelling, more parameters can be tested then is possible by each package alone. For example, different defect parameters, optical generation profiles, and 3D effects can be attempted in Sentaurus simulations while Griddler handles inhomogeneous areal distribution and varied
metallization patterns. Work done by David Berney Needleman on structural defect modeling has also opened up this platform for mc-Si inhomogeneous grain and dislocation defects [REF].

5.7 Future Work

Experimental validation of the model with measured data (e.g. PL images, I-V curves, etc.) from solar cells that are made of Cz-Si wafers with ring defects is a first next step. Including further calibration of the PL image contrast used to designate different defective areas and non-defective areas. There is a phenomenon with the PL technique called “carrier smearing” due to lateral carrier diffusion away from the actual defects [69]. This means that the PL image might show the ring defects covering a larger area than they do in reality. For the saturation current maps imported into Griddler this may exaggerate the impact of the rings on carrier performance. There is a desmearing method using the continuity equation that can be implemented into PL image processing to determine if this issue is large with ring defects [70].

We investigated the impact of oxygen ring defects on solar cell efficiency in this chapter. A step further would be a comparative study of the ring defects before and after different TR treatments. Oxygen defects pose a large drop in efficiency for some portion of every Cz ingot, with the help of predictive process modeling, whether TR is an effective process can be determined as shown in Chapter 4. Then using the PL images of post-TR samples which the ring defect are removed, the end-to-end simulation can predict how a cell should perform after different TR process conditions.

Another future development could be to integrate the I2E process model into the current end-to-end modelling framework. With the I2E process model, a solar cell can be modeled after the TR process when the rings are removed showing the baseline for the cell without rings and 20.19%. Using the I2E Impurity calculator described in Chapter 4, whether the TR process will work for a certain solar cell can be established given input precipitate density and total precipitated and interstitial oxygen. With this information, before and after cell efficiencies can be found in Griddler, determining roughly what concentration of defects are in the rings with PL and recombination contrast comparison. For the cell studied in this case, the total oxygen content is unknown, so I2E cannot be implemented. However, for a full predictive multiscale model this is a measurement that must be included in the procedure, and should be tested in future work.
6.1 Introduction

Oxygen mitigation through the tabula rasa (TR) process has been presented as one approach to tackle the factors limiting PV growth including cost, capital expense (capex), and performance of current crystalline silicon PV modules. However, there are several limitations with implementing TR on a manufacturing line that were enumerated in Chapter 3. There are more strategies with which to tackle high efficiency, low capex, and low cost issues including thinning down silicon wafers [71]. Thinner wafers are defect tolerant that could potentially mitigate or lessen the oxygen defect problem while also lowering material costs [72].

Silicon is the largest single cost-component of a module, and thinner wafers use less silicon. Over half of total module capex lies in feedstock production, crystallization, and wafering which is nearly proportional to wafer thickness [6]. Higher performance is enabled due to the higher voltage of thinner cells. Thin cells are also inherently defect-tolerant, allowing the adoption of lower-cost, lower capex but more defective feedstock and crystallization techniques such as upgraded metallurgical silicon (UMG-Si). This defect tolerance derives from three advantageous physical effects: (1) higher operating voltage, (2) shorter diffusion length requirements for excellent carrier collection, and (3) higher lifetimes for many injection-dependent defects [73][74][75]. The keys to enabling these advantages are excellent surface passivation and light absorption.

The defect tolerance of thin silicon is not a new idea, but it has not been adopted industrially for several reasons. The spot price of silicon, peaking in 2008 at $475/kg, has been hovering around $15/kg in 2017[76], giving no incentive for thinning wafers as silicon is currently considered cheap. Also, thin silicon cells present a handling concern on a manufacturing line as more cells will be lost to breakage. New methods and tools for handling, crack detection, and transfer would
need to be added to the current manufacturing process to prevent yield loss from damaging the less robust thin cells [77] [78]. Given the relatively cheap price of polysilicon feedstock and the problems with implementing thin cells, manufacturers have not taken on thin silicon. However, in the rapid growth scenario, thin silicon is a way to lower capital expenditure while maintaining high efficiencies. Experimental and modeling validation of thin defect tolerance has been explored by Needleman et al. [79] comparing 60 µm vs. 145 µm wafers. Half of these wafers were intentionally contaminated with iron at a concentration of $3 \times 10^{13}$ cm$^{-3}$. Simulations showed that the efficiency potential of thin silicon cells is high, however this study also revealed the importance of superior surface passivation which is required to reach this potential due to surface limitations.

I hypothesize that taking advantage of the defect tolerance of thin cells might be the better solution to deal with oxygen ring defects as well as other extrinsic defects present in material rather than implementing new high temperature processes that need to be optimized for each input material quality. To explore this assertion and the thin silicon advantage more generally, I ask several relevant research questions, (1) At what material quality (as-grown defect concentration) does thin silicon perform better than thicker silicon wafers? (2) What are the efficiency limitations of thin silicon given excellent light trapping and surface recombination velocities? (3) How do wafers containing ring defects specifically perform using thin cells?

### 6.2 Experimental and Modeling details

To show the thin silicon advantage including defect tolerance, silicon heterojunction (SHJ) solar cells shown in Figure 28 were made at the pilot line at Arizona State University (ASU) by Andre Augusto, from commercial grade $n$-type Cz, thickness of 200 µm, resistivity of 3-5 Ω-cm. Two different quality materials are used as measured through effective lifetime. The “standard quality Cz” had an effective lifetime of $\tau_{\text{eff}} = 2.5$ ms, and “lower quality” had $\tau_{\text{eff}} = 1.1$ ms. Thinning the wafers was accomplished with alkaline wet etching + RCA cleaning and conditioning. The “thick” cells are 170µm, and the “thin” cells for this study are 60µm. Hydrogenated amorphous layers with a thickness of 7 nm each were deposited using plasma enhanced chemical vapor deposition (PECVD). Indium tin oxide (ITO) is sputtered on the front and rear surface and silver is sputtered on the rear making electrical contact and reflecting light back into the absorbing layers. The cell is then a ITO/p+/i/Cz/i/n+/ITO-IR/Ag stack. After all layers are deposited or sputtered,
the cell is annealed for 45 min at 200 °C. The cells were measured at ASU using the quasi steady state photo conductance (QSSPC) method using a Sinton lifetime tester WCT-120.

![Figure 28: Silicon heterojunction device.](image)

These were made as Arizona State University and modeled with thick and thin Cz-Si absorbers.

Modeling of the cells was done using the SHJ model developed by Ling et al. [80] in Sentaurus Device [61] with parameters from Filipič et al. [81]. The purpose of the model is to validate with the experimental results and then use it to test the limits of what thin silicon can accomplish in terms of defect tolerance while not sacrificing cell performance. Also, the importance of surface recombination velocity and light absorption can be better understood.

### 6.3 Results

#### 6.3.1 Surface Recombination Velocity

As a continuation of the work done in [79] the first thing to tackle is the importance of surface recombination. Making a thin cell that is adequate to prove defect tolerance requires superior surface passivation. Therefore, using the device model we ask the question: How good of a surface recombination velocity (SRV) is necessary to not limit the cell over the bulk lifetime so that defect tolerance can be tested? SRV's on silicon surface can range from 0.25 cm/s [82] to the thermal velocity of an electron at ~10^7 cm/s. An example is given by a high efficiency industrial PERC cell as recorded in [83], with rear SRV of 90 ± 30 cm/s using an ICP AlO_x/SiN_y stack.

Surface contributions to limiting lifetime are more prominent in thin cells because the higher injection of thinner cells allows a surface of similar passivation to a thick cell impact lifetime more as a greater number of carriers are available for recombination at the surface. Figure 29 shows the potential of good SRV for both thin and thick cells with the effect more pronounced...
for the thinner cells. In this figure, similar light absorption is assumed, pushing thin cells to perform better than thick cells for almost the full range of effective lifetimes and SRVs. In reality, the thicker cell is likely to absorb better than the thinner cell, generating a higher photocurrent which would push the thicker cells to outperform thin cells in some cases. It can be seen that at lower lifetimes (higher defect levels) and lower SRV's (good surface passivation), the thinner cells

![Figure 29: A plot of two devices of different thicknesses while sweeping SRV (cm/s), and effective lifetime.](image)

outperform the thicker cell efficiencies by about 1% (abs.), 5% (rel.). With the light absorption closer to reality, it can be seen that for cells $\tau_{\text{eff}} > 1$ ms for effective lifetime and SRV > 100 cm/s, the thicker cells might perform better.

The impact of the surface is investigated for the experimental cells which were shown to be limited by surface through recombination modeling done by Andre Augusto. The surface accounts for 50% of the bulk recombination in the thicker cells, and more than 80% of the total bulk recombination in the thinner cells.

Modeling the experimental cells shows some discrepancies in both light trapping and surface effects. First, the generation current that is modeled is below that of the cell which indicates the generation profile created does not account for adequate light trapping of the thin cells in reality. Secondly, the open circuit voltage in reality is much lower than the model suggests. The SRV used in the model was 2 cm/s which corresponds to the measured SRV before ITO was sputtered. It is probable that the ITO sputtering damaged the surface passivation increasing the SRV substantially.

**SHJ Model assumptions:**
- $n$-type single crystalline material
- Resistivity, 3.09 Ω-cm
- SRV, varied between 10 to 1000 cm/s
- Optical generation profiles created using Opal2 with random upright pyramid surface
Another reason why the $V_{oc}$ is lower than expected could be that the higher injection regime promised by thinner cells is not necessarily achieved due to inadequate absorption, so the $V_{oc}$ is not benefitting from the thin cell, high injection property.

To determine what SRV would match experimental measurements, simulations were completed while sweeping the surface recombination velocity. Good agreement with experiment was found between 800-1200 cm/s for front SRV and back maintained at 10 cm/s. This high SRV could therefore in reality be split between both front and rear surfaces more evenly, around 400-600 cm/s each. Figure 30 compares the simulations done with the best fit SRV and the 2 cm/s value from before ITO sputtering for both 60 μm to show the discrepancy. The difference in $V_{oc}$ is between 20-30 mV, a trend that holds for both thick and thin cell.

**Figure 30: Simulated vs. experimental $J-V$ curves of thin Cz-Si.** Simulations were done with both lower quality, $\tau_{\text{eff}} = 1.1$ ms in (a) and standard quality, $\tau_{\text{eff}} = 2.5$ ms in (b), demonstrating the higher SRV of around 800 cm/s needed for fit $V_{oc}$ to approach the measured.
It can be speculated that if even better SRV is maintained for the cells without ITO sputtering damage, the thinner cell advantage would continue and the model would not need to be calibrated with SRV as was needed in Figure 30.

The two thicknesses are compared in Figure 31 showing an increase in $V_{oc}$ for thin over thick cells of between 15-20 mV for both simulation and experiment. The generation current in the experimental cell is still higher than simulated accounting for the discrepancy in efficiencies due to inadequate light absorption in the simulation. Also, in Figure 31 (a) showing the lower quality material, the thinner cells achieve higher efficiencies than the thicker cells, while for the standard Cz-Si in Figure 31 (b), the thinner cells lose in performance to the thicker cells. This demonstrates the defect tolerance of thinner cells in experiment and simulation. Given the cost saving that could come from using lower quality Cz-Si over standard Cz-Si, as well as savings from using less material for thinner cells, an argument can be made for using thin cells as a high efficiency, low cost solution.

![Figure 31: Thick vs. thin cell J-V curves.](image)

Both simulated and experimental demonstrate the bump in $V_{oc}$ for thinner cells in both lower quality (a) material with $\tau_{eff} = 1.1 \text{ ms}$, and standard quality Cz-Si material (b) with $\tau_{eff} = 2.5 \text{ ms}$. 
In its most idealized form, simulations show that with SRV of 2-3 cm/s, $V_{oc} = 758$ mV is possible pushing potential efficiencies for 60 µm silicon wafers to 23.71% for standard material, and 22.94% for lower quality material. With more advanced light trapping techniques, these efficiencies can be even higher as $J_{sc}$ increases.

### 6.3.2 Defect Tolerance

The limits of defect tolerance are also explored for thin vs. thick cells of varying material quality and excellent surface passivation, SRV = 1 cm/s front and 10 cm/s rear. Figure 32 shows the theoretical SHJ device performances given common impurities, $[\text{Fe}] = 1 \times 10^{14}$, $[\text{Fe}] = 1 \times 10^{12}$, $[\text{Ni}] = 1 \times 10^{10}$ [atoms/cm$^3$]. These simulations show that at lower lifetimes (i.e. higher defect levels), thin cells perform better than thick cells. Even with high iron concentrations at $[\text{Fe}] = 1 \times 10^{14}$, thin cells can theoretically reach above 19%. According to these simulation results, thin cells could allow for the use of more defective material while maintaining the high performance of current thick wafer devices. With appropriate passivation, theoretical device performance for thin Si cells could be > 24%.

![Figure 32: Theoretical efficiency potentials of thick and thin devices with different effective lifetimes.](image)

SRV = 1 cm/s. Thinner cells perform better at lower lifetimes, and the phenomena of thinner cells operating at higher minority carrier injection is demonstrated clearly. Three metal impurity lifetime curves including $[\text{Ni}] = 1 \times 10^{10}$, $[\text{Fe}] = 1 \times 10^{12}$, and $[\text{Fe}] = 1 \times 10^{14}$ are shown to show device potentials for cells with impurities such as these.
6.3.3 Defect Tolerance for Oxygen Mitigation

Now that the importance of SRV, and the defect tolerance of thin cells have been established, the question remains if using thinner cells might be the better option over tabula rasa for dealing with oxygen defect mitigation.

The end-to-end modeling techniques as described in Chapter 5 are a good option for exploring this question. Cells with different amounts of oxygen related defect rings are simulated for both thick and thin cells to determine thin cell tolerance to oxygen rings. As can be seen in Figure 33 (a), the point at which the concentration of oxygen defects become lifetime limiting for 180 μm thick cells is around $5 \times 10^9 - 1 \times 10^{10} \text{ cm}^{-3}$ for the minority carrier injection in which these cells normally operate ($< 10^{15} \text{ cm}^{-3}$). In Figure 33 (b) is a representative ring defect from [19] with calibrated PL image that shows the lifetime dropping from around 6 ms outside the defect area to ~1-2 ms within the ring which can be found on the lifetime graph at in Figure 33 (a). As first mentioned in Chapter 5, the point where oxygen defects no longer influence effective lifetime is $N = 1 \times 10^9 \text{ cm}^{-3}$.

![Figure 33](image.png)

**Figure 33:** Minority carrier lifetime components of samples with oxygen defects. These include radiative recombination, auger recombination and the contribution of oxygen defects ($N$). It can be seen that the increasing oxygen defects decrease the lifetimes until this is the dominant contribution to lifetime.

For the thinner cells, it is expected that the lifetime limiting number of oxygen defects will prove to be more than the $5 \times 10^9 - 1 \times 10^{10} \text{ cm}^{-3}$, so that the thinner cells can tolerate higher concentration of ring type defects without loss in performance. As was explained in previous sections and can be seen in Figure 34, thinner cells present a trade-off between increase in open
circuit voltage ($V_{oc}$) and loss of light absorption ($J_{sc}$). It can be seen for the more defective portion of the oxygen ring cells at $[N] = 1 \times 10^{11}$ cm$^{-3}$, the 50 µm cell performs better due to higher injection, but this is a tradeoff in the non-defective portion represented by the $[N] = 0$ cm$^{-3}$ cell which losses significantly in current density. From this, it can be seen that for thinner cells to perform better than thick with oxygen rings there must be a ratio of defective area to non-defective area that maximized both current density and voltage for thin cells.

**Figure 34: J-V curves for cells of different thickness and defect concentration.**

The best performing is the thick, device with no defects, however, if ring defects are present, the thinner cell with higher open circuit voltage performs better.

Using the multiscale end-to-end modeling framework described in Chapter 5, a two-diode fit was done on Sentaurus generated J-V curves for a range of defect concentrations for a 50 µm and 100 µm cell to compare with the 180 µm simulations. In Figure 35, the $J_{01}$ values for each thickness are shown together. At the oxygen defect concentrations between $[N] = 1 \times 10^{10}$ cm$^{-3}$ and $[N] = 1 \times 10^{12}$ cm$^{-3}$, the thinner cells show a significant decrease in dark saturation current, indicating a better performing cell. As the concentration range between $[N] = 1 \times 10^{10}$ cm$^{-3}$ and of $[N] = 1 \times 10^{11}$ cm$^{-3}$ has been shown in Chapter 5 to be the most likely concentration within ring defects, this could mean that thin cell devices with ring defect materials could perform better than thicker devices.
Figure 35: Dark saturation current ($J_0$) plotted for several oxygen defect concentrations. A drop for thinner cells at defect concentrations between $1 \times 10^{10}$ and $1 \times 10^{12}$ is shown.

Table 4: Results from Griddler simulations using cells of different thicknesses. These include 50, 100, and 180μm and defect concentrations from $1 \times 10^9$ to $1 \times 10^{12}$ and both binary and gradient image processing.

<table>
<thead>
<tr>
<th>$N_t$ range [cm$^{-3}$]</th>
<th>$N_t=1 \times 10^{11}$ [cm$^{-3}$]</th>
<th>$N_t=1 \times 10^{12}$ [cm$^{-3}$]</th>
<th>$N_t=1 \times 10^{11}$ [cm$^{-3}$]</th>
<th>$N_t=1 \times 10^{12}$ [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{OC}$ [mV]</td>
<td>636</td>
<td>617</td>
<td>634</td>
<td>610</td>
</tr>
<tr>
<td>$J_{SC}$ [mA/cm$^2$]</td>
<td>40.43</td>
<td>40.43</td>
<td>40.43</td>
<td>40.43</td>
</tr>
<tr>
<td>$FF$ [%]</td>
<td>77.24</td>
<td>76.42</td>
<td>76.46</td>
<td>75.53</td>
</tr>
<tr>
<td>$\eta$ [%]</td>
<td>19.84</td>
<td>19</td>
<td>19.58</td>
<td>18.64</td>
</tr>
<tr>
<td>$V_{mpp}$ [mV]</td>
<td>523</td>
<td>499</td>
<td>519</td>
<td>491</td>
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<tr>
<td>$J_{mpp}$ [mA/cm$^2$]</td>
<td>37.95</td>
<td>38.1</td>
<td>37.72</td>
<td>37.99</td>
</tr>
<tr>
<td>average $J_{01}$ [fA/cm$^2$]</td>
<td>193.4</td>
<td>2114.2</td>
<td>225.4</td>
<td>3324.0</td>
</tr>
<tr>
<td>average $J_{02}$ [nA/cm$^2$]</td>
<td>17.4</td>
<td>1.4</td>
<td>28.8</td>
<td>2.9</td>
</tr>
<tr>
<td>$J_{01}$, within rings [fA/cm$^2$]</td>
<td>233.0</td>
<td>5721.0</td>
<td>324.46</td>
<td>9177.81</td>
</tr>
<tr>
<td>$J_{02}$, within rings [nA/cm$^2$]</td>
<td>46.0</td>
<td>0.4</td>
<td>78.61</td>
<td>4.54</td>
</tr>
<tr>
<td>$J_{01}$, outside rings [fA/cm$^2$]</td>
<td>172.0</td>
<td>172.0</td>
<td>172</td>
<td>172</td>
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<tr>
<td>$J_{02}$, outside rings [nA/cm$^2$]</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
This theory is tested by mapping the new $J_{01}$ and $J_{02}$ values for different cell thicknesses using the PL image from Chapter 5, and modeling these in Griddler. The results are shown in Table 6.1, and the efficiencies are plotted in Figure 36. Efficiencies are the highest for the non-defective cells, but for the cells with defects, the 50 $\mu$m cells perform better for both $1 \times 10^{11}$ and $1 \times 10^{12}$ cm$^{-3}$. The gradient image processing shows the thicker cell performing slightly better.

![Figure 36: Cell efficiencies plotted for several cell thicknesses of 50, 100 and 180 $\mu$m.](image)

6.4 Discussion & Preliminary Conclusions

Several questions were explored in this chapter. One question was at what material quality is thin silicon a better choice. To explore this question, experimental results on thick and thin cells of different quality were modelled. The importance of surface passivation for thin cells is explored as it has limited experimental results. Thinner cells are more susceptible to surface recombination due to operating at higher injection, and having a smaller thickness such that more carriers can reach the surface. Modeling the experimental results shows a discrepancy in the SRV between simulation and experiment. This can be explained by ITO sputtering damaging on the surface such that a loss in 15-20mV occurs in the experimental cells. A range of SRV's are tested and the SRV that matches the experiment is between 400-800 cm/s. Also, the thick and thin cells are compared demonstrating the advantage of the thin cell for lower quality material, performing $\sim$0.3% (abs.)
better for both simulation and experiment. For the standard Cz-Si material, the thicker cell performs better by ~0.2 – 0.7\% (abs.).

Another question asked was: What are the efficiency limitations of thin silicon given excellent light trapping and surface recombination velocities? To study this question, a range of simulations was run with different effective lifetimes at 50 \( \mu \)m, and 180 \( \mu \)m. At low lifetimes, thin cells perform better, and SRH lifetime curves representing different defect levels are pictured to show where a cell would operate given different levels of defects. The efficiency potential of thin silicon cells was found to be above 24\% for SHJ cells with equivalent light trapping to thicker cells. With high levels of contamination such as concentrations at \([Fe_i] = 1\times10^{14}\), thin cells are shown to be able to reach above 19\%, higher than the efficiency of the 180 \( \mu \)m cells. This modeling work shows that cells could allow for the use of more defective material while maintaining the high performance of current thick wafer devices.

The last question addressed in this chapter is whether thin cells might be a good option for dealing with the specific problem of oxygen ring defects in silicon. It is shown that thinner cells perform better than thicker cells in the defective area. Outside of the defective area, the thicker cells prove better. Therefore, it is a tradeoff between the two area to determine the optimum. By using the multiscale end-to-end modeling package described in Chapter 5, preliminary results can be mapped out of at what point thinner cells become the better choice. The cross over point for thickness appears to be between 50-100\( \mu \)m where 100\( \mu \)m cells do not perform better than 180 \( \mu \)m cells with these defect concentrations but 50 \( \mu \)m cells do. Also, there appears to be a cross over point for defect concentration around \(1\times10^{11}\), below which thinner cells do not benefit from defect tolerance enough to overcome the higher light absorption of the thicker cells.

Using 50-100 \( \mu \)m cells could save one- to two-thirds the material cost for the solar industry today if the cells maintained the same efficiencies. It has been shown here that this is possible with appropriate light trapping and passivation. Furthermore, due to defect tolerance, worse material that is lower cost could potentially be used for these thinner cells, adding another advantage for using thinner cells. Several concerns exist for handling of such thin cells on a manufacturing line. These concerns are under research currently including a crack detection system designed for thinner cells as well as wire snipping tools that use less force.
6.5 Future Work

A good question to explore as a next step is whether thin silicon or *tabula rasa* (TR) are the better option for solar manufacturers when aiming to control oxygen defects. If optimizing for the highest efficiency cell, TR would appear to be the better option as it can erase ring defects completely. However, when cost is taken into consideration, thinner cells may take care of the oxygen rings enough such that efficiencies are kept in a profitable range, a new high temperature step is not needed, and between one- and two-thirds of the material costs are saved. However, the thin silicon option would require a high up front cost to change a manufacturing line enough to avoid yield loss from breakage of thinner cells. With the appropriate retrofits, this could be the better option in the long term. A full cost benefit analysis of each option should be completed to weigh these considerations.
To scale up photovoltaics to the capacity needed to help in the fight against climate change, several paths are presented for research including increasing efficiency, lowering variable costs, and lowering the capital expenditure for starting a new plant (fixed costs). One problem that currently negatively affects efficiency and also creates yield loss (thereby increasing variable cost) are oxygen related defects in monocrystalline silicon (Cz-Si) which makes up about 40% of the entire solar market. These defects are present in 1/4th to 1/3rd of all Cz-Si ingots. Oxygen defects are recombination active in several forms, the most harmful being large precipitates. Interstitial oxygen is a non-recombination active form of oxygen in silicon, and therefore creating a process that will reliably put oxygen in interstitial form without otherwise negatively affecting the cell is desired.

One method for mitigating oxygen defects is a high temperature processing step called *tabula rasa* (TR), described in detail in Chapter 3, that could be added to a cell manufacturing line. This manufacturing process addition is predicated upon several new oxygen measuring techniques being added to industrial capabilities including Fourier Transform Infrared spectroscopy for measuring interstitial oxygen content and also either defect etching or potentially Transmission Infrared Microscopy for oxygen precipitate measurement. More work is being done to determine the best precipitate measuring method. With these measurements, a predictive process model like I2E, presented in Chapter 4, can be employed to guarantee that TR will accomplish complete oxygen precipitate dissolution, putting oxygen in a non-recombination active form.

To build this predictive capability, a kinetic model created in the PVlab was adopted for oxygen defects and an experiment to find out the energy limiting step in the TR process was performed. During these experiments several important things about TR were observed including best practices for setting up a TR furnace as listed in Chapter 3. Also, the TR process is shown to
be highly dependent on input wafer quality especially with regard to oxygen precipitate size. A range of precipitate sizes is found to be the most likely explanation for why more and more precipitates dissolve at higher temperatures. Even at the highest temperature (1290°C) and longest time (30 min) process, not all precipitates dissolved. This indicates that some precipitates are too large to dissolve at this temperature and that these remaining precipitates above the critical size are slowly dissolving to the solid solubility limit.

The result of the experiment was that the process is found to be kinetically limited, meaning that the activation energy extracted from precipitate dissolution curves was found to be equal to the migration enthalpy recorded in literature. With this knowledge, Fick’s Law of diffusion is used in I2E to predict the dissolution for different TR steps. It is found that I2E is effective for material with small enough precipitates such that they are below the critical size at that temperature. The oxygen defects present in solar materials are general nano-precipitates so the high likelihood that all oxygen is in a small enough size to dissolve makes the use of I2E very promising.

Oxygen defect modeling was also extended beyond I2E to include a multiscale end-to-end modeling platform that starts with nanoscale oxygen defect parameters input into Sentaurus device modeling for small unit cells. Next, double diode fits of Sentaurus results are performed, and the parameters ($J_{01}$ and $J_{02}$) from these fits are used to make current maps from PL images. The current maps are used as inputs for the finite element solver, Griddler to capture the inhomogenous effects of oxygen rings on cell performance. This multiscale modeling platform is used to demonstrate the impact on cell performance from ring defects. Two different image processing techniques are tested including binary ($[N] = 1 \times 10^{11}$ defects/cm$^3$) and gradient images which give between 1.7% - 2.7% (rel.) drop in efficiency. If the binary image is used with $[N] = 1 \times 10^{13}$ defects/cm$^3$, up to 13% (rel.) drop in efficiency is demonstrated. These results indicate that an average of around 450 fA/cm$^2$ are added to $J_{01}$ and 3 nA/cm$^2$ added to $J_{02}$ for areas inside ring defects. Experimental validation of the model with measured data from solar cells that are made of Cz-Si wafers with ring defects is the first next step for this work. Also, integrating the I2E process model into the end-to-end modelling framework would enable a more powerful predictive model for use in industry.

TR is a promising solution for oxygen defect mitigation but additional thermal budget and new equipment costs could prove prohibitive. Another potential method for mitigating oxygen defects is using thin silicon cells below 100 μm. This has several advantages including defect
tolerance, and lower material cost due to less material being used. Defect tolerance in thin devices comes from (1) higher operating voltage, (2) shorter diffusion lengths due to less thickness, and (3) higher lifetimes for many injection-dependent defects [73][74][75].

Modeling of the potential of thin silicon devices demonstrates this defect tolerance as lower quality material is shown to perform better in thin devices over thicker devices. Lower quality material performs ~0.3% (abs.) better for both simulation and experiment in thinner devices, while standard Cz-Si material performs ~0.2 – 0.7% (abs.) better in thicker materials. Therefore, an optimal point could be found when the small drop in efficiency is worth the tradeoff for thinner cells with a 2-3× material cost reduction.

Physically the reason thinner cells do not perform as well in higher quality materials is due to the lesser light absorption in thinner cells as well as the need for better surface passivation. Therefore, at higher lifetimes or with poor surface quality, thinner cells do not perform as well as thicker cells. If excellent surface passivation (SRV = 1 – 5 cm/s) or advanced light trapping techniques are employed in thinner cells, the potential for >24% silicon heterojunction cells with thin absorbers is shown to be possible. If a harmful amount of impurities is introduced to the cell described above, for example concentrations of [Fei] = 1×10^{14}, then thin cells can still reach efficiencies of over 19%, around a 1% (abs.) efficiency gain over thick cells with these defects.

The multiscale end-to-end modeling package developed for determining the impact of inhomogeneous defects on cell performance was also used to show the difference between thin and thick cells with ring defects. From Sentaurus device simulations, the area outside the rings is shown to perform better with thick cells (180µm), and the area inside the ring defect is shown to perform better with thinner cells (50µm). Within the ring defects, the thickness at which thinner cells begin to perform better is between 50-100µm, where 100µm perform worse than 180 µm cells with these defect concentrations, but 50 µm cells perform better. Also, when oxygen defect concentrations reach below [N] = 1×10^{11} cm^{-3}, thinner cells no longer perform better than thick cells. From preliminary modeling results, thinner cells perform better at defect concentrations of [N] = 1×10^{11} and 1×10^{12} cm^{-3} when using the binary image processing, while the gradient image processing shows little difference between the 180µm and 50µm cell performance.

The question remains whether the thinner cell approach is a better option than TR. The answer to this is not straightforward as it depends on the constraints of the industry as well as further research done on the TR process and thin silicon manufacturing. If optimizing for the
largest yield of highest efficiency cells, then TR is most likely the better option as it rids cells of ring defects entirely, especially with a predictive model guaranteeing this outcome. A cost analysis is needed of how much adding TR to a cell line costs vs. how much extra profit is earned by gaining back the yield previously lost to oxygen defects.

Also, there may be a point at which the effects of oxygen defects could be suppressed enough by using thin silicon that the cost of adding TR would not be worth its implementation. For example, if polysilicon prices rise precipitously, then thinner cells will start to become an attractive option due to the reduction in material cost of 2-3x. If the costs of retrofitting a cell line to handle thinner cells is already being spent and is not a part of the cost analysis for comparing TR vs. thin cells, then the gain in efficiency from thin cell defect tolerance may make TR no longer a good option.

With this work several tools are now in place to answer relevant industry questions about oxygen defect mitigation. These include a TR setup at MIT with high temperature capabilities, a predictive process model developed for oxygen dissolution during the TR process, and the multiscale end-to-end modelling used to predict the cell efficiencies of inhomogeneous defects for both thin and thick cells. With the appropriate cost modeling, these tools can help guide industry decisions with regard to oxygen defect mitigation as the silicon solar cell market continues to evolve.
REFERENCES


