DEPOSITING HIGHLY CRYSTALLINE THIN FILM SILICON FOR PHOTOVOLTAIC
SOLAR CELLS UTILIZING METAL SURFACE WAVE PLASMAS

BY

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THESIS

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This thesis aims to explore the ability of the Metal Surface Wave Plasma (MSWP) to create low damage, high speed deposited silicon thin films for solar photovoltaics. Studies characterizing thin films have been performed in the past, but very few utilizing the MSWP. Due to the high electron densities and low electron temperatures characteristic of MSWPs, it is shown that this type of plasma is an ideal candidate for large area, high speed, low damage thin film deposition. The quantitative methods of examining films created by the MSWP system are analyzed through a series of diagnostic tools including: scanning electron microscopy, transmission electron microscopy, profilometry, x-ray diffraction and Raman spectroscopy. This work comprehensively discusses and compares different analytical techniques and methodologies – a shortcoming of prior works. In addition, it is demonstrated that the MSWP system can deposit tandem junction morphologies, ranging from microcrystalline to amorphous silicon films. This validates MSWPs as a robust PECVD source to deposit thin films quickly, yet flexible enough to deposit both amorphous and microcrystalline silicon.
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NOMENCLATURE

a-Si(:H) (Hydrogenated) Amorphous Silicon
µc-Si(:H) (Hydrogenated) Micro-Crystalline Silicon
PV Photovoltaic
SiH$_4$ Silane Gas
RF/VHF/UFH Radio Frequency/Very High Frequency/Ultra High Frequency
e$^-$ Electron
γ Photon
PECVD Plasma Enhanced Chemical Vapor Deposition
SEM Scanning Electron Microscope
TEM Transmission Electron Microscope
XRD X-Ray Diffraction
EPR Electron Paramagnetic Resonance
W Watts
mTorr milli-Torr [pressure]
MFC Mass Flow Controller
lpm Liters Per Minute
scmm Standard Cubic Centimeter per Minute
nm/s Nanometers per Second
cm$^{-1}$ Inverse Centimeters
°C Degrees Celsius
AM 1.5 Air Mass Coefficient (1 is travelling through atmosphere to sea level)
EM ElectroMagnetic (field)
RF Radio Frequency
Chapter 1: Introduction

The world currently depends on fossil fuels for everything from power plants to commercial goods production. These natural resources are used and relied upon in almost all industrialized processes, and their growing scarcity is a factor responsible for today’s global tensions and conflicts. The use of these fuels also releases large quantities of greenhouse gases into the atmosphere, adversely affecting the local and global environments, in addition to affecting the health of the local populace. An alternative source of energy to gain independence from finite, carbon producing energy is an obvious decision that many global leaders are identifying and addressing.

Among the competing clean energy solutions, photovoltaic solar cells prove to be one of the most promising. All solar cells utilize the energy of the sun, but PV cells use the incoming photons as a direct source of energy to knock free electrons from the atomic lattice structure, generating electric potential. The PV effect was first observed by Alexandre-Edmond Becquerel in 1839 in an electrolytic fluid [1]. The first PV cell was built, as we recognize these devices today, by Bell Laboratories in 1954 [2]. Since then, large strides have been made in efficiency, output power and ease of production. Manufacturing processes have improved, bringing down the production price per unit, and efficiency has increased, boosting watts per unit price up. Within the foreseeable future, the PV industry will be approaching a tipping point where the unit cost per watt for PV cells reaches parity with coal, oil or even natural gas.

Advancing PV solar cell technology is motivated by practical, economical and societal benefits. There is mounting evidence that carbon emissions are causing shifts in the global climate which can destabilize local, regional and worldwide climate cycles [3]. Rising sea levels, increasing number and strength of seasonal storm systems, and strengthening drought conditions stand to destroy billions of dollars in agricultural products and capital investments. Solar PV can stabilize a world currently hungry for oil produced in volatile regions of the world; removing dependency on less stable countries and economies. Solar PV also allows for more diffusive electric grids, allowing one to generate energy close to where it is
consumed, without affecting the local environment. This provides a more stable energy grid, with less focal nodes susceptible to hackers, terrorists or accidental blackout events.

The future of solar PV use can be solidified by bringing down the price per watt of electricity generated using PV systems. To achieve this, a concerted effort on several fronts must take place to raise efficiencies, increase deposition speeds, increase film quality, increase lifetime, and to reduce module/installation costs. Efficiency, film quality and deposition speed will be discussed in detail in the proceeding chapters.

1.1 Solar Photovoltaics

There are several different types of solar cells, made from different materials. The first solar cells developed by Bell Labs were made from selenium. In the years after, engineers and scientists developed cells using silicon, cadmium-indium-gallium-(di)selenide, quantum dots, gallium-arsenide, cadmium telluride, copper indium diselenide and many other materials.

The efficiencies of solar cells have been steadily rising since the late 1960s. The National Renewable Energy Laboratory compiles a road map showing the most promising PV cells and their efficiencies. Each year they add to the image displayed below in Figure 1.
The current record holder for the highest recorded efficiency on a PV solar cell is held by Solar Junction at 44%. It is important to note that the efficiencies of these systems occur under concentrated radiation conditions. The record setting cell was operating under a luminosity equivalent of 947 suns.

Most cells are evaluated based on their performance under the global Air Mass (AM) 1.5 spectrum, not under concentrated conditions. The global AM 1.5 spectrum is an industry standard assumption used by many manufacturers, academic institutes and governing bodies to evaluate the efficiency of cells under standard operating conditions. The AM 1.5 spectrum mimics the spectral luminosity and wavelength characteristics of light passing through a cloudless sky, at 25 km visibility, at sea level, with 1.42 cm water vapor at 48.2° off of zenith. The global AM 1.5 spectrum, as opposed to direct AM 1.5, assumes a

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1 Image was downloaded from http://www.nrel.gov/ncpv/ (Last updated 7/23/2012)
non-normal irradiance from reflected photons [4]. An illustrated explanation can be seen below in Figure 2. The AM 1.0 spectrum is not used since most of the population of the world does not live near or on the equator, but further north or south, near the tropics.

![Figure 2: Illustration of the AM 1.5 Spectrums (direct and global) and the nature of the assumptions made. Global AM 1.5 is used as the industry standard spectrum to evaluate PV cell efficiencies. [4]](image)

There are currently two main techniques used to produce silicon for PV cells. The first method, named after Jan Czochralski, is the process of growing single crystals of semiconductor materials. First discovered in 1916, the Czochralski Process is now the cornerstone of semiconductor production methods and has reached a high level of development. When used for photovoltaic application, this process proves to be materially wasteful (due to the kerf loss used to saw the thin silicon wafers from the large, grown ingot). The second method is to grow silicon thin films using a chemical vapor deposition (CVD) process. This allows silicon to be utilized more effectively and in a more sparing manner. This technology is now becoming competitive with the Czochralski Process due to the constant push towards thinner devices and higher efficiencies.

The most important goal when building large scale PV production plants is achieving a competitive cost per watt. Due to the modest energy density of solar radiation and low conversion efficiencies for PV cells,
the cost of materials in the production process strongly affects competitiveness. As the global market for silicon expands, commodity prices will rise due to demand. This will make silicon thin film deposition a more cost effective process than the Czochralski Process.

Solar photovoltaics utilize the photoelectric effect to generate electricity. A brief description of the phenomenon is given here. Suppose an incoming photon $\gamma$ with a particular frequency $f$ is incident on a material surface. The photon has a characteristic energy proportional to the frequency given by $E = hf$. If the photon’s incident energy exceeds the work function (binding energy of an electron) of the material being irradiated, then an electron is liberated from the material. Any extra energy the photon carried that was not necessary for the liberation of the electron results in an increase of the liberated electron’s kinetic energy. If the initial photon energy is less than the work function, the electron remains within the system in an excited state or reemits a photon as it drops to ground state energy. A basic diagram showing this phenomenon is shown below in Figure 3.

![Diagram of photoelectric effect](image)

**Figure 3:** (a) Photo induced excitation of the valence electron does not exceed work function required for liberation (b) incoming photon has enough energy to liberate electron from valence band and into the conduction band.
A PV solar cell must harness the photoelectric effect in order to create a voltage differential between two electrodes, which can then be used to power various devices via an electromotive force. The basic PV cell achieves this voltage differential through the use of a p-n junction. A p-n junction is the physical mating of two similar materials which are doped with different dopants. A dopant contributes charge carriers (adds or subtracts available electrons) to the material it dopes. The most common dopants used in the semiconductor industry are phosphorus (n-type, electron donor) and boron (p-type, hole donor). When a p-n junction is made, the n-type junction donates electrons to the p-type to fill holes. As this happens, an electric field is formed to inhibit this drift of electrons. This movement creates a diode that promotes charge flow, otherwise known as drift current. The region between the n- and p-type materials where the field is active is known as the depletion zone. There are no charge carriers in the depletion zone.

The diode formed by the p-n junction has a forward voltage, which means electrons can travel only one way through the junction. The light induced charge separation then generates an electric vector field that drives current through attached loads. Putting the cells in a series configuration allows higher voltages to be achieved. An inverter is often used to take the generated DC (direct current) and convert this charge flow to AC (alternating current), allowing transmission over the electric grid.

1.2 Multi-Junction Solar Cells

Until the advent of multi-junction solar cells, researchers endeavored to find a material which can absorb a broader percentage of the electromagnetic spectrum reaching the surface of the earth. In lieu of finding a single, perfectly absorbent material, research shifted toward the combination of two or more layers which together could capture a greater range of incident wavelength light.

A multi-junction solar cell is a combination of two or more materials stacked on top of one another to augment the light absorption spectrum. This increases the absorption bandgap of the cell, allowing more wavelengths of incident sunlight to be converted into electron-hole pairs. This raises efficiency and sunlight utilization per area for any multi-junction solar cell.
A graph showing the absorption cross sections is shown below in Figure 4. The a-Si thin film is more efficient at absorbing and converting shorter, more energetic wavelength light. This is due to the unordered spacing between the microlattice network of silicon constituting the thin film. In contrast, the μc-Si absorption cross section lies farther to the right, where the longer, less energetic photons are more readily absorbed. Both silicon phases share some overlap, but superimpose to cover a larger area of the standard AM 1.5 global spectrum.

![Absorption Bandgap Diagram](image_url)

Figure 4: Absorption bandgap for hydrogenated a-Si and microcrystalline-Si. Combining both phases of silicon into one multi-junction cell allows greater utilization of all incident light generated by the sun.

A cut-through diagram of a single junction amorphous cell and a tandem junction a-Si/μc-Si cell is shown below in Figure 5.

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3 Diagram from Applied Materials External presentation at AVS PAG Meeting by Yi Zheng et al
The ordering of the tandem junction cells is an important decision during construction. Since the shorter wavelength (more energetic) photons have a shorter penetration depth, it is critical to place the corresponding absorbent material on the top of the structure, closer to the incident light. It is also important to note that amorphous silicon can reach a high level of absorbance with a shorter thickness. This is shown neatly in Figure 6 below. Measurements were taken with the Varian/Cary 5 G spectrophotometry system. The spectrophotometer shines a large wavelength range of light with known intensity through a given sample and measures the intensity of the light passing through. By measuring the initial intensity and the final intensity, one can calculate the absorption of a material in a range of photon energies.

---

4 Diagram from Applied Materials External presentation at AVS PAG Meeting by Yi Zheng et al
A 550 nm thick a-Si film (with a crystalline fraction $X_c = \sim 16\%$) has a 99.99\% opacity for high energy photons. A much thicker $\mu$-Si film (1.33 microns) has less absorbance for double the thickness.

The theoretical maximum efficiencies of solar cells were first outlined by William Shockley and Hans Queisser at Shockley Semiconductor in 1961. The treatment started from first principles and an assumption of a 1.1 eV silicon bandgap as well as an ideal solar spectrum with 100 mW/cm$^2$. The maximum theoretical efficiency was found to be 29\% [5].

A similar treatment was carried out by Alexis De Vos for tandem PV structures. De Vos was able to calculate maximum theoretical efficiencies by taking into account a particular cell’s illuminosity by solar irradiance and considering the electroluminescence of other cells in the tandem set. While subjected to one solar irradiance, a tandem structure has a maximum efficiency of 42\%, a triple tandem 49\%, and so on. An infinite number of tandem cells has a theoretical maximum efficiency of 68\% under AM 1.5.
lighting conditions. The efficiencies are boosted further to 86% under concentrated lighting conditions [6].

1.3 Introduction to Metal Surface Wave Plasmas

There are myriad methods to generate plasmas, each with their own characteristics which make them better for certain processes and tools. When considering thin film deposition using a Plasma Enhanced Chemical Vapor Deposition (PECVD), high densities and low electron energies are ideal for fast growth, high quality films. Higher plasma densities translate to higher gas precursor breakdown, which creates more radical groups important for film growth. Incidentally, low electron temperatures are needed to minimize high energy ion bombardment on the growing film. These high energy ions bombarding into the film are responsible for creating dislocations in the growing film lattice structure, disrupting ordered growth. These dislocations then act as sponges to soak up charge carriers once the film is utilized as a solar PV structure. If charge carriers fall into these dislocations, they are unable to contribute to the generation of a current.

In plasmas, densities are generally coupled to plasma temperatures. This creates a direct relationship between poor film quality and high deposition rates. Metal surface wave plasmas are ideal due to the inherently low electron temperatures (<2 eV) and high electron densities (>10^{12} cm^{-3}). The electron temperatures are limited due to most of the energy coupled into the system being deposited just above the sheath layer. This thin layer above the sheath works to absorb and ionize most of the gas in a very thin cross-sectional depth spread over the injection port area. As one moves away from the injection port, the temperature drops through collisional processes while the density drops more slowly over a larger distance. The MSWP also scales very well with power, meaning one can scale the plasma density with increasing input power independently changing the electron temperature. This behavior is demonstrated in Figure 7. Since we want to minimize process volume (saves on capital expenditures, process gas and pump size), MSWPs provide excellent characteristics for gas processing very near the target or substrate (in the range of 1-3 cm).
Figure 7: Shirai et al. measured the density and electron temperature for the 2.45 GHz surface wave plasma. As power is increased, the electron temperature remains stable and low, while the electron density increases linearly. [7]

MSWPs also allow for easier area scaling capabilities because of their inherently modular construction and locality effects, e.g. one MSWP system can be placed next to a second similar one without any first order influences (direct change in electron density or temperature) of one system on the other. Since the MSWP plasma can expand and cover a large area radially from the feedthrough location, MSWPs create the ideal large throughput devices needed for materials processing.

A simplified cut through of the MSWP feedthrough device is drawn below in Figure 8.
An amplifier operating at 900 MHz creates a high energy RF signal which is propagated to the MSWP antenna through a series of impedance transformers. The feedthrough coupler reduces the power lost by impedance matching the different components. The EM excitation then reaches the radially slotted antenna, through which the EM wave is launched into the vacuum volume.

Provided a small amount of free charge carriers (electrons), the RF signal will inductively couple and begin to transfer energy into the nascent plasma through a cascade of electron-neutral atom collisions. The resulting ions will begin to excite and ionize surrounding species, quickly bringing the plasma to steady state densities shown in Figure 7. Unlike most plasma generation devices, the MSWP utilizes one conventional electrode surface (the antenna) and uses the high density plasma layer just above the sheath as a lossy conductor to propagate EM fields away from the injection location. The EM fields travel with minimal losses in the sheath region where charge densities are lower.

Once ejected from the antenna dielectric construct, the EM field will traverse the sheath, deposit energy into the plasma, reflect back into the sheath region, and continue this cycle. Thus it is possible for a MSWP to excite a plasma area much larger than the feed through area. As long as there is enough power driven into the system, it is possible to create surface wave plasmas which cover areas many multiples larger than the antenna geometry. A basic illustration of the concept is shown below in Figure 9.

![Figure 9: 2D Surface wave plasma conceptual diagram. The blue represent conducting material (eg. copper, aluminum), yellow represents dielectric material (eg. polyethylene, alumina) and red represents plasma.](image.png)
The VHF radial injector is designed to broadcast and couple with the plasma efficiently. Once the plasma ignites, a standing wave is created. The surface excitation mode of plasmas was first observed by Trivelpiece et al [8]. Many of the surface charge wave’s properties were derived by regarding the plasma as a dielectric and solving the resulting field equations. MSWPs have been studied extensively since the 1970s and their geometrical functionality can be found through numerous references such as Zakrzewski et al 1977 [9], Moisan et al 1974-75 [10]- [11] and Shivarova et al 1978 [12].

1.4 Motivation

Thus far, it has been shown that the further increase in the efficiency of PV solar cells is of great importance. As conversion efficiencies increase, PV solar will reach a tipping point to begin replacing more conventional sources of energy. To facilitate this, PV solar must become more economical (decreasing $/W to <$1/W) by large throughput tools that churn out a significant number of cells quickly. When it comes to large area plasma processing, several methods are currently used, but the MSWP has great large scale uniformity, scalability, low electron temperatures and high carrier densities.

In order to demonstrate the applicability of the MSWP in depositing good quality films, a method of film characterization is needed. SEM, TEM, XRD, Raman Spectroscopy, Ellipsometry, spectroscopic photometry and EPR are all tools that can be used to analyze films. However, for several reasons (destructive, inaccurate speculative model needed or long sample data collection time) Raman emerges as the best option. If used to collect and analyze data correctly, Raman spectroscopy can reveal the phase (amorphous or crystalline) of deposited silicon in the thin film, giving information on the stress/strain of the film as well as the average equiaxed crystal grain size of the μc-Si:H. The goal of this work is to demonstrate proper methodologies and techniques to speedily collect and analyze the aforementioned characteristics of silicon thin films deposited by MSWPs.
Chapter 2: Literature Review

A detailed review of current literature reveals there are similar efforts proceeding to maximize deposition rate, crystallinity fraction and quality (minimize defect density). In order to maximize these values, several analytical techniques have to be proven and shown to measure these parameters reliably.

Houben et al [13] prepared samples in a diode type reactor using very high frequency (VHF) PECVD on glass and silicon substrates. Substrate temperatures were kept steady at 200° C and the dilution ratio was changed between 2:98 to 6.2:93.8 [ratio of SiH₄:H₂ flow rates]. Total gas pressure was held at 300 mTorr. Excitation frequency was 94.7 MHz at 5 W input power, an order of magnitude less than the frequency and powers used in this work. The objective of the study was to investigate the structural characteristics upon the change in the Silane dilution in hydrogen VHF PECVD and to provide insight into the film formation process.

Houben found that with increasing Silane concentration, there is a precipitous drop in $I_{C-RS}$ (Raman crystallinity). Below in Figure 10, Houben plots the findings from XRD crystalline analysis on the right ordinate and Raman crystalline analysis on the left ordinate. There is a strong correlation between Silane flow-rate concentration and crystallinity in the film, supported by a close agreement between XRD and Raman analysis.
Figure 10: Houben et al plotted the crystalline fractions calculated from XRD ($X_{\text{C-XRD}}$) and Raman spectroscopy ($I_{\text{C-RS}}$) against varying Silane concentrations. $X^{111}$ (◊), $X^{222}$ (○) and $X^{311}$ (Δ). As Silane concentrations are increased, the crystal fraction of deposited films decreases, reaching almost purely amorphous. At low Silane concentrations, crystallinity saturates at close to 80%. [13]

The $I_{\text{C-RS}}$ (Raman crystallinity) was calculated by fitting three Gaussian peaks at 480, 500 and 520 cm$^{-1}$ (α-Si:H, μc-Si:H and c-Si:H). The ratio $I_{\text{C-RS}}$ is of the integrated scattering intensity of the crystalline phase to the total scattering intensity is given by:

$$I_{\text{C-RS}} = \frac{I_C}{I_C + I_A}$$  \hspace{1cm} (2.1)

Where $I_C = I_{500} + I_{520}$ and $I_A = I_{480}$. ‘I’ denotes the area of the Gaussian peaks that were fitted to the spectra. In this method, the 520 cm$^{-1}$ and 500 cm$^{-1}$ are treated as idealized peaks and all samples are analyzed on that basis. The maximum crystallinity found during the study was 0.8, which did not increase even after thermal annealing.

The Raman crystallinity ($I_{\text{C-RS}}$) was checked by calculating the crystallinity using XRD. Three peaks were used to calculate the $X_{\text{C-XRD}}$: 28.44°, 47.4° and 56.12° corresponding to the {111}, {220} and {311} lattice plane reflections. The crystalline volume fraction was then calculated from
\[ X_{C-XRD} = \frac{I_{hkl}}{(I_a + \kappa_{hkl}I_{hkl})} \]  

(2.2)

In equation 2.2, \( I_{hkl} \) represents the area under the \{hkl\} crystalline diffraction peak, \( I_a \) was chosen as the area under the first diffraction maximum of the appropriately scaled a-Si:H reference diffractogram, and \( \kappa_{hkl} \) corrects for the proportionality between scattering volume and intensity \( \left( \kappa_{hkl} = \frac{I_{hkl}^{ref}}{I_a^{ref}} \right) \). Here, 

\( I_{hkl}^{ref} \) designates the integral intensity obtained from a thermally crystallized microcrystalline film and \( I_a^{ref} \) is the integrated intensity measured from the a-Si:H reference sample as described above under identical experimental conditions.

The volume fractions are calculated independently for each crystallographic orientation: \( X_{C-XRD}^{111} \), \( X_{C-XRD}^{220} \) and \( X_{C-XRD}^{311} \). There is a slight discrepancy between the different \( X_{C-XRD} \) values, but amount to a negligible effect from a slight deviation from the single-crystal powder pattern.

Using the Scherrer Formula (equation 4.4.2) in conjunction with XRD analysis and TEM images, Houben was able to find the average volumetric crystal grain size grown during different dilution conditions. The results are plotted below in Table 1.

<table>
<thead>
<tr>
<th>Silane concentration (%)</th>
<th>n</th>
<th>( \delta \pm \Delta \delta ) (nm)</th>
<th>s (nm)</th>
<th>( \delta^{111} ) (nm)</th>
<th>( \delta^{220} ) (nm)</th>
<th>( \delta^{311} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>296</td>
<td>12.1 \pm 0.4</td>
<td>6.7</td>
<td>35.1</td>
<td>10.7</td>
<td>14.1</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>10.7 \pm 0.4</td>
<td>6.8</td>
<td>13.9</td>
<td>10.0</td>
<td>14.4</td>
</tr>
<tr>
<td>5.7</td>
<td>302</td>
<td>8.2 \pm 0.3</td>
<td>5.4</td>
<td>8.6</td>
<td>6.9</td>
<td>10.5</td>
</tr>
<tr>
<td>5.9</td>
<td>231</td>
<td>8.1 \pm 0.2</td>
<td>3.3</td>
<td>7.2</td>
<td>6.0</td>
<td>9.6</td>
</tr>
<tr>
<td>6.2</td>
<td>52</td>
<td>7.9 \pm 0.6</td>
<td>4.5</td>
<td>5.2</td>
<td>5.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Table 1: Changes in crystal grain size due to varying Silane concentrations are shown using TEM and XRD analyses. [13] As Silane concentrations increase, there is a nominal decrease in the grain size, most pronounced for the <111> crystal orientation. Crystal sizes shrink seven times from 35 to 5 nm for a change of 2 to 6.2% Silane concentration.
A study similar to that of Houben was carried out by Sakuma et al [14]. Sakuma identifies the high-density (>10^{11} \text{ cm}^{-3}) and low electron temperature (~2 \text{ eV}) characteristics of UHF discharges. At first, the total pressure was optimized to ensure the highest possible crystallinity for a given dilution ratio between SiH_4 and H_2. This is shown in Figure 11 below.

![Raman peaks plot](image)

**Figure 11:** Raman peaks are plotted for four different pressure and dilution conditions. There is a noticeable sharpening in the peak centered at 520 cm\(^{-1}\) as pressure decreases, indicating more crystalline content. [14]

Sakuma found that as the pressure decreases, the crystalline peak becomes more defined and centered on ~520 cm\(^{-1}\). The amorphous content is also reduced as the pressure is decreased. The H\(_\alpha\)/Si* value is the ratio of the Optical Emission Spectroscopy of those two compounds within the plasma during that test recipe.

Sakuma found as the hydrogen flow rate was decreased, while keeping total pressure the same (50 mTorr), the Raman intensity and definition of the µc-Si:H peak became greater. He concludes that the total pressure is a more dominant parameter rather than the H\(_2\) dilution ratio for determining the film crystallinity, as well H\(_2\) gas injection not being necessarily essential for promoting crystalline growth in this high-density microwave plasma. This is visualized below in Figure 12.
As Silane flowrate increases, the peak bows out at 480 cm\(^{-1}\), indicating a larger amorphous Silicon content. [14]

Another test carried out was to vary the axial distance of the quartz plate (upon which deposition took place) from the plasma source device. The overall effect of changing the distance from 6 to 15 cm was minimal, resulting in a 2 Å/s difference.

Figure 13: Varying deposition rate as a function of substrate deposition and plasma source gap. As the sample substrate is moved further from the plasma source, the deposition rate decreases slightly. [14]
Thus by using high power (<2 kW) and UHF (2.45 GHz) as outlined by Shirai et al [7], Sakuma was able to attain highly crystallized and photoconductive μc-Si film at a high deposition rate of 4.7 nm/s. Though the deposition system used by Sakuma was very similar to the one used in this work, Sakuma failed to create a quantitative method of analyzing Raman spectra collected from the films. This meant that all comparisons were qualitatively carried out, reducing the interpretive range of the work’s data when comparing to other sources in literature.

Smit et al carried out a study to determine the material structure of microcrystalline silicon from the Raman spectra [15]. Ruling out XRD, TEM and ellipsometry as too time consuming or ambiguous as diagnostic tools for determining crystalline fraction in silicon films, Smit discusses several approaches to using Raman spectroscopy. Ultimately, the method used involves first subtracting all Raman spectra by a standard a-Si:H film spectrum. The result is denoted as μc-Si:H – A×a-Si:H – B, where ‘B’ is a flat background to correct for the dark counts and background light. Due to differences in signal strength caused by differences in sample alignment and film composition, the amorphous spectrum is scaled by a factor ‘A’. The values for this constant (A) are calculated by a least-squares routine which minimizes the residual in the regions in the spectrum outside the transverse optical (TO) phonon peak (200 – 440 cm\(^{-1}\) and 560-850 cm\(^{-1}\)). The TO phonon is an excitation mode that occurs almost exclusively in the crystalline phase of silicon. The justification for this method is that the μc-Si:H spectrum cannot contain peaks at the a-Si:H acoustical (longitudinal acoustic [LA] and transverse acoustic [TA]) phonon energies.
Figure 14: Smit et al. shows graphically the Raman spectrum manipulation to isolate phase contributions to total spectrum. The top spectrum is the acquired sample spectrum, below that is the weighted a-Si:H spectrum, and below that is the isolated µc-Si spectrum. The dashed line is a c-Si reference sample. [15]

In Figure 14 above, we can see the resulting spectrum following the isolation of the a-Si:H contribution. The dashed line represents a pure crystalline reference sample spectrum. The wider peak centered around ~520 cm$^{-1}$ is from the µc-Si minus the a-Si weighted by a factor of 0.49.

Once the peaks are differentiated, Smit follows with a calculation of the crystalline fraction. Smit asserts that it is not possible to obtain absolute values because the detection efficiency for each phase is usually unknown. However, the ratio of the two peak areas can be used to find the ratio of amorphous to microcrystalline silicon. The ratio needs to be corrected for the difference in the cross sections of the two phases for the reasons mentioned above. For the TO phonon mode, Smit uses a ratio of 0.8 ($\sigma_{\text{c-Si:H}}/\sigma_{\text{a-Si:H}}$).

It is noted that this ratio changes (0.7-0.9) depending on the crystallite size (5-15 nm) [16].

It must be ensured that only the TO phonon mode from the a-Si:H spectrum is used, so Smit breaks down the a-Si:H spectrum into the four phonon modes using Gaussian line profiles (TO - transverse optical, LO
- longitudinal optical, LA - longitudinal acoustic, TA - transverse acoustic). This is shown below in Figure 15.

![Figure 15: Smit et al isolated the four excitation modes in a collected silicon Raman spectrum. It becomes evident which phonon modes contribute to the collected Raman sample spectrum. [15]](image)

The peak area of the TO phonon mode for a-Si:H is scaled by 0.8 to account for the difference in absorption cross sections. The factor A (0.49), calculated earlier by a least squares method, is also applied to the TO a-Si:H phonon peak. The crystalline contribution is calculated by integrating the isolated μc-Si:H spectrum from 440 cm\(^{-1}\) to 560 cm\(^{-1}\). Smit performed a series of hydrogen flow rate tests and plotted the calculated crystallinities in Figure 16 below.
Figure 16: Smit et al calculated silicon thin film crystallinity as a function of hydrogen flowrate into the reaction chamber. Low levels of H$_2$ flowrate into the process volume resulted in highly amorphous films. Increasing H$_2$ flowrates quickly saturates film crystallinity near 80%. [15]

Inspection of Figure 16 reveals that the crystalline fraction saturates around a value of 0.8. The author explains that this may be due to grain boundaries, which can be considered disordered material. A counter argument is also mentioned that for fully nanocrystallized silicon films (with crystal sizes around 5 nm), the amorphous Raman content is less than 0.1. The author concedes that the grain boundaries may not necessarily result in a saturation of the crystalline fraction at 0.8, but instead may be a feature of the deposition system and parameters used in the study.

<table>
<thead>
<tr>
<th>SiH$_4$ flow (sccm)</th>
<th>XRD$^a$</th>
<th>Raman</th>
<th>Raman [480] vs. [520]$^b$</th>
<th>Raman (3 Gauss)</th>
<th>Raman (5 Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>58±9</td>
<td>52±4</td>
<td>72±4</td>
<td>46±10</td>
<td>38±6</td>
</tr>
<tr>
<td>14</td>
<td>50±6</td>
<td>46±4</td>
<td>69±3</td>
<td>40±17</td>
<td>31±6</td>
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<td>12±2</td>
<td>11±4</td>
<td>46±2</td>
<td>3±1.5</td>
<td>5.3±2.5</td>
</tr>
</tbody>
</table>

*Note: cryst indicates crystalline and am indicates amorphous.*

Table 2: Smit et al compared XRD data and three Raman methods for calculation of silicon thin film crystallinity. Three different SiH$_4$ flowrates were tested and evaluated. [15]
Smit finally compares his methodology with several other techniques, shown in Table 2 above. While varying SiH$_4$ flowrate, the films are analyzed by XRD (column 2) and Raman. Using the raw Raman data, Smit calculated crystallinity using his own outlined technique (column 3), employing the ratios of the peak height at 520 cm$^{-1}$ for μc-Si:H and 480 cm$^{-1}$ for a-Si:H (column 4), a 3 Gaussian fit show in Figure 17 (a) below, and a 5 Gaussian fit shown in Figure 17 (b) below.

![Figure 17: Two different fitting methodologies discussed by Smit. (a) A 3-peak method is used, peaks are centered at 461, 501 and 517 cm$^{-1}$. (b) A 5-peak method is applied to optimally fit the collected Raman spectrum. Peak locations are at 402, 475, 490, 510 and 517 cm$^{-1}$. [15] Smit concludes that the analytical technique developed in the study is advantageous to other methods due to its more accurate crystallinity when compared to XRD measurements.](image-url)
Chapter 3: Experimental Setup

The chamber used in this set up utilized a loadlock chamber and a primary (main) deposition chamber assembly, using a transfer arm to move samples between the two chambers. Both the loadlock and main chamber were pumped by isolated turbomolecular pumps, backed by a dry roughing pump. Each chamber also had a roughing pump to reduce chamber pressure from atmosphere (used for evacuating the loadlock after loading/unloading).

The linear transfer arm is able to transfer samples from the loadlock to the main chamber through a large 8” gatevalve. The sample tray attaches to the linear transfer arm and can hold up to 6 sample coupons (6”x6”). Once loaded onto the vertically adjustable pedestal within the main chamber, the linear transfer arm is retracted, and the gatevalve is shut to isolate the main chamber from the loadlock.

The pedestal (upon which the sample tray seats) is mounted to an adjustable bellows which is powered by three electric motors, allowing the user to move the pedestal up/down. The gap between the sample coupons and the plasma source may be variably adjusted. The height adjustable pedestal is electrically isolated and heated. Through biasing with a variable voltage source, the pedestal can heat sample coupons to temperatures upwards of 500° C.

A detailed schematic of the system assembly is shown below in Figure 18.
The metal surface wave plasma system used in the experimental setup is proprietary, loaned to the Center for Plasma Material Interaction (CPMI) from Starfire Industries, LLC. The MSWP system was developed by Starfire over several years utilizing the experience of a team of engineers. Due to contractual obligations, we are unable to show schematics or pictures of the actual plasma source.

An example of a feedthrough system designed for 2.45 GHz is shown below. The bottom cavity structure acts as a waveguide to couple power from the magnetron to the vacuum feedthrough device. The key to creating a useful device is to maximize the power broadcasting on the vacuum side of the feedthrough. Similarly, we can minimize the reflected power at the injection port on the atmosphere side.

**Figure 18:** A 2-dimensional schematic showing MSWP deposition system complete with loadlock, main chamber and vacuum subsystem.

### 3.1 RF Feedthrough System
A modeling campaign was carried out to increase the coupling efficiency of the driving RF source to the broadcasting antenna. This was done by modeling in COMSOL multi-physics, using the EM wave package. A cut-away plot of the COMSOL model is shown above in Figure 19. The model’s geometric parameters were varied based on quarter wavelength optimization until a maximum electric field was realized in the vacuum process space just above the circularly symmetric antenna. Through experimental testing coupled with EM modeling, this method of maximizing electric field proved successful in creating high efficiency feedthroughs.

The RF subsystem consisted of a Novasource wave form generator, which powered a 5 W pre-driver amp into a 2-way splitter. The splitter then fed into a voltage variable attenuator on one branch, and a voltage variable phase shifter followed by another voltage variable attenuator. On both branches, the next component was the main driver amplifiers. These amps are nominally rated for 130 W at 900-1000 MHz.
Once the RF waveform passed through and was amplified, the two branches pass through separate circulators. Each circulator is connected to a 100 W dummy load, which ensures that any backwards moving waveform is shunted away from the sensitive amplifiers. After passing through the circulators, the waveforms pass through directional couplers with a power meter each. Each power meter allows voltage amplitude measurement of the forward traveling waveform in each branch. The branches (and their associated high power travelling waveforms) are then combined in a 2-way high power waveguide combiner. This high power combined line passes through another directional coupler to measure total power forward and reflected. The final component is a variable linear slug tuner which allows impedance matching between the amplifier system and the feedthrough/plasma system. The entire RF assembly is capable of operating at a maximum forward power of ~200 W (due to losses in the lines and phase matching).

3.2 Gas Injection System

The injection methodology used to insert precursor gasses into the system was of utmost importance. Film uniformity is very dependent on the type of gas injection used. Over the course of several designs, it became evident that creating an optimal gas injection tool could be a whole project on its own, thus only two iterations were developed based on uniformity studies carried out by profilometry/Raman spectroscopy over 14/6 points across the sample area respectively.
Figure 20: A stainless steel gas manifold was used as an injection system for the Silane and Hydrogen gas precursor mix. Pictured above in Figure 20 is the gas injection system. The precursor gas of Silane and Hydrogen was mixed and conveyed to the gas manifold through a stainless steel bellows (not pictured). The 1/8” holes in the stainless steel tubing (x26) were plugged with a porous ceramic (ARON Ceramic Inorganic Adhesive D). This allowed the gas to diffuse out at greater angles of injection into the vacuum chamber during PECVD and to limit the flooding of the excitation area.

The diffusive ceramic gas injector also reduced the geometric size of the gas cavity with respect to the frequency of the driven antenna. At the antenna’s operating frequency, with the pressures under consideration in this study, cavity geometries would generate a high density Hollow Cathode Discharge (HCD). The HCD discharge effect would have introduced severe film non-uniformities due to higher electron densities, and for this reason, a high temperature porous ceramic was employed to reduce flow diameters below those that would create HCDs.
Chapter 4: Tools Used to Evaluate Films

4.1 Scanning Electron Microscope

For the purposes of analyzing the surface and cleaved morphologies of the samples generated in this study, the JEOL 6060 Low Vacuum Scanning Electron Microscope (SEM) was utilized. The 6060LV (as it is hereafter referred to) has excellent second electron imaging and backscattered electron imaging resolution. The optically active area can accept specimens up to 5 inches in diameter, and has an optimum resolution of 3.5 nm at high vacuum ($10^{-4}$ mTorr, 30 kV, 6 mm Working Distance).

A brief discussion is given to introduce the reader to SEM operation and analysis. An SEM works by creating a large voltage gradient which accelerates electrons from a thermionic emission point. This beam is accelerated to the desired voltage which is user controlled (ranges up to 30 kV). As the beam is accelerated, it is collimated and tightened by several condenser lenses. The beam then usually passes through a scanning coil, which allows the beam to scan in a raster fashion over a controlled sample area.

When the primary electron beam interacts with the target, several interactions can occur. The electrons lose energy by repeated random scattering and absorption with a teardrop shaped volume into the thickness of the sample (known as the interaction volume). The size of the interaction volume is dependent on the incident electron’s energy, the atomic number of the sample and the specimen’s density. The interaction of the electron with the sample results in the reflection of high-energy electrons by elastic scattering, secondary electron emission by inelastic scattering and the emission of electromagnetic radiation. Each of these can be detected by specialized detectors installed within the specimen chamber.

4.2 Profilometry

In order to measure the deposition thickness of each sample, an area of the sample coupon was masked to prevent film deposition. When the sample was removed, it was possible to measure the total thickness of
film deposited during the process by measuring the height difference between masked and unmasked areas.

The profilometer used for the purposes of this study was the Dektak 3030. The Dektak 3030 profilometer has a high vertical resolution of 2 nm in 131 µm. It utilizes a diamond tipped stylus which is moved laterally across the sample for a specified distance. The profilometer can measure small surface variations by the resulting vertical displacement of the stylus position. A schematic of the underlying principle at work is shown below in Figure 21. The profilometer proved an effective and quick method for quantitatively assessing sample thicknesses to guide sample recipe optimization.

4.3 Raman Spectroscopy

Raman Spectroscopy was used to determine film crystallinity and amorphous content. The device used for the purposes of this study was the NanoPhoton 11 Raman Spectroscope. The Raman spectroscope is able to measure molecular vibrations and optical phonons in the 50-10,000 cm\(^{-1}\) range. The measured phonons are reported in wavenumbers (cm\(^{-1}\)) as this corresponds to the spatial frequency of the phonon. The wavenumber can be thought of as energy (specifically energy lost per incident photon upon interacting with the sample material) via Planck’s relation: \(E = h\nu\). \(E\) is the energy, \(h\) is Planck’s
constant and $\tilde{\nu}$ is the wavenumber. The wavelength of light used for the purposes of this study was 532 nm.

In a solid, a small part of the energy of an incoming photon can be used to excite a lattice vibration (phonon). The remaining energy escapes as a photon with slightly less energy compared to the incoming photon. This energy shift is denoted as a Raman shift. In a pure crystalline sample, the momentum conservation law selects only phonons with zero momentum, because the momentum of the photon is negligibly small. In mono-crystalline silicon, only the optical phonon with energy 64 meV has zero momentum and this leads to the sharp peak at a Raman shift of 520 cm$^{-1}$. In a-Si:H, the momentum selection rule is relaxed and a variety of phonon modes and energies are allowed. A broad peak centered at 480 cm$^{-1}$ then dominates the Raman spectrum. A $\mu_c$-Si:H sample spectrum can be considered a mix of the c-Si and a-Si:H spectra. [15]

![Raman spectrum showing the silicon phase contributions to the total scanned spectrum](image)

**Figure 22:** Raman spectrum showing the silicon phase contributions to the total scanned spectrum (c). a-Si contributes a broad peak centered at 480 cm$^{-1}$ (b) while $\mu_c$-Si contributes a thin, sharp peak centered at 520 cm$^{-1}$ (a). [15]
Raman spectroscopy works by using a laser source to excite vibrational, rotational and other low frequency modes within a sample substance. The laser photons undergo inelastic scattering with the sample material, exciting a certain mode, and lose a related amount of energy. The shift in energy, once picked up by a diode, gives us information regarding the excitation modes within the sample material. Once the wavelength of the reflected light is determined, it is possible to calculate a Raman Shift (ω) using the equation below:

$$\omega [cm^{-1}] = \left( \frac{1}{\lambda_0 [nm]} - \frac{1}{\lambda_1 [nm]} \right) \times \left[ \frac{10^7 nm}{cm} \right]$$ (4.3.1)

The Raman Shift for a given excitation frequency will yield a curve resembling Figure 22 above. The plot is of waveshift (cm\(^{-1}\)) on the abscissa and intensity on the ordinate. We can see that the 520 cm\(^{-1}\) waveshift dominates in crystalline samples. Upon measuring this curve, the precise location of the peak and the peak’s $\Delta \omega_{\text{Ref-Meas}}$ shift from a pure crystalline reference Raman spectrum can be calculated. The Raman shift difference can then be used to calculate the crystalline grain size by equation 3.3.2 below.

$$d_{\text{Raman}} = 2\pi \sqrt{\frac{B}{\Delta \omega_{\text{Ref-Meas}}}}$$ (4.3.2)

Where $B = 2.0 \text{ cm}^{-1} \text{ nm}^2$, which captures disorder-induced line broadening from silicon [17] [18]. $\Delta \omega$ is the shift of the peak for the $\mu$-c-Si:H sample compared to that of c-Si. The raw data file is then exported for peak fitting and calculations. An explanation of the peak fitting method is included in Chapter 5.2: Data Analysis Methodology for Crystal Fraction. Once the Raman spectra is fitted for the three Gaussian fit, a Raman crystallinity fraction ($X_{c-Raman}$) can be calculated using equation 3.3.2

$$X_{c-Raman} = \frac{l_c + l_{ic}}{l_c + I_{ic} + l_a}$$ (4.3.3)
Where $I_C$ is the crystalline excitation peak centered at $\sim 520$ cm$^{-1}$, $I_{IC}$ is the intermediary crystalline peak centered at $\sim 500$ cm$^{-1}$, and $I_A$ is the amorphous peak centered at 480 cm$^{-1}$. Before each sample scan carried out in this study, a reference crystalline sample was scanned to adjust instrumental peak shifts. This was used to center the crystalline peaks more accurately, allowing greater precision on $X_{C-Raman}$ and $d_{Raman}$ calculations.

It is important to note here that the calculated Raman crystallinity provides a lower limit for the actual crystalline volume fraction. Previous authors have pointed out that the amorphous phase is strongly overestimated if the signal at 480 cm$^{-1}$ is related solely to the amorphous phase [19]. Furthermore, the Raman cross-section of crystallites larger than 30 Å is smaller than that of a-Si for a given excitation wavelength [16] and the optical absorption coefficient at the wavelength of excitation is significantly higher for an amorphous sample than for a microcrystalline sample.

### 4.4 X-ray Diffraction

X-ray Diffraction (XRD) is a method of characterizing materials with repeating crystal structures up to size limit of about 150 nm. The XRD machine used in the study was the Phillips XPert. In XRD, an incident beam of x-rays is directed at a sample material, while rotated through a series of angles in conjunction with a rotating sample stage and detector. For the tests carried out in this study, a glancing angle 2θ scan was performed. This meant that the x-ray incident angle was kept at $<5^\circ$ with respect to the sample surface. The x-ray detector and sample stage were rotated through from a 2θ range of 15° - 85°.
In order to fully understand the fundamentals of XRD, one must understand the principals of crystalline and amorphous atomic structures. Amorphous materials have structures where the atoms are arranged in a random way, similar to what we find in a liquid. Glass, for example, is an amorphous material. Crystalline materials are atoms arranged in a repeating, organized structure (lattice). Within crystalline materials, there is a smallest element that one could describe the entire substance with. This repeating element is called a unit cell. The dimensions of this cell are described by three axes (a, b, c) and the angles between them (alpha, beta, gamma).

When an electron is in an alternating electromagnetic field, it will oscillate with the same frequency as the field. When an x-ray is projected onto atoms of a sample in an XRD tool, the electrons around the atoms oscillate with the same frequency of the incoming x-ray beam. In almost all directions, destructive interference will be observed. Only in certain directions, depending on the lattice structure, will there be constructive interference of these excitations, allowing x-ray beams to leave the sample in certain directions. As the incident beam is rotated through different angles, information regarding the characteristic properties of the material under investigation can be obtained by analyzing the strength of the reflected beam.

Figure 23: XRD 2θ scan diagram depicting incident x-ray angle relationship to sample stage angle and x-ray detection device.
When discussing x-ray reflections from a series of parallel planes inside the crystal lattice, a common feature is the consideration of the orientation and interplanar spacing of the reflection planes. These planes are defined by three integers (h, k, l), otherwise known as indices. A given set of planes with indices h, k and l split the a-axis into h segments, the b axis into k segments, and the c-axis into l segments. Three examples can be seen below, demonstrating the atomic structure within a unit cell using the Miller Indices described above.

![Figure 24: Three example crystalline lattice structures with their corresponding Miller Indices.](image)

The crystal fraction of analyzed samples can be calculated using equation 4.4.1.

$$X_{C-XRD} = \frac{I_{hkl}}{I_{a} + \kappa_{hkl}I_{hkl}}$$

---

5 Image obtained from [www.scintag.com](http://www.scintag.com), Chapter 7: Basics of X-ray Diffraction. Scintag was acquired by Applied Research Laboratories, a Thermo Electron Company, and link is now dead.
Here, $I_{hkl}$ represents the area under the \{hkl\} crystalline diffraction peak, $I_a$ was chosen as the area under the first diffraction maximum of the appropriately scaled a-Si:H reference diffractogram. The calibration of $\kappa_{hkl}$ corrects for the proportionality between scattering as $\kappa_{hkl} = \frac{I_{hkl}}{I_a}$. Similar to Raman spectroscopy, the crystal size can be calculated using the XRD diagnostic tool. This is done by using the Scherrer’s equation.

$$d_{XRD} = \frac{k\lambda}{(B\cos\theta_B)}$$

(4.4.2)

Where $k$ is 0.9, $\lambda$ is the wavelength of the x-ray radiation (0.154 nm), $B$ is the FWHM of the peaks (in radian units of $2\theta$), and $\theta_B$ is the angular position of the peak.

### 4.5 Transmission Electron Microscopy

A transmission electron microscope is an instrument for observing and analyzing the micro/nanostructure of a thin sample using an adjustable beam of electrons in parallel mode (no raster). A complex electron optical system (utilizing electromagnets) is used to form the electron probe that illuminates the entire area of interest. Several independent lens imaging systems are used to form a real space image or diffraction pattern (reciprocal space) within a wide range of magnifications. The system used to gather images in this work was the JEOL 2010 LaB6 TEM. A schematic of the internal structure of the TEM in Figure 25 shows the complexity of the device discussed.
Figure 25: Cutaway diagram depicting internal components for Transmission Electron Microscope.

The electron beam is generated by thermionic emission from the heating of a lanthanum hexaboride (LaB$_6$) crystal at the very top of the machine. The electron stream is accelerated through a high voltage gradient generated by an external power supply up to 200 kV. The beam is condensed, aligned and astigmatism is removed by a series of quartet aligned electromagnets (in Figure 25 above: gun align, beam align, image align, projector align). The electrons pass through the sample material, creating a unique diffraction pattern. This pattern is converted into an image by the CCD camera and the native software.
Chapter 5: Description of Research Results

Using a combination of TEM, Raman Spectroscopy and XRD, film crystallinity and grain size of the silicon thin films was quantified. Power delivered through the amplifier system and the substrate temperature was varied to produce a series of silicon thin films with varying phase and crystallographic qualities. By performing congruent diagnostics and consulting methods in literature, a best practice procedure is developed.

5.1 Raman Laser Power

When examining a sample specimen with Raman spectroscopy, the first settings one needs to dial in are Raman shift range and laser power. The Raman shift range is given by the grating size used and the center wavenumber selected; 600/nm and 1500 cm\(^{-1}\) for this study. Subsequently, the Raman shift range was between 78 – 1365 cm\(^{-1}\). This allowed observation of all silicon features with good resolution, as well as providing enough non-silicon thin film data to calculate an accurate baseline. This was chosen by referring to the RRUFF standard Raman spectrum data for silicon [20]. A plot of the standard Raman spectrum is shown below in Figure 26. The peak for a pure crystalline sample was found to occur at 520.42 cm\(^{-1}\).
Figure 26: RUFF crystalline silicon reference spectrum

With the central peaked crystallinity information measured and the Raman shift range set, an incident Raman laser power study was carried out to determine the maximum laser power one could use without damaging the silicon film. All analyses were conducted using the LU PLAN Fluorescent x20 Lens in the XY-imaging mode (line scan). This correlates to a 0.5 mm² sampled area on each sample.

Determining the proper laser power required several tests to be carried out on thin films to observe the effects the laser would have on the silicon film. A sample with an initially moderate crystallinity was placed in the Nanophoton Raman sample stage, and was subjected to successive scans from the Raman laser. In Figure 27 below, the crystallinities are plotted for increasing, then decreasing laser powers.
Figure 27: Raman laser power test performed successively in one location. 3-peak method was applied to scans to determine crystallinity.

As the laser power was increased from 0.1 mW, the measured intensity spectra showed less crystalline fraction, reaching a minimum crystalline content of 20% $X_C$ at 5.9 mW. As the laser power was decreased, each repeat data point yielded a similar crystalline fraction.

The same procedure was carried out on an initially amorphous sample with $X_C = \sim 9\%$. As the power was increased from 0.1 mW to 1.2 mW, there was very little change in the calculated crystallinity fraction. At approximately 2 mW, there was a discontinuous increase in crystallinity, but the trend reversed at maximum laser power. When the same data points were taken in reverse order, there was another discontinuous increase in crystalline fraction. At 2 mW, there was a $\sim 27\%$ increase in crystallinity to 49%. Reducing power levels kept the detected crystalline content steady around 50%, never reaching levels before high laser power exposure.
The physical process of crystallinity change observed in Figure 27 and Figure 28 occurs depending on the initial crystalline content of the thin film being analyzed. In higher crystalline content films, the high powered laser penetrates deeper into the sample material, potentially detecting more of the deep amorphous film content, or perhaps even the glass substrate. Once the high power laser is used, the amorphous content in the film is sufficiently energized to allow a reordering of the random growth structures. These reenergized atoms fall into the ordered lattice structure of microcrystalline silicon. This process is essentially annealing films on a microscopic level.

Visible scarring of the sample surface is evident when laser power levels exceed some threshold value depending on the film’s material properties. The visual scarring can be used as a warning for any analyses done with silicon using Raman spectroscopy. The blemishing of the surface can be seen in Figure 29.
Figure 29: An amorphous sample is visually scarred by using high laser powers during Raman spectroscopy. These scans ultimately changed the crystalline content due to reordering of the silicon in the a-Si atomic structure. The top most scan has the lowest power at 0.3 mW and does not visually scar the film.

Upon conclusion of the incident laser power study, 0.3 mW was determined to be the best laser energy level to use for diagnostic procedures since this power level prevented permanent damage to the amorphous content of the silicon film and also had high enough power to probe deep into the films while preventing luminescence of the glass substrate.

5.2 Data Analysis Methodology for Crystal Fraction

Several methods of examining the collected Raman spectra were analyzed and compared. The three methods were Subtraction Method, 2-Peak Method and 3-Peak Method. As time progressed and our experience with Raman and silicon thin films became more refined, The 3-Peak Method clearly became the most accurate and was subsequently employed throughout this effort.

All methods used data collected from the NanoPhoton 11 Raman Spectroscope using the 532 nm laser at the aforementioned optimized laser power of 0.3 mW. The shift range was set to 78 – 1365 cm\(^{-1}\). A 20 second exposure was taken and the collected spectrum was imported into Microsoft Excel. Immediately after collecting the sample spectrum, another spectrum was collected from a reference c-Si standard sample. The standard reference spectrum was used to eliminate any instrumental shifts that could result in
a shift to the collected spectra. The collected reference spectrum was compared to the RRUFF standard reference, and corrections were made to the reference sample curve so that the peaks of both it and the RRUFF spectrum match. This correction was then applied to the measurement of the sample which preceded the reference sample measurement. An example of the correction made is shown below in Figure 30.

![Comparison of Corrected/Original RefSample to RRUFF Standard Spectrum](image)

**Figure 30:** Triple Raman measurements of RRUFF (blue), original reference sample (green) and corrected reference sample (red). The original reference sample is shifted to peak match the RRUFF crystalline silicon sample. Correction made amounted to -3.61 cm$^{-1}$.

Once this correction was calculated and applied to the sample spectrum in question, interpretation of the data while accounting for instrumental drift was achieved. In the example shown above, the correction amounted to -3.61 cm$^{-1}$.

As a final step before calculating crystallinity in the sample, the raw data has to be manipulated to remove the glass coupon contribution to the Raman intensity. A 5th order polynomial fit is applied to the data in
the ranges of 300-400 cm\(^{-1}\) and 600-700 cm\(^{-1}\). The calculated baseline is then subtracted from the initial spectrum, yielding a flat-baseline modified curve. The process is depicted below in Figure 31 through Figure 33.

Figure 31: Spectrum intervals selected for fifth order polynomial baseline fit to isolate silicon phase signal contribution. Intervals are 300-400 cm\(^{-1}\) and 600-700 cm\(^{-1}\) (highlighted in blue).
Figure 32: Fifth order polynomial baseline fit is made and plotted in green.

Figure 33: Fifth order polynomial baseline fit is subtracted from original Raman spectrum. Raman spectrum is now ready for crystalline calculation methods.
This routine was applied to all collected Raman data in order to isolate and remove glass-substrate or contaminant signal contribution to the Raman spectrum.

**Subtraction Method**

Once a corrected sample spectrum was in hand, the first developed method of calculating crystallinity was applied. The subtraction method assumes that an amorphous component will always be a part of any obtained spectrum. This standard amorphous component, once isolated and properly weighted, can be used to subtract the amorphous contribution from any collected spectrum. The remainder of the area under the spectrum curve is then assumed to be a crystalline contribution. The two areas under each fitted curve are calculated and a crystallinity fraction is computed using equation 5.2.1 below.

\[ X_{C-Sub} = \frac{I_{\mu C}}{I_{\mu C} + I_A} \]  \hspace{1cm} (5.2.1)

The Subtraction method is demonstrated below in Figure 34 using the same example that was shown previously in Data Analysis Methodology for Crystal Fraction.
Integrating the areas under the amorphous curve and subtracting it from the total curve by applying equation 5.2.1 yields a crystallinity of 81%.

Figure 34: Subtraction method fits an amorphous phase Gaussian at $480 \text{ cm}^{-1}$ and subtracts that area from the rest of the curve. The remainder of the area is used to compute the crystallinity fraction.

Decomposing the spectrum into two components through subtracting a “typical” normalized a-Si peak has been utilized by some authors beginning the early 1980s. However, there is a growing consensus that there is too strong a variation in the profiles of a-Si. These variations are most commonly found on the low energy side of the transverse optical peak, where longitudinal optical modes are expected [16].
2-Peak Method

The 2-Peak Method is more firmly grounded in theory, as it fits Gaussian curves to the a-Si and μc-Si peaks independently. The crystalline Gaussian fit is rooted to the μc-Si phase peak at 520±3 cm\(^{-1}\), while the a-Si Gaussian fit is left to float in order to minimize the integrated residual value. The fitting procedure iterates until the calculated integral of the residual is minimized. In Figure 35 below, the whole sample scan is plotted in blue (with dots). The μc-Si Gaussian fit is plotted in blue (without dots), a-Si Gaussian fit is plotted in black, total fitted spectrum is plotted in red and the residual is plotted in green.
Figure 35: 2-Peak method is depicted above. The original spectrum is plotted in blue (with dots), amorphous fit is plotted in black, crystalline fit is plotted in blue, and total Gaussian fit is plotted in red. The residual is then calculated and plotted in green.

Integrating the area under the μc-Si, and dividing it by the total area under both Gaussian fits (using equation 5.3.2) we calculate $X_{C} = 30\% \pm 9\%$.

$$X_{2-peak} = \frac{I_{\mu c}}{I_{\mu c} + I_{A}}$$ (5.3.2)
3-Peak Method

The 3-Peak Method builds on the 2-Peak by adding an additional peak between the a-Si and µc-Si. The new peak represents a transition phase of nanocrystalline silicon (nc-Si). The crystalline grain sizes are much smaller than µc-Si, but not as diffuse and unordered as a-Si. This peak is left to float between 500-515 cm$^{-1}$. Its behavior in a PV cell is similar to µc-Si and has almost identical absorption bandgaps.

![Graph showing 3-peak method](image)

Figure 36: 3-peak method shown with a-Si, nc-Si and µc-Si Gaussian fits at 480 cm$^{-1}$, 500-515 cm$^{-1}$ and 520 cm$^{-1}$. (a) Plots the residual remainder of the sample spectra minus the fitted 3-peak Gaussian (b) the sample spectra in red, overlaid with the sum of the 3-peak Gaussian fit (c) the 3-peak Gaussians plotted individually.

As shown above in Figure 36, the whole sample scan is plotted in the middle chart in red, overlaid with the summation of the three Gaussian fits. On the bottom most chart, the three individual Gaussian fits are plotted. The residual (sample spectrum minus 3-peak Gaussian fit) is plotted in chart (a).
Physically, this method best reflects the underlying processes in crystalline film growth. There is a soft transition between a-Si and μc-Si phases, and this is represented by the nc-Si Gaussian curve. It captures the smaller grains that contribute to crystalline-like behavior of the film, but are too small to excite the TO phonon mode restricted to μc-Si.

Integrating the areas under each Gaussian curve, and using equation 5.3.3 below, we calculate a value for $X_C = 61\%$.

$$X_C = \frac{I_{\mu C} + I_{nC}}{I_{\mu C} + I_{nC} + I_A}$$  \hspace{1cm} (5.3.3)

When comparing the three methods discussed in the subsections above, the 3-Peak method proved to be the most robust and accurate method of interpreting Raman data. For highly crystalline samples, the Subtraction Method estimates a reasonable crystallinity, but when a sample has crystalline content closer to 25-55%, the Subtraction Method severely overestimates the amorphous content of the film. This is similar to the 2-Peak Method, which overestimates the a-Si content regardless of the composition the film. Unless otherwise noted, the crystallinity percentages calculated in this paper utilize the 3-Peak Method.

### 5.3 Determining Grain Size

Using Raman spectroscopy also gives the ability to calculate an average crystalline grain size for a given sample. By using the method developed in Chapter 44.3: Raman Spectroscopy, we can use a given spectra to calculate the average micro/nano-crystalline Si grain size.

In order to see the effect of various crystal grains on the Raman spectra, multiple samples were deposited at various temperatures to create different deposition characteristics, which would lead to a variance in the film grain size.
As the temperature was increased from 150° C to 400° C, its effect on crystalline content can be seen below.

**Figure 37:** Raman spectra for Si thin films deposited at various temperatures. Deposition parameters were as follows: 160 W FWD, <3 W RFL, 100 mTorr, 10sccm SiH₄, 400 sccm H₂, 285° C

At temperatures below 150° C, there is no presence of a µc-Si:H peak around 520 cm⁻¹. As substrate temperature increases to 200° C, there is a large peak which develops around the microcrystalline location. As temperature rises, the amorphous contribution to the spectrum drops and the peak becomes more centered around 520 cm⁻¹. Using the 3-peak method, we can calculate the crystallinities of these samples. A demonstration of the procedure is carried out in Appendix A: Raman 3-Peak and 2-Peak Method. For the plot in Figure 37 above, we have calculated and tabulated the crystallinities below in Table 3.
Table 3: Calculated crystallinity and grain size values for Si thin films deposited under varying substrate temperatures

Also included in Table 3 are the calculated grain sizes. An example of one of these calculations is shown in Appendix B: Raman Crystal Size Example. If we plot the change in crystal size as a function of substrate temperature, we can see there is an optimal growth regime occurring ~350°C. Temperatures above this result in a decreasing grain size. A graphical representation of this trend is shown below in Figure 38.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Xc</th>
<th>FWHM [cm-1]</th>
<th>Peak Location [cm-1]</th>
<th>Δω [cm-1]</th>
<th>Raman Crystal Size d [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.2%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>26.2%</td>
<td>10.252</td>
<td>516.92</td>
<td>3.4993</td>
<td>4.8</td>
</tr>
<tr>
<td>250</td>
<td>52.0%</td>
<td>9.5669</td>
<td>518.1</td>
<td>2.3193</td>
<td>5.8</td>
</tr>
<tr>
<td>285</td>
<td>56.4%</td>
<td>9.5084</td>
<td>518.33</td>
<td>2.0893</td>
<td>6.1</td>
</tr>
<tr>
<td>350</td>
<td>62.5%</td>
<td>9.1941</td>
<td>518.65</td>
<td>1.7693</td>
<td>6.7</td>
</tr>
<tr>
<td>400</td>
<td>58.9%</td>
<td>9.4276</td>
<td>518.44</td>
<td>1.9793</td>
<td>6.3</td>
</tr>
</tbody>
</table>
A corollary to using the Raman data is to examine all the samples with XRD and perform a similar analysis. The XRD spectra are plotted for the same samples below. They are offset for easier viewing.

![XRD Spectra](image)

**Figure 39:** XRD Spectra for Si thin films deposited at various temperatures. Process parameters are identical to samples in Figure 38

At 150° C, there is a very strong amorphous background spectrum, indicating a complete lack of microcrystalline structures in the sample. As the temperature increases, a peak emerges at ~28° (indicating a 111 orientation). At 250° C, the 220 and 311 crystallographic orientations become apparent. At 350° C, the peaks become more resolved, but further increases in temperature have little effect.

By using the Scherrer’s equation (equation 4.4.2), we can calculate and plot the grain size as calculated by XRD analysis. This is carried out on three peaks detected by the XRD machine: 111, 220 and 311 crystallographic orientation.
Figure 40: XRD calculated grain sizes plotted for Si thin films deposited at various temperatures.

The 111 orientation growth is the preferred growth orientation. This is due to the 111 oriented surface being the lowest energy state a Si atom can occupy. Having an uncontaminated, high vacuum chamber allows the Si to migrate along the substrate surface before the arrival of another Si atom. The term “preferred growth” has supplanted “preferred orientation” because the latter was borrowed from the community’s understanding of sample preparation by powder compaction, while the former has the physical meaning of highly mobile atoms along a surface falling into low energy potential wells. Since growth of the 111 orientation is preferred, it dominates the other orientations. Furthermore, in a high vacuum system, the probability of growth on an already nucleated grain is larger than the nucleation (and growth) of a new grain structure.

The grain size calculated by Raman is about 2x lower than the grain size calculated by XRD. This is because Raman analyzes the bulk film material with a much larger penetration depth, whereas the XRD
peak analysis is conducted on one specific grain orientation, focused on a very small depth near the surface of the film. The tables with the specific grain sizes for each orientation are tabulated below.

Table 4: Calculated values using XRD on Si thin films at various temperatures for 111 crystallographic orientation.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Location [cm-1]</th>
<th>FWHM Deg [cm-1]</th>
<th>Deg Corrected</th>
<th>Rad</th>
<th>XRD Crystal Size d [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>28.124</td>
<td>2.1089</td>
<td>4.35745921</td>
<td>0.036432924</td>
<td>4.3</td>
</tr>
<tr>
<td>250</td>
<td>28.399</td>
<td>0.55082</td>
<td>0.213402672</td>
<td>0.00806264</td>
<td>19.5</td>
</tr>
<tr>
<td>285</td>
<td>28.379</td>
<td>0.48443</td>
<td>0.144672425</td>
<td>0.006638504</td>
<td>23.7</td>
</tr>
<tr>
<td>350</td>
<td>28.415</td>
<td>0.51806</td>
<td>0.178386164</td>
<td>0.007371535</td>
<td>21.4</td>
</tr>
<tr>
<td>400</td>
<td>28.411</td>
<td>0.48819</td>
<td>0.148329476</td>
<td>0.006721885</td>
<td>23.5</td>
</tr>
</tbody>
</table>

Table 5: Calculated values using XRD on Si thin films at various temperatures for 220 crystallographic orientation.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Location [cm-1]</th>
<th>FWHM Deg [cm-1]</th>
<th>Deg Corrected</th>
<th>Rad</th>
<th>XRD Crystal Size d [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>47.412</td>
<td>1.7924</td>
<td>3.12269776</td>
<td>0.030841987</td>
<td>6.6</td>
</tr>
<tr>
<td>285</td>
<td>47.401</td>
<td>1.4654</td>
<td>2.05739716</td>
<td>0.025034357</td>
<td>8.2</td>
</tr>
<tr>
<td>350</td>
<td>47.437</td>
<td>1.4713</td>
<td>2.07472369</td>
<td>0.02513955</td>
<td>8.2</td>
</tr>
<tr>
<td>400</td>
<td>47.474</td>
<td>1.7413</td>
<td>2.94212569</td>
<td>0.029936979</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Table 6: Calculated values using XRD on Si thin films at various temperatures for 311 crystallographic orientation.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Location [cm-1]</th>
<th>FWHM Deg [cm-1]</th>
<th>Deg Corrected</th>
<th>Rad</th>
<th>XRD Crystal Size d [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>56.052</td>
<td>1.7087</td>
<td>2.82965569</td>
<td>0.029359196</td>
<td>8.5</td>
</tr>
<tr>
<td>285</td>
<td>56.097</td>
<td>1.2921</td>
<td>1.57952241</td>
<td>0.021935133</td>
<td>11.3</td>
</tr>
<tr>
<td>350</td>
<td>56.084</td>
<td>1.5309</td>
<td>2.25365481</td>
<td>0.026201193</td>
<td>9.5</td>
</tr>
<tr>
<td>400</td>
<td>56.101</td>
<td>1.2891</td>
<td>1.57177881</td>
<td>0.021881298</td>
<td>11.4</td>
</tr>
</tbody>
</table>

At lower temperatures, the rate of growth and total content of the higher order crystallographic orientations is so small that the XRD machine cannot resolve the small signals above the noise.

These measurements were then corroborated with TEM scans to see how accurate Raman and XRD techniques are. Images were taken using the JEOL 2010 LaB6 TEM at 120 kV of acceleration voltage.
Figure 41: TEM image taken of silicon thin film deposition at 150°C, 160 W FWD power, 5 sccm of SiH₄, 100 mTorr total pressure. Grain sizes are an average size of 6-10 nm in diameter.

Figure 42: TEM image taken of silicon thin film deposition at 200°C, 160 W FWD power, 5 sccm of SiH₄, 100 mTorr total pressure. Grain sizes are an average size of 6-9 nm in diameter.
Figure 43: TEM image taken of silicon thin film deposition at 250° C, 160 W FWD power, 5 sccm of SiH$_4$, 100 mTorr total pressure. Grain sizes are an average size of 11-15 nm in diameter. The image is darker due to the prepared film being slightly thicker than previous images.

Figure 44: TEM image taken of silicon thin film deposition at 300° C, 160 W FWD power, 5 sccm of SiH$_4$, 100 mTorr total pressure. Grain sizes are an average size of 12-16 nm in diameter. Dark spots are nucleation sites for grain structures which grow out of the film. These have grown up and out of the film, resulting in poor focus on them. These become more prevalent under deposition parameters more conducive to crystalline growth.
Figure 45: TEM image taken of silicon thin film deposition at 350° C, 160 W FWD power, 5 sccm of SiH₄, 100 mTorr total pressure. Grain sizes are an average size of 18-19 nm in diameter. Dark spots are nucleation sites for grain structures which grow out of the film. These have grown up and out of the film, resulting in poor focus on them. These become more prevalent under deposition parameters more conducive to crystalline growth.

Figure 46: TEM image taken of silicon thin film deposition at 400° C, 160 W FWD power, 5 sccm of SiH₄, 100 mTorr total pressure. Grain sizes are an average size of 15-18 nm in diameter. Dark spots are nucleation sites for grain structures which grow out of the film. These have grown up and out of the film, resulting in poor focus on them. These become more prevalent under deposition parameters more conducive to crystalline growth.
It is crucial to note that TEM interacts with the electronic structure of individual atoms, and thus does not differentiate between amorphous or crystalline structures. Raman and XRD interact with repeating, organized atomic lattice structures which generate specific phonons or resonate with the excitation wave. Thus in the pictures above, it is not possible to differentiate between a-Si and μc-Si grains.

Figure 41 through Figure 46 support the trend observed with Raman and XRD. The average grain size was measured using Iconico OnScreen calipers calibrated to the legend in the bottom left corner of each image. There is a natural variability in the grain size, as the seeding and initial growth phase is non-uniform due to surface inconsistencies on the sample substrate.

For the 150° C case in Figure 41, there are grain structures 6-10 nm in diameter. These grains were undetected by Raman and XRD, meaning that they were purely amorphous in content. As the temperature increased, grain sizes grew to a maximum of 18-19 nm at 350° C. Increased temperatures allow deposited Si atoms to be more mobile along a growing grain surface. This both enhances crystallinity and increased growth rate, allowing larger grains to be formed before another seed begins.

At 400° C, the trend turns over and grains become smaller again. This is in part due to an enhancement of preferred etching by H radicals in the plasma during deposition. The H radicals generated from the cracking of the SiH₄/H₂ precursor gas act as an etchant on the surface of the developing film. As temperatures are increased, this effect is amplified.

5.4 Tandem Silicon Structure

As a final demonstration of the capabilities of the MSWP, a tandem amorphous and microcrystalline film was deposited. A one micron thick layer of μc-Si:H was deposited on a one micro thick layer of a-Si:H. The growth of the film took place in one continuous deposition run, meaning the plasma was on continuously. The total pressure was kept 100 mTorr, at a substrate temperature of 285° C, at a gap distance of 1”. The flowrate for SiH₄ was kept to 30 sccm (330 sccm of H₂) for deposition of a-Si:H.
Once a micron layer was achieved, the SiH\textsubscript{4} flowrate was reduced to 10 sccm (335 sccm of H\textsubscript{2}) for deposition of μc-Si:H.

The sample was cleaved and Whink solution was used as a wet chemical etch to prepare the cleave surface. The SEM image of this surface can be viewed below in Figure 47.

![SEM Image](image.png)

**Figure 47:** Tandem phase silicon deposition of microcrystalline above an amorphous silicon thin film. The tandem phase films sit atop a glass substrate, shown at the base of the image.

Identical tests were carried out to measure the deposition rate during each silicon phase deposition step. The thicknesses of deposited films were measured using profilometry on a partially masked sample. The deposition lengths were timed in order to calculate a deposition rate. For μc-Si:H, a deposition rate of 3.1 nm/s was achieved. For a-Si:H, a deposition rate of 7.3 nm/s was achieved.
Chapter 6: Conclusion

In the effort to create more efficient Si solar cells, tandem junction PV devices need to be made. Tandem junction cells capture more of the sun’s energy by combining two or more mismatched bandgap materials. A promising material for tandem junction cells is silicon. In the microcrystalline phase, Si absorbs low energy photons (red to infrared). While in the amorphous phase, Si absorbs high energy photons (green to UV). Combining these two distinct phases of Si into one film deposited in one process would be a boon to the PV industry; allowing a reduction in costs, increase in cell efficiency and an improvement in production throughput.

In demonstrating the metal surface wave plasma source as an ideal source for multiphase silicon deposition, a method to evaluate the films was needed. Diagnostic tools such as TEM, SEM, ellipsometry and XRD were evaluated. TEM and SEM require long sample preparation times and give qualitative film data. Ellipsometry requires prior knowledge of the film material in order to build a model, with which experimental data can be used to back out film features. XRD also requires long data collection times to acquire spectra with good resolution and accuracy.

The best option was identified as Raman Spectroscopy, as it allows quick data collection (~20 seconds) and has excellent penetration depth depending on the adjustable laser power. A method was then needed to interpret the sample specific spectrum to determine volumetric phase percentage in order to optimize deposition parameters.

Subtraction, 2-peak Gaussian and 3-peak Gaussian fit methods were examined. It was found that the Subtraction method over estimates the crystalline content of a given film. This is because a normalized a-Si fit peak is unable to accurately capture the variances of samples. The 2 peak method drastically underestimates the crystalline content of the film. It fails to capture the nanocrystalline content of a given Si thin film. The 3-peak method was found to be the most accurate technique to calculate film crystallinities when comparing values to XRD.
A method was also devised to determine grain sizes in Si thin films using Raman Spectroscopy. By collecting spectra from a standardized silicon wafer before and after measuring the Si thin film sample, we were able to determine the μc-Si peak shift with great accuracy. Once the peak of the spectrum was found, it was compared to a standard spectrum attained from RRUFF. The locations of the peaks were compared, and a peak shift was calculated. This peak shift was then used to calculate grain size using equation 4.3.2.

By comparing the results with TEM images, it becomes evident that Raman spectroscopy using a 3-Peak Method of analysis is a superior diagnostic method when compared to ellipsometry or XRD. This is due in large part to the reduction of sample preparation time, obviation of vacuum systems, and the ability to create a simple quantitative analytical method to analyze large batches of samples.

Throughout the course of the study, it is shown that MSWPs are capable of depositing highly crystalline and highly amorphous silicon thin films. Furthermore, it is quantitatively shown that the crystalline thin films have large grain sizes. These large grains are vital to cell efficiency, as they reduce the number of grain boundaries. Grain boundaries act to reduce charge carrier lifetime, thus bringing down overall efficiency.
Chapter 7: Future Work

The metal surface wave plasma generates high electron densities, which allow it to deposit both amorphous and microcrystalline silicon quickly. MSWPs also have low electron temperatures, meaning that ion acceleration in the sheath impinging on the sample surface is kept very close to the plasma potential. This property of MSWPs was largely unexplored in this study, and remains to be quantitatively proven.

Sample films were deposited to conduct electron paramagnetic resonance (EPR) studies, but the limitations on the sample size dimensions presented a significant challenge. Devices available to conduct our studies accepted very small sample coupons. With a limited sample size, our films were unable to generate a large enough signal above noise to interpret confidently.

EPR works by detecting dangling bonds in a material. The dangling bonds present in a PV thin film are structural dislocations in the atomic lattice or dangling Si bonds between grains in the film. These dangling bonds are intended to be hydrogenated by the H radicals generated in the plasma, thus preventing a drop in cell efficiency. If a bond is not hydrogenated, it provides a location for charge carriers to reabsorb into the film, thus dropping the current and reducing efficiency.

By conducting EPR, one can measure the dangling bond density of a film, and have a quantitative measurement of film quality. This allows greater feedback into parameter optimization to deposit high quality, highly crystalline thin films. The reduction of dangling bonds also reduces the effect of the Staebler-Wronski effect (a drop in initial cell efficiency over time due to light induced degradation).

Further work should be continued to rectify minor differences in the measured and calculated crystallinities and grain sizes from TEM, XRD and Raman spectroscopy. Ideally, identical samples from a single deposition would be used iteratively with each tool. In this study, multiple depositions were carried out under similar parameters, which were then used for each tool respectively. This methodology was employed due to the limitation of sample size accepted by the TEM device.
A final objective, which is within reach but out of the immediate scope of this study, is to create a complete cell to measure a real efficiency of a device created using MSWPs. Steps were taken toward accomplishing this, but due to limited progress, completed results cannot be included in this work.

Creating a completed cell would provide the most accurate benchmark by which to compare the efficacy of MSWPs to deposit high quality films for solar PV. O-carborene was purchased and utilized to dope films (p-type). N-type doped wafers were purchased to deposited films on. An in-situ sputtering device was installed to deposit aluminum, and silver ink was acquired for front body contacts. As work progresses towards a completed cell, a final device efficiency measurement would prove a great boon to displaying the capabilities of the MSWP.
Appendix A: Raman 3-Peak and 2-Peak Method

Two approaches were explored for the analyzing of collected Raman spectra. The two methods had been used in the literature, though ultimately, the 3-Peak method proved to be more accurate and robust. The 2-peak method assumes that the Raman laser excites two phonon modes. One from the amorphous content at 480 cm\(^{-1}\) and another from the µc-Si at ~520 cm\(^{-1}\). Though this provides a good estimate of the crystalline content, it is inferior to the 3-peak method.

The 3-peak method is more physical accurate since it takes into account a range of crystal size growths which occur during film deposition. In addition to the 2-peaks mentioned above, a third is added at ~505 cm\(^{-1}\) in order to represent smaller, more diffused crystal grains which are scattered throughout the film material.

A comparison of the two methods is shown below.
The 2-peak method tends to underestimate the crystallinity fraction of analyzed films since it fails to accommodate smaller crystal grains. These smaller grains excite shorter phonon modes, which cause the crystalline curve to bow out to the left, toward the amorphous peak. This bow can be seen more neatly in the analyzed spectrum below. The spectrums are identical, but a much more accurate fit is obtained when accounting for the non-uniformity of microcrystals in the silicon film.
Appendix B: Raman Crystal Size Example

Once the Raman spectrum for a given sample is analyzed using the 3-Peak method in Appendix A: Raman 3-Peak and 2-Peak Method, we can analyze the spectra further to back out a grain size estimate.

Then by using equation 3.3.2

$$d_{\text{Raman}} = 2\pi \sqrt{\frac{B}{\Delta \omega}}$$

We can plug in the peak shift of the µc-Si:H peak at ~520 cm$^{-1}$. For the example given above, we have a peak located at: µc-Si:H = 518.65 cm$^{-1}$. The standard reference c-Si peak collected before this sample was centered at 520.4193 cm$^{-1}$, resulting in a peak shift of $\Delta \omega = 1.7693$ cm$^{-1}$.

We can plug these values into equation 3.3.2 and get a $d_{\text{Raman}}$ value as calculated below.
\[ d_{Raman} = 2\pi \sqrt{\frac{2.0 \text{ cm}^{-1} \text{ nm}^2}{1.7693 \text{ cm}^{-1}}} = 6.68 \text{ nm} \]
Appendix C: XRD Crystal Size Example

Once a sample is deposited, it is taken to the XRD Xpert 2. A glancing angle $2\theta$ scan is performed using a spot size of 1 mm x 5 mm with a nickel filter. The spectrum acquired from a predominately microcrystalline sample looks similar to the example spectrum shown below (100 mTorr, 400 C, 160 W, 1” gap, 10 sccm SiH$_4$).

Once the spectrum is collected, it is converted into a .csv file and imported into Igor Pro 6.3. Once in Igor, the data can be manipulated, have the baseline removed and fitted.
The $<111>$ peak is isolated and a fifth order polynomial is used to fit the amorphous glass sample baseline (area highlighted in blue). The baseline is green. This is then subtracted from the spectrum to get a pure spectrum from the crystalline content of the sample. The spectrum with the baseline removed is shown below.
Once we have the pure crystallographic contribution to the spectrum, we can fit the data using a Gaussian fitting routine native to Igor.
The fitting procedure iterates itself to minimize the residual left from the subtraction of the real data by the fitted plot. The fitting routine iterates this process until the residual is unable to be minimized further. The statistics of the fitted Gaussian are then displayed neatly in a new window (labeled “Multipeak Fit 2 Results” shown in the picture above). The values important to the crystal size calculation are: the peak location and the FWHM of the Gaussian fit.

From the example above, we have a peak location of 28.411° and a FWHM of 0.81289°. We can then apply the Scherrer’s Equation:

$$d_{XRD} = \frac{k \lambda}{(B \cos \theta_B)}$$

Where k is 0.9, λ is the wavelength of the x-ray radiation (0.154 nm), B is the FWHM of the peaks (in units of 2θ), and θ_B is the angular position of the peak.

$$d_{XRD} = \frac{(0.9)(0.154 \text{ nm})}{(0.81289 \times \frac{\pi}{180}) \cos \left(28.411 \times \frac{\pi}{180}\right)} = 11.12 \text{ nm}$$

This grain size is valid only for crystals in the 111 orientation. A similar treatment is undertaken for the 220 and 311 orientations.
Appendix D: Gas Plumbing Subsystem Diagram
Appendix E: Igor 3-Peak Fitting Code

#pragma rtGlobals=1 // Use modern global access method.

//include ".\TN020 Procedures"
//include ".\Multi-peak Fitting 2.0"

Macro RamanBaselineSubtraction()
    if( exists("g_w") == 0 )
        InitPeakMacros()
    endif
    TN020BStartup_Raman()
End

Proc TN020BStartup_Raman(w)
    String w=g_w
    Prompt w,"Select Y-Wave for Analysis:" ,popup, WaveList("S*",";","Text:0")
    Silent 1;PauseUpdate
    InitializeMostEverything_Raman(w,"Wavenumber_cm_1_","_None_;")
    InitBaseLineFit_Raman(w,"Wavenumber_cm_1")
    AddRegionToFit_1()
    AddRegionToFit_2()
    FitBaselineAtRegions_Raman(w,"Wavenumber_cm_1_","W_BaselineFit","_New_;")
End

fStartMultipeakFit2()

    SetAxis left 0,100
    SetAxis bottom 300,700
End

Proc InitializeMostEverything_Raman(w,wx,wb)
    String w=g_w,wx=g_wx,wb=g_b
    Silent 1;PauseUpdate
    g_wx=wx; SBs(wb)
    if( exists(w) != 1 )
        Abort "Wave "+ w+" doesn't exist!"
    endif
    g_w=w
    Redimension/D $w
    SameLen(w,"W_BaseRegion");W_BaseRegion=NaN;SameLen(w,"W_AreaRegion");W_AreaRegion=NaN
    Mk("W_EstAmpsY",2);Mk("W_EstCentersX",2);Mk("W_EstWidthsX",2);Mk("W_EstCentersP",2);Mk("W_EstEdgesP",4);
    Mk("W_AreaNoBase",2);Mk("W_AreaX1",2);Mk("W_AreaX2",2);
    Mk("W_BasePM",2);Mk("W_PeakPM",2)
    if(exists(wx)==1)
        Redimension/D$wx
    endif
    if(exists(wb)==1)
End
Redimension/D $wb

AppWv_Raman(w,wx,"");HideAreaTags()

End

Proc AppWv_Raman(w,wx,ax)
    String w,wx,ax
    String wn=WinName(0,1)
    Variable inGraph=0
    //
    if(strlen(wn)==0)
        ax = "Display ">
        if(exists(w)==1)
            ax+=GetWavesDataFolder($w,2)
        endif
        //
    else
        //
        DoWindow/F $wn
        //
        ax="AppendToGraph"+ax+" ">
        if(exists(w)==1)
        //
            ax+=GetWavesDataFolder($w,2)
        //
            CheckDisplayed/W=$wn $w
        //
            inGraph= V_Flag != 0
        //
        endif
        //
        endif
        //
        if(exists(w)==1)
            if( !inGraph )
                if( ?inGraph )
                    ax=+" vs "+GetWavesDataFolder($wx,2)
                endif
            endif
        Execute ax
        ColorWaves()
    endif
    endif
End

Proc InitBaseLineFit_Raman(w,wx)
    String w=g_w,wx=g_wx
    Silent 1;PauseUpdate
    g_w=w;g_wx=wx
    fbar_wr="W_BaseRegion"
    SameLen(w,"W_BaseRegion");AppWv("W_BaseRegion",wx,"");Modify
    mode(W_BaseRegion)=1;W_BaseRegion=NaN;AppCrs(w)
End

Proc AddRegionToF1_1()
    Silent 1;PauseUpdate
    variable i=CalculateFitRegionLow_1()
    variable j=CalculateFitRegionHigh_1()
    CheckTwo Cursors(g_w);W_BaseRegion[i,j]=$g_w[p]
End
Proc AddRegionToFit_2()
    Silent 1;PauseUpdate
    variable i=CalculateFitRegionLow_2()
    variable j=CalculateFitRegionHigh_2()
    CheckTwoCursors(g_w);W_BaseRegion[i,j]=$g_w[p]
End

Proc FitBaselineAtRegions_Raman(w,wx,wr,fit)
    String w=g_w,wx=g_wx,wr=fbar_wr,fit=fbar_fit
    Silent 1;PauseUpdate
    g_w=w;g_wx=wx;fbar_wr=wr;fbar_fit=fit
    ChkLen(w,wx);ChkLen(w,wr)
    String ow="W_BaselineFit", wtmp="W_tmp", opts="", SameLen(w,ow)
    Variable tt=0, typ=floor(strsearch(S_funcs,fit,0)/10)
    if (exists(wx)==1)
        opts+="/X="+wx
    endif
    if (exists(wr)==1)
        Dup(wr,wtmp)
        $wtmp=(numtype($wtmp)==0)
        opts+="/W="+wtmp
        ar_ex=3
    else
        ar_ex=1
    endif
    tt=str2num(fit[7,8])-1
    String command="CurveFit "+fit[1,7]+"", $w"+opts
    Execute command
    KillWv(wtmp)
    Mk("W_BaseCoefs",2);W_BaseCoefs={NaN,K0,K1,K2,K3,K4};Redimension/N=(2+tt)
    W_BaseCoefs
    Mk("W_BasePM",2);W_BasePM={1,0,numpnts($w)-1,typ,tt};Dup("W_BasePM","W_PM")
    if (exists(wx)==1)
        $ow=PolyMorph(W_BaseCoefs,$wx[p])
    else
        $ow=PolyMorph(W_BaseCoefs,x)
    endif
    AppWv(ow,wx,"")
    SBs(ow)
    ar_wfit=ow
    ar_ow=ow+"Res"
End

Proc SubtractBaseline_Raman(w,wx,wb,ow)
    String w=g_w,wx=g_wx,wb=rb_b,ow=rb_ow
    Silent 1;PauseUpdate
    g_w=w;g_wx=wx
    ChkLen(w,wx);ChkLen(w,wb)
    String cw,dcw,tcw="W_tmp0",tdcw="W_PM"
if(exists(ow)!=1)
    NewWv(w, "NoBase"); ow=S_Wave
else
    SameLen(w, ow)
endif
rb_ow=ow
if(exists(wb)!=1)
    cw="W_BaseCoefs"
dcw="W_BasePM"
    if(numtype($dcw[1])!=0)
        Abort "Run Fit Peaks first!"
    endif
endif
    Variable terms=$dcw[4],s=$dcw[1],e=$dcw[2],funcs=$dcw[0]
    Dup(cw, tcw); Redimension/N=(2+terms) $cw
    Dup(dcw, tdcw); Std$dcw[0]=1
    wb="W_tmp"; SameLen(w, wb); $wb=NaN
    if(exists(wx)==1)
        $wb[s,e]=PolyMorph($tcw, $wx[p])
    else
        $wb[s,e]=PolyMorph($tcw, x)
    endif
endif
$ow=w-$wb
AppWv(ow, wx, ""), ModifyGraph zero(left)=1
KillWv(wb); KillWv(tcw)
g_w=ow
SBs("_None_"
End

///////////////////////////////////////////////////////////////////////
////////////
//
///////////////////////////////////////////////////////////////////////
Functions for Calculating Area for Baseline Fit

Function CalculateFitRegionLow_1()
    variable i
    wave Wavenumber_cm_1_
    for (i=0; i<numpnts(Wavenumber_cm_1_); i+=1)
        if (Wavenumber_cm_1_[i]>300)
            break
        endif
    endfor
    return i-1
End

Function CalculateFitRegionHigh_1()
    variable i
    wave Wavenumber_cm_1_
    for (i=0; i<numpnts(Wavenumber_cm_1_); i+=1)
        if (Wavenumber_cm_1_[i]>350)
            break
        endif
endfor

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Function CalculateFitRegionLow_2()
    variable i
    wave Wavenumber_cm_1_
    for (i=0; i<numpnts(Wavenumber_cm_1_); i+=1)
        if (Wavenumber_cm_1_[i]>550)
            break
        endif
    endfor
    return i-1
End

Function CalculateFitRegionHigh_2()
    variable i
    wave Wavenumber_cm_1_
    for (i=0; i<numpnts(Wavenumber_cm_1_); i+=1)
        if (Wavenumber_cm_1_[i]>700)
            break
        endif
    endfor
    return i
End
References


