MASTER

Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

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Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

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Abstract

Amorphous hydrogenated silicon nitride (a-SiNₓ:H) has an important application as antireflection coating, and surface and bulk passivating layer on crystalline silicon solar cells. In this study, the feasibility of the expanding thermal plasma technique for the deposition of a-SiNₓ:H at high rates (typically 20 nm/s) has been investigated. By implementation of high rate deposited a-SiNₓ:H films in multicrystalline silicon solar cells, promising antireflection and bulk passivating qualities have been demonstrated.

In order to assist future optimization of the process, the growth mechanism of a-SiNₓ:H using a SiH₄-N₂ type of plasma has been studied. As a starting point for this study, a previously proposed growth model (Smith et al., J. Vac. Sci. Technol. B 8, 551 (1990)) has been used. In this model, the a-SiNₓ:H growth is portrayed by surface reactions of activated nitrogen with an a-Si:H-like top layer.

The plasma densities of viable candidate species for respectively the a-Si:H growth and 'nitridation' reactions have been investigated. Using threshold ionization mass spectroscopy (TIMS), the atomic N density has been measured in both the non-depositing 'source plasma' without SiH₄, and during deposition conditions. A very high N density of ~10⁻⁹⁻¹⁰⁻²⁰ m⁻³ has been revealed in the source plasma and during 'standard' deposition conditions. Using cavity ringdown spectroscopy (CRDS), SiH₃ densities of ~10⁻¹⁸⁻¹⁰⁻¹⁹ m⁻³ have been observed during deposition, and SiH densities of ~10⁻¹⁶⁻¹⁰⁻¹⁷ m⁻³. At these densities, SiH₃ can almost fully account for the Si growth flux, while SiH has a contribution in the order of percentages. The high N radical density in the plasma could certainly account for the N growth flux. If the N radicals indeed are responsible for the growth, the sticking probability of N is estimated to be in the order of a few percent.

Furthermore, a new infrared absorption measurement technique, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), has been installed for in situ studies on as-deposited a-SiNₓ:H films. With this technique, the infrared absorptions by Si-N, Si-H and N-H bonds have been monitored as a function of the film thickness. From the revealed depth information, a relatively homogeneous bonding configuration is observed as a function of the film depth, compared to a-Si:H growth.

In addition, the ATR-FTIR technique has been used to find more evidence for the growth model of Smith. If this model is applicable, it should be possible to create a-SiNₓ:H at the surface of an a-Si:H film, by modifying the a-Si:H film with a N-containing plasma. This has indeed been confirmed in a 'nitridation' experiment, in which an as-deposited a-Si:H film has been exposed to an Ar/N₂ plasma. The measured changes in the infrared absorption spectrum suggest that the plasma treatment results in the creation of an a-SiNₓ:H surface layer with a depth of ~2 nm. This has been found to occur without strong dependence on the substrate temperature in the range of 100-400°C, which is in line with the only weakly temperature dependent N/Si content of the films during normal deposition conditions.

As a conclusion, both the plasma studies and the nitridation experiment corroborate the proposed a-SiNₓ:H growth model of Smith et al. As an extension to this model, the measured radical densities in the plasma indicate that the formation of the a-Si:H-like layer can almost fully be accounted for by SiH₃ radicals, while the role of the activated nitrogen could well be filled in by the N radical.
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Chapter 1

Introduction

1.1 Technology assessment

An important strategy for achieving a reduction of the global $\text{CO}_2$ emission, is making clean energy sources economically more competitive with fossil energy sources. This master thesis project is closely related to this subject, as one of the goals is the enhancement of the production speed, i.e. the reduction of the production costs of multicrystalline silicon solar cells. To increase their efficiency, solar cells are generally produced with an anti reflection (AR) coating. Such an AR coating consists of a transparent $\lambda/4$ film, where the optical thickness (the product of the refractive index $n$ and film thickness $d$) is optimized for the most energetic part of the solar light spectrum (see Fig. 1.1). The still reflected light gives the cells, which look gray metallic without AR-coating, their typical dark blue color.

![Fig.1.1](image)

Fig.1.1: The working of a $\lambda/4$ anti reflection coating: light that is reflected on the internal surface interferes destructively with incoming light. Typically used parameters for solar cells are $n=2.1$, $d=70\text{nm}$ and $\lambda=625\text{ nm}$.

Until recently, $\text{TiO}_x$ ($n=2.0$) was the most commonly used AR material for most types of cells, as it can be produced by atmospheric pressure chemical vapor deposition (AP-CVD) at relatively low cost. However, for (multi-)crystalline silicon cells, hydrogenated amorphous silicon nitride ($\text{a-SiN}_x\text{H})$, is found to have a number of advantages. Apart from being a suitable material for AR coatings, $\text{a-SiN}_x\text{H}$ is known to reduce the recombination rate of charge carriers at the surface of solar cells. This surface passivation effect is especially important for highly efficient and very thin (expensive) monocrystalline silicon (c-Si) solar cells. Importantly for the less efficient but cheaper multicrystalline silicon (mc-Si) solar cells.

Defects (e.g. dangling bonds) and grain boundaries in the bulk of mc-Si act as trapping centers for minority charge carriers and therefore as recombination centers for electron-hole pairs. The resulting reduced lifetime of the charge carriers leads to a decreased collection at the electrodes, and hence to a lower cell efficiency. It is known that the bulk dangling bonds can be passivated by atomic hydrogen. One way to let the hydrogen reach the dangling bonds, is by hydrogen effusion from an $\text{a-SiN}_x\text{H}$ film deposited on top of the mc-Si cell. The effusion is realized by annealing the cell at a temperature of 850-
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900°C*. After the annealing process, cell efficiencies are seen to increase, due to an increased internal quantum efficiency (IQE) for long (red) wavelengths. This indeed indicates a bulk effect, as long wavelength light is able to penetrate deep into the cell.

However, although a-SiN$_x$:H films clearly increase solar cell efficiencies, their implementation in the cells has to compete with the relatively cheap production process of TiO$_x$ AR coatings. A-SiN$_x$:H films are traditionally deposited by plasma deposition radio frequency (RF) wave generated plasmas, and more recently also with microwave (MW) plasma's (ECN), at low pressures (~10$^{-5}$ mbar). With these techniques only low growth rates (0.01-1nm/s) can be achieved, which makes the implementation of a-SiN$_x$:H films in solar cells relatively expensive. Therefore in the plasma-group, a-SiN$_x$:H deposition with a cascaded arc generated expanding thermal plasma (ETP) has been investigated. With this plasma, a-SiN$_x$:H deposition rates of ~20nm/s are in principle possible.

In this master thesis project, two issues have been addressed. The feasibility of ETP-films as AR coating and as bulk passivation layer has been investigated by implementation of the films in a series of n$^+$p mc-Si solar cells. This was done in cooperation with Energieonderzoek Centrum Nederland (ECN) and Shell Solar Helmond. The solar cells produced with ETP a-SiN$_x$:H have shown promising results, which indicate that the ETP technique is viable for industrial production of a-SiN$_x$:H coatings for solar cells.

While the ETP process will be improved by further fine-tuning of the plasma parameters, also fundamental insight in the deposition mechanism can be of value to control and improve the process in the future. Therefore, also efforts have been made to gain more understanding of the plasma and surface processes that lead to a-SiN$_x$:H deposition. It has been investigated which reactive species are present in the plasma, that could be responsible for the deposition. As a starting-point, published information on conventional a-SiN$_x$:H depositing plasmas is used, as well as knowledge of ETP deposition of hydrogenated amorphous silicon (a-Si:H) in the group. The combination of both has enabled aimed investigation of candidate reactive depositing species in the plasma.

Strongly related to the deposition mechanism are the basics of the bulk passivation process. The amount of bulk passivation depends on various film properties, among which the hydrogen bonding configuration (i.e. bonded to Si or N) and the film density. Furthermore, the transparency of the films is related to their optical bandgap, which depends on the general bonding configuration as well. For these reasons, the H-bonding configuration in the deposited films has been investigated with a sensitive in-situ infrared absorption measurement technique.

In the following section, a brief description will be given of the cascaded arc expanding thermal plasma, with attention to the relevant properties for a-SiN$_x$:H deposition. As an illustration, the feasibility of the ETP films as AR and bulk passivation layer is then demonstrated by showing the test results of a solar cell in section 1.2.2. In section 1.3, a treatment of some of the present knowledge of the a-SiN$_x$:H deposition process is given, followed by a more precise target formulation of the second part of this research. Finally, the contents of this report are given.

* In solar cell production, the hydrogen effusion is generally combined with the metallization step (application of electrodes), in a so-called 'firing through' process. In this process, silver from a screen-printed silver-paste metallization pattern on top of the cell, diffuses through the a-SiN$_x$:H AR coating to the mc-Si.
1.2 ETP-deposited a-SiN\textsubscript{x}:H as antireflection and bulk passivating material for multicrystalline silicon photovoltaic cells

An important characteristic of the expanding thermal plasma (ETP), from an industrial point of view, is its ability to maintain a high dissociation rate at high gas flows. This enables very high deposition (or etching) rates for several materials. For example, a-Si:H deposition rates of 10 nm/s and a-SiN\textsubscript{x}:H deposition rates of over 20 nm/s have been achieved, where conventional MW and RF plasmas reach only deposition rates of maximum 1 nm/s. Furthermore, due to absence of a bias-voltage, the substrate is free from ion-bombardment during deposition.

A useful property of the ETP for scientific studies, in which well-defined and reproducible experiments are of value, is the fact that it is a remote plasma: the plasma source and the substrate chamber are geometrically separated. A large pressure difference between the plasma source and the downstream chamber enables tuning of the plasma parameters to a large degree independently from the substrate properties. Furthermore, the plasma source itself can be kept free from undesired deposition, by injection of the deposition precursor gas in the expansion chamber.

In the next section, a description is given of the ETP plasma technique.

1.2.1 Cascaded arc generated expanding thermal plasma: general characteristics

The expanding thermal plasma setup consists of a high-pressure cascaded arc plasma source and a low-pressure deposition chamber, which are schematically depicted in Fig.1.2. The plasma source is used to create reactive species for the dissociation of the deposition precursor gas (SiH\textsubscript{4} for a-SiN\textsubscript{x}:H deposition). It is operated on a non-depositing gas mixture (Ar, H\textsubscript{2}, and N\textsubscript{2} for a-SiN\textsubscript{x}:H deposition), at typical pressures of 0.5 bar when the plasma is ignited. Inside the source, the plasma is close to thermal equilibrium and can be characterized by a high electron density $n_e=10^{22}\text{ m}^{-3}$ and electron and heavy particle temperature of ~1eV. This relatively high heavy particle temperature leads to almost full dissociation of the injected gases.

The plasma expands through a nozzle into the deposition chamber, which has a resulting pressure of typically 0.1-0.3 mbar. Initially, the pressure gradient leads to a supersonic expansion of the plasma, and after a stationary shock, the plasma expands subsonically to the other end of the chamber. Near the shock region at approximately 5 cm from the arc nozzle, the deposition precursor is admixed into the plasma with an injection ring, to become ionized and dissociated by the plasma species. The resulting depositing ionic and neutral radical species drift to a substrate, which is placed on a temperature-controlled holder at 38 cm from the arc nozzle (or 72 by placing an extension). To deposit films with a reproducible thickness, an automatic shutter has been installed in front of the substrate holder.

In the next section, we will discuss the properties of a-SiN\textsubscript{x}:H films deposited with this technique, with main focus on their application as AR and bulk passivating coating on solar cells.

* This is often more difficult in for instance RF or MW generated plasmas, where the substrate (which is generally being modified during the process) either actively or passively takes part in the electronic setup.
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Fig. 1.2: The cascaded arc thermal plasma source (left), and the complete expanding thermal plasma setup (right). The cascaded arc plasma source consists of a stack of electrically insulated copper plates, with concentric holes (Ø4mm) for inlet of gases. The plasma is generated by means of a current controlled arc discharge between three tungsten cathode tips at one side of the plates and the anode at the other side. Typical currents are 10-75 A, and the power dissipated is 2-5 kW. Typical used gas flows are 55 sccs (standard cubic centimeters per second) Ar, 0-10 sccs H₂ and 0-12 sccs N₂, with downstream injection of 1-10 sccs SiH₄. The resulting mixture of ionic and neutral radical species expands towards the substrate holder, which is temperature controlled (0-500°C). A helium back flow is used to increase thermal contact between the holder and substrate. The reactor windows allow for several process diagnostics of which some are discussed in this report.

1.2.2 ETP-deposited a-SiNₓ:H for mc-Si solar cells

A-SiNₓ:H can be deposited with the ETP deposition technique, using an Ar/H₂/N₂ gas mixture in the cascaded arc, and SiH₄ as precursor in the expansion chamber. As shown in Fig. 1.3, the refractive index is tunable by varying the N₂/SiH₄ gas flow ratio. The resulting films have a refractive index that ranges from 1.7 (N-rich) to 3.25 (no N). This is useful for AR applications.

* An important alternative gas mixture for a-SiNₓ:H deposition is the combination of Ar/H₂ in the arc, with SiH₄ and NH₃ as precursor gases in the chamber. In this report, we will concentrate on the N₂ mixture.
Chapter 1: Introduction

To explore the functionality of ETP-deposited a-SiN$_x$:H as AR and bulk passivating coating on mc-Si solar cells, the films have been implemented in a number of test solar cells. By extending the chamber length and tuning the plasma parameters, conditions were found that result in films with a thickness and refractive index variation of less than 5% on a 4 inch (round) wafer, which is sufficiently homogeneous for the 10x10cm$^2$ (square) test solar cells. Using ellipsometry, conditions for a suitable refractive index and thickness of ~2.1 and ~70nm were determined. Cells were produced with ETP-a-SiN$_x$:H, deposited under 5 different plasma settings (10 cells for each condition$^*$), in cooperation with ECN. In Fig.1.4a-b, a reflection measurement and internal quantum efficiency (IQE) of one test group with an efficiency ($P_{electric}$ /$P_{light}$) of ~11% is shown$^{24}$. As references, a regular state-of-the-art (~13%) cell with MW plasma-deposited a-SiN$_x$:H (deposited at ECN) is shown, as well as another ‘ETP cell’ which is not annealed and has no bulk passivation$^†$.

$^*$ In practice, groups of 10 cells are processed for each condition, to average out the effect of the quality of the mc-Si wafers, processing variations, and accidentally broken wafers. To enable comparison between different groups, they are build with more or less identical sets of mc-Si wafers, by distributing wafers that were ‘neighbors’ before being sawed over the different groups.

$†$ The non-passivated cell is made using a ‘reverse scenario’ processing of the cell. First the metallization process is completed, including the annealing step. Then the a-SiN$_x$:H coating is deposited without annealing. In this way, the hydrogen is not allowed to effuse into the wafer, and no bulk passivation takes place.
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Fig. 1.4: (a) Reflectivity measurement, and (b) IQE measurement of a test solar cell with ETP deposited a-SiN\textsubscript{x}:H coating, as processed and measured at ECN\textsuperscript{24}. As references, a regular cell with MW deposited a-SiN\textsubscript{x}:H and a non-passivating cell are shown as well:

- Group 1 has an ETP-deposited a-SiN\textsubscript{x}:H AR coating,
- Group 2 has an ETP-coating as well, but has not been annealed, i.e. exhibits no bulk passivation,
- Group 3 has a ‘regular’ a-SiN\textsubscript{x}:H coating that is deposited with a microwave SiH\textsubscript{4}/NH\textsubscript{3}/H\textsubscript{2} plasma. This was done at ECN.

The IQE measurements are displayed relative to the IQE of the non-passivating ETP cell (g2).

From the reflection measurement (Fig.1.4a) it follows that the ETP-cells have similar AR properties as the ECN reference cell. This indicates that the ETP a-SiN\textsubscript{x}:H material is suitable for application in AR coatings. However, after annealing of the cell, the reflected power in the blue (short wavelength) region increases a lot, which is attributed to absorption by the film itself.

From the IQE measurements (Fig.1.4b), it can be seen that in the longer wavelength (‘red’) region, the ETP cell exhibits an increased efficiency compared to the cell with non-passivating (non-annealed) a-SiN\textsubscript{x}:H. This is evidence for bulk passivation by ETP a-SiN\textsubscript{x}:H films. Still, the conventionally produced cell still has a better performance in this region.

In the shorter wavelength (‘blue’) region, the ETP cell has a much lower IQE than the conventional cell. Apparent from both reflection and IQE measurements, an increased blue absorption by the ETP a-SiN\textsubscript{x}:H film itself takes place after the annealing. This is attributed to a lower optical bandgap compared to the MW material\textsuperscript{1}. A lower bandgap can be caused by different bonding configurations: more Si-Si bonds lead to a lower bandgap, while more Si-N bonds increase the bandgap. Furthermore, it is observed that the films undergo a densification due to the annealing step.

So, although the first steps have been taken towards high rate deposition of AR and bulk passivating a-SiN\textsubscript{x}:H coatings on mc-Si solar cells, there is still room for improvement. As shown, the ETP films are yet not as ‘good’ as films deposited with optimized conventional techniques. One possible way to improve the film qualities, which most certainly is being followed in the industry, is by further fine-tuning of the plasma parameters. In this project however, a goal is to gain more insight in the a-SiN\textsubscript{x}:H deposition process. Knowledge of the plasma chemistry and of the process of bulk passivation can be of great value for the optimization of a-SiN\textsubscript{x}:H AR coatings in the future.

\* Experiments with ETP a-SiN\textsubscript{x}:H deposition using NH\textsubscript{3} instead of N\textsubscript{2} indicate that it is possible to deposit a-SiN\textsubscript{x}:H films with higher bandgaps at the same refractive index.
Chapter 1: Introduction

As a starting point for the investigation described in the following chapters, we will discuss some of the existing published work on a-SiNx:H deposition mechanisms in the next section. As the expanding thermal plasma is not very common yet, most work is based upon MW and RF generated plasmas.

1.3 A-SiNx:H deposition mechanisms

A remarkable conclusion in ref.1 and 2, is that the plasma chemistry is relatively simple in a SiH4/N2 RF plasma. Using mass spectrometry, it has been shown that apart from N atoms and SiHx radicals, Si2H6 (disilane) and H2 are the only measurable products in this kind of plasma. When using sufficiently high RF power and increasing the N2/SiH4 flow ratio beyond a critical level, there is an excess of N atoms to react with SiHx, and even no disilane is being formed anymore by SiHx radicals reacting with each other.

Creating more active N in the plasma (by either increasing the N2/SiH4 flow ratio or increasing the RF power*) results in an increased N/Si ratio in the film, a lower refractive index, and an increased N-H/Si-H bond ratio. Beyond the critical N2/SiH4 flow ratio, films with only hydrogen bonded to N can be produced with a RF plasma. In that case, the lack of Si-H is thought to be a result of enough N impinging on the surface to displace all the H from the Si-Hx bonds.

As no Si-N containing products are seen in the RF plasma, the a-SiNx:H deposition process must occur by direct reaction of SiHx radicals and activated nitrogen at the substrate surface. A proposed deposition model that is in line with these observations, consists of the formation of an a-Si:H-like layer, followed by nitridation of this layer by the activated nitrogen from the plasma. During deposition, the film then would consist of a growing a-SiNx:H layer, with a more Si-rich surface layer on top all the time. This model, schematically depicted in Fig.1.5, has been used as a reference for our investigations.

It has not yet been specified which species are forming the a-Si:H top layer, and neither which species establish the nitridation. From extensive previous studies on the a-Si:H depositing ETP plasma, it is known that SiH3 is the most important deposition precursor in that plasma (when H2 is admixed). Therefore, SiH3 is expected to play an important role during a-SiNx:H deposition as well. The activated nitrogen could be atomic N, although in ref.3 also excited N2 is suggested based upon emission spectroscopy measurements.

Fig.1.5: Proposed a-SiNx:H growth model: a Si-rich top layer is formed by the SiH3 precursor, which becomes 'nitridated' by atomic N radicals from the plasma.

* Apart from increasing the N2/SiH4 flow ratio, also increasing the power results in creation of relatively more N radicals in a RF plasma. While SiH4 dissociates already at relatively low plasma powers, more energy is needed to dissociate the much stronger N2 bond. Therefore, increasing the plasma power does not affect the SiHx density much (as SiH4 is being dissociated already anyway), but does lead to more N radicals.
In the next section, the steps that are taken to verify the model are discussed, and an overview of the contents of this report is given.

### 1.4 Goal of this investigation and outline of the report

To determine if the discussed model is applicable for the ETP process, the plasma species that are involved in this model are investigated. The SiH$_3$ and SiH densities in the plasma have been measured using cavity ringdown spectroscopy (CRDS), and the N radical density has been measured using threshold ionization mass spectrometry (TIMS). Also, an attempt is made to measure H. It is verified whether the measured radical densities are high enough to explain the film deposition rate.

Parallel to the plasma investigations, the deposited films have been investigated using attenuated total reflection (ATR) infrared spectroscopy, a for this purpose newly installed technique. Using this technique, the infrared absorptions of SiH$_x$, NH$_x$ and SiN bonds have been followed in as-deposited a-SiN$_x$:H films. An attempt to find more evidence for the proposed deposition mechanism is made, by verifying whether a-SiN$_x$:H can indeed be created by ‘nitridation’ of a-Si:H, by exposing an a-Si:H film to a N-containing plasma.

In chapter 2, the relevant theory behind the three used measurement techniques CRDS, TIMS and ATR-FTIR spectroscopy, and the followed measurement procedures are described in detail. In chapter 3 the measured radical densities in respectively the non-depositing source plasma (before SiH$_4$ injection), and the depositing plasma are presented, as well as an estimate of the contribution to the film growth of each radical. In chapter 4, an in situ film study with use of the ATR technique is presented. Measured SiH and NH densities in different types of a-SiN$_x$:H films are discussed, as well as the mentioned nitridation experiment. Finally, in chapter 5 a number of conclusions are drawn.
Chapter 2

Plasma and surface measurement techniques

In this chapter, three of the measurement techniques that have been used are presented, as well as the followed measurement procedures. To measure the densities of radical species in the plasma during the a-SiNx:H deposition process, both cavity ringdown spectroscopy (CRDS) and threshold ionization mass spectrometry (TIMS) have been used. The CRDS technique is well described elsewhere, so just a brief introduction to the general technique is given in section 2.1, along with the used theory and followed procedures to measure SiH and SiH$_3$ in the a-SiNx:H depositing plasma. The TIMS measurement procedure is not as common in the group yet, and is therefore described in more depth in section 2.2, on the basis of the density measurement procedure of atomic N. In section 2.3, the newly set-up attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) technique is explained, and a description of the specific used setup is given.

2.1 Cavity ring down spectroscopy (CRDS): SiH and SiH$_3$ radical density

CRDS measurements have been carried out of both the SiH and SiH$_3$ radical densities in the a-SiNx:H depositing Ar/H$_2$/N$_2$/SiH$_4$ plasma. These radicals have been measured previously in the a-Si:H depositing plasma$^4$.$^5$. The measurement procedure is described in detail in ref.$^6$, and therefore here only a short overview of the technique is given, together with the specific experimental details.

2.1.1 The basics of CRDS

Cavity ring down spectroscopy is a very sensitive laser absorption technique, which is based upon measuring the rate rather than the absolute magnitude of the absorption. The main components of a CRDS setup are depicted schematically in Fig.2.1.

![Fig.2.1: A schematic representation of the CRDS setup, with an example of measured light intensity.](image)

A cavity is created using two highly reflective plano-concave mirrors. When a light pulse is coupled into this cavity from one side, it will travel back and forth between the mirrors. As the mirrors do not have a perfect 100% reflectivity however, the intensity of the trapped light decreases slightly upon each reflection, resulting in an exponential decay with a time constant or ringdown time $\tau_{\lambda 0}$ that is given by$^7$:

$$\tau_{\lambda 0} = \frac{d}{c \left| \ln(R_\lambda) \right|},$$

where

- $d$: path length of the cavity
- $c$: speed of light
- $R_\lambda$: reflectivity of the mirrors at wavelength $\lambda$.
with $d$ the distance between the mirrors, $c$ the speed of light, and $R_A$ the mirror's reflectivity. This decaying light intensity is measured using a detector that collects the amount of light that is transmitted from the cavity at the second mirror. The ringdown time $\tau_{A0}$ is determined by fitting linear functions to the natural logarithm of the measured signal after each light pulse. The ringdown time is averaged over typically 64 laser shots.

When an absorbing medium (in our case: the studied plasma) is placed between the mirrors in the cavity, the light intensity decreases more rapidly due to the absorption. The ringdown time is then given by:

$$\tau_A = \frac{d/c}{\ln(R_A) + A_A}, \tag{2}$$

with $A_A$ the absorption per pass for the laser wavelength $\lambda$ used. The absorption per pass $A_A$ by the plasma can be deduced from equation (1) and (2):

$$A_A = \frac{d}{c} \left( \frac{1}{\tau_A} - \frac{1}{\tau_{A0}} \right). \tag{3}$$

As visible, neither the mirror reflectivity nor the laser light intensity has to be known to obtain the absorption per pass $A_A$.

Finally, to convert a measured absorption $A_A$ to a density, the wavelength dependent cross section $\sigma_\lambda$ and the density profile of the plasma has to be known. When assuming a cylinder-symmetric profile of the plasma, the density profile at a certain distance from the source can be obtained from a radial scan of the absorption using Abel inversion. For simplicity however, a cylindrical plasma with homogeneous density over a diameter length $I$ is often assumed. In that case, the density $n$ can be obtained from

$$A_A = \sigma_\lambda n I. \tag{4}$$

### 2.2.2 CRDS on SiH$_3$

In the next sections, the experimental details of the SiH$_3$ measurements are treated. In section A, the relevant spectroscopy of SiH$_3$ is treated, followed by the measurement procedure in section B.

#### A. SiH$_3$ spectroscopy

For the SiH$_3$ density measurement, ~215 nm light is used to measure the electronic transition $^2A^e \rightarrow X^2A^e$ from the ground state ($X$) to the first electronic excited state ($A$) of SiH$_3$. The $A$ state of SiH$_3$ is a pre-dissociative state because its energy level is close to the energy level of the dissociative state of SiH$_2$ + H. A rather large probability exists that the excited electron will "jump" to the dissociative state, without changing the molecular energy (see Fig.2.2).

---

* Absorption can in principle not be distinguished from other mechanisms that decrease the light intensity (e.g. scattering), and therefore it is actually more appropriate to talk about "cavity loss". For simplicity, we will speak about absorption in the considered cases in this report.
Chapter 2: Plasma and surface measurement techniques: Cavity ringdown spectroscopy

The lifetime of any vibrational level (a,b,c...) in the A state is inversely proportional to the probability of this jump, and is therefore relatively short for each vibrational level. According to Heisenberg's uncertainty principle, short lifetimes correspond to less well-defined energies (i.e. broad energy intervals). The resulting spectrum of the measured transitions to the various A states therefore consists of a number of broad overlapping spectral lines. The resulting spectrum is very broad, and the individual transitions can not be distinguished. In Fig.2.3 the previously measured absorption in a Ar/H$_2$/SiH$_4$ plasma is shown in the wavelength range 200-260nm.

In principle, other broad band absorption processes apart from absorption by SiH$_3$ might cause the measured spectrum of Fig.2.3 as well. For the Ar/H$_2$/SiH$_4$ plasma however, the attribution of the absorption to SiH$_3$ is supported by previous TIMS measurements. Furthermore, although not yet conclusive, it has been shown that in the Ar/H$_2$/SiH$_4$ plasma, Raleigh scattering and scattering by Si clusters do most probably not give a large contribution to the absorption, based upon spectral analysis.⁶
Although the spectrum has just been measured at one point in the a-Si$_3$H depositing Ar/H$_2$/N$_2$/SiH$_4$ plasma so far, we assume for the moment that this is true for this plasma as well.

**B. SiH$_3$ Measurement procedure**

In the used setup (see Fig.2.1), the light pulses are generated using a tunable dye laser (Sirah Precisionscan-D), pumped by a Nd:YAG laser (Spectra-Physics Quanta Ray DCR-11). Also a filter is used to reduce the light intensity. The mirrors (which simultaneously act as vacuum seals) are positioned at a distance $d$ of 1.08m from each other. The light that leaks out of the cavity is filtered again using a band pass filter. As light detector a photo multiplier tube (PMT) is used.

For the measurement of the SiH$_3$ density in the Ar/H$_2$/N$_2$/SiH$_4$ plasma, the broadband absorption is measured over a small range at its maximum around 215 nm. Mirrors with a reflectivity of ~96% around 215 nm have been used. For estimating the density $n$ with equation (4), a cross section $\sigma$ of 2.4·10$^{-21}$m$^2$ at 215 nm is used as given by Lightfoot et al.$^9$. The mirror distance $d$ is 1.08m, and a plasma diameter $l$ of 0.40m is used.$^*$

### 2.2.3 CRDS on SiH

In this section, the experimental details of the SiH measurements are treated. In section A, the relevant spectroscopy of SiH is treated. In sections B and C, the measurement procedure and rotational and vibrational temperature measurements are explained. In the following sections D and E, the measured spectra and background absorptions are discussed.

**A. SiH spectroscopy**

For the SiH density measurement, one line is measured in the $Q_1$ branch ($\Delta J=0$) of the $A^2\Delta \leftrightarrow X^2\Pi$ transition of SiH$^*$ around 414 nm. In Fig.2.4 both a previously measured and simulated spectrum of the $Q_1$ branch of SiH is shown$^6$.

![Absorption spectrum of SiH](image)

**Fig.2.4:** Part of a simulated and measured spectrum of the $A^2\Delta \leftrightarrow X^2\Pi$ electronic transition of SiH, as previously measured in a Ar/SiH$_4$ plasma$^6$. In the simulations only the $A^2\Delta (v'=0) \leftrightarrow X^2\Pi$

$^*$ The densities that follow from this approximation have for the SiH$_3$ radical been shown to agree with axial densities obtained from radial density profile measurements$^4$.

$^9$ A more detailed description of the spectroscopy for SiH is given in ref.$^6$. 

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(v'='0) band is taken into account. In this work, the rotational line $Q_{1}(11.5)$ is used to determine the SiH density and the relative height of $Q_{1}(14.5)$ and $R_{1}(1.5)$ absorptions are used to determine the rotational temperature (for one plasma condition only).

The various absorption peaks in this branch correspond to the different rotational states of the radical, and are labeled according to the rotational quantum number $J$ of each state. The amount of absorption $A_{J}$ depends on the density $n$ of SiH in the specific corresponding state, integrated over the pathway $l$ through the plasma, and the cross section $\sigma_{J}$ for the corresponding transition. If we again assume a homogenous plasma density, the density of one particular state can be obtained from equation (4). As the absorption is integrated over the peak, also an integrated cross section $\sigma_{J}$ is used, which is obtained from

$$\sigma_{J} = \int_{A} \sigma_{J} \, d\lambda = B_{ik} \, h \lambda_{ik},$$

with $\lambda_{ik}$ the wavelength of the transition from level $i$ to $k$, and $h$ Planck’s constant. $B_{ik}$ is the Einstein absorption coefficient that is obtained from the program LIFBASE, for simulating spectra of diatomic molecules.

The total ground state density is the sum of the densities of each rotational state. One way to determine the total ground state density would be by scanning a complete rotational transition branch. In practice however, only one rotational state density (i.e. one peak) is measured for each plasma condition. To deduce the total ground state density from the density of this particular state, a calculation is made of the relative occupation distribution of all rotational and vibrational states in the ground state. This distribution depends on the vibrational and rotational temperature. In our case, a Boltzmann distribution over the various rotational state densities is assumed.

**B. Measurement procedure**

For the SiH measurements, the same setup as for the SiH$_3$ measurements is used. Mirrors with a reflectivity of 99.6% around 414 nm have been used. The $Q_{1}(11.5)$ SiH peak is measured at 413.5 nm, as indicated in Fig.2.4.

An example of an absorption spectrum is shown in Fig.2.5. The scans are measured from higher to lower wavelengths. The ring down time of the non-absorbing Ar/H$_2$ plasma is used as baseline to determine $\tau_{0}$ (equation (3)).

* Integrated absorptions (i.e. peak areas) are used rather than the absorptions at one wavelength, as the height/width of a peak depends on the temperature (Doppler broadening) and the line profile of the laser.
Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

Fig.2.5: Absorption spectrum during a-SiNₓ:H depositing plasma (Ar flow 55, H₂ 5, N₂ 8, SiH₄ 4 sccs, arc current 45 A). Around 413.6 nm both the Q₁(11.5) peak and extra unidentified peaks are visible. Furthermore, there is a broadband background absorption, which increases when N₂ is admixed to the plasma. The measured spectrums feature a shift in wavelength of about 1 nm (which is corrected for in the plot) and an erroneous wavelength scale factor, due to the alignment of the specific laser setup. By comparing a measured SiH spectrum to a simulated spectrum, a scaling factor of 1.174 has been estimated, which has been used to scale down the fitted peak areas.

A number of aspects are visible in the spectrum:
- The Q₁(11.5) peak around 413.5 nm is present. The surface of this peak is the integrated absorption A₁ which is used in equation (5) to calculate the density of this SiH state.
- At least two extra absorption peaks are present next to the SiH peak. These peaks are of yet unknown origin.
- Apart from the peak absorptions, also a broadband absorption by the plasma occurs in this wavelength range when silane and nitrogen are fed into the plasma.

A fitting procedure is applied to deconvolute the absorptions by the SiH peak and the unidentified peaks, by using three gaussian peaks (see Fig.2.6).
C. Rotational and vibrational temperature, and relative state occupation

As mentioned, to obtain the total ground state density from a single measured rotational state density, the rotational and vibrational temperatures have to be known.

One way to estimate the rotational temperature in the plasma, is by comparing the relative height of the various absorption peaks in a measured spectrum to a simulated spectrum, using LIFBASE\textsuperscript{10}. Again, to save time, just a small part of the spectrum is measured. In our case, the $Q_1(14.5)$ and $R_2(1.5)$ rotational transition peaks are compared (as indicated in Fig.2.4), which have a relative height that varies strongly with the rotational temperature. For the plasma condition with flow rates Ar 55 sccs, SiH$_4$ 8 sccs, N$_2$ 10 sccs, H$_2$ 5 sccs and arc current 45A, a rotational temperature of 1400K has been estimated in this way.

The vibrational temperature is not measured in the a-SiN$_x$:H depositing plasma. In the a-SiH$_x$ depositing plasma however a vibrational temperature of ~3000K is measured\textsuperscript{11}, by optical emission spectroscopy (OES). As the relative state occupancy does not depend strongly on the vibrational temperature anyway, this value is taken as an approximation.

These temperatures and the assumption of a Boltzmann distribution have been used to calculate the relative rotational state occupancies in the SiH ground state. For the $J=11.5$ groundstate a relative occupation of 1.97% has been estimated in this way\textsuperscript{5}.

D. Extra peaks in spectrum during Ar/H$_2$/SiH$_4$/N$_2$ plasma

We have considered a number of possible candidates to explain the appearance of the unknown peaks in the spectrum, by simulating the corresponding spectra, which are depicted in Fig.2.7.
Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

**Fig.2.7:** A comparison between the Q_{1}(11.5) SiH peak + unknown peaks as measured in a Ar/H\textsubscript{2}/N\textsubscript{2}/SiH\textsubscript{4} plasma, and simulated spectra of SiN, N\textsubscript{2}+, and SiH\textsuperscript{10}.

- SiN: As the extra peaks are only present when both SiH\textsubscript{4} and N\textsubscript{2} are fed into the plasma, SiN seems a good candidate. The simulated spectrum of SiN does however not match the measured extra peaks.
- N\textsubscript{2}+: N\textsubscript{2}+ has been a promising candidate, as its absorption spectrum has peaks in the 414 nm region and even one peak on the exact position of our peak. However, the N\textsubscript{2}+ spectrum does not fully coincide with the measured spectrum.
- SiH: Another considered possibility is the formation of higher excited vibrational states ("hot bands") of SiH, that might be created in a reaction path involving nitrogen. LIFBASE is used to calculated the possible transitions from \(v'=0,1,2,3\) to \(v'=0,1,2\). Again, the extra absorption peaks in the vicinity of the Q\textsubscript{1} peak do not match the measured spectrum. The mentioned observation that the peaks are only present when both SiH\textsubscript{4} and N\textsubscript{2} are fed into the plasma, already makes N\textsubscript{2}+ and SiH less probable candidates anyway.

E. The broadband absorption

**a-Si:H plasma:** A broad band absorption at the 414 nm region has been observed earlier\textsuperscript{12} in the a-Si:H depositing (Ar/H\textsubscript{2}/SiH\textsubscript{4}) plasma. Of the various candidates for this absorption, the possibility of Raleigh scattering and absorption by Si clusters is thought to be unlikely in that plasma, based upon the measured wavelength dependence, although this is not conclusive. Some correlation to the measured SiH\textsubscript{3} density has been observed. Therefore, the background absorption in the a-Si:H depositing plasma could be caused by a species in the plasma, of which the production mechanism is related to the SiH\textsubscript{3} density.

**a-SiN\textsubscript{2}:H plasma:** When N\textsubscript{2} is added to the plasma, an increase by a factor of \(\sim 3\) of the absorption level occurs (see Fig.2.5). The absorption increases with either both increasing N\textsubscript{2} or SiH\textsubscript{4} flows, and decreases slightly with increasing H\textsubscript{2} flow. Again, for SiH\textsubscript{4} and H\textsubscript{2} flow variations, this trend is observed for SiH\textsubscript{3} in the a-SiN\textsubscript{2}:H depositing plasma as well (the SiH\textsubscript{3} density has not been measured as function of the N\textsubscript{2} flow rate). Possible candidates are broadband absorption by electron detachment processes from negative ions, which probably have a too low cross section \(\sigma\sim10^{-22}\) m\textsuperscript{2} to explain the large absorption, and excitation to a pre-dissociative state similar to the SiH\textsubscript{3} case.
2.2 Threshold ionization mass spectrometry

The plasma density of atomic N has been measured using a mass spectrometer. Measuring radical species using a mass spectrometer requires a specific approach, which is usually referred to as threshold ionization mass spectrometry (TIMS), or in some cases as appearance potential mass spectrometry (APMS). After an introduction on quadrupole mass spectrometry in general and our setup specifically, the TIMS technique and the particularly used method to measure and analyze the spectra adapted from ref.13 will be treated in this section.

2.2.1 Quadrupole mass spectrometry

In Fig.2.8, the quadrupole mass spectrometer that has been used in our setup is depicted schematically, along with a description of its main components. In general, the relation between the counted detection rate \( S \) (counts/s) and the measured species density inside the ionizer cage \( n_{\text{ionizer}} \) can be written as

\[
S = \alpha J(E) \cdot I_e \cdot \epsilon \cdot (m/e) \cdot \beta \cdot \theta \cdot (m)
\]

with \( \sigma(E) \) the electron energy dependent cross section for electron impact ionization, \( I_e \) the (adjustable) electron beam current through the ionizer cage, and \( \alpha \) the efficiency of the mass spectrometer. The efficiency \( \alpha \) can be described by the product \( \alpha = l \beta (m/e) \theta (m/e) \), of \( l \) the length of the ionizer cage, \( \beta \) the extraction efficiency of the ionizer (chance for ions to reach the mass filter), \( \theta (m/e) \) the mass to charge ratio \( m/e \) dependent transmission probability through the mass filter, and \( \theta (m/e) \) the \( m/e \) dependent efficiency of the channeltron and the detector. Since we are interested in only singly ionized ions, the expression for \( \alpha \) can be written as \( \alpha = l \beta (m) \theta (m) \).

While the beam current \( I_e \) can be regulated accurately, and reported values for the ionization cross section \( \sigma(E) \) can be found in the literature respectively, the absolute efficiencies in \( \alpha \) are difficult to estimate and may even change in time. This makes obtaining absolute densities from mass spectrometry a difficult task. In practice therefore, the efficiencies are usually reduced to a known relationship, by using a measurement of a reference gas with known density.

![Schematic picture of the used mass spectrometer](image)

**Fig.2.8:** Schematic picture of the used mass spectrometer, which is a modified version of the Hiden Analytical 300 quadrupole mass spectrometer (PSM upgrade: the detector has been blocked from photons from the source by adding a Bessel box type of energy analyzer). From right to left the main components are: 1. The 50μm extraction orifice (pinhole), for extracting plasma particles while maintaining a low pressure. The pressure of the mass spectrometer is typically 10^{-7}-10^{-5} mbar during plasma operation. 2. The ionizer cage with filament. The electron energy (typically 70eV) and current (typically 50μA) are adjustable in a large range. 3. The mass/charge filter, consisting of a quadrupole mass filter. 4. The channeltron detector.
2.2.2 Beam and background density

The density of species in the ionizer cage \( n_{\text{ionizer}} \) is a sum of the beam (or 'line of sight') component of species extracted from the plasma, and the background contribution

\[
n_{\text{ionizer}} = n_{\text{Beam}} + n_{\text{Background}}.
\]

It is important to notice that of both contributions, only the beam component is directly proportional to the species density in the plasma. The detection rate of the beam component is proportional to the plasma density, because densities inside the ionizer cage determine the detection rate, rather than particle fluxes. Although the flux through the pinhole is generally higher for faster (lighter) particles, the residence time of these particles spent in the ionizer cage is inversely proportional to their velocity. On the other hand, the background density (i.e. the density of particles that are allowed to re-enter the ionizer cage) does depend on the incoming flux and the pumping speed of the specific species. In the case of radical species, also the wall recombination probability \( \gamma \) of the specific radical strongly influences the background density.

Methods to separate the beam signal from the background include beam modulation (e.g. by chopping), and multi-stage differential pumping. As our setup however is (yet) not equipped with either of both, a proportionality factor \( C \) is introduced given by

\[
C = \frac{n_{\text{Beam}} + n_{\text{Background}}}{n_{\text{Beam}}},
\]

\[ C \approx 1 - \frac{1}{35} \] for non-radical species with a wall loss probability \( \gamma = 0 \), assuming a pumping speed of 50-60 \( \text{l/s} \). However, for radical species that do have a wall loss probability \( \gamma > 0 \), \( C \) will have a smaller value, decreasing to 1 for radicals with unit wall loss probability \( \gamma = 1 \).

2.2.3 Radical density measurement: threshold ionization mass spectrometry

While the discussion in the previous section mostly applies to mass spectrometry in general, the measurement of radicals involves a specific approach. In this section, radical density measurement using threshold ionization mass spectrometry (TIMS) is explained by using the example of N-radical measurements, as performed for this study.

Typically applied electron ionization energies in mass spectrometry (~70eV) are high enough for the dissociation (cracking) and ionization of any molecule from the plasma. With these energies therefore, it is not possible to measure radical densities in the plasma, as the directly ionized radicals can not be distinguished from identical radicals that are created by dissociative ionization of their parent molecules. As radicals are often present in much lower density than their parent molecules, their detection rate would in many cases be drowned by the detection rate of their cracked parents.

To get round this problem, TIMS utilizes the energy difference (typically >2eV) that exists between the ionization energy threshold of a radical \( (E_i) \) and the dissociative ionization energy threshold of its parent molecule \( (E_a) \). For instance, there is a 10eV gap between the thresholds of ionization of atomic N and dissociative ionization of \( \text{N}_2 \):

\[
\begin{align*}
\text{N} + e & \rightarrow \text{N}^+ + 2e & E_i = 15.18 \text{ eV} \\
\text{N}_2 + e & \rightarrow \text{N}^+ + \text{N} + 2e & E_a = 25.26 \text{ eV}
\end{align*}
\]

When using ionization energies between both ionization energy thresholds, just the N radicals from the plasma can be ionized and detected while the parent molecules are left intact. This is demonstrated in
Chapter 2: Plasma and surface measurement techniques: Threshold ionization mass spectrometry

Fig. 2.9, in which an electron energy scan of the detection rate at 14 amu (the mass of atomic N) is shown, both during an Ar/N2 plasma and with the plasma turned off at constant gas flows.

Two regions are visible in the measured detection rates of N in Fig. 2.9. From 15.18 eV only N radicals from the plasma are ionized and detected, while from 25.26 eV an additional signal due to N radicals created by dissociative ionization of N2 can be seen. Therefore, the detection rate in region I is used for obtaining the density of N radicals.

However, when the plasma is turned off (also shown in Fig. 2.9), there still is a small detection rate left. This is attributed to radicals created by thermal dissociation (or pyrolysis) of N2 close to the filament. Naturally, this additional source of radicals is present during plasma operation as well. Therefore, to correct for this pyrolysis contribution to the signal, the count rate after turning the plasma off (at constant gas flows) is subtracted from the count rate during plasma on. But, as visible in the second region, the N2 density is higher when the plasma is off, because of a lower gas temperature and the absence of gas consumption. Therefore the plasma off pyrolysis signal is scaled down first, using the ratio of the detection rates at high (~70 eV) ionizing energies during the plasma turned on and turned off respectively. For this scaling factor, it is assumed that the N density is much smaller than the N2 density, such that the plasma N radical signal becomes negligible compared to the N2 signal at high ionization energies. To summarize, the plasma radical signal $S$ is corrected for the pyrolysis contribution using the equation:

$$S_{\text{plasma\_radical}} = S_{15-25\text{eV}\_\text{plasma\_on}} - \frac{S_{70\text{eV}\_\text{plasma\_on}}}{S_{70\text{eV}\_\text{plasma\_off}}} \cdot S_{15-25\text{eV}\_\text{plasma\_off}}$$ (4)

It should be noted that in the case of N, the contribution of pyrolysis to the radical count rate is relatively small due to the high N2 bond strength. Having obtained the detection signal of plasma N radicals, the next step is to obtain a density from this signal, which is discussed in the next section.
2.2.4 Converting detection rates to densities

![Graph: N and Ar detection rates vs electron energy, linear scale.](image)

Fig.2.10: Measured N and Ar detection rates vs electron energy, linear scale. The energy scale has been calibrated using the ionization threshold of Ar (40 amu) at 15.7 eV, which is always present in the studied processes.

In figure 10, measured N detection and Ar detection rates are shown, close to their respective ionization threshold energies. As visible, both detection rates are nearly proportional to the electron energy. It is in fact generally observed that just above the threshold energy, the electron impact ionization cross section is to a good approximation a linear function of the electron energy:

\[
\sigma^{X\to X^+} = \lambda^{X\to X^+} (E - E_{\text{threshold}}), \tag{5}
\]

with \(E\) the electron energy, \(E_{\text{threshold}}\) the threshold energy and \(\lambda^{X\to X^+}\) the slope. Values for the slope of the cross section \(\lambda^{X\to X^+}\) can be deduced by fitting ionization cross section vs. electron energy series of the specific species X. This is illustrated in Fig.2.11, in which reported electron impact ionization cross sections \(\sigma(E)\) of N and Ar are shown as a function of the electron energy. By linearly fitting, for N and Ar slopes have been obtained of respectively \(\lambda_N = 4.61 \times 10^{-22} \text{ m}^2/\text{eV}\) and \(\lambda_{Ar} = 1.63 \times 10^{-21} \text{ m}^2/\text{eV}\).

![Graph: Ionization cross sections of nitrogen and argon](image)

Fig.2.11: Electron impact ionisation cross sections of nitrogen and argon\(^{14,15,28}\)
By substituting the equation for the cross section \( \sigma \) in the equation for the detector count rate \( (I) \), we can write for the relation between ionizer density and detection rate:

\[
n_{\text{ionizer}} = \frac{A^{X\rightarrow X^+}}{\alpha d \lambda^{X\rightarrow X^+}},
\]

in which \( A^{X\rightarrow X^+} \) is (analogously to \( \lambda^{X\rightarrow X^+} \)) defined as the slope of the measured detection rate close to the ionization threshold. As already mentioned in section 2.2.1 however, the extraction efficiency \( \beta \), mass filter transmittance \( t(m) \) and channeltron detector efficiency \( \Theta(m) \) that determine the overall mass spectrometer efficiency \( \alpha \), are unknown. Therefore, usually a known reference density is measured as well. One previously often used species as reference, is the radical parent molecule. The radical parent can be measured with unchanged mass spectrometer settings by just increasing the electron energy beyond the threshold for dissociative ionization. E.g. in the case of \( N \) measurements, the parent molecule \( N_2 \) is dissociatively ionized into \( N^+ \). With this approach, \( \beta \) and \( \Theta(m) \) are supposedly totally eliminated as the same particle (e.g. \( N^+ \)) passes through the mass filter and detector.

However, recently Harmeet Singh et al.\(^{13} \) pointed out that in comparison to “normal” ionization, the extraction efficiency \( \beta \) could be 2 to 50 times smaller for dissociatively ionized particles due to a totally different velocity distribution after ionization, due to the Frank Condon effect. To eliminate \( \beta \), the reference gas should be measured using “normal” ionization instead of dissociative ionization. An equal extraction efficiency \( \beta \) upon (non-dissociative) ionization has indeed been reported\(^{13} \) for a large number of gases, among which \( Ar, H_2, N_2, CO_2, O_2 \).

As \( Ar \) gas is always present in the plasma processes under study, the \( Ar \) density (with plasma power turned off) is used as the reference. Using equation (6), the measured radical density in the plasma \( n_{X}^{\text{on}} \) can be expressed with the measured signal slopes \( A^{X\rightarrow X^+} \) (plasma on), \( A^{Ar\rightarrow Ar^+} \) (plasma off) and the \( Ar \) reference density \( n_{Ar}^{\text{off}} \) as:

\[
\frac{n_{X}^{\text{on}}}{n_{Ar}^{\text{off}}} = \left( \frac{A^{X\rightarrow X^+}}{A^{Ar\rightarrow Ar^+}} \right) \left( \frac{\lambda^{Ar\rightarrow Ar^+}}{\lambda^{X\rightarrow X^+}} \right) \frac{t(m_{Ar}) \Theta(m_{Ar})}{t(m_{X}) \Theta(m_{X})}.
\]

Still left are the mass filter transmission \( t(m) \) and channeltron/detector efficiencies \( \Theta(m) \). For the product of both \( t(m)\Theta(m) \), a \( m^2 \) dependence has been measured\(^{20,23} \), which has been used in the calculations.

### 2.2.5 Further experimental details for the \( N \) radical measurements

For each measured plasma condition, 4 ionization energy scans are made, which are listed in table 1. These scans are repeated during plasma off to obtain the detection rate of the \( Ar \) reference density, as well as the correction for pyrolysis.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Mass</th>
<th>Ionization threshold</th>
<th>Energy scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ( N\rightarrow N^+ )</td>
<td>14 amu</td>
<td>15.18 eV</td>
<td>14-35 eV ( \rightarrow ) plasma ( N ) radicals + pyrolysis</td>
</tr>
<tr>
<td>B ( N_2\rightarrow N^+ )</td>
<td>25.26 eV</td>
<td></td>
<td>68-72 eV ( \rightarrow ) dissociatively ionized ( N_2 )</td>
</tr>
<tr>
<td>C ( Ar\rightarrow Ar^+ )</td>
<td>40 amu</td>
<td>15.7 eV</td>
<td>14-22 eV ( \rightarrow ) Ionized ( Ar ) close to threshold</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td>68-72 eV ( \rightarrow ) not used for the ( N ) measurements</td>
</tr>
</tbody>
</table>

With these measurements and equation (7), the density of \( N \) inside the mass spectrometer ionizer cage can be obtained, with respect to the \( Ar \) density inside the ionizer cage.
Unfortunately however, the ratio of the densities in the ionizer cage is not necessarily equal to the ratio of densities in the plasma, as follows from the discussion in section 2.2.2 on the beam and background densities in the mass spectrometer. While Ar does not get lost to the steel walls of the mass spectrometer, the N radicals do have a probability to recombine at the surface. In Fig.2.12, two reported measurements of the recombination probability of atomic N on steel are shown, in two different pressure ranges\textsuperscript{29,30}. As visible, at higher pressures the recombination probability is relatively low in the order of a few percents. This is attributed to shielding of the wall by N\textsubscript{2}. At pressures below 10\textsuperscript{-1} mbar however, a sharp increase of the wall recombination probability of nitrogen has been observed. As a best approximation for the much lower operating pressure of the mass spectrometer of 10\textsuperscript{-6}-10\textsuperscript{-7} mbar, a unity recombination probability \( y_N = 1 \) is assumed. This means that while for the Ar reference density a proportionality factor of \( C = 35 \) (as defined in section 2.2.2) is used to account for the background density, for the N measurements a factor of \( C = 1 \) used as only the beam component is thought to be observed.

\textbf{Fig.2.12: The wall recombination probability of atomic N on steel as a function of the pressure.}\textsuperscript{29,30}
2.3 Attenuated total reflection infrared spectroscopy

In this section, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is explained. This technique has been used to measure SiHₓ, NHₓ, and SiN bonds in as-deposited a-SiNₓ:H films. An introduction to the technique is given, followed by a description of the followed measurement procedure.

2.3.1 The principle of ATR spectroscopy: the evanescent wave

Consider a beam of light that travels within a transparent medium which has a higher refractive index than the surrounding medium (e.g. light in glass surrounded by air). When the light encounters the edge of the medium, a part of the light reflects at the interface, with a reflection coefficient R that depends on the angle of incidence \( \theta \). Total reflection of the light takes place when the angle is larger than the critical angle \( \theta_c \):

\[ \theta_c = \arcsin\left(\frac{n_1}{n_3}\right), \tag{1} \]

with \( n_{il} \) the ratio \( n_3/n_1 \) of the refractive index of the surrounding medium to the refractive index of the denser medium (see Fig.2.13).

Fig.2.13: Total internal reflection occurs when the angle of incidence \( \theta \) exceeds the critical angle \( \theta_c \).

However, even though the reflection is complete, it is known that there is an electrical field beyond the interface. The amplitude of this field oscillates with the frequency of the light, but decreases exponentially in amplitude with distance from the interface:

\[ E = E_0 e^{-z/d_p}, \tag{3} \]

with \( E_0 \) the field amplitude at the surface, \( z \) the distance from this surface, and \( d_p \) the penetration depth. Therefore the field is named the evanescent wave. A schematic picture of this field is shown in Fig.2.14.
The penetration depth beyond the interface is proportional to the wavelength $\lambda$ of the reflected light, decreases with increasing angle of incidence $\theta$, and is given by

$$d_p = \frac{\lambda}{2\pi \left( \sin^2 \theta - n_{3i}^2 \right)^{1/2}}.$$  

with $n_{3i}$ the ratio of vacuum over film refractive index.

As long as the external medium is transparent, no energy is transported via this wave, as without magnetic field the Poynting vector equals zero. However, if the contacting medium is absorbing, some light energy is lost. The resulting reflectivity $R$ is not equal to 100% anymore, and is said to be attenuated. This effect, which is being employed in ATR spectroscopy, can be observed at home: holding a glass filled with water, one can distinguish the lines of his/her fingerprints when looking at the light reflections inside the glass.

In Fig.2.15, the core of each ATR setup, the ATR crystal is depicted schematically. It consists of a light transparent material, which is cut in a trapezoid shape. The edges are polished such that light can enter the crystal at large angles with respect to the top surface, higher than the critical angle of equation (1). Depending on the crystal length, one or more total internal reflections take place, which trap the light inside the crystal until it reaches the opposing edge. The number of reflections $N$ depends on the length and thickness of the crystal and the angle of incidence, and is given by
\[
N = \frac{l}{2rt \tan \theta},
\]

with \(l\) the crystal length and \(t\) the thickness of the crystal.

When a film is brought into contact with the ATR crystal, which in our case is done by direct deposition, absorptions by the film can be measured utilizing the evanescent wave. In ATR-FTIR spectroscopy, an FTIR spectrometer is used as light source, and a separate IR detector at the other side of the crystal is used to collect transmitted light. The possibility of using multiple reflections makes the technique relatively sensitive compared to single reflection or transmission techniques. A second advantage is the possibility of in situ measurements.

In the next section, a number of possible pathways of the light through the crystal and film are discussed, and the corresponding magnitudes of absorptions are determined.

### 2.3.2 Converting absorbances to densities

Depending on the refractive indexes of the film and the crystal, at least three possible pathways for the light are possible, which are depicted in Fig. 2.16:

- **a)** When the refractive index of the film is low enough, the light still totally reflects at the crystal-film interface. This is the **attenuated total reflection (ATR)** mode. Although the light does not enter the film, absorptions by the film take place because of the evanescent wave, as discussed.

- **b)** When the refractive index of the film matches the refractive index of the crystal, the light penetrates the film and reflects at the film-vacuum surface. This is the **multiple internal reflection (MIR)** mode.

- **c)** In all other cases, one part of the light reflects at the crystal surface, while the other part reflects at the film-vacuum interface. A complicated pathway results, which for the moment is left out of consideration.

Each pathway has its own absorption rate, of which the ATR and MIR cases are discussed, in the following subsections.
a) ATR: effective thickness of a thin film

In transmission measurements (see also the appendix), the absorption \( A \) is usually obtained by comparing measured intensities with and without the absorbing medium between light source and detector. The transmission of the measured object is then given by

\[
T = \frac{I}{I_0} = \exp(-\alpha d),
\]

with \( \alpha \) the absorption coefficient of the film, and \( d \) the thickness of the measured material. In practice, people often work in absorbance, which is defined as

\[
\text{Abs} = -10 \log\left(\frac{I}{I_0}\right) = -10 \log(\exp(-\alpha d)) = \log(e) \cdot \alpha d = \alpha d / 2.30,
\]

with \( I \) and \( I_0 \) the measured light intensity with and without absorbing medium. The advantage of working in absorbance is that the absorbance is linear in both absorption coefficient and thickness, unlike the absorption \( A \).

A similar approach can be used for the ATR measurements. However, we can not use the actual thickness of the film as in equation (7), because the absorption by attenuated total reflection is also determined by the penetration depth and magnitude of the evanescent wave. Therefore, an 'effective thickness' \( d_e \) is defined, which accounts for the field strength of the evanescent wave. The effective thickness is a rather complex function of the absorption coefficient \( \alpha \) and wavelength \( \lambda \), but can be simplified for thin films by the assumption that the electric field of the evanescent wave is constant over the film. In that case \( d_e \) can be approximated by

\[
d_e = \frac{n_{21} E_0^2 d}{\cos \theta},
\]

with \( n_{21} \) the ratio of film over crystal refractive indexes, \( d \) the thickness of the film and \( E_0 \) the electric field amplitude of the evanescent wave close to the interface. For parallel and perpendicular polarised light, this field strength is given by
Chapter 2: Plasma and surface measurement techniques: attenuated total reflection IR-spectroscopy

\[ E_\perp = \frac{2\cos\theta}{\sqrt{1-n_{31}^2}}, \quad \text{and} \quad E_{\parallel} = \frac{2\cos\theta}{\sqrt{1-n_{31}^2}} \left( \frac{(1+n_{32}^4) \sin^2 \theta - n_{31}^2}{(1+n_{31}^2) \sin^2 \theta - n_{31}^2} \right)^2, \tag{9} \]

with \( n_{32} \) the ratio of vacuum over film refractive indexes, \( n_{31} \) the ratio of vacuum over crystal refractive indexes and \( \theta \) the angle of incidence. Combining (8) and (9) gives the effective thickness \( d_e \) for parallel and perpendicular polarized light:\(^7\):

\[ d_{\perp} = \frac{4n_{21} \cos\theta}{(1-n_{31}^2)}, \quad \text{and} \quad d_{\parallel} = \frac{4n_{21} \cos\theta}{(1-n_{31}^2)} \left( \frac{(1+n_{32}^4) \sin^2 \theta - n_{31}^2}{(1+n_{31}^2) \sin^2 \theta - n_{31}^2} \right). \tag{10} \]

When the film is thin, \( 2\pi d < \lambda/10 \) (i.e. \( d < 160 \) nm for 10\(\mu\)m light), and the absorption coefficient is small, \( \alpha < 1.25n/\lambda \) (i.e. \( \alpha < 6 \cdot 10^4 m^{-1} \) for 10\(\mu\)m light in a film with refractive index of 2.1), these relations are correct within a few percent. For too high absorbances, the effective thickness is overestimated by equation (10), and hence the calculated density underestimated. The effective thickness may be greater or smaller than the actual film thickness by a large factor, and decreases with increasing angle of incidence. Also, the effective thickness for parallel polarization may be greater or smaller than that for perpendicular polarization, depending on whether \( n_{32}^4/n_{31}^2 \) is greater or smaller than 1\(^*\). In the next section, examples of effective thicknesses for two used crystal types (made of Si and ZnSe) are given.

To summarize, the ATR absorptions can be treated analogously to transmission absorptions, by using the effective thickness \( d_e \) instead of \( d \), as explained above. For an ATR crystal with \( N \) internal reflections, we could write for the absorbance of a thin film, analogously to equation (7):

\[ \text{Abs} = -10 \log\left( \frac{I}{I_0} \right) = N\alpha d_e / 2.30. \tag{11} \]

In practice, absorption peaks are integrated over their width. The bond density is calculated using the relation

\[ n_{\text{bond}} = K \int \frac{\alpha}{\omega} d\omega, \tag{12} \]

with \( K \) a proportionality constant (reciprocal absorption cross section). Combining equation (11) and (12), the bond density is obtained from absorbances measured with an ATR crystal by

\[ n_{\text{bond}} = \frac{2.30 \cdot K}{Nd_e} \int \frac{\text{Abs}}{\omega} d\omega. \tag{13} \]

b) Multiple internal reflection

In case of matching refractive indexes, the light will enter the film undeflected and reflect at the film-vacuum surface. The film absorption \( A \) of the light in MIR mode during each reflection is then determined by the light pathlength in the film \( l = 2d/cos\theta \) and absorption coefficient \( \alpha \). Hence, we can write for the absorbance

\[ \text{Abs} = \alpha(2d/cos\theta) / 2.30, \tag{14} \]

\(^*\) For the used crystals Si and ZnSe, the perpendicular field strengths are respectively 0.96 and 1.06 times as large as the parallel field when measuring films with a refractive index of 2.1.
with \( d \) the film thickness. To compare the resulting absorbance to absorbances in ATR mode, we can define a relative “effective thickness” for MIR reflections as

\[
\frac{d_r}{d} = \frac{2}{\cos \theta},
\]

which in contrary to the ATR case increases with increasing angle of incidence.

### 2.3.3 The experimental setup

In Fig.2.17, the measurement setup is presented. Both silicon and zinc selenide ATR-crystals, with 60° angles, have been used. The crystals have been positioned inside the reactor vessel using a modified substrate holder to enable deposition and in situ measurements. A FTIR spectrometer has been applied as light source, and a liquid nitrogen cooled IR-detector as detector. In the initial experiments with the Si crystal, an aluminum-plated off-axis parabolic mirror (\( f=32 \) cm) has been used to focus the light beam upon the ATR-crystal. As vacuum windows KBr windows have been used (transparent range KBr: \( \sim400-50000 \) cm\(^{-1} \)). However, the focal length of the off-axis parabolic mirror has turned out somewhat too short to suit our setup (and larger focal lengths are not easily available). Therefore in the second series of experiments with the ZnSe crystal, an NaCl lens (\( f=50 \) cm, transparent range NaCl: \( \sim600-500000 \)) and also larger NaCl windows have been used. First, the used crystal materials Si and ZnSe are discussed.

**Fig.2.17:** The ATR-FTIR setup. A FTIR spectrometer (Bruker Vector 22) is used as light source, linked to an IR detector\(^{(6)} \) (Bruker) with a PC\(^{(9)} \). An NaCl lens\(^{(5)} \) (\( f=50 \) cm) is used to focus the initially \( \varnothing -5 \) cm IR beam onto the crystal edge. The light enters and leaves the reactor through NaCl vacuum windows\(^{(4)} \), and is focussed on the detector, using a gold plated off-axis parabolic mirror (\( f=7 \) cm). The dimensions of the ATR crystals are \( l\times w\times t=50 \times 20 \times 0.5 \) mm\(^3 \), with edges cut at 60°. The actual angle of incidence in this setup is 68°. Used crystal materials are Si (\( n=3.4 \rightarrow \theta=62.3° \rightarrow N=26 \)) and ZnSe (\( n=2.4 \rightarrow \theta=63.3° \rightarrow N=25 \)).
Measurement procedure

In Fig. 2.20, a series of absorbance spectra is shown. For this series, first a background spectrum has been taken of the bare crystal. Then a series of accumulating depositions are made on the crystal, of which the spectra are taken between each deposition. The spectra are averaged typically $400$ times, which takes approximately $3-4$ minutes.

The peaks can be de-convoluted using reported peaks assignments by Bustarret et al.\textsuperscript{18}, which are listed in table 1. The proportionality factors (reciprocal absorption cross sections) that relate the integrated normalized absorption to the density of the specific bands are listed as well. These factors are estimates, as the film composition does affect the absorption strength. As the de-convolution is not always straightforward, in most cases overall proportionality values for the Si-H and N-H bond types have been used\textsuperscript{19}. In section 4.1, a more in depth treatment of a number of deposition series is given.

![Graph showing absorbance spectra](image)

**Fig. 2.20:** A-SiN$_x$:H deposition series on ZnSe. This is obtained by taking the difference between absorbance spectra measured after short cumulative a-SiN$_x$:H depositions and one initial background spectrum taken before the depositions. A baseline correction has been performed. Visible are the SiN stretching mode (845-870 cm$^{-1}$), SiH$_x$ stretching ($\sim 2100$ cm$^{-1}$), NH$_x$ bending and stretching modes (1175, 3340 cm$^{-1}$), and NH$_2$ bending and stretching modes (1540, 3450 cm$^{-1}$)\textsuperscript{18}. The plasma conditions for this particular series are Ar 55, H$_2$ 5, N$_2$ 10 and SiH$_4$ 4 sccs.

For the measurements, one ATR crystal can be used several times, by cleaning it with an Ar/CF$_4$ etching plasma after a measurement is finished. The transparency of the crystal does degrade however as a result of the various treatments. One crystal lasts typically 10-20 deposition series.
Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

Table 1: SiH, NH and SiN peak assignments, and the proportionality factors between bond densities and integrated absorption of the corresponding peaks, as reported by Bustarret et al.\textsuperscript{18} As in practice de-convolution of the peaks is not always possible, an overall proportionality constant for the SiH\textsubscript{x} and NH\textsubscript{x} absorptions as reported by Landford et al.\textsuperscript{19} has been used as well.

<table>
<thead>
<tr>
<th>Wavenumber (cm\textsuperscript{-1})</th>
<th>Bondtype</th>
<th>(K \times 10^{19} \text{cm}^{-2}) (Bustarret/Langford)</th>
</tr>
</thead>
<tbody>
<tr>
<td>845-870</td>
<td>SiN stretching</td>
<td>2.07 (1.25&lt;N/Si&lt;1.45)</td>
</tr>
<tr>
<td>1175</td>
<td>NH bending</td>
<td>2.07</td>
</tr>
<tr>
<td>1540</td>
<td>NH\textsubscript{2} bending</td>
<td>2.07</td>
</tr>
<tr>
<td>2005</td>
<td>SiH-Si\textsubscript{3} stretching</td>
<td>7</td>
</tr>
<tr>
<td>2065</td>
<td>SiH\textsubscript{2}-Si\textsubscript{2} stretching</td>
<td>11</td>
</tr>
<tr>
<td>2082</td>
<td>SiH-NSi\textsubscript{2} stretching</td>
<td>17</td>
</tr>
<tr>
<td>2140</td>
<td>SiH-N\textsubscript{2}Si, SiH\textsubscript{2}-NSi stretching</td>
<td>11</td>
</tr>
<tr>
<td>2175</td>
<td>SiH\textsubscript{2}-N\textsubscript{2} stretching</td>
<td>40</td>
</tr>
<tr>
<td>2220</td>
<td>SiH-N\textsubscript{3} stretching</td>
<td>20</td>
</tr>
<tr>
<td>3340</td>
<td>NH stretching</td>
<td>12</td>
</tr>
<tr>
<td>3450</td>
<td>NH\textsubscript{2} stretching</td>
<td>50</td>
</tr>
</tbody>
</table>

3250 absorption peak

During the experiments on both the Si and ZnSe crystal, strong absorptions around 3250 cm\textsuperscript{-1} have been detected. It was found that the absorptions almost completely disappear overnight, when the chamber is pumped down to \(10^{-7}\) mbar using turbo pumps. This is demonstrated in Fig.2.21, in which a background spectrum in the morning is shown with respect to a background taken at the end of the previous day. When pumping with the roots pumps again (base pressure \(\sim 10^{-5}\)) the absorption peaks begin to re-appear again, even before deposition. Also, the initial deposition causes a major increase of the absorption. The absorptions could be related to species from the roots pump, or the helium back flow that is applied for temperature control of the substrate. A possible candidate for the peaks is Si(OH)\textsubscript{x}. ZnOH is considered too, but the absorptions take place on the Si crystal as well. As the absorptions overlap with the NH\textsubscript{x} absorptions, special care has to be taken during the analysis.

![Fig.2.21: Unknown absorption peaks. This spectrum is taken in the morning, with the spectrum taken at the end of the previous day as reference.2.3.4](image-url)
2.3.4 Comparison between Si and ZnSe ATR crystal materials

Two different materials have been used for the ATR-crystals, each with their own advantageous properties:

- Silicon (Si) has a refractive index of 3.42, and therefore measurements on a-SiN:Hx (n~2.1) are ATR measurements. An advantage is the fact that Si is used as solar cell material as well, and it is relatively inexpensive. A main disadvantage is the early cutoff (transparent range Si ≈ 1000-10000 cm⁻¹), and the rapidly decreasing transmission at temperatures above 200°C due to intra-band transitions.

- Zinc selenide (ZnSe) has a refractive index of 2.4, which means that the measurements are only in ATR mode provided that the (IR) refractive index of the measured a-SiNx:H film does not exceed 2.14 (equation (1)). ZnSe is relatively expensive and brittle, but is well transparent up to 400°C. Furthermore, the transparent range of ZnSe ≈ 500-17000 cm⁻¹.

In Fig.2.18, baseline transmission spectra of both crystal types are shown as a function of the temperature.

![Temperature spectra](image)

**Fig.2.18:** The transmission spectrum of a) the Si-ATR-crystal, and b) the ZnSe crystal, both at various temperatures between room temperature and 400°C. The intensities are in arbitrary units, but can be compared for the different crystals. The ZnSe crystal is transparent in the full temperature range, while the Si crystal becomes almost fully opaque at 400°C.

Using equation (10), we can calculate the relative effective thickness (as defined in section 2.3.3) for both crystals. Using the IR refractive index of the film, the effective thickness for Si equals \( \frac{d}{d'} = 0.60 \times n_{film} \), while for ZnSe \( \frac{d}{d'} = 0.91 \times n_{film} \), in our specific setup. In other words, for the ZnSe crystal we would expect absorption peaks that are higher by a factor of approximately 1.5 compared to peaks of the same film type on Si. An actual comparison is made between ATR measurements on Si and ZnSe crystals, by doing a deposition series with identical plasma settings on both crystals. Unfortunately, an unassigned peak at 3250 cm⁻¹ as discussed in the previous section appeared in the ZnSe series. Therefore, we used the absorption spectrum of only one deposition step, i.e. the spectrum of 0.6s of a-SiNx:H deposition on top of a ~40nm thick a-SiNx:H film, as depicted in Fig.2.19.

![Temperature spectra](image)
Fig. 2.19: Comparison between ZnSe and Si ATR crystals. The spectra are shown of 0.6s a-SiNx:H deposition on top of already deposited a-SiNx:H, for both crystal types. Deposition parameters: Ar 55, H2 5, N2 10, SiH4 4 sccs.

The ratios of the absorption peak maxima (ZnSe/Si) are 1.39 and 1.36 for the NHx and SiHx peaks respectively, which is in reasonable agreement with the expected ratio of 1.5.
Chapter 3

Plasma radical densities during a-SiN\textsubscript{x}:H deposition

In this chapter, the measurements performed on the a-SiN\textsubscript{x}:H depositing plasma are presented. The deposition reaction scheme as described in chapter 1, i.e. nitridation of an a-Si:H-like top layer, has been used as a starting point for the plasma measurements. This model suggests that a-Si:H depositing radicals together with 'nitridating' species, either atomic N radicals or possibly excited N\textsubscript{2} molecules, bring about the deposition of a-SiN\textsubscript{x}:H. In this study, an attempt is made to find out which exact radicals establish the deposition. In section 3.1, first dissociation mechanisms of the SiH\textsubscript{4} precursor are discussed, which play an important role in the a-Si:H depositing plasma and could occur in the a-SiN\textsubscript{x}:H depositing plasma as well. In section 3.2, measured densities of radicals in the non-depositing source plasma that might be responsible for the dissociation of SiH\textsubscript{4} are presented. In section 3.3, measured densities of N and SiH\textsubscript{3} in the depositing plasma are shown. Also the SiH density has been measured. In section 3.4 the plasma densities are discussed in correlation to film composition and growth rate as measured by ERD and ellipsometry. It is verified whether the measured N and SiH\textsubscript{3} densities are high enough to explain the deposition rate. Finally, in section 3.5 some other observations in the plasma are presented.

3.1 Precursor dissociation mechanisms

As discussed in chapter 1, the dissociation of SiH\textsubscript{4} takes place in a low pressure deposition chamber, by means of an Ar/H\textsubscript{2}/N\textsubscript{2} plasma that is generated in a high-pressure cascaded arc plasma source. We will first consider which of the species that are emanating from the plasma source could dissociate SiH\textsubscript{4}. Previous Langmuir probe measurements on the plasma have pointed out that the electron temperature in this plasma is relatively low at 0.3-0.4 eV, which means that electrons most likely do not play a major role in the precursor dissociation reactions. Furthermore, it is shown that the ion density decreases from \(10^{19} \text{ m}^{-3}\) (mainly Ar\textsuperscript{+}) to \(10^{17} \text{ m}^{-3}\) (mainly NH\textsuperscript{+}) when hydrogen and nitrogen are admixed to the plasma.\textsuperscript{23}

From previous studies on the a-Si:H depositing plasma, both ions and atomic H are known to provide reaction pathways that lead to the dissociation of SiH\textsubscript{4}. Ar\textsuperscript{+} can dissociate SiH\textsubscript{4} by dissociative charge exchange in the reaction:\textsuperscript{5}

\[
\text{Ar}^+ + \text{SiH}_4 \rightarrow \text{SiH}_n^+ + p\text{H}_2 + q\text{H} + \text{Ar} \quad (n \leq 3, n + 2p + q = 4),
\]

which is a relatively efficient reaction. Subsequent dissociative recombination reactions of SiH\textsubscript{n}\textsuperscript{+} with electrons lead to the production of SiH\textsubscript{n} (n\textless=2) radicals, which are very reactive, both in the plasma with SiH\textsubscript{4} and on the surface. As mentioned, the ion density is however low in the Ar/H\textsubscript{2}/N\textsubscript{2} plasma when H\textsubscript{2} is added to the plasma. In that case (just as in the case of a-Si:H deposition) the following reaction\textsuperscript{5} is thought to become predominant:

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

Subsequent H-abstraction reactions of the SiH\textsubscript{3} radicals with H may occur, but as long as there is no abundance of H, the SiH\textsubscript{3} radical is expected to be produced in much higher density than the SiH\textsubscript{n} (n\textless=2) radicals.

Because of the lack of Si-N containing species in an Ar/N\textsubscript{2}/SiH\textsubscript{4} RF plasma as reported by Smith et al.\textsuperscript{1,2}, atomic N is not expected to be very reactive with SiH\textsubscript{4} in the plasma phase, but dissociation reactions of SiH\textsubscript{4} involving N can still be possible. Therefore we have measured the densities of both H and N in the source plasma, as presented in the following section.
3.2 N and H radical densities from the Ar/N\textsubscript{2}/H\textsubscript{2} plasma source
(without SiH\textsubscript{4} injection)

![Graph showing N density in Ar/N\textsubscript{2}/H\textsubscript{2} plasma source](image)

Fig.3.1: Atomic N density in a Ar/N\textsubscript{2}/H\textsubscript{2} plasma [Ar 55, H\textsubscript{2} 5, N\textsubscript{2} 0-10 sccs, 45A], as a function of the N\textsubscript{2} flow, as measured with TIMS.

In Fig.3.1, the N density in the Ar/H\textsubscript{2}/N\textsubscript{2} source plasma is shown as a function of the N\textsubscript{2} flow. The density has been measured using TIMS (chapter 2.2), at the position of the substrate holder. The N density increases with increasing N\textsubscript{2} flow to 1-2·10\textsuperscript{19} m\textsuperscript{-3}, i.e. the production of N is not limited by the capacity of the plasma source. The order of magnitude of the absolute density is in agreement with TALIF measurements, where a density of 5·10\textsuperscript{19} m\textsuperscript{-3} was determined during a pure 25 sccs N\textsubscript{2} plasma at a pressure of 0.20 mbar\textsuperscript{25}. As shown in the same figure, the addition of H\textsubscript{2} reduces the N density by approximately 50%.

Unfortunately, atomic H is generally more difficult to measure. We have been able to detect atomic H using the TIMS technique, but the relative error due to time-dependent artifacts in these results is too high to present the H density series. However, the measurements suggest an absolute density in the range of 2·10\textsuperscript{18}-7·10\textsuperscript{19} m\textsuperscript{-3}.

The main conclusion is that the measurements suggest that both neutral N and H are present in high enough density in the source plasma for the majority of precursor dissociation reactions in the depositing plasma. In the next section N and SiH\textsubscript{x} radical density measurements in the depositing plasma (i.e. with SiH\textsubscript{4}) will be presented.

3.3 N, SiH\textsubscript{3} and SiH radical densities in the Ar/H\textsubscript{2}/N\textsubscript{2}/SiH\textsubscript{4} depositing plasma

In Fig.3.2, the measured N density is shown, but now with SiH\textsubscript{4} being added to the downstream plasma, using the injection ring. Interestingly, the SiH\textsubscript{4} addition leads initially to a steep increase of the N density by a factor of 5-6, to a very high density of ∼10\textsuperscript{20} m\textsuperscript{-3}. This is followed by a gradual decrease with increasing SiH\textsubscript{4} flow. The remarkably sharp initial increase in N density is not expected and not understood yet. In fact, the possibility of reactions of atomic N with SiH\textsubscript{x} in the plasma and at the surface would more likely result in a lower density, because more N atoms are consumed per unit of time. If we reverse this reasoning, the fact that SiH\textsubscript{4} addition leads to an increase in N density supports the idea that atomic N is indeed not very reactive with SiH\textsubscript{x}. It should be noted however, that TIMS is a local measurement technique (unlike e.g. CRDS, where the density is integrated over the line of sight through the plasma). Therefore, apart from new reaction mechanisms, a possible explanation for the jump could be

* Depending on the proportionality factor for the background density inside the mass spectrometer, which depends on the wall recombination probability of atomic H, as discussed in chapter 2.2.
a confinement of the plasma due to the silane injection, i.e. N atoms might have a lower diffusivity to the wall upon SiH₄ addition. An increased density by a factor of 5 would correspond with a decreased "diameter of the plasma" by a factor of \( \sqrt{5} \). Such a confinement can not be seen in the CRDS measurements without making a radial scan of the density. Another possibility to be considered is the availability of SiH₃ related reaction pathways leading to dissociation of (excited) N₂, although such reactions would require a lot of energy as the N₂ bond is a relatively strong bond. A third possible explanation is a decreased consumption of N in reactions with H, because of H being consumed in the precursor dissociation reactions (reaction 2).

The subsequent gradual decrease of the N density can be explained by an increased consumption of N on the surface, due to a higher incorporation rate of N in the a-SiNₓ:H film that is being grown with increasing growth rate as the SiH₄ flow is increased. This will be verified with ERD data in section 3.4.

![Fig.3.2: Atomic N density in an Ar/N₂/H₂/SiH₄ plasma [Ar:55, H₂:5, N₂:10, SiH₄:0-12 sccs], as measured with TIMS.](image-url)

CRDS density measurements of SiH₃, the other expected main radical, and SiH are shown in Figs.3(a) and (b). A density of 1-2\( \times 10^{19} \text{ m}^{-3} \) is measured for the ‘standard’ a-SiNₓ:H deposition conditions with 8 sccs SiH₄. The addition of N₂ to the plasma leads to a density which is about twice as high as same condition without N₂. This could indicate that N is involved in dissociation reactions with SiH₄, but the increased density may as well be explained by a higher reactivity of the plasma due to a higher power usage of the arc. The arc plasma source is current controlled, not power controlled, and at higher gas flows usually a higher voltage (and hence more power) is needed to maintain the same current through the plasma. This explanation could apply for the increased SiH density upon N₂ addition as well.
Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

As visible from Fig.3.3, the SiH₃ density is about two orders higher compared to the SiH density. This large difference between both densities indicates that the proposed reaction scheme (2), in which SiH₃ is created by H abstraction reaction from SiH₄, is dominant over reaction (1), as expected. The flattening-off trend of SiH may be explained by a competition of SiH creation (either by reaction (1) or reaction (2)), and loss in reactions of SiH with SiH₃.

The fact that both SiH₃ and N radicals are present in high densities supports (at least does not contradict) the proposed deposition model of nitridation of an a-Si:H-like layer (section 1.3). In the next section, a quantification is done of the contribution of the SiH₃ and N radicals to the film growth, by comparing the radical densities in the plasma to the growth rate and composition of the films.

3.4 Contribution of SiH₃, SiH and N radicals to the film growth

In Fig.3.4a, the a-SiNx:H film growth rate is shown as a function of the SiH₄ flow, at a constant N₂ flow of 10 sccs. In Fig.3.4b, the N/Si ratio in the deposited films deposited under the same plasma conditions is shown. As the growth rate increases nearly linearly with the SiH₄ flow, the film composition changes from a N-rich film to Si-rich film. At very low SiH₄ flows, the films become nearly stoichiometric Si₃N₄; it is not possible to produce films with much higher N/Si ratios than 1.33. Evidently, the change from N-rich to Si-rich films must be caused by the changed ratio of N and SiH₃ radicals present in the plasma. In this section, it is investigated to what extent the measured N and SiH₃ densities in the plasma can explain the film composition and growth rate.

Fig.3.3: SiH₃ (a) and SiH (b) density in an Ar/H₂/N₂/SiH₄-plasma vs. SiH₄ flow [Ar 55, H₂ 5, N₂ 10, SiH₄ 0-15 sccs], as measured using CRDS.
Chapter 3: Plasma radical densities during a-SiN$_x$:H deposition

![Graph](image1)

**Fig.3.4:** A-SiN$_x$:H film growth rate (a) and N/Si ratio (b) vs. SiH$_4$ flow [Ar 55, H$_2$ 5, N$_2$ 10, SiH$_4$ 1-15 sccs], as determined with FTIR and ERDA respectively.

In Fig.3.5a, the densities of N, Si and H atoms in the films are shown for the same flow series. Apparently, at lower growth rates the films become more dense. By multiplying the film composition with the growth rate, the number of H, Si and N atoms that are incorporated in the films per second is obtained, as shown in Fig.3.5b. The Si implementation rises approximately linearly with the SiH$_4$ flow, as does the SiH$_3$ density (Fig.3.3) in the plasma. For SiH$_4$ flows higher than 2 sccs, the N incorporation increases slightly, while the plasma density of N slightly decreases (Fig.3.2). The fact that the N implementation abruptly decreases at low SiH$_4$ flows can well be explained by the stochiometric film limit. Thus, so far the Si and N incorporation rates seem to correlate well to the SiH$_3$ and N densities in the plasma.

![Graph](image2)

**Fig.3.5:** The film composition (a) in absolute atomic densities of N, Si and H, as measured with ERDA, and (b) the film composition multiplied with the growth rate: the incorporation rate of N, Si and H atoms.

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As a next step, an estimate is made of the incorporation rate of Si and N, but now on basis of the densities and expected sticking and surface reaction probabilities of the SiH₃, SiH and N radicals respectively. This is done using the following expression:

\[
\text{Implementation rate} = \frac{1}{2} n v \frac{s}{1 - \beta/2}
\]  

(1)

with the implementation rate in (atoms/m²s), \(n\) the thermal velocity of the considered radical in front of the substrate, and \(s\) and \(\beta\) the sticking and surface reaction probability respectively. As an estimate for the thermal velocity, a temperature of 1000K used, which is in between the substrate temperature and the rotational temperature of 1400K of SiH as measured by CRDS (section 2.1).

When for SiH₃ an overall reaction probability of 0.3 is used, as reported for a-Si:H deposition conditions, the measured SiH₃ density at 8 sccs SiH₄ flow would lead to an Si incorporation rate of \(-5.4 \times 10^{16}\) atoms/cm²s. This is \(-80\%\) of the total Si incorporation rate as determined with ERDA. Of SiH, both the sticking and surface reaction probabilities are reported to be close to 0.95 in ref.27. With these values, a Si implementation rate of \(-2.4 \times 10^{15}\) atoms/cm²s is estimated, which is 3-4% of the total Si implementation rate. Due to the low SiH density, the absolute error in the contribution to the total Si incorporation is relatively small. For SiH₃ however, the density, reaction probability, velocity etc. have to be known with greater accuracy to obtain the total Si incorporation rate. Still, while contributions of other Si depositing species apart from SiH should be investigated, the SiH₃ radical density explains the greater part of the Si incorporation rate.

The measured N density at the same plasma condition is certainly high enough for the observed N incorporation rate. When the N radicals indeed are responsible for the growth, the measured radical density and N growth flux suggest a surface reaction probability of \(-0.01-0.02\). This value does have the same order of magnitude as the expected recombination probability of 1-4% of atomic N on steel, on basis of extrapolation to the deposition pressure of 0.20 mbar of the reported recombination probabilities (Fig.2.12 in section 2.2).

In Fig.3.6a, the N implementation rate divided by the atomic N density in the plasma, which is a measure for the overall surface reaction probability provided that atomic N is indeed the nitrogen source, is plotted as a function of the SiH₄ flow. Unfortunately, there are only a few points available, as we do not have corresponding ERD measurements for all the plasma conditions. However, some trends can be seen. For the N radicals, the decreased reaction probability at low SiH₄ flows is understood by the fact that the stochiometric limit is reached. When the SiH₄ flow is increased, an a-SiNx:H layer can be formed which has a lower than stochiometric N/Si ratio, which effectively increases the sticking probability. Fig.3.6a then suggests that at SiH₄ flows of 2 sccs or more, the surface reaction probability of N has reached its maximum, and remains constant for films deposited with higher SiH₄/N₂ flow ratios.

In Fig.3.6b the Si implementation rate divided by the SiH₃ density is shown as well. For the SiH₃ radicals, the sticking and surface reaction probability are not expected to vary as much, which is indeed reflected by the relative constant line in Fig.3.6b, except at low SiH₄ flow. At low SiH₄ flows, other radicals than SiH₃ may well become the predominant Si-sources. When there is relatively more H available per SiH₄ molecule, subsequent H-abstraction reactions (reaction 2) may result in the creation of more reactive SiH₄ (n=2) radicals. The trends in Fig.3.3 also suggest that the SiH density initially increases sharper than the SiH₃ density.
Chapter 3: Plasma radical densities during a-SiN$_2$:H deposition

Fig. 3.6: (a) $N$ incorporation rate in the film divided by the atomic $N$ density in the plasma, and (b) $Si$ incorporation rate divided by the $SiH_3$ density in the plasma. Provided that the $N$ and $Si$ in the film originate from atomic $N$ and $SiH_3$ in the plasma, these ratios are expected be constant as long as the sticking and surface reaction probabilities are constant. Deviations from a constant incorporation rate/plasma density are in the case of $N$ thought to be caused by a decreased sticking probability due to the stochiometric film limit, and in the case of $Si$ to be caused by contribution of other radicals than $SiH_3$ to the film growth.
Chapter 4

In situ film study

In this chapter the in situ a-SiNₓ:H film studies performed with the ATR-FTIR technique, as introduced in chapter 2.3, are presented. With this technique, the infrared absorptions by Si-H, N-H and S-N bonds have been monitored in a number of experiments. In sections 4.1, three measured deposition series are discussed, which have been deposited with a varied SiHₓ/N₂ flow ratio. In section 4.2, the variation in depth of the a-SiNₓ:H films is discussed. In section 4.3, a study in which the growth mechanism is investigated more closely is described.

4.1 N-rich – Si-rich a-SiNₓ:H films

In Fig.4.1, IR absorbance spectra that are made during three a-SiNₓ:H deposition series are depicted. The films have been deposited on a ZnSe ATR crystal. Three plasma conditions with a high, medium and low N₂/SiHₓ flow ratio were used, by maintaining an N₂ flow of 10 sccs and using 1, 4 and 8 sccs SiHₓ respectively. The resulting films have a N/Si-content that varies from nearly N-rich to Si-rich. The spectra are measured after a number of short cumulative depositions, each time interrupted for the measurement. One measurement takes approximately 5 minutes.

In the spectra, respective absorption peaks of SiN stretching (700-1000 cm⁻¹), NH bending (1175 cm⁻¹), NH₂ bending (1540 cm⁻¹) and SiHₓ (2005-2175 cm⁻¹), NH (3340 cm⁻¹) and NH₂ (3450 cm⁻¹) stretching modes are visible, as indicated in the middle graph. Also, some oxygen related absorption peaks are present of SiO (1050 cm⁻¹), possibly SiOH (broad around 3250 cm⁻¹) as well as an absorption around 2264 cm⁻¹ which is thought to be caused by SiHₓ with an oxygen environment. First we will consider the differences between the film types, by comparing the spectra of films with an approximately equal thickness of ~40 nm.

In Fig.4.2, the SiN stretching + NH bending, SiHₓ and NHₓ stretching peaks are singled out, shown from left to right. From top to bottom, the three film types ranging from nearly N-rich to Si-rich are organized. As visible, with decreasing SiHₓ flow, the absorption by SiHₓ decreases relative to the NHₓ absorption. The trend of NHₓ and SiHₓ roughly follows the N/Si ratio (Fig.3.3) in the film, but at 1 sccs SiHₓ, practically all the hydrogen that is present in the film is bonded to N. Furthermore, the SiHₓ absorption peak shows a shift to higher wavenumbers when relatively more N is present in the films. This is due to the generally observed fact that absorptions by Si-H bonds shift to higher wavenumbers when the electronegativity of the back-bonded atoms to Si is increased. N has a higher electronegativity than Si.

With decreasing SiHₓ/N₂ flow ratio (resulting in more N-rich films), an increasing SiO peak around 1050 cm⁻¹ appears. Also a number of yet unassigned, possibly O-related absorptions at 2264, 3170 and 3250 cm⁻¹ are present. The increasing O content with decreasing SiHₓ flow can be explained by the lower growth rate. A lower growth rate while having a constant pressure of oxygen in the chamber would result in relatively more oxygen incorporated in the film. Another explanation is found in a more porous structure of the films due to a higher relative N density in the plasma.
Fig. 4.1: Deposition series of nearly N-rich (top), intermediate and Si-rich (bottom) a-SiNx:H films. Plasma conditions are [Ar 55, H2 5, N2 10, SiH4 1-4-8 sccs respectively].
Fig. 4.2: Comparison of N-rich (top row) – Si-rich (bottom row) ~40 nm thick films, deposited with 1-4-8 sccs SiH₄ and 10 sccs N₂ respectively. From left to right, the SiN, SiHₓ and NHₓ absorptions are shown.
In table 1, the integrated absorbances of the de-convoluted peaks of Fig.4.2 are shown. Peak positions and proportionality constants for the several bond types as reported by ref.18 and ref.19 are used for the assignment and density estimation of the bonds. For the density calculation, equation (13) of section 2.3 is used, using IR refractive indices. The trend of the total Si-H and N-H density is according to expectation. The estimated densities however turn out smaller compared to ex situ FTIR measurements and ERD densities by a factor of ~2-4. As a conclusion, the ATR technique is perhaps less suitable for absolute density measurements, as many variables are involved.

Table 1: Film parameters of N-rich, medium and Si-rich films, plasma conditions: [Ar 55, H₂ 5, N₂ 10, SiH₄ 1-8 sccs, T 350°C], as deposited on a ZnSe ATR crystal (25 reflections). The total deposition time is 5 seconds (in 0.5-2 second intervals). The refractive index and growth rate are extrapolated values from measurements of films deposited at 300 and 400 °C. The densities are calculated using the effective thickness concept as discussed in chapter 2.3.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Bond assignment</th>
<th>K_{int/land} (10¹⁹cm²)</th>
<th>Integrated Absorbance (x10⁻²²cm⁻³)</th>
<th>Density (x10⁻²²cm⁻³)</th>
<th>Integrated Absorbance (x10⁻²²cm⁻³)</th>
<th>Density (x10⁻²²cm⁻³)</th>
<th>Integrated Absorbance (x10⁻²²cm⁻³)</th>
<th>Density (x10⁻²²cm⁻³)</th>
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<tbody>
<tr>
<td>845-870</td>
<td>SiN</td>
<td>0.63</td>
<td>130.04</td>
<td>1.47</td>
<td>120.96</td>
<td>1.15</td>
<td>95.29</td>
<td>0.83</td>
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<td>1025</td>
<td>SiO</td>
<td>63.52</td>
<td>--</td>
<td>37.58</td>
<td>--</td>
<td>17.94</td>
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<td>1175</td>
<td>NH b.</td>
<td>2.07</td>
<td>24.62</td>
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<td>6.29</td>
<td>0.14</td>
<td>3.42</td>
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<td>1540</td>
<td>NH₂ b.</td>
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<td>0.70</td>
<td>0.01</td>
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<td>0.01</td>
<td>0.10</td>
<td>0.00</td>
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<td>SiH-Si₁</td>
<td>14</td>
<td>0.23</td>
<td>0.02</td>
<td>0.10</td>
<td>0.01</td>
<td>0.45</td>
<td>0.04</td>
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<tr>
<td>2065+ 2081</td>
<td>SiH₂-Si₂</td>
<td>14</td>
<td>00</td>
<td>0.86</td>
<td>0.07</td>
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<td>2140</td>
<td>SiH-N₂Si₁ +SiH₂-NSi</td>
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<td>00</td>
<td>1.90</td>
<td>0.16</td>
<td>2.44</td>
<td>0.19</td>
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<td>1.98</td>
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<td>2220</td>
<td>SiH-N₃</td>
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<td>00</td>
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<td>0.04</td>
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<td>2264</td>
<td>?</td>
<td>14</td>
<td>00</td>
<td>0.39</td>
<td>0.03</td>
<td>0.10</td>
<td>0.01</td>
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<td>Total SiHₓ</td>
<td>0.33</td>
<td>0.03</td>
<td>5.44</td>
<td>0.45</td>
<td>7.23</td>
<td>0.58</td>
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<td>3170</td>
<td>?</td>
<td>3.13</td>
<td>--</td>
<td>0.71</td>
<td>--</td>
<td>0.38</td>
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<td>3250</td>
<td>?</td>
<td>3.03</td>
<td>--</td>
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<td>0.34</td>
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<tr>
<td>3346</td>
<td>NH s</td>
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<td>7.78</td>
<td>0.99</td>
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<td>0.28</td>
<td>1.45</td>
<td>0.14</td>
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<tr>
<td>3470</td>
<td>NH₂ s</td>
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<td>0.47</td>
<td>0.06</td>
<td>0.17</td>
<td>0.02</td>
<td>0.27</td>
<td>0.03</td>
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<td>Total NHₓ</td>
<td>8.25</td>
<td>1.05</td>
<td>2.77</td>
<td>0.31</td>
<td>1.72</td>
<td>0.17</td>
<td></td>
<td></td>
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</table>
4.2 Depth information

Apart from investigating different film types, the deposition series have also been intended to gain depth information (e.g. possible initial growth features, surface and bulk composition) of the a-SiNₓ:H films. However, while during a-Si:H growth changes in the film composition can be observed in absorption peak shifts, during a-SiNₓ:H such clear peak shifts have not been observed. Only a peak shift of the NH bending from 3360-3345 cm⁻¹ with increasing film thickness occurs several times, possibly related to a transition from a surface-like to a more bulk-like environment of the NH bonds. In Fig 4.3, the integrated absorbances of the de-convoluted peaks of the deposition series from Figs.4.1-2 with 4 sccs SiH₄ is shown. As visible, the areas increase almost linearly. Although not apparent from the graphs, the ratio of the total SiHₓ over NHₓ absorbance peaks does vary with thickness, and increases from -2 to -3. In a number of other deposition series it is also seen that the largest absorption peak (being either SiHₓ or NHₓ) increases most, which is not fully understood yet, but is most likely to be attributed to the measurement technique.

![Deposition time (s) vs. Integrated absorbance](image1)

**Fig.4.3:** The total integrated absorbances of de-convoluted SiHₓ and NHₓ peaks as a function of the film thickness.

Even when depositing at low growth rate, as shown in Fig.4.3, the peak evolution is apart from broadening relatively linear in deposition time. Apparently, the bonding configuration during a-SiNₓ:H deposition is relatively homogenous in time and depth.

![Deposition time (s) vs. Absorbance](image2)

**Fig.4.3:** Deposition at low growth rate[ Ar 35, H₂ 2, N₂ 1, SiH₄ 1 sccs, Iarc 12.5A, 100°C]
4.3 Nitridation of an a-Si:H film

Using the ATR-FTIR technique, an experiment is performed to find more evidence for the deposition model of Smith et al. As discussed in the section 1.3, this model explains a-SiNₓ:H growth by reactions at the surface of activated nitrogen with an a-Si:H-like top layer. If this model is indeed applicable, then it should be possible to create a-SiNₓ:H by depositing an a-SiH film and exposing this film to an N containing plasma. This has been verified in the experiment described in this section.

An a-Si:H film has been deposited on a Si ATR crystal, and has subsequently been exposed to an Ar/N₂ plasma. The resulting changes in the IR spectrum have been monitored. First, the possible influence of other plasma species than atomic N on the film has been examined, by measuring the effect of a pure Ar plasma on the H-bonding configuration of an a-Si:H film.

4.3.1 Ar plasma treatment of a-Si:H

For examining the effect of an Ar plasma on a-Si:H, a 12 nm thick a-Si:H film has been deposited on a Si ATR crystal, with the plasma conditions Ar 35, H₂ 2, SiH₄ 1 sccs, 12.5A, 60s. The IR spectrum of this film is shown in Fig.4.5. The SiHₓ peak can be fitted with two large gaussians at 2003 and 2080 cm⁻¹, which correspond to SiH and SiH₂ respectively, a sharp smaller absorption peak at 2130 cm⁻¹, which is related to SiH₃ at the surface, and a peak at 2224 cm⁻¹, which is thought to be SiHₓ with O backbonds. Also broad absorption around 3250 cm⁻¹ occurs. As we are interested in the changes in the film due to the Ar plasma treatment, the measured spectrum of crystal + a-Si:H film is used as a background for the following spectra.

An Ar plasma (Ar 55 sccs, 45A) has been applied on the film for respectively 2s, 8s and 30s, while after each time a spectrum is measured. In Fig.4.5, the resulting changes in the spectrum with respect to the original film spectrum are shown, together with the original spectrum. Negative absorbances correspond to bonds that have disappeared due to the Ar plasma, while positive peaks correspond to creation of new bonds. As visible, after 2s a small sharp negative peak at 2140 appears, which is likely from removed surface SiH₃ bonds. It has about 2% the size of the original peak, which indicates that about 0.3 nm of the top surface has been removed, which corresponds to just one monolayer*. After 40s, also bonds with absorptions at lower wavenumbers disappear, which is attributed to etching of SiH₂ somewhat deeper into the film. Creation of new absorptions takes place around 2200 cm⁻¹, only after longer time, and at 3250 cm⁻¹, which is a small broad band absorption. Both are thought to be related to oxygen incorporation into the film. Therefore, the decreased SiH₂ absorption could for a part also be described by a peak shift to higher wavenumbers due to O backbonds.

Conclusively, the main effect of the Ar treatment seems to be removal or oxygen backbond implementation of (near-)surface SiH₃ and SiH₂ bonds.

* This is only a rough estimation in which it is assumed that the Si-H bond density is constant throughout the film, and that the proportionality constants are equal for all Si-H, absorptions.
4.3.2 Ar/N₂ plasma treatment: nitridation of a-Si:H

Having observed the effect of a pure Ar plasma, now the effect of an Ar/N₂ plasma on an a-Si:H film is investigated. For this experiment an a-Si:H film is grown using the same conditions as for the Ar-treatment experiment. Again, an IR absorption spectrum has been measured of this film (Fig.4.6)*, which is used as background for the subsequent actions. This time the effect of an Ar/N₂ plasma (Ar 55, N₂ 10 sccs, 45A) is monitored. In Fig.4.6 the changes in the spectrum of the film due the subsequent Ar/N₂ plasma treatments are depicted.

First of all, a large negative peak appears in the 2005-2150 cm⁻¹ region, which corresponds to the disappearance of SiHₓ bonds. Furthermore, newly created SiHₓ absorptions emerge around 2180-2220 cm⁻¹, and there is also creation of NHₓ bonds as visible in the 3300-3500 cm⁻¹ region. As a second observation, the size of the negative SiHₓ and positive NHₓ peaks do not change much with increasing plasma time. Most effects take place after 0.5s. Because the newly created SiHₓ peaks around 2180-2220 cm⁻¹ appear immediately, they can initially most likely not be attributed to oxygen related processes. Therefore, these absorptions are thought to emerge solely because of incorporation of N backbonds into existing SiHₓ bonds in the film. This could happen by insertion reactions into existing Si-Si bonds, or by N occupying a dangling bond. Only after longer time, also oxygen backbonds are thought to contribute to further increase of the 2180-2220 cm⁻¹ absorptions.

In Fig.4.7a-b, the SiHₓ and NHₓ absorption peaks after 0.5s of Ar/N₂ plasma treatment are shown individually. In the accompanying table 2, the peak assignments are denoted, along with the estimated peak areas and widths. Negative areas correspond to absorption peaks that have disappeared, while positive areas indicate newly created absorptions. If we again compare the total area of the disappeared SiHₓ peaks to the peak size of the original film, an affected film depth of ~2 nm is suggested.

*Although the a-Si:H film is similar to the film of the AR-treatment, a lower absorbance is measured. This can be attributed to the fact that a number of films have been deposited on the crystal for previous experiments already. The altered refractive index, as well as the thickness of the resulting layers influence the field strength and hence the absorption rate of the evanescent wave (i.e. change the 'effective thickness' of the a-Si:H film).
Plasma and in situ film studies on silicon nitride growth for photovoltaic applications

![Graph showing absorbance with wavenumber (cm⁻¹) on the x-axis and absorbance on the y-axis. The graph includes a line graph for 12 nm a-Si:Hx and a line graph for NHx with markers indicating the change due to Ar/N₂ plasma treatment.]

**Fig. 4.6:** Ar/N₂ plasma treatment of an a-Si:H film. Both the original a-Si:H spectrum and the change due to the Ar/N₂ plasma are depicted.

<table>
<thead>
<tr>
<th>Peakpos.</th>
<th>Assignment</th>
<th>Width (cm⁻¹)</th>
<th>Area (int.abs.)</th>
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</thead>
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<tr>
<td>2005</td>
<td>SiH</td>
<td>62</td>
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<tr>
<td>2065</td>
<td>SiH₂</td>
<td>28</td>
<td>-0.08</td>
</tr>
<tr>
<td>2113</td>
<td>SiH₃(sur)</td>
<td>52</td>
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</tr>
<tr>
<td>2141</td>
<td>SiH₃(sur)</td>
<td>15</td>
<td>-0.16</td>
</tr>
<tr>
<td>2182</td>
<td>N₂-SiH₂</td>
<td>27</td>
<td>+0.09</td>
</tr>
<tr>
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<td>N₂-SiH</td>
<td>55</td>
<td>+0.20</td>
</tr>
<tr>
<td>3160</td>
<td>SiOH?</td>
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<td>3253</td>
<td>SiOH?</td>
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<td>NH</td>
<td>59</td>
<td>+0.17</td>
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<td>NH</td>
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<tr>
<td>3497</td>
<td>NH₂</td>
<td>38</td>
<td>+0.08</td>
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</tbody>
</table>

![Graph showing absorbance with wavenumber (cm⁻¹) on the x-axis and absorbance on the y-axis. The graph includes a peak at 3160 cm⁻¹ with an Area of 0.05, at 3253 cm⁻¹ with an Area of 0.15, at 3340 cm⁻¹ with an Area of 0.17, at 3401 cm⁻¹ with an Area of 0.28, and at 3497 cm⁻¹ with an Area of 0.08.]

**Fig. 4.7:** The changes in SiHₓ and NHₓ absorptions after 0.5s Ar/N₂ plasma, de-convoluted.
4.3.3 Nitridation vs temperature

It has been investigated whether the nitridation process depends on the surface temperature. From previous work it is known that the N/Si ratio in a-SiNx:H does not depend strongly on the temperature. E.g. the N/Si ratio of films deposited with an SiH₄ flow of 8 sccs and N₂ flow of 10 sccs, ranges from 0.66 to 0.75 for substrate temperatures during deposition of 200-500°C. Therefore, if the nitridation experiment is relevant for the growth process, no strong influence of the temperature is expected of the nitridation too.

To verify this, the nitridation experiment has been repeated at different temperatures, ranging from 100 to 400°C. The a-Si:H films have been deposited under the same conditions as above, but during 120s, and at the same temperatures of 100-400°C as during the Ar/N₂ plasma treatment. After each deposition, the ATR crystal is cooled to 100°C for measuring a spectrum, because the Si crystal is only transparent up to 200°C. Then, the crystal is heated to the measured temperature for the Ar/N₂ plasma treatment. The Ar/N₂ plasma treatment is performed at the same conditions as described above, during 60s. Then, the crystal is cooled again for measurement of the changed spectrum.

As visible in Fig.4.8, for all temperatures a similar effect of the Ar/N₂ plasma, i.e. removal of SiHₓ absorptions and creation of N or O backbonded SiHₓ and NHₓ, is observed. The different shape of the SiHₓ removal peaks correspond to the initial a-Si:H films (not shown), so it is not possible to draw conclusions for the nitridation process from this. The larger creation around 2200 cm⁻¹ and 3340 might be attributed to a more porous structure of the film grown at lower temperature. A more porous structure would allow atomic nitrogen and also oxygen to permeate deeper in to the film. In the future, this experiment should be repeated with identical initial a-Si:H.

The main conclusion however from the temperature series is that the nitridation process is not really thermally activated, as it takes place at all temperatures in the range 100-400°C.

Fig.4.8: Ar/N₂ plasma treatment of a-Si:H as function of the temperature.
Chapter 5: Conclusions

Conclusions

A study has been performed on the feasibility of high-rate (~20 nm/s) deposited a-SiNx:H using the cascaded arc generated expanding thermal plasma. By implementation of the films in multicrystalline silicon solar cells, promising antireflection and bulk passivating qualities have been demonstrated.

To support future optimization of the deposition process, a study is made on the a-SiNx:H growth process using a SiHJN2 plasma. As a starting point, a proposed growth model by Smith et al. has been used. In this model, the a-SiNx:H deposition process is portrayed by surface reactions in which an a-Si:H-like top layer, formed by a-Si:H depositing radicals, becomes 'nitridated' by activated nitrogen from the plasma. The densities of, on basis of available knowledge on the a-Si:H depositing plasma, viable candidate species for the a-SiH-like layer formation and nitridation reactions have been measured.

Cavity ringdown spectroscopy (CRDS) has been applied to measure the densities of SiH3 and SiH radicals in the Ar/H2/SiHJN2 plasma. Threshold ionization mass spectrometry (TIMS) has been applied to measure N radical densities. From these densities and an estimated typical gas temperature deduced from the measured SiH rotational temperature of 1400K, an estimate is made of the individual contributions of SiH3, SiH and N radicals to the growth. These contributions are compared to the growth flux as obtained by composition measurements by ERD and measured deposition rates.

From these studies, the following conclusions can be drawn:

- SiH3 has a high density in the plasma of ~1-4·1019 m-3, while SiH has a density of ~0.5-1·1017 m-3. At these densities, SiH3 can almost fully account for the Si growth flux, while SiH has a contribution in the order of percentages. The large contribution of SiH3 is reflected in the nearly linear dependence of the Si incorporation rate to the SiH3 density, except at low SiH4 flows, where other growth precursors are becoming increasingly important.

- A very high atomic N density of ~1019-1020 is measured in the Ar/H2/SiHJN2 plasma. This high density could well account for the N-incorporation rate in the a-SiNx:H films during deposition. The measured growth flux then indicates that the N radical has a sticking probability of ~2%.

Besides, an in situ technique for infrared absorption measurements, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), has been installed. This technique has been used to monitor the Si-N, Si-H and N-H bonding configurations of as-deposited films as a function of film thickness, to gain depth information of the films.

In addition, with the ATR-FTIR technique an experiment is performed to find more evidence for the proposed a-SiNx:H growth model of Smith. If this model is applicable, it should be possible to create a-SiNx:H at the surface of an a-Si:H film, by modifying the a-Si:H film with a N-containing plasma. This has been verified in a 'nitridation' experiment, in which an as-deposited a-Si:H film has been exposed to an Ar/N2 plasma. From these studies the following conclusions can be drawn:

- The monitored IR absorptions during series of short subsequent a-SiNx:H depositions, do not exhibit large peak shifts and increase nearly linear with time. This suggests a relative homogeneous growth of a-SiNx:H in time and depth as far as the bonding configuration is concerned.

- It is demonstrated that a-SiNx:H can be created by exposing a-Si:H to an Ar/N2 plasma. The measured changes in the infrared absorption spectrum suggest that the plasma treatment results in the creation of an a-SiNx:H surface layer with a depth of ~2 nm. This 'nitridation' process does not show a large dependence on the substrate temperature within the range of 100-400°C, which supports the relevancy of this experiment to a-SiNx:H deposition, where no large temperature dependence of the N/Si ratio is observed either.

As a conclusion, both the plasma studies and the nitridation experiment corroborate the proposed a-SiNx:H growth model of Smith et al. As an extension to this model, the measured radical densities in the plasma indicate that the formation of the a-Si:H-like layer can almost fully be accounted for by SiH3 radicals, while the role of the activated nitrogen could well be filled in by the N radical.
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Appendix: absorption vs. absorbance

\[ I = T + R + A \]

\( A = \) absorption, \( T = \) transmission, \( R = \) reflection

Transmission (without reflection):
\[ I = I_0 \exp(-\alpha d) \]

\[ T = \frac{I}{I_0} = \exp(-\alpha d) \]

\[ A = 1 - T = 1 - \exp(-\alpha d) \]

\( A = \alpha d \), if \( \alpha d < 1 \)

\[ \text{Abs} = -10 \log\left(\frac{I}{I_0}\right) = -10 \log(\exp(-\alpha d)) = \log(e) \cdot \alpha d = \alpha d / 2.30, \quad \text{Abs} = \text{absorbance} \]

\( n = K A_{\text{int}} \)

with \( A_{\text{int}} = \int \alpha \omega^{-1} d\omega \)

\( n = \) density absorbing species,
\( K = \) reciprocal absorption cross section

\( A_{\text{int}} = \) normalized integrated absorption coefficient

Attenuated total reflection, thin film limit (\( 2\pi d < 0.1 \lambda, k < 0.1 \))

\[ \frac{d_{\text{eff}}}{d} = \frac{4n_{21} \cos \theta}{1 - n_{31}^2} ; \]

\[ \frac{d_{\text{eff}}}{d} = \frac{4n_{21} \cos \theta}{1 - n_{31}^2} \left( \frac{(1 + n_{32}^4) \sin^2 \theta - n_{31}^2}{(1 + n_{32}^4) \sin^2 \theta - n_{31}^2} \right) \]

\( d_{\text{eff}} = \) effective thickness

\[ N = \frac{l}{2t \tan \theta}, \quad N = \text{number of reflections}, \quad l = \text{crystal length}, \quad t = \text{crystal thickness}, \quad \theta = \text{angle to surface normal} \]

\[ n = \frac{2.30 \cdot K}{Nd_{\text{eff}}} \int \frac{\text{Abs}}{\omega} d\omega \]