Towards the Development of a Horizontal Ribbon Growth Process to Produce Thin, Monocrystalline Silicon Sheets via the Stabilization of the (111) Plane in Undercooled Melts

by

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Abstract

A new manufacturing process that directly produces thin, monocrystalline silicon wafers would significantly reduce the cost and energy used to make high efficiency, crystalline-silicon solar panels. Although alternative silicon wafer manufacturing processes have been pursued for decades, only the Horizontal Ribbon Growth (HRG) process has ever demonstrated monocrystalline silicon ribbons. Unfortunately, these ribbons have been too thick for commercial use and the HRG process model cannot explain either its inability to produce thin ribbons or what conditions destabilize this process at high pull rates. This work therefore develops a new understanding of how the HRG process stably grows monocrystalline silicon ribbons and investigates a new approach to overcome its inherent process limitations.

This work develops the first analytical thermal model of the HRG process that consistently predicts the conditions that destabilize the process and the final ribbon thickness. For the HRG process parameters reported by Kellerman, this model calculates that 25-55% of the latent heat generated at the leading-edge solidification interface can stably dissipate through the undercooled liquid ahead of the interface. These results support Kellerman’s theory that the HRG ribbon’s leading-edge solidification interface is stabilized by the growth kinetics of the (111) plane. Process windows made from this model reveal the HRG process’s inherent limitations in producing thin ribbons, which necessitates a new approach for growing monocrystalline silicon ribbons.

This work develops a new approach for growing monocrystalline silicon ribbons where an angled (111) leading-edge solidification interface propagates in a defined silicon film. This involves designing and constructing a high temperature semiconductor demonstration furnace that melts, seeds, and solidifies a silicon film by rapidly extracting heat from the ribbon surface with a helium jet at rates up to 92 W/cm². This work develops a fine-gauge thermocouple apparatus that directly measures the temperature profile of a silicon film’s solidification interface as it travels through this furnace. Measured temperature profiles of the thin silicon film’s solidification interface show predicted high levels of undercooling in the liquid ahead of the interface. This work presents the silicon seeds grown in the demonstration furnace and outlines next steps to enable stable monocrystalline growth.
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Chapter 1: Introduction

1.1 Introduction:

Photovoltaic cells directly convert high energy photons, typically from sunlight, into electricity. Since their invention in the early 1950s, photovoltaics have expanded from niche applications in the space industry to a presence in the world energy market. Over the last decade, the solar panel industry has grown 35-44% annually [1, 2]. Despite this impressive growth, solar panels still do not provide an economic alternative to utility power for most situations without subsidy [3].

Over 57% of the energy used to produce a crystalline silicon photovoltaic cell is presently incurred during the manufacturing of the silicon wafer substrate[4, 5]. Today, high quality monocrystalline silicon wafers are made by wire-sawing silicon ingots produced by the Czochalski (CZ) process. This sawing process wastes over half the silicon ingot as kerf or sawdust. The CZ process is slow and requires expensive, sophisticated crystal growth equipment. A manufacturing process that could directly create thin sheets of monocrystalline silicon could dramatically reduce the energy consumption and cost of solar panel manufacturing.

Although there have been many attempts to develop a process for directly producing silicon sheets for photovoltaics, only the Horizontal Ribbon Growth (HRG) process has ever demonstrated the potential to produce monocrystalline material. The HRG process grows a silicon ribbon on the surface of an open crucible of melt which is then horizontally removed over the edge of the crucible, as shown in Figure 1.1a. It was originally thought that this process could achieve high process rates because the long, leading-edge solidification interface could dissipate the majority of its latent heat directly through the solid ribbon above the interface, as shown in Figure 1.1b[6, 7]. This approach was first proposed by William Shockley in 1962, and the first demonstration of monocrystalline silicon material was achieved by Kudo in 1980 [6, 7].
Figure 1.1: a) Illustration of the Horizontal Ribbon Growth (HRG) process where a silicon ribbon grows on the surface of a crucible of melt and is subsequently pulled horizontally off the edge the crucible. [8] b) The latent heat dissipated from the leading-edge solidification interface is traditionally thought to be removed via heat loss from the ribbon surface directly above the solidification interface [6, 7]

Unfortunately, the HRG process has not been able to stably grow silicon ribbons thin enough for commercial solar cells. To date, the thinnest ribbons grown by the HRG process have been over 600 μm, compared to the wafer thickness typically used for solar cell manufacturing of under 200 μm. Furthermore, this process has been shown to destabilize at process rates faster than 2 mm/sec [6], resulting in the facetted dendritic growth [9] shown in Figure 1.2b.

Figure 1.2: a) Mirror surface of a stably grown monocrystalline silicon ribbon produced by the HRG process [9] and b) the surface of a ribbon where the interface became unstable and decayed into facetted dendrites [9]
The thermal models developed for the HRG process have not been able to explain its inability to produce thin ribbons or what conditions destabilize the process at high pull-rates [6, 8, 10, 11]. Furthermore, Kellerman has recently provided new evidence that suggests the leading-edge solidification interface of the HRG process does not resemble the long, “slender wedge” profile illustrated in Figure 1.1b. Instead, Kellerman proposes that the leading-edge solidification interface is formed by a flat (111) plane held at a fixed $\theta_{111}$ to the surface, as shown in Figure 1.3. This new evidence suggests that the latent heat generated at the leading-edge solidification interface dissipates through the liquid ahead of the interface, the ribbon surface above the (111) plane, and the melt-supported ribbon downstream of the leading edge solidification interface.

![Figure 1.3: Proposed profile of the HRG's leading-edge solidification interface where a flat (111) plane holds the angle $\theta_{111}$ to the interface. Heat extracted from the surface of the liquid, ribbon surface above the (111) plane, and melt-supported ribbon downstream of the leading edge solidification interface all potentially dissipate a significant amount of latent heat from the leading-edge solidification interface.](image)

Kellerman’s reported insights have tremendous implications for our understanding of the HRG process and its prospective potential to grow thin silicon ribbons. Silicon’s (111) plane grows via a “step-and-spread” mechanism that stabilizes its solidification interface in process conditions that would destabilize all of silicon’s other growth directions.[12-14] Leveraging the stability of this (111) plane potentially allows for a process where the latent heat generated at the leading-edge interface dissipates through the liquid ahead of the interface.

However, the potential of the HRG process to yield commercially viable, thin ribbons still remains unclear. Although Kellerman has published many key attributes of produced ribbons and the conditions that give rise to the instability of the HRG process, there is no representative HRG thermal model that can interpret these conditions or assess the feasibility of proposed process improvements. To
understand the thermal conditions that destabilize the HRG process from these reported values, this work develops a new analytical model of the HRG process that assumes a flat, angled-leading-edge solidification interface that can remain stable when exposed to undercooled liquid. This work uses this model to understand the heat transfer involved at the HRG process' leading-edge solidification interface and the inherent limitations of this process to produce thin ribbons. Temperature profiles made by this model with Kellerman's reported conditions support the theory that a significant fraction of the latent heat generated from the (111) leading-edge interface dissipates through the liquid ahead of the solidification interface. Furthermore, this model reveals that there is no process window for the conditions presented by Kellerman for producing ribbons thin enough for commercial solar cell use ($t_f < 200 \, \mu m$) and therefore presents different conditions to improve process performance.

This work then experimentally investigates one approach for growing monocrystalline ribbons that propagates an angled (111) leading-edge solidification interface in a defined silicon film. As illustrated in Figure 1.4, constraining the geometry of the ribbon not only limits the ribbon thickness, but potentially also enables significantly higher maximum process rates than the HRG process.

![Figure 1.4: Concept illustration of the proposed process for growing monocrystalline silicon ribbons where an angled (111) plane is propagated in a silicon film. The oxide isolates the silicon film from the supporting substrate.](image)

To explore the potential of the proposed process, this work designed and constructed a high-temperature semiconductor demonstration furnace that melts, seeds, and solidifies a silicon ribbon with a high intensity cooling profile. Figure 1.5 shows a concept illustration of the constructed furnace and a silicon film growing in the cool zone. We also develop the material system for encapsulating a silicon seed in a non-nucleating, structural oxide and supporting the seed through the furnace. This work develops a fine-gauge thermocouple apparatus that directly measures the temperature profile of a silicon film's solidification interface as it travels through this furnace. Measured temperature profiles of
the thin silicon film's solidification interface show predicted high levels of undercooling in the liquid ahead of the interface. Silicon seeds grown in the demonstration furnace exhibit the beginnings of a stable monocrystalline silicon interface. However, small tears in the oxide nucleate new grains ahead of the interface, thus resulting in polycrystalline ribbons. This work concludes with outlining future steps to enable monocrystalline silicon films.

Figure 1.5: Conceptual diagram of the demonstration furnace for investigating the potential of propagating an angled (111) interface in a defined silicon film

1.2 Thesis Organization:

This work reviews the opportunity, feasibility, and technological capability of directly producing high quality sheets of monocrystalline silicon that are thin enough for commercial solar cells in Chapter 2. Chapter 3 then develops a thermal model of the HRG process and presents options for developing a commercially viable monocrystalline ribbon process that stably dissipates latent heat through the liquid ahead of the interface. Chapter 4 proposes a process design for growing monocrystalline silicon ribbons by directly solidifying thin, encapsulated films of silicon. This chapter also discusses the desired thermal profile of the process and the design and construction of the experimental furnace. Chapter 5 discusses the material systems developed to define and maintain a silicon film in the demonstration furnace and the fine-gauge thermocouple assembly used to measure the temperature profile of the solidifying
ribbon. Chapter 6 discusses the furnace’s measured cooling intensity in the cool-zone and the directly measured temperature profiles of the silicon films’ solidification interface. Chapter 7 concludes this work and recommends future work. Detailed descriptions of each chapter are found below.

1.2.1 Overview of Chapter 2: Literature Review and Background

The goal of this chapter is to understand the opportunity, feasibility, and technological capability of directly producing high-quality sheets of monocrystalline silicon. It begins by describing how the motivation for developing kerf-less silicon wafer processes has evolved since the 1950s and the present commercial context for developing a monocrystalline silicon ribbon manufacturing process. This chapter reviews the crystal growth mechanics relevant to silicon solidification systems and outlines the different conditions for stably growing a monocrystalline solidification interface. This work then goes on to discuss the status of existing silicon ribbon manufacturing processes, specifically how the HRG process has uniquely demonstrated the ability to stably grow monocrystalline silicon ribbons. Chapter 2 continues by discussing this process’ present limitations in producing commercially viable ribbons and how existing process models do not predict these limitations. This chapter calls for a new analytical model of the HRG process and for a deeper understanding of the conditions needed to sustain the stable growth of a monocrystalline ribbon process with an angled (111) leading-edge solidification interface.

1.2.2 Overview of Chapter 3: Horizontal Ribbon Growth Heat Transfer Model with (111) Leading-Edge Solidification Interface

This chapter develops the first analytical thermal model of the HRG process that consistently predicts the conditions that destabilize the process and the final ribbon thickness. To determine reasonable assumptions for this model, Appendix A develops a series of scaling relationships and simple heat transfer models to approximate the heat flows in both the liquid and solid ribbon bordering the leading-edge solidification interface. A MATLAB script combines these analytical models and, for a given set of process conditions, determines the steady-state horizontal thermal profiles in both the liquid and solid ribbon bordering the leading edge interface and the final ribbon thickness. For the process conditions reported by Kellerman, results from this model support the theory that the HRG process can remain stable even when a significant fraction (25-55%) of the latent heat generated at the leading-edge interface dissipates through undercooled liquid ahead of the interface. However, this program also shows that ribbons thin enough for commercial solar cells are not possible for the process conditions reported by Kellerman. Process windows created from the model suggest that higher cooling intensities
or lower levels of contamination could enable thinner HRG ribbons. However, this model claims that the cooling intensities needed for <200 μm ribbons are almost double what has been achieved to date, thus calling for substantial engineering development. This identified limitation of the HRG process necessitates the new approach for growing monocrystalline silicon ribbons developed in Chapter 4.

1.2.3 Overview of Chapter 4: Process and Equipment Design for Growing Monocrystalline Silicon Films

Chapter 4 presents a new approach for growing monocrystalline ribbons that propagates an angled (111) leading-edge solidification interface in a defined silicon film and outlines its potential advantages over the HRG process. For this proposed process, this work designs and constructs a demonstration furnace that can melt, seed, and solidify a ribbon with an intense cooling profile. This involves designing a cool zone that impinges a high intensity cooling jet on the surface of the ribbon to dissipate latent heat from the ribbon's solidification interface. For this proposed cool zone, this work calculates the expected heat extraction intensity for each mechanism of heat loss from the ribbon surface as a function of the jet's temperature. Insights from these calculations guide the design and construction of the heater assemblies, the high intensity cooling jet, and the apparatus for moving and supporting a thin film of silicon through the furnace. This chapter concludes with a presentation of the complete demonstration furnace constructed to investigate this approach for growing monocrystalline silicon ribbon films.

1.2.4 Overview of Chapter 5: Materials and Methods: Silicon Film Preparation, Fine-Gauge Thermocouple Apparatus and Procedure for Acquiring Temperature Profiles

Chapter 5 presents the materials, apparatus, and procedure for measuring the thermal profile of the demonstration furnace and of the silicon film's solidification interface as it travels through the furnace. This involves developing a material system that defines a thin, silicon film that can remain stable as it melts and solidifies in the demonstration furnace. This chapter describes the development of a fine-gauge thermocouple assembly that remains in direct contact with the silicon film as the film melts and solidifies while traveling through the demonstration furnace. This chapter concludes by discussing the procedure used for measuring the thermal profile of the film as it melts, seeds, and crystallizes in the demonstration furnace.

1.2.5 Overview of Chapter 6: Measured Thermal Profiles and Experimental Results

Chapter 6 presents the measured cooling intensity of the demonstration furnace and the temperature profiles of a silicon film's solidification interface as it travel through this furnace's cool zone. This chapter shows a linear relationship between the demonstration furnace's cooling intensity and the flow rate through the helium jet. This chapter also shows that positioning the helium jet too close (<7 mm) to the
edge of the graphite chuck in the hot zone causes an undesirable thermal profile in the hot zone. Thermal models fitted to the measured temperature profiles reveal the demonstration furnace can impose up to a 92 W/cm² cooling intensity on the surface of the silicon film. Measured by the fine-gauge thermocouple apparatus developed in Chapter 5, Chapter 6 also presents the temperature profiles of a silicon film’s solidification interface as it travels through the demonstration furnace. Temperature profiles of the thin silicon film’s solidification interface exhibit the predicted high levels of undercooling in the liquid ahead of the interface. This chapter concludes by presenting the silicon seeds grown in the demonstration furnace that exhibit the beginnings of a stable monocrystalline silicon interface. However, small tears in the oxide nucleate new grains ahead of the interface, thus resulting in polycrystalline ribbons. This work concludes with outlining future steps to enable monocrystalline silicon films.

References:

Chapter 2: Background and Literature Review

2.1 Chapter Overview

Manufacturing processes that directly produce sheets of high quality silicon material for semiconductor applications have been pursued since the first silicon-based devices were demonstrated in the 1950s. Although there have been many proposed approaches and the understanding of silicon crystal growth has advanced significantly, a “kerfless” silicon ribbon technology has never replaced the original, incumbent technology for producing high quality monocrystalline silicon wafers: wire sawing ingots grown via the Czochralski process which wastes over half of the silicon as kerf. The goal of this chapter is to understand the opportunity, feasibility, and technological capability of directly producing high quality sheets of monocrystalline silicon that are thin enough for commercial solar cells.

This chapter begins by describing how the motivation for developing kerfless silicon wafer processes has evolved since the 1950s and the present commercial context for developing a monocrystalline silicon ribbon manufacturing process. This work reviews the crystal growth mechanics relevant to silicon solidification systems and establishes the different conditions for stably growing a monocrystalline solidification interface. This chapter discusses the status of existing silicon ribbon manufacturing processes, specifically how the Horizontal Ribbon Growth (HRG) process has uniquely demonstrated the ability to stably grow monocrystalline silicon ribbons. We then discuss the shortcomings of existing HRG process models in predicting the HRG process’ behaviors and difficulty in producing commercially viable ribbons. We call for a new analytical model of the HRG process and work to understand the temperature profiles needed to sustain the stable growth in the process. A brief summary of each major section is provided below.

Evolution of Silicon Wafer Demand in the Solar Panel Manufacturing Industry: The solar panel industry in 2014 consumed over 90% [1] of global silicon production and was the most critical market for a prospective large volume silicon wafer process. This work reviews the evolution of silicon wafers’ end-use, focusing on the crystalline silicon solar panel industry. This section briefly contextualizes today’s silicon wafer market and the relevance of a “kerfless” monocrystalline silicon ribbon process.

Review of Crystal Growth Mechanics for Silicon: This section reviews the theory of and criteria necessary for stably propagating a silicon solidification interface. Silicon is a highly anisotropic material: different crystallographic planes grow via different mechanisms that require different respective conditions for
advancing and remaining stable. This work reviews these mechanisms and distinguishes how silicon’s (111) plane can uniquely maintain a stable interface as it propagates into an undercooled melt with a negative temperature gradient ahead of the interface. This section ends with discussing how the Horizontal Ribbon Growth (HRG) process has demonstrated monocrystalline growth by leveraging the stability of silicon’s (111) interface.

Solidification Processes for Producing Continuous, Monocrystalline Silicon Ribbons: This section briefly reviews the two main approaches for producing kerfless silicon ribbons. It discusses the HRG process’ reported successes and limitations in producing monocrystalline material and the observed behaviors of the process. We review the existing heuristic explanations and thermal models of the HRG process and discuss their limitations in predicting the observed process behaviors. This work identifies that no analytical model of the HRG process has yet been developed that incorporates the growth kinetics and temperature requirements of silicon’s (111) interface. This section concludes by calling for a new solidification model of the HRG process and identifying the need to directly measure and quantify the thermal conditions that enable a stable HRG process.

2.2 Evolution of Silicon Wafer Demand in the Solar Panel Manufacturing Industry

Solar cells convert high energy photons into electricity via the photoelectric effect. Unlike other approaches for converting energy sources into electricity, solar cells can directly generate electricity without any moving parts or high temperatures. These attributes make solar cells the obvious choice for remote power generation where fuel delivery and maintenance are difficult. The initial motivation behind their development in the 1950s was for powering devices in space. However, the high cost of semiconductor manufacturing at the time limited their use beyond this niche application.

The cost of solar cell manufacturing was greatly reduced via advancements made by the microelectronics industry. The invention of the bipolar transistor in the late 1940s motivated significant work on improving the materials and processes needed for semiconductor manufacturing. The solar industry directly benefited from the resulting economies of scale and the improved performance of silicon-based devices. By the 1970s, these advancements had lowered manufacturing costs enough to enable photovoltaics’ terrestrial use in applications like small electronics and remote power generation [2].

By the late 1990s, the processing of silicon substrates into solar cells had become more or less standardized, and a solar panel’s silicon substrate determined its cost and efficiency. At the time, the
cost of manufacturing a silicon wafer was up to 70% of the cost of the panel or up to 50% of the fully installed solar system (including BOS electronics and installation). Solar panel production was divided between “high efficiency” solar panels that used monocrystalline wafers produced by the Czochalski process and inexpensive solar panels that used polycrystalline wafers produced by the Bridgeman process. Although more expensive to manufacture, an installation using high efficiency monocrystalline solar panels required fewer panels, less real-estate, and less installation hardware than a system using panels made with polycrystalline wafers. Therefore, the final cost of electricity produced by either panel-type was competitive, and the most economic option was case-specific. Monocrystalline and multicrystalline photovoltaic panels had comparable market share by 2005.

The driving economics of silicon wafer production and thus photovoltaic manufacturing changed dramatically in the late 2000s. The rapid expansion of primarily Chinese solar panel and silicon wafer manufacturing capacity brought about tremendous economies of scale and improved logistics that resulted in the cost of panels plummeting from over $4.90/Wp in 2005 to $1.28/Wp in 2011. This trend continued, and in July 2015, worldwide panel prices were as low as $0.6/Wp. With such low solar panel prices, the cost of the installation and the BOS electronics now play a much larger role in the final installed cost of a solar system. The higher efficiency panels that proportionally require less installation hardware now have a significant cost advantage over lower efficiency systems.

2.2.1 High Efficiency Panel Use of High-Lifetime, Monocrystalline Wafers

The maximum theoretical efficiency of a crystalline silicon solar cell with a “classic cell architecture” is 29.8% in the AM1.5G spectrum and up to 38% in concentrated light. Most commercially available cells exhibit power conversion efficiencies typically between 16.5-18%, but solar cells fabricated with advanced cell architectures can achieve significantly higher efficiencies by generating and harvesting charge carriers from a given spectrum more readily. Solar panels using these advanced cells have demonstrated efficiencies of up to 22.9% commercially and up to 25.6% in laboratory testing using the AM1.5G spectrum.

These advanced cells can only achieve high efficiencies when created on silicon wafers exhibiting a high carrier “lifetime.” A silicon wafer’s “lifetime” is the average amount of time that a carrier (generated by an incoming photon) can remain in the conduction band before it thermally decays back to the valence band. The lifetime of a silicon wafer is limited by its most electronically active defects which can include dislocations, grain boundaries, and the precipitates of non-metallics in the silicon lattice.
As monocrystalline silicon wafers produced by the CZ and Float-Zone process do not have grain boundaries, dislocations, or high levels of contamination, they are typically the wafers used for these high efficiency cell architectures.[13] Although significant work in boosting the lifetimes of polycrystalline wafers produced from the Bridgeman process has been pursued, advanced architecture solar cells produced on monocrystalline wafers still exhibit superior efficiencies. [13-17] As the FZ process is generally too expensive for commercial solar panels, the only manufacturing process that presently yields the high lifetime monocrystalline silicon wafers needed for the high efficiency solar cell architectures is the CZ process.

2.2.2 Opportunity in Kerfless Monocrystalline Silicon Ribbon Manufacturing Process

Unfortunately, wire-sawing CZ ingots is a capitally intensive process that constitutes up to 90% of the total energy used in the making of a solar panel. First, the CZ process is a slow, crystal growing process (generally limited to 50 mm/hr [18]) and requires many expensive crystal pullers for a given material production rate. Depreciation and maintenance of this equipment is estimated to account for approximately $0.04/W_p of the final cell. [19] Second, because the CZ crystal does not produce net-shaped silicon sheets, a consumable-intensive wire-sawing process is required to produce silicon wafers. This wire-sawing process wastes up to half of the ingot as kerf or sawdust, requires expensive abrasive slurries, and creates micro-cracks on the surface of the produced wafers that have to be etched off with a subsequent HNA acid bath. [10] The single-use wire and silicon slurries cost approximately $0.05/W_p, and the cost of the silicon presently lost as kerf during the sawing of the silicon wafers is estimated to be $0.08/W_p.[20] Given that the total CZ wafer manufacturing cost is estimated to be $0.25 - $0.30/W_p and there were over 10 billion silicon wafers -purchased by the photovoltaic industry in 2014, there is tremendous opportunity in developing a new process for rapidly producing net-shaped sheets of high lifetime monocrystalline silicon. [20]

2.3 Review of Solidification Growth Mechanisms for Silicon

Growing a high quality, monocrystalline ribbon in a volume of liquid silicon requires a stable, planar solidification interface. A solidification interface’s growth rate is determined by how readily latent heat macroscopically dissipates from the solidification interface and the kinetics of how readily atoms join the surface. The rate at which latent heat dissipates from the solidification interface relates to the macroscopic growth rate \( R \) by the Stefan equation as:

\[
R = \frac{\Delta H}{\rho c_p T} \frac{1}{\sqrt{\frac{\alpha}{\pi}}} \left(1 + \frac{\alpha}{\pi}ight)
\]
where $K_s$ and $K_l$ are the thermal conductivity of the solid and liquid, $G_s$ is the thermal gradient in the solid, $G_l$ is the thermal gradient in the liquid, $\rho$ is the material's effective density, and $h_{l/s}$ is the latent heat. The kinetics of how readily atoms stably join an interface depends on the interfacial energy between the liquid/solid phase, the thermal properties of the solidifying material, and the defects that intersect with the interface. [21] The material properties are related to the thermal driving and opposing energetic forces for solidification as:

$$dG = \left( \frac{h_{l/s} \Delta T}{T_m V_s} + \frac{d\sigma}{dx} \right) dx$$

where $\Delta T$ is the temperature of the atom below the equilibrium melting temperature $T_m$, $V_s$ is the volume of the joining atom, and $\sigma$ is the interfacial energy between the liquid/solid interface. A simple interpretation of Equation 2.2 is that the relative strength of the interfacial energy determines the level of undercooling required to advance a solidification interface.[22] As solidification occurs only when adding a new atom to the surface lowers the system’s overall energy, high interfacial energy can give rise to significant energy barriers that limits the rate of solidification. [21] Overcoming these thermodynamic barriers requires either relatively high levels of thermal undercooling or energetically favorable sites (like defects) at the surface.

2.3.1 Sharp and Diffuse Interface Growth Mechanisms

In classic Jackson’s solidification theory, interfaces that must overcome a large thermodynamic barrier to propagate are classified as “sharp” interfaces, and interfaces that require relatively low thermal driving forces to propagate are classified as “diffuse” interfaces.[23] Attaching an atom to a diffuse interface does not require overcoming a high level of undercooling or an energetically favorable site and thus forms a rough interface as illustrated in Figure 2.1b. These diffuse or rough interfaces grow rapidly with any thermal undercooling of the liquid ahead of the interface as:

$$v_{step} = \beta_{step} \Delta T$$

where $v_{step}$ is the velocity of the propagating lateral interface, $\beta_{step}$ is the step kinetic coefficient, $\Delta T$ is the thermal undercooling at the solidification interface. The step kinetic coefficient for silicon has been calculated and measured by several studies to be between 0.2-0.8 m/s K. [24-26] The kinetics of this growth mechanism typically do not limit the advancement of a solidification interface, and thus the shape of their interface is typically determined by that of the equilibrium melting temperature isotherm.
In contrast, advancing a “sharp” solidification interface requires either a high level of undercooling or an energetically favorable site that does not increase the interfacial energy of the surface. These interfaces advance via “step-flow” mechanisms: an atomic step is initiated on a flat interface via a high level of undercooling and then rapidly grown parallel to the surface, as illustrated in Figure 2.2a. Because adding more atoms to an existing step does not increase the surface's interfacial energy, the parallel “spreading” is not limited by the same thermodynamic barrier that is needed to orthogonally propagate the interface. Instead, this parallel “lateral growth” scales linearly with undercooling and is generally limited like a diffuse interface: by the rate of heat extraction from the interface. The kinetics and growth rate of a sharp interface are therefore limited by the rate at which atomic steps can be generated at the surface.

Energetically favorable sites on a “sharp” surface are formed by either defects on the interface or via the two-dimensional nucleation of steps. Using a defect or dislocation that intersects the interface to create a step for lateral growth is known as the Frank mechanism of growth or screw-dislocation mechanism. As illustrated in Figure 2.2b, atoms attaching to this local point spiral around this source at rates comparable to that of the continuous growth mechanisms of diffuse interfaces.

When there are no dislocations or other energy-lowering defects on the surface, steps are initiated via two-dimensional nucleation. For this growth mechanism, a new single-layer of atoms is nucleated on an
otherwise flat interface, as illustrated in Figure 2.2c. The average rate of nucleation [25] on the surface of a propagating sharp interface is given by:

\[
I_{2DN} = \left( \frac{\beta_{\text{step}}}{\alpha} \right) (\Delta T^3) \left( \frac{h_{\text{step}} h_{l/s}}{(2\pi k_0 T)^2} \right) e^{\frac{-\pi a^2}{h_{\text{step}} h_{l/s} k_0 T^2}}
\]

where \(I_{2DN}\) is the rate of 2D nucleation, \(\alpha\) is the free energy of an interface per unit length, \(\beta_{\text{step}}\) is the step kinetic coefficient, \(\Delta T\) is the thermal undercooling at the solidification interface, \(h_{\text{step}}\) is the height of the generated step as illustrated in Figure 2.2a, \(h_{l/s}\) is the latent heat of solidification, \(k_0\) is the Boltzmann constant, and \(T\) is the temperature of the interface. Once a stable nucleation occurs, this solid phase grows from the step laterally along the surface by diffuse growth mechanisms. This lateral growth rate has been related to the orthogonal propagation of the (111) interface by Voronkov [27, 28] to be:

\[
R_{111} = 1.33 h_{\text{step}} \left( I_{2DN} v_{\text{step}}^2 \right)^{1/3}
\]

where \(R_{111}\) is the rate of propagation normal to the surface. For many semiconductor materials, this nucleation-flow mechanism is necessary for the propagation of a single growth direction. For silicon, the (111) plane uniquely advances by this mechanism when a critical level of undercooling is achieved at the interface, calculated by Voronkov et al. to be 3.7° C. [25]

At increased levels of undercooling, the kinetics of this nucleation-spread mechanism approach that of diffuse interfaces at increased levels of undercooling. Cahn claims that this nucleation-spread mechanism resembles a diffuse interface when the critical radius of a nucleating step approaches the width of the step. [21, 22] Brice and Bruton [29], however, predict that a sharp interface resembles a diffuse interface when the time between subsequent step generations on the surface becomes comparable to the time for a step to propagate across the length of the interface. Buta et al. used nonequilibrium molecular dynamics simulations to understand the window for when step-flow processes could be assumed in silicon [26]. Buta estimates that 2D-nucleation could be assumed to be the mechanism of growth until the liquid undercooling ahead of the solidification interface reaches 40 K, with a corresponding \(\theta_{\text{crit}} \sim 0.2\). [26] For comparison, Voronkov calculated the anisotropic growth factor at the critical level of undercooling of 3.7 K to be on the order of \(\theta_{3.7K} \sim 10^5\), indicating an extremely flat interface when growth is initiated. [27] The dependence of the growth rate on undercooling as the interface transitions from a flat “sharp” surface to a rough “diffuse” surface is shown in Figure 2.3. [30]
2.3.2 Solidification Fronts Formed by Diffuse and Sharp Surfaces

For materials like silicon that exhibit a singular plane (111), both sharp and diffuse kinetics can simultaneously shape a solidification interface. Solidification interfaces formed by both surface types in convex and concave thermal profiles are shown in Figure 2.4. In this CZ process example, the shape of the solidification interface for orientations deviating from the (111) singular plane follows the equilibrium or melting temperature isotherm, and the sharp, facetted plane forms a mirror-flat interface offset from the equilibrium isotherm. The largest distance between the faceted interface and the respective equilibrium isotherm is determined by the relative amount of undercooling required to activate 2D nucleation.

![Figure 2.4: Solidification interface of a CZ ingot with a convex and concave thermal profile. Note that the position of the singular plane is always behind the equilibrium isotherm but ahead of other growth orientations so as to not provide sources of steps. [27]](image)
2.3.3 Solidification Interfaces Stability Criterion for Continuous Silicon Crystal Growth

Maintaining a stable solidification interface is critical for growing defect-free, monocrystalline ribbon. Interface “instability” refers to the situation where, if a perturbation arises on an otherwise flat solidification interface, this perturbation would not disappear and, in fact, would be encouraged to grow out further from an otherwise planar interface. This perturbation is reinforced because the liquid ahead of the solidification interface preferentially grows the perturbation faster than the liquid at the planar interface.[31] Amplifying this perturbation is possible when the liquid *ahead* of the solidification interface is thermally undercooled or the liquid *at* the solidification interface is constitutionally supercooled. If the liquid ahead of the solidification interface is thermally undercooled, then a perturbation will grow preferentially because the latent heat is more readily diffused away from the geometry of a perturbation. If the liquid at the solidification interface is constitutionally supercooled, then the effective melting temperature of that liquid is higher at the interface and solidification is suppressed. A perturbation that interacts with “cleaner” liquid away from the interface will be preferentially grown with respect to the interface. A stable process can never give rise to a self-reinforcing perturbation.

Constitutional supercooling arises when impurities are preferentially segregated and concentrated in the melt ahead of the solidification interface. Increased concentration of these impurities raises the liquid’s equilibrium melting temperature, and stability can only be maintained when a thermal gradient in the liquid compensates for the melting temperature alteration. The liquid thermal gradient ($G_l$) needed to prevent this interface instability is traditionally calculated to be:

$$\frac{G_l}{R} \geq \frac{m_i C_o (1 - k)}{k D_L}$$  \hspace{1cm} (2.6)

$R$ is the rate of solidification, $m_i$ is the slope of the liquidus line of the material for a given impurity, $C_o$ is the bulk concentration of an impurity, $k$ is the partition coefficient, and $D_L$ is the diffusivity of a given impurity into the given liquid.

2.3.3.1 Stability Criterion for Diffuse Solidification Interfaces

To remain stable, a *diffuse* solidification interface cannot advance faster than [21]:

$$R_{max} \leq K_s G_S \left( \rho h_{i/s} + \frac{K_i m_L C_o (1 - k)}{k D_L} \right)^{-1}$$  \hspace{1cm} (2.7)
Achieving high, stable solidification rates requires relatively low impurity concentrations and sufficient temperature gradients in the solid and liquid phase near the solidification interface. Both Kellerman and Kalejs recognize that low initial levels of contamination \( C_o \) in the silicon melt are necessary for maintaining stable growth. [32, 33] Maintaining low contamination levels is particularly challenging. Although high purity silicon feedstock exhibits low concentrations of metallic impurities \( C_0 < 10 \text{ ppt} \), concentrations of metallic impurities in liquid silicon are typically higher \( C_0 \approx 10 \text{ ppm} \) because of impurities that diffuse into the silicon from the containing crucible.\[34\]

Silicon ribbon processes are traditionally limited to low growth rates to prevent high, destabilizing concentrations of impurities at the solidification interface. Metallic impurities in liquid silicon have relatively small equilibrium partition coefficients \( k < 10^{-3} \) and relatively low diffusion coefficients \( D \sim 10^{-4} - 10^{-5} \text{ cm}^2/\text{s} \) \[35\] which gives rise to an effective segregation coefficient of one at growth rates higher than 1 cm/min. \[36\] To prevent interface instability via constitutional supercooling, silicon ribbon processes like Edge-Fed Growth and String Ribbon traditionally maintain a positive \( G_i \) (requiring more heat to be extracted through the solid crystal) which limits their growth rates to less than 4 cm/min. \[36-38\] It is important to note that high concentrations of impurities at the solidification interface can result in the precipitation of solid particles ahead of the interface that can nucleate a new grain or cause significant stress/defects in the final crystal.

When a sufficient thermal profile cannot be maintained across a silicon solidification interface at a given process rate, a diffuse interface destabilizes into facetted dendrites.\[39\] Fujiwara has shown that all of silicon’s diffuse planar interfaces (\(<100>, <112>, \text{ and } <110>\) directions) destabilize to form zig-zag facets bound by (111) planes when the solidification interface advances too rapidly.\[40\] As shown in Figure 2.5, the destabilizations of these diffuse interfaces are attributed to the evolution of a negative temperature gradient at the crystal-melt interface. It is important to note that in these studies, a (111) interface could not be destabilized at growth rates even greater than 200 \( \mu \text{m/s} \). \[41\]
When this maximum solidification rate is exceeded, the interface for any growth direction deviating from the $<111>$ is expected to break down and form facetted cells, as shown in Figure 2.6. [42, 43] The resulting “corrugated” structure forms solute-rich grooves between these facet-bound cells which eventually precipitate, stress, and generate threading dislocations in the final crystal material. [44, 45] These dislocations and the concentration of metallic impurities degrade the final electrical performance of the material. It is important to note the length scale for a surface transitioning from planar to unstable growth is on the order of $10^{-4}$ m.

**Figure 2.5:** The destabilization of a silicon solidification interface into a zig-zag facetted interface when a negative thermal gradient is formed in the melt ahead of the solidification interface. [41]

**Figure 2.6:** Breakdown of silicon interface into (a) corrugated cell structure for propagation rates of 164 $\mu$m/s and the (b) corresponding isochrones with an imposed furnace thermal gradient of 8 K/mm. [39]
2.3.3.2 Stability Criterion of Sharp Solidification Interface

Silicon’s (111) plane is a “sharp” interface that advances via a combined “step-flow” mechanism when the liquid phase at the interface is undercooled between 3.7 and 40 K. [26] The (111) plane’s highly anisotropic mechanism for growth has been shown to effectively stabilize the solidification interface, allowing for high stable growth rates with relatively high impurity gradients and negative values of $G_i$. [41] A modified stability criterion for sharp, anisotropic surfaces was developed originally by Sekerka et al. and later improved by Chernov. [46-48] This expression relates the thermal gradient necessary to maintain stability for a given process rate to the thermal undercooling, the constitutional supercooling, and the anisotropic growth factor, as given by:

$$\frac{G_i}{R} \geq \frac{m_L C_o (1 - k)(1 - \theta)}{k D_L} - \frac{h_{ij} \theta}{c_p (\alpha_i + \alpha_s)}$$  \hspace{0.5cm} (2.8)

where $\alpha_i$ and $\alpha_s$ are the thermal diffusivities of the liquid and solid. For a high anisotropy growth factor $\theta \gg 1$, Equation 2.8 shows that interface stability is possible in undercooled melts with negative thermal gradients. Voronkov calculated $\theta$ for silicon to be approximately $10^5$ [27] at the critical level of undercooling, and Buta et al [26] used nonequilibrium molecular dynamics simulations to find that $\theta \sim 0.2$ at an undercooling of 40 K. This high value of $\theta$ has motivated Voronkov to claim the (111) interface is “immune” to undercooling-driven instabilities. He furthermore advocates rapidly growing dislocation-free crystals by advancing a $<111>$ oriented crystals with a flat isotherm.[21, 27]

No commercialized crystal growth process to date claims stably seeding and orthogonally growing the (111) interface to be the strategy for rapidly creating dislocation-free silicon ribbons. However, the stability of a sharp semiconductor interface growing into undercooled melts with negative thermal gradients has been observed and recognized by several studies.[21, 30, 39, 43, 49] For example, Peteves grew dislocation-free gallium crystals at 1.4 mm/s with interface undercooling of 10 K by propagating the (111) interface.[49]

A process that could stably grow silicon crystals where latent heat dissipates through the liquid ahead of the solidification interface could theoretically be significantly faster than existing processes. As the thermal conductivity of silicon’s liquid phase is approximately three times greater than its solid phase, heat extraction through the liquid could enable significantly higher process rates than those achieved by multicrystalline vertical ribbon processes. Furthermore, the thermal gradient and the corresponding thermal stress in the solidified ribbon could be substantially reduced.
2.4 Solidification Processes for Producing Continuous, Monocrystalline Silicon Ribbons

The thermal profiles in the liquid and solid phase bordering a solidification interface dictate the geometry and behavior of the interface. As discussed in Section 2.3, the thermal profile in the liquid phase determines the interface’s stability, and the thermal profile in the solid phase determines the stress and defect profiles in the solid. Combined, the thermal profiles govern the shape of the interface and the rate of solidification.

The leading edge of the ribbon’s solidification interface is typically shaped (or at least indicated) by the melting temperature isotherm. Latent heat released from the interface flows normal to this isotherm by conduction. The maximum rate at which heat can stably dissipate away from the solidification interface determines the maximum growth rate of a process.

The shape and orientation of the solidification interface with respect to the pull direction traditionally distinguishes vertical and horizontal silicon ribbon growth processes. As illustrated in Figure 2.7a, the solidification interface of vertical ribbon processes is normal to the pull direction, whereas the solidification interface of horizontal processes is traditionally believed to be almost orthogonal to the pull direction and thus to maintain the shallow angle shown in Fig.2.7b. Dissipating latent heat from the ribbon surface directly above this long “slender wedge” solidification interface theoretically allows for high process rates compared to vertical processes where the latent heat dissipates through a solidification interface equal to the thickness of the growing ribbon.

![Figure 2.7](image)

Figure 2.7: (a) Vertical and (b) horizontal ribbon solidification interfaces and orientation of heat loss [50]

Vertical and horizontal silicon ribbon processes have had their respective successes to date. Vertical ribbon processes (Edge-Fed Growth, String Ribbon) have been commercialized by several companies (Mobile Tyco, Schott Solar, and Evergreen); however, the produced ribbons have been polycrystalline...
and defect-ridden and have yielded only lower efficiency solar cells.[36, 40, 51, 52] Today, there is no active production of vertically grown silicon ribbons.[4] On the other hand, horizontal ribbon growth (HRG) processes have demonstrated monocrystalline ribbons at higher growth rates than that achieved by vertical processes.[33, 53] Although HRG processes achieved promising results as early as 1980, the HRG process has never been able to produce silicon ribbons thin enough to be commercially viable for solar cells. Silicon solar cells typically use wafers that are thinner than 200 μm, and, to date, the HRG process has not been able to produce ribbons thinner than 600 μm.[33] Unfortunately, attempts to grow thinner ribbons with the HRG processes have been unsuccessful, and the experimental findings are not readily predicted by or consistent with published solidification models of the process. To date, no HRG process has been commercialized.

2.4.1 HRG Process Achievements and Behaviors

The majority of HRG development work has been pursued by private industry, so there is limited information available that characterizes produced HRG ribbons and the respective equipment used to grow this material. However, Kellerman’s 2013 DOE¹ Report reveals several telling process behaviors and ribbon attributes that provide critical insight into the growth mechanisms and associated heat transfer involved with the HRG process.

Kellerman reports successfully growing a stable monocrystalline ribbon at 2 mm/s with 120 W/cm² cooling intensity at the solidification interface. The growing ribbon’s surface corresponds to silicon’s (100) plane, and the (111) solidification interface is maintained at 54.7° to the surface as shown in Figure 2.8a. The corresponding thickness of the final ribbon is reported to be just over 600 μm, and ribbons produced with lower cooling intensities are thicker. Chapter 3 uses Kellerman’s published cooling rate (120 W/cm²), stable process rate (2 mm/s), and ribbon thickness (600 μm) to understand the thermal profiles at the HRG leading-edge solidification interface.

As shown in Figure 2.8b, Kellerman also presents a close-up photograph and surface profile of a grown HRG ribbon that may provide critical insight into the crystal growth kinetics involved at the leading-edge of the ribbon’s solidification interface. Voronkov describes periodic “ridges” similar to those shown on the ribbon surface that are created by the surface-tension mechanisms involved with advancing the

¹ Department of Energy (United States).
(111) plane in silicon. [25] This “ridged” surface is consistent with the leading-edge solidification interface being advanced by the step-and-spread mechanism unique to “sharp” interfaces.

Figure 2.8: (a) Proposed HRG ribbon interface growth direction with a (100) top surface and facetted leading-edge solidification interface angled at approximately 55° from the surface. (b) Photograph of HRG ribbon showing characteristic ridged surface indicating facetted growth [33].

These insights have profound implications on our understanding of the heat transfer involved at the leading-edge solidification interface and of how the HRG process can be made to remain stable at high process rates. As discussed in Section 2.3, a sharp interface requires thermal undercooling (of at least 3.7°C) of the liquid ahead of the interface to advance and is relatively very stable when exposed to destabilizing impurities and thermal gradients in the melt. Furthermore, a sharp interface is inherently flat and aligned with the orientation of the <111> plane (54.7° to the surface in Kellerman’s process), regardless of the thermal profile in the solid or liquid phase. As shown in Kellerman’s heuristic illustration of the ribbon in Figure 2.8a, this would mean the leading-edge is not analogous to the melting temperature isotherm.

Kellerman’s DOE report also provides a critical insight into the thermal conditions that destabilize the HRG process. As shown in Figure 2.9, a ribbon stably growing at 2 mm/s destabilizes into facetted
dendrites when the pull rate is marginally increased to 2.1 mm/s. Because a solidification interface remains stable until a critical $G_L/R$ is exceeded (as discussed in Section 2.3), it can be assumed that increasing the pull rate causes the thermal profile in the liquid ahead of the solidification interface to exceed this critical value for the HRG process. This is a critically important and possibly unforeseen limitation of the HRG process. Because a facetted interface is considered “immune” to undercooling-related instabilities (as discussed in Section 2.3.3.2), Voronkov claims this is only true when the facetted interface is aligned orthogonally to the isotherms in the process. As the (111) interface maintains a 54.7° angle to the pull direction (and thus likely misaligned to the isotherms in the liquid), one could expect that the interface’s stability is not infinite.

![Figure 2.9](image)

**Figure 2.9:** Increasing the pull rate of the HRG process destabilizes the interface into polycrystalline growth as (a) illustrated by Kudo and (b) shown by Kellerman [33, 53].

### 2.4.2 Review of Existing HRG Heat Transfer Models

This section provides an overview of the existing thermal models of the HRG process and their respective shortcomings in explaining their behavior. The HRG process was originally proposed by William Shockley in 1962 [54], was first demonstrated by Kudo in 1980, and is now being pursued by Kellerman, the first to recognize the stability introduced by the (111) interface in 2013. [33, 53, 55]

However, no analytical thermal model that incorporates the stability criteria and kinetics of growing silicon’s (111) interface has been proposed for the HRG process.

The original thermal models developed for the HRG process are simple and predict that the solidification interface resembles a long “slender-wedge” that enables high process rates. [55, 56] An improved “blunt-tip” model of the process, where a curved leading edge of the solidification interface was formed by the thermal boundary layer created by the active cooling device, was developed by Zoudetsky in 1980. [57] Both these models assume the shape of the solidification interface is defined by the melting
temperature isotherm and do not account for the kinetics of the (111) plane. Both of these models also assume the temperature profile in the melt plays no role in the heat transfer at the leading-edge of the solidification interface. They both predict that for the thermal conditions reported by both Kudo and Kellerman, thin ribbons should be possible at significantly faster rates. Further detailed descriptions of “slender-wedge” and “blunt-tip” model are found below.

In 2009, Brandon et al. developed a preliminary solidification phase-field model of the HRG process where the leading-edge interface grows into undercooled melt several degrees below the equilibrium melting temperature.[33] This solidification model adapted the kinetics-limited phase-field model originally developed by Olesiien and Weinston in 2004.[58] Unfortunately, Brandon’s model was not able to simulate the HRG process in a way that predicted the growth conditions and stability limits observed experimentally. Brandon’s only published results show an HRG ribbon growing stably into undercooled liquid at much slower process rates than what has been experimentally demonstrated. Further details about the heuristic models developed by Brandon and Kellerman for the HRG process are discussed below.

### 2.4.2.1 Slender Wedge Model

The traditional “Slender Wedge” model of the HRG process is strictly a thermal model that assumes the solidification interface resembles a long “slender wedge” where the isotherms maintain a high aspect ratio \( \ell_x/\ell_y = \Delta > 100 \) as illustrated in Figure 10a.[50, 53-56] For high aspect ratios, this model postulates that because the majority of latent heat is extracted orthogonally to the pull direction, high process rates are possible for relatively shallow furnace thermal profiles. The governing analytical model asserts that the thermal gradients in the pull and orthogonal directions can be related geometrically for steady-state systems, where the thermal gradient maintained in the pull direction \( G_x \) is equal to the quotient of the thermal gradient orthogonal to the pull direction and the aspect ratio \( G_y = G_x/\Delta \).

![Figure 2.10: Solidification interface shape predicted by the (a) “slender wedge”][57]
Although this model’s promise of high process rates has motivated multiple HRG projects, it does not explain why the HRG process cannot produce thin ribbons and does not accurately predict the level of heat extraction needed for high process rates, as discussed in Chapter 3. The “slender wedge” model assumes that the thickness of the ribbon grows linearly as it is exposed to the cooling profile, and therefore thinning a ribbon could be achieved by either increasing the process rate or limiting the rate of heat extraction. However, no ribbon produced to date has been thinner than 600 μm, and typical reported thicknesses are in excess of 1 mm.[33, 53] Furthermore, the model predicts that the long solidification interface enables process rates 100X faster than vertical ribbon processes just with radiative heat extraction from the surface of the ribbon. However, the fastest confirmed pull-rates of the HRG and vertical ribbon process have been 120 mm/s and 60 mm/s, respectively, and it should be noted that the HRG process achieved those rates with high intensity active cooling. [33, 36]

2.4.2.2 Boundary-Layer Thermal Model

Given the limitations of the “slender wedge” model, Zoutendyk proposed an HRG solidification model in 1980 where the shape of the leading-edge interface is defined by the thermal boundary layer of a high-intensity active cooling device on the surface of the liquid melt.[57] As illustrated in Figure 11b, this model assumes that an active cooling device creates a thermal boundary layer ($\delta_T$) in the melt which scales with the momentum boundary layer ($\delta_V$) formed by a plate (the ribbon) dragging across the surface of the melt. The heat transferred through this boundary layer is balanced by the latent heat released from the solidification interface and the heat conducted into the melt. Contrary to the long, nearly horizontal melting temperature isotherm predicted by the “slender wedge” model, this model predicts a relatively short, blunt-tip leading edge of the solidification interface.

![Figure 2.11: Illustration of Zoutendyk's Boundary-Layer Model for the HRG process][57]
2.4.2.3 Blunt-Tip Facetted Interface Model

Helenbrook’s phase-field FEM model of Kellerman’s HRG process recognizes the presence of a (111) interface at the leading-edge solidification interface, as illustrated in Figure 2.12. [33] This model assumes the surface of the growing ribbon is the (100) orientation (the preferred surface for solar cells), which is bound by the (111) plane oriented at 54.7° to the surface of the grown ribbon.

![Figure 2.12: Heuristic model of Varian’s Floating Silicon Process incorporating growth kinetics of facetted growth. The imposed cooling profile \(q''(x)\) is assumed to be Gaussian and imposed on the solid, and leading-edge of the interface is a perfectly flat (111) plane [33]](image)

A fundamental assumption of both Zoutendyk and Helenbrook’s heuristic model is that the latent heat generated at the leading-edge solidification interface dissipates through only the solid ribbon. And unlike the long solidification interface assumed by the “slender wedge model,” both models assume that the length of the leading-edge solidification interface is comparable to the thickness of the wafer. Conducting heat through this relatively thin solidification interface presents a significant challenge as the surface of the growing ribbon is supported by thermally conductive melt that can dissipate heat orthogonal to the pull direction. Heat dissipation into the melt below the surface of the ribbon can substantially reduce the amount of heat extracted from the leading-edge of the solidification interface and also create a relatively thick ribbon. Given the proposed thin interface length and the fact that the HRG process extracts heat through only one side of the ribbon, the thermal models proposed by both Zoutendyk and Helenbrook imply that the HRG process should not be able to achieve process rates greater than vertical ribbon processes for a given cooling rate.

However, the HRG process has demonstrated significantly higher process rates than those achieved with vertical processes. Kudo and Kellerman have reported HRG process rates of 415 mm/min (unconfirmed).

---

2 Finite element method.
and 120 mm/min respectfully [33, 53], whereas vertical growth processes typically achieve rates between 20-50 mm/min.[37] Although the reported HRG processes used active cooling devices that provided higher cooling intensities at the solidification interface than passive thermal radiation (which is the cooling approach for vertical processes), it is not clear that these cooling devices alone can account for this dramatic difference if we assume that all the latent heat generated from the interface dissipates through the solid.

As discussed in Section 2.4.1, Kellerman advocates that HRG’s high process rates may be enabled by the stability of the (111) plane. This has profound implications for our understanding of the heat transfer involved at the leading-edge solidification interface as this plane can stably grow into undercooled melt. Although Kellerman does not provide any heat transfer model for the HRG process that accounts for this undercooling, he does reason that a significant fraction of the latent heat generated at the leading-edge solidification interface may dissipate through this undercooled liquid. Preliminary figures in Kellerman’s DOE report illustrate a level of undercooling in the liquid ahead of the solidification interface, but there is no described model or discussion about how this insight may guide future process development efforts. Chapter 3 develops a new analytical model of the HRG process where heat extraction through the liquid can dissipate latent heat from the leading solidification interface.

2.5 Need for New Analytical HRG Process Model and Temperature Characterization

Even with Kellerman’s recent reported successes in demonstrating high-speed monocrystalline silicon growth, it is still not clear whether the HRG process could produce ribbons thin enough for commercial solar cell use. Kellerman has claimed that one approach for boosting HRG’s process rate is to increase the heat extraction intensity of the cold sink, but there is no available heat transfer model that readily supports that this improvement alone (if even possible) would be sufficient. As there is no published model of the HRG process that incorporates the kinetics of propagating a (111) leading-edge interface, it is also not clear that increasing the heat extraction intensity would enable thinner (commercially viable) ribbons.

Because the behavior of the HRG process is not readily predicted by existing models, this work calls for a new analytical model of the HRG process that can elucidate approaches for creating thinner monocrystalline ribbons. Unlike the strictly thermal “slender wedge” model, this new model must account for silicon’s anisotropic crystal growth kinetics and must involve a comprehensive understanding of the heat transfer involved at the leading-edge of the growing ribbon’s solidification interface. As the goal of this work is to understand the feasibility of stably growing thin monocrystalline
silicon ribbons, this model should provide insight into the limitations of the HRG process and should present options for producing thinner ribbons at faster growth rates. Furthermore, as the HRG process has been successful in producing monocrystalline silicon ribbons, a working model of the process would guide the development of HRG-like processes for materials other than silicon.

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Table 1: Measured material parameters and modeling constants used for silicon crystal growth

References


Chapter 3: Horizontal Ribbon Growth Heat Transfer Model with (111) Leading-Edge Solidification Interface

3.1 Introduction and Chapter Overview
The Horizontal Ribbon Growth (HRG) process has been pursued for decades and has been uniquely able to produce monocrystalline silicon ribbons at high process rates.[1-4] However, the heat transfer involved at the HRG ribbon’s leading-edge solidification interface has not been well understood. As discussed in Chapter 2, the original models developed for the HRG process have not been able to explain its inability to produce ribbons thinner than 600 μm or why the process destabilizes at pull rates exceeding 2 mm/s.

In 2014, Kellerman provided the first report of the HRG process that disclosed specific details about grown ribbon attributes, furnace heat extraction intensities, and process conditions that destabilize the ribbon’s interface. Kellerman’s report is also the first to advocate that the HRG process’ leading-edge solidification interface is shaped by a flat (111) interface. As discussed in Chapter 2, this has tremendous implications for our understanding of the HRG process: this “sharp” interface can uniquely grow into an undercooled liquid without breaking down into facetted dendrites. If the HRG process can leverage the stability of silicon’s (111) plane to rapidly grow monocrystalline ribbons, then undercooled liquid ahead of the interface may dissipate a significant fraction of the latent heat generated at the leading-edge interface.

This goal of this work is to develop a new analytical model of the HRG process that accounts for the crystal growth kinetics of the (111) plane to understand the potential of the HRG process for producing thin, monocrystalline ribbons. Insights from this model could reveal how improving process parameters (like heat extraction intensity at the interface) could yield thinner ribbons and higher process rates and could indicate what conditions destabilize the process. Insights from this model would guide future work and the design of new processes that more readily produce thin monocrystalline silicon ribbons. Finally, a working model and understanding of the process could be used to develop an HRG-like process for producing monocrystalline ribbons of materials other than silicon.
This chapter develops an analytical model of the HRG process as follows. Section 3.2 begins by revealing the shortcomings of Kudo's model in predicting the process rates reported by Kellerman and proposes a new approach for modeling the heat transfer involved at the leading-edge solidification interface. Appendix A then develops a series of scaling relationships to determine reasonable assumptions for the heat flows in both the liquid and the solid ribbon bordering the leading-edge solidification interface. This chapter then constructs a complete HRG model by combining thermal models of the solid phase (Section 3.2.1) and liquid phase (Section 3.2.2) near the leading-edge of the solidification interface. In Section 3.2.3, this work determines the thermal profile at the solidification interface for a given set of process parameters. Iterating these models with a MATLAB script calculates the steady-state position of the solidification interface in a given cooling profile, the fraction of latent heat dissipated through the liquid, and the final thickness of the HRG ribbon. In Section 3.3, these models yield process windows for the HRG process, paths to growing thinner monocrystalline ribbons, and an understanding of the thermal conditions that destabilize the process at high growth rates.

3.2 HRG Process Thermal Model Background and Overview

The original HRG thermal model presented by Kudo forms a control volume around the leading edge solidification interface, as shown in Figure 3.10. For high process rates, Kudo proposes that heat extracted from the surface of this control volume \( q_0 \) dissipates 99% of the latent heat needed to grow a ribbon \( t_f \) thick at a process rate \( V \).[1] For the high process rates and thicknesses proposed, the resulting interface must maintain a very shallow angle (\( \theta_{dif} \ll 90^\circ \)). It should be noted that modeling the leading-edge solidification interface as this diffuse “slender-wedge” profile has been performed as recently as 2014 by Daggalou [5] and 2010 by Appapillai. [6]

![Diagram](image)

**Figure 3.1:** Control volume (dashed red) around the leading-edge solidification interface of an HRG ribbon.
In 2013, Kellerman presented experimental evidence that suggests the leading-edge solidification interface is shaped by a (111) plane held at a fixed angle $\theta_{111} = 54.7^\circ$. As shown in Figure 3.2, this angle yields a relatively short control volume around the leading-edge solidification interface of length $L = t_f \cot \theta_{111}$.

![Figure 3.2: Control volume (dashed red) around the angled (111) plane held at $\theta_{111}$](image)

Balancing the heat transfer across the control volume surfaces outlined in Figure 3.2 is simply found by:

$$\rho h_{l/s} V t_f = q_0 t_f \cot \theta_{111} \quad (3.9)$$

where $\rho h_{l/s}$ is the latent heat ($J/m^3$). Given that Kellerman has reported the heat intensity on the surface of the ribbon ($q_0 = 120 W/cm^2$) and $t_f$ cancels out from Equation 3.9, the maximum ratio of the process rate expected by Kudo's thermal model compared to that demonstrated by Kellerman ($V_{exp} = 2 \, mm/s$) is:

$$\frac{V}{V_{exp}} \approx \frac{q_0 \cot \theta_{111}}{\rho h_{l/s} V_{exp}} \approx 0.1 \quad (3.10)$$

According to Kudo's approach, Kellerman's results should not have been possible since heat extraction from the control volume surrounding the leading-edge solidification interface is an order of magnitude less than what is needed to achieve the demonstrated process rates. This study aspires to address the conflict and proposes that the latent heat generated at the leading-edge solidification interface dissipates through both the liquid and solid region bordering this interface. This study therefore develops analytical heat transfer models of how heat extracted from each the surface of each control volume illustrated in Figure 3.3 dissipates latent heat from the leading-edge solidification interface. This involves deriving representative heat transfer models for each region bordering the solidification
interface in Appendix A and then combining these models with an iterative MATLAB script to find a steady-state thermal profile and ribbon thickness for a given set of process parameters. For a cooling profile of length $L$, this model determines the relative position of the solidification interface $x$, and the corresponding horizontal thermal profiles in each of the control volumes illustrated in Figure 3.3.

![Diagram](image)

**Figure 3.3:** Three independent control volumes formed around the liquid, leading-edge solidification interface, and diffuse ribbon. Heat extraction from the top surface of these control volumes determine the position of the leading-edge solidification interface, the thermal profile in the liquid ahead of the ribbon, and the final ribbon thickness.

### 3.2.1 Thermal Model for the Diffuse Solid Ribbon:

Unlike vertical ribbon processes where only the leading-edge solidification interface is in contact with the liquid reservoir, both the leading-edge solidification interface and the melt-side surface of an HRG ribbon are in contact with the melt. Therefore, heat extracted from the surface of the ribbon can dissipate latent heat from both the leading-edge interface shaped by the (111) plane and the diffuse, melt-side surface. As shown in Figure 3.4, the simultaneous growth rates of both the leading-edge interface ($V$) and melt-side interface ($t$) are determined by how readily latent heat is dissipated from their respective interfaces. This study assumes that latent heat generated at the leading-edge interface dissipates through *both* the solid ribbon and the undercooled liquid bordering the interface, as discussed in Appendix A. On the other hand, this study assumes heat extraction through only the solid ribbon grows the melt-side interface, as exposure to any level of undercooling would destabilize this interface:
Figure 3.4: Heat extraction from the leading-edge solidification interface through the liquid and solid ribbon determines parallel growth rate of the leading-edge interface (V). The remaining fraction of heat extracted from ribbon surface grows the melt-side interface (t̅).

As discussed in Appendix A, a fraction of the heat extracted from the surface of the ribbon (Q_{sx}) conducts latent heat away from the leading-edge solidification interface and the remainder dissipates latent heat from the melt-side interface. For a cooling profile imposed on the control volume illustrated in Figure 3.5, this model assumes a uniform q₀ for a distance x_a. Heat extracted from the melt-side interface grows the ribbon to a final thickness (t_f = t₀ + Δt). To the right of the control volume outlined in Figure 3.5, this model assumes no heat extraction from the top surface of the ribbon; however, this model does assume the ribbon is heated by the liquid melt at temperature T_m with heat transfer coefficient (h). These assumptions result in this model presenting a lower-bound on the final thickness of the ribbon, because further heat extraction from the ribbon surface away from the leading-edge interface would continue to thicken the ribbon.
Figure 3.5: Illustration of the silicon ribbon bordering the leading-edge solidification interface supported by a silicon melt. Heat extracted through the surface of the control volume (dashed red) results in a two-dimensional thermal profile that grows the leading-edge and melt-side interface.

By weighing the respective distance between the surface of the ribbon and each solidification interface, Appendix A reasons that the fraction of $q_0$ that extracts heat from the leading-edge interface ($q_{sx}$) fits the exponential function of $x_1$ as:

$$q_{sx}(x_1) = q_0(Ae^{-Bx_1} + C) \quad (3.11)$$

where $A$, $B$, and $C$ are constants fitted to the exponential curve. It should be noted that $B$ scales with $t_0$.

To approximate the heat flow through the left side of the control volume outlined in Figure 3.6 ($Q_{sx}$), this study approximates the parallel heat flow through the ribbon as a fin with a modified cooling intensity ($d_{sx}$). The remaining heat flow grows the ribbon profile $t(x_1)$, as illustrated in Figure 3.6.
Figure 3.6: Illustration of thermal model for the horizontal heat transfer that approximates the ribbon contained in the control volume as a one-dimensional fin model with a modified expression of the heat extracted through the surface \( q_{sx}(x_1) \).

Heat conduction orthogonal to the pull direction from the diffuse, melt-side interface therefore determines \( t(x_1) \) as:

\[
\frac{dt(x_1)}{dx} = \frac{q_0 - q_{sx}(x_1)}{\rho h_{l/s} V} \quad (3.12)
\]

Integrating Equation 3.12 finds the thickness profile of the ribbon adjacent to the leading-edge solidification interface as:

\[
t(x_1) = \frac{q_0}{\rho h_{l/s} V} \left( (1 - C)x_1 + \frac{A}{B} (e^{-Bx_1} - 1) \right) + t_0 \quad (3.13)
\]

Given expressions for \( q_{sx}(x_1) \) and \( t(x) \), this work approximates the horizontal thermal profile in the ribbon as:

\[
\frac{\partial^2 T_1}{\partial x_1^2} - \frac{V}{\alpha_s} \frac{\partial T_1}{\partial x_1} - \frac{q_{sx}(x_1)}{k_s t(x_1)} = 0 \quad (3.14)
\]

where \( \alpha_s \) is the thermal diffusivity of solid silicon and \( k_s \) is the thermal conductivity of solid silicon. The horizontal temperature profile of the ribbon to the right of the control volume \( T_2(x_2) \) is approximated as:
\[
\frac{\partial^2 T_2}{\partial x_2^2} - \frac{V}{\alpha_s} \frac{\partial T_2}{\partial x_2} - \frac{h(T_2 - T_m)}{k_s t(x_1 = x_a)} = 0
\]  
(3.15)

Boundary conditions for the ribbon thermal profile assume that the edge of the control volume \((x_1 = 0)\) is \(T_m\) and that the heat flow and temperature at the control volume’s right boundary is continuous with the ribbon downstream from the leading-edge solidification interface \((T_1(x_a) = T_2(0), \frac{\partial T_1(x_a)}{\partial x_1} = \frac{\partial T_2(0)}{\partial x_2})\). Boundary conditions specifically for \(T_2\) are that the final temperature of the ribbon away from the control volume is the equilibrium melting temperature \((x_2 \to \infty, T_2 \to T_m)\). The final horizontal temperature profile in the control volume is approximated by:

\[
T_1(x_1) = \frac{Aq_0 e^{-bx_1}}{Bk_s t_0 \left(B + \frac{V}{\alpha_s}\right)} - \alpha_s \left(\frac{V}{\alpha_s} \left(\frac{C_1 e^\frac{V}{\alpha_s} x_1}{k_s t_0} + \frac{Cq_0}{k_s t_0 x_1}\right) + C_2\right)
\]  
(3.16)

where \(C_1\) and \(C_2\) are coefficients. This yields the final temperature profile for the ribbon to the right of the control volume as:

\[
T_2(x_2) - T_m = C_3 e^{s_3 x_2}
\]  
(3.17)

where the coefficients and exponential factors are:

\[
s_3 = \frac{V}{\alpha_s} - \sqrt{\left(\frac{V}{\alpha_s}\right)^2 + \frac{4h_2}{k_s t(x_1 = x_a)}}
\]  
(3.18)

\[
C_1 = \frac{Vq_0}{k_s t_0 \alpha_s} \left(\frac{1}{s_3} \left(C\alpha_s + A e^{-bx_a}\right) - \left(A \left(1 - e^{-bx_a}\right)\right) - C\alpha_s x_a\right)
\]  
(3.19)

\[
C_2 = \frac{T_m}{Bk_s t_0 \left(B + \frac{V}{\alpha_s}\right)} + \frac{\alpha_s}{V} C_1
\]  
(3.20)
Finally, this study compares $Q_{sx}$ to the latent heat dissipated at the leading-edge interface via calculating the horizontal thermal gradient ($G_s$) in the ribbon at ($x_1 = 0$) as:

$$R_s = \frac{k_s G_s}{\rho h_{l/s} V} = \frac{-k_s}{\rho h_{l/s} V_{\exp}} \left( \frac{q_0}{k_s t_0} \left( \frac{A}{V_{\exp} \alpha_s} + \frac{C \alpha_s}{V_{\exp}} \right) + C_1 \right)$$  \hspace{1cm} (3.22)

\textbf{ii. 3.2.2 Thermal Model of the Liquid Ahead of the Leading-Edge Interface:}

Appendix A reasons that the heat extracted from the surface of the liquid ahead of the solidification interface conducts almost exclusively from the leading-edge solidification interface for the short distances involved with the HRG process. For this preliminary HRG process model, we assume that heat extracted from the surface of the liquid ahead of the interface conducts heat from the leading-edge interface as a one-dimensional fin where the isotherms in the liquid are orthogonal to the pull direction.

We approximate the steady-state thermal profile of the liquid ahead of the solidification interface contained within the control volume illustrated in Figure 3.6 to be:

$$\frac{\partial^2 T}{\partial x^2} + \frac{V}{\alpha_l \alpha_t} \frac{\partial T}{\partial x} - \frac{q_0}{k_l t_0} = 0$$  \hspace{1cm} (3.23)

where $\alpha_l$ is the thermal diffusivity of liquid silicon, and $k_l$ is the thermal conductivity of liquid silicon.
Assumed boundary conditions are that the temperature of the solidification interface is the melting temperature of silicon \(T_m=1414^\circ\text{C}\), and the temperature of the incoming liquid a distance \(x_i\) away from the interface is \(T_m + \Delta T\). The resulting temperature profile of the liquid is then:

\[
T(x) = C_1 + C_2 e^{-\frac{vx}{a}} - \frac{q_0 \alpha x}{V k_i t_0}
\]

with the coefficients:

\[
C_2 = \frac{\Delta T + \frac{q_{sy} \alpha x_i}{V k_i t_0}}{e^{-\frac{vx_i}{a}} - 1}
\]

\[
C_1 = T_m - C_2
\]

For the process rate and cooling intensity reported by Kellerman, the percentage of latent heat \(R_l\) generated at the leading-edge solidification interface that dissipates through the liquid scales with the respective thermal gradient in the liquid \(G_l\) at \(x = 0\) as follows:

\[
R_l = -\frac{k_i G_l}{\rho h_i/s V} = \frac{k_i}{\rho h_i/s V} \left(\frac{q_{sy} \alpha_s}{k_i t_0 V} + \frac{C_2 V}{\alpha_i}\right)
\]

**3.2.3 Combined HRG Analytical Thermal Model:**

This section combines the analysis presented in Sections 3.2.1 and 3.2.2 to create a complete thermal model of the HRG process. As illustrated in Figure 3.8, the combined HRG thermal model assumes that all the heat extracted from the surface of the liquid and the facetted interface has constant intensity \((q_0)\) and that \(q_{sx}(x_1)\) diminishes exponentially at increasing values of \(x_1\).
The total heat flow dissipating through the solid phase of the ribbon is then the combined heat extracted through the surface of the facetted interface \( Q_f \) and the diffuse ribbon \( Q_{sx} \) as:

\[
Q_{solid} = Q_f + Q_{sx} = t_0(k_sG_s + q_0\cot\theta_{111})
\]  

(3.28)

and the heat extracted through the liquid near the interface \( Q_{liq} \) is:

\[
Q_{liq} = k_tG_t t_0
\]

(3.29)

For a total cooling profile of length \( L \), the position of the leading-edge solidification interface relative to the start of the cooling profile is:

\[
x_l = L - t_0\cot\theta_{111} - x_a
\]

(3.30)

For a given \( L, q_0, \) and \( V \), the MATLAB script iterates numerically through different values of \( x_l \) until the latent heat generated at the leading-edge interface balances the heat extracted from the interface as:

\[
Q_{solid} + Q_{liq} = Q_{lat} = \rho h_f s V_{exp} t_0
\]

(3.31)

For this calculated value of \( x_l \), this script determines the final horizontal temperature profiles in the liquid and solid ribbon and the final thickness of the ribbon exiting the cool zone \( t_f \). Section 3.3 uses
this script to understand how varying different process parameters affects the thermal profiles and thickness of the final ribbon. Section 3.3 also provides possible explanations for HRG behaviors and identifies several approaches for improving the HRG process performance.

iii. 3.3 HRG Process Model Results and Discussion:

This section discusses the results and insights brought about by the HRG process models developed in Section 3.2. We describe the findings specific to each of the independent models developed for the solid and liquid thermal profiles in Section 3.3.1 and 3.3.2 respectively before discussing the results from the complete model in Section 3.3.3. Section 3.3.4 discusses potential paths forward for improving the HRG process.

3.3.1 Thermal Profile and Thickness Profile of the HRG Ribbon

For $q = 120 \text{ W/cm}^2$, $V = 2 \text{ mm/s}$, and a cool zone over the solid ribbon of length $x_a$, the model developed in Section 3.2.1 yields the temperature profile and the ribbon’s corresponding thickness profile as shown in Figure 3.9. As expected, the surface temperature of the ribbon (blue) near the leading-edge interface initially decreases; however, the ribbon surface reaches a temperature minimum ($x_{\text{min}}$) before reaching the edge of the cooling profile ($x_{\text{min}} < x_a$). This minimum ($x_{\text{min}}$) arises because the ribbon to the right of the control volume (downstream) conducts heat from the supporting liquid melt. It is important to note that heat extracted to the right of this minimum ($x_1 > x_{\text{min}}$) does not dissipate latent heat from the leading-edge interface; however, heat removed from the surface of the ribbon to the right of this minimum does continue to thicken the ribbon (green).
Figure 3.9: Example temperature and corresponding thickness profile for a cooling profile ending at $x_a = 0.5$ mm and an initial thickness of $t_0 = 200 \mu m$.

Figure 3.12 shows the relative position of this temperature minimum ($x_{min}/x_a$) as it relates to the cooling profile length ($x_a$) and the assumed initial thickness of the leading-edge interface ($t_0$). As expected, $x_{min}/x_a$ decreases as $x_a$ increases, indicating that an increasing fraction of the heat extracted from the surface of the solid ribbon does not dissipate heat generated at the leading-edge solidification interface. Furthermore, Figure 3.12 shows that for a given $x_a$, thin ribbons reach higher values of $(x_{min}/x_a)$ more readily than thicker ribbons.
Figure 3.10: Relative position of the surface temperature minimum ($X_{min}/x_a$) for increasing values of $x_a$

Figure 3.11 shows how the melt downstream from the cool zone can impact the thermal profile and final thickness ($t_f$) of the silicon ribbon. Specifically, Figure 3.11 shows how $t_f$ increases with respect to $x_a$ and how a smaller initial value of $t_0$ results in the ribbon growing relatively faster because conduction to the leading-edge solidification interface scales with the ribbon thickness.

Figure 3.12 shows that the heat conducted from the leading-edge interface through the diffuse ribbon ($Q_{sx}$) relative to the total latent-heat generated at the leading-edge interface for Kellerman's reported cooling intensity and process rate. This Figure shows that the fraction of the heat dissipated through the solid ribbon ($R_s$) is significantly less than 1 for all listed thicknesses. Even for thin ribbons ($t_0 = 50 \mu m$), a cooling zone length greater than 1 mm ($20 \times t_0$) dissipates only about half of the latent heat generated at the leading-edge. And although a larger value of $x_a$ could result in a situation where ($R_s = 1$), this would also give rise to a significantly larger and possibly undesirable final $t_f$, as shown in Figure 3.11.
Figure 3.11: Relative ribbon thickness \( \frac{t_f}{t_0} \) for increasing values of \( x_\alpha \).

Figure 3.12: Relative heat conducted through diffuse ribbon \( R_s \) for increasing values of \( x_\alpha \).
3.3.2 Thermal Profile of the Liquid Ahead of the Leading-Edge Interface

The model developed in Section 3.2.2 yields the liquid temperature profiles ahead of the leading-edge interface shown in Figure 3.13 for the cooling intensity reported by Kellerman and different assumed values of $t_0$ and $x_I$. This figure shows that for large enough values of $x_I$, a negative thermal gradient ($G_I$) develops in the liquid ahead of the leading-edge interface that conducts latent heat away from the facetted interface ($x = 0$). The magnitude of $G_I$ and the minimum temperature achieved in the liquid both scale with $1/t_0$ and $x_I$. For relatively low values of $x_I$, the $G_I$ at the solidification interface is positive and therefore does not dissipate heat away from the interface.

\[ t_0 = \{50, 150\} \mu m \]

\[ x_I = \{0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0\} \]

**Figure 3.13:** Thermal profile of the liquid for $q = 120 \text{ W/cm}^2$ and varying ribbon thicknesses and cooling profile lengths. Solidification interface assumed at $x = 0$.

Figure 3.14 shows that the relative amount of heat dissipated from the solidification interface scales inversely with $t_0$ and $x_I$ and that a relatively large value of $x_I$ is needed to develop a significant $G_I$. This is because, similar to the profile in the solid ribbon, heat extracted from the surface of the melt to the left of the temperature minimum does not conduct heat away from the leading-edge interface. Therefore, only a fraction of $x_I$ conducts heat away from the interface, while the remaining area conducts heat exclusively from the liquid in the reservoir.
Figure 3.14: Fraction of latent heat generated from the interface that dissipates through the liquid ahead of the interface as a function of the cooling profile length.

3.3.3 Combined HRG Temperature Profile and Process Sensitivity:

The complete model of the HRG process developed in Section 3.2.3 yields the thermal profile of the liquid and solid shown in Figure 3.15, assuming \( L = 1 \) mm, \( t_0 = 50 \) μm, and the \( q_0 \) and \( V \) reported by Kellerman. As indicated by the dashed line, the position of the liquid-solid interface \( (x_f) \) for these conditions is over 300 μm from the start of the cooling profile. The temperature profile of the liquid begins at \( T_m + 1 \), then cools below \( T_m \) and finally gives rise to a negative thermal gradient \( (G_f) \) at the leading-edge of the solidification interface. This work assumes that the temperature of the facetted interface is \( T_m \) and a “negative” \( G_f \) is one where the temperature decreases as it moves away from the solidification interface.
Figure 3.15: Temperature profile of a ribbon with an assumed 50 μm leading-edge thickness, exposed to a 1 mm long cooling profile with an intensity of 120 W/cm².

Varying the parameters of this thermal model shifts the position of $x_l$ and the temperature profiles of both the liquid and solid phase bordering the interface. As shown in Figure 3.16a, increasing the process rate ($V$) shifts $x_l$ towards the end of the cool zone, which results in a stronger $G_l$ ahead of the leading-edge interface. On the other hand, increasing the value of both $L$ and $q_0$ results in the position of the solidification interface approaching the start of the cool zone, as shown in Figures 3.16b-c. It is important to recognize that smaller values of $x_l$ are analogous to relatively more latent heat dissipating through the solid ribbon and less heat dissipating through the liquid.
Figure 3.16: Temperature profiles of the solid and liquid phase in the cool zone interface for increasing values of (a) \( V \), (b) \( q_0 \), and (c) \( L \).

As the relative amount of heat dissipated through the liquid phase directly scales with the values of \( (G_l) \) at the solidification interface, Figure 3.16 (a) and (b) calculate how \( R_l \) scales with \( V \), \( q_0 \), and \( L \) where:

\[
R_l = \frac{-k_l G_l}{\rho h_l / s V} \tag{3.32}
\]

Figure 3.17 a-c calculates \( R_l \) and \( t_f \) using the conservative estimate that \( t_0 = 50 \mu m \). Figure3.17a shows how increasing \( V \) results in higher values of \( R_l \), and Figure3.17a shows increasing \( L \) results in lower relative \( R_l \). Figure 3.17b shows that for large enough values of \( L \) and \( q_0 \) \((L = 2 \text{ mm}, q_0 = 140 \text{ W/cm}^2)\), all the latent heat generated from the leading-edge solidification interface can dissipate exclusively
through the solid ribbon for $V = 2 \text{ mm/s}$, as indicated by the star. However, the significant heat extraction through the ribbon also results in $t_f > 550 \mu m$, as indicated by the star in Figure 3.17c.

![Diagram](image1)

**Figure 3.17:** (a) For an assumed cool zone length of $L = 1 \text{ mm}$, the fraction of latent heat dissipated through the liquid ($R$) scales with the pull rate ($V$) and heat extraction intensity ($q_0$). (b) The relative fraction of latent heat dissipated through the liquid for increasing values of $L$ and (c) the final ribbon thickness, assuming $V = 2 \text{ mm/s}$.

It is important to recognize that Figure 3.17 reveals a fundamental link between the heat extraction in the liquid and the final ribbon thickness. If we assume that the HRG process destabilizes at a critical value of $R_i/V$, then we must assume that increasing a ribbon's stable pull rate must involve increasing the heat extraction through the solid ribbon, which can be achieved by increasing $L$. And because increasing the heat extraction through the solid ribbon simultaneously increases its thickness, the thickness of an HRG ribbon is coupled to its maximum process rate for a given $V$ and $q_0$. Therefore,
Figure 3.17 presents the first analytical explanation for why Kellerman has struggled to yield thin ribbons at increasing pull rates.

### 3.3.3.1 HRG Stability Limits and Process Windows

This work creates Figure 3.18 and 3.19 by iterating the complete model of the HRG process developed in Section 3.2.3 through different values of $V$ and $L$ to calculate the steady-state values of $R_I$ and $t_f$. Negative values of $R_I$ (-0.4, -0.2) indicate that $G_I$ is negative and that the fraction of latent heat generated at the leading-edge interface dissipating through the liquid is 40% and 20% respectively. Alternately, positive values indicate that the solid ribbon dissipates all the heat from the interface (along with that flowing from the liquid) and that the thermal gradient in the melt is also positive. The line marked by zeros is the threshold for which the solid ribbon exclusively dissipates latent heat from the leading-edge interface ($R_I = 0$). Figures 3.18 and 3.19 differ only in the assumed $t_0$, where Figure 3.18 assumes that $t_0 = 200 \mu m$ and Figure 3.19 assumes $t_0 = 75 \mu m$.

As expected, both Figure 3.18 and 3.19 shows that $t_f$ increases with $L$ and decreases with $V$, and more negative values of $R_I$ correspond to thinner ribbons ($t_f$). To approximate the critical value of $R_I$ that destabilizes Kellerman’s HRG process, this study determines the value of $L$ in Figure 3.18a for the reported ribbon thicknesses and rate at which the process destabilizes ($t_{\text{reported}} \approx 600 \mu m$ and $V_{\text{reported}} = 2 \text{ mm/s}$). For this value of $L$, this study then identifies the corresponding value of $R_{\text{crit}} > -0.5$ in Figure 3.18b, as indicated by the stars in both figures. For Figure 3.19a-b, which assumes $t_0 = 75 \mu m$, this study identifies $R_{\text{crit}} \approx -0.2$. Before discussing the implications of this finding, it is important to note that there are many factors that influence this prediction of $R_I$ not addressed in this modeling effort. First, this model assumes that $t_{\text{reported}}$ is the same as $t_f$, which may not be the case as the ribbon thickness beyond the modeled cool zone may change significantly before the ribbon detaches from the liquid melt reservoir. Second, this heat transfer analysis does not account for any flow or surface-driven influences, such as Marangoni convection, which has been shown to be significant in other ribbon processes [7]. This study therefore advocates that Kellerman provide further descriptions of the thickness profile of the solidification region to corroborate this model.

The result of a negative value of $R_I$ for Kellerman’s reported process parameters for reasonable estimates of $t_0$ supports the theory that the (111) interface stabilizes the leading-edge interface in the HRG process. If we assume a stable process cannot go beyond the identified values of $R_{\text{crit}}$, Figures 3.18
and 3.19 also reveal that there is no combination of $V$ and $L$ for $q_0 = 120 \text{ W/cm}^2$ that yield values of $t_f < 200 \mu m$, which is consistent with Kellerman's noted difficulty in producing thin ribbons. The only combinations found in Figures 3.18 and 3.19 for this value of $t_f$ correspond to $R_i > 0.5$. The model results are consistent with the experimental observations reported by Kudo and Kellerman, and provide an explanation for their respective inability to yield thin ribbons at high process rates.
Figure 3.18: a) calculated $t_f$ assuming $t_0 = 200 \, \mu m$ and b) corresponding calculated $R_t$ for different values of $V$ and $L$, given $q_0 = 120 \, W/cm^2$. The star in a) determines the effective value of $L$ for Kellerman’s reported $t_f$ and $q_0$. The star in b) uses this identified value of $L$ to identify the associated value of $R_t$ achieved at the stability limit.
Figure 3.19: a) calculated $t_f$ assuming $t_0 = 75 \mu m$ and b) corresponding calculated $R_f$, for different values of $V$ and $L$, given $q_0 = 120 \ W/cm^2$. The star in a) determines the effective value of $L$ for Kellerman’s reported $t_f$ and $q_0$. The star in b) uses this identified value of $L$ to identify the associated value of $R_f$ achieved at the stability limit.
Although this study does not predict any process design window for $q_0 = 120 \text{ W/cm}^2$, an iterative MATLAB script was developed to find combinations of $V$ and $L$ where $R_l > R_{crit}$ and $t_f < t_{crit}$. The shaded red region shown in Figure 3.20 corresponds $t_{crit} = 500 \mu m$ and $R_{crit} = 0$. For this design process window, the stability criterion shapes the upper bound of this process window and the maximum allowable ribbon thickness undercuts the lower bound of the process window. The star in Figure 3.20 indicates $V_{max}$ for $q_0 = 120 \text{ W/cm}^2$ where the stability limit intersects with the maximum allowable ribbon thickness criteria. A noteworthy characteristic of this process window is that the slope of the prescribed Thickness Limit line is greater than that of the Stability Limit, resulting in the converging “shooting-star” shape. This indicates an inherent limitation of the HRG process that, for a given $q_0$, increasing $V$ lowers $t_f$ up until a critical point where the process destabilizes, hence coupling the maximum process rate with a minimum ribbon thickness.

![Figure 3.20: HRG process window formed by the criteria $t_f < t_{crit} = 500 \mu m$ and $R_l > R_{crit} = 0$](image)
ii. **3.3.3.2 Paths to Thin Ribbons and Higher Process Rates:**

To identify paths for the HRG process to achieve higher pull rates and thinner ribbons, an iterative script determines $V_{\text{max}}$ (as indicated by the star in Figure 3.20) and its corresponding $L$ for a given $q_0$ and $R_{\text{crit}} = -0.2$. Figures 3.21a-b plot these identified values of $V_{\text{max}}$ for their associated values of $L$, $q_0$, and $t_f$. Figure 3.21a shows that a higher values of $q_0$ result in an HRG process requiring a smaller $L$ for a given $V_{\text{max}}$, and Figure 3.21b shows that this smaller value of $L$ translates to significantly thinner ribbon at the maximum pull rate. This study therefore recommends that future HRG work focus on increasing the cooling intensity. Both of these plots assume $t_0 = 50 \mu m$.

![Figure 3.21: (a) Minimum cool zone length required to achieve a $V_{\text{max}}$ for different $q_0$ and (b) the minimum $t_f$ resulting from a given $V_{\text{max}}$](image)

Figures 3.21a-b also suggest that thinner ribbons may be possible at lower process rates with a smaller cool zone length. Although it may be feasible to create a high intensity cool zone $L < 1 \text{ mm}$ wide, we advocate pursuing approaches that do not compromise $V_{\text{max}}$. We show that allowing for more negative values of $R_{\text{crit}}$ yields a similar trend of enabling higher stable pull rates and thinner ribbons. As shown in Figure 3.22, tolerating a more substantial negative thermal gradient in the melt allows for more heat to be extracted through the liquid ahead of the interface which translates to thinner ribbons.

This study proposes that a practical approach to enabling more negative values of $R_{\text{crit}}$ would be to seed a (111) plane orthogonal to the pull direction. As discussed in Chapter 2, Voronkov asserts that a facetted interface is immune from undercooling-related instabilities only when the thermal gradient in the liquid is *orthogonal* to the pull direction. As the (111) plane maintains a 54.7° angle in the process...
pursued by Kellerman, this work proposes that the propagation of the angled facetted interface has limited stability when growing into the undercooled melt. Appendix A provides scaling arguments that strongly suggest the isotherms in the liquid near the leading-edge interface are well-approximated to be orthogonal to the pull direction. Therefore, this study proposes seeding the (111) interface such that it is well-aligned with the thermal profile would stabilize the interface for more significant values of $R_{crit}$.

![Graphs showing minimum cool zone length and maximum pull rate](image)

Figure 3.22: (a) Minimum cool zone length required to achieve a $V_{max}$ for different $R_{crit}$ and (b) the corresponding minimum $t_f$ resulting from a given $V_{max}$, given $q_0 = 120 \text{ W/cm}^2$

iii. 3.4 Conclusions and Future Work:

This work investigates the heat transfer involved in the HRG process. We review the limitations of existing HRG heat transfer models and calculate their respective shortcomings in predicting the behaviors of the HRG process in Appendix A. This investigation reveals that the impressively high process rates achieved by the HRG process to date can only be possible if a significant amount of the latent heat generated at the leading-edge interface can stably dissipate through undercooled liquid ahead of the interface. This discovery called for a new working model of the HRG process. Creating this new model required developing assumptions about the heat transfer both in the liquid and solid bordering the leading-edge solidification interface, and the result provided an unprecedented understanding of the limitations of the HRG process and identified paths to increase the process performance. The model results are consistent with the experimental observations reported by Kudo and Kellerman, and provide an explanation for their respective inability to yield thin ribbons at high process rates.
Future work includes using this understanding of the heat transfer involved with leading-edge solidification interface to develop better manufacturing processes for creating high quality silicon ribbons. We hope that these new insights about HRG process motivate further investigation into creating thin, high quality crystals by propagating a faceted interface into an undercooled melt.

References:

Chapter 4: Process and Equipment Design for Growing Monocrystalline Silicon Films

4.1 Chapter Overview and Introduction:

Chapter 3 reveals the HRG process’ limitations for producing thin, commercially viable silicon ribbons at high process rates. This chapter begins by proposing a new ribbon process that propagates an angled (111) leading-edge solidification interface in a defined silicon film and discussing its potential advantages over the HRG process. For this proposed process, we design and construct a demonstration furnace that can melt, seed, and solidify a growing ribbon with an intense cooling profile. We design a cool zone that impinges a high intensity cooling jet on the surface of the ribbon to dissipate latent heat from the ribbon’s solidification interface. For this proposed cool zone, we calculate the expected heat extraction intensity for each mechanism of heat loss from the ribbon surface as a function of the jet’s temperature. Insights from these calculations guide the design strategy of the demonstration furnace’s temperature zones and how their temperatures are monitored. Section 4.4 discusses the specific design and construction of the heater assemblies, the high intensity cooling jet, and the apparatus for moving and supporting a thin film of silicon through the furnace. This chapter concludes with a presentation of the completed demonstration furnace constructed to investigate this approach for growing monocrystalline silicon ribbon films.

4.2 Process Design for Growing Monocrystalline Silicon Films

From the options presented at the end of Chapter 3, this work experimentally investigates one approach for growing monocrystalline ribbons that proposes to limit the final ribbon thickness. As illustrated in Figure 4.1, we propose a ribbon process that propagates an angled (111) leading-edge solidification interface in a defined silicon film. Similar to the HRG process, this process seeds the ribbon such that the (111) plane holds a 54.7° to the surface, resulting in a (100) surface orientation for the final ribbon (as is presently used for solar cells). This process proposes to define and isolate a silicon film by encapsulating it in a thin, structural oxide that prevents the liquid film from both deforming via surface tension mechanisms and chemically reacting with the environment. A thin substrate supports and moves the silicon film through the hot and cool zone of the furnace. The supporting substrate should structurally support the liquid film in the hot zone but should otherwise have minimal impact on the temperature profile in the hot zone.
Figure 4.1: Concept illustration of a monocrystalline ribbon process where an angled (111) plane propagates in a defined liquid silicon film

Constraining the geometry of the growing ribbon near the leading-edge solidification interface not only limits the ribbon thickness, but potentially also enables significantly higher maximum process rates than the HRG process for three reasons. First, the proposed process could extract heat from both surfaces of the growing silicon ribbon, thereby enabling higher effective cooling intensities at the surface of the ribbon. Second, as a significant fraction of the heat extracted from the surface of an HRG ribbon grows the melt-side interface instead of dissipating latent-heat from the leading-edge interface, this proposed process would eliminate that thermal profile dilution, and all heat extracted from the film surface would conduct from the leading-edge solidification interface. Finally, given the same cooling profile, faster pull rates than the HRG process may be possible because the encapsulated silicon film is not readily contaminated by the furnace environment (carbon dissolution in the melt). This may enable a “cleaner” silicon liquid phase ahead of the interface and therefore enable more latent heat to dissipate through the liquid without destabilizing the process.

4.3 Process Cool Zone Design using an Impinging Helium Jet:

4.3.1 Background for High Intensity Jet in Solidification Processes

The cooling intensity (W/m²) imposed on the surface of the growing silicon ribbon near the solidification interface determines the temperature profile in the solid and liquid and therefore the maximum pull rate of a proposed process. The goal of this work is to design a finite, targeted cooling zone for the demonstration furnace that imposes an intense cooling profile on the surface of the ribbon and to approximate its heat extraction intensity.

Several approaches to rapidly extract heat from a surface via direct contact with a cooling metal or liquid have been explored. In strip and die casting, a chilled die rapidly extracts heat from a solidification...
interface via conduction. In quenching, heat rapidly dissipates from an interface via conduction to a liquid or via phase change occurring directly on the surface. Unfortunately, these traditional, high-intensity cooling approaches require direct contact with a potentially contaminating cooling die or liquid and are therefore not usable for this semiconductor process.

Non-contact cooling strategies for rapidly extracting latent heat from the surface of a ribbon include convection via targeted cooling jets, thermal radiation, and conduction to a cold sink through a thermally conductive gas. Kudo’s original “demonstration” of the HRG process and Kellerman’s early efforts extracted latent heat from the ribbon surface with helium jets focused at the solidification interface.[1, 2] Later efforts by Kellerman extracted heat from the ribbon surface via conduction through a thermally conductive layer of helium to an actively chilled cold sink, resulting in the reported 120 W/cm².[2] Zoutendyk’s original modeling work of the HRG process also assumed the latent heat was dissipated to a cold sink via conduction.[3, 4] In the commercially implemented vertical silicon ribbon and ingot growing processes, including String Ribbon, Edge-Fed Growth, and the Czochralski process, heat dissipates from the solid crystal surface near the solidification interface via thermal radiation alone.[5-9]

4.3.2 Cool Zone Heat Extraction Design Methods:

To extract latent heat from the solidification interface of the ribbon in the proposed demonstration furnace, the demonstration furnace impinges a helium slot jet on the surface of the ribbon. As illustrated in Figure 4.2 below, heat extraction from the surface of the ribbon in the cool zone ($q_{tot}$) is therefore the sum of radiation losses from the substrate ($q_{sub}$), heat conducted to the jet apparatus ($q_{cond}$), radiation losses from the ribbon surface ($q_{rad}$), and forced convection from the impinging jet ($q_{conv}$), as:

$$q_{tot} = q_{sub} + q_{cond} + q_{rad} + q_{conv}$$  (4.1)

This section derives expressions for each of these heat transfer mechanisms, compares their respective intensities, and then calculates the range of possible process rates for the demonstration furnace.
4.3.2.1 Thermal Radiation Heat Intensity ($q_{\text{rad}}^{i}$):

As illustrated in Figure 4.2 above, the three radiating surfaces that border the solidification interface are liquid silicon, solid silicon, and a thin, carbon fiber based substrate. Thermal radiation from these surfaces scales with their respective effective emissivity coefficients as:

$$q_{\text{rad}}^{i} = \varepsilon_i \sigma (T_{Si}^4 - T_c^4)$$

(4.2)

where $\sigma$ is the Stefan-Boltzmann constant, $\varepsilon_i$ is the effective emissivity of the radiating surface, $T_{Si}$ is the temperature of the silicon surface, and $T_c$ is the effective temperature of the cold sink. Kawamura reports the spectral emissivity of liquid silicon to be approximately 0.2 for all relevant wavelengths [1], and Tanaka reports the black-body emissivity for liquid and solid silicon to be between 0.2-0.3 and 0.4-0.5 respectively, as shown in Figure 4.3a.[2] Jain et al., however, shows that the total emissivity of silicon varies significantly with its respective doping and temperature, as shown in Figure 4.3b.[3] This study conservatively assumes that the effective emissivity of liquid silicon is 0.2 and the emissivity of solid silicon is 0.7. Finally, Burchell reports the effective emissivity of a carbon-fiber based composite is approximately 0.8 at the melting temperature of silicon.[4]
4.3.2.2 Conduction to the Cold Sink ($q_{\text{cond}}$):

This study assumes that rate of heat conducted from the surface of the ribbon to the jet or cold sink ($q_{\text{cond}}$) scales linearly with the distance between the cold sink and the ribbon ($\Delta x$) and the effective thermal conductivity of the gas ($k_{\text{gas}}$) as:

$$q_{\text{cond}} = k_{\text{gas}} \frac{\Delta T}{\Delta x}$$ (4.3)

Although pure helium exhibits high thermal conductivity [5, 6], its conductivity decreases significantly when diluted with other gas species [7]. Diluting helium gas with only 5% argon decreases its thermal conductivity from 0.47 W/m K to 0.13 W/m K. [5-7] This study assumes that the conductivity of the gas is that of undiluted He ($k_{\text{gas}} = 0.47$) and that the distance between the cold sink and the ribbon surface is $\Delta x = 1$ mm.

4.3.2.3 Heat Intensity of Forced Convection via Jet Impingement ($q_{\text{conv}}$):

A gas jet impinging on a surface can yield significantly higher convective heat transfer coefficients than those resulting from the forced convection of flow parallel to a cooling surface.[17] Several studies have documented how different jet types, flow dynamics, and surface shapes determine the dynamics and overall heat transfer coefficients of a flow. [17, 18] This section uses these studies to approximate the convective heat intensity created by a slot jet impinging the surface of the ribbon in the proposed demonstration furnace. First, we identify an appropriate Nusselt number correlation from the literature, modify it for the gas properties of Helium, and then use it to calculate the heat transfer coefficient.
on the ribbon surface. We then develop an analytical model of the heat transfer \( q_{\text{conv}} \) between the flowing helium and the ribbon surface and use it to approximate the average convective heat intensity \( q_{\text{conv}}^{\text{avg}} \).

The Nusselt number \( (Nu) \) of a jet flow impinging a surface depends on the jet nozzle type, the flow’s effective Reynold number \( (Re_D) \), surface roughness \( (f) \), the Prandtl number of the gas \( (Pr) \), and distance between the jet and the cooling surface \( (Z) \) relative to the hydraulic diameter of the jet \( (D_h) \) as:

\[
Nu = C Re_D^n Pr^m f Z / D_h
\]  

(4.4)

where \( C, n, \) and \( m \) are measured constants. [8, 9] The \( Nu \) relates to the heat transfer coefficient \( (h_{\text{conv}}) \) for a jet impinging on a surface as:

\[
h_{\text{conv}} = \frac{Nu k_{\text{gas}}}{D_h}
\]  

(4.5)

For the proposed slot jet in the demonstration furnace, a maximum He flow rate \( (\dot{V}) \) of 1 liter/s is possible, and a minimum slit width of 200 \( \mu m \) can be machined into a graphite nozzle. For a jet slit \( (L_{\text{slit}}) \) that spans 7.5 cm, a maximum possible Reynolds number \( (Re_D) \) is then:

\[
Re_D = \frac{\rho_{\text{He}} (2t_{\text{slit}}) (\frac{\dot{V}}{t_{\text{slit}} L_{\text{slit}}})}{\mu_{\text{He}}} \approx 100
\]  

(4.6)

where \( \mu_{\text{He}} \) is the viscosity of the cooling gas (He). For a uniform slot jet, studies agree that laminar flow can be assumed for \( Re_D < 2500 \), where \( D_h \) is twice the slit width \( (t_{\text{slit}}) \).[10] For these low expected values of \( Re_D \), Choo et al. have investigated the local and average heat transfer coefficients for a slot jet flow and have reported the plots given in Figure 4.4. Figure 4.4a reveals that, for the proposed jet’s low \( Re_D \), the local Nusselt number \( (Nu_x) \) and thus local heat transfer coefficient \( (h_x) \) is fairly constant at relatively large distances from the jet axis \( (x) \). Furthermore, Figure 4.4b shows that the maximum Nusselt number \( (Nu_0) \) is fairly insensitive to \( Z \).

We therefore use a modified version of Choo’s recommended expression for a slot jet’s average Nusselt number \( (Nu_{\text{avg}}) = 0.0784 Re_D^{0.74} \left( \frac{Z}{D_h} \right)^{-0.15} \) to approximate a convective heat transfer coefficient.

However, the numerical coefficient \( (0.0784) \) of Choo’s expression is a function of \( Pr \) and was evaluated for air. As air exhibits a much higher value of \( Pr \) than Helium, we define this numerical value to be a function of \( Pr \) and a coefficient \( C \) as:
0.0784 = \text{CP}_{\text{air}}^m \hspace{1cm} (4.7)

This calculated value of $C$ is then used along with Martin’s value of $m$ for a slot jet ($Pr_{gas}^{0.42}$) [9] to modify Choo’s correlation to be:

$$Nu_{avg} = CPr_{He}^{0.42}Re_D^{0.74}(\frac{Z}{D_h})^{-0.15} \hspace{1cm} (4.8)$$

![Figure 4.4: Reported variation of expected $Nu$ for a slot jet with low $Re_D$ with (a) distance from the jet center ($x$) and (b) distance of the jet from the surface ($Z$).][11]

Given this expression for $Nu_{avg}$ and the corresponding $h_{conv}^{avg}$, this study approximates the heat extraction intensity ($q_{conv}(x)$) from the ribbon surface using the model illustrated in Figure 4.5. This model assumes that helium from the slot jet flows symmetrically to both the right and left of the slot jet and creates a laminar flow on the ribbon surface. Heat dissipated from the surface of the ribbon ($Q_{conv}(x)$) raises the bulk gas temperature ($T_g(x)$) as it flows from the jet’s center axis.

![Figure 4.5: Incremental control volume fitted over the gas flowing from the jet across the ribbon surface. Convective heat from the ribbon surface raises the temperature of the gas.][82]
$Q_{\text{conv}}(x)$ thus balances the heat absorbed by the bulk gas ($Q_{\text{gas}}(x)$) as:

$$Q_{\text{gas}}(x) = -Q_{\text{conv}}(x)$$

(4.9)

Therefore, the $T_g(x)$ increase as it flows over the ribbon surface as:

$$Q_{\text{gas}}(x) = 0.5 \rho_{He} \dot{V} c_p (T_g(x + dx) - T_g(x))$$

(4.10)

where $c_p$ is the specific heat of helium gas. Finally, $Q_{\text{conv}}(x)$ scales with the temperature difference between the flowing gas and the melting temperature of silicon ($T_m$) as:

$$Q_{\text{conv}}(x) = h_{\text{conv}} w dx (T_g(x) - T_m)$$

(4.11)

where $w$ is the width of the gas jet, and $dx$ is the distance spanned by the incremental control volume.

Equations 4.10-4.11 combine to solve for the temperature of the helium as a function of position with the initial conditions of $T_g(x = 0) = T_g^0$, and the temperature of the ribbon surface is constant and equal to $T_m$, yielding:

$$T_g(x) = T_m + (T_g^0 - T_m) e^{\rho_{He} \dot{V} c_p}$$

(4.12)

$q_{\text{conv}}(x)$ is then simply found as:

$$q_{\text{conv}}(x) = h_{\text{conv}}^{avg} (T_g(x) - T_m)$$

(4.13)

Figure 4.6 plots $q_{\text{conv}}(x)$ for different initial gas temperatures ($T_g^0$) and values of $Z$. The peak heat extraction occurs at the stagnation point and diminishes at increasing distances from the jet center axis. Furthermore, Figure 4.6 shows that $q_{\text{conv}}(x)$ is most sensitive to $T_g^0$ and minimally affected by $Z$, suggesting that maintaining a low jet temperature in the furnace is a priority.

Finally, this study approximates the average rate of convective heat loss ($q_{\text{conv}}^{avg}$) from the surface of the ribbon as:

$$q_{\text{conv}}^{avg} = \frac{1}{x_f} \int_0^{x_f} q_{\text{conv}}(x) dx$$

(4.14)

where $x_f$ is the distance from the jet center, assumed from the plot to be around 7 mm. This distance is consistent with the thermal model fitted to the cool zone in the demonstration furnace, as discussed in Chapter 6.
Figure 4.6: Convective heat intensity ($q_{conv}(x)$) for varying initial gas temperatures ($T_g^0$) and jet offset distances ($Z$).

### 4.3.2.4 Total Cool Zone Heat Extraction Intensity

For the expected heat extraction via radiation, convection, and conduction from the surface of the ribbon in the demonstration furnace, Figure 4.7 presents the respective calculated heat extraction intensities ($q_i$) as a function of the jet's (cold sink's) temperature ($T_c$). Furthermore, Figure 4.7 scales these respective $q_i$'s on the second y-axis by an expected cool zone length ($L_{cool} = 4 \text{ mm}$), ribbon thickness ($t_w = 300 \mu\text{m}$), and silicon's effective latent heat ($\rho_{Si} h_{Si}$) as:

$$V_{pull} = \frac{q_i L_{cool}}{\rho_{Si} h_{Si} t_w}$$

(4.15)

It is important to note that this calculated $V_{pull}$ does not indicate a maximum stable pull rate for the proposed silicon ribbon process. Rather, $V_{pull}$ only indicates an upper-bound on a process pull rate by assuming all heat extracted from the surface dissipates latent heat from the solidification interface.

The calculated heat intensities for the different mechanisms of heat extraction plotted in Figure 4.7 were used to guide the design of the demonstration furnace. Figure 4.7 shows that the heat extraction intensity via all mechanisms can be significant in the cool zone and that the conductive/convective heat extraction from the jet exceeds that of thermal radiation for $T_c < 1000 \, ^\circ\text{C}$. The cool zone of the demonstration furnace therefore prioritizes well-insulating the cool zone from the hot zone and directly
monitoring the temperature of the cold sink to understand the process heat extraction intensity. Furthermore, it should be noted that this plot is consistent with and provides good reasoning behind Kellerman's reported 120 W/cm² heat extraction intensity. With this guidance, Section 4.3 now designs and constructs the proposed demonstration furnace.

![Figure 4.7: Heat extraction intensity and maximum corresponding pull rates for different heat transfer mechanisms on the surface of the ribbon as a function of cold sink temperature.](image)

### 4.4 Demonstration Furnace Design and Construction:

This section discusses the design and construction of a demonstration furnace that uses a helium jet to dissipate latent heat from the solidification interface of a silicon film. This section first describes a conceptual diagram of the proposed furnace and then goes on to describe the design, construction, and assembly of different furnace components.

As shown in Figure 4.8 below, the demonstration furnace has two functional, thermally isolated temperature zones. The Hot Zone (HZ) should raise the temperature of a silicon film uniformly above the melting temperature ($T_m$), and the Cool Zone (CZ) rapidly dissipates latent heat from the solidification
interface. Suspended between a heater and a thermally conductive thermal mass that buffers temperature fluctuations in the HZ, a thin substrate carries a silicon film through the HZ and CZ at rate $V$. To control and monitor the temperatures and cooling profile imposed on the ribbon surface, pyrometers spot both the HZ ($T_h$) and CZ ($T_c$). The following sections describe the designs and construction of these different furnace components.

**Figure 4.8:** Conceptual diagram of the substrate-based process demonstration furnace

4.4.1 Hot Zone Design:

4.4.1.1 Serpentine Heater Design: To raise the hot zone above $T_m$, we designed and manufactured resistive serpentine heaters using Tokai’s G330 graphite. At peak power, a Control Concept’s 1032a SCR delivers 240V to a 6:1 transformer that supplies 100 Amps to these heaters at 40 Volts. [12] As shown in Figure 4.9 below, 0.75” graphite rod connectors support and provide the electrical connection to these serpentine heaters. These rods are supported outside the furnace by two aluminum clamps that are electrically isolated from the aluminum furnace shell.
4.4.1.2 Vacuum Support Chuck: To smooth the thermal profile of the silicon film in the HZ, a graphite vacuum chuck that spans the width of the substrate (3") and the length of the hot zone (5.25") was designed. Because tension “curls” the thin substrate and therefore prevents good thermal contact between the mass and silicon film, vacuum channels were machined into the thermal mass to deliver a downward suction pressure on the substrate edges. As shown in Figure 4.10, a thin graphite sheet with a fine plenum covers rests on top of this thermal mass such that suction is only transmitted to the substrate not supporting the silicon film. This avoids a thermal gradient across the HZ. Suction via an external pump is channeled through the annulus of the quartz rods supporting the thermal mass. Also, the quartz support rods are sheathed by a second set of quartz rods that deliver purge gas (Argon) to the HZ. Gas flowing through the space between the support rods and outer quartz rods cools the quartz rods to prevent their sagging in the HZ.
Figure 4.10: a) Vacuum grooves cut into the thermal mass that channel vacuum from the connecting quartz tube. b) thin graphite cover plate that channels vacuum to the edges of the substrate through the plenum cutouts. The substrate support lip prevents the substrate from sagging near the cool-zone.

4.4.1.3 Hot-Zone (HZ) Insulation Assembly: To achieve high temperatures and minimize the cooling needs on the aluminum furnace shell, a series of Fiberform® insulation components were custom cut for the HZ, as shown in Figure 4.11. These components minimize hot zone radiation losses and minimize the paths for non-purge gases to enter the hot zone.

4.4.2 Cool Zone (CZ) Design: To create the high intensity cooling profile described in Section 4.3, this study designed and constructed a graphite cooling jet that can deliver over 1 L/s of helium to the substrate surface. As shown in Figure 4.12 below, helium flows through a gas-connection assembly mounted on the top-side of the furnace, through a connecting graphite support tube, and finally to a 200 μm slit that releases to the furnace enclosure. The jet slit is 3.5" in length.
4.4.3 Pyrometer Temperature Monitoring and Feedback Control: To monitor and to control the temperature of both the hot zone ($T_h$) and cooling jet ($T_c$), we mounted two Raytek Marathon FA1B pyrometers [13] on the top of the furnace that spot the edge of the vacuum chuck and the center of the jet respectively, as shown in Figure 4.13. As these pyrometers measure temperature from the intensity of 1 µm wavelengths emitting from a surface, we cleared a line of sight through the CZ insulation and top aluminum frame, as shown in Figure 4.14b. To cool and protect the pyrometers from corrosive furnace gases, a gas purge line (green) is connected to their aluminum fixtures, as shown in Figure 4.15. The pyrometer readings are used in real-time by a National Instruments CompactDAQ that feeds into LabView.
Figure 4.12: Solidworks model and constructed graphite gas jet assemble and path for cooling gas flow.

Figure 4.13: Top view of Raytek pyrometer spots to measure $T_h$ and $T_c$. 
Figure 4.14: Holes cut into insulation for Raytek pyrometers to spot the edge of the vacuum chuck and the center of the jet from the top of the furnace. a) insulation cutaway when top mounted on the furnace and b) insulation cutaway through insulation on the furnace top.

Figure 4.15: Support structure for helium jet and pyrometers and (b) Solidworks model of total cold zone (CZ) assembly.

4.4.4 Substrate Support Chassis and Gas Enclosure Chamber: To tension the substrate as it carries a silicon film through the furnace, we designed and constructed the substrate chassis system shown in Figure 4.16. This system consists of two rail-mounted chassis that clamp the ends of the substrate at the entrance and exit of the furnace. A lead-screw drives the chassis attached to the substrate on the “entrance side”, and an aluminum bar (not shown) rigidly connects and maintains the distance between the two chassis as it “threads” the substrate through the furnace. With this assembly, the complete furnace assembly spans over 3 m, and the travel distance of the substrate through the furnace is 90 cm. The chassis threads the substrate through the furnace at pull rates between 0.3 mm/sec and 5 mm/s. To
prevent ambient gases from entering the furnace through the substrate entrance and exit, the substrate support system is enclosed in a chamber that is also mildly purged, as shown in Figure 4.17.

Figure 4.16: Substrate, substrate rail chassis, and furnace gas enclosure (a) constructed and (b) in Solidworks

Figure 4.17: Top view of complete furnace with gas enclosure and substrate support system

4.4.5 Complete Furnace Assembly: The demonstration furnace can reach over 1550 °C in less than 40 minutes and takes roughly 30 minutes to purge with argon gas at 10 SCFH. This HZ has stably run for over 250 hours (lifetime) and has never had to be replaced. All sides of the aluminum shell are cooled with an active water cooling system. As shown in 4.19, gold coated viewing windows on the front-side of the furnace allow for comfortable viewing of the HZ and CZ during experiments. Chapter 6 discusses the temperature profiles of the furnace for different process conditions and setups.
Figure 4.18: Completed and assembled substrate-based demonstration furnace

Figure 4.19: Demonstrated furnace on and at temperature
References

Chapter 5: Silicon Film Preparation, Fine-Gauge Thermocouple Apparatus and Procedure for Measuring Temperature Profiles

5.1 Chapter Overview and Introduction

This work aims to measure the heat extraction intensity of the cool zone in the demonstration furnace and the temperature profile of a silicon film’s solidification interface as it travels through this respective cooling profile. Figure 5.1 illustrates an example temperature profile of the film’s solidification interface. To capture this proposed measurement, Section 5.2 develops a material system that defines a thin, silicon film that can remain stable as it melts and solidifies, and Section 5.3 discusses a fine-gauge thermocouple assembly developed to stably, repeatedly, and directly measure a representative thermal profile of the silicon film’s solidification interface. This chapter also describes the procedure used for melting, seeding, and growing silicon films in the demonstration furnace in Section 5.4.

Figure 5.1: Conceptual diagram of the temperature profile measurement in the demonstration furnace
5.2 Material System for Maintaining a Stable Silicon Film in the Demonstration Furnace

5.2.1 Problem Statement:

This work develops a material system for isolating and maintaining a flat silicon film that remains stable and does not chemically react with any materials in the furnace hot zone while exposed to temperatures \( T_m \) for extended periods of time. The proposed material system must also not strongly react with liquid silicon, contaminate the silicon seed, or catalyze the nucleation of new silicon grains in the undercooled liquid ahead of the solidification interface.

5.2.2 Silicon Seed Preparation:

Appapiali and Greenlee [1] both showed that a liquid silicon film encapsulated in a dry, thermally-grown oxide (0.6-1 \( \mu \)m) can remain planar and achieve high levels of undercooling before nucleating a silicon grain. Appapiali found that oxide-encapsulated liquid silicon films could be undercooled up to 100°C before a nucleation event occurred, whereas other encapsulating materials like SiNₓ triggered a nucleation event in only a few degrees of undercooling. These findings are consistent with other undercooling measurement studies performed on various SiNₓ and SiO₂ based substrates [2, 3]. Furthermore, these measured undercoolings are only a fraction of the 300 °C undercooling achieved by Li et al while levitating pure liquid drops of silicon. [4]

This study therefore used the following procedure to encapsulate thin silicon wafers in a thermally grown oxide. First, p-type (100), 200 \( \mu \)m thick solar-grade silicon wafers were cut down along the natural break lines (along (111) planes) to produce 1” X 4” seed wafers. These samples were then etched in HNA acid bath [5, 6] to remove microcracks from the surface and yield a final seed thickness of 170 \( \mu \)m. These wafers were then cleaned in an RCA bath to remove surface organics.[7] Finally, the silicon samples were loaded into a semiconductor-grade quartz tube furnace held at 1100 °C. After a 20 hour dwell in a dry-oxygen environment, a 0.8-1 \( \mu \)m [1, 8] oxide grew around the seed wafer, as shown below in Figure 5.2.

When melted and resolidified in an oxidizing atmosphere, the encapsulated silicon seeds maintained their original dimensions and presented a shiny, metallic surface, as shown in Figure 5.3a. However, this oxide was found to be unstable in the low oxygen, reducing atmosphere present in the demonstration furnace. As shown in Figure 5.3b, the oxide on a seed heated in an argon atmosphere sublimed to speckle the otherwise green oxide. This degradation occurred most strongly at the edges of the samples.
which had the most exposure to the furnace argon flows. Without this encapsulating oxide to isolate the liquid silicon, the silicon seed strongly reacted with the supporting substrate when heated above $T_m$. This resulted in either the sample being heavily contaminated by the substrate, as shown in Figure 5.3b or completely infiltrating the supporting substrate, as was the case in Figure 5.3c. The sample in Figure 5.3b was supported by a non-wetting ceramic substrate (Lytherm 1530) and the sample in Figure 5.3c was supported by a non-woven carbon fiber substrate produced by Advanced Carbon Materials.

Figure 5.2: 170 μm silicon wafers (1" X 4") encapsulated in a thermally grown oxide grown in 20 hour dwell at 1100 °C

Figure 5.3: S2 and S6 differ only in atmosphere type. S6 (right) shows “pits” in the oxide where it is believed the reducing atmosphere reacted with the thermally grown oxide.
5.2.3 High Purity Fumed Silica Spray Coating:

Because the demonstration furnace is made almost exclusively out of carbon-based components, this work investigated different coatings to stabilize the thermally grown oxide in an Argon atmosphere. After testing over 42 coating combinations in a tube furnace, this study identified two options for keeping the oxide intact and stable in the demonstration furnace. First, this study found that a silicon seed encapsulated in a densified CVD coating of SiNₓ maintained the same dimensions after it was melted and resolidified. The silicon seeds presented in Figure 5.4 below both were both coated with 2 μm of SiNₓ and then densified at 900°C in a Nitrogen environment for 1 hour. Unfortunately, it was found that the oxide sublimed out from underneath this SiNₓ coating, such that only the silicon seed and CVD coating remained. This was determined by weighing the samples before and after a hot phosphorous bath (dissolves SiNₓ) and a hydrofluoric acid bath (dissolves oxides). As would be predicted for a sample coated only SiNₓ, the melted silicon seed shown in Figure 5.4 was polycrystalline and very brittle compared to the original seed.

![Melted Seed](image)

Figure 5.4: Silicon seed samples encapsulated in densified SiNₓ coating that were a) partially melted and resolidified in the demonstration furnace and b) fully melted in a tube furnace purged with argon.

The second identified option to stabilize this oxide was to spray coat the surface of the ribbon with high purity fumed silica. As shown in Figure 5.5a, this work placed silicon seeds onto a hot plate maintained at 250°C and used an airbrush to spray several coatings of a 1:3 solution of Cabot’s L90 fumed silica and DI water on both of their respective surfaces. This work found that the airbrush settings could significantly impact the density and homogeneity of the coatings, as shown in Figure 5.5b and 5.5c. The gas settings that yielded the sample shown in Figure 5.5b were used for all the samples that characterized the temperature profile in the demonstration furnace.
As shown in Figure 5.6, L90 coated samples were able to stabilize the thermally grown oxide as the silicon seed melted and recrystallized in the demonstration furnace. Coated samples were able to preserve the original oxide coloring, however the total weight of the oxide marginally decreased while in the furnace. From visual inspection of the walls in the demonstration furnace, it seems that the L90 also sublimes at high temperatures and then recondenses as a light irredescent blue coating on cool surfaces. However, this coating deterioration does not happen so fast that the oxide is left unsupported as there is a significant coating left on the samples exiting the furnace.
5.2.4 Supporting Substrate:

But even with the support of the L90 coatings, silicon seeds that were melted and resolidified in the demonstration furnace would adhere to the supporting substrate at point contacts. As silicon contracts in volume when it melts, the oxide coating can be locally stretched where melting is initiated on the surface of the ribbon. As shown in Figure 5.7 below, “Melt Spots” can arise on the surface of the seed if the wafer is uniformly being raised slowly above the melting temperature. These molten pockets locally stretch and create little tears in the oxide that lead to liquid silicon bonding to the supporting substrate. Although this can be mitigated by slowly backing the silicon seed into the furnace hot zone such that a linear melt front develops instead of the local melt pools, liquid silicon can still erupt from the oxide at the edges and end of the oxide during solidification. This occurs chiefly because the solidification front (with volume expansion) results in mass flow to the liquid ahead of the interface. This accumulates to form an increasingly thick liquid film that eventually erupts through the oxide at the end of the silicon film. Although this would not occur in a continuous manufacturing process, this phenomenon does arise and can result in the silicon seed adhering to its supporting substrate and the vacuum chuck.

To prevent the silicon film from adhering to the substrate in the demonstration furnace, this work made two process adjustments. First, this work slowed down the rate at which the silicon seed was brought into the furnace hot zone. This resulted in fewer surface melt pools and instead brought about a more continuous melt front. Second, this work began supporting the silicon film on a thin, non-woven high purity silica fiber substrate instead of the carbon substrate that spans the furnace. This silica fiber substrate provides the same stability as the carbon fiber substrate and can be replaced with every seed crystal.
Figure 5.7: a) Molten spots formed on the surface of the silicon wafer as it begins to melt. b) Magnified surface image that shows the center of the molten spots made contact with the substrate supporting the wafer. It is not clear if the silicon made contact with the substrate before or after it resolidified.

For measuring the temperature profiles in the furnace, the procedure here-in discussed to encapsulate a silicon seed with a thermally grown oxide and coat it fumed silica fulfilled the requirements needed to maintain a stable film. However, this study recommends future work to develop oxide-based materials further for a manufacturing-scale process.

5.3 Fine-Gauge Thermocouple Assembly for Measuring the Temperature Profile of the Silicon Film’s Solidification Interface in the Demonstration Furnace

5.3.1 Problem Statement:

The analysis performed in Chapter 3 and 4 suggests that the length of the cool-zone surrounding the solidification interface will be on the order of a few millimeters, therefore measuring a representative temperature profile would require a spatial resolution on the order of 100 μm. Furthermore, as the temperature difference between the melting temperature and the undercooking of the liquid ahead of the solidification interface may be as little as a few degrees, capturing a representative temperature profile requires a resolution on the order of a single degree at $T_m = 1414^\circ C$.

5.3.2 Measurement Approach:

This study therefore considered optically measuring the silicon film’s temperature profile in the solidification furnace. FLIR produces several MWIR cameras that exhibit a 25 μm resolution pixel size and reported accuracies of $2^\circ C$ or +/- 2% for this temperature range [9]; however, implementing an optical system in the existing demonstration furnace to spot the solidification interface was considered too challenging and therefore not pursued for the following reasons. First, the clearance between the jet
and the expected surface of the solidification interface is approximately 1 mm and there is much needed insulation isolating the jet from the hot zone that would obstruct a camera spot angled from top of the demonstration furnace. Second, viewing the solidification interface from the side of the furnace is prohibited by the connector tubes of the jet. And although spotting the substrate from the bottom floor of the furnace could be possible, it is unclear if or how the thermal profile in the silicon ribbon translates through the thermally insulating nonwoven silica substrate on which it rests. Furthermore, even if a proper viewing angle could be achieved in the demonstration furnace, the reflection of radiation from the different bodies in the furnace, all exhibiting different emissivities and temperatures, could affect a temperature measurement of the solidification interface. Finally, as discussed in Chapter 4, the emissivity of coatings on the silicon seed crystal as well as the silicon seed itself could vary significantly around the solidification interface, which would also affect any temperature reading from the surface.

This study therefore considered and chose to measure the temperature profile of the solidification interface by the direct contact of a fine-gauge thermocouple on the ribbon surface. C-type thermocouples can measure temperatures up to 2330 °C with an accuracy of 1% of the reading at $T_m$. The tungsten-based wire can withstand the reducing atmosphere in the demonstration furnace, and thermocouples beads as fine as 0.003” are readily available.[10]

5.3.3 Fine-Gauge Thermocouple Apparatus Design and Assembly:

However, using a fine gauge thermocouple to accurately, stably, and repeatedly measure the temperature profile of the solidification interface in the demonstration furnace is nontrivial. First, it is critically important that the presence of the thermocouple minimally affect the geometry of the film, and although the thermocouple must be in direct contact with the seed during solidification for an accurate measurement, it must not adhere to the film. Furthermore, it is critically important that any coating or cover placed on the thermocouple be thin enough to allow for the thermocouple to register the fast temperature response expected in the furnace. Also, as the thermocouple measures temperature by producing a voltage, it is important that the thermocouple remain electrically isolated from the supporting carbon substrate and sources of electrical noise the furnace. Finally, as C-type thermocouples can be embrittled by the carbon-heavy atmosphere in the demonstration furnace, it is critically important to shield the thermocouple wire from the environment while in the hot zone.

This study threaded a fine-gauge, 0.003” C-type thermocouple through a series of thin-walled capillary quartz XRD sample holders manufactured by the Charles Supper Company. These high quality quartz tubes have 10 μm wall thicknesses and outer diameters (OD) ranging from 100-1000 μm with an OD
tolerance of +/- 10 µm. As shown in Figure 5.8a, one end of these sample holders opens to a 2 mm funnel through which a fine-gauge wire can be threaded, and the end of 3" of a 300 µm OD quartz capillary tube is sealed. These smooth, quartz capillary tubes are pliable and can therefore be softly pressed against the liquid silicon film, without tearing the oxide or significantly deforming the geometry, as shown in Figure 5.8b. The same fine-gauge thermocouple assembly can therefore be repeatedly used to directly measure temperature profiles of silicon films solidification interfaces.

![Figure 5.8: a) Charles Supper Company quartz capillary XRD tube with an OD of 300 µm through which a fine-gauge thermocouple wire is threaded and b) the imprint of this quartz capillary tube on the silicon film that was melted and resolidified in the demonstration furnace](image)

To support the thermocouple bead 14" inside the demonstration furnace and ensure that its wires are electrically insulated before terminating in an OMEGA iNet-555 DAQ, this study developed the thermocouple assembly illustrated in Figure 5.9a. As shown in this concept diagram, the thermocouple bead rests at the end of a 500 µm quartz sample holder, and one of the two wires extending from this bead is electrically insulated by a 200 µm quartz capillary tube. Upon exiting the funnel of the 500 µm quartz sample holder, both wires are threaded into a standard ceramic thermocouple sheath that guides these wires out of the furnace. To interconnect the quartz sample holder with this ceramic sheath and create a positive pressure of carbon-free argon in the assembly, the funnel of the quartz holder and ceramic sheath are encased in a 5 mm OD quartz sheath. The end of this 5 mm OD quartz tube was flame-polished to a smaller inner diameter than the funnel of the 500 µm quartz sample holder to ensure the assembly remained in the quartz sheath. Figures 5.9b-d provide photographs of the constructed thermocouple assembly that correspond to this conceptual diagram.
Figure 5.9: a) Concept diagram of fine-gauge thermocouple assembly encased in quartz capillary tubes and the structural support system that guides the wires out of the demonstration furnace. b-d) Photographs of the constructed fine-gauge thermocouple assembly.

To measure the temperature profile of the furnace, the fine-gauge TC assembly is fastened to an extension from the substrate support chassis as shown in Figure 5.10. The end of the quartz sheath connects to a yellow argon purge line taped to the substrate support chassis. The TC wires exit through small holes cut in this gas purge line and interconnect with the iNet-555 DAQ that rests on the substrate support chassis. Figure 5.10 shows the substrate support chassis in the seed-loading position, such that the TC bead rests just at the exit of the furnace. Section 5.4 discusses the procedure for loading a silicon seed into the demonstration furnace with this TC assembly.

When the substrate support chassis moves to the seed-melting position, the silicon seed (not shown) and the TC bead rest in the hot zone of the demonstration furnace, as shown in Figure 5.11a-b. Figure 5.11a shows the demonstration furnace with top and front walls removed to see reveal the TC bead relative to the heaters and the vacuum chuck. As shown by the close-up photograph in Figure 5.11b, the TC bead rests approximately 1.5 cm from the edge of the vacuum chuck in the hot zone when in the seed-melting position. If the top wall of the furnace were installed, we would see the jet positioned to the right of the vacuum chuck in Figure 5.11b.
5.4 Procedure for Loading a Seed and TC Assembly in the Demonstration Furnace:

To measure the temperature profile of a silicon film in the demonstration furnace, a 1" wide silicon seed was placed over two 0.5" strips of the non-woven silica substrate described in Section 5.2.4. The bead of the TC assembly rested between these two strips and firmly pressed against the silicon seed. The 1 mm thick silicon carbide plates shown in Figure 5.12 therefore weighted down the silicon seed such that
it lay flush to the silica substrate. These plates also ensured that the high gas flow from the cooling jet did not lift silicon seed or substrate in the cool zone. To clear the cooling jet, it was critical that the height of the substrate stack and silicon seed did not exceed 2 mm.

![Figure 5.12: Silicon seed substrate assembly. (a) Fine-Gauge thermocouple positioned between two non-woven quartz fiber substrates. (b) Silicon seed resting on top of thermocouple assembly and weighted down by silicon carbide plates. (c) Melted and resolidified seed after the temperature profile measurement](image)

### 5.5 Temperature Profile Measurement Procedure

To acquire a temperature profile of the demonstration furnace, the procedure outlined in Figures 5.13-5.16 was executed. As shown in Figure 5.13 below, the silicon seed and TC assembly were mounted on
thin carbon substrate at the furnace exit. Although not shown, the silica substrate rested below the silicon seed and the thermocouple bead rested approximately 5 mm from the end of the seed (facing the hot zone). Driven by a lead-screw, the substrate support chassis then reverses the seed assembly into the furnace, as shown in Figure 5.14.

Once reaching the “seed-melting” position in the furnace, the substrate support carriage stops, and a fraction of the silicon seed rests in the hot zone. After a given dwell period, a portion of the seed has melted, as shown in Figure 5.15.
Once the TC registers a temperature above $T_m$, the cooling jet is turned on. After another dwell period where the temperature of the furnace stabilizes. For this demonstration furnace, it typically takes 20 seconds for the jet to cool from its steady-state temperature without gas flow of around 1000 °C to approximately 700 °C. At this point, provided the TC bead is still registering a temperature above $T_m$, the support chassis then begins to pull the silicon seed to the right, underneath the cooling jet, as shown in Figure 5.16.

**Figure 5.15:** Schematic of critical components when reversing the silicon seed into the demonstration furnace

**Figure 5.16:** Schematic of critical components when the silicon seed is being solidified by the helium jet in the cool zone
Chapter 6 presents two thermal profile measurements using the procedure outlined above. The first is the temperature profile of the silicon seed’s solidification interface as it grows by the procedure described in Figures 5.13-5.16. Second, this work measures the heat extraction intensity in the cool zone for different flow gas rates through the jet and different positions of the jet relative to the graphite chuck. To measure the cooling intensity of the cool zone, this work executes the procedure outlined in Figures 5.13-5.16 with the hot zone temperature roughly 100 °C below the melting temperature of silicon. The cooling intensity is then found by fitting a one-dimensional fin model to the measured profiles that does not include the solidification interface.

References:

10. TEMPERATURE, O., Thermocouple Tolerances: American Limits of Error ASTM E230-ANSI MC 96.1
Chapter 6: Measured Thermal Profiles and Experimental Results

6.1 Introduction:

In Chapter 2, Kellerman proposes that the HRG process leverages the stability of silicon’s (111) interface to rapidly grow monocrystalline ribbons by dissipating latent heat through the liquid ahead of the leading-edge interface. Modeling work performed in Chapter 3 reveals the process-inherent challenge of growing thin ribbons at accelerated process rates and therefore inspires a new process where a (111) interface propagates in a defined silicon film. Chapter 4 designs and constructs a demonstration furnace to investigate this proposed approach. Chapter 5 develops a material system for defining a silicon film, an apparatus to measure the temperature of its solidification interface, and the procedure for melting and seeding a film in the demonstration furnace.

This chapter presents the temperature profiles measured by the fine-gauge thermocouple directly in contact with the silicon film as it travels through the demonstration furnace. Section 6.2 presents the temperature profiles measured in the demonstration furnace where the hot zone is below \( T_m \) to determine the effective heat transfer coefficient in the cool zone \( h_{cz} \) and the cool zone temperature \( T_{cz} \). This section shows how the cooling intensity of the cool zone scales linearly with the flow rate of the jet and determines the cool zone’s maximum values of \( h_{cz} \) and \( T_{cz} \) by fitting these curves to a one-dimensional thermal model. This section shows that the jet must be positioned a minimum of 7 mm from edge of the hot zone to avoid a significant thermal profile in the graphite chuck. Both the cooling intensity and the response of the cool zone to different furnace parameters are shown to be readily predicted by the modeling work in Chapter 4.

Section 6.3 presents the measured temperature profiles of the silicon film’s solidification interface as it travels through the cool zone. For high pull rates and the maximum cooling intensity in the demonstration furnace, the fine-gauge thermocouple apparatus developed in Chapter 5 captures temperature profiles where the liquid ahead of the solidification interface is significantly undercooled. This fine-gauge thermocouple apparatus repeatedly and consistently measures the expected undercooled liquid profile ahead of the interface. This section compares these preliminary measurements to the HRG solidification process model and recommends future work for developing this proposed process where a (111) plane propagates in a defined silicon film.
This chapter concludes by presenting the microstructure of silicon seeds melted and recrystallized in the demonstration furnace. Section 6.4 shows that small tears created in the oxide film created during the melting of the silicon film result in the liquid silicon contacting the supporting substrate and nucleating grains ahead of the solidification interface. So although the silicon seeds initially grow a monocrystalline interface, the samples exhibit a dendritic, polycrystalline microstructure after a few millimeters. This section concludes with recommending future work to stabilize this oxide.

6.2 Demonstration Furnace Thermal Profiles:

6.2.1 Measured thermal profiles and process behavior

As discussed in Chapter 5, this study characterizes the thermal profile of the demonstration furnace at temperatures below $T_m$ by reversing the silicon film into the hot zone, waiting for the temperature to stabilize, and then pulling the silicon film through the cool zone. The temperature profiles presented in Figure 6.1 begin when the silicon film starts traveling in the direction of the cool zone at 100 mm/s. These measured profiles are captured by the fine-gauge TC apparatus while the jet is positioned approximately 1 cm away from the edge of the vacuum chuck and differ only in the flow rates through the jet. As expected, Figure 6.1 shows that increasing the flow rate through the jet results both in a greater measured thermal gradient across the silicon ribbon as well as a lower temperature minimum. Figure 6.1 also shows that the temperature of the silicon film reaches a minimum in the cool zone before rising to the ambient temperature of the furnace away from the cool zone.

For the temperature profiles presented in Figure 6.1, Figure 6.2 plots the average thermal gradients measured by the fine-gauge thermocouple assembly in the cool zone relative to the flow rate through the jet. This figure shows that the measured thermal gradient scales linearly with the gas flow rate through the helium jet.
Figure 6.1: Temperature profiles measured by the fine-gauge thermocouple apparatus as it travels with the silicon film through the demonstration furnace at 100 mm/s. The different curves correspond to different runs where only the gas flow rate is varied.

Figure 6.2: Measured average thermal gradient in the cool zone as a function of the flow rate through the cooling jet and a linear fit line.
6.2.2 Fitted Demonstration Furnace Heat Transfer Model

To understand the maximum possible heat transfer coefficient \(h_{cz}\) and the effective temperature \(T_{cz}\) of the cooling profile acting on the silicon film through the cool zone, this work fits a one-dimensional heat transfer model to the measured thermal profiles presented in Figure 6.1. As the expected Biot number \(Bi_{ex}\) of the thermocouple and thin silicon film is approximated to be much less than 1:

\[
Bi_{ex} = \frac{h_{ext}}{k_{ex}} \approx \frac{(800)(5e^{-4})}{60} \ll 1
\]  

(6.1)

it is assumed the thermocouple and silicon wafer exhibit the same thermal profile and can be reasonably treated as a combined one-dimensional entity. We therefore model the combined thermocouple and silicon film as it travels through the cool zone to be a three-part fin. As indicated in Figure 6.3, we assume that the first section of the fin spanning a distance \(x_0\) has no heat extracted from the surface, that the second region of the fin is actively cooled by the jet \(x_{jet}\), and that the final region of the fin slowly reaches the temperature of the demonstration furnace adjacent to the cool jet \(x_1\).

![Figure 6.3: Illustration of the thermal model fitted to the thermal profile data presented in Figure 6.3.](image)

We model the cool-zone bordering the vacuum chuck to be a one-dimensional fin, where the first section of the fin spans a distance \(x_0\) and has no heat extracted from the surface. This model also assumes the second region of the fin is actively cooled by the jet \(x_{jet}\), and the final region of the fin slowly reaches the temperature of the demonstration furnace adjacent to the cool jet \(x_1\).

The temperature profile of the silicon film and thermocouple assembly for \(0 < x < x_0\) is therefore approximated to be:
\[ (k_{si}t_{si} + k_{tc}t_{tc}) \frac{\partial^2 T}{\partial x^2} + V(\rho_{si}c_{si}t_{si} + \rho_{tc}c_{tc}t_{tc}) \frac{\partial T}{\partial x} = 0 \]  

(6.2)

where \(k_{si}\) and \(k_{tc}\) are the thermal conductivity of silicon and the thermocouple respectively, \(t_{si}\) and \(t_{tc}\) are the effective thickness of the silicon film and thermocouple respectively, \(\rho_{si}\) and \(\rho_{tc}\) are the density of the silicon film and thermocouple respectively, \(c_{si}\) and \(c_{tc}\) are the specific heat of the silicon film and thermocouple respectively, and \(V\) is the pull rate. The temperature profile of the silicon film and thermocouple assembly for \((x_0 < x < x_0 + x_{jet})\) is therefore:

\[ (k_{si}t_{si} + k_{tc}t_{tc}) \frac{\partial^2 T}{\partial x^2} + V(\rho_{si}c_{si}t_{si} + \rho_{tc}c_{tc}t_{tc}) \frac{\partial T}{\partial x} - h_{cz}(T - T_{cz}) = 0 \]  

(6.3)

And the temperature profile of the silicon film and thermocouple assembly for \((x_0 + x_{jet} < x < x_0 + x_{jet} + x_1)\) is therefore:

\[ (k_{si}t_{si} + k_{tc}t_{tc}) \frac{\partial^2 T}{\partial x^2} + V(\rho_{si}c_{si}t_{si} + \rho_{tc}c_{tc}t_{tc}) \frac{\partial T}{\partial x} - h_{df}(T - T_{df}) = 0 \]  

(6.4)

where \(h_{df}\) is the heat transfer coefficient between the ribbon and demonstration furnace for the region downstream from the cooling jet, and \(T_{df}\) is the temperature of the demonstration furnace downstream from the cooling jet. Temperature boundary conditions for the temperature profiles include \(T(x = 0) = T_{start}\) and \(T(x \to \infty) = T_{df}\). Also, this model assumes the temperature profile is continuous at the boundaries between the different fin sections.

Figure 6.4 shows this one-dimensional heat transfer model (blue solid curve) fitted to the measured thermal profile of the silicon film (blue dashed curve) traveling through the cool zone of the demonstration furnace for \(V = 100\) mm/min, \(\dot{V} = 80\) SCFH, and the jet axis positioned 1 cm from the graphite chuck. This fitted thermal profile assumes \(h_{cz} = 1500\) W/m²°C, \(T_{cz} = 800\) °C, \(x_0 = 3\) mm, and \(x_{jet} = 14\) mm. The values of \(T_{start}\) and \(T_{df}\) were taken from the data directly. Assuming that the chief mode of heat transfer from the ribbon to the furnace was thermal radiation, this model reasonably assumes \(h_{df} = 400\) W/cm²°C. For the fitted values of \(h_{cz}\) and \(T_{cz}\), the effective cooling intensity \(q_{df}\) for a film surface at \(T_m\) would be approximately \(q_{df}(T_m) \approx 92\) W/cm². This cooling intensity is comparable to that of Kellerman’s process (120 W/cm²) and what we would expect, given the modeling work performed in Chapter 4. The assumed value of \(T_{cz}\) is also comparable to what is measured by the pyrometers in the furnace in real time when gas is flowing through the jet at high rates. The modeling work performed in Chapter 4 also supports that our approximation of \(x_{jet}\) is also reasonable.
Figure 6.4: Temperature profiles measured of the silicon film for a jet intensity of 80 SCFH, a pull rate of 100 mm/min, and a distance of 1 cm (blue) and 0 cm (red) between the jet axis and the vacuum jet.

To understand how the position of the jet relative to the graphite chuck affects the thermal profile of the hot zone, we positioned the cooling jet such that the jet axis was aligned with the edge of the vacuum chuck. For a maximum jet flow rate of 80 SCFH, the measured temperature profile (dashed red curve) shows how the jet at the edge of the vacuum chuck creates an undesirable thermal gradient in the hot zone and cools the hot zone well below the melting temperature. To prevent the jet from cooling the hot zone, it is positioned 1 cm away from the edge of the graphite chuck to measure the more dramatic temperature profiles of the silicon film's solidification interface that are discussed in Section 6.3. The model (solid red) fitted to the measured thermal profile used the same value of $h_{CZ}$ and $T_{CZ}$ used to fit the blue curve. The chief difference between these two fitted profiles was that the thermal profile for the fitted to the on-axis jet curve shifted the values of the jet positions to $x_0 = 0$ mm and $\frac{x_{jet}}{2}$. 

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6.3 Temperature Profile of Silicon Film Solidification Interface

6.3.1 Measured Temperature Profiles of the Silicon Film Solidification Interface

This work measured the temperature profile of a silicon film’s solidification interface using a fine-gauge thermocouple that directly contacts the film as it travels through the hot and cool zone of the demonstration furnace. Executing the procedure described at the end of Chapter 5, we sought to measure liquid thermal profiles that exhibited the thermal undercooling needed to advance silicon’s (111) plane and dissipate latent heat from a stable monocrystalline interface at high process rates. These measurements are used to discern future work for developing this proposed process for manufacturing monocrystalline silicon ribbons.

Figure 6.5 shows two measured temperature profiles of the solidification interface where the jet was aligned with and 1 cm away from the edge of the graphite chuck. Both measurements were taken with $V = 100$ mm/min and $\dot{V} = 40$ SCFH, and both profiles show that the liquid silicon films undercooled below the melting temperature before rising up to the effective melting temperature. Interestingly, both profiles show the solidification interface to be several degrees below the equilibrium melting temperature of silicon (1414 °C). Both temperature profiles exhibit well-defined negative thermal gradients in the liquid adjacent to the solidification interface. As discussed in Chapter 2, this is to be expected as silicon’s (111) plane must be undercooled at least 3.7 °C to initiate growth. It is also expected that the position of the solidification interface would move towards the end of the graphite chuck when the jet is positioned 1 cm away from the edge.

Figures 6.6 shows the measured temperature profiles of silicon films traveling at $V = 100$ mm/min with the jet positioned 1 cm away from the edge of the graphite chuck, where the jet was flowing $\dot{V} = 40$ SCFH for the blue curve and $\dot{V} = 80$ SCFH for the green curve. Unexpectedly, the higher jet flow rate brought about a more dramatic cooling profile in the liquid bordering the interface, and the thermal profile measured in the solid ribbon bordering the interface did not change substantially. This may be because the silicon film and TC bead were still in the hot zone during solidification, and heat transfer to the graphite vacuum chuck dissipates the high intensity cooling profile. The expected response of the film’s temperature profile to different process parameters is discussed in Section 6.3.2.
Figure 6.5: Temperature profiles of the silicon film's solidification interface as measured by the fine-gauge thermocouple for different positions of the jet relative to the graphite chuck.

Figure 6.6: Measured solidification profiles of silicon films traveling at $V = 100$ mm/min with the jet positioned 1 cm away from the edge of the graphite chuck, where the jet was flowing $\dot{V} = 40$ SCFH for the blue curve and $\dot{V} = 80$ SCFH for the green curve.
6.3.2 Thermal Model of Proposed Silicon Film Solidification Process

The goal of this section is to calculate what the temperature profiles of a working silicon film process would resemble and discuss the paths to enabling higher process rates in a given demonstration furnace. As previously discussed in Chapter 4, the proposed silicon ribbon process can be modeled as a one-dimensional fin, where the thermal profile of the ribbon on either side of the cool zone is approximated by:

\[
(k_{si}t_{si}) \frac{\partial^2 T}{\partial x^2} + V(\rho_{si}c_{si}t_{si}) \frac{\partial T}{\partial x} = 0
\]  

(6.5)

where \( k_{si} \) is the thermal conductivity of either solid or liquid silicon, \( \rho_{si} \) is the density of either solid or liquid silicon, and \( c_{si} \) is the specific heat of either solid or liquid silicon. In a cool zone of length \( L \), the thermal profile is found by:

\[
(k_{si}t_{si}) \frac{\partial^2 T}{\partial x^2} + V(\rho_{si}c_{si}t_{si}) \frac{\partial T}{\partial x} - h_c(T - T_{cz}) = 0
\]  

(6.6)

Similar to the assumptions made in Section 6.2, we would expect the temperature profile to be continuous at the boundaries between the different fin sections. As shown in Figure 6.7, we expect the ribbon’s solidification interface to be inside the cool zone where heat is extracted both from the bordering liquid and solid ribbon. The thermal profiles presented in Figure 6.7 all show the expected undercooling profile in the liquid ahead of the solidification interface as well as a sharp temperature profile in the solid ribbon. The blue trace indicates the region of the film in the cool zone. Figure 6.7b presents the calculated horizontal temperature profiles of silicon films with different thicknesses being chilled by the same cooling intensity. This figure shows that thinner ribbons require shorter cool zones and the liquid ahead of the interface does not achieve the high undercooling that occurs with thicker ribbons. This low level of undercooling is critically important for avoiding the nucleation of a new grain ahead of the solidification interface.

Figure 6.8 presents the calculated temperature profiles of silicon films with different cooling intensities. As the expected radiation from the surface of the ribbon at the melting temperature of silicon to a cold sink is assumed to be approximately 40 W/cm², this plot presents these curves as multiples of this radiation heat intensity. As expected from our previous discussions of the HRG process and the results presented in Figure 6.7, a higher cooling intensity requires a shorter cooling profile and results in less undercooling in the liquid ahead of the solidification interface.
Figure 6.7: Solidification model for the proposed process for growing a silicon film in a high intensity cooling profile indicated by the blue traced line. a) The calculated horizontal temperature profile of a silicon film being chilled by a cooling profile of length L. Heat generated at the leading-edge interface dissipates through both the liquid and solid. b) The calculated horizontal temperature profile of silicon films of different thicknesses being chilled by the same cooling intensity.

Figure 6.8: Calculated thermal profiles of silicon ribbons for different cooling heat intensities
Figures 6.7 and 6.8 show that, like the HRG process, higher cooling intensities enable higher process rates for growing monocrystalline silicon films. Unlike the HRG process, the calculated thermal models presented here suggest that thinner ribbons are both possible and potentially yield a more stable thermal profile in the liquid ahead of the solidification interface. From this one-dimensional thermal model of the proposed film process, this work advocates for developing thinner silicon films and a cool zone with a higher cooling intensity and shorter cool zone length.

6.4 Silicon Seeds Melted and Resolidified in the Demonstration Furnace

This section presents silicon seeds that were melted and resolidified in the demonstration furnace with and without the fine-gauge thermocouple assembly. The 1” wide silicon seeds presented in Figure 6.9 were melted and solidified while resting on the fine-gauge thermocouple assembly. These seeds all have distinct imprints of where the thermocouple assembly was pressed into the film. Also, the portion of the seed crystal that rests on the TC assembly without contacting the quartz fiber substrate melted back more than the surrounding crystal. This region is also distinctively smoother than the rest of the melted seed, most likely because it was not in contact with the disturbing, non-woven quartz substrate. However, the entire melted portion of the seed exhibited a shiny, metallic surface indicating that the oxide was kept stable enough to prevent significant reaction with the supporting substrate. Also, the thickness of the final silicon seeds were comparable to the original seed thickness.

Figure 6.9: Silicon Seeds melted and solidified while resting on the fine-gauge thermocouple assembly and non-woven quartz fiber substrate.
Silicon seeds that were melted and resolidified in the demonstration furnace without the fine-gauge thermocouple assembly are presented in Figure 6.10. Supported by the non-woven quartz fiber substrate, these samples present the desired even temperature profile across the seed width, indicating a uniform temperature hot zone orthogonal to the pull direction. Although the first few millimeters of the silicon seeds exhibited monocrystalline growth, the seeds unfortunately transitioned to polycrystalline dendritic growth. Upon closer inspection, this transition to polycrystalline microstructure coincided with what appear to be small tears created in the oxide by the expansion and contraction of the seed crystal during melting and solidification. These tears allow liquid silicon to interact with surrounding surfaces that both contaminate and potentially result in the nucleation of new grains in the undercooled liquid silicon film.

Figure 6.10: Silicon seeds melted and resolidified in the demonstration furnace resting on non-woven quartz fiber substrates. a) The top surface and b) bottom surface of the solidified seeds show how contact with the non-woven quartz fiber substrate distorts and reacts with the seed crystal. c) The bottom of the silicon seed crystal has small point contacts with the non-woven substrate. d) As silicon contracts volumetrically when melting, the thermally grown oxide becomes distorted and develops tears that allow for the liquid silicon to interact with surrounding surfaces.
To keep the oxide film coating as intact as possible, silicon seeds were then melted and resolidified in the demonstration furnace while being supported by a polished quartz plate instead of the non-woven substrates. The resulting 1” wide samples presented in Figure 6.11 exhibit a smoother surface and a longer region (up to 1 cm) of seeded monocrystalline growth before decaying into polycrystalline material. Although using thin quartz plates would be cost prohibitive for a manufacturing process, these high quality films indicate that future work should focus on developing smoother substrate surfaces.

An SEM image and electron backscatter diffraction (EBSD) scan of the border between the un-melted and melted region of the silicon seed are presented in Figure 6.12. The SEM image shows that the melted silicon seed (right side of scan) exhibits a much rougher surface than the un-melted seed (left side of scan). Because the spray-coated silica layer seems to agglomerates into clusters of that length scale, we believe the small “craters” that speckle the surface of the melted film are imprints of the silica coating. The corresponding EBSD scan (the color indicates silicon’s grain orientation) in Figure 6.12b shows that the (100) orientation of the seed is also present in the melted film bordering the un-melted region.

Figure 6.13 presents the EBSD scan of a typical polycrystalline portion of a film resolidified on a quartz plate. The film’s microstructure is characterized by a dominant bulk grain orientation (which is not the original (100) seeded orientation) that is speckled by small sub-millimeter grains. The nucleated grains are expected, given the observed tearing in the oxide and the measured thermal undercooling of the liquid ahead of the interface. The domination of this alternate grain orientation is also expected, as the seeded orientation is kinetically limited by the (111) plane and would therefore be slower than any other orientation that were to evolve. This work therefore concludes that this proposed process can only yield monocrystalline material if both the solidification interface remains stable and the nucleation of new grains ahead of the interface is prevented. Developing an improved material system for encapsulating silicon seeds and supporting them through a furnace is therefore necessary to overcome the present limitations of this proposed monocrystalline film process.
Figure 6.11: a) silicon seeds encapsulated in a thermally grown oxide and spray coated with fumed silica that were supported by a thin polished quartz substrate in the demonstration furnace. b) Silicon seeds after oxides removed via a 30 second exposure to hydrofluoric acid.
Figure 6.12: a) SEM image of the seed crystal (left side of the image with the smooth surface) and the melted and resolidified seed (right side of the image with the rougher surface). b) EBSD scan of this transition region that shows the grain orientation (001) is seeded.

Figure 6.13: EBSD scan of the polycrystalline region of the film. The film exhibits small sub-millimeter size grains interspersed with an otherwise homogenous grain orientation. It is important to note the orientation of the bulk phase is not (100).

6.5 Future Work Recommendations

This work recommends the following list of action items to continue development of a commercially viable, monocrystalline silicon ribbon manufacturing process.
Chapter 7: Conclusions and Contributions

The goal of this work was to identify and pursue an approach for growing commercially viable, monocrystalline silicon ribbons. Starting from Kellerman's 2013 DOE report that proposes the leading-edge solidification interface of the HRG ribbon is shaped by a \((111)\) interface, this work developed the first analytical model of the HRG process that readily explains and is consistent with the observed HRG process behaviors. For Kellerman's reported process parameters, this analytical model showed that a significant fraction of the latent heat generated at the leading-edge solidification interface dissipates through the liquid ahead of the solidification interface. These findings support the notion that the kinetics of a \((111)\) leading-edge solidification interface stabilizes the HRG process, allowing for significantly higher process rates than other silicon ribbon manufacturing processes. This modeling work also investigated how increasing the process cooling intensity or the threshold for destabilizing the HRG process could yield thinner ribbons. Although we found that both of these approaches could reduce the ribbon thickness significantly from the present minimum of 650 \(\mu\)m to 200 \(\mu\)m, the calculated small cooling profile lengths (<1 mm) and high intensity cooling profiles (> 200 W/cm\(^2\)) present a significant engineering challenge.

To overcome these identified limitations of the HRG process, this work proposed a process modification where the \((111)\) leading-edge solidification interface propagates in a defined silicon film supported by a substrate. This proposed approach constrains the ribbon thickness. The proposed approach also achieves a significantly higher effective cooling intensity at the leading-edge solidification interface compared to the HRG process for two reasons. First, this modification allows for heat extraction through both sides of the ribbon. Second, unlike the HRG process, heat extraction from the ribbon surface in this process is not diluted by the melt-side solidification interface.

To investigate this proposed process, we designed and constructed a high temperature semiconductor furnace that could melt, seed, and grow a silicon ribbon in a high intensity cooling profile comparable to the profile reported in the Kellerman HRG process. We designed a rail and chassis system that tensions a thin substrate through the proposed furnace and a vacuum chuck system that keeps the liquid film flat as it travels through the hot and cool zones. We also designed a series of graphite serpentine heaters and insulation components that yield an even, flat thermal profile in the hot zone. To create the desired high cooling intensity, we modeled the heat transfer for the ribbon surface as it travels through the cool zone. We then designed a graphite slot jet that impinges helium on that surface. Using this work's
developed fine-gauge thermocouple assembly, we measured that this jet creates an effective 92 W/cm² cooling intensity in the cool zone. Silicon seeds melted and re-solidified in this demonstration furnace exhibited a desired flat, planar solidification interface.

This work developed a novel fine-gauge thermocouple assembly that could directly measure the temperature profile of a silicon seed as it melted and then traveled through the demonstration furnace. Separated and protected from the silicon seed by only a sheath of quartz 10 μm thick, this fine-gauge thermocouple assembly was durable enough to release from the silicon seeds and then be reused for up to 10 measurements before the sheath became severely devitrified. At the same time, this fine-gauge TC assembly had a fast enough response time to capture the expected undercooling and negative thermal gradient in the liquid ahead of the solidification interface. The fine-gauge TC assembly repeatedly captured and well-defined the expected thermal profile in the liquid ahead of the leading-edge interface, where the measured undercooled region was less than 500 μm long. This fine-gauge TC also measured the temperature of the solidification interface to be several degrees below the melting temperature of silicon, which Chapter 2 showed to be necessary for advancing a silicon solidification interface. The measured temperature profiles of the solidification interface revealed also that the seed crystal solidified before reaching the end of the hot zone, thus necessitating future work in developing the demonstration furnace architecture.

Several of the silicon seeds that were melted and re-solidified in the demonstration furnace exhibit single crystal microstructure at the very beginning of the seed. However, the seed quickly becomes polycrystalline after only a few millimeters. Upon close inspection, we find that the melting of the silicon seed locally creates small tears in its encapsulating oxide. Although this does not seem to be problematic for the top surface of the ribbon, the bottom surface of the ribbon creates point-contacts with the non-woven quartz fiber substrate where liquid melt “leaks” from these tears. This study believes that the escaped undercooled liquid silicon in contact with the substrate nucleates grains and thus gives rise to the observed polycrystalline microstructure samples.
**Horizontal Ribbon Growth Process Modeling:**

- To refine the analytical model developed here and better approximate the thermal profiles involved at the leading-edge solidification interface, this work advocates that Kellerman publish details about the thickness profile of the HRG silicon ribbons and the lengths of the HRG process’ cooling profiles. Specifically, understanding the thickness of the leading-edge solidification interface would constrain the proposed model so it can better approximate the horizontal thermal gradients.

- This work also recommends expanding this HRG model to account for the role of impurity segregation at the leading-edge solidification interface and the corresponding effects of constitutional supercooling. This would provide insight into exactly which impurities play a large role in the destabilization of the interface and would guide future efforts in “cleaning up” the melt. Furthermore, this also would identify what dopants could be used for an HRG process (based on their segregation properties).

- This work further recommends developing a full-scale FEM phase-field model of the HRG process to refine our understanding of the two-dimensional thermal profile in the liquid and the solid ribbon. A more sophisticated modeling effort could solve for the leading-edge solidification interface thickness, account for the heat transfer driven by convection in the melt, and calculate the leading-edge thermal profile created by a non-uniform rate of heat extraction. Helenbrook and Kellerman have attempted to develop such a model, and this work advocates for the publication of the full model and its corresponding process windows in detail.

**Demonstration Furnace Design and Construction:**

- Although the demonstration furnace hot zone was able to create a homogenous temperature profile across the width of the silicon seed, it also exhibited a significant thermal gradient along its length in the pull direction. Because super-heating the liquid seeds degrades and eventually destabilizes the oxide films, this thermal gradient prevents seed crystals from backing up “too far” into the hot zone. To grow longer samples, this study proposes shortening the graphite vacuum chuck and using insulation to reduce the effective hot zone length to only 1”. This would enable the process to grow longer films in a continuous fashion.

- This work recommends abandoning the slot jet cooling apparatus for a more targeted, high intensity cooling approach. The fine-gauge thermocouple assembly measured the effective
length of the cooling profile created by the helium slot jet to be approximately 14 mm, which is supported by the modeling work performed in Chapter 4. However, thermal profiles in Chapter 6 show that the proposed process requires only a fraction (less than half) of that cooling length. Furthermore, the fine-gauge thermocouple measured that the edge of the hot zone is cooled by the flowing helium gas such that the film solidifies before exiting the hot zone. This work therefore advocates for a different cooling approach where, similar to that of the HRG process described by Kellerman, heat is extracted from the surface of the ribbon by conduction to an actively cooled heat sink. By removing the large footprint of the helium jet and constraining the cool zone to only the finite region underneath this cool sink, we believe that the more dramatic cooling profiles necessary for this approach are possible.

**Temperature Profile Measurement Instrumentation:**

- We also advocate for developing an IR-based approach for measuring the temperature profile of the cool zone in the demonstration furnace. Specifically, mounting an IR camera to the floor of the demonstration furnace that measures the temperature of the substrate as it exits the hot zone could be extremely helpful for understanding the heat intensity of the cool zone in the demonstration furnace. However, we maintain that the direct contact measurement of the TC bead to the silicon film is the best approach for measuring the temperature profile of a film’s solidification interface.

**Material Development of the Silicon Seed Coating and Supporting Substrate**

- The chief limitation of the proposed process to grow monocrystalline silicon ribbons is the material system used to coat and support the silicon seed. As originally shown by Appapillai, this study maintains that an oxide-based coating is the best option for growing a monocrystalline silicon film where the liquid ahead of the interface undercools significantly below the melting temperature. However, the present structural fumed silica spray coating and/or the supporting fibrous substrate tears this oxide and nucleates new grains that prevent single-crystal growth. This work specifically believes that developing a *flat and smooth* supporting substrate would minimize the disturbance of this oxide coating. Appapillai and Greenlee both showed that supporting an oxide-encapsulated silicon seed with flat silicon carbide plates enabled the production of smooth films. This work recommends a priority be given to developing this material system.
A.2 Scaling Analysis to Identify Dominant Heat Flows in HRG Process

A.2.1 Heat Extracted through Solid Ribbon with Angled (111) Plane Interface Scaling Analysis

As illustrated in Figure A.1, the heuristic model presented by Kellerman assumes that the surface of the growing ribbon is the (100) orientation (preferred surface for solar cells), which is bound by the (111) plane oriented at 54.7° to the surface of the grown ribbon. This model assumes that the latent heat generated from the leading-edge interface dissipates only through the solid ribbon. This subsection therefore develops two simple models of the heat transfer through this solid ribbon to approximate the fraction of latent heat dissipated from the leading-edge interface, given Kellerman’s reported cooling profiles. Chapter 3 uses the second model to approximate the heat transfer in the solid ribbon and the ribbon’s thickness profile.

![Figure A.1: Heuristic model of Varian’s Floating Silicon Process incorporating growth kinetics of facetted growth. The imposed cooling profile \( q''_{wcl}(x) \) is assumed to be Gaussian and imposed on the solid, and leading-edge of the interface is a perfectly flat (111) plane [1].](image)

The first model calculates the heat extracted through the solid ribbon by assuming that the isotherms in the control volume illustrated in Figure A.2 are parallel to the angled interface. As shown, this control volume encloses the entire “sharp” interface which is pulled to the right at rate \( V \). Assuming that the liquid ahead of the interface plays a negligible role in the heat transfer at the leading-edge solidification interface \( q_{lx}, q_{ly} = 0 \), heat generated at the solidification interface must dissipate through the control volume boundaries orthogonal \( q_{sx} \) and parallel \( q_{sy} \) to the pull direction.
Appendix A:

A.1 Limitations of Traditional Silicon Ribbon Heat Transfer Models:

Although the HRG process has produced monocrystalline silicon ribbons at high process rates, the shape of the solidification interface and the corresponding heat transfer in both the liquid and solid phase are not well understood. Kellerman has presented evidence that indicates a significant amount of the latent heat generated at the leading-edge solidification interface dissipates through the undercooled liquid ahead of the interface, which is not accounted for in the existing HRG process models. To date no analytical thermal model has been developed that assumes the leading-edge solidification interface is shaped by a (111) plane maintained at a fixed angle to the pull direction.

This work therefore develops scaling relationships to create simple models of the heat transfer in both the liquid and solid ribbon bordering the leading-edge solidification interface in the HRG process. These models are used in Chapter 3 to approximate how heat extracted from the surface of the liquid and solid regions determine the final ribbon thickness and thermal profile in the liquid. We then use Kellerman’s recently reported process parameters ($q_{sy} = 120$ W/cm$^2$, $V = 2$ mm/s) to understand if these preliminary models predict a significant fraction of latent heat dissipating through the liquid ahead of the interface.

It is important to recognize that the simple models developed by this Appendix are meant to approximate the heat transfer involved with the HRG process’s leading-edge solidification interface. The thermal profile in the liquid and solid region bordering the solidification interface are three-dimensional and would require advanced phase-field modeling programs to accurately solve for. The simple models developed here for the heat transfer in the pull direction and the complete simulations carried out in Chapter 3 aim to only capture and explain the HRG’s behavior. As the destabilization of the HRG process, the undercooling of the liquid ahead of the interface, and the HRG’s challenge in producing thin ribbons is captured by these simple models, we believe that this work can readily guide future development work without the need for advanced software packages. The MATLAB scripts presented in Appendix B and C approximate the HRG thermal profiles and create process windows for the varying parameters in less than one minute computing time.
For a steady-state process, the heat transfer across the control volume surfaces outlined in Figure A.2 balances the latent heat generated at the interface, as given by:

\[ \rho h_{l/s} V \tau = \tau \left( q_{sx} + q_{lx} + \cot \theta_{111} (q_{ly} + q_{sy}) \right) \]  \hspace{1cm} (A.33)

where \( \rho h_{l/s} \) is the latent heat (J/m\(^3\)), \( q_{sx} \) and \( q_{sy} \) are respectively the heat transferred through the solid ribbon, and \( q_{lx} \) and \( q_{ly} \) are the heat transferred through the liquid. If the isotherms are parallel to the solidification interface, \( q_{sx} \) can be related geometrically to \( q_{sy} \) as:

\[ q_{sx} = q_{sy} \tan \theta_{111} \approx 1.4 (q_{sy}) \]  \hspace{1cm} (A.34)

It is important to note that the fixed geometry of the “sharp” interface results in \( q_{sx} \) being independent of the ribbon thickness. For Kellerman’s reported value of \( q_{sy} \), the maximum process rate \( (V_{sat}) \) expected with this parallel isotherm assumption is only a fraction of what was experimentally demonstrated \( (V_{exp} = 2 \text{ mm/s}) \), as shown by:

\[ \frac{V_{sat}}{V_{exp}} = \frac{q_{sx} \tan \theta_{111} + q_{sy} \cot \theta_{111}}{\rho h_{l/s} V_{exp}} \approx \frac{2.1 (q_{sy})}{\rho h_{l/s} V_{exp}} \approx 0.22 \]  \hspace{1cm} (A.35)

This study therefore also investigates the possibility that the isotherms in the illustrated control volume are not parallel to the angled facet plane. For this assumption, we approximate \( q_{sx} \) by calculating the thermal profile in the solid ribbon adjacent to the leading-edge solidification interface, as outlined in Figure A.3. Unlike the control volume containing the leading-edge interface in Figure A.3, this control volume contains a diffuse solidification-interface which is analogous to the melting temperature isotherm. Heat extracted from the surface of this control volume \( (q_{sy}) \) must therefore originate from the latent heat generated at either the leading-edge solidification interface or the diffuse, melt-side ribbon surface. Heat conducted from the facetted edge \( (q_{sx}) \) contributes to the maximum process rate.
(V), and heat conducted from the melt-side ribbon surface determines the growth rate of the ribbon orthogonal to the pull direction (t).

**Figure A.3:** Geometry of leading-edge solidification interface and respective growth rates

To approximate $q_{sy}$, this study now estimates the length ($L$) and height ($t_0 + \Delta t$) of the control volume outlined in Figure A.3. For an assumed starting ribbon thickness ($t_0$), an upper-bound of ($t_0 + \Delta t$) can be found by assuming that all the heat extracted from the surface of the control volume grows the ribbon orthogonal to the pull direction as:

$$Lq_{sy} = \rho h_{ij} V \Delta t$$

where $\Delta t$ is the increased thickness of the ribbon at the end of the control volume. Assuming that the orthogonal growth rate ($\dot{t}$) is constant, the angle of the melt-side solidification interface with respect to the surface ($\theta_{MS}$) can be found geometrically as:

$$\tan \theta_{MS} = \frac{\Delta t}{L}$$

Substituting Equation A.36 into Equation A.37, the maximum upper-bound of $\theta_{MS}$ for $q_{sy} = 120$ W/cm² is less than 9°. This small angle signifies that away from the facetted leading-edge solidification interface, the isotherms in the ribbon are near parallel to the cooling surface, and minimal heat is conducted parallel to the pull direction. However, for distances close to the leading-edge solidification interface, a significant fraction of $q_{sy}$ may conduct parallel through the edge of the control volume ($q_{sx}$). To determine the magnitude of $q_{sx}$, this study compares the distance between a point on the surface of the ribbon and the leading-edge solidification interface to the respective distance between that point on the ribbon surface and the melt-side interface, as illustrated in Figure A.4. These relative distances
(δ_{LE}(x), δ_{MS}(x)) reflect the effective thermal resistances between the surface of the ribbon and each respective solidification interface.

**Figure A.4:** Distance between the surface of the ribbon and the respective solidification interfaces governs orientations of the isotherms and the relative percentage of heat flow to each interface.

Assuming both solidification interfaces are analogous to the melting temperature isotherm, heat flow parallel (q_x(x)) and orthogonal (q_{MS}(x)) to the pull rate is related to the temperature difference between a point on the surface of the ribbon and the melting temperature (ΔT(x)):

\[ ΔT(x) = q_x(x)δ_{LE}(x) = q_{MS}(x)δ_{MS}(x) \]

where the distance between a point on the surface of the ribbon and the melt-side interface as a function of x is:

\[ δ_{MS}(x) = \frac{t_0}{cosθ_{MS}} + (x - t_0tanθ_{MS})sinθ_{MS} \] (A.38)

and the distances between a point on the surface of the ribbon and the leading-edge interface as a function of x is:

\[ δ_{LE}(x) = (x + t_0cotθ_{111})sinθ_{111} \] (A.39)

for values of x less than:

\[ x_{crit} = \frac{t_0}{sinθ_{111}}(secθ_{111} - cosθ_{111}) \] (A.40)

For values of x greater than x_{crit}, the minimum distance between a point on the surface of the ribbon and the leading-edge interface is found as:
\[ \delta_{LE}(x) = \left( x^2 + t_0^2 \right)^{1/2} \]  

(A.41)

Assuming a constant rate of heat extraction from the surface of the ribbon \( q_{sy} \), this study approximates the \( q_x \) relative to the total \( q_{sy} \) as:

\[
\frac{q_x(x)}{q_{sy}} = \frac{q_x(x)}{q_{MS}(x) + q_x(x)} = \frac{\delta_{MS}(x)}{\delta_{LE}(x) + \delta_{MS}(x)}
\]

(A.42)

Figure A.5a shows the calculated values of \( q_x(x) \) for different assumed initial ribbon thickness values \( (t_0) \). This figure shows that, at the edge of the control volume (distance to the interface = 0), more than half of \( q_{sy} \) conducts heat from the leading-edge solidification interface. For increasing values of \( x \), this fraction decreases until reaching an asymptotic value of around 0.2. Normalizing the \( x \)-axis of Figure A.5a by \( t_0 \) to form Figure A.5b shows that the relative value of \( (q_x/q_{sy}) \) is independent of \( t_0 \). Figure A.5b also shows that for distances greater than 3\( t_0 \), over two-thirds of the heat extracted from the surface of the ribbon \( q_{sy} \) originates from the melt-side interface.

**Figure A.5:** a) Fraction of heat extracted from the surface of the ribbon that is conducted from the leading-edge solidification interface as a function of distance for different initial thicknesses b) Normalized fraction of heat extracted from the surface of the ribbon coming from the leading-edge solidification interface

The fraction of heat conducted to the leading-edge solidification interface can be approximated by the exponential curve fitted to the model in Figure A.5b is given by:

\[
q_x(x) = q_{sy}(Ae^{-Bx} + C)
\]

(A.43)
where $A$, $B$, and $C$ are constants fitted to the exponential curve. It should be noted that $B$ scales with the initial ribbon thickness of the ribbon at the left edge of the control volume ($t_0$). Chapter 3 determines $q_{sx}$ by modeling the ribbon illustrated in Figure A.3 as a one-dimensional fin with heat extraction from the surface equal to that approximated by A.43. Chapter 3 also uses the expression for $q_{MS}(x)$ to approximate $i(x)$.

To understand if this model where extracted from the surface of the control volume illustrated in Figure A.3 enables higher rates of heat dissipation than the previous model where isotherms are parallel to the interface, we now approximate $q_{sx}$. A very conservative assumption of the dimensions of the control volume illustrated in Figure A.3, given the plots in Figure A.5, is $L = Nt_0$, where $N = 3$ and $R = q_x/q_{sy} = 50\%$. These assumed values translate to a rate of heat dissipation from the solid ribbon, relative to that needed for Kellerman’s process rate, of:

$$\frac{V_{sol}}{V_{exp}} = \frac{q_{sx} + q_{sy} \cot \theta_{111}}{\rho h_{i/s} V_{exp}} = \frac{q_{sy}(NR + \cot \theta_{111})}{\rho h_{i/s} V_{exp}} \approx 0.34 \tag{A.44}$$

As the conservative values used for A.44 yield a much higher rate of heat extraction than that found by A.35, this study concludes that the isotherms near the solidification interface are steeper than the angle of the (111) plane. Furthermore, the low relative values of heat extracted through the solid ribbon (calculated by Equation A.35 and A.44) support the theory that a significant amount of heat generated at the leading-edge solidification interface dissipates through the undercooled melt ahead of the interface. Given that silicon’s (111) plane can grow stably into an undercooled melt, this next section develops a scaling argument and simple heat transfer model for the dissipation of latent heat through the liquid.

**A.2.2 Latent Heat Dissipation through Liquid Ahead of Interface Scaling Analysis**

For the HRG process, no analytical model has yet been proposed for how heat extracted from the liquid ahead of the solidification interface dissipates the latent heat generated at the leading-edge interface. This section develops a scaling argument and simple heat transfer model of the liquid and calculates its respective ability to dissipate the latent heat generated at the leading-edge interface for Kellerman’s reported process rate.

This work proposes that the thermal profile of the liquid ahead of the solidification interface is shaped by a developing thermal boundary layer ($\delta_{yt}$) formed by the active cooling profile ($q_{sy}$) and the presence
of the solidification interface (indicated by the melting temperature at leading-edge solidification interface), as illustrated in Figure A.6.

Figure A.6: Liquid Thermal Profile Ahead of the Solidification Interface

Similar to how $q_{sy}$ dissipates latent-heat generated from either the sharp or diffuse interface of the solid ribbon in A.2.1, this study assumes that $q_{sy}$ extracts heat from either the melt reservoir or the leading-edge solidification interface in the liquid. The resulting fraction of heat that flows orthogonally to the pull direction ($q_{yi}$) is countered by heaters below the liquid melt, and heat that conducts parallel to the pull direction ($q_{xi}$) dissipates latent heat generated at the solidification interface. The magnitudes of these two heat flows scale with the temperature difference between a point on the surface of the liquid and the melting temperature of silicon ($\Delta T$) and the distance between this respective point and each melting temperature isotherm ($\delta_{yl, \delta_{xl}}$). This study approximates $q_{xi}$ by weighing these relative distances as:

$$R = \frac{q_{xi}}{q_{sy}} = \frac{q_{xi}}{q_{yi} + q_{xi}} = \frac{\delta_{yl}}{\delta_{yl} + \delta_{xl}}$$  \hspace{1cm} (A.45)

This study approximates $q_{yi}$ by the heat extraction across a thermal boundary-layer formed in the liquid ahead of the interface. It is important to note that the traditional boundary-layer model does not account for the infinite-temperature source created by the leading-edge of the solidification interface a distance $L$ away from the beginning of the cooling profile. Assuming that the thermal boundary layer scales with the characteristic velocity of the process, $q_{yi}$ and the expected vertical thermal boundary layer $\delta_{yl}$ can be approximated as:

$$q_{yi} = k_i \frac{\Delta T}{\delta_{yl}} = k_i \frac{\Delta T}{2 \sqrt{\alpha_i t^*}} = k_i \frac{\Delta T}{2 \sqrt{\alpha_i x / V}}$$  \hspace{1cm} (A.46)
where \( k_t \) is the thermal conductivity of the liquid silicon, \( \Delta T \) is the temperature difference between the surface and temperature of the bulk fluid, \( \alpha_t \) is the thermal diffusivity of the liquid, \( t^* \) is the characteristic time of the boundary, and \( x \) is the distance from the start of the cooling profile. The presence of this solidification interface locally creates a strong thermal gradient parallel to the pull direction that scales with the surface temperature of the liquid as:

\[
q_{xl} = k_t \frac{\Delta T}{L - x} \tag{A.47}
\]

Figure A.7a plots \( \delta_{y_t} \) on the first y-axis and the respective \( R = q_{xl}/q_{y_t} \) on the second y-axis for a cooling profile that begins \( L = 1 \) mm ahead of the solidification interface. It is important to recognize that this approximation of the thermal profile in the liquid is better suited for the proposed silicon film process than for the HRG thermal profile. This work advocates for future work developing a more comprehensive model for the two-dimensional thermal profile in the melt. Because silicon is a thermally diffusive material, Figure A.7a shows the thermal boundary layer (in blue) grows quickly and that the relative thermal resistance to the leading-edge solidification interface \( (\delta_{x_t}/\delta_{y_t}) \) diminishes as it approaches the solidification interface. Figure A.7b shows that \( q_{xl} \gg q_{y_t} \) for increasing values of \( L \), suggesting that heat extracted through the liquid can readily dissipate heat away from the leading-edge interface. And unlike the heat transfer in the solid ribbon, where a significant fraction of the heat removed from the surface thickens the ribbon, heat extracted from the surface of the liquid almost exclusively dissipates latent heat from the leading-edge solidification interface.
As supported by Figure A.7b, heat conduction to the solidification interface dominates at even large distances from the interface, justifying a simple one-dimensional model to characterize the thermal gradient in the liquid near the solidification interface. Chapter 3 develops a comprehensive thermal model of the heat transfer through the liquid; however, this study now simply approximates this thermal profile by fitting a control volume over the liquid in front of the solidification interface with height $t_0$. Heat conducted to the leading-edge interface in this control volume is therefore approximated by:
Assuming that the temperature at the solidification interface is $T_m$ and the very conservative assumption that the thermal gradient in the pull-direction goes to zero at $x_0 = 0.5$ mm away from the interface, the thermal gradient of the liquid ahead of the interface is simply:

$$\frac{\partial T}{\partial x} = \frac{q_{sy}}{k_1 t_0} (x - x_0)$$  \hspace{1cm} \text{(A.49)}$$

Finally, for $t_0 = 0.05$ mm, the heat dissipated by the liquid compared to the latent heat generated at the interface at Kellerman’s reported process rate is given by:

$$\frac{V_{liq}}{V_{exp}} = \frac{k_1 t_0}{\rho h_{l/s} t_0} \left| \frac{\partial T}{\partial x} \right|_{x=0} = .70$$  \hspace{1cm} \text{(A.50)}$$

Equation A.50 shows that not only is the dissipation of a significant amount of latent heat through the interface is possible, but that the ratio of heat through the liquid well complements that extracted through the solid ($\frac{V_{sol}}{V_{exp}} \approx .22 \text{ or } .34$), as found in Section A.2.1. This calculation supports Kellerman’s theory that latent heat dissipates through undercooled liquid ahead of the interface.[1]

### A.3 Future Work

Although Kellerman’s report attributes the high growth rates of monocrystalline material to the stability of a facetted silicon interface, no quantitative understanding of the heat transfer and the inherent implications have ever been presented. Without a governing understanding of the heat transfer that enables HRG’s high process rates, the experimental results achieved to date have only provided mysterious hints as to the potential of this technique. The original analytical “slender wedge” model [2] of the HRG process has misled several attempts to commercialize the HRG process as recently as 2014 [3]. This work therefore calls for the development for a more comprehensive model of the HRG process that exploits this finding.