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Plasma-deposited polycrystalline silicon film growth and characterization

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Award date:
2012

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Plasma-deposited polycrystalline silicon
Film growth and characterization

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September 2011 - July 2012
PMP 12-07

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Abstract

Polycrystalline silicon thin-film solar cells are considered to be a recognized route for low-cost photovoltaics. Absorber layers consisting of polycrystalline silicon aim to combine the high efficiency of wafer-based silicon solar cells with the low-cost manufacturing typical of thin-film technology. However, polycrystalline silicon solar cells require a relatively thick absorber layer of typically \( \sim 2 \) \( \mu \)m, while on the other hand conventional deposition techniques like PECVD and HWCVD exhibit a low deposition rate on the order of 1 nm/s. Therefore, an alternative deposition technique capable of attaining high polycrystalline silicon deposition rates, while maintaining a high film quality, is highly desirable. To this end, the feasibility of depositing polycrystalline silicon by an expanding thermal plasma (ETP), which has proven to be able to deposit various other functional thin films at high deposition rates (1-60 nm/s), is investigated in this thesis.

The work in this thesis has been guided by three main research topics. First, since the deposition of polycrystalline silicon was never achieved in ETP, feasibility studies were carried out. Two approaches for poly-Si deposition were undertaken, i.e. an alternative method in which film deposition is alternated with an atomic hydrogen treatment and, secondly, a high-temperature route. The high-temperature route (>600 °C) proved to lead to poly-Si deposition at a deposition rate up to 18 nm/s. Additionally, from these studies, the role of growth radicals present in the plasma in poly-Si film deposition has been elucidated.

The second part of the thesis focuses on a fundamental understanding of the development of crystal grains in poly-Si films. With the use of in-situ and ex-situ characterization techniques, various phases of film growth have been identified. It was found that the initial film growth consists of an amorphous incubation layer, typically 100-400 nm thick. After this thickness, a structural relaxation of the amorphous silicon surface takes place due to a build-up of stress, which leads to the formation of crystalline nuclei. From these nuclei, crystalline film growth proceeds in a columnar fashion, with a strong preferential (220) crystal orientation. Since depositions are carried out at an elevated temperature, there is ample thermal energy for the amorphous network in the incubation layer to relax to the crystalline state, leading to the formation of small randomly-oriented grains within this incubation layer.

Thirdly, the possibility of applying ETP-deposited poly-Si films in a p-i-n solar cell configuration was initiated. For the determination of the optimal poly-Si film properties for solar cell applications, the absorbance of these layers was characterized. More precisely, the role of film thickness and surface roughness in spectral absorbance was highlighted. Additionally, since film roughness is crucial for light trapping purposes, the interplay between deposition conditions and roughness was elucidated. Based on the developed understanding, a few deposition conditions have been selected for the production of p-i-n solar cells in collaboration with the Helmholtz institute in Berlin.
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Chapter 1

Introduction

1.1 The terawatt challenge

The current world energy consumption, which is at a staggering 15 TW, is dominantly based on fossil fuels.[1] Over the past decades there has been a growing consensus on the need to switch to alternative sources of energy, motivated by various factors; The world energy consumption is increasing rapidly, which can be attributed in particular to the enormous economic and population growth in India and China. This trend is opposite to the depletion of fossil fuels, particularly oil and natural gas. Additionally, the dependence of (mostly) the Western countries on foreign energy sources poses a political risk. And finally, there is the worldwide problem of climate change, which is induced by the $\text{CO}_2$ released during the combustion of fossil fuels. The tragedy of climate change is that it mostly affects the developing countries, whereas the rich are responsible for most of the $\text{CO}_2$ production.

The considerations shown above clearly indicate that there is an urgent need for an increased contribution of non-fossil, renewable energy sources to the world energy production. In order for renewables to make a significant contribution in the foreseeable future, their power output will have to increase to the order of terawatts in the next few decades: the terawatt challenge.[2]

As it can be seen in figure 1.1, the current contribution of renewables to the energy mix is minor. Although hydroelectric power is a very cheap and reliable energy source, there has been little increase in its production over the last decade. The simple reason for this is that most places where hydroelectric power generation is feasible have already been exploited. The combustion of biofuels and waste has the largest contribution of the renewables, but it should be noted that this mostly stems from rural cooking activities in third-world countries.

Although the contribution of other renewables like geothermal, wind and solar energy is currently negligible, their share will increase in the near future. It has been estimated that biomass, wind and geothermal energy can only practically contribute up to 10 TW.[3] On the other hand, more than $10^5$ TW of solar power strikes the Earth, of which it is estimated that 600 TW can technically be harvested.[1] Therefore photovoltaics (PV)
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Figure 1.1: The global energy production as obtained from the International Energy Agency website. Mtoe denotes million tonnes of oil equivalent, which is a unit of energy. 1 Mtoe ≈ 42 GJ.

is an eligible candidate to meet the terawatt challenge.

1.2 The current status of photovoltaics

In 1954, Chapin et al. from Bell Labs presented the first crystalline silicon solar cell. Since then, crystalline silicon has been the mostly-used material for solar cells. The contribution of PV to the world energy supply has remained negligible for over 60 years after the production of the first solar cell. The main reason is that the energy cost of solar cells has been unable to compete with electricity from the grid. However, in the last decade there has been a true revolution in the production of solar cells, as can be seen in figure 1.2. This can mostly be attributed to two factors. Firstly, innovations in solar cell design and production lead to higher efficiency and/or lower cost per Wp. Secondly, the introduction of very successful financial incentives, most notably the German feed-in tariff system, made PV financially attractive for consumers. This newly-created huge market, supported by a guaranteed long-term financial incentive, formed a suitable environment for a solid base of PV companies to originate. Competition between these companies and economies-of-scale have driven the PV cost down drastically, with the current spot price being below 1 €/Wp. However, recent cuts in subsidies (e.g. Germany, Italy) have drastically reduced the demand, bringing many companies to bankruptcy. This

1 Wp (Watt-peak) is a measure of the nominal power a solar cell delivers under standardized conditions, i.e. an irradiance of 1000 W/m², an AM1.5 spectrum and a cell temperature of 25 °C.

demonstrates that PV will need to become cost-competitive (i.e. to achieve grid-parity) without financial incentives.[5]

![Figure 1.2: The global installed PV capacity, as reproduced from the 2011 Market Report of the EPIA.][6] The figure for 2011 is an estimate.

The major cost of mono- and multicrystalline solar cells resides in the silicon material use. The production of crystalline silicon is an energy-intensive process and up to 50% of the material is lost during wafer sawing, known as kerf loss. Moreover, wire-sawing can currently only obtain thicknesses down to a minimum of 180 µm, whereas only 40 µm is needed for sufficient light absorption. Green et al. calculated that even for a c-Si film of only 1 µm an efficiency of ∼20% can be obtained when advanced surface passivation and light trapping schemes are employed.[7] This indicates that major advances in the price/W_p ratio can be made for silicon solar cells by going to thinner films.

Several thin film techniques strive to reduce the cost per W_p by decreasing the material consumption. Also, most thin films can be applied on low-cost substrates like polymer foils, glass and stainless steel. The versatility in substrate material and even the availability of flexible substrates greatly enhances the applicability of PV, for example the integration in buildings and even clothing.

Figure 1.3 shows the market shares of the dominant solar cell types as of 2009. Although the crystalline silicon technologies still have the major market share, thin film solar cells have gained momentum in the past decade. Especially CdTe solar cells have a considerable share, although there are environmental concerns because of the use of the heavily-toxic cadmium. Also CI(G)S (Copper Indium (Gallium) Sulfide) solar cells

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[6]: Image linking to Figure 1.2
[7]: Image linking to Figure 1.3
CHAPTER 1. INTRODUCTION

are receiving a lot of attention, especially since relatively high efficiencies of almost 20% can be achieved.

The remaining thin-film solar cells are silicon-based. Amorphous silicon (a-Si:H) photovoltaics is a rather mature technique, with efficiencies reaching up to 10%.[8] Because of the maturity of this type of solar cell and the fundamental properties of a-Si:H little gain in efficiency is to be expected.

Ribbon silicon refers to wafers of silicon that are made directly by crystallization from a silicon melt crucible. There are various ribbon Si growth processes, but all involve the slow extraction of the silicon wafer from the melt. Due to a controlled temperature gradient, the wafer is grown by crystallization from the melt. Typical wafer thicknesses are in the range of 200-300 µm with grain sizes up to the millimeter range. In contrast to wafers made from ingots, no wafer sawing takes place which leads to a more efficient silicon usage. Among the mostly-used silicon ribbon growth techniques are edge-defined film-fed growth (EFG), string ribbon (SR) and ribbon growth on substrate (RGS). Despite the lower crystal quality and higher impurity concentrations compared to ingot-based wafers, relatively high efficiencies of 18% for lab-made cells and 16% for industrial cells.

1.3 Thin film crystalline silicon solar cells

Another approach to achieve high efficiencies for thin-film solar cells is to deposit thin films consisting of crystalline silicon grains, which is known as polycrystalline silicon (poly-Si). In contrast to microcrystalline silicon (µc-Si:H) which is also used as an absorber layer in photovoltaics, poly-Si contains (almost) no amorphous tissue. In this work, a film is said to be polycrystalline when its crystalline fraction is above 95%. The rationale behind using poly-Si as an absorber layer, is that it can combine the advantages of thin-film technology, e.g. low material use and roll-to-roll processing, with the efficiency of crystalline silicon solar cells. Unfortunately, the presence of grain boundaries and defects in these thin-film poly-Si layers hinders their efficiency, as will be elucidated further in subsection 1.3.3.

3For a-Si solar cells the reported efficiency is the stabilized efficiency, since during light-soaking the efficiency initially decreases rapidly due to the well-known Staebler-Wronski effect (SWE).[9]

4µc-Si:H is multiphase material, consisting crystalline silicon grains (typically ~30 nm) embedded in an amorphous matrix. Typically, µc-Si:H films for photovoltaic applications have a crystalline volume fraction of 60%.
1.3.1 Pathways to poly-Si thin-films

Polycrystalline thin films for solar cells are mainly obtained by three distinct routes:

- Solid phase crystallization (SPC) of a-Si:H
- Direct deposition
- Epitaxial thickening of seed layers

Solid phase crystallization refers to the crystallization of amorphous silicon, a process which is activated by thermal energy. Using SPC, poly-Si thin films can be produced in a two-step process, which consists of the deposition of (hydrogenated) amorphous silicon followed by thermal annealing at elevated temperatures of typically 600 °C. The crystallization process has been schematically drawn in figure 1.4. During the annealing step, the thermal energy allows the amorphous silicon network to relax from its metastable state to the global minimum of free energy, which corresponds to the crystalline state.

![Figure 1.4: Schematic of the free energy of the silicon network as a function of its configuration.](image)

More specifically, the SPC process can be described by various phases, as schematically depicted in figure 1.5. In the incubation phase, hydrogen effuses from the bulk amorphous silicon upon annealing and structural relaxation of the silicon network takes place. After the so-called incubation time, small randomly oriented nuclei of crystalline silicon appear homogeneously in the bulk of the matrix, that subsequently grow in the grain growth phase until the grains coalesce and the film is entirely crystalline.

The SPC process has already been studied in great detail, and a clear correlation between the film microstructure, incubation time and final grain size has been found by
Chapter 1. Introduction

Sharma et al. [11] Amongst others, the final grain size is dependent on the parameter $R^*$, which represents the distribution of hydrogen over vacancies and voids in the silicon network. This hydrogen distribution can be determined by infrared spectroscopy, as shown in the cartoon in figure 1.6. Hydrogen bonded in mono- or divacancies contributes to an absorption band around 2000 cm$^{-1}$, which is called the low stretching mode (LSM). A higher stretching mode (HSM) around 2100 cm$^{-1}$ belongs to hydrogen bonded on nanosized voids (up to tens of nanometers in size), as will be elaborated in section 2.2.1 of the experimental details. The parameter $R^*$ represents the ratio of these two absorption band and is defined as:

$$R^* = \frac{A_{HSM}}{A_{LSM} + A_{HSM}}$$

Where A denotes the peak area of the LSM and HSM peaks in the absorption spectrum.

Films exhibiting low $R^*$ (i.e. vacancy dominated material) show a high nucleation rate, resulting in a small final grain size. With increasing $R^*$, the divacancy density of the films is reduced and the final grain size increases. However, for very high $R^*$ values the dominant presence of large voids in the amorphous matrix hinders the growth of large grains. The second important microstructural parameter is the medium range order (MRO), which represents the correlation of the position of silicon atoms in the amorphous matrix on a 3-25 Å range. [11] MRO can be determined by the FWHM of the amorphous silicon diffraction peak in X-ray diffraction (XRD). Films with a high medium range order exhibit a small incubation time. Based on their experimental work, it is postulated that the more ordered areas around the divacancy constitute the nucleation centers in amorphous silicon.

SPC can produce films with grain sizes as large as $\sim 1 \mu m$. [12] However, open circuit voltages of SPC solar cells are generally not very high, which is attributed to the poor intragrain quality. Also, due to the hydrogen outdiffusion during annealing, posthydrogenation is needed for effective dangling bond defect passivation and the need for long...
Figure 1.6: Cartoon of vacancies and voids in a a-Si:H network and their respective contributions to the low and high stretching mode.

(∼10 hour) annealing makes the SPC process both time and energy consuming. Nonetheless, CSG solar has successfully commercialized this technique and has demonstrated a 10.3% cell efficiency. [13]

Besides the two-step process for obtaining polycrystalline silicon films by SPC of amorphous silicon, it is also possible to directly deposit polycrystalline silicon using various CVD techniques like PECVD[5] and HWCVD[6]. By a proper choice of the substrate temperature, growth radical flux (composition) and ion bombardment towards the substrate there are regimes where crystal grains nucleate during growth, as it will be elaborated in section 3.3.1.

At this point, following Rath et al. it is convenient to divide the direct deposition in two regimes depending on the substrate temperature. [14] In the low-temperature regime (< 600 °C) it is possible to deposit on inexpensive glass substrates, and since hydrogen does not out-diffuse during deposition there is less need of post-hydrogenation for effective grain boundary passivation. For the high-temperature regime (> 600 °C) generally more expensive heat-resistant substrates and posthydrogenation are required. Nonetheless, the high-temperature can be promising since larger grain sizes are typically obtained and the intragrain defect density decreases with the growth temperature.

[5] PECVD: Plasma enhanced chemical vapour deposition. In this deposition technique, growth radicals are created by collisions of precursor molecules with energetic electrons in a plasma. A parallel-plate configuration is a typical PECVD plasma source. Another common configuration of PECVD is electron cyclotron resonance chemical vapour deposition (ECR-CVD) where a plasma is generated by a microwave source.

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Directly-deposited poly-Si is an inhomogeneous material. A schematic of typical poly-Si film growth is depicted in figure 1.7. Like in the deposition of microcrystalline silicon (mc-Si:H), crystal grains develop after a certain incubation layer thickness of amorphous tissue, after which the grains compete in growth. Therefore, the layer consists of an amorphous interlayer, a region of many small grains, followed by the fewer larger grains that survive. Since the amorphous and small-grain region are detrimental to performance, understanding and control of these regions is prerequisite for the development of device-grade poly-Si.

One approach to avoid the amorphous incubation layer is the use of a polycrystalline silicon seed layer. During poly-Si deposition on the seed layer, the grains in the seed layer are epitaxially thickened and no amorphous interlayer is formed. Several kinds of seed layers exist, most of which are based on metal-induced crystallization.

At the Interuniversity Microelectronics Centre (IMEC) in Belgium poly-Si seed layers formed by aluminum induced crystallization (AIC) are being researched. Their AIC seed layers are prepared by the following steps. First an alumina substrate is covered by a spin-on oxide in order to reduce its roughness. Then a 200 nm layer of aluminum is deposited by electron-beam high-vacuum evaporation, followed by a 250 nm a-Si film. This stack is annealed at 500 °C for 4 h, during which the layer order is interchanged and the amorphous film is fully crystallized. This
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process is also known as aluminum-induced layer exchange (ALILE). The aluminum top layer is removed by wet etching to expose the poly-Si layer for epitaxial thickening. In order to improve the final poly-Si grain size, the aluminum layer can either be oxidized by exposure to air or treated by HNO₃ prior to a-Si deposition, increasing poly-Si grain sizes to 15 and 50 µm, respectively.\[17, 18\]

The ALILE process can also be done with a reversed layer stacking order, as is used by, for example, Jaeger et al.\[16\]. In this case first a-Si is deposited on a glass substrate, followed by the aluminum deposition. Like in ALILE the layers interchange position during annealing, but now the poly-Si layer is on top after the layer exchange. Because of this reversed order, this technique is coined reversed aluminum-induced layer exchange (R-ALILE).

A schematic of a full solar cell stack prepared from a R-ALILE seed layer is shown in figure 1.8. After the R-ALILE process, the glass substrate is coated with an aluminum layer, that is contaminated with silicon islands (hillocks), followed by the poly-Si seed layer. A great benefit of this reversed approach is that an aluminum back contact is automatically formed and there is no need for a wet etch step to remove the aluminum layer.

1.3.2 Overview of polycrystalline silicon solar cells

An overview of polycrystalline solar cell reports, deposited by either direct deposition, SPC or seed layer thickening, is shown in table 1.1. To the author’s knowledge, these values are among the highest reported poly-Si solar cell efficiencies of the above-mentioned approaches. Solar cells produced by epitaxial wafer thickening have shown efficiencies up to 16%, but such approaches are omitted here since they are not truly thin-film technologies.\[19\]

CSG solar has commercialized the SPC approach and has shown cell efficiencies around 10%, with module efficiencies on the 8.8% efficiency level. The cell consists of a p-n+ junction, where the 1.5 µm absorber layer is a crystallized PECVD-deposited a-Si:H. The borosilicate substrate is pre-coated with silica beads to enhance light trapping, as is reflected in the rather high short circuit current density of 28 mA/cm². For these cells, post-processing is crucial to obtain a high $V_{oc}$. The $V_{oc}$ is actually doubled after a short RTA treatment at 900 °C and plasma hydrogenation step, that lead to a reduction of the intragrain defect density and better grain boundary passivation, respectively.\[13, 20\]

Poly-Si solar cells made by direct deposition also show potential, as can be seen from the table. The so-called STAR-cell (Surface Texture and enhanced Absorption with a back Reflector) from Kaneka Corporation has the highest efficiency (10.7%) in the table.\[21\]. The STAR-cell is a p-i-n cell with a 1.5 µm absorber layer which is deposited by PECVD. The high $V_{oc}$ value of 539 mV suggests a high crystal quality. The high short circuit density can be attributed to excellent light management. The use of a rough back reflector and the self-structured roughness of the poly-Si layer enhance the optical path length. The columnar grain morphology of the (220)-oriented i-layer also aids in current collection, as will be explained in section 1.3.3.

The highest solar cell efficiency made from an ALILE seed layer is a heterojunction
CHAPTER 1. INTRODUCTION

<table>
<thead>
<tr>
<th>Affiliation</th>
<th>Technique</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSG Solar</td>
<td>SPC</td>
<td>500</td>
<td>28</td>
<td>-</td>
<td>10</td>
<td>[13, 20]</td>
</tr>
<tr>
<td>Kaneka Corporation</td>
<td>Direct</td>
<td>539</td>
<td>25.8</td>
<td>-</td>
<td>10.7</td>
<td>[21]</td>
</tr>
<tr>
<td>Osaka University</td>
<td>Direct</td>
<td>503</td>
<td>20.6</td>
<td>71.3</td>
<td>7.3</td>
<td>[22]</td>
</tr>
<tr>
<td>IMEC</td>
<td>AIC</td>
<td>534</td>
<td>20.7</td>
<td>73</td>
<td>8.0</td>
<td>[17, 18]</td>
</tr>
<tr>
<td>W. Schottky Institute</td>
<td>R-ALILE</td>
<td>440</td>
<td>18</td>
<td>63</td>
<td>5.2</td>
<td>[16]</td>
</tr>
</tbody>
</table>

Table 1.1: Overview of the top solar cell efficiencies demonstrated by the various poly-Si preparation techniques.

cell from IMEC. [17] [18] The cell structure is shown in figure 1.9. On top of the AIC seed layer, a thin epitaxial p+ layer is deposited by thermal CVD that acts as a back-surface field and also aids in lateral conductivity. The p+ BSF layer is then thickened with a p-layer for light absorption. The total poly-Si thickness is in the 2-4 µm range. A heterojunction emitter is formed by the deposition of both an i- and n+ a-Si:H layer. Defect passivation is done by plasma hydrogenation at 400 °C. A remarkable observation by Gordon et al. was that the efficiency of these cells did not increase anymore when developing larger grains. This has been attributed to a poor intragrain quality, characterized by a lot of electrically active defects. The electrical activity of these defects is attributed to the high level of contaminants such as Cu, Al, C and O, whose concentrations were found to be on the level of $\sim 10^{17}$ cm$^{-3}$. The role of intragrain quality is also addressed in the next section.

Figure 1.9: The AIC solar cell structure as made at IMEC. Reproduced from reference [18].

1.3.3 Towards higher efficiencies

As seen in table 1.1, the efficiencies obtained from thin-film polycrystalline silicon are not nearly on par with efficiencies typical of wafer-based solar cells. The aim of this section is to describe the main loss mechanisms and potential routes towards more efficient polycrystalline silicon thin-film solar cells.
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In the past, the main aim for improving efficiency was maximizing the grain size. Grain boundaries reduce the charge carrier mobility due to scattering and can act as recombination (trapping) centers. Therefore, an increase in efficiency is expected with increasing grain size, since the larger the average grain size is, the less grain boundaries charge carriers meet (and get trapped in) before extraction. Although this generally holds, also the grain morphology can play a crucial role. For example, in directly-deposited poly-Si films that exhibit a strong preferential (220) orientation, grain growth occurs in a columnar mode. Even though the lateral dimension of the grains can be small, charge carrier collection is effective due to the columnar grains extending over the film thickness. Additionally, the bond-angle deviation between the columnar grains is low, making them electrically inactive. In the case of a randomly-oriented poly-Si film the grain boundaries can be more recombination-active due to significant bond-angle deviations. The advantage of columnar (220) growth is nicely displayed by Matsui et al., where an increase in short circuit current density is correlated with the preferential (220) orientation. Additionally, Nakahata et al. have reported an anisotropic conductivity for (220) poly-Si films, where the conductivity perpendicular to the film is about five times higher than the lateral conductivity.

The observation that the efficiency hardly increases for grains larger than about one micron has lead to the insight that also the intragrain quality is of major importance. Impurity incorporation can make defects electrically active and induce deep levels within the bandgap, which especially happens for films prepared by ALILE that have a high amount of aluminum contamination. But more importantly, by performing a systematic study on poly-Si solar cells fabricated by various techniques, Wong et al. have identified that electronic levels induced by dislocations limit the charge carrier lifetime and thus solar cell efficiency. Clean dislocations in silicon induce shallow 1D bands just below the conduction band and above the valence band ($\sim 60 - 85$ meV), as shown in figure 1.10. They demonstrated that the transition between these two bands is the dominant route for non-radiative recombination in poly-Si solar cells, indicating that control on the dislocation density is necessary for attaining higher efficiencies.

In the case of direct deposition, understanding and control over the nucleation layer

Figure 1.10: Schematic of the DOS diagram of silicon, with additional levels induced by dislocations and impurities. [25]

\[ \text{Conduction band} \]
\[ \text{Valence band} \]
\[ \text{1D electron band} \]
\[ \text{1D hole band} \]
\[ \text{Energy} \]
\[ \text{Localized states} \]
\[ \text{Density-of-states} \]
thickness and nuclei density is also necessary. The undesired nucleation layer should be kept as thin as possible. Nucleation density is preferably low, so that there are little small grains that compete. However, a low nuclei density increases the thickness over which the grains coalesce, thereby increasing the incubation layer thickness.

An approach to obtain high open circuit voltages is the use of thinner absorber layers. Unfortunately, the short circuit density decreases for thin layers due to incomplete light absorption. For this reason, polycrystalline silicon solar cells are often deposited on textured glass or coated with a high-roughness transparent conductive oxide (TCO) to enhance light scattering. Yamamoto et al. have shown with their STAR-cell that an absorber thickness as low as 2 µm can lead to a 10.7 % efficiency when employing light trapping schemes.\[21\] The ability to directly deposit high-roughness poly-Si absorber layers could further enhance the optical confinement and, eventually, substituting the use of textured glass. This possibility is explored in chapter 5 for poly-Si layers deposited by an expanding thermal plasma (ETP).

1.3.4 Insights in poly-Si deposition

Poly-Si has historically been successfully deposited by a variety of techniques, including (VHF)-PECVD, ECR-CVD and HWCVD. Through systematic studies on these systems, a basic understanding of the relation between deposition parameters (i.e. temperature, growth radical flux, ion bombardment) and film properties can be found in literature. These findings are reviewed in this section, along with a summary of experimental reports on poly-Si deposition by the above-mentioned techniques.

Ion bombardment plays a decisive role in the formation of crystallites in poly-Si deposition. High energy ions (> 16 eV) can create defects in the crystallites or even prevent nucleation from occurring (\[14, 29\]). Also, in the case of the very similar μc-Si:H deposition process, high energy ions are known to randomize the preferential orientation.\[14\]

On the other hand, ions with an energy below 16 eV are considered to be beneficial for crystallite formation. A high flux of low-energy ions provides the surface with additional energy, thereby enhancing the surface diffusion, which can allow the use of lower substrate temperatures.\[14\] So generally, a high flux of low-energy ions can accommodate low temperature crystal growth, whereas high-energy ions disrupt crystal growth. For PECVD, this criterion limits the power that can be coupled to the plasma (and thus the deposition rate) in a parallel-plate configuration. In order to increase the deposition rate while keeping ion energy low, higher excitation frequencies or the high-pressure depletion (HPD) regime are used. \[30, 31\]

In addition to the nature of the ion bombardment, the growth radical flux (composition) is of major influence on the film properties. It is generally accepted that a predominant SiH$_3$ flux leads to device-grade films. This is attributed to the high surface diffusion length of the silyl radical, as opposed to the more reactive SiH$_x$ (x < 3) radicals and polysilanes.\[29\] Thanks to the high surface diffusion length, the radical is able to find the energetically more favourable sites on the surface, which typically are crystalline configurations.

It is widely accepted that atomic hydrogen is a crucial element for the transition
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from amorphous to $\mu\text{c-Si:H}$ or poly-Si. In PECVD, the crystallinity critically depends on the $\text{H}_2/\text{SiH}_4$ dilution ratio, whereas in HWCVD the ability to form crystallites at low substrate temperatures is attributed to the high hydrogen flux originating from the catalytic cracking of silane at the filament. Although the precise role in facilitating crystal growth is not known, various models have been proposed to explain the experimental findings. [29, 32]

The surface diffusion model states that the precursor surface diffusion length is increased by the flux of atomic hydrogen impinging on the surface. It is hypothesized that the atomic hydrogen recombines at surface dangling bonds, thereby making the surface less reactive and thus enhancing the diffusion length. Additionally the hydrogen exchange reactions are highly exothermic, providing the surface species with additional energy for diffusion. Because of the enhanced diffusion length, the precursor can find the energetically more favorable sites. [33]

Another point of view is considered by the etching model. The etching model is based on the experimental observation that the deposition rate is seen to decrease for higher $\text{H}_2/\text{SiH}_4$ dilution ratios. It is stated that the atomic hydrogen preferentially etches strained Si-Si bonds, that can be replaced by rigid Si-Si bonds. [34] This mechanism is thought to enhance the structural order of the silicon, thereby facilitating crystal growth. [35, 36]

The third model is the chemical annealing model, which is used to explain the fact that thin layers (several mono-layers) of amorphous silicon can be crystallized by exposure to atomic hydrogen. This is exploited in the layer-by-layer technique (LBL), which is a cyclic deposition technique where the deposition of a thin layer of a-Si:H is alternated with a hydrogen exposure cycle that crystallizes the a-Si:H. [34, 37] The chemical annealing model states that atomic hydrogen permeates the subsurface and thereby rearranges the Si-Si bonds, allowing them to relax to the crystalline state. [32] This structural rearrangement has also been observed by Sriraman et al., who performed a computational analysis of the effect of atomic hydrogen impinging on a layer of a-Si:H using a combination of density functional theory (DFT) and molecular dynamics (MD). An increase in the Si-Si pair correlation function was found upon atomic hydrogen exposure, which basically means the material is crystallized. [38]

Temperature is a parameter that is critical in deposition related parameters like surface diffusion and surface composition. Thermal desorption of surface hydrides, which typically happens at temperatures >400 °C, is one example. [29] As stated earlier, a high temperature provides the surface species with sufficient thermal energy to diffuse across the surface, thereby finding the energetically more favourable sites. Therefore, a higher temperature is usually accompanied by a higher crystallinity. Additionally, surface temperature can affect the preferential orientation. Sun et al. reported an increase in the (220) orientation with increasing temperature for their microcrystalline silicon films, prepared by reactive hydrogen plasma sputtering of silicon. [39]
CHAPTER 1. INTRODUCTION

1.4 Research goals and thesis outline

In this thesis, the possibility of using an ETP for polycrystalline silicon deposition is explored. The expanding thermal plasma has been extensively investigated in our group, both in terms of the Ar-SiH$_4$-H$_2$ plasma chemistry and in terms of the deposition of hydrogenated amorphous silicon (a-Si:H) and µc-Si:H. But despite being a well-studied deposition system, no experimental conditions resulting in the deposition of polycrystalline silicon are known to date.

Nonetheless, the expanding thermal plasma may prove to be a promising tool for poly-Si deposition. Compared to other deposition techniques, the ETP generally has a higher deposition rate (e.g. several tens of nm/s for a-Si:H). Given the relatively low poly-Si deposition rate of typically a few nm/s or less for conventional deposition techniques, along with the required absorber thickness of several microns for photovoltaic applications, the advantages of achieving a high deposition rate by ETP are evident.

On the other hand, the deposition of poly-Si at high deposition rates with an ETP will probably prove to be challenging. The ETP is known to deliver a very little amount of ion bombardment (i.e. ion energies < 2-3 eV), especially when molecular hydrogen is admixed in the arc (as will be explained in section 2.1). The absence of ion bombardment for providing additional energy to the surface for surface diffusion, along with a high deposition rate will make it hard to achieve crystal growth.

The feasibility of depositing poly-Si with an ETP is the topic of chapter 3. The main research questions that are addressed are:

- Is it possible to deposit poly-Si with an expanding thermal plasma?
- How do growth radicals affect the film phase?
- Can a high deposition rate be achieved?

To this end, two approaches for poly-Si deposition have been explored. The first one consists of depositing using a pulsed silane flow in order to alternate deposition with hydrogen treatment. The effect of the hydrogen treatment, which is thought to increase film crystallinity, is investigated. The second approach consists of depositions in the high-temperature regime (> 600 °C). For these depositions, the dependence of film properties like crystallinity and resistance to oxidation on the growth radicals is systematically studied.

Chapter 4 focuses on the growth mechanism of crystal grains in our poly-Si films. The main research topics in this chapter are:

- How do crystal grains develop during deposition? Do the poly-Si films have an incubation layer like in µc-Si:H and if so, how is it controlled by the deposition parameters?
- How does the preferential crystal orientation depend on deposition parameters? Can films with the beneficial (220) orientation be deposited? Does the preferential
orientation prevail from the start of crystalline film growth or does it develop over the film thickness?

To answer these questions films have been analyzed both by *ex-situ* and *in-situ* characterization techniques. *Ex-situ* XRD analysis on a series of films of different thicknesses has been used to investigate the evolution of the crystallite properties during deposition. *In-situ* spectroscopic ellipsometry (SE) has been used for real-time monitoring of the film thickness and roughness. Additionally, *in-situ* SE allows for the investigation of the presence of an amorphous incubation layer. By combining the results of these studies, a growth model for poly-Si growth in our setup is presented, which has been verified by TEM imaging.

Since it is planned to produce p-i-n solar cells from our poly-Si films, their optical absorbance should be considered as well. Therefore, the following topics are addressed in chapter 5:

- How does the film absorbance depend on the film thickness? What thickness would be needed for the application in a p-i-n solar cell?
- Can poly-Si films with a native texture be deposited? And if so, what is the effect of the film roughness on light trapping?
- Which deposition parameters influence the film roughness? Can we understand why?
- Is it possible to produce p-i-n solar cells from the deposited poly-Si films? How do solar cell parameters ($\eta$, $V_{oc}$, $J_{sc}$ and FF) depend on the properties of the intrinsic poly-Si absorber layer?

These questions are addressed in three parts of the chapter. In the first part, the absorbance of a thickness series of poly-Si films is measured to determine the effect of film thickness and roughness on absorbance. The effect of roughness on absorbance has been further clarified by comparison of the absorbance of a series of 1 µm SPC poly-Si of variable surface roughness. In the second part, the role of deposition parameters on surface roughness has been investigated by performing a detailed AFM analysis and the rationale behind the observed trends is presented. The last part is on the production of p-i-n solar cells using an intrinsic poly-Si absorber layer deposited by ETP, in a collaboration with the Helmholtz institute in Berlin. Unfortunately, these experiments are still underway. Therefore, an overview of the planned depositions is presented, along with a motivation for the chosen deposition conditions.

In the following chapter the experimental setup is described. A detailed description of the expanding thermal plasma deposition setup is given, along with the accompanying Ar-H$_2$-SiH$_4$ plasma chemistry. Additionally, the experimental techniques adopted during these studies are explained.
Chapter 2

Experimental Setup

In this chapter the experimental setup used for deposition will be discussed, along with the most used analysis techniques. First the ETP setup is described, including the Ar-H$_2$-SiH$_4$ plasma chemistry in the ETP. In subsequent sections fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, XRD, SE and the UV-VIS absorbance setup are treated in detail, since these analysis techniques have been extensively used throughout the project.

2.1 The Expanding Thermal Plasma

The ETP is a plasma enhanced chemical vapor deposition (PECVD) technique that has been developed at the Eindhoven University of Technology. It has been shown that the ETP setup is a very viable tool for the deposition of various functional thin films, especially for solar cell applications. Among these are a-Si:H and mc-Si:H films as solar cell absorber layers, silicon nitride (a-SiNx:H) films as antireflection coating, silicon oxide (SiO$_2$) as a surface passivation layer and aluminum-doped zinc oxide (ZnO:Al) acting as a transparent conductive oxide.

A schematic of the ETP setup is depicted in figure 2.1. The deposition chamber consists of a cylindrical stainless steel vessel, 80 centimeters long and 50 centimeters in diameter. During depositions the chamber is evacuated by roots blowers, otherwise it is pumped down by a turbo pump, reaching a base pressure of 10$^{-6}$ mbar.

The plasma is struck in a cascaded arc, which is a dc plasma source (see figure 2.1 right). The discharge is created by a potential drop between three cathode tips and a grounded anode plate, which are separated by alternating cascaded plates of copper and boronitride. The source gas is argon, often mixed with hydrogen, which is flown through the plasma channel. During a typical deposition 15 A of current is driven through each cathode tip and, depending on the plasma composition, this results in a power dissipation of a few kilowatts.

The plasma in the arc has an electron density of $\sim$10$^{22}$ m$^{-3}$ and both the electron and heavy particle temperature are $\sim$1 eV. This thermal nature of the discharge is due to the relatively high pressure of a few hundred mbar in the arc, leading to efficient
CHAPTER 2. EXPERIMENTAL SETUP

Figure 2.1: Schematics of the ETP setup (left) and the cascaded arc (right).

momentum transfer between electrons and heavy particles.

The plasma exits the arc through a nozzle and expands into the deposition chamber, which is kept at around 0.1 mbar by the roots blowers. Due to the large pressure difference between the arc and the deposition chamber, the plasma expands supersonically into the chamber. After a few centimeters there is a stationary shock, after which the expansion becomes subsonic with a typical speed of 1000 m/s. The electron density and temperature drop to respectively $\sim 10^{17}$ - $10^{19}$ m$^{-3}$ and $\sim 0.1$-0.3 eV during the expansion.

At five centimeters from the arc an injection ring is placed. Up to 10 sccs of SiH$_4$ is injected into the vessel, where it is dissociated by reactive species emanating from the arc. The dissociation reactions will be discussed in subsection 2.1.1. No power is coupled to the plasma as it expands into the deposition chamber, so it becomes a recombining plasma.

Sample placement is done through a load-lock. Two different substrate heaters have been used throughout this thesis. The first heater is able to heat up to 600 °C and is electronically controlled. Also, helium backflow is possible for optimal thermal contact between the heater and sample. Another heater was used to reach substrate temperatures exceeding 600 °C, which consists of a molybdenum spiral for ohmic heating welded onto a substrate holder. A heat shield is placed around the heater to minimize radia-
CHAPTER 2. EXPERIMENTAL SETUP

tive losses. Although the substrate holder can reach temperatures exceeding 1000 °C, the maximum substrate temperature is around 800 °C due to poor thermal contact. Substrate temperatures were measured by a thermocouple. In the case of deposition on quartz, the thermocouple was placed inside a hole drilled into the side of the quartz plate. In the case of deposition on (oxidized) wafers the thermocouple was glued to the wafer surface by thermal paste. The temperature during deposition was controlled manually by adjusting the current through the heating element. Due to the manual temperature control there was a spread of up to 10 °C in the set deposition temperature.

A remarkable feature of the ETP is the fact that it is a truly remote plasma; Due to the enormous pressure difference between the arc and the deposition chamber, the plasma upstream is not or hardly influenced by the conditions in the reactor. This is in contrast to for example most PECVD systems, where the plasma is in direct contact with the deposition surface and plasma-surface interactions have a major influence on the plasma itself. The decoupling of the plasma creation and the plasma-surface interactions make the ETP a very versatile technique, as this greatly increases the available parameter space. This is not only beneficial for optimization of deposition conditions, but also for fundamental studies on the plasma and surface reactions.

2.1.1 Controlling growth radicals in an Ar-H₂-SiH₄ plasma

In the past, the Ar-H₂-SiH₄ plasma chemistry in the ETP has been investigated in great detail, especially in the PhD thesis of Kessels. The information on the plasma chemistry from these studies can be conveniently used for the work in this thesis, since very similar plasma settings were used. Therefore, the most important findings will be reproduced below.

As stated before the ETP technique is a remote plasma, which means that the plasma creation in the arc, the dissociation of silane in the plasma expansion and the deposition process can be described more or less independently. Therefore, first the plasma creation in the arc and mainly the effect of adding molecular hydrogen will be discussed. Then the
dissociation mechanism of silane in the deposition chamber due to the reactive species emanating from the arc is treated for various hydrogen flows. Finally the effect of plasma parameters on the growth flux of the various silyl radicals will be made clear.

The discharge is created in the arc, through which (for most experiments) 55 sccs of argon is flown. If no hydrogen is added, the arc is a source of argon ions which are produced in the breakdown. At the typical setting of 45 A the ion fluence from the arc is about 3 sccs, corresponding to an electron/ion density of $\sim 10^{19} \text{m}^{-3}$ at a position of 6 centimeter from the arc outlet. The electron temperature at this position is around 0.3 eV. The addition of hydrogen to the flow drastically changes the reactive species coming from the arc. Adding hydrogen changes the dominant specie from Ar$^+$ to ArH$^+$ for low H$_2$ flows and to H for high H$_2$ flows of up to 10 sccs. More importantly, the molecular hydrogen leads to a strong reduction in the electron temperature and the ion flow from the arc, which drop to respectively $\sim 0.15$ eV and 0.08 sccs for a H$_2$ flow of 10 sccs. Also, the flux of atomic hydrogen greatly exceeds the ion flux, effectively rendering the arc a source of reactive H instead of an ion source.

The dissociation pathway of silane greatly depends on the type of reactive species emanating from the arc, and thus on the hydrogen flow. In the thesis of Kessels, a reaction scheme for the dissociation process is presented for the two limiting cases of a low H$_2$ flow ($\ll 2$ sccs) and high H$_2$ flow ($\gg 5$ sccs).

In the case of no or low H$_2$ flow, the main reactive species from the arc is Ar$^+$, which is accompanied by a high electron density. The first step in silane dissociation is dissociative charge transfer from Ar$^+$ to SiH$_4$.

$$\text{Ar}^+ + \text{SiH}_4 \rightarrow \text{Ar} + \text{SiH}_n^+ \ldots (n \leq 3) \quad (2.1)$$

This reaction is followed by dissociative recombination with electrons, due to the high electron density at this condition.

$$\text{SiH}_n^+ + e \rightarrow \text{SiH}_m + \ldots (m \leq 2) \quad (2.2)$$

These lower radicals are very reactive with SiH$_4$ and can therefore create polysilanes by sequential addition of silane molecules, especially at higher SiH$_4$ partial pressures.

$$\text{SiH}_m + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_p + \ldots \text{etc} \quad (2.3)$$

The electron density in the expansion is reduced through reaction $2.2$. When the electron to silane density ratio becomes $\lesssim 10^{-3}$ the dissociative recombination in reaction $2.2$ is no longer dominant and ion-molecule polymerization reactions lead to the formation of cationic clusters with up to 10 Si atoms, as determined by mass spectrometry.\[47\]

$$\text{Si}_p\text{H}_q^+ + \text{SiH}_4 \rightarrow \text{Si}_{p+1}\text{H}_r^+ + \ldots \text{etc} \quad (2.4)$$

For H$_2$ flows $\gtrsim 5$ sccs the arc becomes a source of mainly H atoms, rendering the hydrogen abstraction of silane the most prominent reaction.

$$\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2 \quad (2.5)$$
There is also still a small flux of hydrogen ions coming from the arc, which undergo dissociative charge transfer reactions with silane

\[
H^+ + SiH_4 \rightarrow H + SiH_4^+(n \leq 3)
\]  

(2.6)

Because of the low electron density at high H\textsubscript{2} flow, the main reaction of these silyl ions is the polymerization reaction in equation \ref{polymerization}. The precise deposition conditions used in this thesis are mentioned in the corresponding chapters.

2.2 Characterization techniques

2.2.1 Fourier Transform Infrared Spectroscopy

FTIR is an analysis technique that provides information on the chemical bonding in a material. It is based on the absorption of infrared light by a material, which leads to excitation of vibrational modes (or even rotational modes for gas-phase spectroscopy) specific to certain bond configurations.

Since the various vibrational modes each have a specific eigenenergy, the part of the infrared light passing a sample that matches that eigenenergy is strongly absorbed and appears as an absorption band in a FTIR spectrum. However, the bond must have a net dipole moment for light absorption to occur, since otherwise the transition dipole moment is zero. For this reason the linear symmetric molecule N\textsubscript{2} does not absorb IR light, whereas CO\textsubscript{2} does show strong absorption features.

The vibrational energy levels of film species all belong to a specific normal mode of vibration. In the case of for example a SiH\textsubscript{2} group, there are six normal modes of vibration, which are schematically drawn in figure 2.3. Note that for each normal mode in the figure, the two green arrows represent the movement direction during the first half of the oscillation period, whereas the red arrows represent the movement in the second half of the period.

In the figure the atoms are drawn as free-standing, which makes their normal modes well-defined. However, in reality the vibrational modes are influenced by their bonding environment, which can both shift the resonance energy and lead to absorption band broadening. This will be made clear by a few examples. An FTIR spectrum of gas-phase species shows very sharp peaks, since the gas-phase molecules have little interaction and therefore the vibrational modes are well-defined. Peaks of species adsorbed on a surface do show broadening, since there will be a distribution of their vibrational energy levels due to influences of for example the local surface geometry and the nature of surface species that are adsorbed on neighbouring surface sites. In bulk species, the peak shift and broadening effects are even more pronounced. For example, the energy of the bulk Si-H stretching mode is dependent on whether the H-atom is located at a vacancy or at the surface of a nanosized void, as will be elucidated below. So an FTIR spectrum can not only provide information on the kind of bonds in the material, but also on the microstructure in which these bonds reside.
The basic component of any FTIR spectrometer is a Michelson interferometer, as shown in Figure 2.4. The working principle of FTIR can best be explained by first considering a monochromatic source and no sample, and in the end generalize to the case of a polychromatic source as the superposition of an infinite amount of monochromatic sources.\cite{48}

The Michelson interferometer consists of an IR source which strikes a beamsplitter at a 45° incidence. The beamsplitter (ideally) reflects half of the light and transmits the other half. The reflected part of the light is directed perpendicularly onto a planar movable mirror, whereas the transmitted part is directed onto a fixed mirror. The light reflected from both mirrors is combined again at the beamsplitter, where it is directed towards the detector. This light interferes either destructively or constructively, depending on the optical path difference between the two beams. Also, a compensator plate is added to compensate for the optical path difference due to the beamsplitter, since otherwise the beam that is directed towards the movable mirror would have an additional phase shift due to an additional pass through the beamsplitter.

If the distance between the front side of the beam splitter and the movable mirror is equal to the distance between the back side of the beamsplitter and the fixed mirror, the optical path for both beams is identical upon arrival at the detector, leading to constructive interference. If the movable mirror is moved backwards by a quarter-wavelength, the optical path difference becomes half a wavelength, and no light is detected due to destructive interference. The light intensity as measured by the detector as a function of the mirror displacement can be described as follows: \cite{48}

\[
I(x) = B(k) \times \cos (2\pi kx)
\]  

(2.7)
CHAPTER 2. EXPERIMENTAL SETUP

In this equation, \( x \) is the mirror displacement, \( k \) is the wavenumber of the light and \( B(k) \) is the intensity of the source at this wavenumber. Note that the detector measures \( I(x) \), while the quantity \( B(k) \) is desired since it contains information on the absorption of the light by the sample.

In the case of a broadband light source, the light measured at the detector is the superposition of the interference of all the wavelengths that constitute the beam. Therefore, the intensity measured by the detector can be found by integration of equation 2.7 over all wavenumbers.

\[
I(x) = \int_{-\infty}^{\infty} B(k) \times \cos(2\pi kx)dk
\]  

(2.8)

The intensity profile as a function of mirror displacement is known as an interferogram. The spectrum of the source, \( B(k) \) can be obtained from the interferogram by applying a Fourier transform to equation (2.9).

\[
B(k) = \int_{-\infty}^{\infty} I(x) \times \cos(2\pi kx)dx
\]  

(2.9)

The absorbance spectrum of a thin film can be found by comparing the FTIR spectrum of the bare substrate (in our case c-Si) to the spectrum of the substrate with the deposited thin film.
CHAPTER 2. EXPERIMENTAL SETUP

In this subsection, the most important silicon-hydride and oxidation modes that arise in the spectra of amorphous, microcrystalline and polycrystalline silicon thin films are discussed.

In a-Si:H hydrogen can reside in either vacancies or on the surface of nanosized voids. It has been shown by Smets et al. that the hydrogen stretching mode in a-Si:H is different for these two configurations.\textsuperscript{[49]} Hydrogen in a vacancy has a so-called low stretching mode (LSM) around 1980-2010 cm\textsuperscript{-1}, while hydrogen on the surface of nanosized voids has a high stretching mode (HSM), around 2070-2100 cm\textsuperscript{-1}. The hydrogen distribution in a-Si:H (or mc-Si:H) can thus be determined from the LSM and HSM peaks in an FTIR spectrum. This is quantified by the microstructure parameter $R^\ast$, which is defined as the HSM integrated absorbance over the total hydrogen stretching mode absorbance:

$$R^\ast = \frac{A_{\text{HSM}}}{A_{\text{LSM}} + A_{\text{HSM}}}$$

(2.10)

Therefore, a high $R^\ast$ represents a high fraction of voids in the film.

In the case of $\mu$-Si:H and poly-Si:H, hydrogen bonded to crystal grain surface gives rise to three additional narrow high stretching modes (NHSM) at 2083, 2103, and 2137 cm\textsuperscript{-1}, which correspond to mono-, di- and trihydride configurations, respectively.\textsuperscript{[50, 51]} The presence of NHSM modes typically indicates that the crystal grains are bound by voids instead of amorphous silicon, rendering the film prone to oxidation.\textsuperscript{[51, 52]}

A typical FTIR spectrum of a a-Si:H thin film is shown in figure 2.5. The spectrum was recorded using a Bruker Tensor 27 FTIR spectrometer, in the range of 450-7000 cm\textsuperscript{-1} and with a resolution of 4 cm\textsuperscript{-1}.

![FTIR spectrum of a-Si:H](image)

Figure 2.5: A typical FTIR spectrum of a-Si:H, showing the fringes, the low and high H stretching mode and the SiH\textsubscript{x} wagging mode.
CHAPTER 2. EXPERIMENTAL SETUP

The most prominent feature in the spectrum are the fringes, which arise due to internal reflections of the beam in the a-Si:H thin film. These fringes can be used to determine the thickness and refractive index of the film, using a simple three-layer model as described in reference [53]. The LSM and HSM modes show up as absorption bands, as well as the SiH\textsubscript{x} wagging modes around 600-680 cm\textsuperscript{-1}.\[52\] Additionally, the total hydrogen content of the film can be determined by integration of the wagging mode, as described in reference [54]. This specific mode is used, since every hydrogen bonded in the bulk contributes to this mode.

Oxidation of a silicon film can be seen in an FTIR spectrum by the presence of a Si-O-Si antisymmetric stretching mode around 1050 cm\textsuperscript{-1} and by the shift of the hydrogen stretching mode to 2200-2250 cm\textsuperscript{-1} due to oxygen bonded to the Si-Si backbon. In the 700-900 cm\textsuperscript{-1} region, various oxidation peaks are convoluted, which are the Si-O-Si symmetric stretching, O-Si-H deformation, Si-O stretching and O-H bending of SiOH modes.[55, 56]

2.2.2 Raman Spectroscopy

Like IR spectroscopy, Raman spectroscopy provides information on the vibrational states of a material. It is based on the inelastic scattering of light, which was first observed by Raman et al. in 1928.\[57\] In Raman spectroscopy, a sample is illuminated by a high-intensity laser. The light can be scattered by three distinct mechanisms. Figure 2.6 shows these three scattering mechanisms for a simplified system consisting of only two vibrational states. IR absorption is shown for comparison.

![Figure 2.6: Schematic representation of the three scattering mechanisms for a system consisting of only two vibrational states. IR absorption is shown for comparison.](image)

Elastic Rayleigh scattering is by far the most dominant scattering mechanism. A photon distorts the electron cloud of a molecule, through which it is scattered. In figure 2.6, this corresponds to excitation from the \(n\) or \(m\) vibrational state to a higher virtual state, followed by relaxation to the original state. Rayleigh scattering scales with the fourth power of the frequency of the incident light. This is also the reason why the sky...
is blue; The blue part of the solar spectrum is scattered more efficiently by molecules in the atmosphere than the red part. Note that unlike (IR) absorption, there is no need for the incident light to match a certain electronic transition for the scattering to occur.

Inelastic Stokes (or Raman) scattering is a far less efficient process, by a factor of $\sim 10^6 - 10^8$. In Stokes scattering, nuclear motion is induced. The scattered photon has an energy which is its energy prior to scattering minus the energy of the induced vibrational motion. This shift in energy is the Stokes or Raman shift. In figure 2.6, this is visualized as excitation from the lower energy state $n$ to a virtual energy state, followed by relaxation to the higher energy level $m$.

Inelastic anti-Stokes scattering is very similar to Stokes scattering. Anti-Stokes scattering is the scattering of a photon from a molecule which is already vibrationally excited. The molecule is demoted to a lower vibrational energy level, transferring this energy to the scattered photon. This also leads to a Raman shift, but towards a higher energy. Since at room temperature most systems are typically dominantly in their vibrational ground-state, anti-Stokes scattering is even more inefficient than Stokes scattering. However, by comparing the intensity of Stokes and anti-Stokes shifts, information on the population of the vibrational system, and thus its temperature, can be obtained.

One might wonder what the advantage of Raman is over for example FTIR, since both techniques provide information on the vibrational states of a system. In fact the techniques are complementary since a vibrational mode that is Raman-active is not necessarily IR-active, and vice versa. This is due to different selection rules for both processes. Whereas a bond must have a net dipole in order to be IR-active, it appears that a vibrational mode is only Raman-active if the electric field of an incident photon induces a change in the polarizability tensor. Most antisymmetric modes change the net dipole moment, whereas changes in the polarizability occur most frequently for symmetric modes. Nonetheless, modes can certainly be both IR and Raman-active. Only for centrosymmetric systems a mode can not be both IR and Raman active, which is known as the mutual exclusion rule.

The discussion above described the Raman effect by molecular vibrations. In the case of a solid, these vibrations are represented by phonon modes.

Raman spectroscopy is an excellent tool for silicon thin film characterization, since it can easily distinguish between amorphous, microcrystalline and poly/monocrystalline silicon. Typical Raman spectra of these three silicon phases are shown in figure 2.7.

In a crystalline solid, the momentum-conservation rule requires that the phonon mode has zero momentum, since the momentum of a photon is negligible with respect to most phonon momenta. Crystalline silicon only has a peak at 520 cm$^{-1}$, which corresponds to the zero-momentum Si-Si transverse optical (TO) mode with an energy of 64 meV.

In amorphous silicon, the zero-momentum selection rule is relaxed, and contributions from linear acoustic (LA), transverse acoustic (TA), linear optical (LO) and TO Si-Si phonon modes are visible in a Raman spectrum. The positions of these modes are summarized in table 2.1.

As can be seen in figure 2.7, the mc-Si:H spectrum shows the TO modes from both
CHAPTER 2. EXPERIMENTAL SETUP

Figure 2.7: Typical normalized Raman spectra of a-Si:H, µc-Si:H and poly-Si.

<table>
<thead>
<tr>
<th>Material phase</th>
<th>Phonon mode</th>
<th>Peak position (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>TO</td>
<td>520</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>TO</td>
<td>475 ± 10</td>
</tr>
<tr>
<td></td>
<td>LO</td>
<td>380 ± 10</td>
</tr>
<tr>
<td></td>
<td>TA</td>
<td>300 ± 10</td>
</tr>
<tr>
<td></td>
<td>LA</td>
<td>140 ± 5</td>
</tr>
</tbody>
</table>

Table 2.1: The various Raman-active phonon modes in c-Si and a-Si:H \[59, 60\]

a-Si:H and c-Si. As proposed by Tsu et al., the crystalline fraction \(X_c\) can be determined from the integrated areas of these two TO modes. \[61\]

\[
X_c = \frac{I_c}{I_c + \gamma I_a}
\]  

(2.11)

In this, \(I_c\) and \(I_a\) denote the integrated areas of the crystalline and amorphous TO modes, respectively. The factor \(\gamma\) accounts for the difference in Raman scattering cross section between amorphous and crystalline silicon. Most authors take \(\gamma\) to be around 0.8 for mc-Si:H. However, it appears that the Raman cross section for crystallites in mc-Si:H is strongly dependent on the crystallite size. Bustarret et al. have found an empirical formula for \(\gamma\) as a function of crystallite size \(d\) (\(d\) in nanometers). \[62\]

\[
\gamma(d) = 0.1 + \exp\left(-d/25\right)
\]  

(2.12)

Therefore, care must be taken in the determination of \(X_c\), especially for films with
large crystallites where the deviation from the commonly-used $\gamma$ value of 0.8 can be significant.

Raman spectra were taken with a Renishaw InVia Raman spectroscope. The laser excitation wavelength was 514 nm. Scans were made in the 20-1000 cm$^{-1}$ Raman shift region with a resolution of 1.6 cm$^{-1}$. The laser power was set to 5 mW and the acquisition time was fixed at ten seconds.

2.2.3 Spectroscopic ellipsometry

In this work, SE has been used in-situ to gain insight in the growth process of polycrystalline silicon. In an SE measurement, light with a known polarization state is shone on the thin film at an oblique angle, and the change in the polarization state after reflection is measured. From this data physical information on film properties like optical constants and thickness can be extracted, even for multilayer systems. However, SE is an indirect measurement, i.e. in order to obtain physical information a suitable optical model of the thin film has to be made and fitted to the measurement, as will be explained later.

As stated earlier, the principle of SE relies on the change in polarization state upon reflection from a sample. This process is schematically shown in figure 2.8.

Figure 2.8: Schematic drawing of linearly polarized light striking a surface, which is reflected as elliptically polarized light.[63]

Linearly polarized light strikes the sample at an angle of 45°. $E_i$ is the electric field vector of the incident light, which is decomposed in the $s$ and $p$ polarizations. The subscript $i$ is used for the incident quantities, whereas the subscript $r$ is used for quantities after reflection. Due to a difference in dipole induction in the sample for the $s$ and $p$ polarizations, these two polarizations undergo a different change in amplitude and phase. In ellipsometry, the two values ($\Psi$, $\Delta$) are measured, which are indicated in figure 2.8. $\Psi$ is the ratio of the $s$ and $p$ amplitudes, whereas $\Delta$ is the induced phase difference between the two components.

In the case of a simple, thick sample the optical constants of the material can be calculated directly from the measured ($\Psi$, $\Delta$).[63] However, generally the film of interest
can be comprised out of different layers, with even for example thin oxide layers in between. The various reflections from these interfaces make the interpretation of \((\Psi, \Delta)\) much less trivial. Other complicating factors are for example surface roughness, void incorporation in the film or even mixed-phase films.

Fortunately, modeling of the thin-film of interest makes it possible to extract a plethora of physical film properties from the spectroscopically measured \((\Psi, \Delta)\). Typically, modeling of a multilayer system is done using a software package (in our case CompleteEASE) as follows. A model comprised of a stack of layers with corresponding layer thicknesses is defined in the software, which is thought to be representative of the physical system. Since the dielectric functions of the materials are known, the expected \((\Psi, \Delta)\) response of this model can be calculated. The result is compared to the measured \((\Psi, \Delta)\), and model parameters (e.g. layer thicknesses, void content, roughness and substrate temperature) are varied iteratively to fit the calculated \((\Psi, \Delta)\) to the measured \((\Psi, \Delta)\).

If the dielectric function of a layer is not known, this dielectric function can also be obtained from the spectroscopically measured \((\Psi, \Delta)\) by fitting. The dielectric function of the layer is in this case represented by a B-spline, which is forced to be Kramers-Kronig consistent. In this work, a B-spline is used to discriminate between amorphous and crystalline silicon growth, as will be elaborated in chapter 4.

For our \textit{in-situ} measurements, a Woollam rotating compensator ellipsometer was used. Scan times were set to 1 second, as this was found to be a good compromise between temporal resolution and signal-to-noise ratio. The \textit{SE} source and detector were mounted to two viewports of the chamber, which have an \(75^\circ\) angle with the substrate. Prior to deposition, the substrate (mostly a Si \((100)\) wafer with 450 nm of oxide) was brought to the deposition temperature and was scanned for a longer time. This allowed for a precise determination of the starting layer. The film model used for modeling is presented in chapter 4.

2.2.4 X-ray Diffraction

XRD is an analysis technique that can provide information on the crystal structure of a material. Its working principle is based on destructive and constructive interference of coherent X-ray radiation that is diffracted on a periodic structure, like a crystal of atoms. The working principle can most easily be demonstrated by considering the simple case of diffraction from a two dimensional square lattice with spacing \(d\), as shown in figure 2.9.

Two cases are shown: Constructive (a) and destructive (b) interference. A coherent X-ray beam is incident on the crystal with an angle \(\theta\) with respect to the surface. The beam is diffracted isotropically by the periodic atoms. Depending on the angle \(\theta\), photons from successive crystal planes will either interfere constructively or destructively. In the case of figure 2.9a, the path length difference between the top and bottom plane is exactly one wavelength, thus leading to constructive interference. In 2.9b, the path length difference is only half a wavelength, so the two photons cancel out due to destructive interference. With some basic geometry, it can be shown that the path length difference
between the top and bottom plane is $2d\sin \theta$. The criterion for constructive interference is that the path length difference must equal a multiple of the x-ray wavelength, which is stated in Bragg’s law:

$$2d\sin \theta = n\lambda \quad (2.13)$$

This holds for the simplistic case of diffraction from successive planes in a cubic lattice. In general, constructive interference does not necessarily have to arise from successive planes. Moreover, the plane spacing depends on the orientation of the crystal with respect to the surface normal. In the example shown above, diffraction occurs from successive (100) planes, where (hkl) denote the so-called Miller indices. If the sample would be tilted by 45 degrees, diffraction would occur from (110) planes, whose spacing is $d/\sqrt{2}$. The decreasing plane spacing with increasing Miller indices has been visualized in figure 2.10, which shows three sets of planes in a two-dimensional cubic lattice with increasing Miller indices.

This can be generalized to an arbitrary (hkl) plane by substitution of the plane (100) (110) (210).
CHAPTER 2. EXPERIMENTAL SETUP

spacing \(d\) in 2.13 by:

\[
d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.14)
\]

Where \(a\) is the lattice parameter. Thus, for example, for a known crystal, the crystal orientation can be determined by scanning the full \(\theta\) range, and looking at which value(s) of \((hkl)\) a signal is detected.

However, not every \((hkl)\) plane can lead to constructive interference. It appears that depending on the crystal structure (e.g. BCC, FCC, diamond) there are certain selection rules on the values of \((hkl)\) that can lead to constructive interference. Crystalline silicon which has a diamond structure serves as a perfect example: An XRD spectrum of silicon shows a peak for the \((220)\) orientation, but no peak for \((110)\) can be observed, even though these two combinations of \((hkl)\) represent the same direction in the crystal.

The origin of these extra selection rules stems from diffraction of other atoms in the crystal basis, which were not taken into account in the derivation of Bragg’s law above. To be more precise, although Bragg’s law might predict constructive interference from a certain plane at a certain angle \(\theta\), it is possible that diffracted radiation from other atoms in the crystal basis interferes destructively (or even constructively) with the diffracted beam from the considered plane. This effect makes it so that the diffraction intensity is dependent on the crystal plane, and can even make the intensity zero for some planes, leading to the before-mentioned selection rules.

These selection rules can be easily determined mathematically, by phase-wise addition of the contribution of all the atoms in the crystal basis to the diffracted beam. This summation, which determines the diffracted beam intensity, is known as crystal structure factor \(F\) and is calculated as follows:

\[
F(hkl) = \sum_j f_j e^{2\pi i (hu_j + kv_j + lw_j)} \quad (2.15)
\]

In this equation, the index \(j\) denotes the atoms in the unit cell over which is summed. \(f_j\) is a proportionality constant which is dependent on the atom in consideration. The parameters \(u_j, v_j\) and \(w_j\) denote the relative coordinates of the atoms in the unit cell in \(x, y\) and \(z\) direction, respectively.

Applying this to several common Bravais lattices, the selection rules summarized in table 2.2 can be found.\(^{64}\) Silicon has a diamond lattice, which can be interpreted as a combination of two interpenetrating face-centered cubic (FCC) lattices with a translation of \((1/4, 1/4, 1/4)\). Therefore, the diamond lattice has the same selection rules as the FCC Bravais lattice, along with some additional selection rules arising from the double FCC lattice basis. The selection rules for the diamond lattice can be shown to be the following:

\[
h^2 + k^2 + l^2 = 3, 8, 11, 16, 19, 24, 27, 32, \ldots \quad (2.16)
\]
Table 2.2: Selection rules for constructive interference from (hkl) planes for various Bravais lattices

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Reflections present for</th>
<th>Reflections absent for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive</td>
<td>all</td>
<td>none</td>
</tr>
<tr>
<td>Body-centered</td>
<td>h+k+l even</td>
<td>h+k+l odd</td>
</tr>
<tr>
<td>Face-centered</td>
<td>h, k and l unmixed (all even or all odd)</td>
<td>h, k and l mixed</td>
</tr>
</tbody>
</table>

This explains the absence of the (100) peak in an XRD spectrum of crystalline silicon; the sum of the squares of (hkl) is one, which does not comply with the selection rule. However, if the measured sample has crystals with the (100) orientation in the direction of the surface normal, they will show up as a (400) peak in the XRD spectrum, since this diffraction peak does meet the selection rule.

Figure 2.11: Powder diffraction XRD spectrum of silicon, showing the main diffraction peaks.

The effect of the crystal structure factor $F$ can also be seen in a powder diffraction spectrum. In powder diffraction, the measured sample consists of a crystalline material that is ground to tiny crystals. Since these crystals are randomly oriented, all possible crystal orientations with respect to the surface normal are equally present. Therefore, any difference in intensity of the various diffraction peaks stems from the difference in crystal structure factor. A typical powder spectrum of silicon is shown in figure 2.11 as taken from the RRUFF database\(^1\). It is clearly visible that the peak intensity is plane-dependent.

When looking at preferential crystal orientations in for example polycrystalline materials, it is very important to take the powder diffraction spectrum into account. Only

\(^1\)Website: http://www.rruff.info
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After dividing the peaks in an XRD spectrum of a polycrystalline material by their respective powder diffraction peak heights, it is possible to reveal a preferential orientation. In the case of a randomly oriented polycrystalline film, all the peaks will have the same height after division. If a certain crystal orientation prevails preferentially, it will show up as the highest peak after division.

As a final note on XRD, it is also possible to deduce information on crystallite size from a spectrum. As the crystallite size decreases, the width of the diffraction peak increases. The reason for this can be made clear using a very simple argument and by looking at two limiting cases: Diffraction from only two successive planes, like in figure 2.9, and the case of diffraction from an infinite crystal. When diffraction occurs from only two successive planes, there will still be some constructive interference when slightly deviating from the Bragg angle. To be more precise, the diffracted beam intensity will only drop to zero when going from the Bragg angle to the angle for destructive interference, so from (a) to (b) in figure 2.9. Therefore, the diffraction peak in an XRD spectrum would be very broad in this case. On the other hand, in the case of an infinite crystal there will only be a diffraction peak exactly at the Bragg angle, and consequently the diffraction peak is a Dirac delta peak (ignoring instrumental broadening). To see why, consider the case of diffraction from an infinite crystal, at such an angle that the diffracted beams from the first two planes are out of phase by for example 1/10 of the wavelength. If there were only two planes, there would still be constructive interference. However, diffraction from the fifth plane will have a 1/2 wavelength difference, leading to destructive interference with the beam diffracted from the first plane. For an infinite crystal, this will hold for any wavelength difference between successive planes, since there will always be diffraction from a plane that exactly cancels with diffraction from another plane. The only exception is diffraction at the Bragg angle at which diffraction from all planes is exactly in phase, which explains the Dirac delta peak for an infinite crystal.

The average crystallite size can be estimated from an XRD spectrum by applying Scherrer’s formula:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$ (2.17)

In this equation, $\tau$ is the average crystallite size, $\lambda$ the wavelength of the used x-ray (Cu K-α), $\beta$ the full width at half maximum of the diffraction peak, and $\theta$ the diffraction angle. K is a dimensionless constant, known as the shape factor. It is dependent on the shape of the crystallite, and is usually taken as 0.89 for spherical crystals. Note that the Scherrer formula provides a lower limit on the crystal size, since additional broadening arises due to instrumental imperfections. An extensive review on the Scherrer formula and the various shape factors can be found in reference [65].

XRD measurements have been performed on a Panalytical X’pert Pro MRD. Soller slits were placed on both the incident and diffracted side to reduce the influence of scattered signals. A nickel filter was used to attenuate radiation of the copper X-ray source other than the K-α radiation. Scans were taken in the 20-60° 2θ range.
CHAPTER 2. EXPERIMENTAL SETUP

2.2.5 UV-VIS Absorbance measurement

The light absorbance of poly-Si films has been determined by a UV-VIS absorbance setup. A simplified schematic of the working principle is depicted in figure 2.12. Two operating modes are displayed. On the left, the setup is configured to measure the transmittance of the sample, whereas on the left it is configured to measure the reflectance.

In transmittance mode, a beam from the light source, which is tuneable over a wavelength range of 240-2400 nm, strikes the sample. In this case the sample is positioned in the superstrate configuration. The part of the light that is transmitted by the sample, either after being scattered or going straight-through, enters an integrating sphere. The straight-through component of the light is scattered by a white reflector at the back of the setup. By comparing the signal of the integrating sphere to the case when there is no sample placed, the percentage of transmittance can be determined. By varying the source wavelength, the transmittance as a function of wavelength is obtained. Additionally, by removing the reflector in this measurement mode, the amount of diffusely transmitted light can be measured instead of the total amount of transmitted light.

In reflectance mode, the sample is placed at the position of the white reflector in transmittance mode. Light that is reflected is measured by the integrating sphere. Again, the percentage of reflectance can be determined by comparing the signal with and without sample, and the source wavelength is varied in order to obtain the reflectance as a function of wavelength.

Since all the light that is shone on the sample should either be transmitted, reflected or absorbed, the absorbance of the film as a function of wavelength can be obtained from the transmittance and reflectance by the following equation:

\[ A(\lambda) = 1 - T(\lambda) - R(\lambda) \]  \hspace{1cm} (2.18)

Figure 2.12: Simplified schematic of the working principle of the UV-VIS absorbance setup. On the left the setup is in transmittance mode, on the right the setup is in reflectance mode. Samples are measured in the superstrate configuration.
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In this equation, $A$, $T$ and $R$ are the film absorbance, transmittance and reflectance, respectively.

Measurements were performed with a Shimadzu UV-3600 spectrophotometer. Measurements were taken in the 450-1100 nm wavelength region. 450 nm was taken as the lower bound, since this was the cut-off wavelength of the used glass and quartz substrates. The upper bound of 1100 nm was taken since this approximately matches the bandgap of c-Si (1.12 eV).
Chapter 3

Towards polycrystalline silicon deposition by ETP-CVD

3.1 Introduction

In this chapter the feasibility of depositing poly-Si by an expanding thermal plasma is explored. Although the expanding thermal plasma is a technique capable of depositing device-grade a-Si:H at high deposition rates, poly-Si deposition was never attempted by ETP. As stated in the outline, the expanding thermal plasma may have some specific advantages with respect conventional techniques such as a high deposition rate and the absence of high-energy ion bombardment.

Two approaches to explore the feasibility of poly-Si deposition have been followed. The first approach is a low-temperature route (<600 °C) in which the SiH$_4$ in an Ar-H$_2$-SiH$_4$ plasma is pulsed to allow for low-temperature crystal growth. This approach is inspired by the LBL technique, where short depositions of a-Si:H are alternated by an atomic hydrogen treatment that leads to crystallization of the film. The effect of the hydrogen treatment on the film crystallinity in our system was investigated and a tentative explanation for the observed results is given. The reason for taking the pulsed-deposition approach was because for the ETP setup no experimental condition for poly-Si deposition at substrate temperatures <600 °C is known, despite the extensive investigation of parameter space in the past.

The second approach is a high-temperature route (>600 °C). As mentioned before, this high deposition temperature has specific disadvantages like the incompatibility with inexpensive glass substrates, diffusion of impurities across films and the need for post-hydrogenation of the poly-Si for dangling bond passivation. Nonetheless, in order to achieve full crystal growth the high substrate temperature may be necessary to compensate for the lack of ion bombardment-enhanced surface diffusion in ETP at the substrate. For this approach, the role of growth radicals and temperature on the film properties is investigated.
CHAPTER 3. TOWARDS POLYCRYSTALLINE SILICON DEPOSITION BY ETP-CVD

3.2 Pulsed deposition for low-temperature crystal growth

For the pulsed silane deposition experiments a fast-acting ALD valve was connected to the silane line, which has an open shutter time of ten milliseconds and a variable ‘off time’. In order to see if this approach can enhance film crystallinity, the optimized deposition condition for µc-Si:H was taken as the starting point. In this condition, the arc current is set to 45 A and gas flows are set to 55 sccs of Ar, 30 sccs of H₂ and 0.33 sccs of SiH₄. The substrate temperature was set at 250 °C or 580 °C. The deposition temperatures and off-times used for depositions are summarized in table 3.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Off-time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>250</td>
<td>0.67</td>
</tr>
<tr>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>250</td>
<td>1.2</td>
</tr>
<tr>
<td>250</td>
<td>1.5</td>
</tr>
<tr>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>580</td>
<td>0</td>
</tr>
<tr>
<td>580</td>
<td>10</td>
</tr>
<tr>
<td>580</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 3.1: Deposition temperatures and off-times used for the pulsed depositions.

For depositions at 250 °C, the ‘off-time’ has been varied between zero (continuous deposition) and two seconds. It has to be noted that although the ALD valve only opens for ten milliseconds during a deposition cycle, the chamber residence time is approximately 1.2 s, as inferred from QMS measurements. Therefore, for off-times lower than 1.2 s, there is no effective separation between the deposition and hydrogen treatment cycles and the deposition is more or less continuous. For these low off-times the deposition is effectively carried out at a higher hydrogen/silane dilution ratio, and therefore a higher crystallinity is expected. Only for off-times above the chamber residence time there is an effective hydrogen treatment that can affect film properties.

The Raman spectra for the various off-times are shown in figure 3.1(a). For these films, the total deposition time was kept constant at 400 seconds. The corresponding film crystallinity is displayed in figure 3.1(b).

For off-times well below the chamber residence time an increase in film crystallinity with respect to the continuous deposition is observed, as expected. For off-times above the chamber residence time, the crystalline fraction decreases rapidly, as seen by the decrease in the 520 cm⁻¹ TO peak of c-Si, indicating that the hydrogen treatment induces an amorphization of the film.

FTIR spectroscopy indicates a microstructural change for increasing off-time, as shown in figure 3.2. In the case of continuous deposition the film is dominated by NHSM (hydrogen bonded on crystal grain surfaces) and hardly any LSM is detected (i.e. low density of hydrogen in vacancies). The hydrogen treatment increases both the LSM and HSM contribution, while decreasing the NHSM peaks. It is tempting to suggest that because of the observed decrease in NHSM the pulsed deposition results in films where the grain boundaries are better passivated by amorphous tissue. However, care must be taken since also the crystalline content is decreased when increasing the off-time. The presence of the convoluted oxidation peaks in the 800 - 1200 cm⁻¹ region
for all the films also indicates that no enhanced crystal grain passivation takes place or that the amorphous tissue itself is prone to oxidation.

Because of the unexpected decrease in crystallinity, the influence of pulsed deposition on film crystallinity was investigated further at a higher deposition temperature of 580 °C and at longer hydrogen treatment times of 10 and 20 seconds. Figure 3.3 shows the resulting Raman spectra. Again, the film crystallinity is decreased significantly by the hydrogen treatment as seen from the decrease of the 520 cm\(^{-1}\) c-Si TO peak. FTIR shows that the films are oxidized and contain no hydrogen, most probably due to outdiffusion that readily occurs at this high deposition temperature.

The decrease in crystalline fraction with hydrogen exposure time was also observed by van Sark et al. in the case of μc-Si:H deposited by RF PECVD.\(^6\) Unfortunately, no explanation was given for their similar observation. In our case, a few tentative explanations for the observed decrease in crystallinity are proposed: the conventional LBL technique typically less than one monolayer is deposited during the deposition cycle.\(^3\) In our case, the thickness determined by SE shows that 2-3 nm of film is deposited per pulse. This is possibly too large to have effective crystallization by the hydrogen. Also the energy of the impinging hydrogen ions and radicals could be the culprit. Boland et al. attribute the crystallization of the film to the selective removal of strained Si-Si bonds by hydrogen etching.\(^3\) In their case PECVD is used which features the presence of higher ion bombardment with respect to the expanding thermal plasma, both in terms of particle flux and ion energy. Therefore the etching conditions in our setup may be

\(^1\) An experimental reason could be that the amount of silane that is injected per pulse is dependent on the off-time. Since the ALD valve is connected downstream from a MFC that is set to a SiH\(_4\) flow of 0.33 sccs, pressure can build up in the gas line upstream during the off-time leading to a higher silane injection during the deposition cycle. However, QMS showed that the m/e=31 peaks (corresponding to SiH\(_3\)) right after a SiH\(_4\) pulse were similar for the different off-times. Additionally, the fact that 2-3 nm is deposited per pulse independently of the off-time suggests a similar amount of silane per pulse.
such that no preferential etching takes place. Moreover, in the computational analysis of hydrogen-induced crystallization by Sriraman et al. that was mentioned in the introduction chapter, incident hydrogen atoms are given an energy of up to 5 eV which could indicate that excited hydrogen is required for successful crystallization. Also, it could be that the microstructure of our ETP-deposited amorphous tissue is different (i.e. hydrogen bonding configuration, network order) from the amorphous silicon microstructure in the above-mentioned studies, making it less susceptible to hydrogen-induced crystallization. Finally, the decrease in crystallinity could be explained by atomic hydrogen etching of the crystalline nuclei. In the experimental conditions used (i.e. the standard \( \mu \)c-Si:H condition) crystal nuclei develop even when no hydrogen treatment is performed. During the off-time, it seems plausible that atomic hydrogen is able to etch these nuclei, which could explain the decrease in crystallinity with off-time.

These results indicate that crystalline film growth by pulsed-deposition is non-trivial. Although many authors have reported on the successful crystalline film growth by the LBL technique, we have demonstrated that the effect of the hydrogen treatment can also reduce film crystallinity. From our results, it seems that the chamber residence time, the amount of deposition per pulse and the hydrogen plasma treatment (both time and nature of the hydrogen plasma) can play a major role in the film crystallinity. For a detailed analysis on the effect of the hydrogen treatment on the film surface, in-situ techniques like SE or ATR-FTIR could be employed. However, this route was not further investigated in this thesis and the possibility of depositing poly-Si at temperatures exceeding 600 °C was explored.
CHAPTER 3. TOWARDS POLYCRYSTALLINE SILICON DEPOSITION BY ETP-CVD

Figure 3.3: Raman spectra of µc-Si:H films for various hydrogen treatment times at 590 °C.

3.3 High temperature deposition of polycrystalline silicon

The second approach is the use of a high substrate temperature to obtain crystal growth. Since the use of temperatures >600 °C prohibits the use of glass substrates, depositions were performed either on quartz plates and/or (oxidized) silicon wafers.

For the first experiments the substrate temperature was controlled at 700 °C and the gas flows were varied in order to find a condition that results in poly-Si deposition, and more importantly, to elucidate the role of growth radicals on the material properties of the deposited film. Depositions were carried out both on samples of quartz and c-Si wafer. The SiH$_4$ flow was kept relatively low in order to keep the deposition rate low, since crystalline growth is more challenging to achieve at high deposition rates. For some conditions, the arc current and/or the argon flow was reduced as well in order to further reduce the deposition rate. Various conditions and the resulting film phase, determined by Raman spectroscopy, are shown in table 3.2.

<table>
<thead>
<tr>
<th>Arc current (A)</th>
<th>Ar flow (scce)</th>
<th>H$_2$ flow (scce)</th>
<th>SiH$_4$ flow (scce)</th>
<th>Film phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>55</td>
<td>0</td>
<td>0.33</td>
<td>a-Si</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>0</td>
<td>0.13</td>
<td>a-Si</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>10</td>
<td>0.33</td>
<td>µc-Si</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>30</td>
<td>0.33</td>
<td>µc-Si</td>
</tr>
<tr>
<td>45</td>
<td>25</td>
<td>30</td>
<td>0.33</td>
<td>µc-Si</td>
</tr>
</tbody>
</table>

Table 3.2: Various deposition conditions and the resulting film phase at 700 °C.

The observed effect of the deposition conditions on film phase is discussed below.
From these experimental results, the role of growth radicals on the film phase is deduced, as will be discussed in the next section (3.3.1).

As seen from the table, for both conditions where no hydrogen is admixed in the arc the film phase is amorphous, even when using a very low arc current and low argon and silane flows. Adding high amounts of hydrogen (10 and 30 sccs) leads to a microcrystalline phase, indicating once again the importance of hydrogen in achieving crystal growth.

Since these initial experiments at 700 °C did not result in the deposition of a poly-Si film, the substrate temperature was raised to 800 °C for further experiments. Table 3.3 shows the resulting film phases at 800 °C for a different set of conditions.

<table>
<thead>
<tr>
<th>Arc current (A)</th>
<th>Ar flow (sccs)</th>
<th>H₂ flow (sccs)</th>
<th>SiH₄ flow (sccs)</th>
<th>Film phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>55</td>
<td>0</td>
<td>0.1</td>
<td>a-Si</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>5</td>
<td>0.33</td>
<td>µc-Si/poly-Si</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>10</td>
<td>2.5</td>
<td>poly-Si</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>10</td>
<td>10</td>
<td>a-Si</td>
</tr>
</tbody>
</table>

Table 3.3: Various deposition conditions and the resulting film phase at 800 °C.

Again, for the first condition with no hydrogen admixed in the arc, the film is amorphous. However, two conditions that lead to a crystalline film were identified. For a hydrogen flow of 5 sccs and a silane flow of 0.33 sccs FTIR shows that the film is highly oxidized. Also, Raman shows a very limited remaining amorphous content. However, the film produced using 10 sccs of hydrogen and 2.5 sccs shows no sign of amorphous tissue and is stable to oxidation, indicating a dense film.

The poly-Si film deposited by this initial unoptimized deposition condition has been analyzed by Raman spectroscopy, X-ray diffraction, AFM and scanning electron microscopy (SEM). In the Raman spectrum (figure 3.4(a)) only the c-Si TO peak is visible, indicating full crystallinity. However, the TO peak is slightly shifted to 519 cm⁻¹, which could indicate stress in the film. [67]

X-ray diffraction (figure 3.4(b)) reveals a very strong preferential orientation. The (220) peak at 47.4° 2θ is much higher than the (111) and (311) peak. The FWHM of the (220) peak is only 0.14° 2θ, whereas the (111) and (311) peaks are much broader, with a FWHM of 0.27 and 0.30° 2θ, respectively. This suggests a much larger perpendicular grain size for (220)-oriented grains, which is a strong indication of the desirable columnar growth, typical of (220) oriented films.

Cross-sectional SEM shows a film thickness of 2.5 µm (figure 3.5). Since the deposition time was 300 seconds, an unoptimized deposition rate in excess of 8 nm/s was achieved, which is considerable for poly-Si deposition. It is noteworthy that when using the same plasma conditions but a lower substrate temperature of 400 °C, Kessels et al. obtained an amorphous silicon film at a deposition rate ~3 nm/s.

Under these conditions, they found from aperture-well experiments that the overall surface reaction probability was ~0.3-0.4. [68] At 800 °C, the deposition rate is nearly
three times higher, indicating an overall surface reaction probability close to unity at this elevated substrate temperature. This in turn suggests that the growth surface is strongly different. Most likely the surface hydrogen coverage is drastically lower due to thermal desorption of surface hydrides at this higher temperature, which renders the surface much more reactive. The decrease of surface hydride coverage with increasing substrate temperature has been reported by various authors.\[33, 69\]

Looking at the zoomed SEM images in figure 3.5, some small pores are visible even  

\[\text{As shown in appendix A.1, a deposition rate of 8 nm/s and a surface reaction probability of 1 suggests a silyl radical flux of } 4 \times 10^{20} \text{ atoms/m}^2\text{s, which is very close to the experimentally determined } 3 \times 10^{20} \text{ atoms/m}^2\text{s, which justifies this assumption.}\]
though FTIR did not reveal any appreciable oxidation. Also, the film microstructure is inhomogeneous. At the bottom of the film, small facets are visible, indicating small grains. Towards the top of the film, larger grains develop. The grain boundaries are observed to be predominantly vertical, although the growth does not look as columnar as for example the poly-Si films prepared by HWCVD at the Utrecht University. An appreciable surface roughness due to crystal growth is also visible in the SEM image, which may prove to be useful for light trapping.

The surface morphology has also been determined by AFM. Figure 3.6 shows a 3D image of a 2x2 μm² AFM scan. This scan has been made with a NT-MDT Solver AFM using a TiN-coated tip (NSG01). The image reveals that the surface is dominated by a pyramid-like morphology. The features have a height up to 120 nm and a lateral dimension of typically ~200 nm. The RMS roughness of this film is ~20 nm, which is close to 1% of the film thickness. The effect of deposition conditions on surface roughness and light trapping will be explored further in Chapter 5.

### 3.3.1 The role of growth radicals in poly-Si deposition

An attempt has been made to explain the observed film phases by the predominant growth radicals for the various H₂ and SiH₄ flows, using the Ar-H₂-SiH₄ plasma chemistry as treated in section 2.1.1 of the experimental details chapter.

As discussed in the experimental setup, for conditions where no hydrogen is admixed in the arc, the dissociation of silane occurs purely by dissociative charge transfer from positive argon ions (reaction 3.1), followed by dissociative recombination with electrons (reaction 3.2), leading to the very reactive SiHₙ radicals (n ≤ 2).

\[
\text{Ar}^+ + \text{SiH}_4 \rightarrow \text{Ar} + \text{SiH}_n^+..(n \leq 3) \quad (3.1)
\]

\[
\text{SiH}_n^+ + e \rightarrow \text{SiH}_m + ..(m \leq 2) \quad (3.2)
\]

The reason for the fact that films prepared without hydrogen flow are amorphous is thought to be the low surface diffusion of these reactive growth radicals, along with the lack of atomic hydrogen reaching the surface.

When hydrogen is admixed to the arc, the arc becomes a source of atomic hydrogen. The role of this hydrogen in deposition is two-fold: the atomic hydrogen impinging on the surface seems to have a crucial role for crystallinity, as summarized by the various
models discussed in section of the Introduction chapter. Secondly, the atomic hydrogen dissociates the injected silane through (sequential) hydrogen abstraction (reaction 3.3).

\[ \text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2 \]  

(3.3)

It is stated that the H\textsubscript{2}/SiH\textsubscript{4} dilution ratio R is critical in determining whether the film will be microcrystalline or polycrystalline and whether the film is prone to oxidation, as will be elaborated below.

The effect of the hydrogen dilution ratio on the presence of the lower radicals in the plasma is shown by optical emission spectroscopy (OES) measurements. Figure 3.7(a) shows the emission intensity from the Si\textsuperscript{*} and SiH\textsuperscript{*} excited species for various hydrogen and silane flows. The arc current and argon flow were fixed at 45 A and 55 sccs, respectively.

![Figure 3.7(a)](image)

Figure 3.7: (a) Si\textsuperscript{*} \((4s^1 P^0 - 3p^2 1S)\) emission intensities for various silane and hydrogen gas flows. (b) The corresponding SiH\textsuperscript{*} \((A^2\Delta - X^2\Pi)\) emission intensities.

At very high dilution ratios R, a lot of atomic hydrogen is available for silane dissociation. Therefore, there will be an increased contribution of SiH\textsubscript{x} \((x \leq 2)\) radicals, which are produced by sequential hydrogen abstraction reactions, to film growth. As seen in figure 3.7(a), this is especially the case for SiH\textsubscript{4} flows below 1 sccs, but not so much for higher SiH\textsubscript{4} flows. These reactive SiH\textsubscript{x} \((x \leq 2)\) radicals are detrimental to crystallinity due to their low surface diffusivity. Additionally, the low diffusivity leads to voids in the film, making the films prone to oxidation. On the other hand, the high flux of hydrogen is beneficial for crystallinity. Looking at the results in both tables, the conditions with a low SiH\textsubscript{4} flow \((\leq 0.33 \text{ sccs})\) and high R value \((30 \text{ and 90 for } 700 \text{ oC}, 15 \text{ for } 800 \text{ oC})\) result in microcrystalline films, where the film with R=15 is very close to polycrystalline. Additionally, all these films show oxidation, which is attributed to the low diffusivity of the growth precursors.

For very low dilution ratios, for example when using 10 sccs of hydrogen and silane flow, the film is amorphous. This could be attributed to a lack of atomic hydrogen flux.
towards the surface, since atomic hydrogen is being depleted by the large amount of silane via the hydrogen abstraction reaction. However, for this condition also the high deposition rate due to the high silane flow could be the culprit.

For an intermediate R value of 4 poly-Si is obtained that is also resistant to oxidation. It is thought that at this intermediate dilution condition, it is likely that the interaction between one hydrogen atom and one silane molecule will occur just once, leading to mainly SiH$_3$ radicals and less SiH$_x$ ($x \leq 2$) radicals. The prevailing SiH$_3$ growth radical is good for obtaining crystallinity and avoiding voids in the film thanks to the high diffusion length of this precursor. Also, the silane flow is not high enough to deplete all the atomic hydrogen, leaving a sufficient flux of atomic hydrogen to assist in crystallization.

### 3.4 Conclusions

In this chapter, the feasibility of depositing poly-Si by ETP was explored. Two approaches followed to obtain poly-Si deposition have been presented. In the low-temperature route, pulsed deposition of silane was used to achieve crystal growth. However, pulsed deposition showed to induce a decrease in film crystallinity. Although the exact reason for the decrease in crystallinity is not known, a few hypotheses have been addressed. The first reason could be that too much silicon is deposited per pulse, preventing effective selective etching of strained Si-Si bonds. Also the absence of considerable H ion bombardment during the hydrogen treatment cycle could be the culprit. Nonetheless, since this route did not provide any promising results for poly-Si deposition, the second route was followed, i.e. the high-temperature route.

For films deposited at temperatures at 700 and 800° C, it was proposed that the H$_2$/SiH$_4$ flow ratio is of crucial influence on both the film crystallinity and porosity. At a very high dilution ratio, a high H flux impinges on the growth surface, promoting crystallinity. However, the presence of repeated hydrogen abstraction reactions in the gas phase leads to reactive SiH$_x$ ($x \leq 2$) silyl radicals, that tend to lead to less crystallinity and porous films. Therefore, films at high dilution ratios showed (micro)crystallinity, but were very sensitive to oxidation.

For low hydrogen flows, there is little or no flux of atomic hydrogen towards the surface, and the main growth radicals are SiH$_x$ ($x \leq 2$) silyl radicals that originate from dissociative charge transfer of silane molecules with argon ions, followed by dissociative recombination with electrons. Thus all films deposited at a low hydrogen flow showed to be amorphous, even at 800° C.

It was found that an intermediate dilution ratio of 4 leads to a promising poly-Si film. Raman indicated full crystallinity and XRD showed a strong preferential (220) orientation, along with a large perpendicular grain size for the (220) grains. SEM shows that the film still contains some pores, and that the grain morphology is inhomogeneous, with larger grains at the top of the surface. To conclude, it has been demonstrated that it is feasible to deposit poly-Si by ETP. Moreover, in view of the low deposition rates typical of conventional techniques, the high unoptimized deposition rate of 8 nm/s is very promising.
4.1 Introduction

In the previous chapter, initial results on the direct deposition of poly-Si were presented. XRD showed a strong preferential (220) growth, and a strongly inhomogeneous grain morphology was observed in the SEM image, with small grains at the bottom of the film growing to larger grains towards the top of the film. The aim of this chapter is to gain insight in the evolution of the grain morphology and orientation during deposition.

The dependence of the preferential orientation on the film thickness has been investigated. In literature it is common to report preferential orientations of poly-Si films, but very limited studies are dedicated to the evolution of the preferential orientation with film thickness. Since SEM revealed an evolution of the grain morphology from small crystals to more columnar growth, it is speculated that a change in preferential orientation may occur. XRD has been performed on a thickness series to determine whether the preferential (220) orientation is present from the onset of crystal growth or whether it develops during film deposition.

Furthermore, in-situ SE has been employed for the characterization of film growth. Spectroscopic ellipsometry is able to distinguish between amorphous and crystalline growth, and is therefore an excellent tool to check for the presence of incubation amorphous layer in our films, as already observed in µc-Si:H growth. The growth of poly-Si under various deposition conditions has been monitored by in-situ SE in order to investigate the presence of an incubation layer (and its thickness), and its dependence on the deposition conditions.

This chapter is concluded by a proposed model able to explain the observed inhomogeneous grain morphology as seen in the SEM image, and also the different phases of film growth that were found from XRD measurements on the thickness series and the in-situ SE measurements. Furthermore, this model has been verified by TEM imaging.
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4.2 Experimental details

A thickness series for the ex-situ XRD analysis has been deposited using the initial deposition conditions defined in the previous chapter. Depositions were carried out on quartz substrates. Deposition times were varied between 10 and 1200 seconds in order to have a large range in thickness (∼80-9600 nm).

For in-situ SE analysis, oxidized (∼450 nm) silicon wafers were used for deposition. The reason for using oxidized wafers instead of bare silicon wafers is that the SiO$_2$ layer generates a better contrast between the silicon wafer and the poly-Si film, essential for the SE modeling. Also, the surface of an oxidized wafer is comparable to that of quartz, which can be of importance for crystal growth. A scan time of one second was used, as this was found to be a good compromise between temporal resolution and signal-to-noise ratio. Note that since deposition rates in the order of 10 nm/s are achieved, the film thickness increases on the order of 10 nm during an SE measurement with a scan time of 1 s. Therefore these measurements represent the 'effective' film during an acquisition. For the in-situ SE analysis, the initial poly-Si deposition condition was taken as the starting point. From this starting condition, the silane flow has been varied between 1 and 7.5 sccs and the substrate temperature was set to either 690 or 740 °C. Additionally, two depositions have been carried out at a higher hydrogen flow of 30 sccs. The deposition time was kept constant at 200 s.

4.3 Results and discussion

4.3.1 X-ray diffraction on a poly-Si thickness series

The thickness series that was deposited for the ex-situ XRD analysis has first been characterized by Raman spectroscopy, which showed full crystallinity for all the films. Even the film with a deposition time of just 10 s shows no amorphous signature. Since this film has a thickness of ∼80 nm, which is much less than the penetration depth of the Raman laser, this suggests that there is no (or a very thin) amorphous incubation layer.

XRD gonio measurements in the 20-60 ° 2θ range have been carried out on this thickness series. The resulting peak intensities of the (111), (220) and (311) diffraction planes for these films are shown in figure 4.1. The peak intensities have been obtained by integration of the area under the peak (after baseline subtraction) and subsequent normalization to the corresponding powder diffraction peak intensity.

Two regimes in the film growth can be observed. For deposition times t < 50 s, the three peak intensities overlap (see inset in figure 4.1), indicating a completely random grain orientation. For larger deposition times the (220) intensity increases, whereas the (111) and (311) intensities remain constant.

Since Raman shows no sign of an amorphous incubation layer, these results suggest a nucleation of randomly oriented crystal grains at the onset of film growth. After a certain thickness, preferential growth of (220) grains takes over, resulting in a linear increase of (220) intensity with thickness.
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Figure 4.1: Peak intensities of the (111), (220) and (311) diffraction peaks for various deposition times. An enlarged view for short deposition times is shown in the inset. For this condition, the deposition rate was \( \sim 8 \) nm/s.

4.3.2 Monitoring poly-Si growth by \textit{in-situ} SE

The poly-Si growth has been investigated further with \textit{in-situ} SE. From the XRD results it is known that there is a transition from a random crystal growth to a preferential (220) growth. It is hypothesized that the preferential (220) growth could originate from a larger crystal growth rate for this orientation with respect to the other orientations. If this is true, it may be possible to see an increase in deposition rate when going from random growth to preferential (220) growth. \textit{In-situ} SE was used to investigate this, as it is an excellent tool to monitor film thickness during growth. Additionally, it can be used to discriminate between amorphous and crystalline growth, allowing for an investigation of an amorphous incubation layer, if present. The model used for SE modeling in the CompleteEASE software is presented in the in-set on page 51.
For SE modeling of the film, the following layers have been implemented in the CompleteEASE software.

- **Silicon substrate**
  A temperature-dependent silicon substrate dielectric function was applied to take into account the changes in the substrate at high deposition temperatures.

- **Oxide layer**
  The wafer oxide layer was modeled by the Sellmeier equation. A Sellmeier is used to fit the dispersion of light in an optically transparent medium.

- **Poly-Si layer**
  The optical response of the deposited layer is fitted by a B-spline. In this way, the effective dielectric function of the deposited film can be determined, making it possible to distinguish between amorphous and crystalline growth.

- **Surface roughness**
  The surface roughness has been modeled by a 5-layer graded EMA layer. The two EMA constituents are voids and a medium of which the dielectric function is coupled to the bulk layer. This approach, instead of the standard roughness model (50% voids, 50% material), was required for obtaining satisfactory fit results. This is expected to originate from the fact that the surface morphology is pyramid-like, as seen in the AFM image of figure 3.6. This is confirmed by the fact that during fitting, the grading results in an increase of void content as a function of the roughness layer thickness.
Since in-situ SE is used to discriminate between amorphous and crystalline growth, it is instructive to look at the dielectric functions of these silicon phases. To this end, simulated $\varepsilon_2$ curves have been generated with the CompleteEASE software, as shown in figure 4.2(a).

Figure 4.2: [a] Simulated $\varepsilon_2$ curves of c-Si at room temperature, c-Si at 800 °C, c-Si with 10 nm roughness and of amorphous silicon. [b] Spectral penetration depth of light in crystalline silicon.

The black spectrum corresponds to the dielectric function of crystalline silicon at room temperature. Two absorption peaks are observed. As can be seen in figure 4.3, these correspond to the direct E1 and E2 transitions at the $\Lambda$ and X points in the band diagram of c-Si, respectively.[63, 70]

The red curve represents the dielectric function of a silicon wafer with 10 nm of surface roughness (50% c-Si, 50% voids). The roughness has a clear effect on the dielectric response. The E1 and E2 peaks are seen to decrease and there is an apparent shift to lower energies. This decrease is ascribed to the void content of the roughness layer. Since the penetration depth of the light is $\leq 20$ nm at the energies of the E1 and E2 peaks (see figure 4.2(b)), the voids ($\varepsilon_2=0$) in the roughness layer constitute a large part of the effective $\varepsilon_2$. Also, since the penetration depth at the energy of the E2 peak is lower than at the E1 peak, the effect of roughness on the E2 peak is more prominent, explaining why the E1 peak is higher than the E2 peak for the rough silicon surface. The dielectric function of c-Si also has a clear dependence on the temperature, as can be seen from the blue curve. At higher temperatures, there is an overall shift...
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to lower energies. Amorphous silicon (teal line) has a broad feature in its $\varepsilon_2$ spectrum, represented by a Tauc-Lorentz oscillator.

![Figure 4.4: Evolution of the effective dielectric function of the bulk layer, as obtained from a B-spline fit.](image)

**In-situ** SE was performed by deposition on an oxidized wafer using our initial poly-Si condition. From the b-spline fit in the model, it is possible to see the evolution of the film dielectric function during deposition, as shown in figure 4.4. It is observed that the film phase during the first 17 s of deposition (corresponding to a thickness of 160 nm) is amorphous, as can be seen by comparison with the teal line in figure 4.2(a). After this thickness, the film dielectric function gradually develops towards the one corresponding to poly-Si, as observed by the development of the two distinct $E_1$ and $E_2$ absorption peaks. Note that these peaks only reveal information on the first $\sim$20 nm of film due to the low penetration depth at this photon energy. With increasing deposition time, the $E_1$ and $E_2$ peaks decrease and the $E_1$ peak becomes more prominent than the $E_2$ peak, indicating the development of an appreciable surface roughness.

The fact that SE shows an amorphous growth for the first $\sim$160 nm of film is remarkable, since films with a deposition time of 10 and 20 seconds (corresponding to a film thickness of $\sim$80 and $\sim$160 nm, respectively) for the XRD thickness series are completely crystalline, as inferred from Raman measurements.

The film thickness and roughness during deposition have been determined by fitting of the SE data. The result is shown in figure 4.5. The film thickness is seen to increase linearly, without a clear variation of deposition rate at the transition from a randomly-oriented to a (220)-oriented film. However, the film roughness evolution shows a remarkable feature. A prominent dip is visible, which has a minimum occurring at about 17 s of deposition. This dip in roughness occurs precisely where the transition from amorphous to crystalline growth is seen in the b-spline fit, indicating a correlation between the two phenomena.

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Figure 4.5: Evolution of the film thickness and roughness during deposition, as determined from in-situ SE.

Fujiwara et al. reported on a very similar observation in the deposition of μc-Si:H by PECVD in several papers [63, 71, 72, 73]. They investigated crystal nucleation in their (220)-oriented μc-Si:H by a combination of in-situ SE, in-situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), stress measurements and TEM. Just like in our case, they observed a dip in roughness in the SE data and occurrence of this dip corresponds to the onset of crystal growth, as verified by TEM. Also, they found a decrease in this transition thickness with an increasing hydrogen dilution, suggesting a prominent role of hydrogen in nucleation. In the ATR-FTIR data an increase of a Si-H mode at ~1937 cm$^{-1}$ corresponding to a so-called Sid-complex is observed during deposition up to the amorphous-crystalline transition, followed by a sharp decrease right after the transition. The Sid-complex corresponds to hydrogen inserted into strained Si-Si bonds, as shown in figure 4.6. A linear correlation between the Sid-complex mode intensity with film stress was found. Also, it was observed that for varying deposition conditions crystal nucleation always occurred at a film stress of ~750-800 MPa.

From these experimental observations, they proposed the following nucleation mechanism for their μc-Si:H films. During deposition, atomic hydrogen inserts into strained Si-Si bonds to form Sid-complexes, thereby increasing film stress. Due to the increased film stress, the subsequent deposited layers will have more strained Si-Si bonds, facilitating the formation of more Sid-complexes. This positive feedback loop leads to an increase of film stress during deposition. At a critical film stress, the film surface rearranges and relaxes, leading
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to a minimum in roughness and is accompanied by the formation of crystal nuclei.

Their proposed nucleation mechanism can shed some light on the question why the pulsed deposition of the previous chapter did not result in an enhanced crystallinity. In conventional LBL deposition a sub-monolayer of deposited silicon is treated with hydrogen, resulting in the formation of Sid-complexes and a corresponding increase in film stress. However, in our depositions typically 2-3 nm of a-Si:H per pulse was rapidly deposited on top of a a-Si:H surface that is treated with a hydrogen plasma. It is speculated therefore, that under our experimental pulsing conditions there is no build up of stress, leading to nucleation.

It is thought that also in our case the dip in roughness corresponds to a nucleation event. The main reasons are the similarities in roughness evolution between our experiments and those of Fujiwara et al. and also the simultaneity of the transition from amorphous to crystalline growth and the roughness dip. To investigate this claim further, the experimental window has been further extended. At a hydrogen flow of 10 sccs, two substrate temperatures of 690 and 740 °C were considered, and the silane flow was varied between 1 and 7.5 sccs. The resulting deposition rates, as determined from in-situ SE, are shown in figure 4.7.

![Deposition rate as a function of silane flow at a H2 flow of 10 sccs.](image)

Figure 4.7: Deposition rate as a function of silane flow at a H2 flow of 10 sccs.

The deposition rate is seen to increase with increasing silane flow, which is attributed to an increased growth precursor flux. The deposition rate also increases with temperature, indicating that growth is thermally activated. For a silane flow of 7.5 sccs at 690 °C the film is amorphous, which could indicate a too high deposition rate for crystal growth and/or a depletion of atomic hydrogen by silane. Note that a deposition rate of more than 18 nm/s is achieved at 740 °C and a SiH4 flow of 7.5 sccs, which is considerable.

Figure 4.8 shows the evolution of film roughness as function of the film thickness for these samples. At 690 °C, the film with 1 sccs of silane flow seems to have two dips in roughness. However, the amorphous-crystalline transition in the B-spline fit is observed for the second dip at 275 nm of film thickness, indicating that the first dip is
not related to the amorphous-crystalline transition. The origin of the first dip at ∼40 nm of thickness is unknown, but it is very well possible that this is related to very similar observations made by Wank et al. in the deposition of a-Si:H by ETP. They attribute this dip in roughness to the coalescence of islands during initial growth, which leads to a lower roughness due to the removal of valleys in between these islands. Additionally, as observed by Fujiwara et al., a significant reduction of the a-Si:H bulk H-content during coalescence leads to a collapse in surface roughness.

The deposition with 5 sccs of silane does not show a clear dip, but the transition to crystalline growth also occurs at the onset of the increased roughness at a film thickness of ∼400 nm. At 740 °C, all films again show a clear dip in roughness followed by an increase in roughness which in each case corresponds to the amorphous-to-crystalline transition.

Figure 4.8: Film roughness versus film thickness for varying silane flows, at 690 °C (a) and 740 °C (b). The transition thickness of each film is marked by a green circle.

Figure 4.9 displays the transition thicknesses of these films, which were determined from the onset of the increasing roughness after the dip. It is observed that a higher deposition temperature results in a lower transition thickness. Also, there seems to be a trend towards a higher transition thickness for higher silane flows, although the amount of data points is insufficient to claim this. However, in view of the nucleation mechanism proposed by Fujiwara et al., the increase in transition thickness with silane flow could be explained. In the silane dissociation mechanism in ETP, for higher silane flows more atomic hydrogen is depleted by hydrogen abstraction reactions from the silane molecules, leaving an insufficient amount of hydrogen to form Sid-complexes. To support this hypothesis, an attempt to quantify the SiH$_3$/H arrival ratio at the surface for these various silane flows has been made, and is presented in appendix A.2. For the standard condition (2.5 sccs of silane) the SiH$_3$/H arrival ratio has been estimated to be around one. The ratio was however found to increase over one order of magnitude going from 1 to 7.5 sccs of silane, supporting the notion that less hydrogen is available for the formation of Sid-complexes at higher silane flows. Additionally, at a higher deposition
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rate, there is less time for hydrogen to incorporate in Sid-complexes. Therefore, less hydrogen is incorporated in Sid-complexes, leading to a more gradual increase of film stress with thickness.

![Graph showing transition thickness as a function of silane flow.](image)

Figure 4.9: Amorphous-crystalline transition thickness as a function of silane flow.

To further investigate the influence of atomic hydrogen on the transition thickness, two depositions at 740 °C and a higher hydrogen flow of 30 sccs have been carried out, with a silane flow of 1 and 2.5 sccs. Unfortunately, we have not been able to get a satisfactory fit of the SE data. However, in the case of 2.5 sccs of silane, the transition is visually seen to occur around 12 seconds of deposition, as opposed to 17 seconds when using only 10 sccs of hydrogen. This indicates that the atomic hydrogen promotes the transition to crystal growth.

![SEM image and X-ray diffraction pattern.](image)

Figure 4.10: Cross-sectional SEM image (a) and X-ray diffraction pattern (b) for a film deposited with 1 sccs of silane and 30 sccs of hydrogen at 740 °C.
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More interestingly, for 1 sccs of silane growth seems to start of crystalline, as qualitatively evaluated by the shape of the pseudo-dielectric function in the SE data. This would indicate that there is no incubation layer or that it is so thin that the temporal resolution of the SE scans is insufficient to detect it. A cross-sectional SEM image of this film is shown in figure 4.10 (a).

The image reveals a structure that seems more columnar than the film of figure 3.5 with a much smaller lateral grain size. A considerable self-structured roughness is observed. The transition between the ~400 nm wafer oxide (bright area in the image) and the deposition is vague due to wafer cleaving, making it hard to check whether an incubation layer is visible.

X-ray diffraction (figure 4.10 b) reveals another remarkable feature of this film. Like all the other films, the preferential orientation is (220). In the region of the (311) diffraction peak a few other peaks are observed, which however are related to the measurement and not the sample. However, at 26.9° 2θ an additional peak is clearly visible. This peak was not observed or hardly visible in other samples.

This peak has been assigned to Σ₃ twin grain boundaries that are present between columnar (220) grains.[14] Figure 4.11 schematically displays this Σ₃ boundary between (220) oriented grains. These grain boundaries are of the [110] tilt type, and are known to be electrically inactive.[14,31] However, as seen in figure 4.11, this type of grain boundary can be interpreted as a monolayer of wurtzite silicon in between cubic silicon. The band gap of WZ-Si is ~0.3 eV lower than that of cubic-Si. Therefore Kondo and Matsuda proposed that this monolayer of WZ-Si acts as a quantum well, leading to states within the band gap of the cubic-Si that act as trapping sites for carriers. They claim that because of this, solar cells made from films with a high density of these twin boundaries typically exhibit a low open circuit voltage.[31]

Since SEM (figure 4.10 a) revealed a highly columnar structure with small lateral grains, the density of Σ₃ grain boundaries is high and therefore we also attribute the peak at 26.9° 2θ to these boundaries. It is speculated that the high hydrogen dilution ratio leads to a high nucleation density, which reduces the lateral grain size, as was also observed by Fujiwara et al.[71] So although these films are highly columnar which should be beneficial for current collection in a p-i-n solar cell, the open circuit voltages may be low in view of the observation of Kondo and Matsuda.

Σ₃ cubic          WZ          cubic
Σ₃ cubic          WZ          cubic

Figure 4.11: Schematic of the Σ₃ twin grain boundary peak and the corresponding band diagram.[31]
4.3.3 Proposed growth mechanism

As stated earlier, there seems to be a contradiction between the results from the thickness series and in-situ SE results. For the deposition conditions used for depositing the thickness series, in-situ SE reveals an amorphous growth for the first $\sim 17$ seconds, whereas films deposited for shorter times than this transition time are fully crystalline according to the ex-situ characterization. Based on the experimental observations, the following growth mechanism for our films is proposed, as also displayed in figure 4.12.

![Figure 4.12: Schematic of the proposed growth mechanism of our poly-Si films.](image)

At the start of the deposition the layer is amorphous, followed by nucleation of crystal nuclei at the surface at a film thickness of $\sim 160$ nm, as inferred from the film dielectric function and dip in roughness, respectively. After the nucleation event, grain growth proceeds with a preferential (220) orientation. This is seen in the XRD data, where (220) preferential growth takes place for films deposited for more than 20 seconds (corresponding again to a film thickness of $\sim 160$ nm). Therefore, the growth is very similar to the $\mu$c-Si:H films of Fujiwara et al.\textsuperscript{[71]} However, due to the high deposition temperature, we expect that the SPC of the amorphous incubation layer readily takes place during deposition. The SPC of the amorphous tissue leads to randomly oriented grains in the incubation layer, which explains the full crystallinity and random orientation of the films that are thinner than the transition thickness.

To verify this hypothesis, the sample deposited with a silane flow of 2.5 sccs at a temperature of 740 $^\circ$C has been analyzed by TEM. Various TEM images are displayed in the inset on page 61. The top image shows the 1.64 $\mu$m poly-Si film on top of the oxide layer. A columnar structure is clearly visible. The middle image is a BFTEM image (28,500x) showing the interface between the poly-Si and the oxide. A clear transition from small crystals to columnar growth is visible at a poly-Si film thickness of $\sim 100$ nm. This thickness coincides with the onset of the roughness dip observed in the in-situ SE data, as can be seen in figure 4.8 (right). This confirms again that the roughness dip corresponds to a transition in the film growth from amorphous to preferential (220) columnar poly-Si growth. The bottom image shows a HRTEM (600,000x) image of the SiO$_2$/poly-Si interface. Small crystal grains (below 100 nm grain size) of various orientations are discernible, which confirms that the incubation layer is fully crystalline after the deposition. The small size of these randomly-oriented grains is thought to originate from a high nucleation rate during SPC, caused by the high deposition temperature of...
740 ° which is well above the crystallization temperature of amorphous silicon (\(\sim 600 \, ^\circ C\)).

An experiment that could further support this growth model would be the deposition of a very thin amorphous layer (thinner than the amorphous-crystalline transition thickness) at the standard poly-Si condition and monitoring the film phase by *in-situ* SE. The model predicts that SPC of this thin amorphous layer should take place within 200 seconds (which was our standard deposition time) at the high deposition temperature.
4.3. RESULTS AND DISCUSSION

Poly-Si

1.64 ± 0.03 µm

SiO₂

0.46 ± 0.01 µm

Si

BFTEM (28,500x)

Nucleation layer (~100 nm)

Columnar grains

HRTEM (600,000x)

Various orientations

Nucleation layer (≈100 nm)

Silicon dioxide/poly-silicon interface
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4.4 Conclusions

In this chapter, poly-Si film growth has been investigated further by X-ray diffraction and in-situ SE. XRD revealed a change in crystal orientation with increasing film thickness. Thin films (≲200 nm) exhibit a random orientation, whereas thicker films are preferentially (220) oriented. In-situ SE showed that for the same deposition conditions, the first ∼160 nm of film growth is amorphous, which seems to contradict the fact that thinner films are observed to be fully crystalline. Based on these experimental observations, a growth model has been proposed. At the transition from amorphous to crystalline growth, a dip in roughness is observed which is attributed to a structural relaxation that leads to crystal nucleation. From this thickness growth is preferentially (220) oriented. The full crystallinity and random orientation of films with a thickness below the transition thickness is attributed to solid phase crystallization of the amorphous incubation layer during deposition. This hypothesis has been verified by TEM images.

Additionally, it was found that temperature, silane and hydrogen flow play a major role in determining the film properties. The transition thickness was found to decrease strongly with an increasing deposition temperature. Also, there seems to be a trend of a higher transition thickness with a higher deposition rate. Finally, increasing the hydrogen flow to 30 sccs was found to promote the transition. At this higher hydrogen flow, the transition time was seen to decrease from 17 to 13 seconds when using 2.5 sccs of SiH$_4$ and no transition was visible when using 1 sccs of SiH$_4$.

For this last sample, SEM revealed a highly columnar structure with a small lateral grain size. The presence of a satellite peak at 26.9° 2θ in the XRD spectrum confirms that the film features a high density of grain boundaries between columnar (220) grains. It is hypothesized that the small lateral grain size is due to a high nucleation density at this high hydrogen dilution, as was also observed by Fujiwara et al. [71].
Chapter 5

Optical properties of poly-Si and solar cell performance

5.1 Introduction

In the previous chapters it has been shown that the ETP is capable of depositing polycrystalline silicon at very high deposition rates (up to 18 nm/s). Additionally, a thorough understanding of the crystal grain growth has been obtained. Due to these promising results, it was decided to investigate the performance of ETP-deposited polycrystalline silicon as an intrinsic absorber layer in a p-i-n solar cell on quartz. However, for successful solar cell application, not only the crystal properties are of importance, but also the optical performance. Therefore, this chapter focuses on the optical absorbance of our poly-Si films. More precisely, the effect of film thickness and roughness on the absorbance is investigated.

To this end, the absorbance of two different series of poly-Si films has been determined. Firstly, the absorbance of the thickness series of directly-deposited poly-Si from chapter 4 has been measured. The SEM and AFM images in the previous chapters reveal a self-structured surface roughness due to crystal growth for our directly-deposited poly-Si films, which is thought to favour light trapping. Therefore, the absorbance of this series is affected by both the film thickness and the surface roughness.

In order to separately elucidate the effect of poly-Si film roughness on light trapping, a second poly-Si series has been deposited. This series consists of a-Si:H films of constant thickness (1 µm) but varying surface roughness, which have been crystallized by SPC. Due to the equal film thickness and mass density, absorbance differences in this series originate from differences in surface morphology, allowing for a precise determination of the role of the film surface morphology on light trapping.

Additionally, since film roughness is desired for optimal light trapping in photovoltaic applications, the effect of deposition conditions on the surface roughness of directly-deposited poly-Si films is explored in this chapter. For this purpose, the films deposited for the in-situ SE series have been investigated by AFM. The observed dependence of roughness on the deposition parameters has been explained by a difference in crystal
nucleation density, as will be explained in section 5.4.

By combining the insights achieved in this thesis work, a few deposition conditions have been chosen for the production of a full p-i-n solar cell stack on quartz. At the moment of writing, these experiments are underway. Therefore, the planned depositions are reviewed, along with the rationale for choosing these conditions. The solar cell production will be carried out in collaboration with the silicon photovoltaics department of the Helmholtz institute in Berlin.

### 5.2 Influence of poly-Si thickness and roughness on absorbance

The absorbance of the poly-Si thickness series from chapter 4 has been measured by the UV-VIS absorbance setup, as discussed in section 2.2.5. The absorbance spectra of these films are shown in figure 5.1. The absorbance increases with the deposition time (the deposition rate was $\sim 8$ nm/s). Some spectra exhibit clear fringes due to interference effects.

![Light absorbance spectra of direct poly-Si for various deposition times.](image)

Figure 5.1: Light absorbance spectra of direct poly-Si for various deposition times.

For thick films the long-wavelength absorbance is seen to increase. This suggests that the increase of film absorbance (and thus the optical path length) with film thickness should not only be attributed to an increased film thickness, but also to enhanced light scattering due to an increased film roughness. Therefore, the film surface morphology of these films has been investigated by atomic force microscopy (AFM).
Table 5.1: 10x10 µm$^2$ AFM scans, showing the evolution of surface morphology for different deposition times.
AFM images of the film surface morphology for various deposition times are shown in table 5.1. With increasing deposition time the film morphology is seen to evolve from a smooth surface to a surface with a clearly visible crystal grain structure. The decrease in grain density with film thickness suggests a competition in grain growth. Also, for ten seconds of deposition the film is very smooth and no surface grains are observed, even though the film is fully crystalline. After twenty seconds of deposition the scan does show grains, which indicates that surface crystal nucleation takes place in between these two deposition times. This is in line with the in-situ SE results of the previous chapter, where nucleation was observed after 17 seconds of deposition.

This decrease in grain density with film thickness has been quantified by determining the grain density from the AFM data. The resulting grain densities of this thickness series are shown in figure 5.2. After an initial jump in grain density due to the nucleation event, the grain density reduces drastically due to competitive growth. This also demonstrates that the growth is not purely columnar, since in that case no decrease in grain density with film thickness would be observed. The effective average surface grain size of these films is also displayed, as was calculated by taking the square root of the reciprocal grain density.

Figure 5.2: The crystal grain density as a function of film thickness as obtained from AFM measurements. The average grain size is also displayed.

The RMS surface roughness of these films is reported in figure 5.3. The film roughness is seen to increase near-linearly with deposition time. Between ten and twenty seconds, the nucleation event is visible as the slope of the surface roughness changes.

To facilitate an easier comparison of the absorbance of these films, their absorbance has been quantified by calculating the theoretical maximum short circuit current density ($J_{sc}$) upon AM1.5 illumination\(^1\). This has been done under the assumption that each photon in the wavelength range of 450-1100 nm leads to one extracted charge carrier.

\(^1\)A datasheet containing the AM1.5 spectrum has been obtained from the NREL website (http://rredc.nrel.gov/solar/spectra/am1.5/).
Figure 5.3: RMS roughness of a poly-Si thickness series as determined by AFM. The red dotted line is a guide to the eye.

(i.e. an internal quantum efficiency of 1). The wavelength of 450 nm was taken as the lower limit since this is the cut-off for the quartz substrate, and 1100 nm was taken as the upper limit as this corresponds to the bandgap energy of c-Si. The mathematical procedure used for the calculation of \( J_{sc} \) is shown in the inset.

---

**Mathematical procedure for determining \( J_{sc} \)**

For the determination of \( J_{sc} \) it is desired to count the photons that are absorbed per second. The AM1.5 spectrum is in the form of a spectral intensity, having the dimension \([W/m^2\text{nm}]\). This has been converted to a spectral photon flux by dividing by the photon energy:

\[
\Phi(\lambda) = \frac{I(\lambda)}{E(\lambda)} = \frac{I(\lambda) \times \lambda}{hc} \left[ \frac{\text{#photons}}{m^2 \times s \times nm} \right]
\] (5.1)

The total \( J_{sc} \) originating from photons in the 450-1100 nm range is obtained by integration of the product of spectral photon flux, absorbance and the elementary charge \( e \):

\[
J_{sc} = \int_{450}^{1100} \Phi(\lambda) \times A(\lambda) \times e \, d\lambda \left[ \frac{I}{m^2} \right]
\] (5.2)

In our case, this integral has been replaced by a numerical sum.
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The calculated $J_{sc}$ values versus the film thickness, accompanied by the RMS roughness are displayed in figure 5.4.

Figure 5.4: Maximum short circuit current density as calculated from the measured absorbance curves, along with the RMS roughness of these films. For comparison, the best-performing poly-Si solar cells mentioned in the introduction are indicated in the graph.

The maximum short circuit current density is seen to increase with film thickness, in correspondence with the observed increase of spectral absorbance with increasing film thickness in figure 5.1. As indicated by the blue dotted line in figure 5.4, the maximum $J_{sc}$ increases logarithmically with the film thickness for the three thinnest films. This is in line with Lambert-Beer’s law, which states that light intensity shows an exponential decay in an absorbing medium. However, the thicker and rougher films deviate from this trend, as shown by the red dotted line. It is thought that the additional absorbance (and thus higher $J_{sc}$) of these films originates from the increased optical light path due to scattering at the rough surface.

The best-performing poly-Si solar cells, as mentioned in the introduction, are indicated in the graph. As can be seen, the theoretical maximum $J_{sc}$ of the ETP-deposited poly-Si is in all cases lower than the experimentally reported values, even though an internal quantum efficiency of 1 was assumed. However, it should be noted that the absorbance measurements are done on bare poly-Si on quartz, whereas the processed solar cells make use of additional light trapping techniques like a backreflector and rough substrates.

5.3 Absorbance of SPC poly-Si films of varying roughness

Unfortunately, although the results shown above indicate a beneficial effect of surface roughness on the absorbance for our films, the effect of film roughness and thickness...
cannot be completely decoupled. In order to separately investigate the effect of film roughness on the absorbance, another approach has been taken. Films of a-Si:H of constant thickness (\(\sim 1 \mu m\)) have been deposited by ETP and crystallized by SPC. Typically, poly-Si prepared by SPC of a-Si:H is very smooth with a RMS roughness in the nanometer range. However, by going to ultra-high growth rate conditions in the ETP, a-Si:H films with a higher roughness can be deposited. The a-Si:H films were grown using an arc current of 45 A, and argon, hydrogen and silane flows were 55, 10 and 10 sccs, respectively. The substrate temperature was controlled at 450 °C. The gate valve position was throttled in order to control the chamber pressure, and thereby also the deposition rate. The deposition rate was determined as a function of chamber pressure, as shown in figure 5.5(a) and found to increase with chamber pressure.

![Graph showing linear fit of a-Si:H deposition rate as a function of chamber pressure.](image1)

![Graph showing RMS roughness before and after SPC as a function of deposition rate.](image2)

Figure 5.5: (a) Linear fit of the a-Si:H deposition rate as a function of the chamber pressure. Deposition rates were obtained by dividing the film thickness, as obtained by fitting of interference fringes in the FTIR spectra, by the deposition time. (b) RMS roughness before and after SPC as a function of deposition rate.
Table 5.2: 10x10 μm² AFM scans, showing the surface morphology for different deposition rates.
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Using the found relation between deposition rate and chamber pressure, a series of a-Si:H films with a thickness of 1 \( \mu \text{m} \) (\( \pm 10 \) nm) was deposited by choosing the appropriate deposition time. These films were crystallized by thermal annealing at 600 \(^\circ\)C for 12 hours. Figure 5.5(b) shows the film roughness, both prior to and after crystallization. The RMS roughness value increases with deposition rate, and the roughness after crystallization is seen to be similar to the roughness prior to crystallization.

AFM images also show a similar surface morphology for as-deposited and crystallized films. AFM images of the crystallized films for varying deposition rates are shown in table 5.2.

As can be seen from the table, the increased deposition rate changes the surface morphology from very smooth to a surface that is dominated by cauliflower-like features. The origin of these features for high deposition rates is unknown at the moment. One explanation could be a change of the film growth due to the formation of large silane clusters in the plasma at higher pressures, as was also observed by Kessels et al. when using identical experimental conditions in the same plasma setup.\(^{[47]}\)

By comparing the absorbance of the 1 \( \mu \text{m} \) SPC poly-Si films exhibiting different roughness, the effect of surface morphology on the absorbance can be deduced. The absorbance spectra of these films are shown in figure 5.6. A clear overall increase of the absorbance spectra is seen with increasing roughness, and a film with a roughness of only 16 nm already has a much higher overall absorbance than a smooth film. The fringes of these film seem to have the same periodicity, indicating a similar film thickness. Also, the fringe intensity decreases for rougher films due to a reduction in internal reflections.

![Figure 5.6: Light absorbance spectra of 1 \( \mu \text{m} \) SPC poly-Si films.](image)

The theoretical maximum short circuit current density of these films has been calculated in the same way as in the case of the films of the thickness series. The result is shown in figure 5.7. The maximum \( J_{sc} \) of these 1 \( \mu \text{m} \) films increases monotonically with the film roughness and reaches almost 20 mA/cm\(^2\) for a roughness of \( \sim 18 \) nm.
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Figure 5.7: Maximum short circuit current density as calculated from the measured absorbance curves.

However, care must be taken in interpreting this data and comparing it to the absorbance of the directly-deposited poly-Si. It is known that a-Si:H films that are deposited at very high growth rates contain voids, and therefore light refraction at these voids can also lead to an enhanced optical path length. However, TEM images of films grown under the same conditions in the same reactor by Sharma et al. show that the void content of these films is negligible, except for the film grown at the highest deposition rate.[76] Additionally, not only the value of the RMS roughness is of importance for light scattering, but also the surface morphology plays a role. The directly-deposited poly-Si films exhibit a pyramid-like surface morphology, whereas the crystallized poly-Si films have cauliflower-like features. Therefore, a direct comparison based on the RMS roughness on absorbance value is not possible. Nonetheless, the beneficial effect of surface roughness has been demonstrated.

5.4 Effect of deposition conditions on poly-Si roughness

Since a high surface roughness is desirable for photovoltaic applications, the effect of the deposition conditions on the poly-Si film roughness has been investigated. For this purpose, the poly-Si samples used for the in-situ SE analysis in chapter 4 have been analyzed by AFM. Since these films are not of equal thickness, a comparison is made based on the film roughness divided by the film thickness. This approach is validated by the observation that the film roughness increases near-linearly with film thickness, as can be seen in figure 5.3. The roughness-to-thickness ratio of these films is displayed in figure 5.8.

As can be seen from the figure, the film roughness is greatly dependent on the film temperature. Films deposited at 690 °C have a roughness around 2% of the film
Figure 5.8: Film roughness divided by film thickness for varying silane flow and temperature.

thickness, whereas films deposited at 740 °C have a roughness in the range of 1-1.5% of the film thickness. There seems to be some variation of the roughness with varying silane flow, but no clear trend is discernible.

The precise reason for the temperature-dependence of the film roughness is unknown at the moment. Since films deposited at lower temperatures have a thicker amorphous incubation layer (see chapter 4), a smaller fraction of the film thickness consists of crystal growth, which would suggest a lower roughness-to-thickness ratio for these films instead of the observed higher roughness-to-thickness ratio. One explanation could be a temperature-dependence of the crystal nucleation density. A lower nucleation density would lead to a competitive growth between less grains, giving rise to a larger lateral grain size (and thus a higher RMS roughness) for equal film thickness.

In order to verify this hypothesis, the grain density of these poly-Si films has been determined by AFM. Figure 5.9 displays the surface grain density versus the film thickness minus the incubation layer thickness. The reason for subtracting the incubation layer thickness is that this part of the film does not play a role in the competitive grain growth during deposition. As can be seen from the figure, the grain density decreases with film thickness, similar to what was observed for the thickness series. More importantly, the grain density for films deposited at 690 °C are observed to have a lower grain density than films prepared at 740 °C, which is a strong indication that indeed the initial nucleation density is lower for films deposited at a lower temperature.
5.5 Solar cell application

As stated in the introduction of this chapter, a few poly-Si deposition conditions have been chosen for the production of the i-layer in a p-i-n solar cell. The main goal of the characterization of the produced solar cells is to investigate the influence of film thickness, roughness and nucleation layer thickness on the solar cell performance. The solar cell absorbance is expected to increase with film thickness and roughness, whereas it is expected that the fine-grained nucleation layer is detrimental to the solar cell performance.

Various substrates with a 30 nm n⁺ a-Si:H layer have been obtained from the Helmholtz institute, which have been crystallized by SPC at 600 °C. On top of these layers the poly-Si i-layers, using various deposition conditions, will be deposited by ETP. The chosen deposition conditions are displayed in table 5.3, and a motivation for choosing these conditions is given below. These samples will be sent to the Helmholtz institute for further processing.

Looking at the poly-Si solar cells in table 1.1 in the introduction chapter, it is seen that these cells exhibit a short circuit current density in excess of 20 mA/cm². By looking at the theoretical maximum $J_{sc}$ of our films, a film thickness above 3 micron would be needed to obtain a similar $J_{sc}$, whereas the cells in table 1.1 have an absorber layer thickness of only ~2 µm. However, the absorbance of our films has been measured without the application of back-reflection and a rough transparent conductive oxide, which could further reduce this thickness requirement. For the investigation of the film thickness on the solar cell performance, a thickness series ranging from 1 to 5 micron.
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<table>
<thead>
<tr>
<th>Sample</th>
<th>H&lt;sub&gt;2&lt;/sub&gt; flow (sccs)</th>
<th>SiH&lt;sub&gt;4&lt;/sub&gt; flow (sccs)</th>
<th>Temperature (°C)</th>
<th>Thickness (nm)</th>
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</thead>
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<td>740</td>
<td>1000</td>
</tr>
<tr>
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<td>2.5</td>
<td>740</td>
<td>2500</td>
</tr>
<tr>
<td>Berlin03</td>
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<td>2.5</td>
<td>740</td>
<td>5000</td>
</tr>
<tr>
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<td>2.5</td>
<td>690</td>
<td>1000</td>
</tr>
<tr>
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</tr>
<tr>
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<td>2500</td>
</tr>
<tr>
<td>Berlin07</td>
<td>10</td>
<td>7.5</td>
<td>740</td>
<td>2500</td>
</tr>
</tbody>
</table>

Table 5.3: Overview of the deposition conditions for the poly-Si i-layer for application in a p-i-n solar cell stack.

will be deposited at our standard condition (samples Berlin01-Berlin03).

Two samples (Berlin04 and Berlin05) of 1 and 2.5 micron will be deposited at a lower temperature of 690 °C. The lower temperature will lead to a higher roughness and thicker nucleation layer. By comparing these two samples to Berlin01 and Berlin02, the effect of deposition temperature on solar cell performance can be deduced.

Sample Berlin06 has the same deposition conditions as sample Berlin02, except for the higher hydrogen flow of 30 sccs. It is known from the in-situ SE study that the amorphous-crystalline transition occurs earlier for this higher hydrogen flow. Since these two conditions also have a similar roughness-to-thickness ratio, it is thought that a comparison between these two samples can elucidate the effect of the nucleation layer on the solar cell performance.

Finally, one sample will be deposited at a higher silane flow of 7.5 sccs. This condition has been chosen to see whether an acceptable solar cell performance can be obtained at a high deposition rate close to 20 nm/s.

5.6 Conclusions

In this chapter, the correlation between film thickness, surface morphology and absorbance has been investigated. UV-VIS absorbance measurements on a thickness series of directly-deposited poly-Si revealed an increase in absorbance for thicker films, especially in the long-wavelength region. AFM showed a near-linear increase of RMS roughness with film thickness, which has been attributed to crystal growth. The theoretical maximum $J_{sc}$ of these films under AM1.5 illumination has been calculated from the measured absorbance curves. For thin films ($\leq$400 nm) with a low roughness, the film absorbance increases logarithmically with the film thickness, which is in line with Lambert-Beer’s law. However, for thicker films a steeper increase of absorbance with thickness was observed. Scattering at the rough interface has been assigned as the reason for this increased absorbance.

To decouple the effect of surface roughness on the film absorbance from the film
thickness, a series of 1 µm SPC poly-Si samples with a roughness varying between 3 and 16 nm was deposited. A clear increase of film absorbance with roughness was observed. Unfortunately, a direct comparison with the directly-deposited poly-Si films could not be made due to the different surface morphology.

Since a high surface roughness is beneficial for current generation in a solar cell, the effect of deposition parameters on roughness was determined. It was found that the surface temperature plays a decisive role in the roughness, with films deposited at 690°C having a roughness around 2% of the film thickness, whereas films deposited at 740 °C have a roughness in the range of 1-1.5% of the film thickness.

By combining the knowledge on the dependence of the film grain morphology and absorbance characteristics gained in this and the previous chapters, a few deposition conditions were chosen to deposit a poly-Si i-layer for a p-i-n solar cell stack. Unfortunately, results on solar cell performance are still underway.
Chapter 6

Conclusion and Outlook

In this thesis, the deposition of poly-Si thin films by an expanding thermal plasma has been investigated. More specifically, three main research topics have been addressed, as stated in the introduction:

- Is it possible to deposit poly-Si with an expanding thermal plasma?
- How do crystal grains develop during deposition?
- In view of solar cell applications, what are the optical properties of ETP-deposited poly-Si films?

These topics have been treated in chapters 3-5. The main conclusions drawn in these chapters are summarized in the sections below.

6.1 The feasibility of depositing poly-Si by ETP

In order to investigate the feasibility of depositing poly-Si by an expanding thermal plasma, two routes have been taken. The first route consisted of a pulsed deposition, where the silane gas flow in an Ar-H₂-SiH₄ plasma is pulsed. This was carried out in order to alternate deposition with a hydrogen plasma treatment, which is thought to aid in film crystallization. However, it was found that for silane 'off-times' above the chamber residence time the film crystallinity decreased due to the hydrogen treatment.

Although the precise reason for this unexpected trend is not known, various possible reasons have been proposed. Among these are a too high deposition thickness per pulse, which prevents hydrogen induced crystallization, a varying amount of SiH₄ per pulse for different off-times, which changes the plasma chemistry and finally the possibility that the hydrogen radical and ion fluxes/energies in the ETP setup are not suitable for crystallization. The use of in-situ techniques to monitor the film properties like SE and ATR-FTIR could be of great help to gain further understanding in this respect.

The second approach was a high-temperature route, as it was found that a substrate temperature of ~800 °C is needed for direct poly-Si deposition. By varying the deposition
conditions and monitoring the plasma by OES, it was found that the film phase is critically dependent on the growth precursors.

In short, it was found that SiH$_3$ dominated growth, in combination with a sufficient atomic hydrogen flux results in the deposition of good quality poly-Si. Depositions without hydrogen admixed in the arc result in amorphous films, which is thought to originate from a lack of H flux towards the surface and from the very sticky SiH$_x$ ($x\leq2$) growth radicals. Films deposited at high H$_2$/SiH$_4$ dilution ratios were found to be crystalline but porous, which is attributed to the low surface diffusivity of sticky SiH$_x$ ($x\leq2$) growth radicals. At very low dilution ratios films are found to be amorphous, which is attributed to a depletion of the atomic hydrogen by the silane. A good quality poly-Si film was deposited at an intermediate dilution ratio (R=4).

This film initial poly-Si film was found to have an inhomogeneous grain morphology, with small grains at the bottom of the film, evolving into a columnar grain morphology. The film exhibits a self-structured pyramid-like surface morphology and has a preferential (220) orientation. A high unoptimized deposition rate of 8 nm/s was achieved.

### 6.2 Crystal growth in ETP-deposited poly-Si

In chapter 4, the crystal growth was investigated more in detail by a combination of in-situ SE and ex-situ XRD on a thickness series. Based on the observations, the following growth model was proposed. Film growth is initially amorphous, as observed by in-situ SE. After a certain incubation layer thickness, structural relaxation of the surface takes place, which has a corresponding dip in the surface roughness and a transition from amorphous to crystalline growth. From this thickness, crystals grow in a preferential (220) direction, as observed by XRD. Due to the high deposition temperature, solid phase crystallization of the amorphous incubation layer takes place, leading to the formation of small ($\leq100$ nm) randomly oriented grains in the incubation layer. This growth model has been verified by TEM, which shows a clear transition between randomly oriented small grains in the incubation layer to columnar (220) growth. Therefore, novel insights in the evolution of crystal growth in ETP-deposited poly-Si have been gained. Additionally, these insights might not only be applicable to ETP, but also to other high-temperature poly-Si deposition techniques where SPC of the amorphous incubation layer can play a role. It is also important to stress that these novel insights were only obtainable thanks to the use of in-situ techniques, which revealed a dynamic behaviour (i.e. SPC of the incubation layer), a process which could have never been observed by ex-situ techniques.

Furthermore, it was found that the incubation layer thickness is highly dependent on the substrate temperature and growth precursors. A high substrate temperature and hydrogen flow promote the transition, whereas a high SiH$_4$ flow (and thus a high deposition rate) leads to a thicker incubation layer. To conclude, despite the presence of an incubation layer, it has been demonstrated that the ETP is capable of depositing poly-Si at a high deposition rate (up to 20 nm/s) and with the beneficial (220) orientation. An interesting follow-up research topic would be to investigate the effect of substrate
biasing, which could potentially reduce the required deposition temperature.

6.3 Optical properties of poly-Si and its application in solar cells

In the final chapter, the effect of film thickness and surface morphology on absorbance was investigated. By comparing the absorbance of a thickness series of direct poly-Si, it was found that the film absorbance increases super-logarithmically with thickness, which is attributed to the rough pyramid-like surface morphology for thicker films.

The absorbance of a series of 1 µm SPC poly-Si films of varying roughness was measured in order to decouple the effect of film roughness from the thickness on absorbance. The overall absorbance was found to almost double when going from a film with 3 nm roughness to a film with 18 nm of roughness, demonstrating the beneficial effect of surface roughness on light trapping. Unfortunately, a one-to-one comparison with direct poly-Si cannot be made, due to a different surface morphology.

For directly-deposited poly-Si, it was found that the substrate temperature has a major influence of the film roughness. For a deposition temperature of 740 °C, the film roughness/thickness ratio is ~1-1.5%, whereas it is ~2% for films deposited at 690 °C. An increase in nucleation density with increasing substrate temperature was put forward as a possible explanation for this observation.

Some deposition conditions have been chosen for processing in a full p-i-n solar cell stack in collaboration with the Helmholtz institute in Berlin, but no results are available at the time of writing.
Acknowledgments

In this section, I would like to thank the people that have been important to me during this graduation project, both scientifically and personally.

To start with, I would like to deeply express my gratitude to the technicians of the P&MP group: Joris Meulendijks, Cristian van Helvoirt, Janneke Zeebregts and Ries van de Sande. Without their expertise and enthusiasm, I could not have achieved the results presented in this thesis. Especially Ries is thanked for his extensive help on the heater, even though it broke down so many times. I wish you all the best for your retirement, which will be a great loss to the P&MP group.

Secondly, I would like to thank Jan-Willem Weber for his great contribution in setting up the spectroscopic ellipsometry measurements (together with Gianfranco Aresta). Not only did you encourage me to do in-situ SE, your deep understanding of the SE technique also proved of great value for the data analysis!

Great thanks go to Wytze Keuning and Marcel Verheijen for making lamella’s for the TEM scan and performing the TEM scan, respectively. Marcel, you are thanked for the fruitful discussion of the TEM result. Wytze, you are also deeply thanked for fruitful discussions on XRD results, making SEM images and for performing HF-dips. Your expertise on all the instruments of P&MP makes you invaluable to the group.

Kashish, special thanks go to you. Not only for being my daily supervisor, but also for being a good friend. We have worked together for a few years now, and I think it is safe to say we make a mean team!

Adriana, I think most of my thanks should go to you. We met three years ago for an OGO project, and since then I stayed at P&MP as an AFM operator, did my bachelor project, my internship in Colorado and my graduation project, all under your guidance. You arranged our internship in Colorado, where I had the time of my life, and for that I am very grateful.

I would also like to thank the students in the student room for making the student room not only a place to work, but also for the occasional laugh! Especially Bas, Nick and René, with whom I’ve spent my time in Colorado, you have proven to be great friends and we share many great memories.

Erwin, you are thanked for providing me with the bible of depo II, which is your PhD thesis. It has provided me with the knowledge of the system I needed to perform the research in this thesis. Additionally, I am very grateful for the PhD position on heterojunction solar cells you have offered me.
CHAPTER 6. CONCLUSION AND OUTLOOK

I would of course also like to thank my family and my girlfriend Cherelle. You provided me with a warm home and everything I needed to work on my graduation project, for which I’m very grateful. This year hasn’t been the easiest, especially with my father fighting cancer. Dad, I’m very happy you recovered!

To end with, I would like to say that I’ve really enjoyed my years at P&MP! The group spirit is great, and I’ve made many friends over the years. Fortunately, I will stay for another four years in this group for a PhD position, working on a new challenge. So luckily I will not have to miss out on the almost daily ’vlaai’, the weekly Borrel, the yearly football tournament and the great PhD graduation parties!
Appendix A

Determination of radical fluxes

A.1 Calculation of silyl flux

As stated in section 3.3, it is plausible that during high-temperature poly-Si deposition the silyl radicals have a sticking coefficient close to unity, most likely due to a very reactive hydrogen-deficient surface. Using this notion, together with the experimentally determined deposition rate of 8 nm/s, it is possible to make an estimate for the flux of silyl radicals (which is mostly SiH$_3$) at our standard condition (55 sccs argon, 10 sccs hydrogen, 2.5 sccs silane).

Since every impinging silyl radical contributes to growth, the growth flux is equal to the silicon atomic density times the deposition rate:

$$\Phi = n_{Si} \times R_{dep}$$ (A.1)

The atomic density of silicon can be calculated from the lattice constant $a$, which is 5.431 Å and the fact that in the diamond lattice of c-Si there are 8 atoms per unit cell

$$n_{Si} = \frac{8 \text{ atoms}}{a^3} = 5 \times 10^{28} \text{ m}^{-3}$$ (A.2)

The growth flux is then:

$$\Phi = n_{Si} \times R_{dep} = 5 \times 10^{28} \times 8 \times 10^{-9} \times 4 \times 10^{20} \frac{\text{atoms}}{\text{m}^2\text{s}} = 4 \times 10^{20} \frac{\text{atoms}}{\text{m}^2\text{s}}$$ (A.3)

Kessels et al. have experimentally determined this growth flux to be $3 \times 10^{20} \frac{\text{atoms}}{\text{m}^2\text{s}}$ under identical conditions on the same plasma setup. The fact that a very similar value is obtained by assuming a sticking coefficient of unity justifies this approach.

A.2 Approximating the flux ratio

In this section, it is attempted to get an estimate on the SiH$_3$/H arrival ratio at the substrate holder. This will be done using a number of assumptions and simplifications.
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Therefore, the resulting ratio should be considered as an indication for the order of magnitude of the SiH$_3$/H arrival ratio and not as the exact value.

The SiH$_3$/H arrival ratio will be calculated for the conditions used for the in-situ SE series. (55 sccs of argon, 10 sccs of hydrogen and 1-7.5 sccs of SiH$_4$). Fortunately, the SiH$_3$ densities for these conditions have been determined experimentally by Kessels et al. and are used as an input for the calculations [47].

However, the atomic hydrogen flux towards the substrate holder under these conditions should also be known for the calculation of the SiH$_3$/H arrival ratio. The atomic hydrogen density in front of the substrate holder under these conditions is only known for a silane flow of 0 and 10 sccs. For no silane flow, the hydrogen density is ∼ $5 \times 10^{17}$ m$^{-3}$ [40]. For a silane flow of 10 sccs, the hydrogen density has been estimated from modeling work by Kessels et al. to be ∼ $4 \times 10^{16}$ m$^{-3}$ [77].

The atomic hydrogen density as a function of silane flow has been estimated using the assumption that an increase in SiH$_3$ density with silane flow corresponds to a decrease in atomic H density due to the hydrogen abstraction reaction:

$$SiH_4 + H \rightarrow SiH_3 + H_2$$  \hspace{1cm} (A.4)

With this assumption, the atomic H density as a function of SiH$_3$ density has been calculated by:

$$n_H(n_{SiH_3}) = n_H(SiH_4=0) - \frac{n_{SiH_3}}{n_{SiH_3(SiH_4=10)}} \times (n_H(SiH_4=0) - n_H(SiH_4=10)) \hspace{1cm} (A.5)$$

In this equation, the known input parameters are:

- $n_H(SiH_4=0)$, the atomic hydrogen density when no silane is injected (5 × 10$^{17}$ m$^{-3}$)
- $n_{SiH_3(SiH_4=10)}$, the SiH$_3$ density for a silane flow of 10 sccs (3 × 10$^{18}$ m$^{-3}$)
- $n_H(SiH_4=10)$, the atomic hydrogen density for a silane flow of 10 sccs (∼ 4 × 10$^{16}$ m$^{-3}$)

The experimentally determined SiH$_3$ densities, along with the calculated hydrogen densities are shown in figure A.1.

From these densities, the SiH$_3$/H arrival ratio can be calculated. It is assumed that the fluxes can be obtained from the simple relation:

$$\Phi = \frac{nv}{4} \hspace{1cm} (A.6)$$

Which is only valid for a Maxwellian distribution and completely neglects the presence of any flow fields. The SiH$_3$/H arrival ratio is the ratio of the fluxes, i.e.:

$$\text{Ratio} = \frac{n_{SiH_3}}{n_H} \times \frac{v_H}{v_{SiH_3}} = \frac{n_{SiH_3}}{n_H} \times \frac{1}{\sqrt{31}} \hspace{1cm} (A.7)$$

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Figure A.1: Experimentally determined SiH₃ densities and calculated hydrogen densities.

The $\sqrt{31}$ factor originates from the greater thermal velocity of the atomic H due to the lower mass with respect to the SiH₃ radical (1 versus 31 AMU). The calculated flux ratios are shown in figure A.2.

Figure A.2: Calculated flux ratios as a function of silane flow.

As can be seen from the figure, the flux ratio varies over one order of magnitude going from 1 to 7.5 sccs of silane, although the error becomes increasingly large for higher silane flows.
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