MODELING AND EXPERIMENTAL PROCESS OPTIMIZATION FOR A SiH$_4$ + H$_2$
SURFACE WAVE PLASMA DISCHARGE FOR SILICON PHOTOVOLTAICS

BY

JASON A. PECK

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Nuclear, Plasma, and Radiological Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2014

Urbana, Illinois

Master’s Committee:

Professor David N. Ruzic, Adviser
Professor Davide Curreli
Abstract

A surface wave plasma source was used for the deposition of amorphous (a-Si) and nanocrystalline (nc-Si) silicon thin films for the manufacture of silicon solar cells. This source was optimized for 900 MHz microwave excitation. The process gases used were silane (SiH₄) and hydrogen (H₂). The plasma source was shown to be advantageous in depositing films at very high deposition rate, exceeding 2 nm/s for nc-Si, while deposition of a-Si was observed at 10 nm/s and could be increased if a higher flowrate mass flow controller was used. Film thickness was measured via profilometry with verification through SEM imaging, while the crystallinity was determined via peak fitting of Raman spectra. A distinct transition from nc-Si to a-Si was observed between 1% and 2.5% SiH₄ concentration, increasing for higher source power and decreasing for lower substrate temperature. An optimal substrate temperature was found for depositing nc-Si: 285°C for 1.0 W/cm², and 350°C for 0.5 W/cm². Expansion of the nc-Si process window to higher deposition rates was shown to be possible by higher source power.

Film nanostructure of nc-Si was determined by XRD, Raman analysis, TEM, and EPR. Calculation of grain size for 100 nm films yielded 5±1 to 15±2 nm from 200°C to 400°C. EPR analysis of a-Si and nc-Si revealed that defect density increased with crystallinity. Due to adverse deposition conditions, calculated defect densities for the surface wave source ranged from 1.2±0.3·10¹⁶ cm⁻³ for a-Si to 7.3±1.2·10¹⁷ cm⁻³ for nc-Si. However, a ceteris paribus comparison with films made by radio frequency capacitively-coupled
discharge (RF CCP) showed that a-Si made by the latter method had $7.4 \pm 0.7 \cdot 10^{17}$ cm$^{-3}$, a factor of 6 worse than a-Si produced via surface wave. The low oscillation height of ions due to high frequency, as well as low sheath potential due to low electron temperature $T_e$, combined to generate high quality Si thin films relative to the RF CCP industry standard.

Numerical modeling of the SiH$_4 +$ H$_2$ model was achieved using the volume-averaging formulation of Kim and Lieberman.$^{[49]}$ An extensive literature study for the physical parameters of cross sections and rate coefficients accompanies this work. 40 gas species and 62 reactions were tracked, as well as the surface reactions involved in deposition. The result of the plasma simulations predicted experimentally observed trends in deposition rate vs. silane concentration (accurate within 10-25%) and total pressure, although it diverged from what was seen experimentally in varying source power. $T_e$ for 100% H$_2$ was found to be 2.7 eV at 100 mTorr and 2.5 eV at 200 mTorr, coincident with Langmuir probe measurements. Basic plasma trends such as decreasing $T_e$ for higher pressure and constant $T_e$/increasing $n_e$ with power were predicted by the model, as well. Most importantly, the influence of hydrogen abstraction via incident H flux was correlated with increased crystallinity, coinciding with what was observed experimentally and what is argued in literature.$^{[68]}$

Finally, solar cells were manufactured on n-type Si wafer with the surface wave and RF sources for comparison. While the RF-made cell did not produce any measurable voltage or current, the surface wave produced a functioning solar cell with very low efficiency.
Although this device was far from industry standards due to the CPMI’s and author’s lack of skill and resources to manufacture photovoltaics, it is a basic illustration of the advantages of the low-damage MSWP source over conventional industry methods.
Acknowledgements

It would be foolish to begin presenting the progress and results I’ve obtained over the past two years without first giving credit to all who have helped me to this point. Firstly, my adviser David Ruzic has provided not only exceptional direction in my research but also encouragement and validation for my accomplishments, as well as guidance in my failures.

The funding company of this work, Starfire Industries, LLC, has also given brilliant feedback on the direction of the project from the outset. I have shared countless conversations with CEO Brian Jurczyk, along with engineers Piyum Zonooz and Mike Reilly, learning invaluable technical and research practices. With little to no experience planning a project for the long term, they quickly coached me into setting reasonable goals and achieving them. In particular, the experience of interacting with a customer in an industry relationship was a lasting benefit from this project.

Post-doctorate researchers Ivan Shchelkanov, Kishor Kalathiparambil, and especially Davide Curreli (now professor), assisted me immensely in technical guidance on plasma physics and experimentation. My fellow graduate students of the Center for Plasma-Material Interactions (CPMI) – Peter Fiflis, Soonwook Jung, Michael Christenson, to name just a few – also generously offered their advice, help, and sometimes equipment when requested. Undergraduates Alex Knicker, Nick Rivera, Stephen Kleppinger, Vikrum Joshi, and Jesus Sanchez also lent their help to the experiment through either volunteering or
regular work. Conversations with Antonio Mei and Allen Hall are also gratefully acknowledged.

On the note of material diagnostics, the Frederick Seitz Materials Research Lab furnished the opportunity for equipment usage, including X-ray diffractometry (XRD) via the Phillips XPer 2, Raman spectroscopy via the Nanophoton RAMAN-11 Microscope, scanning electron microscopy (SEM) on the JEOL 6060LV, JEOL 7000F, and Hitachi S-4700 devices, profilometry with the Dektak 3030 profilometer, and absorption studies on the Varian 500G spectrophotometer. Catalin Chiritescu and Julio Soares offered valuable technical help on multiple occasions. Mark Nilges of the Illinois EPR Research Center assisted in conversation and training for electron paramagnetic resonance (EPR/ESR) measurements. Finally, Dane Sievers of ECE offered assistance through the Everitt Lab cleanroom’s four point probe and aluminum evaporator chamber.

This work is partially funded by the National Science Foundation under Grant No. IIP-1127557. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the NSF.

I’m grateful to my parents for encouraging my passions and strengths as I endeavored into engineering. I am also immensely fortunate to have a wife who provides continued love and support in spite of the time I devote to my schooling. I dedicate this work to my daughter, whose playful adventurousness will one day drive her to find a passion like mine.
Table of Contents

1: Introduction – *The Need for Solar* ................................................................. 1
   1.1 – Fossil Fuels Today ...................................................................................... 1
   1.2 – Nuclear Power ......................................................................................... 1
   1.3 – Renewable Energy ................................................................................... 2

2: Background ....................................................................................................... 3
   2.1 – The Solar Industry ................................................................................... 3
   2.2 – The Niche of Solar Power ........................................................................ 4
   2.3 – Photovoltaic Basics ................................................................................ 4
      2.3.1 – Band Structure ................................................................................... 6
      2.3.2 – Vacuum Purity and Defects ............................................................... 7
      2.3.3 – Heterojunction Devices .................................................................... 11
   2.4 – Aim of This Work ................................................................................... 14

3: Mathematical Development of the 0-Dimensional Plasma Model .................. 15
   3.1 – Overview and Basic Equations ............................................................... 15
   3.2 – Mean Free Path for Ion and Neutral Wall Flux ...................................... 18
   3.3 – Reaction Rate Coefficients .................................................................... 23
   3.4 – Power Balance ....................................................................................... 25

4: Discussion of Reaction Kinetics in a Silane-Hydrogen Discharge .................... 28
   4.1 – Electron Impact Ionization ..................................................................... 28
   4.2 – Electron Impact Excitation .................................................................... 30
   4.3 – Dissociative Excitation .......................................................................... 33
   4.4 – Dissociative Attachment ........................................................................ 36
   4.5 – Cation-Anion Recombination ................................................................. 37
   4.6 – Dust Formation Kinetics ........................................................................ 38
   4.7 – Surface Reactions ................................................................................... 40
   4.8 – Summarized List of Reactions Included in the Model ......................... 42

5: The Experimental Apparatus ............................................................................ 45
   5.1 – Chamber and Discharge Geometry ....................................................... 45
   5.2 – The Surface Wave Plasma Source ......................................................... 45
   5.3 – Power Delivery ...................................................................................... 48
   5.4 – Gas Delivery ......................................................................................... 49
   5.5 – Temperature Control ............................................................................ 51
   5.6 – Deposition Process ............................................................................... 55
   5.7 – Routine Film Analysis ........................................................................... 57
      5.7.1 – Profilometry Measurement for Thickness ....................................... 57
5.7.2 – Raman Spectroscopic Analysis of Crystallinity .......................................................... 58
5.8 – Comparison with RF Capacitively Coupled Plasma ...................................................... 61
5.9 – Doping Technique and Calibration .................................................................................. 62
6: Results and Discussion ............................................................................................................ 67
  6.1 – Particle Mitigation ............................................................................................................. 67
  6.2 – Optimization of the Parameter Space .............................................................................. 68
    6.2.1 – SiH4 Concentration ..................................................................................................... 68
    6.2.2 – Substrate Temperature .............................................................................................. 71
    6.2.3 – Total Pressure ............................................................................................................ 74
    6.2.4 – Source Power ............................................................................................................ 75
    6.2.5 – Discharge Gap .......................................................................................................... 77
    6.2.6 – Ternary Mixtures ..................................................................................................... 80
  6.3 – Results of the Numerical Plasma Model ........................................................................... 82
    6.3.1 – Stability and Convergence .......................................................................................... 82
    6.3.2 – Silane Concentration Study ...................................................................................... 85
    6.3.3 – Power Study ............................................................................................................. 87
    6.3.4 – Total Pressure Study ............................................................................................... 90
    6.3.5 – Comparison of Plasma Parameters with Langmuir Probe Data .................................. 93
  6.4 – Grain Size Calculation via Raman, TEM, and XRD ............................................................. 95
  6.5 – Electron Paramagnetic Resonance (EPR) Characterization of Defects .............................. 98
  6.6 – Manufacturing a PV Device ............................................................................................ 105
7: Conclusions .......................................................................................................................... 108
8: Future Work .......................................................................................................................... 111
9: Bibliography ......................................................................................................................... 113
1: Introduction – The Need for Solar

1.1 – Fossil Fuels Today

The United States has faced challenges in finding sufficient sustainable energy for the increasing power demands of its citizens. In 2012, 37% of supplied energy came from coal utilities.\[^{60}\] Coal, while low-cost, faces the issue of emissions and environmental impact, especially as the concept of global warming gains more widespread credibility and recognition. Natural gas is abundant and has been particularly cheap in recent years, and the supply has been further increased through the process of “fracking” – hydraulic fracturing of bedrock via fluid injection to allow natural gas to diffuse out of the shale background. The recent surge in natural gas usage has manifested as an increase from 30% of 2012 national energy usage to an estimated 40% in 2014.\[^{60}\]

1.2 – Nuclear Power

In the case of nuclear power, it keeps pace with generally 20% of US electricity coming from the fission plant infrastructure in the US. Many have been persuaded against the advantages of nuclear due to manifestations of mismanagement and operator error (e.g. Chernobyl, Three Mile Island, and the more recent Fukushima-Daiichi disaster), but companies like Areva, General Atomic, and Sargent & Lundy are working to implement advanced reactor designs that include passive safety mechanisms and alternative power cycles, such as liquid metal fast reactors, gas-cooled pebblebed designs, or molten salt-cooled
thermal reactors. However, design challenges and material limitations keep these options roughly two decades on the horizon, albeit necessary to relieve the current plants operating well past their initial design criteria.

1.3 – Renewable Energy

Looking to the long-term, utility-scale implementation of renewable energy must be accomplished to supplement the phase-out of fossil fuels and the gradual technological shift in nuclear. Wind power has gained footing, representing 3.46% of the US energy production. This work will focus primarily on the complementary technology, solar power, harnessing the sun’s radiated energy for human use. This is primarily achieved through the capture of visible and ultraviolet (UV) light in components called “photovoltaics,” semiconductor devices that convert light into electricity. They come in a variety of forms, from single-element materials to complicated alloys, single-layer to multi-layer structures. The most prevalent and easy to manufacture of these devices is silicon-based. This work will focus on the deposition of the Si films which compose the core component of the photovoltaic cell.
2: Background

2.1 – The Solar Industry

Solar energy throughout the world has gained somewhat disappointing momentum since its popularization in the 1990’s. Despite government subsidies in the past decade that have favored green energy, often specifically tailored toward solar power, solar only represents 0.11% of the nation’s energy usage.\textsuperscript{[60]} Part of the implementation issues may be attributed to the intermittent nature of solar. The variability in generated power culminates with a lack of proven, economic energy storage options, as large-scale battery storage is simply not viable.

For solar photovoltaic (PV) cells, cost of production tends to be a major limitation of large scale adoption of solar. With China’s targeted subsidies toward green energy and artificially low currency value, American companies have been unable to compete with Chinese silicon photovoltaics. Their subsidies of green energy has bottomed out much of the solar market, extinguishing much of the silicon PV production in first world countries. A well-published case of this involved the Silicon Valley startup, Solyndra, who had produced CIGS (advanced solar chalcopyrite alloys – copper indium gallium selenide/sulfide) photovoltaics in a cylindrical geometry for increased light absorption. With approximately $0.5B in DOE loans, the company was hit hard by China’s sudden production of silicon PV cells, ultimately filing for bankruptcy.\textsuperscript{[58]} Similarly, companies like semiconductor giant Applied Materials have backed out of solar. With a goal of depositing of multilayer amorphous/crystalline silicon (a-Si/c-Si) thin film devices, also known as a heterojunction or
tandem cells, they sought to produce photovoltaics of higher efficiency. However, their SunFab plant struggled with low deposition rates and large area deposition, ultimately phasing the division out in 2010, relocating or laying off ~500 workers.\textsuperscript{[59]}

2.2 – The Niche of Solar Power

On a rural scale, however, the ability to obtain electric power without access to an electrical grid has found resonant applications in developing countries, India in particular. This nodal implementation of electricity through standalone means such as solar has allowed countries to completely bypass the sluggish establishment of a national, regional, or even local power grid when there is little incentive for a company to do so. This accelerates innovation and gives individuals in these countries the ability to channel creativity and entrepreneurship through technology such as cell phones and laptops. Possibly the most immediate improvement solar brings to these countries is access to clean and safe lighting, reducing kerosene consumption. For Bangladesh in 2011, the two lowest income groups were found to use three times as much kerosene as the top two.\textsuperscript{[62]} Purchase of even one solar panel in these areas is seen as an investment that pays immensely over time. In first world countries, sustainability-minded individuals can outfit their homes with large area panels to supplement their energy needs.

2.3 – Photovoltaic Basics

Photovoltaics are semiconductor devices that essentially work like light-emitting diodes (LEDs) in reverse – absorbing light and creating an electrical current that can power
a device or be stored for later use. Understanding a semiconductor begins with studying its *band structure*, a representation of the allowed energy levels of electrons in the material. While a single atom has orbitals that represent what potential energy and angular momentum the electron has, when many atoms are joined together, the discrete energy levels join to become a distribution of allowed states.

![Diagram](image)

*Figure 1: Representation of the joining of multiple quantum wells, roughly representative of individual atoms. As the spacing decreases (a → c), discrete energy states become a "band" of energies due to inter-well tunneling and interaction.\[\text{33}\]*

In semiconductors, this can be summarized into a bound state, or “valence band” denoting that the electron is tied to the valence shell of its atom, and a “conduction band” where the electron is mobile. The energy difference between the two is referred to as the “band gap.” What separates semiconductors from conductors is the presence of this band gap (valence electrons in metals are typically almost entirely free, representative of a Fermi gas), and in contrast to insulators, this band gap is small (typically <2 eV). What drives a PV cell to operate is the solar excitation of valence band electrons into the conduction band, leaving a missing electron, or *hole*, in the valence band. Production of these electron-hole
(e-h) pairs due to incident light can be collected as current; thus, solar power is converted into electrical power. The performance factor, or efficiency, is how well the device converts incident power, and is governed primarily by four factors: band gap, electron dispersion, defects present, and physical light-capturing design.

2.3.1 – Band Structure

![Band Structure of Si and GaAs](image)

Figure 2: Band structure vs. wave vector $\vec{k}$ in silicon (left) and gallium arsenide (right). [33] Arrows represent likely transitions from valence to conduction band. $E_g = 1.12$ eV in Si and 1.42 eV in GaAs.

In Figure 2, energy of each band is plotted vs. allowed electron momentum. In GaAs, for an electron to move from the valence band to the conduction, the most likely pathway is a transition from $\Gamma_{15}$ to $\Gamma_1$ (marked with red arrow), where the maximum of the valence band meets the minimum of the conduction band. This transition requires only a change in energy while momentum remains constant. This is ideal for photonic excitation, where photons carry very little momentum relative to their energy due to their absence of mass. This makes for a very efficient conversion of photons to e-h pairs.
However, in the case of silicon, the valence maximum $\Gamma_{25}$ is misaligned from the conduction band minimum $X_1$, so an electronic transition requires both energy and momentum, requiring a third body, such as an atomic oscillation, or phonon. The difference between the direct band gap of GaAs and the indirect band gap of Si make GaAs a much better candidate for photonic interactions.

In spite of having an indirect band gap, silicon has historically been the go-to PV material. It has been said that the three things man does best are steel, cement, and silicon, referring to the massively successful and blossoming market of silicon-based electronics worldwide. As a single-atom material, it is straightforward to grow and produce. As an electronic material, its band structure and carrier transport properties are well-understood. Due to the sheer natural abundance, minimal health and environmental risks, and low cost, it's no surprise that silicon initially became the benchmark for PV devices.

2.3.2 – Vacuum Purity and Defects

To produce PV cells, a vacuum chamber is typically needed, and an ionized gas is used to chemically deposit the film material. This ionized gas is a state of matter known as plasma, and the process is called plasma-enhanced chemical vapor deposition (PECVD). In the case of silicon, the process gas is typically a mixture of silane (SiH$_4$) and a buffer gas, either hydrogen, helium, or argon. The film is “doped,” or filled with deliberate impurities to add free charge carriers to the device. This is typically a p-i-n design:
- a layer of silicon filled with group III electron “donor” atoms (boron, aluminum, gallium, producing “p-type” Si),
- a thick (proportional to the absorption depth), un-doped layer for light absorption,
- and a layer of “n-type” silicon, doped with group V electron “acceptor” atoms (phosphorous, arsenic, antimony).

This p-i-n junction allows for e-h pair excitation by photons in the intrinsic layer while the electric field formed by the p/n layers accelerates it to the electrodes.

From the effective mass approximation and Bloch theorem for a regular crystal lattice, a conduction band electron or a valence band hole will behave as a free particle with an effective mass $m^*$, typically smaller than its rest mass $m_0$. Any perturbation that these charge carriers – vacancies, impurities, even thermal vibrations of atoms or polar oscillations of valence electrons – provide scattering centers that inhibit electron mobility. This can be seen in Fermi’s 2nd Golden Rule (derived by Dirac)\cite{33}:

\begin{equation}
S(k, k') = \frac{2\pi}{\hbar} |\langle k' | V' | k \rangle|^2 \delta(E(k) - E'(\bar{k}') \pm \hbar \omega)
\end{equation}

where $S(\bar{k}, \bar{k}')$ denotes the transition probability per unit time for scattering to occur, $\bar{k}$ and $\bar{k}'$ are wavevectors representing initial and final states, $\hbar$ is the normalized Planck’s constant, $V'$ is the perturbing potential, and $\omega$ is the angular frequency of the time-dependent component of $V'$ (assuming the perturbation is harmonic). Thus, depending on the form and strength of the perturbation, scattering and recombination will occur with a larger magnitude. A thin film PECVD system is in need of superb base pressure and cleanliness to guarantee uncontaminated films. The effects of primary vacuum contaminants
– oxygen, hydrocarbons, water vapor, even nitrogen – can be detrimental in the growth and quality of the film.

![Figure 3: Examples of point defects in a crystal structure: (a) perfect lattice – no defect, (b) vacancy-induced deformation, (c) ionized “shallow” impurity (without deformation), and (d) interstitial deformation.][33]

In terms of film contamination, air leaks into the chamber must be avoided at all costs. Oxygen is particularly poisonous to silicon devices. Stationed in the middle of silicon’s band structure, it provides an array of states to “trap” electrons. Conversely, nitrogen has been known to increase hardness of silicon by immobilizing dislocations, having industrial applications in the form of Si$_3$N$_4$ as a mechanically protective coating or diffusion barrier.\[^{35}\]

Unfortunately, in the presence of both oxygen and nitrogen, a variety of defects may form in the event of an external chamber leak. O-H, O-N, and larger clustered bonds serve as polar defects which drastically increase the loss of e-h pairs.\[^{34}\]  Hydrocarbons alone, whether from

external contamination of the sample, poor vacuum etiquette during chamber maintenance, or backstreaming of pump oil, can implant carbon impurities in the film. While carbon shares the same valence properties as silicon and thus doesn’t behave like a doping impurity, its small size will induce a lattice deformation that serves as a scattering potential, however weak.

Luckily, various steps can be taken to optimize chamber cleanliness. Helium leak detection, involving a mass spectrometer (SRS RGA100 quadrupole gas analyzer was used in this work) and a stream of helium gas external to the chamber, tracks the mass 4 peak over time, corresponding to helium presence. Leaking connections can be pinpointed from a spike in the vacuum helium peak. For residual water vapor adsorbed on vacuum walls, chamber “baking” to temperatures above 100°C will degas these adsorbed molecules from the system. Finally, replacing a standard oil roughing pump with a dry pump (Edwards iL600n model) – a finely machined rotary pump that uses no oil for seal – removes the worry of hydrocarbon backstreaming through the pumping line. Through persistent applications of these techniques, a chamber base pressure on the order of $10^{-8}$ Torr was achieved.

Other film defects are not as easy to avoid as external contaminants. Dangling bonds (unbonded Si electrons) and grain boundaries are both emphasized points of this work. These mechanisms go hand-in-hand, as will be seen later. The effects of deposition conditions on film structure and overall defect density must be understood to create photovoltaics with competitive efficiencies. Techniques such as electron spin/paramagnetic
resonance (ESR/EPR) and transmission electron microscopy (TEM) will assist in exploring the best conditions to enhance solar cell performance. Other defects that promote recombination and lower efficiency are interfacial defects arising from the bonding of dissimilar materials (film-film or film-substrate) due to strain and dislocations in either or both lattices.

2.3.3 – Heterojunction Devices

In 1961, William Shockley and Hans Queisser\(^2\) published a detailed balance of quantum processes in a p-n junction assuming no defects, radiative losses being the only mechanism for recombination of e-h pairs. Their coupling of an approximate solar spectrum with the band gap of the material produced a theoretical maximum efficiency of the PV cell as a function of band gap. Scientists have since calculated this limit with the ground-level solar spectrum after it has passed through the atmosphere.\(^1\)

Figure 4: Theoretical and empirical values for solar cell efficiency vs. band gap.\(^3\) Silicon’s \(E_g = 1.12\) eV sits near the maximum of this curve.
The mechanisms shaping the curve in Figure 4 are simple. At low band gap, the high energy tail of the solar spectrum is wasted since blue/purple and UV photons can only impart $E_g$ per photon. At high $E_g$, much fewer photons are capable of exciting e-h pairs simply due to the lack of energy for the transition to occur. In a real device, non-ideal issues such as reflective losses and film defects prevent single-film photovoltaics from attaining this maximum efficiency. To bypass this, a multilayer heterojunction device can be used to harness the whole solar spectrum more efficiently.

Figure 5: Applied Materials schematic of a single p-i-n junction (top-left) to a dual junction a-Si/c-Si device (top center). Quantum efficiencies of a-Si and μc-Si junctions relative to the solar spectrum are shown (bottom-left). [63]
As seen in Figure 5, the addition of the lower band gap (1.12 eV) microcrystalline (μc-Si) junction to the larger band gap (1.7 eV) a-Si junction expands the range of capture into the infrared range of solar emissions. The absorbing layer consists of a thick layer of intrinsic material for light absorption with limited scattering due to the absence of ionized impurities. The junction is made by sandwiching the film with thin layers of p- and n-type silicon, setting up a built-in field to drive e-h current to the respective electrodes. Finally, a “tunnel diode,” a highly-doped n-p junction, is needed between the junctions to account for the mismatch in band structure of the two materials. Interfacial losses can be further reduced by replacing the tunnel diode with a region of graded composition to “smooth out” the energy bands of the joined materials, as seen in Figure 6.

Figure 6: Abrupt (a) and gradual (b) transitions of materials with dissimilar band gaps, given by Schubert.\[^{64}\] The abrupt change in the conduction band, represented as $\Delta E_c$, serves as a potential barrier that the electrons must tunnel through, increasing the resistivity of the layer.
2.4 – Aim of This Work

The focus of this work is threefold – to characterize a microwave surface wave plasma (MSWP) source for the production of silicon thin films that are:

- high deposition rate,
- high quality/low defect, and
- flexible in process conditions between a-Si and μc-Si for the production of heterojunction devices.

Experimental exploration of the process space is accompanied with rigorous material diagnostics of the Si films, as well as numerical simulations of the SiH$_4$ + H$_2$ plasma discharge, correlating the deposition conditions with the films produced.
3: Mathematical Development of the 0-Dimensional Plasma Model

3.1 – Overview and Basic Equations

To correlate trends observed in deposited thin films with plasma processes, a numerical model was necessary to characterize the plasma under various process conditions. This model, like any chemical plasma model, follows the creation and loss of each significant and interacting species:

\[
\frac{\partial n_j}{\partial t} = \left( \sum_i \alpha_{ij} R_i \right)_j - \frac{A}{V} \Gamma_j
\]

Table 1: List of species included in fluid model

<table>
<thead>
<tr>
<th>Positive Ions</th>
<th>Neutrals</th>
<th>Excited State</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsuperscript{2+}, H\textsuperscript{3+}</td>
<td>H, H\textsubscript{2}</td>
<td>H\textsuperscript{2}\textsuperscript{01}, H\textsuperscript{2}\textsuperscript{02}, H\textsuperscript{2}\textsuperscript{03}, H\textsuperscript{2}\textsuperscript{02}, H\textsuperscript{2}J\textsuperscript{13}</td>
<td>SiH\textsubscript{5} , e\textsuperscript{-}</td>
</tr>
<tr>
<td>SiH\textsubscript{2+}, SiH\textsubscript{3+} , SiH\textsubscript{4+}</td>
<td>SiH\textsubscript{2}, SiH\textsubscript{3}, SiH\textsubscript{4}</td>
<td>H\textsubscript{2}(a\textsuperscript{3}Σ\textgreek{g} \textsuperscript{+}), (B\textsuperscript{1}Σ\textsuperscript{u} \textsuperscript{+}), (C\textsuperscript{1}Π\textsuperscript{u}), (c\textsuperscript{3}Π\textsuperscript{u}), (d\textsuperscript{3}Π\textsuperscript{u}), (Σ\textsuperscript{Rydberg})</td>
<td></td>
</tr>
<tr>
<td>Si\textsubscript{2}H\textsubscript{4+}</td>
<td>Si\textsubscript{n}H\textsubscript{2n+1}, Si\textsubscript{n}H\textsubscript{2n+2}</td>
<td>H(b\textsuperscript{3}Σ\textsuperscript{u} \textsuperscript{+}), H\textsuperscript{n=2}, H\textsuperscript{n=3}</td>
<td></td>
</tr>
<tr>
<td>(2 \leq n \leq 7)</td>
<td></td>
<td>SiH\textsubscript{4}\textsuperscript{13}, SiH\textsubscript{4}\textsuperscript{24}</td>
<td></td>
</tr>
</tbody>
</table>

Subscript \(j\) denotes the species, and \(\Sigma_i\) is a sum over every reaction in the model. All plasma species, 40 in total, are listed in Table 1. An example of the particle balance for H\textsubscript{2}\textsuperscript{+} is given:

\[
\frac{\partial n_{H_2^+}}{\partial t} = R_{22} - (R_1 + R_7 + R_8 + R_{59}) - \left( \frac{A}{V} \Gamma_{H_2^+} \right)_{substrate} - \left( \frac{A}{V} \Gamma_{H_2^+} \right)_{antenna}
\]

with \(R_i\) giving the volumetric reaction rate for each reaction involving H\textsubscript{2}\textsuperscript{+}; in this case, reaction 22 is the production through ionization, and 1, 7, 8, and 59 are losses through anion-cation recombination, charge exchange with H\textsubscript{2}, electron-ion recombination, and
charge exchange with SiH₄, respectively. \( R \) is the reactivity of the reaction, a product of interacting species:

\[
R_i = k_i n_{i1} n_{i2}
\]

where, if reaction \( i \) is a 2-body process, \( n_{i1} \) and \( n_{i2} \) are number densities of the two interacting educts \([\text{m}^3 \text{ or cm}^3]\), and \( k_i \) is the integrated rate coefficient for the given temperature. Expressions for \( k \) are given in the following section. For the remaining terms in eq. (2), \( \alpha_{ij} \) is a stoichiometric term that is positive if species \( j \) is a product, negative if a reactant, or zero if not involved or equally balanced on both sides of the reaction. The magnitude corresponds to new species produced, e.g. the recombination reaction:

\[
H_3^+ + e \rightarrow 3H
\]

would have \( \alpha_{l,e} = \alpha_{l,H_3^+} = -1 \), and \( \alpha_{l,H} = 3 \). Thus, both chemical loss and production are accounted for in this term. The final term in (2), represents wall loss. \( \Gamma \) is the flux to the wall; in the case of neutrals:

\[
\Gamma_{\text{neutral}} = \frac{1}{4} h_i n v_{th} \frac{\beta}{2-\beta}
\]

where \( h_i \) is the center-to-edge ratio, \( v_{th} = \sqrt{\frac{2k_{i \text{gas}}}{m}} \) is thermal velocity, and \( \beta \) is the wall loss probability \((0 \leq \beta \leq 1)\). The factor \( \frac{\beta}{2-\beta} \) is the fractional loss of incident flux, as seen in Danko\[6\] and Kim.\[49\] The \( \frac{1}{4} \) term originates from the velocity distribution being isotropic: \( \langle \cos^2 \theta \rangle = 1/2 \) and the surface capturing only \( 1/2 \) of the geometry. The center-to-edge ratio \( h_i \) is given by Kim et al.\[49\] by the following:
with $L$ being the distance from the center of the plasma to the edge. In the case of the axially asymmetric surface wave source, two different lengths must be considered: the length from the plasma to the antenna (taken to be 1 mm) and from the plasma to the substrate (25 mm). The volume-averaging of the set of reactions represented by eq. (2) would make the model 0-dimensional, but accounting for nonuniform plasma geometry and center-to-edge ratios improves the accuracy of the result. Both surfaces in question have the same area $A = 176 \text{ cm}^2$ with the associated plasma volume $V = AL_{\text{sub}} = 176 \text{ cm}^2 \times 2.5 \text{ cm} = 440 \text{ cm}^3$. Loss coefficient $\beta$ is composed of sticking probability $s$ and recombination probability $\gamma$ where $\beta = s + \gamma \leq 1$. Diffusion coefficient $D$ in eq. (7) is calculated for neutral species:

$$\frac{1}{1 + \frac{4L\beta}{D(2-\beta)}}$$

In the case of ions, the flux is:

$$\Gamma_{\text{ion}} = h_{\text{ion}} n u_{\text{ion}}$$

where $u_{\text{Bohm}} = \sqrt{\frac{k_BT_e}{m_i}}$, the Bohm velocity in the case of a collisionless sheath. Contrary to neutral flux, the factor of $\frac{1}{4}$ does not appear due to being anisotropically accelerated across the sheath. The center-to-edge ratio in this case is a weighting between high and low pressure regimes:

$$h_{\text{ion}} = \frac{h_{\text{hp}} + bh_{\text{ip}}}{1+b}$$
where the weighting factor is $b = \frac{\lambda T_e}{L T_{\text{gas}}}$. The low pressure ratio is identical to that of Godyak with the assumption of electronegativity $\alpha \to 0$:

\begin{equation}
    h_{lp} = \frac{0.86}{(3+\frac{L}{L})^{1/2}}
\end{equation}

while the high pressure case is governed by ambipolar diffusion:

\begin{equation}
    h_{hp} = \frac{\pi D_{\text{amb}}}{L u_{\text{Bohm}}} \approx \frac{\pi T_e \lambda}{L u_{\text{Bohm}} v_{\text{thm}}}
\end{equation}

The determination of $u_{ion}$ is done in a similar fashion:

\begin{equation}
    u_{ion} = \frac{v_{\text{th}} + bu_{\text{Bohm}}}{1+b}
\end{equation}

The system of 40 species balance equations must be solved simultaneously, while the power balance determines electron temperature. This was achieved via the first-order ODE solvers of Matlab: ode45() or ode113().

3.2 – Mean Free Path for Ion and Neutral Wall Flux

The determination of mean free path $\lambda$ for the center-to-edge ratio $h_l$ requires an understanding of the cross section of interaction between the species and the neutral background. For neutral species diffusing to the walls, a crude, hard-sphere approximation can be made based on the effective neutral particle radius:
Figure 7: Schematic of impact parameter $b_{\text{coll}}$ for a hard-sphere collision between two particles radius $r_1$ and $r_2$ in the lab frame.

The above diagram depicts the situation of hard-sphere collisions, most valid in the simplest case of ground-state H. All neutral species have had three axial dimensions $(d_1, d_2, d_3)$ calculated to determine an effective diameter:

\[(14) \quad d_{\text{eff}} = \sqrt{d_1 d_2 d_3}\]

Thus, the cross section can be determined from the impact parameter:

\[(15) \quad \sigma = \pi \left( \frac{d_{\text{eff}}}{2} + \frac{d_{\text{effbg}}}{2} \right)^2\]

where subscript $j$ denotes the neutral species in question, and $bg$ denotes the interacting background species (either H$_2$ or SiH$_4$). Dimensions of all relevant species are listed in Table 3 with calculated cross sections for collisions with H$_2$ and SiH$_4$. In the majority of Si$_n$H$_m$ geometry, a 109.5° bond angle is assumed, correlating to tetrahedral structure. Species SiH$_n$ for $n = 2, 3, 4$ were approximated as equal in size. For Si$_n$H$_{2n+1}$ and Si$_n$H$_{2n+2}$, $n \geq 4$, the largest and smallest isomers were evaluated for a linear average. Isomeric structure was obtained from Mellor.$^{[51]}$
### Table 2: Calculated dimensions and effective radius of neutral species

<table>
<thead>
<tr>
<th>Species</th>
<th>Name</th>
<th>(d_1)</th>
<th>(d_2)</th>
<th>(d_3)</th>
<th>(d_{\text{eff}})</th>
<th>(\sigma_{\text{H}_2})</th>
<th>(\sigma_{\text{SiH}_4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>hydrogen</td>
<td>(2a_H)</td>
<td>(2a_H)</td>
<td>(2a_H)</td>
<td>1.06, 4.2, 13.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>hydrogen (diatom)</td>
<td>(2a_H)</td>
<td>(2a_H)</td>
<td>(2a_H + b_{HH})</td>
<td>1.26, 5.0, 14.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{SiH}_4)</td>
<td>silane</td>
<td>(\sqrt{2}c)</td>
<td>(\sqrt{8}/3c)</td>
<td>(3/2c)</td>
<td>2.97, 14.28.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{SiH}_3)</td>
<td>silyl</td>
<td>&quot;&quot;</td>
<td>&quot;&quot;</td>
<td>&quot;&quot;</td>
<td>2.97, 14.28.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{SiH}_2)</td>
<td>silylene</td>
<td>&quot;&quot;</td>
<td>&quot;&quot;</td>
<td>&quot;&quot;</td>
<td>2.97, 14.28.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}_2\text{H}_6, \text{Si}_2\text{H}_6)</td>
<td>disilane</td>
<td>(\frac{2}{3}b_{\text{HSi}} + 2a_H + b_{\text{SiS}})</td>
<td>(\sqrt{8}/3c)</td>
<td>(\sqrt{2}c)</td>
<td>3.43, 17, 32.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}_3\text{H}_7, \text{Si}_3\text{H}_8)</td>
<td>trisilane</td>
<td>(\frac{2}{\sqrt{3}}c + \frac{1}{3}b_{\text{SiS}})</td>
<td>(\frac{2}{3}c + 2\sqrt{\frac{8}{3}b_{\text{SiS}}})</td>
<td>(\sqrt{\frac{8}{3}c})</td>
<td>4.48, 26, 44.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}_4\text{H}_9, \text{Si}<em>4\text{H}</em>{10})</td>
<td>n-tetrasilane</td>
<td>&quot;&quot;</td>
<td>(\frac{2}{3}c + \frac{1}{3}b_{\text{SiS}})</td>
<td>&quot;&quot;</td>
<td>5.04, 31, 50.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>5\text{H}</em>{11}, \text{Si}<em>5\text{H}</em>{12})</td>
<td>iso-tetrasilane</td>
<td>(\frac{3}{2}b_{\text{SiS}} + \frac{1}{3}c)</td>
<td>(\frac{3}{2}b_{\text{SiS}} + \frac{1}{3}c)</td>
<td>(\frac{1}{3}b_{\text{SiS}} + c)</td>
<td>3.63, 19, 34.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>6\text{H}</em>{13}, \text{Si}<em>6\text{H}</em>{14})</td>
<td>n-pentasilane</td>
<td>(\frac{2}{\sqrt{3}}c + \frac{1}{3}b_{\text{SiS}})</td>
<td>(\frac{2}{3}c + \frac{4}{\sqrt{3}}b_{\text{SiS}})</td>
<td>(\frac{8}{\sqrt{3}}c)</td>
<td>5.49, 36, 56.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>7\text{H}</em>{15}, \text{Si}<em>7\text{H}</em>{16})</td>
<td>neo-pentasilane</td>
<td>(\sqrt{2}(c + b_{\text{SiS}}))</td>
<td>(\frac{8}{\sqrt{3}}(c + b_{\text{SiS}}))</td>
<td>(\sqrt{2}(c + b_{\text{SiS}}))</td>
<td>6.41, 46, 69.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>8\text{H}</em>{17}, \text{Si}<em>8\text{H}</em>{18})</td>
<td>n-hexasilane</td>
<td>(\frac{2}{\sqrt{3}}c + \frac{1}{3}b_{\text{SiS}})</td>
<td>(\frac{2}{3}c + \frac{5}{\sqrt{3}}b_{\text{SiS}})</td>
<td>(\frac{8}{\sqrt{3}}c)</td>
<td>5.87, 40, 61.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>9\text{H}</em>{19}, \text{Si}<em>9\text{H}</em>{20})</td>
<td>2,3-disilylettrasilane</td>
<td>(\frac{2}{\sqrt{3}}(b_{\text{SiS}} + c) + b_{\text{SiS}})</td>
<td>(\frac{8}{\sqrt{3}}b_{\text{SiS}} + \frac{2}{\sqrt{3}}c)</td>
<td>(\frac{3}{2}b_{\text{SiS}} + \frac{2}{\sqrt{3}}c)</td>
<td>6.48, 47, 70.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>{10}\text{H}</em>{21}, \text{Si}<em>{10}\text{H}</em>{22})</td>
<td>n-heptane</td>
<td>(\frac{2}{\sqrt{3}}c + \frac{1}{3}b_{\text{SiS}})</td>
<td>(\frac{2}{3}c + \frac{6}{\sqrt{3}}b_{\text{SiS}})</td>
<td>(\frac{8}{\sqrt{3}}c)</td>
<td>6.23, 44, 67.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Si}<em>{11}\text{H}</em>{23}, \text{Si}<em>{11}\text{H}</em>{24})</td>
<td>2,3-trisilylettrasilane</td>
<td>(\frac{2}{\sqrt{3}}(b_{\text{SiS}} + c) + b_{\text{SiS}})</td>
<td>(\frac{8}{\sqrt{3}}b_{\text{SiS}} + \frac{2}{\sqrt{3}}c)</td>
<td>(\sqrt{3}b_{\text{SiS}} + \frac{2}{\sqrt{3}}c)</td>
<td>6.56, 48, 71.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Physical parameters:

\(b_{\text{HSi}} = 1.47\,\text{Å}\) \(a_H = 0.529\,\text{Å}\) \(b_{\text{SiS}} = 2.32\,\text{Å}\) \(a_{\text{Si}} = 1.11\,\text{Å}\) \(b_{HH} = 0.74\,\text{Å}\) \(c = b_{\text{HSi}} + a_H\)

The calculation of ion-neutral mean free path is similarly nontrivial. An approximate solution applies the potential of an electric dipole:

\[
U(r) = E \cdot \vec{p}
\]
where $\vec{E}$ is the electric field the dipole experiences, and $\vec{p}$ is the dipole moment. For an ion represented as a point charge, the two expressions become:

$$U(r) \approx \frac{e}{4\pi \varepsilon_0 r^2} \cdot \frac{ae}{4\pi \varepsilon_0 r^2}$$

(17)

In this case, $\alpha$ is the polarizability [F-m$^2$] and $r$ is the spacing between the ion-neutral pair.

For relative energies much larger than the potential of eq. (17), the interaction is negligible. Thus, the threshold for an effective impact parameter is found by setting these values equal:

$$\varepsilon = \left(\frac{e}{4\pi \varepsilon_0 r_{coll}^2}\right)^2 \alpha$$

(18)

Solving for the impact parameter yields:

$$r_{coll} = \left(\frac{\alpha e^2}{16\pi^2 \varepsilon_0^2}\right)^{1/4}$$

(19)

Calculation of the transport cross section is then straightforward:

$$\sigma(\varepsilon) = \pi r_{coll}^2 = \pi \left(\frac{\alpha e^2}{16\pi^2 \varepsilon_0^2}\right)^{1/2} = \frac{e}{4\pi \varepsilon_0} \left(\frac{\alpha}{\varepsilon}\right)^{1/2}$$

(20)

This result is identical to that given by Raizer$^{[53]}$, instead given in Gaussian units.

For a gas temperature $T_{gas}$, the cross-section must be integrated over the Maxwell-Boltzmann distribution to represent a mean value:

$$\langle \sigma \rangle = \int \sigma(\varepsilon) f(\varepsilon) d\varepsilon = \frac{4\pi}{\sqrt{2\pi m_r}} \left(\frac{1}{k_b T_{gas}}\right)^{3/2} \int_0^\infty \frac{e^{\sqrt{\varepsilon}}}{4\varepsilon_0 \varepsilon^{1/2}} e^{-\frac{e}{k_b T_{gas}}} d\varepsilon$$

(21)

where $\varepsilon$ is the center of mass energy, and $m_r$ is the reduced mass. With the $\varepsilon^{-1/2}$ term in $\sigma$ cancelling out the $\varepsilon^{1/2}$ term in $f(\varepsilon)$, the definite integral significantly simplifies to:
This approximate expression happens to be inversely proportional to the root of reduced mass \([\text{amu}]\) and thermal energy, bearing a striking similarity to Hickman's\(^{[23]}\) ion-ion interaction scaling law (70). Polarizability data was obtained for SiH\(_4\) from Srinivas\(^{[52]}\) \((\alpha'_{\text{SiH}_4} = 34.1a^3_{\text{Bohr}} = 5.05 \cdot 10^{-24} \text{ cm}^3\) ) and H\(_2\) from Ishiguro\(^{[54]}\) \((\alpha'_{\text{H}_2} = 5.3a^3_{\text{Bohr}} = 0.78 \cdot 10^{-24} \text{ cm}^3\) ), where \(\alpha'\) is the polarizability volume, convertible to SI units via the relation \(\alpha[\text{SI}] = 4\pi\varepsilon_0\alpha'\). The calculated cross sections for \(T = 500K\) are exhibited in Table 3.

<table>
<thead>
<tr>
<th>Ion</th>
<th>(n_r(\text{ion} \rightarrow \text{H}_2)) [amu]</th>
<th>(n_r(\text{ion} \rightarrow \text{SiH}_4)) [amu]</th>
<th>(+\sigma_{\text{H}_2}[\text{Å}^2])</th>
<th>(+\sigma_{\text{SiH}_4}[\text{Å}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2^+)</td>
<td>1.00</td>
<td>1.88</td>
<td>255</td>
<td>472</td>
</tr>
<tr>
<td>(\text{H}_3^+)</td>
<td>1.20</td>
<td>2.74</td>
<td>232</td>
<td>391</td>
</tr>
<tr>
<td>(\text{SiH}_2^+)</td>
<td>1.88</td>
<td>15.5</td>
<td>186</td>
<td>164</td>
</tr>
<tr>
<td>(\text{SiH}_3^+)</td>
<td>1.88</td>
<td>15.7</td>
<td>186</td>
<td>163</td>
</tr>
<tr>
<td>(\text{Si}_2\text{H}_4^+)</td>
<td>1.94</td>
<td>20.9</td>
<td>183</td>
<td>141</td>
</tr>
</tbody>
</table>

*Physical parameters: \(a_{\text{H}_2} = 0.87 \cdot 10^{-40}\text{F.m}^2, a_{\text{SiH}_4} = 5.62 \cdot 10^{-40}\text{F.m}^2, T = 500K\)

It is seen in Table 3 that cross sections for hydrogen ion collisions with SiH\(_4\) are significant due to larger \(\alpha\) and lower \(n_r\). A comparison between calculated data and that of Phelps\(^{[55]}\) shows moderate accuracy for H\(_2^+\) and H\(_3^+\), both with cross sections of \(\approx 100 \text{ Å}^2\) at 0.1 eV. With the \(v^{-1}\) dependence, it is expected that experimental data at thermal energies \((k_BT = 0.043 eV)\) would more closely match the theoretically predicted cross sections in Table 3.
With both neutral-neutral and neutral-ion cross sections defined, the mean free path can be easily calculated:

\[
\lambda = \frac{1}{\sigma_{H_2} n_{H_2} + \sigma_{SiH_4} n_{SiH_4}}
\]

At 100 mTorr and 5% silane concentration, \(\lambda\) for ions range from 0.11 mm for \(H_2^+\) to 0.16 mm for \(Si_2H_4^+\), while \(\lambda\) for neutrals ranges from 9.1 mm for \(H\), 8.1 mm for \(H_2\), 3.5 mm for \(SiH_2\), \(SiH_3\), \(SiH_4\), 2.9 mm for \(Si_2H_5\) and \(Si_2H_6\), down to 0.60 mm for \(Si_7H_{15}\) and \(Si_7H_{16}\).

3.3 – Reaction Rate Coefficients

Calculation of reaction rates is the most laborious step of assembling a plasma model. Extensive searching of references and cross section databases yielded these parameters. For hydrogen reactions, the tabulated database provided by Phelps\(^8\) served as the source for most reactions, with verification from others, such as Kurachi\(^{14}\), as well as the Hayashi\(^{13}\) and SIGLO\(^{16}\) databases. For silane-based interactions (particularly ion-ion pathways), the comprehensive analysis by Perrin, Leroy, and Bordage\(^{25}\) provided a basis for majority of the reactions considered. Other sources were consulted for confirmation on the validity of these values.

Given a set of cross-sectional data \(\sigma(E) \text{ [cm}^2\text{]}\), a vast simplification in assessing scattering events is the identification of a volumetric reactivity \(R \text{ [#/cm}^3\text{-s]}\) for a certain reaction. This reactivity can be expressed as a product of environmental variables:

\[
R = k_{ABC\ldots \rightarrow A'B'C'\ldots} \prod_i = A, B, C, \ldots n_i
\]
where $k$ represents a reaction rate coefficient for a given reaction, and the pi term represents the product of every reactant species $n_i \, [\text{cm}^{-3}]$ involved. The nature of $\sigma(E)$ influences the behavior of $k$, while the number of reactants determines the units. For a single-body reaction, i.e. self-dissociation, de-excitation, or nuclear decay events, $k$ is merely a rate $[1/\text{s}]$ and can either be determined experimentally via electron swarm data or by rigorous quantum analysis. For two-body processes, $k$ takes on units of $[\text{cm}^3/\text{s}]$, and three-body processes $[\text{cm}^6/\text{s}]$. Thus, the reactivity always results in units of $[1/\text{cm}^3\cdot\text{s}]$. In this model, only two-body interactions are incorporated. *(Some molecule-molecule reactions included are implicitly 3-body but low energy.)* For a two-body scattering interaction, the calculation of $k$ is as follows:

\[(25) \quad R = n_A n_B \int_0^\infty v f(E) \sigma(E) dE = n_A n_B k\]

where $v$ is the relative velocity of the incident particle to the target particle and $f(E)$ is the energy distribution function of the incident particle. It should be noted that this formula is not general – it is an approximation for the situation of the target particle being far more massive than the incident particle (in this case, electron impact). This results in a substitution of $\sqrt{\frac{2E}{m_e}}$ for $v$. Another simplification can be made for low temperature discharges in that the target is approximately at rest, relative to the electrons:

\[(26) \quad T_e \gg T_i \approx T_{\text{gas}}\]

Another assumption will be made in a mid-pressure (100~500 mTorr) range, that the electrons are thermalized. This is not necessarily the case very near the surface of the
antenna, but it is a good approximation elsewhere in the plasma. The electron energy
distribution (EEDF) is simply a Maxwell-Boltzmann distribution:

\[
 f_{MB}(E) = \left( \frac{E}{\pi (k_B T_e)^3} \right)^{1/2} e^{-E/k_B T_e} dE
\]

where \( T_e \) is electron temperature and \( k_b = 1.38 \cdot 10^{-23} \frac{J}{K} \), Boltzmann’s constant. This
distribution represents the differential probability to find an electron over a given energy
range. As it describes the array of energies that would be participating in the reaction, it is
necessary in the average to find \( \langle \sigma v \rangle \). This is what simplifies the equations of state of
the system from integral to algebraic equations. The expression becomes:

\[
 k = \langle \sigma v \rangle = \left( \frac{8}{\pi m_e (k_B T_e)^3} \right)^{1/2} \int_0^\infty E e^{-E/b T_e} \sigma(E) dE
\]

One must carefully consider units, as \( T_e \) and \( E \) are normally given in eV, while \( \sigma \)
comes in either \([\text{cm}^2]\), \([\text{m}^2]\) or \([\text{Å}^2]\). As \( \sigma \) is often determined empirically (or an analytical
form may result in an intractable integral), a numerical integration can be easily done for
various \( T_e \). In this study, this was done with trapezoidal rule via the trapz() function of
Matlab.

3.4 – Power Balance

Due to the high frequency and moderate pressure of the discharge, the ions are unable to
gain sufficient energy during the oscillation period. Typical of low temperature plasmas, the
power balance in the plasma falls primarily on the electron population:

\[
 \frac{3}{2} \frac{d}{dt} (n_e \cdot k_b T_e) = \frac{p_{\text{wave}}}{v} - p_{\text{ex}} - p_{\text{el}} - p_{\text{ion}} - p_{\text{wall}}
\]
where \( n_e \) is the electron density, \( T_e \) is electron temperature, \( P_{\mu\text{wave}} \) is microwave power input into the plasma (accounting for losses in the coaxial line with an efficiency factor of 80%), \( V \) is the effective plasma volume, \( p_{\text{ex}} \) is power density of excitation, \( p_{\text{el}} \) is power density loss of electrons to neutrals via elastic scattering, \( p_{\text{ion}} \) is power density put into ionization, and \( p_{\text{wall}} \) is loss of charged species to the wall. In the transient, power is channeled into both adding new electrons into the population: \( \frac{\partial n_e}{\partial t}(\frac{3}{2} k_B T_e) \) and increasing the mean energy of the population itself: \( n_e \left( \frac{3}{2} k_B \frac{\partial T_e}{\partial t} \right) \). With equation (29) coupled to the electron particle balance, the value of the electron temperature \( T_e \) is determined.

The power loss terms \( p_{\text{ex}}, p_{\text{el}}, \) and \( p_{\text{ion}} \) are as follows:

\[
p_m = \sum_i \epsilon_{m,i} R_{m,i} \tag{30}
\]

where subscript \( m \) is the loss mechanism (excitation, elastic scattering, or ionization), \( \Sigma_i \) is a sum over all associated reactions for that mechanism, \( R_i \) is the reactivity of the \( i^{th} \) reaction, and \( \epsilon_i \) is the energy lost. For ionization and excitation, the energy is most commonly the energy transition or appearance potential for the chemical pathway, while elastic scattering must use the collisional energy loss of an electron with a heavy ion:

\[
\epsilon_{el} = 3 k_B T_e \frac{m_e}{m_i} \tag{31}
\]

For wall power loss, the expression for \( p \) takes a different form:

\[
p_{\text{wall}} = \sum_+ (\epsilon_{\text{ion}} + \epsilon_{\text{elec}}) I_+ \beta_+ \tag{32}
\]

where \( \Sigma_+ \) is a sum over all ions, and energy loss per e-i pair is:
\[ \epsilon_{\text{ion}} + \epsilon_{\text{elec}} = T_e \left( \frac{e^2}{2} + \frac{1}{2} \ln \frac{m_i}{2\pi m_e} \right) \]

given in Kim.\[^{49}\] Despite electron mobilities and velocities being considerably higher than that of ions, eq. (33) embodies the quasineutrality condition that governs ambipolar diffusion to the wall and balances electron current with ion current. Loss probability \( \beta = s + \gamma \), the sum of surface sticking and recombination probabilities, is taken to be 1 in the case of ions in a collisionless sheath.

With density rates for all species given by (2) and rate coefficients \( k \) being a function of \( T_e \), the power balance of (29) is the final equation required for the system constraints, solving for \( T_e \) as a function of \( n_e \), electron energy loss mechanisms, and time. With all rate coefficients calculated as a function of \( T_e \), the complete set of 41 equations following 40 species (Table 1) in 62 reactions (Table 4) can be constructed in Matlab and called by ode45 or ode113 for the time-dependent electron temperature and densities of all species.
4: Discussion of Reaction Kinetics in a Silane-Hydrogen Discharge

4.1 – Electron Impact Ionization

Hydrogen ionization reactions have been long understood, and data from Phelps\textsuperscript{[8]} and Mendez et al.\textsuperscript{[26]} was used for calculation of rate coefficients. The primary electron source of the discharge is ionization of H\textsubscript{2}:

\begin{equation}
    e + H_2 \rightarrow H_2^+ + 2e
\end{equation}

resulting in 15.4 eV loss due to the ionization potential. Another pathway possible, although drastically less likely, is dissociative ionization:

\begin{equation}
    e + H_2 \rightarrow H^+ + H + 2e
\end{equation}

However, this requires a larger appearance potential and enthalpy of formation due to the dissociative effect on top of ionization. An interesting choice of Danko et al.\textsuperscript{[6]} and other cited models is the exclusion of H\textsuperscript{+} as a plasma species altogether. While H is a primary species, appearing as a product in many reactions and significant for surface interactions, it is only in a discharge with low pressure and high power/particle ratio where H\textsuperscript{+} becomes dominant.

For dissociative ionization of SiH\textsubscript{4}, data was obtained from Krishnakumar et al.\textsuperscript{[12]} with comparisons on work done by Haaland\textsuperscript{[46]}, Perrin\textsuperscript{[25]}, and Basmer\textsuperscript{[47]}, as these are more recent publications. Works pre-1990 had sometimes quoted detected production of SiH\textsubscript{4}+, but this was often disputed. Haaland\textsuperscript{[46]} undertook a thorough electron swarm analysis using Fourier transform mass spectroscopy (FTMS), bearing in mind the naturally-occurring
isotopes of silicon ($^{28}\text{Si}$: 92.2%, $^{29}\text{Si}$: 4.69%, $^{30}\text{Si}$: 3.09%). Through careful consideration of these natural abundances, he ruled out the production of $\text{SiH}_4^+$ seen in earlier works by their detection of $^{30}\text{SiH}_2^+$. With attention with respect to isotope mass, the correct production of $\text{SiH}_2^+$ and $\text{SiH}_3^+$ could be understood, as well. Perrin et al. agreed that in the majority of studies, the conclusion was that $\text{SiH}_4^+$ was not a stable product, further dissociating by ejecting $\text{H}$, 2$\text{H}$, or $\text{H}_2$.[25]

Haaland[46], Perrin[25], and Basmer[47] all conclusively recognized $\text{H}_2^+$ and $\text{H}^+$ production through electron impact of $\text{SiH}_4$ to be minimal. In Krishnakumar et al.[12], the representative fraction of $\text{H}_2^+$ and $\text{H}^+$ produced was less than 10% of the total for lower energies. This may be attributed to the high threshold for generating these species, both $\approx 24.5$ eV[46], compared to the 12-13 eV appearance potentials for the silicon-ion centers.

From data in [12], the key production pathways for low to mid energies are $\text{SiH}_3^+$ and $\text{SiH}_2^+$, with $\text{SiH}_2^+$ cross-sections being 50% higher. Other sources agree somewhat well – the form of the cross-sectional curve was captured well, with Basmer[47] giving 20% higher values and Haaland[46] underestimating by half (his was an empirical fit based on appearance potential and high-energy measurements). For the purpose of the model, the reactions chosen represent >70% of the total dissociative ionization cross-section:

\begin{align*}
(36) & \quad e + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{H} + 2e \\
(37) & \quad e + \text{SiH}_4 \rightarrow \text{SiH}_2^+ + 2\text{H} + 2e
\end{align*}
Figure 8: Plot of cross-sections for electron impact dissociative ionization of SiH\(_4\) by resultant ion. Open shapes represent data obtained by Krishnakumar\(^{[12]}\), while blackened shapes are by Robertson et al.\(^{[48]}\)

The reverse reaction of recombination was considered for primary ion species:

\[
\begin{align*}
(38) & \quad e + H_2^+ \rightarrow H + H \\
(39) & \quad e + H_3^+ \rightarrow H_2 + H \\
(40) & \quad e + SiH_3^+ \rightarrow SiH_2 + H \\
(41) & \quad e + SiH_2^+ \rightarrow SiH_2 + h\nu
\end{align*}
\]

drawing from rate coefficients included in the work of Perrin et al.\(^{[25]}\)

4.2 – Electron Impact Excitation

As one of the primary energy loss mechanisms, excitation reactions are included in the model. Any atom brought into an excited state will remove energy from the electron population, influencing the electron temperature. While excited state species may have
improved interaction probability compared to the neutral analog, the transition time for an excited → ground state is primarily responsible for whether these excited state species further influence the plasma chemically. If the plasma falls into the following regime:

\[
\tau_m = \frac{1}{v_m} \gg \tau_{1\rightarrow0}
\]

where \(\tau_{1\rightarrow0}\) represents the transition time, and \(\tau_m\) is the collision time, the effects of excited state species may become non-negligible.

The following reactions were included, following Danko's\(^6\) list, as well as others due to availability of cross sections or empirical comparisons:

\[
\begin{align*}
(43) \quad & SiH_4 + e \rightarrow SiH_4^{v13} + e \quad (0.113 \text{ eV}) \\
(44) \quad & \rightarrow SiH_4^{v24} + e \quad (0.27 \text{ eV}) \\
(45) \quad & H_2 + e \rightarrow e + H_2(B^1\Sigma_u^+) \quad (11.3 \text{ eV}) \\
(46) \quad & \rightarrow e + H_2(c^3\Pi_u) \quad (11.75 \text{ eV}) \\
(47) \quad & \rightarrow e + H_2(a^3\Sigma_g^+) \quad (11.8 \text{ eV}) \\
(48) \quad & \rightarrow e + H_2(C^1\Pi_u) \quad (12.4 \text{ eV}) \\
(49) \quad & \rightarrow e + H_2(d^3\Pi_u) \quad (14.0 \text{ eV}) \\
(50) \quad & \rightarrow e + H_2(\Sigma_{Rydberg}) \quad (15.2 \text{ eV}) \\
(51) \quad & \rightarrow e + H_2^{v01} \quad (0.54 \text{ eV}) \\
(52) \quad & \rightarrow e + H_2^{v02} \quad (1.08 \text{ eV}) \\
(53) \quad & \rightarrow e + H_2^{v03} \quad (1.62 \text{ eV}) \\
(54) \quad & \rightarrow e + H_2^{102} \quad (0.044 \text{ eV}) \\
(55) \quad & \rightarrow e + H_2^{113} \quad (0.073 \text{ eV})
\end{align*}
\]
Danko\textsuperscript{[6]} includes the 8.4 eV excitation to SiH\textsubscript{4}\textsuperscript{*}; however, this state has been found to be a pathway for dissociative excitation, rather than a stable excitation. This reaction will be discussed in section 4.3.

The treatment of optical "thickness" is also an important concept for considering excitation in the discharge. In general, because the photon energy is resonant to the electronic or atomic transition it originated from, the photon is likely to be re-absorbed by neighboring gas species. For relevant gas species, the mean free path for a photon can be calculated in the usual manner:

\[ \lambda_{hv} = \sum_i \frac{1}{n_i \sigma_{hv_i}} \]

where \( n_i \) is the density of the \( i^{th} \) gas species, and \( \sigma_{hv} \) is the absorption cross-section at the given photon energy. Normally, the sum can be removed, and only the emitting gas species is considered. In the optically-thick regime, \( \lambda_{hv} < L \), the characteristic length of the discharge geometry. In high pressure situations, such as a DBD plasma display pixel of Ne/Xe (700 Torr fill pressure), photon transport is nontrivial. In the PECVD system under consideration, however, the low pressure of \( \sim 100 \) mTorr remedies this concern. The assumption in this work is that stable excited state species relax promptly before their next interaction.

Other results of electron impact excitation, particularly any resultant metastables, will not be included in the model. The literature does not note any observed metastables of
significant energy or lifetime (longest-lived H transition: \(1^2S_{1/2} \rightarrow 2^2P_{3/2}\), 10.2 eV in 1.6 ns\(^{[29]}\)).

4.3 – Dissociative Excitation

A primary mechanism for formation of silane radicals is the excitation of SiH\(_4\), leading to dissociation:

\[e + \text{SiH}_4 \rightarrow \text{SiH}_n + (4 - n)H + e\]  \hspace{1cm} (57)

Danko et al.\(^{[6]}\) incorrectly include an excitation reaction resulting in a stable excited state SiH\(_4^*\), but similarly to SiH\(_4^+\), this species is electronically unstable and dissociates into respective fragments. While dissociative ionization if SiH\(_4\) is easy to measure due to charged products, dissociative excitation is much more challenging to assess, making the consideration of the primary silane radical, SiH\(_2\) or SiH\(_3\), problematic.

It is generally agreed in literature that, similar to dissociative ionization of silane, SiH and Si are marginal products of the dissociation reaction. Jarnev and Rieter\(^{[18]}\) attribute branching ratios of 0.15 for SiH and 0.13 for Si, although this is disputed by references cited by Spiriopoulos et al.\(^{[17]}\), claiming branching ratios of <0.01 each. Regardless, the theme of low production due to high formation energy applies in this case.

The major discrepancy in the literature is the production of SiH\(_3\) over SiH\(_2\), where [17] gives \([\text{SiH}_3]/[\text{SiH}_2] = 0.17/0.83\) of Potzinger and Lampe\(^{[22]}\), while [18] gives nearly the inverse: \([\text{SiH}_3]/[\text{SiH}_2] = 0.46/0.26\). Kushner discusses these varied branching ratios,
referring to Robertson and Gallagher’s methane (CH₄) dissociation analogy, with Melton and Rudolph’s [CH₃]/[CH₂] = 0.80/0.13 agreeing with this analogy (see [19]). Other groups suggest branching ratios of [SiH₃]/[SiH₂] less than unity (1/5 or 1/8), more closely in line with the popular [SiH₃]/[SiH₂] = 0.17/0.83. This work will focus on a theoretical analysis of SiH₄ dissociation given by Winstead et al.\(^{[15]}\) Possibly the most important recommendation in their formulation is the attribution of the 8.9 eV \(^1\)T₂ (singlet) excited state of SiH₄ to the subsequent dissociation:

\[(58)\]

\[e + \text{SiH}_4 \rightarrow e + \text{SiH}_4(\ ^1\text{T}_2) \rightarrow \text{SiH}_3 + H + e\]

while the 7.8 eV \(^3\)T₂ (triplet) state primarily dissociates as follows:

\[(59)\]

\[e + \text{SiH}_4 \rightarrow e + \text{SiH}_4(\ ^3\text{T}_2) \rightarrow \text{SiH}_2 + 2H + e\]

Figure 9: Reaction rate coefficients for electron impact excitation of SiH₄ resulting in SiH₂ and SiH₃, calculated from data obtained from the Hayashi database\(^{[13]}\) and the work of Kurachi, Nakamura\(^{[14]}\). The
reactivity for the SiH\textsubscript{2} pathway is consistently higher due to the lower appearance potential (7.8 eV) of its associated cross section.

![Calculated Branching Ratio [SiH\textsubscript{3}]/[SiH\textsubscript{2}]](image)

Figure 10: Branching ratio of SiH\textsubscript{3}:SiH\textsubscript{2} calculated by k\textsubscript{SiH\textsubscript{3}}/k\textsubscript{SiH\textsubscript{2}} in dissociative excitation of SiH\textsubscript{4} (based on values shown in Figure 9).

It is anticipated, based on Langmuir probe data from this work, that the electron temperature will vary from \( \approx 5 \) eV near the source down to 1-3 eV at the substrate. Thus, from Figure 10, the branching ratio remains fairly stable between 0.3-0.4.

Other dissociative excitation reactions considered are that of disilane (Si\textsubscript{2}H\textsubscript{6})\textsuperscript{[28]}:

\begin{equation}
(60) \quad e + \text{Si}_2\text{H}_6 \rightarrow \text{SiH}_3 + \text{SiH}_2 + H + e
\end{equation}

which is significant for producing deposition radicals SiH\textsubscript{2}/SiH\textsubscript{3}. Also, hydrogen\textsuperscript{[8]}:

\begin{equation}
(61) \quad e + H_2 \rightarrow H^{n=2} + H^{n=2} + e
\end{equation}

\begin{equation}
(62) \quad e + H_2 \rightarrow H + H^{n=3} + e
\end{equation}
follows the important dissociation reactions above, where $n$ is the principal quantum number. These hydrogen dissociation reactions are of particular interest because they provide a comparison with emission spectra from the experimental plasma (assuming direct excitation of H is minimal).

4.4 – Dissociative Attachment

Dissociative attachment data of SiH$_4$ was taken from the work of Haaland.$^{[21]}$ The cross sections for this reaction manifest as resonant peaks with thresholds 6.5 to 8.9 eV. Their magnitudes are generally smaller than that of electron attachment for hydrogen. However, they become important when considering the fast neutralization reaction:

(63) \[ X^- + Y^+ \rightarrow Z^{(+)} + A^+ \]

where $X$ represents a cation. These reactions are addressed in section 4.5.

Figure 11: Electron attachment cross-sections of SiH$_4$ leading to corresponding products SiH$_3^-$, SiH$_2^-$, and SiH$^-$, as provided by Haaland.$^{[21]}$
As seen in Figure 11, the cross-section for SiH$_3^-$ is larger than the other two species combined. Coupling this with the low appearance potential and enthalpy of formation (2.56 eV), as well as the simple broadness of the cross-sectional peak, it is concluded that SiH$_3^-$ is the only significant silane-derived anion in the discharge. (Larger “particle” anions will not be followed due formation through higher-order reactions.) Thus, the attachment reaction that will be followed is:

(64) \[ e + SiH_4 \rightarrow SiH_3^- + H \]

4.5 – Cation-Anion Recombination

The ion-ion recombination process described in equation (63) is acknowledged by Perrin$^{[25]}$ to be a very efficient one due to the typically low energy of interacting ions and the lack of need for a third body for momentum conservation. Following suit with Danko$^{[6]}$, SiH$_3^-$ was the only anion considered for recombination. Thus, the set of reactions for this type of process are brief:

(65) \[ SiH_3^- + H_2^+ \rightarrow SiH_3 + H_2 \]
(66) \[ SiH_3^- + H_3^+ \rightarrow SiH_4 + SiH_2 \]
(67) \[ SiH_3^- + SiH_2^+ \rightarrow SiH_3 + SiH_2 \]
(68) \[ SiH_3^- + SiH_3^+ \rightarrow SiH_5 + SiH_3 \]
(69) \[ SiH_3^- + Si_2H_4^+ \rightarrow SiH_3 + 2 SiH_2 \]

The importance of these reactions is to provide a loss mechanism for negative ions, since they don’t have the thermal energy to cross the plasma sheath, and electron impact ionization is very unlikely. If the negative ion population should exceed 10-20% of the
electron density, the equations offered in section 4.0 would need to be modified to reflect plasma electronegativity $\alpha$, in this case: $\alpha = \frac{n_{SiH_3}}{n_e}$.

With ion-ion interactions in a microwave plasma governed by diffusion, an approximation may be made that their distribution falls in line with the gas temperature, $T_{gas}$. This allows the use of the scaling model developed by Hickman$^{[23]}$ and applied by Danko,$^{[6]}$ possibly more appropriately in the case of a microwave source. Hickman uses a semi-empirical fit based on Olson’s$^{[24]}$ “absorbing sphere model” (ASM). The result is the following$^{[23]}$:

\[
(70) \quad \frac{1}{k_1 [cm^3/s]} = 4.38 \cdot 10^4 \left( \frac{T[K]}{300} \right)^{\frac{1}{2}} (m_r [amu])^{\frac{1}{2}} (EA [eV])^{0.4}
\]

where $k$ is the reaction rate coefficient, $T$ is the ion temperature ($T_i \approx T_{gas}$), $m_r$ is the reduced mass in amu, and $EA$ is the electron affinity of the anion’s neutral analog. In general, this equation represents that the reactivity is inversely proportional to some power of the temperature, reduced mass, and electron affinity of the interacting species. The calculated values for these reactions at $T_{gas} = 500K$ are obtained from Danko$^{[6]}$, typically larger than $k$ for electron-ion recombination due to significantly larger reduced mass.

4.6 – Dust Formation Kinetics

SiH$_4$ discharges are well-known to produce dust under the right circumstances, plaguing atmospheric DBD devices in particular. Because thin film systems require high purity and controlled deposition conditions, the regimes of a PECVD system in which dust
formation occurs must be avoided. The deposited films are not well-adhered and are usually porous, both of which are unwanted in a photovoltaic material.

Perrin’s\textsuperscript{[25]} analysis for SiH\textsubscript{4} discharges presents pressure-dependent rate-coefficients for the accumulation of larger silane chains:

(71) \[ SiH_4 + H_2 \rightarrow Si_2H_6 \]

(72) \[ Si_2H_6 + SiH_2 \rightarrow Si_3H_8 \]

(73) \[ Si_2H_6 + SiH_3 \rightarrow SiH_4 + Si_2H_5 \]

(74) \[ Si_3H_8 + SiH_2 \rightarrow Si_4H_{10} \]

(75) \[ Si_4H_{10} + SiH_2 \rightarrow Si_5H_{12} \]

(76) \[ Si_5H_{12} + SiH_2 \rightarrow Si_6H_{14} \]

(77) \[ Si_6H_{14} + SiH_2 \rightarrow Si_7H_{16} \]

Particles of Si\textsubscript{n}H\textsubscript{2n+(1,2)} with n \geq 8 are flagged as dust dust and not followed further.

Perrin’s\textsuperscript{[25]} cited rate coefficients for these accumulation reactions (presumably with \( T_{\text{gas}} \) set somewhere between 300 and 600K) are as follows:

(78) \[ k = c \cdot \left( 1 - \frac{1}{1+0.0033p_0} \right) \]

where \( p_0 \) is the pressure of the system, and \( c \) is a constant that loosely represents the interaction potential of the two molecules. It is important to note that for higher pressure, the magnitude of \( k \) increases. The physical explanation for this relates directly back to the neutral mean free path – more collisions means more opportunity for dust particle formation in the gas phase. Luckily, larger silane chains that undergo electron impact ionization or
charge transfer reactions become unstable and dissociate\textsuperscript{[30]}. In the case of electron attachment, however, large anions do remain stable\textsuperscript{[25]}. Synergistically, these molecules typically have larger electron affinities (\(EA_{SiH_2} = 1.124\ e\), \(EA_{Si_5H_{11}} \geq 1.52\ eV\)), but the fast reaction of ion-ion neutralization:

\begin{equation}
X^+ + Y^- \rightarrow Z^{(*)} + A
\end{equation}

has the added chance of dissociating its educts\textsuperscript{[23][24]} due to the release of energy. Thus, the stability of dust is further reduced by this mechanism. Its survival depends on diffusion out of the high density plasma region.

To summarize the description of the process in literature, the longer a silane radical resides in the system undeposited and unpumped, the more it coalesces into a larger chain of \(Si_xH_y\). This implies that a lower pressure, a heated substrate for high sticking coefficient, and a narrow discharge gap (preferably planar for roll-to-roll deposition) will all mitigate the creation of dust in the system.

4.7 – Surface Reactions

With center-to-edge ratios determined for each neutral and ion, the final important mechanism of the model can be put into place – the surface sticking and recombination reactions. The gas/plasma-surface interaction involves two processes: deposition of \(Si_mH_n\) radicals into an open bonding site, and removal of the accompanying hydrogen from the film by H atom exposure. As argued in the experimental results of this work, it is the balance of these two processes that mostly determine the atomic structure and quality of the film.
For ions, the considerable amount of energy gained when traversing the plasma sheath prompts the assumption that the loss probability of ions is $\beta_+ = 1$. Silicon-containing ions ($\text{SiH}_2^+$, $\text{SiH}_3^+$, $\text{Si}_2\text{H}_4^+$) have an imposed sticking probability of $s_+ = 1$ with no recombination. For $\text{H}_2^+$ and $\text{H}_3^+$, $\beta_+ = (s_+, \gamma_+) = (0, 1)$.

For neutrals, the density of $\text{H}$, $\text{SiH}_2$, and $\text{SiH}_3$ is larger than the plasma density and should contribute a much larger portion of the growth/hydrogen treatment, although $\text{H}_3^+$ will be competitive with $\text{H}$ in that it counteracts hydrogen removal from the film. Following Perrin$^{[25]}$, the recombination probability of $\text{H}$ is taken to be $\gamma_H = 1$. For $\text{SiH}_2$, the divalent silyl interacts strongly with the surface it encounters. In Perrin’s work on sticking coefficients$^{[57]}$, a high loss probability of $\beta_{\text{SiH}_2} = 0.95$ was found in literature, assuming a branching of $s_{\text{SiH}_2} = 0.8$ and $\gamma_{\text{SiH}_2} = 0.15$. On the contrary, $\text{SiH}_3$ has a much lower loss probability: $\beta_{\text{SiH}_3} = 0.30 \pm 0.02$ from Kessels et al.$^{[56]}$ and $0.26 \pm 0.02$ from Perrin.$^{[57]}$ Both studies showed $\beta$ to be temperature-independent, but Perrin’s work diverged in that it gave $(s, \gamma) = (0.09 \pm 0.02, 0.16 \pm 0.05)$ at $T_{\text{substrate}} < 275^\circ\text{C}$ against Kessels’ $(s, \gamma) = (0.30 \pm 0.02, 0)$. To avoid this discrepancy, this model will use $T_{\text{substrate}} \geq 285^\circ\text{C}$ to accompany the bulk of experimental data obtained at this temperature.

![Diagram](image-url)

Figure 12: Depiction of the possible reactions incident thermal $\text{SiH}_3$ may cause when interacting with a growing $\text{Si:H}$ film, taken from Perrin.$^{[57]}$
Larger silanes require approximations based on SiH$_3$ and SiH$_4$ physics. Since both gas and substrate temperature are relatively low compared to thermal CVD techniques, saturated silanes ($\text{Si}_n\text{H}_{2n+2}$) are assumed to have loss probabilities near zero, following suit with SiH$_4$. In the case of unsaturated molecules ($\text{Si}_n\text{H}_{2n+1}$), their loss probability will pattern the monovalent SiH$_3$. Thus, H-abstraction of saturated molecules becomes significant:

\[
\text{Si}_n\text{H}_{2n+2} + H \rightarrow H_2 + \text{Si}_n\text{H}_{2n+1}
\]

opening up larger molecules to deposition, rather than gas-phase dust accumulation.

### 4.8 – Summarized List of Reactions Included in the Model

Table 4: List of reactions

<table>
<thead>
<tr>
<th># in Model</th>
<th>Reaction</th>
<th>Energy* [eV]</th>
<th>Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R10</td>
<td>$\text{SiH}_4 + e \rightarrow \text{SiH}_4 + e$</td>
<td>$3kT_i \frac{m_e}{m_i}$</td>
<td>Elastic Scattering</td>
<td>[13][14]</td>
</tr>
<tr>
<td>R21</td>
<td>$H_2 + e \rightarrow H_2 + e$</td>
<td>$3kT_i \frac{m_e}{m_i}$</td>
<td></td>
<td>[8][9][10]</td>
</tr>
<tr>
<td>R22</td>
<td>$H_2 + e \rightarrow H_2^+ + 2e$</td>
<td>15.4</td>
<td>Ionization</td>
<td>[8][9][10]</td>
</tr>
<tr>
<td>R11</td>
<td>$\text{SiH}_4 + e \rightarrow \text{SiH}_3^+ + H + 2e$</td>
<td>11.9</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>R18</td>
<td>$\text{SiH}_4 + e \rightarrow \text{SiH}_2^+ + 2H + 2e$</td>
<td>11.9</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>R19</td>
<td>$\text{Si}_2\text{H}_6 + e \rightarrow \text{Si}_2\text{H}_2^+ + 2H + 2e$</td>
<td>12</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>R8</td>
<td>$H_2^+ + e \rightarrow 2H$</td>
<td>$\approx T_e$</td>
<td>Recombination</td>
<td>[25]</td>
</tr>
<tr>
<td>R9</td>
<td>$H_2^+ + e \rightarrow H_2 + H$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R5</td>
<td>$\text{SiH}_2^+ + e \rightarrow \text{SiH}_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R6</td>
<td>$\text{SiH}_3^+ + e \rightarrow \text{SiH}_2 + H$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R17</td>
<td>$\text{SiH}_4 + e \rightarrow \text{SiH}_3^- + H$</td>
<td>6.5-11</td>
<td>Attachment</td>
<td>[21]</td>
</tr>
<tr>
<td>R1</td>
<td>$\text{SiH}_3^+ + \text{H}_2 \rightarrow \text{SiH}_3 + \text{H}_2$</td>
<td></td>
<td>i-i Recombination</td>
<td>[6]</td>
</tr>
<tr>
<td>R2</td>
<td>$\text{SiH}_3^- + \text{H}_2 \rightarrow \text{SiH}_4 + \text{SiH}_2$</td>
<td></td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>R3</td>
<td>$\text{SiH}_3^- + \text{SiH}_2^+ \rightarrow \text{SiH}_2 + \text{SiH}_3$</td>
<td></td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>R4</td>
<td>$\text{SiH}_3^- + \text{SiH}_3^+ \rightarrow \text{SiH}_3 + \text{SiH}_3$</td>
<td></td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>R36</td>
<td>$\text{SiH}_3^- + \text{SiH}_3^+ \rightarrow \text{SiH}_3 + 2\text{SiH}_2$</td>
<td></td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>R24</td>
<td>$H_2 + e \rightarrow H_2(B^1\Sigma_u^-) + e$</td>
<td>11.3</td>
<td>Excitation</td>
<td>[7][8]</td>
</tr>
<tr>
<td>R25</td>
<td>$H_2 + e \rightarrow H_2(c^3\Pi_u) + e$</td>
<td>11.75</td>
<td></td>
<td>[7][8][10]</td>
</tr>
<tr>
<td>R26</td>
<td>$H_2 + e \rightarrow H_2(a^3\Sigma_u^+) + e$</td>
<td>11.8</td>
<td></td>
<td>[7][8][10]</td>
</tr>
<tr>
<td>R27</td>
<td>$H_2 + e \rightarrow H_2(c^1\Pi_u) + e$</td>
<td>12.4</td>
<td></td>
<td>[7][8][10]</td>
</tr>
<tr>
<td>R28</td>
<td>$H_2 + e \rightarrow H_2(d^3\Pi_u) + e$</td>
<td>14.0</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td># in Model</td>
<td>Reaction</td>
<td>Energy* [eV]</td>
<td>Type</td>
<td>Reference</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>-------------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>R29</td>
<td>$H_2 + e \rightarrow H_2(\Sigma_{Rydberg}) + e$</td>
<td>15.2</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>R35</td>
<td>$H_2 + e \rightarrow H_2^{02} + e$</td>
<td>0.044</td>
<td>(Rot.)</td>
<td>[8][10]</td>
</tr>
<tr>
<td>R14</td>
<td>$H_2 + e \rightarrow H_2^{13} + e$</td>
<td>0.073</td>
<td></td>
<td>[8][9]</td>
</tr>
<tr>
<td>R30</td>
<td>$H_2 + e \rightarrow H_2^{01} + e$</td>
<td>0.54</td>
<td>(Vibr.)</td>
<td>[8][10]</td>
</tr>
<tr>
<td>R31</td>
<td>$H_2 + e \rightarrow H_2^{02} + e$</td>
<td>1.08</td>
<td></td>
<td>[8][9]</td>
</tr>
<tr>
<td>R32</td>
<td>$H_2 + e \rightarrow H_2^{03} + e$</td>
<td>1.62</td>
<td></td>
<td>[8][9]</td>
</tr>
<tr>
<td>R12</td>
<td>$SiH_4 + e \rightarrow SiH_4^{13} + e$</td>
<td>0.27</td>
<td></td>
<td>[14]</td>
</tr>
<tr>
<td>R13</td>
<td>$SiH_4 + e \rightarrow SiH_4^{24} + e$</td>
<td>0.113</td>
<td></td>
<td>[13][14]</td>
</tr>
<tr>
<td>R23</td>
<td>$H_2 + e \rightarrow 2H(b^3_\Sigma^+ \Sigma) + e$</td>
<td>8.9</td>
<td>(Dissoc.)</td>
<td>[8][9][10]</td>
</tr>
<tr>
<td>R33</td>
<td>$H_2 + e \rightarrow 2H^{02} + e$</td>
<td>24.9</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>R34</td>
<td>$H_2 + e \rightarrow H + H^{03} + e$</td>
<td>16.6</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>R15</td>
<td>$SiH_4 + e \rightarrow SiH_3 + H + e$</td>
<td>8.9</td>
<td></td>
<td>[13][14]</td>
</tr>
<tr>
<td>R16</td>
<td>$SiH_4 + e \rightarrow SiH_2 + 2H + e$</td>
<td>7.8</td>
<td></td>
<td>[13][14]</td>
</tr>
<tr>
<td>R20</td>
<td>$Si_2H_6 + e \rightarrow SiH_3 + SiH_2 + H + e$</td>
<td>10.2</td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>R7</td>
<td>$H_2^+ + H_2 \rightarrow H_3^+ + H$</td>
<td></td>
<td>Charge Transfer</td>
<td>[26]</td>
</tr>
<tr>
<td>R37</td>
<td>$SiH_3^+ + SiH_4 \rightarrow Si_2H_4^+ + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R43</td>
<td>$Si_2H_6 + SiH_2^+ \rightarrow SiH_3^+ + Si_2H_5$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R53</td>
<td>$Si_2H_6 + SiH_2^+ \rightarrow Si_2H_4^+ + SiH_4$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R59</td>
<td>$SiH_4 + H_2^+ \rightarrow SiH_3^+ + H_2 + H$</td>
<td></td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td>R60</td>
<td>$SiH_4 + H_3^+ \rightarrow SiH_5^+ + H_2 + 2H$</td>
<td></td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td>R61</td>
<td>$SiH_4 + SiH_2^+ \rightarrow SiH_3^+ + SiH_3$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R62</td>
<td>$SiH_4 + SiH_2^+ \rightarrow Si_2H_4^+ + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R39</td>
<td>$SiH_3 + H \rightarrow SiH_2 + H_2$</td>
<td></td>
<td>H-Abstraction</td>
<td>[25]</td>
</tr>
<tr>
<td>R40</td>
<td>$SiH_4 + H \rightarrow SiH_3 + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R41</td>
<td>$Si_2H_6 + H \rightarrow Si_2H_5 + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R42</td>
<td>$Si_2H_6 + H \rightarrow SiH_3 + SiH_4$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R44</td>
<td>$Si_3H_6 + H \rightarrow Si_3H_7 + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R45</td>
<td>$Si_4H_{10} + H \rightarrow Si_4H_9 + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R46</td>
<td>$Si_5H_{12} + H \rightarrow Si_5H_{11} + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R47</td>
<td>$Si_4H_{14} + H \rightarrow Si_4H_{13} + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R48</td>
<td>$Si_5H_{16} + H \rightarrow Si_5H_{15} + H_2$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R38</td>
<td>$SiH_3 + SiH_3 \rightarrow SiH_4 + SiH_2$</td>
<td></td>
<td>Accumulation</td>
<td>[25]</td>
</tr>
<tr>
<td>R49</td>
<td>$SiH_2 + H_2 \rightarrow SiH_4$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R50</td>
<td>$SiH_4 + SiH_2 \rightarrow Si_2H_6$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R51</td>
<td>$Si_2H_6 + SiH_2 \rightarrow Si_3H_8$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R52</td>
<td>$Si_3H_6 + SiH_3 \rightarrow SiH_4 + Si_2H_5$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R54</td>
<td>$Si_3H_6 + SiH_2 \rightarrow Si_4H_{10}$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R55</td>
<td>$Si_4H_{10} + SiH_2 \rightarrow Si_5H_{12}$</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
</tbody>
</table>
### Table 4 (cont.)

<table>
<thead>
<tr>
<th># in Model</th>
<th>Reaction</th>
<th>Energy* [eV]</th>
<th>Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R56</td>
<td>( \text{Si}<em>2\text{H}</em>{12} + \text{SiH}_2 \rightarrow \text{Si}<em>6\text{H}</em>{14} )</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R57</td>
<td>( \text{Si}<em>6\text{H}</em>{14} + \text{SiH}_2 \rightarrow \text{Si}<em>7\text{H}</em>{16} )</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>R58</td>
<td>( \text{Si}_2\text{H}_5 + \text{Si}_2\text{H}_5 \rightarrow \text{Si}_3\text{H}_8 + \text{SiH}_2 )</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>( -n\text{SiH}<em>{4-n} + H \rightarrow -n\text{SiH}</em>{3-n} + \text{H}_2 ) (s,γ) = (0, 1)</td>
<td>Surface</td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>( \text{SiH}_2 + = \text{SiH}_2 \rightarrow \text{SiH}_4 + = \text{Si} ) (s,γ) = (0.8, 0.15)</td>
<td></td>
<td></td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>( \text{Si}<em>n\text{H}</em>{2n+1} + \text{Surf} \rightarrow \text{Loss} ) (s,γ) = (0.3, 0)</td>
<td></td>
<td></td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>(ion)(^+) + \text{Surf} \rightarrow \text{Loss} ) (s,γ) = (1, 0)</td>
<td></td>
<td></td>
<td>[6][25]</td>
</tr>
</tbody>
</table>

*Energy denotes energy loss from electron population, calculated based on either energy levels or appearance potential.
5: The Experimental Apparatus

5.1 – Chamber and Discharge Geometry

The main chamber consists of a 16.5" outer diameter × 16" tall cylinder with a mounted retractable bellows on the base. With height control via translation of the bellows, a sample tray may be loaded on the heated pedestal and raised to the surface wave plasma source for deposition.

Figure 13: Diagram of the MSWP chamber with retractable bellows and electrical feedthrough on the base for substrate translation and heating. The main chamber turbo pump and load lock are to the left (not pictured). The surface wave plasma source is situated on the top of the chamber. The MSWP source is depicted in Figure 14.

5.2 – The Surface Wave Plasma Source

In a typical unmagnetized plasma, the limit on power input, and subsequently plasma density, follows the following equation:

\[ n_{\text{crit}} = \frac{m_e e^2}{e^2 \omega^2} \]
where $m_e$ is electron mass, $\varepsilon$ is the permittivity, $e$ is the elementary charge, and $\omega$ is the frequency. This originates from the wave dispersion relation:

\begin{equation}
\omega^2 = \omega_p^2 + c^2 k^2 = \frac{n_e e^2}{m_e \varepsilon} + c^2 k^2
\end{equation}

where $\omega_p$ is the plasma frequency, and $\bar{k}$ is the wavevector. When $k = 0$, “cutoff” occurs, and no waves propagate through. Thus, in a normal situation, the maximum density is frequency-limited and any further power input results in electron oscillations that reflect the EM wave. However, evanescent waves for complex propagation (i.e. $Im\{\bar{k}\} \neq 0$) are an essential component of the source design. A full derivation of the wave dispersion of eq. (82) is given in Shah\[4\], while Thorne takes the derivation further, applying a “two-fluid” formalism.\[3\]

![Diagram of surface wave antenna, optimized for 900 MHz. A qualitative representation of the plasma discharge is illustrated as a purple glow. The antenna is roughly 15 cm in diameter.](image)

**Figure 14:** Diagram of surface wave antenna, optimized for 900 MHz. A qualitative representation of the plasma discharge is illustrated as a purple glow. The antenna is roughly 15 cm in diameter.

In a surface wave source, the presence of the dielectric back plate ($Al_2O_3$ – alumina) produces surface plasmon oscillations, or “surface waves” across the interface. This also
occurs in the antenna-plasma interface, allowing a discharge to be produced beyond the critical density limit. The expression for the EM wave for imaginary $k$ becomes:

\[ E = E_0 e^{-\alpha k L} e^{-i\omega t} \]

(83)

This result denotes an oscillatory form parallel to propagation (the interface in question) and an exponential, “evanescent” wave in the direction normal to the surface.\[^{39}\] This evanescent standing wave is an essential mechanism to the design of the surface wave source.

As a microwave, “over-dense” plasma, the skin depth of the incoming EM waves is narrow, proportional to $\delta = 1/\alpha$, and the intensity of the field decays quasi-exponentially as a function of distance from the antenna.\[^{38}\], producing a Chapman-like plasma profile. The wave reflects continuously between the plasma and the antenna surface, dissipating energy in a thin region proportional to the skin depth. Because of this and the high frequency, a key characteristic of the plasma source is the localized deposition of power near the antenna surface. Thus, the transport of silane radicals to the substrate is governed primarily by diffusion, masking any nonuniformities inherent from the antenna design. To summarize, the advantage of this source is four-fold:

- an “over-dense” plasma is formed ($10^{11-12}$ cm$^{-3}$), allowing high deposition rates,
- electron temperature and sheath potential are low ($T_e \sim 1 - 3$ eV), minimizing ion damage,
- source coupling is independent of chamber geometry due to its high frequency, and
- the plasma is generally uniform for sufficiently high pressure due to profile “smoothing” via diffusion.
Figure 15: Schematic of two-leg microwave power system for the MSWP experiment. Despite the choice of 900 MHz, the setup is able to use Type N connectors and RF coaxial cable without appreciable transmission losses.

The excitation source for the surface wave antenna consists of a NovaSource™ function generator and two Stealth™ 800-1000 MHz amplifiers with maximum combined power of ~200 W. Upstream of the amplifiers, two digital attenuators control the input signal in order to produce a symmetric output from both amps. The system follows the typical circulator, directional coupler, and combiner arrangement using 50Ω coaxial cable and Type N connectors. The waveguide combiner is vigorously cooled, as the combination of asymmetric or out-of-phase amplifier outputs can be devastating to the component. A stub tuner matching network is pre-set for matched conditions with-plasma, and the discharge may be initiated via in-chamber DC electrodes. The ability to strike plasma quickly eliminates any variability in process conditions, in contrast to a manual match via adjustment of the stub tuner.
5.4 – Gas Delivery

Gas delivery into the system is achieved via “showerhead” gas manifold with porous outlets to maintain laminar flow into vacuum. Initial tests using a flexible tube with small outlet holes revealed localized deposition correlated to hole placement, prompting the shift to the radially-uniform and flow-throttling design shown in Figure 16.

![Gas ring manifold and flexible source tube](image)

Figure 16: Gas ring manifold and flexible source tube pictured. The inner circle of the manifold surrounds the plasma source, encapsulating a discharge region of ≈ 15 cm diameter.

Mass flow controllers (MFCs) of the following models input the corresponding gases: UNIT 1661e for SiH₄ (50 sccm max), O₂ (2000 sccm max), and a shared H₂/SF₆ line (2000 sccm max); Horiba SEC-7330 for Ar (500 sccm max). These were controlled via NI 6008-USB data acquisition (DAQ) devices interfacing with LabVIEW 11.0. For measuring pressure, both a Pfeiffer Compact FullRange Gauge (PKR 251, 10⁻⁹-10³ Torr) and Compact Capacitance Gauge (CMR 264, 10⁻³-10⁰ Torr) provide readout through the LabVIEW
interface. An Edwards iL600n dry pump and Pfeiffer 520 L/s TMU 521 P (main chamber) and 230 L/s TPH 240 (load lock) turbomolecular pumps maintain system vacuum.

Figure 17: Pressure and instrument diagram (PID) for the MSWP system. A major emphasis in the construction of the flow system was the isolation of the silane line, as well as the ability to purge upstream of the SiH₄ regulator via Ar. Not pictured is a silane burner with compressed air input for controlled reaction of the exhaust gas. Both of these aspects were necessary for safe experimental use of silane.

Due to numerous hazards associated with silane[37], the need for proper purging and tubing isolation is mandatory to minimize the risk of an accident. The SiH₄ cylinder was encased in a reinforced gas cabinet for tamper resistance and fire/explosion protection. All valves are controlled pneumatically to eliminate the need to access the cylinder under routine working conditions. The cylinder itself comes stocked with a restrictive flow orifice (RFO) of 0.01" to restrict flow in the event of a leak. Finally, an upstream Ar cylinder with high pressure
pneumatic valve is capable of purging the regulator and flow line of residual contaminants before silane exposure.

5.5 – Temperature Control

Substrate heating is achieved by a thermally and electrically isolated pedestal that serves as the sample chuck. A 240VAC Variac transformer supplies power to internal heating wires ($\approx 35$ $\Omega$), allowing a temperature range of 20-500°C. While the pedestal is stainless steel with low thermal diffusivity ($\alpha \approx 10^{-5}$-$10^{-6}$ $m^2/s$), the sample tray is aluminum ($\alpha = 8.4 \cdot 10^{-4} m^2/s$), allowing for a uniform temperature profile. On top of this, an operating pressure range of 25-500 mTorr keep convective losses low, so the introduction of process gases doesn’t perturb substrate conditions. The primary mechanism for heat loss, then, is downward through the pedestal shaft, roughly maintaining radial temperature uniformity.

Figure 18: Illustration of heated pedestal (dark gray) with aluminum sample tray (light gray) and glass coupon (light blue). The pedestal is 19 cm in diameter, and the substrate coupons used are 50 x 75 mm Corning borosilicate glass provided by Ted Pella, Inc. Depositions were also conducted on soda-lime glass. A thermocouple (left) is spot-welded to the pedestal surface.
Due to poor thermal contact between the sample tray and the pedestal, the heating time of the sample tray after placement on the pedestal was unknown. It was determined that a pre-heat was necessary to obtain repeatable deposition conditions.

Figure 19: Depiction of contact between the sample tray and the pedestal. The center recession of the pedestal severely limits contact area, reducing it by more than a factor of 2. In reality, the contour of the sample tray doesn’t mate with the pedestal, so even perfect contact in the blue area cannot be assumed.

This pre-heat stage involved flowing high pressure hydrogen into the chamber to facilitate a convective/conductive heat flux in the gap. To quantify the required time, a thermocouple was secured to a glass coupon on the sample tray. Upon placement on the pedestal, the second thermocouple could track the surface temperature as a function of time.
Figure 20: Temperature of pedestal and sample tray after placement at $t = 0$ (chamber base pressure $e^{-8}$ Torr).

Figure 21: Temperature of pedestal and sample tray upon placement at $t = 0$ (13.5 mTorr $H_2$).

The discrepancy between sample temperature and pedestal temperature seen in Figure 20—Figure 21 originates from the poor contact between the thermocouple and the glass. While heat slowly diffuses through glass, heat loss through the length of the conductive thermocouple wire will produce a different steady-state temperature, although the
general form of the curve remains the same. All tests exhibit the characteristic form of Newton’s cooling law:

\[ \Delta T(t) = \Delta T(t = 0) \cdot e^{-t/\tau} \]  

(84)

The thermal time constant \( \tau \) was determined via least-squares fit of the above equation to the glass coupon temperature. The resultant value of \( \tau \) is plotted in Figure 22.

![Thermal Time \( \tau \) vs. Pressure](image.png)

Figure 22: Thermal time constant \( \tau \) vs. chamber pressure of \( H_2 \).

A pre-heat with short thermal time was functionally desirable to reduce preparation time per experiment. The thermal time constant does not decrease significantly with pressure beyond 3 Torr, so maintaining a pressure <5 Torr was ideal as to not disturb the temperature of the pedestal itself. The pre-heat routine decided on was a 7 minute interval of 3 Torr \( H_2 \). 7 minutes, or approximately \( 3\tau \), would be sufficient in reducing \( \Delta T \) to <5% of its initial value, ensuring good repeatability of substrate temperature.
5.6 – Deposition Process

In preparation of depositing H:Si films via $H_2 + SiH_2$ discharge, the $50 \times 75$ mm glass coupon is cleaned via acetone and isopropyl alcohol (IPA) and secured on the aluminum sample tray via metal clips. The tray is screwed onto a magnetically-actuated transfer arm in the chamber load lock. The load lock is pumped down, first with the Edwards iL600n dry pump, and then with the Pfeiffer TPH 240 (240 L/s) turbo pump. Once a sufficient vacuum pressure is reached, the transfer gate is opened. The sample tray can be inserted and placed on the heated pedestal, and then 3 Torr $H_2$ flow is introduced in the pre-heat stage for thermal equilibrium. Any remaining contaminants on the sample tray can be are baked off as it reaches the desired substrate temperature (most commonly $\sim 300^\circ C$).

After the $\sim 10$ minute pre-heat, the pedestal is raised into close proximity to the antenna. The gas pressures are set via MFCs in the LabVIEW software, first the $SiH_4$ and then the $H_2$ to meet the desired total pressure.

To start the discharge, the function generator feeding the amplifiers is triggered. With the stub tuner matching network preset at the matched-with-plasma condition, two DC electrodes strike a secondary plasma to temporarily provide a source of electrons across the discharge gap. The DC-initiated breakdown eliminates any variability in deposition time that may occur with manual matching of the stub tuner. Once the deposition is complete
(run time 5-20 mins.), the source is triggered off, the stage is lowered, and the sample tray is removed via the load lock transfer arm.

![Sample tray and masked glass coupons with deposited H:Si film. The radial pattern of the plasma diffusion and gas ring geometry is evident. Color represents interference fringes, indicative of a thickness gradient.](image)

Following the deposition, a plasma etch of the system is needed for a clean environment for the next run. This discharge consists of 120 mTorr Ar + 50 mTorr SF₆. Due to the high electronegativity of SF₆, the plasma is first initiated with Ar only, and then SF₆ is introduced. The fluorine radicals etch deposited silicon from the antenna and surrounding gas ring. The etching is complete after the plasma shifts from a cyan color to the characteristic pale purple of argon. SF₆ is replaced with O₂ to remove any residual sulfides. Finally, a pure Ar discharge works to remove any adsorbed oxygen that would threaten the purity of the next film made. Films are typically made back-to-back for the purpose of analyzing them in batches via material diagnostic techniques.
5.7 – Routine Film Analysis

5.7.1 – Profilometry Measurement for Thickness

Measurement of film thickness was routine and straightforward via the Dektak 3030 profilometer. This setup consisted of a scanning stylus attached to a linear variable differential transformer (LVDT), an encoder-like device that can precisely measure height changes down to ~50 nm. Variations in height over the 1 cm scan length could be saved to file and analyzed in batch via Matlab program.

Figure 24: Profilometry analysis of a double- (bottom-left) and single-edged mask (others). Upward-curving (top-left) and downward-curving (top-right) substrates, pitting/roughness/particles (bottom-left), and the double-sided mask (bottom-right) offered as a solution to these issues.
Error in thickness measurements was generally associated with sample roughness and substrate/device curvature. As seen in Figure 24, a slight curvature over the relatively large 1 cm scan length can become a significant obstacle in determining film thickness, sweeping away the film step height in the variation. The solution to this issue was overcome by using a double-sided mask for left- and right-edge baseline determination. Through this technique, a quadratic baseline can account for the curvature introduced by the glass substrate and the Dektak device itself, giving accurate thickness measurements for each radial measurement of the deposited film.

5.7.2 – Raman Spectroscopic Analysis of Crystallinity

Raman microscopy is a technique that involves exposing a material with low-intensity laser and measuring the Stokes shift – a slight shift in energy due to collisions with atoms, causing lattice oscillations, also known as “phonons.” The magnitude of the shift corresponds to the energy of the phonon, which are consistently in the infrared range. Thus, a nondestructive pulse of coherent light can divulge information about the atomic structure of the material in question.

Single-crystal silicon exhibits an optical phonon mode that results in a distinct Lorentzian peak at 521 cm\(^{-1}\) (\(\Gamma = 3\) cm\(^{-1}\) linewidth)\(^{[43]}\) in the Raman spectrum. A shift in this peak to higher or lower values can be attributed to film stress or grain size, although the interpretation of the shift is still somewhat disputed.\(^{[42][43]}\) Generally, a smaller crystallite diameter exhibits a broader, red-shifted Raman peak. The limit to amorphous phase is
taken to be when crystallite groups are no larger than $d = 3a_o$, where $a_o = 0.543\ \text{Å}$, the silicon lattice parameter. In the amorphous limit, the spectrum appears as merely a broad Gaussian centered on $\approx 480\ \text{cm}^{-1}$. For the polycrystalline films studied in this work, the spectra observed represent a distribution of crystallite diameters between single-crystal ($d \to \infty$) and amorphous phase ($d < 3a_o$).

In SiH$_4$ + H$_2$ plasma chemistry, the crystallinity of films tends to decrease for increasing silane concentration (SC). Typically, a distinct threshold between amorphous and nanocrystalline growth is observed at some low SC value, typically 1-6\%, depending on the system and plasma source. Part of the focus of this work is to determine the process knobs that grant the ability to deposit nc-Si to higher SC, allowing higher deposition rates of the crystalline phase. This trend is captured in Figure 26.

![Figure 25: Theoretically-calculated Raman peaks for varying crystal diameter, quoted as a multiple of atomic spacing $a_o = 0.543\ \text{nm}$, by Gaïsler et al.\cite{42}](image)

In SiH$_4$ + H$_2$ plasma chemistry, the crystallinity of films tends to decrease for increasing silane concentration (SC). Typically, a distinct threshold between amorphous and nanocrystalline growth is observed at some low SC value, typically 1-6\%, depending on the system and plasma source. Part of the focus of this work is to determine the process knobs that grant the ability to deposit nc-Si to higher SC, allowing higher deposition rates of the crystalline phase. This trend is captured in Figure 26.
Figure 26: Raman spectra for various silane concentration/flowrate (100 mTorr, 160 W, 300°C substrate temperature). Baseline intensity is artificially shifted higher for decreasing flowrate to illustrate spectral distinction.

The analysis of the Raman spectra obtained via the Nanophoton RAMAN-11 Microscope followed a three-peak fitting of Gaussians centered around 480 cm\(^{-1}\), 521±5 cm\(^{-1}\), and 500±5 cm\(^{-1}\), corresponding to amorphous, crystalline, and nanocrystalline contributions. The calculation of the crystal fraction follows from the ratio of integrated peak areas\([42,44,45]\):

\[
f_c = \frac{I_{521} + I_{500}}{I_{521} + I_{500} + cI_{480}}
\]

where \(I\) is the area of each respective peak, and \(c\) is a weighting factor to compensate for improved absorption of the amorphous phase (\(c \approx 0.7 - 0.9\)[45]; 0.8 was used in this work). This method produced a significant reduction in residual compared to the two-peak fit and a more accurate representation of crystallinity, as seen in Figure 27, since the distribution of
crystal sizes could be taken into account. Similar to profilometric analysis, Matlab batch processing was used to determine crystallinity of the films via the three-peak fit.

Figure 27: Two-peak (left) and three-peak (right) Gaussian fit of a nanocrystalline Raman spectrum. The two-peak fit exhibited noticeable residual, simultaneously overestimating the amorphous contribution by encompassing the crystal contribution in the 495-510 cm\(^{-1}\) range. The three-peak fit exhibited an order of magnitude less in residual, broadening the range of crystallinities obtained from a 40% cap in the two-peak fit up to 80% in the three-peak.

5.8 – Comparison with RF Capacitively Coupled Plasma

Maintaining a similar geometry but using an isolated stainless steel plate on the heated pedestal as the live electrode, a 13.56 MHz discharge was set up to compare MSWP-grown films with those made by RF CCP discharge. The antenna and top flange of the chamber were used as the ground electrode.
Figure 28: RF CCP configuration of the heated pedestal setup. The live electrode the sample tray sits on is isolated from the electrically-floating pedestal with ceramic tube legs. The sample tray is left for a very long time (>3 hours) to verify that it is in thermal equilibrium with the pedestal.

5.9 – Doping Technique and Calibration

For manufacturing a p-i-n junction, it was necessary to have a doping method in-situ with the deposition process. Breach of chamber vacuum before the deposition of the top electrode would form an inhibiting oxide layer on the film surface. While ion implantation ex-situ may work if the oxide layer on the film is removed before the top conductor is placed, the uniformity of the dopant into the film would be poor; also, the induced film damage due to ion bombardment would skew the performance of the finished device.

Due to cost and the addition of hazardous gases other than silane, process gases such as diborane (H₆B₂, flammable) and phosphine (PH₃, pyrophoric and highly toxic), an evaporative doping method was pursued instead. Boronization of carbon via evaporation of o-carborane (B₁₀C₂H₁₂), a boron-based fullerene, had been previously investigated at the
CPMI for treating plasma-facing surfaces in fusion devices, so this method was tested in a PECVD situation.

A stainless steel tube was filled with o-carborane and heated to a temperature range of 80-250°C (Figure 29). The entire length of the tube was heated to prevent downstream recrystallization on the tube walls. With o-carborane’s 1 atm melting point at 297°C, only a small vapor pressure in vacuum was desired to achieve the fine doping concentration desired ($\approx 1$ boron per $10^4$ atoms).

![Figure 29: Stainless steel tube filled with o-carborane crystal, separated by the main chamber by a ball valve. Heat tape is wrapped around the length of the tube to prevent condensation downstream. A thermocouple for temperature monitoring is spot-welded to the left end.](image)

Once the evaporator was loaded and at-temperature, the valve was opened and deposition began. As carborane diffused into the discharge gap, it dissociated when exposed to the plasma. To prevent condensation of un-dissociated molecules in the film, the substrate was kept at 305°C, slightly above $T_{melt}$. A key advantage of this technique, as opposed to implantation of energetic ions, is that the films can be doped in distinct layers,
such as p-type, intrinsic, n-type for a junction. Also, ignoring any diffusion of the dopant post-deposition, the doping concentration is expected to be very uniform.

Figure 30: Schematic of a four point probe. The two outer probe tips drive a current, and the inner tips measure the voltage produced.

Measurement of the doping concentration was done via four point probe (4pp) to calculate bulk resistivity. The measured $V/I$ of the 4pp can determine the sheet resistance of the film by the following relation:

$$\rho \left[ \frac{\Omega}{\text{sq}} \right] = \frac{\pi \cdot V}{\ln(2) \cdot I}$$

(86)

The above equation is valid for a film area much larger than the probe size. To find bulk resistivity for film thickness $t \ll s$, all that is needed is to multiply by film thickness:

$$\rho_{o}[\Omega \cdot \text{cm}] \approx 4.53 \cdot \frac{V}{I} \cdot t$$

(87)

Bulk resistivity has been known to scale inversely with doping concentration, the values of which can be determined via Hall effect measurements.
Figure 31: Doping concentration vs. bulk resistivity for p- and n-type silicon.\textsuperscript{[1]} Boron is a p-type dopant, since its 3-electron valence among silicon makes it possible to accept an electron.

![Graph showing doping concentration vs. bulk resistivity](image)

A clear trend is observed in doping concentration. It is important to note that the plot in Figure 31 is for single-crystal Si. For a-Si and nc-Si, the resistivity will be higher due...
to other defects such as grain boundaries. Thus, the actual doping concentration is expected to be higher than what is seen in Figure 32.

The increasing trend in acceptor population demonstrates that the amount of dopant introduced into the plasma increases exponentially with temperature. Although somewhat variable due to the unstable nature of the carborane sublimation, at least an order of magnitude confidence is guaranteed.
6: Results and Discussion

6.1 – Particle Mitigation

In preliminary deposition tests over wide pressure ranges, dust would occasionally accumulate in the center of the deposition pattern. The “film” in this 1-2 cm radius was poorly adhered, and thicknesses sometimes measured an order of magnitude larger than the surrounding area.

![Figure 33: Dust collection at the center of the deposition pattern. The material could be easily removed by a gloved finger. The area of this spot increased with lower substrate temperature.](image)

It was initially suspected that a high silane percentage was the culprit. However, reducing silane percentage did little to mitigate dust in the film. While the entire film was dusty and poorly-adhered for substrates at ambient temperature, it is evident that the primary cause of dust at $T_{\text{substrate}} = 285^\circ C$ was a high total pressure. This agrees with Perrin’s $\text{Si}_n\text{H}_{2n+1}$ accumulation rate coefficients which increase with pressure.\textsuperscript{[25]}
Figure 34: SEM images of dust nanoparticles in the center of the deposition pattern (left and center) and on the edge (right). Deposition conditions were 500 mTorr, 100W, 285°C, 1.4% SiH₄, 1” discharge gap.

As seen in the first and second photos of Figure 34, the dust consisted of generally uniform (50-100 nm) nanoparticles of hydrogenated silicon. The Raman spectra of the dusty regions produced crystallinities between 20-30%, independent of the composition of the surrounding film. Even in the “glass-like” film 4 cm away from the dust spot, the dust seemed to find its way into the developing film, resulting in significant surface roughness and voids (right photo).

With a 1” discharge gap, the necessary length for radicals to diffuse was far larger than the mean free path, resulting in accumulation of silanes SiₙH₂n₊₂. Due to the recipe-independent crystallinity and the accumulation in the flow stagnation point of the gas ring center, it may be concluded that these particles were formed in the gas phase and only deposited once reaching a certain mass. Maintaining operating pressure below 150 mTorr completely eliminated dust formation for a heated substrate.

6.2 – Optimization of the Parameter Space

6.2.1 – SiH₄ Concentration
Once a suitable operating pressure was chosen, the crucial parameter of interest was silane flowrate. An analogous measure of this is silane percentage $\frac{[\text{SiH}_4]}{([\text{SiH}_4] + [\text{H}_2])} \times 100\%$, or silane dilution $\frac{([\text{SiH}_4] + [\text{H}_2])}{[\text{SiH}_4]}$. A concentration-based representation of silane content, rather than absolute flowrate, gives a more system-independent comparison between experimental trends in literature.

![Raman Spectra for 100 mTorr, 285°C](image)

Figure 35: Side-by-side comparison between Raman spectra trends in this work (left, also shown in Figure 26) and Houben. The 94.7 MHz source may be attributed to the observed higher crystalline transition ($S\kappa \approx 6\%$) on the right, vs. roughly 2% the left figure.

As seen in Figure 35, the Raman spectra of deposited films trend very similarly to what is seen in literature, with very small SiH$_4$ percentage producing a prominent peak at 521 cm$^{-1}$, representative of the volumetric crystalline fraction. While Houben’s work shows the emergence of a crystalline peak below 5.9%, this can be attributed to their high power density.
Figure 36: Deposition rate and crystallinity vs. silane flowrate.

Plotting deposition rate against crystallinity, Figure 36 demonstrates a distinct transition from c-Si to a-Si occurring around 18-20 sccm SiH$_4$, (2.5% silane concentration). The deposition rate is strongly linear, implying that silane utilization is very high in the plasma region, resulting in growth rates proportional to SiH$_4$ input. The c-Si→a-Si transition at low silane concentration imposes a limitation on growth for the crystalline phase, which will be the bottleneck of the manufacturing process. Despite this, deposition rates for nc-Si approach a very competitive 3 nm/s, far exceeding the industry standard of 0.5-1.0 nm/s for PV-grade crystalline films. Deposition of a-Si is even faster, reaching 9 nm/s.

The structural difference between nc-Si and a-Si is seen in Figure 37. It is encouraging to note that the control of silicon phase is easily achieved by an easily controlled parameter. Silane flowrate may be adjusted, and the change in deposited phase would develop on the order of seconds, assuming the appropriate pumping speed and volume of the process device.
Figure 37: SEM cross sectional images of nc-Si of 73±6% crystallinity (left) and a-Si with 21±3% crystallinity. With a focus for optimization, the subsequent tests were aimed to understand what parameters could move this “crystalline-transition” to the right, thus allowing the creation of c-Si at higher deposition rates.

6.2.2 – Substrate Temperature

The choice of substrate temperature is very influential on the manufacturing process. The ability to heat uniformly over a large area poses a challenge, especially depending on the narrowness of the margin $\Delta T$ for the determined process window. Also, this temperature will limit the choices of cost-effective polymer substrates to be used in roll-to-roll manufacturing. Thus, it is of interest to find the substrate temperature that optimizes crystallinity for c-Si recipe, presents a comfortable temperature margin to work in, and allows for the use of cheap substrate materials.
It is observed in Figure 38 that a maximum in crystallinity occurs at 285±20°C for 160W source power (or 1.0 W/cm²) source power. For 80W (0.5 W/cm²), this optimized temperature increases to 350 ±20°C. For lower temperature, deposited SiHₓ radicals do not have sufficient thermal mobility to arrange into a crystalline structure. As already discussed from Perrin[^57], the SiH₃ recombination process prevails over sticking at lower substrate temperatures; this diminishes film quality as SiH₂ becomes the uncompleted depositing species, growing very topically compared to SiH₃'s diffusion into the film. On top of this, Kessels[^56] has demonstrated the surface composition at low temperature (100°C) is composed of primarily =SiH₂ and –SiH₃ bonds, while only ≡SiH sites appear at high substrate temperature, denoting efficient hydrogen removal and increased crystalline ordering at higher substrate temperature.
The reduction in required substrate temperature with areal power density confirms that the two parameters are complementary in the crystallization process of the growing film. As illustrated in Figure 40 below, a combination of both allows access to zone “T” and beyond, offering increased crystallite size and reduced void fraction.

Figure 39: Surface composition of deposited H:Si films as a function of substrate temperature: 100°C (a), 250°C (b), and 400°C (c), by Kessels et al.$^{[56]}$

Figure 40: Structure zone diagram for substrate temperature and incident energy, by Anders.$^{[67]}$ The diagonal transitions denote the complementary effects of temperature and source energy on crystallization in film growth.
The low substrate temperature compared to thermal CVD (600-900°C) is a characteristic of PECVD in general. This, coupled with the speed of deposition, is what makes PECVD highly advantageous over traditional CVD techniques.

6.2.3 – Total Pressure

With low total pressure having a noticeable influence on film quality, it was of interest to tune this parameter and observe its effects on the location of the crystalline transition.

![Film Attributes vs. Total Pressure – 25, 50, 100, 150 mTorr](image)

Figure 41: Raman crystallinity and growth rate vs. SiH₄ flowrate for varying total pressures.

From Figure 41, the crystalline fraction and deposition rate were generally unmoving in the 50-150 mTorr total pressure range. A local maximum is observed somewhere between 50-100 mTorr, as seen by the roughly quantitative plot in Figure 42 below. More data in this range would better-refine the locations of these transitions. The crystalline transition at 25 mTorr was unexpectedly low, compared to 50 mTorr and above. It is speculated that
monatomic hydrogen flux to the film surface was reduced disproportionately compared to \( \text{SiH}_x \) flux. This effect will be confirmed in section 6.3.

![Location of Crystalline Transition](image)

Figure 42: Rough quantitative representation of the crystalline transition as a function of total chamber pressure. Error bars denote the observed width of the observed transition.

6.2.4 – Source Power

Varying source power was necessary to predict the effects of shifting to 3.0 W/cm\(^2\) or higher with a conventional 2.45 GHz source. Since the amplifier configuration was limited to 160W (1.0 W/cm\(^2\)) and an abundance of data had been taken at this setting, the power was reduced instead. The effects of increasing power density could thus be inferred by comparing the 1.0 W/cm\(^2\) reference with 0.5 W/cm\(^2\). This will provide guidance in future work where source power will be on the order of kilowatts.
Figure 43: Crystallinity and growth rate at two source power settings – 80W (0.5 W/cm\(^2\)) and 160W (1.0 W/cm\(^2\)).

The result, as seen in Figure 43, demonstrates that the crystalline transition shifts from low SiH\(_4\) flowrate at low power to higher flowrate at higher power. This is in agreement with the conclusion made in section 6.2.2, the energy-temperature effect embodied in Anders’ zone diagram (Figure 40).

On top of this, interpretation of Figure 43 reveals another influencing factor in crystallinity. The linear trend of trend of deposition rate vs. SiH\(_4\) flowrate is constant across 0.5-1.0 W/cm\(^2\). This shows that the process gas utilization of the source is very high, where doubling silane flow doubles deposition rate, even at half power. Thus, doubled power density produces more H via dissociation instead. This surface treatment of monatomic hydrogen results in an abstraction reaction, removing the surface-passivating H-bonds that
are an artifact of deposited SiH$_x$ radicals. Increased hydrogen treatment will, ironically, decrease hydrogen content in the developing film, thus reducing disorder and resulting in a crystalline film. It may then be hypothesized that the crystallinity is dependent on the relative proportion of H to SiH$_x$ flux (with SiH$_2$ being the dominant species). The mechanism is illustrated in Figure 44 below. This has been confirmed recently by Hori$^{[68]}$ using time-dependent VUV absorption spectroscopy, and it can be quantified for the SWP source via the numerical model.

![Figure 44: Illustration of the simultaneous deposition of SiH$_x$ and surface treatment via H. Micro- and nanocrystalline silicon (left) is formed by adequate hydrogen flux relative to the deposition rate, removing hydrogen and allowing increased ordering for Si crystallites to form. Amorphous silicon (right) is deposited at high deposition rate and hydrogen abstraction fails to keep up, resulting in a disordered film.](image)

6.2.5 – Discharge Gap

The length between the antenna and substrate is a crucial parameter governing uniformity of deposition and plasma density at the substrate surface. It is also an aspect of a manufacturing device that is not easily changed, if variable at all.
Figure 45: Growth rate and crystallinity vs. discharge gap width for a nearly-crystalline recipe.

The resultant crystallinity and deposition rate from varying crystallinity in Figure 45 have a few implications. First, the crystallinity rapidly decreases for larger discharge gap. Second, the deposition rate increases for higher gap width. This second effect is the opposite of what is expected – with a larger distance for radicals to diffuse and deposit, it is counter-intuitive to assume larger deposition rates. The true explanation lies in the ability for gas to flow freely across the discharge gap. Since the showerhead gas ring for SiH₄/H₂ input extends ½” down from the antenna surface with gas outlets pointed down, the discharge gap becomes disproportionately restricted from new gas exiting the gas ring as the gap width decreases. The SiH₄ content is more likely to be depleted; at a lower effective silane concentration, the result is the increased crystallinity seen for 0.5”. This is an artifact of a flow system that isn’t optimized for the deposition geometry. The ideal setup would be to flow gas directly through the antenna itself; however, hollow cathode discharges can form
in small holes drilled into the antenna due to high frequency, and the overall machining cost would be prohibitive for a university-level research project.

Figure 46: Radial film thickness and crystallinity profiles for 2” (left) and 1” (right) discharge gap. With spatially-resolved data in Figure 46, it is seen that at 2” discharge gap, diffusion dominates and spherical symmetry presents itself in a center-peaked thickness profile. With 1” gap, the deposition profile is generally uniform across ±4 cm, falling off at the edge of the source, although the local minimum in the center of the deposition pattern is indicative of the plasma profile from the source. At ½”, nonuniformities in in both the crystallinity and thickness profile occurred as a result of gas flow and alignment issues.

Figure 47: Radial thickness and crystallinity profile for ½” discharge gap.
### 6.2.6 – Ternary Mixtures

The addition of a noble gas was of interest to promote overall film crystallization. The use of helium or argon metastables to deliver energy to the film surface was hypothesized to help expand the process window and access the c-Si phase at higher growth rates.

**Figure 48:** Adding argon at a slightly amorphous recipe (100 mTorr, 25 sccm/3.3% SiH$_4$, 160 W, 285°C, 1" gap).

**Figure 49:** Adding helium to a-Si recipe – 25 sccm SiH$_4$.
For a slightly amorphous recipe (100 mTorr 25 sccm/3.3% SiH₄, 285°C substrate, 1” gap, 160W) argon (Figure 48) and helium (Figure 49) were added in hopes to tip the film into a crystalline phase. The deposition rate increased slightly in each case, but the overall phase became increasingly amorphous. The same result occurred with the addition of argon to a c-Si recipe – 10 sccm SiH₄ – with crystallinity decreasing with argon content (Figure 50).

While unsuccessful, these tests revealed two possible explanations on the effects of noble gas addition. First, the replacement of hydrogen with another gas diminished the relative flux of H to the film surface, decreasing crystallinity. Second, the low dimensionality of argon and helium is such that it likely reduced available pathways for dissociation and excitation, increasing the electron temperature. It is conjectured that these mechanisms subsequently increased the sheath potential drop, giving ions slightly more energy to break Si bonds and induce film damage.
6.3 – Results of the Numerical Plasma Model

Three studies were conducted to represent the parameter space – silane concentration, power, and pressure ramping. The respective distances to the wall in all cases were taken to be $L_{antenna} = 1 \text{ mm}$ and $L_{substrate} = 25 \text{ mm}$, representing the localized plasma diffusing to each surface. Both the substrate and antenna were assumed to be at 300°C, coinciding with the surface loss probabilities discussed in section 4.7, and the gas temperature was taken to be 500°C for ion-neutral and neutral-neutral interactions.

6.3.1 – Stability and Convergence

The stability of the discharge at 180W was observed to be limited to 45 mTorr, under which generated electrons would be lost to the walls rather than sustaining the plasma due to the diminished mean free path. This is consistent with experimental results in that 25 mTorr discharges were very difficult to strike and sustain, requiring an initial increase to higher pressures to generate breakdown. The computation time in all cases was pressure-dependent, varying from 20 seconds at 25 mTorr, 15 minutes at 100 mTorr, and 90 minutes at 200 mTorr on a 4GB 1.90GHz AMD A4-3300M processor, following a roughly quadratic relation.

Equilibration time to steady-state solution varied depending on the species; for $H_2^+$, $H_3^+$, and electrons, the population leveled out in $<100 \mu s$ due to Bohm acceleration in the plasma sheath; monatomic hydrogen equilibrated at a similar speed due to its small mass and imposed recombination probability of $\gamma = 1$. However, SiH$_2$ required $\approx 0.5 \text{ ms}$, and
SiH$_3$ $\approx$ 1.0 ms due to large mass and wall loss probabilities less than unity. The threshold for steady-state conditions for all runs was taken to be 1 ms, although 200 mTorr total pressure required slightly longer times of 2 ms. An example of the time-dependent solution is shown in Figure 51.

![Graph showing population of significant species vs. time.](image)

Figure 51: Time-dependent solution of the center plasma composition via Matlab’s ode45(). Conditions used were 100 mTorr, 180W, and 1.4% SC.

Due to the negligible concentration of Si-containing ions, the deposition rate had a characteristic time patterning SiH$_2$/SiH$_3$, since these were the primary deposition species. As seen in Figure 52, the hydrogen deposition rate becomes negative not too long after $t = 0$, signifying that the H-abstraction reaction developed much faster than silane radical
deposition, following the development of the SiH\(_2\)/SiH\(_3\) population. At \(t > 1\, ms\), the deposition is fully-developed and steady state values can be taken.

Figure 52: Discrete deposition rates for the film grown at the substrate for 100 mTorr, 180W, 1.4% SiH\(_4\). These values are obtained by counting of absorbed atoms of the sticking Si\(_x\)H\(_y\) radicals and ions. Plotted in yellow is the gain of hydrogen in the film, while the hydrogen deposition rate is reduced by incident H flux abstracting hydrogen from the film (plotted in green).

Note that for 1.4% SiH\(_4\), Figure 52 displays a larger hydrogen flux than the hydrogen deposition rate due to Si\(_x\)H\(_y\)(+) radicals, which is approximately 2.5\(\times\) the Si deposition rate, representative of roughly equal SiH\(_2\) and SiH\(_3\) sticking on the substrate. If recombination probability of H incident on the film is taken to be 1, there would be no hydrogen in the film. This is due to the assumption that all incident hydrogen flux results in hydrogen removal from the film. For future work, a more accurate assessment of hydrogen content would take into account the hydrogen surface coverage by a Langmuir equation representation.

Given the flux rates for each species, the deposition rate can be obtained by dividing the Si rate \([m^{-2}\cdot s^{-1}]\) by the atomic number density of crystalline silicon: \(5.0\cdot10^{28}\, m^{-3}\). For
amorphous films, the deposition rate will be underestimated, as measurements of a-Si mass density in literature are typically 3-15% less than c-Si (2.33 g/cm$^3$).\textsuperscript{[69]}

6.3.2 – Silane Concentration Study

![Densities of Significant Species vs. Silane Concentration at 100mTorr, 180W](image)

Figure 53: Population of plasma species plotted against silane concentration for 100 mTorr, 180W.

Increasing silane concentration, as shown in Figure 53, steadily increased the plasma density and all SiH$_4$-derived species. The overall H$_3^+$ and H$_2^+$ populations decreased as well, due to SiH$_4$ having a lower ionization potential (13.2-13.9 eV) to H$_2$ (15.4 eV), as well as more power being channeled into SiH$_4$ neutral dissociation. For silyl ions (SiH$_2^+$, SiH$_3^+$, Si$_2$H$_4^+$, SiH$_3^-$), the dependence on silane concentration was essentially linear. SiH$_3^-$ was thankfully a small contributor to the plasma population, only reaching $\approx 0.02n_e$ at 5% SiH$_4$. 
making the electropositive plasma assumption valid. However, SiH$_2$ and SiH$_3$ dependence on SC was observed to be slightly less than linear, as power channeled into SiH$_4$ dissociation became a limiting factor. It is interesting to note that, despite the branching ratio of [SiH$_3$]/[SiH$_2$] = 0.3-0.4 shown back in Figure 10, the higher loss probability for SiH$_2$ compared to SiH$_3$ results in approximately equal concentrations of each radical.

![Figure 54: Electron temperature vs. silane concentration via the numerical model.](image)

The electron temperature $T_e$ is seen to decrease steadily with silane concentration, as seen in Figure 54. With the increase in plasma density and the channels for energy loss brought in by SiH$_4$ – dissociation, lower energy ionization – the electron temperature decreases accordingly.
Figure 55: Deposition rate calculated via the model (x) plotted against experimental data (□).

The predicted deposition rate in Figure 55 coincides with experimental data moderately well, having 10-25% variability. Regarding crystallinity, the ratio of Si atomic deposition rate:H surface flux is plotted against crystal fraction. While a stark distinction is not seen in the model results, the general trend is shown that the deposition rate outweighs monatomic hydrogen surface treatment for higher silane concentration, resulting in amorphous silicon.

Figure 56: Atomic ratio of hydrogen of the deposited film (x) plotted against experimental crystal fraction (□).

6.3.3 – Power Study
As expected, the density of each species increases proportionally with the input power, aside from SiH$_3^-$, which seems to be suppressed by increased plasma density, as the only loss mechanism is recombination with positive ions. The calculated plasma density increases from $2 \cdot 10^{16}$ to $8 \cdot 10^{16}$ m$^{-3}$ from 50 to 200W. Also affirming basic plasma trends, the electron temperature is essentially invariant with input power at low power density, as seen in Figure 58.
However, one interesting divergence from observed data is the deposition rate vs. power. In the experimental data of Figure 43, the deposition rate was generally unchanging whether the applied power was 80 or 160W. For the numerical simulation, Figure 59 shows the deposition rate increasing roughly linearly. It is suspected that this discrepancy shows that in the experimental case, full utilization of the silane is achieved in the narrow “hot” plasma region near the antenna, and convective flow assists in transporting radicals to the substrate. In contrast, the numerical model relies on diffusion alone in determination of wall flux \( I' \) for neutrals, thus scaling linearly with power.

Figure 58: Electron temperature for varying power input at 100 mTorr, 1.4% SiH4.

Figure 59: Numerical (x) and experimental (□) deposition rate vs. source power.
6.3.4 – Total Pressure Study

Varying total pressure was useful in understanding species transport to the walls, as well as thresholds for the stability of the discharge. As already mentioned in section 6.3.1, for total pressures <45 mTorr for 180W, the fractional power loss to the wall was 99.7%. This signified that the mean free path was too small to sustain the discharge.

![Densities of Significant Species vs. Pressure at 180W, 1.4% SiH₄](image)

Figure 60: System composition vs. pressure at 180W, 1.4% SiH₄.

The trend seen in Figure 60 reveals a decreasing plasma density while SiH₃⁻, reaching 10% of \( \approx 0.1n_e \) at 500 mTorr, on the verge of requiring an electronegative formulation. SiH₂ and SiH₃ find maximums around 100 mTorr before decreasing at higher pressures. \( H_2^+ \) rapidly falls away at higher pressures due to increased interaction with \( H_2 \), forming \( H_3^+ \). The low
values shown at 25 mTorr are the results of an unstable discharge, as the mean free path seems to be too large for the given power density. Wall losses, in this case, occupy more than 95% of the power consumption.

Figure 61: Ion populations normalized to the electron density in an H$_2$-only plasma discharge. Results are based on the 13-reaction H$_2$ discharge proposed by Mendez$^{[26]}$.

The increasing disparity between H$_3^+$ and H$_2^+$ in Figure 60 was originally a cause for concern, as the difference reaches two orders of magnitude. A 13 reaction, 6 species model based on those given in Mendez$^{[26]}$ was constructed for an H$_2$-only discharge using identical wall loss equations and geometry. The relative populations of H$^+$, H$_2^+$, and H$_3^+$ are seen in Figure 61. As expected, H$_2^+$ becomes prominent only at low pressure where the mean free path is low enough to prevent collision with H$_2$. At higher pressures, H$^+$ begins to emerge due to an overall increase in monatomic hydrogen concentration. At medium pressures (100 mTorr), neglecting H$^+$ is a valid assumption, particularly in the presence of SiH$_4$, when free H is reduced due to the abstraction reaction in Si-H bonds.
Figure 62: Numerical (x) and experimental (☐) deposition rate vs. total pressure.

The predicted and observed deposition rates shown in Figure 62 vary by as much as a factor of 2; this shows, in part, that the model overestimates the effects of diffusion by calculating significantly higher deposition rates at 50 mTorr. On the other hand, the exclusion of silane depletion in the discharge gap may be the source of the overestimate. However, the overall trend of a peak deposition rate for an optimal pressure is observed, balancing the tradeoff between low gas density for low pressure and low mean free path for high pressure, essentially a Paschen-like effect for neutral radicals.

The electron temperature similarly exhibits a decreasing trend with higher pressure, representative of the energy losses due to increased neutral density. The decrease from 3.0 eV at 50 mTorr to 2.0 eV at 200 mTorr is shown in Figure 63. The 25 mTorr case is not pictured, as the very low electron density with constant power resulted in an electron temperature of $\sim 10^5$ eV, clearly an inaccurate prediction. The correction to this problem with the model was elusive, and its origin is not understood.
Figure 63: Electron temperature vs. total pressure.

6.3.5 – Comparison of Plasma Parameters with Langmuir Probe Data

A comparison with Langmuir probe data for 100% H$_2$ was of interest in comparing predicted data. Using a tungsten wire with a 10 kΩ resistor ballast inserted into the plasma at 0.7 cm away from the antenna, the plasma current to the probe was determined at varied voltage. A sample probe trace is shown in Figure 64:

Figure 64: Langmuir probe trace for 100 mTorr, 160W, 100% H$_2$. Ion current is fitted with a parabola below -20V. Subtracting this current out leaves the electron current.
It is clear in Figure 64 that the resolution of the oscilloscope was not sufficient in providing precise data. Regardless, a parabola was fitted to the current below -20 V and subtracted from the total current to yield electron current only. So long as the applied probe voltage isn’t too large, the electron current is Maxwellian; a fit with \( \ln(I_e) \) will yield a straight line proportional to \( T_e^{-1} \):

![Graph](image)

Figure 65: Plot of \( \ln(I_e) \) with fitted line, slope \( \propto T_e \). Note that, above 28V, the electron current saturates, resulting in the “knee” in the curve.

With \( T_e \) known from the method illustrated in Figure 65, and using the approximation of a thin, collisionless sheath, the electron density could be determined:

\[
\begin{align*}
    n_e &= \frac{I_i^{sat}}{e u_{Bohm} A_{probe}} \\
    \text{where } I_i^{sat} &\text{ is the ion saturation current, found at very negative probe voltage. Because }
\end{align*}
\]

\[
u_{Bohm} = \sqrt{\frac{k_b T_e}{m_i}}
\]

required an ion mass, the measurement of a SiH\textsubscript{4} + H\textsubscript{2} discharge put an
ambiguity on the effective ion mass, since silyl ion concentration is shown to vary relative to H$_3^+$, as seen in Figure 53. On top of this, film deposition on the probe itself was problematic in introducing error, as the probe area increased over time and voltage drop through the film gave false estimates on probe voltage. This was the motivation for the measurements in 100% H$_2$. As seen in Table 5, the electron temperature in both measurement and simulation are within error bounds of each other, decreasing with an increase in pressure. However, the model severely underestimates $n_e$ by a factor of 2-4, predicting a decrease with pressure when measurements show the opposite. This is a shortcoming of the volume-averaging technique; with a majority of the plasma generated near the antenna, the “hot” plasma region is likely to be much more efficient in ionization due to a higher local $T_e$, hence the disparity between numerical and experimental values.

Error on Langmuir probe data incorporates the poor oscilloscope resolution, while the error in model-generated values accounts for the standard deviation across the plasma volume, assuming an exponentially-decaying plasma profile.

<table>
<thead>
<tr>
<th>Table 5: Comparison of Measured and Predicted Plasma Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}$-D Model</td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>100 mTorr H$_2$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>200 mTorr H$_2$</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

6.4 – Grain Size Calculation via Raman, TEM, and XRD
Studying micro/nanostructure of deposited films is essential to understand the carrier lifetime and mobility in silicon, an indirect band gap material, as grain boundaries can serve as a location for recombination in the form of phonons and scattering centers. The impact of temperature on grain size was studied via X-ray diffraction (XRD), Raman spectrum analysis, and transmission electron spectroscopy (TEM).

Figure 66: XRD intensity vs. 2θ for increasing substrate temperature (left), as well as calculated grain size via the Scherrer equation (right).

Figure 67: Calculated Raman crystallinity based on the shift in the 521 cm⁻¹ Stokes peak.
From XRD 2θ data in Figure 66, grain size can be determined from the broadening of each peak via the Scherrer equation:

\[
d = \frac{0.89\lambda}{\beta\cos\theta}
\]

where \(d\) is the crystallite diameter, \(\lambda\) is the X-ray wavelength, \(\theta\) is the angle the peak is found, \(\beta\) is the angle broadening of the peak. The average of each contributor ([111], [200], and [311] orientations) reaches approximately 10±2 nm from 285°C and up. Lower temperatures, significant XRD signal is not seen above the amorphous background.

Complementary to XRD data, Raman estimation of grain size via peak shift of the 521 cm\(^{-1}\) TO phonon appears to underestimate the crystallite size, following a similar trend as XRD but reaching a maximum of 6.6±0.6 nm at 350°C (Figure 67). TEM images are perhaps the most illuminating, with grain size ranging from 6 nm at 200°C up to 13 nm at 400°C. In Figure 68, the a-Si “filler” between grains for the 200°C case disappears at 350°C, but it returns at 400°C, consistent with the decrease in crystallinity seen at high temperatures in Figure 38.

![TEM images of H:Si made with a crystalline recipe (100 mTorr, 10 sccm/1.4% SiH\(_4\), 1” gap, 160W) at 200°C (left), 350°C (center), and 400°C (right).](image)

Figure 68: TEM images of H:Si made with a crystalline recipe (100 mTorr, 10 sccm/1.4% SiH\(_4\), 1” gap, 160W) at 200°C (left), 350°C (center), and 400°C (right).
Overall, the crystallite size was fairly consistent across these three diagnostics. These 5-15 nm grains are considered small, although hydrogen passivation may bypass adverse effects on efficiency by reducing defects and deformation potential observed at grain boundaries. Also, with these films being thin (<100 nm), it is expected that longer deposition would produce larger grains due to the upward fanning effect (see Figure 76).

6.5 – Electron Paramagnetic Resonance (EPR) Characterization of Defects

Since dangling bonds found at grain boundaries are the primary emphasis of study in this work, it was necessary to find a means of measuring them. EPR spectra of the films would provide a signal proportional to the number of unbound electrons.

The fundamental working principle is that all fermions (particles with half-integer spin: \( s = \frac{1}{2}, \frac{3}{2}, \ldots \)) carry an associated magnetic moment; electrons, as well as many nuclei, are fermions. In an external magnetic field, these particles have states which are either “up” or “down”, corresponding to a splitting of energy levels in a potential \( U = -\vec{S} \cdot \vec{B} \) known as the Zeeman effect. Complementary to nuclear magnetic resonance, which probes the spin coupling of atomic nuclei, ESR investigates the spins of electrons. When exposed to an excitation resonant to the material and exposed to a scanning magnetic field, electrons will change state at a certain magnetic field, radiating signal that can be collected by a detector. The intensity and location of these pulses gives information on the atomic and electronic properties of the material.\(^{[40]}\)
Since only the number of unbonded electrons is of interest in this study, the analysis of EPR data is very straightforward. Since the spins are generally uncoupled with any surrounding atoms (\(^{28}\text{Si}\) has spin \(s = 0\)), the peak center is located on the Landé \(g\)-factor of 2.0023. So long as the input power (in this case, 2 mW) does not induce saturation, the emitted signal is proportional to the number of spins in the sample. Free carriers (e-h pairs) in silicon contribute to the signal, as well. Luckily, the concentration of carriers in intrinsic silicon at 300K is \(\sim 10^{10}\) cm\(^{-3}\), far below the expected dangling bond density (\(10^{14-18}\) cm\(^{-3}\)).

Because many factors are dependent on the EPR device settings, a reference sample must be used to gauge a quantitative value to the spin count. 2,2-diphenyl-1-picrylhydrazyl (DPPH) is a very popular reference sample in the field:

![Diagram of the DPPH molecule](image)

Figure 69: Diagram of the DPPH (C\(_{18}\)H\(_{12}\)N\(_{5}\)O\(_{6}\)) molecule. Note the bridge nitrogen which carries the single unbonded electron.

DPPH is significant in that it contains one very weakly-bonded electron. This results in a peak center for \(g = 2.0036\), and EPR signals can be calibrated around this reference. With chemical formula C\(_{18}\)H\(_{12}\)N\(_{5}\)O\(_{6}\) and large molecular weight of 394.32 g/mol, the number of spins/signal [#/a.u.] can be calculated and used as a metric for the H:Si thin film spectra. In this work, three samples, each 180 mg of a mixture of SiO\(_2\):DPPH of 3100:1 mass ratio,
were used to calibrate for each session. The number of expected spins in each sample would be:

\[
N_{\text{spins}} = 0.180 \frac{g}{3100 g_{\text{Mixture}}} \cdot \frac{1}{394.32 \frac{g}{mol}} \cdot 6.022 \cdot 10^{23} \text{mol}^{-1} \approx 8.9 \cdot 10^{16} \text{ spins}
\]

A \approx 10\% variation in measured reference signal was seen, being attributed to the inhomogeneity of the mixture and slight inconsistency in EPR device settings.

Historically, the first derivative of the signal is plotted for data analysis reasons, as it is easier to subtract out a constant baseline via voltage offset rather than remove a linear baseline in the signal itself. Note in the case of Figure 70, a nonzero baseline will produce
an overestimate of the spin count in the sample. While this spectrum of the DPPH reference was obtained in 3 scans and 320× gain, the H:Si thin films needed at least 10 scan averaging and 10^5× gain due to the extremely small signal and linewidth.

![ESR Spin Density v. SiH₄ Concentration](image)

Figure 71: Log-scale plot of defect density against silane concentration.

Plotting defect density vs. silane concentration reveals a decreasing trend in the MSWP films. It may be implied, as asserted by Johnson et al.[36], that hydrogen content manifesting at Si grain boundaries passivates the interface, removing dangling electrons from the film. The fact that the RF films preserve a high defect density despite moderate SiH₄ concentration (4%) can be attributed to the ion energy damage dissociating Si-H bonds throughout the film, causing hydrogen to diffuse out. This process can take place by both SiH₂⁺, SiH₃⁺, Hₙ⁺ (n = 1, 2, 3) impact or the formation of H₂ by hydrogen abstraction:

\[(91) \quad H + H:Surface \rightarrow H₂ + Surface\]
In contrast to the RF case, the MSWP source has an added benefit in that the glass coupon is dielectric and the antenna field is localized, limiting the ion energy $f$ to $e \cdot (V_p - V_f) \approx 3 T_p$, where $V_p$ is the plasma potential, and $V_f$ is the potential of a floating substrate.

**ESR Spin Density v. Raman Crystallinity**

![ESR Spin Density vs Raman Crystallinity Graph](image)

*Figure 72: Crystallinity dependence of defect density in the RF and MSWP H:Si films.*

An upward trend in defect density with crystallinity is seen for the MSWP film. This ties into Figure 71 in that silane concentration and resultant crystallinity are inversely proportional. For larger H flux to the surface relative to SiH$_2^{(+)}$ and SiH$_3^{(+)}$, the H abstraction reaction has more of an effect, removing the hydrogen that becomes implanted in the film carried by silyl (SiH$_3$) and silylene (SiH$_2$) radicals. In the diffusion-driven deposition process of the MSWP source, it can be argued that higher hydrogen content means passivating dangling bonds at the cost of inducing higher disorder (more amorphous).
Figures 73 and 74: Films grown with 100 mTorr total pressure, 30 sccm (4.0%) SiH\textsubscript{4}, 180W power, via MSWP source (left) and RF-CCP (right).

The full width half-maximum (FWHM) of the signal for MSWP films was 2.74±0.21G, while the RF-CCP films had FHWMs of $\Delta B = 3.38 \pm 0.28G$. Comparing this to the observed FWHM of the DPPH samples – $\Delta B = 5.49 \pm 0.26G$ – it may be concluded that the coupling of electron spins to neighboring defects in MSWP-made films is small.\textsuperscript{[40]}

Figure 75: Defect density plotted against film thickness.
A final concern is one of defect density varying with film thickness, as nc-Si films were thinner than a-Si films due to slower deposition rate, with the RF films as an exception. Figure 75 does, in fact, seem to insist this dependency. The physical mechanisms that could cause this are interfacial defects between the substrate and film, as well as the 50 nm “incubation” stage at the onset of deposition, as seen in Figure 76. This results in very small grains fanning upward in the direction of deposition; for thinner films, the ESR signal of a thin film would inevitably represent a higher density of grain boundaries. Thus, a thicker film would demonstrate a lower defect density due to its ability to balance out the average with the larger grains from growth beyond incubation. However, this was not the case, as thinner films (~0.3 μm) consistently produced larger signal than their thicker (~2.2 μm) counterparts. This eliminates any suspicion of thickness dependence on the defect density.

Figure 76: Fanning grain effect of thin film growth for a 76±11% crystalline H:Si film (160W, 1.4% SiH₄, 285°C substrate temperature). Note the incubation stage of early deposition near the substrate.
ESR analysis, in summary, demonstrated an increasing trend of defect density with crystallinity, corresponding to unpassivated grain boundaries at the cost of a more ordered film. Encouragingly, the MSWP source produced films with defects much fewer than those grown by RF-CCP due to drastically reduced ion damage. Finally, the idea of thickness dependence for observed spin densities was ruled out.

6.6 – Manufacturing a PV Device

As this work is a process optimization for depositing solar-grade silicon, a pivotal step was to manufacture a functioning solar cell. It was first necessary to demonstrate the ability to deposit distinct layers of a-Si and nc-Si in a heterojunction style. 1.0 μm of a-Si was deposited on a p-Si wafer substrate, and then 1.1 μm of nc-Si was deposited. The cross-section of this tandem film is seen in Figure 77.

Figure 77: SEM images of the cross section of a tandem a-Si/nc-Si film on p-type Si wafer. The film was prepared in 2% HF solution for 1 hour before the cleave.

With the deposition and doping processes refined, it was possible to grow heterojunctions of appropriate dimensions on n-type wafer substrate. An in-chamber
magnetron sputtering device allowed deposition of indium tin oxide (ITO) for use as a transparent top conductor, albeit not at ideal recipes for transparency and conductivity.

Various cells were deposited and tested for performance, and successful devices were of the following construction:

![Cross section of manufactured PV cell.](image)

Figure 78: Cross section of manufactured PV cell.

In a comparison between PV devices made by identical conditions other than the plasma source, those made by RF capacitively-coupled parallel plate discharge did not function, while those made by MSWP devices had measurable outputs, however small. From the defect densities presented in section 6.5, even the relatively low densities of $10^{17}$ for MSWP a-Si are too high to produce the industry-standard ~10% efficiency of amorphous cells. Also, an unoptimized deposition process of ITO led to highly resistive contacts, and the n-type layer (350 μm wafer) was uncharacteristically large for a solar cell, resulting in the ohmic (linear) I-V curve and poor efficiency seen in Figure 79.
Figure 79: I-V curve for a completed PV cell made via the MSWP source. The suppression of the characteristic "knee" in the curve to a flat line is attributed to a highly resistive top conductor, as well as a very thick n-type layer (350 μm wafer) relative to a conventional cell.
7: Conclusions

This work was very successful in achieving the research goals initially set, as well as changing direction appropriately as new data manifested. The following steps were essential to the success of the project:

- exploration of the parameter space,
- materials analysis of the deposited films,
- optimization of process knobs, and
- explanation of trends via numerical plasma simulation from first principles.

An experimental device was constructed to routinely deposit H:Si films in a clean vacuum environment via PECVD with a surface wave plasma source. With base pressure reaching $10^{-8}$ Torr and an Ar-SF$_6$-O$_2$ etch process to follow each deposition, few opportunities for film contamination occurred. With calibrated pedestal height and substrate temperature settings, as well as a LabVIEW interface for gas flow and power systems, the control on experimental conditions led to sufficient repeatability in deposited films. Hundreds of data points were tested to construct a functional view of the many-dimensional parameter space.

Extensive characterization of the films produced by the surface wave plasma source produced trends similar to literature in the observed crystalline transition vs. silane concentration. A flexible process window was found for simple and fast transition from deposition of a-Si to nc-Si, and the resultant tandem film was illustrated via SEM. Low total pressures (<300 mTorr) and an adequately heated pedestal were shown to avoid dust
formation, producing films with low void fraction. The deposition rate, linear with SiH$_4$ flowrate, indicated the high silane utilization of the MSWP source. The deposition rates for crystalline silicon were high (>3 nm/s) compared to the industry standard for PV-grade silicon films (0.5-1.0 nm/s) and could be further increased with improved system design. The deposition rate for amorphous silicon was superb, reaching upwards of 10 nm/s and producing compact films. Expanding the power capabilities of the plasma source would likely lower the required substrate temperature, opening up a wide range of flexible polymer substrates for commercialization of the source. Increasing power would also allow higher deposition rates for a crystalline recipe by pushing the a-Si/nc-Si transition to higher silane concentration.

The plasma model was predictive in trends for various process knobs, giving values accurate to within 10-25% of experimental deposition rates for 100 mTorr and 180W vs. SiH$_4$ concentration. However, numerical outputs showed deposition rates to be linear with power, while experiments produced constant growth rate across 80 → 160W. Basic plasma trends – e.g. decreasing $T_e$ for increasing pressure, increasing $n_e$ and constant $T_e$ for increasing power – were shown through the model, although experimental data disagrees with the model’s predicted decrease in plasma density at higher pressure, a very unusual deviation. Plasma electronegativity was found to become a concern at 500 mTorr or greater, and stability of the plasma for 1.0 W/cm$^2$ was questionable below 50 mTorr, agreeing with experimental observations. Unfortunately, plasma density was generally underestimated by a factor of 2-5 due to the volume-averaging of the global model. The lack of consideration for
localized power deposition in the “hot” plasma region may also be the source of where model diverges from experiment, as this nonuniformity was only taken into account in the wall loss of the model, not in power density. As recommended in Chapter 8, the solution of the electromagnetic coupling of the antenna with the plasma would shed ample light on the effects of the position-dependent effects of the discharge. The values of $T_e$ were consistent with non-rigorous Langmuir probe measurements of the plasma, although the experimental electron densities were much larger than the values generated in the model. The physical data used as input for the model could be more extensively verified and developed, but this study was sufficient in determining significant ion species and neutral radicals, giving at least a qualitative understanding to compare to experimentally observed trends.

Regarding film structure, grain size of the Si films was average, ranging from 5-15 nm depending on deposition conditions. In the case of defects, EPR analysis of the films showed nearly an order of magnitude improvement in defect reduction compared to films made by RF capacitively-coupled plasma. Negatively, hydrogen content in the film passivated defects at the expense of decreased crystallinity. Finally, a PV cell was made by the MSWP source that performed better than that of the RF CCP source, demonstrating the commercial advantages of this PECVD method over conventional RF discharges.
8: Future Work

For source characterization at various deposition conditions, a more rigorous and higher-resolution study of the MSWP source is needed. The Langmuir probe data obtained in this work breaks down for $T_e$ measurements at lower plasma densities simply due to the inability to resolve the exponential portion of the Maxwellian electron current. On top of this, the fact that the highest density region of the discharge is likely to be non-Maxwellian will skew the results of numerical simulations that adopt the thermal assumption. A determination of the plasma source in the “hot” region near the antenna would be ideal, whether by spectroscopic methods or through a Boltzmann solver. This can be coupled with an extension of the ½-dimensional into a 1 and ultimately 2-D fluid model with appropriate transport physics. Also, despite the extensive literature review done in this work, further study is needed to verify cross sections/rate coefficients and rule out discrepancies in the numerical data.

Further process optimization can be accompanied with in-situ Raman spectroscopy in real-time for crystallinity feedback, and FTIR spectroscopy is recommended for determination of surface or plasma composition, as the bond information for FTIR has been well-understood for decades. This should be done with a narrow channel chamber for SiH$_4$ utilization and roll-to-roll substrate compatibility, as well as a source optimized for gas flow through the antenna. An upgrade to higher power 2.45 GHz source would be conducive for
commercialization of the plasma source, as the market is saturated with 2.45 GHz suppliers due to its application in appliances.

With extensive characterization of deposited silicon films at various conditions, an appropriate extension of this work would be in deposition of polycrystalline silicon as the conductive channel for transistors, as preferential orientation in the [111] plane has already been shown in section 6.4. The incorporation of the MSWP source into plasma processing would be extremely useful in a large area situation, with many antennas multiplexed together. The diffuser in the tool could remain to buffer out source uniformities; however, it may not be necessary, as source-source and source-chamber coupling disappears in the microwave frequency range. Thus, the absence of cross talk and standing waves that are normally a problem in large area RF deposition would not be found with a microwave source.

In addition to PECVD of H:Si, alternative uses of the MSWP source should be explored. Preliminary work with etching has been done with the MSWP source has been done at the CPMI, and it is believed that exceptional etch rates can be achieved with moderate anisotropy. Other options for use include oxygen cleaning and treatment. Given a sufficient power source and design compatibility, the range of applications can be broadened to atmospheric processing of materials, eliminating the necessity for a vacuum chamber. This high density, low particle energy, wide pressure range, plug-and-play surface wave source has many undiscovered uses that would serve industry well.
Bibliography


