In situ infrared spectroscopy for plasma-assisted ALD of SiNₓ films

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Abstract

Silicon nitride (SiN$_x$) is being used extensively as material in industrial applications, such as in solar cells and integrated circuits. However, the downscaling of integrated circuits, in particular of transistors, imposes new, strict requirements on the material. Not only the quality, but also the conformality, uniformity and thickness of the material should be controlled on nanometer scale. Atomic layer deposition (ALD) is a candidate to fulfill these requirements. For the development of suitable ALD processes, the factors that rule film quality and growth should be known. Therefore, fundamental understanding of the surface chemistry and reaction mechanisms is crucial. In this work, the plasma-assisted ALD process of SiN$_x$, employing BTBAS (SiH$_2$[NH(C$_4$H$_9$)]$_2$) as precursor and N$_2$ plasma as co-reactant, has been studied with in situ infrared spectroscopy and a reaction mechanism for the ALD film growth is proposed.

The ALD process, developed in the PMP research group in 2013, was first transferred to a home-built ALD setup. This setup was extended with a sample manipulator and a novel resistive heating method, to enable infrared spectroscopy in transmission mode over the full ALD temperature window of the SiN$_x$ process. The material properties of the grown films were determined to be similar to the previously developed process, where, despite slightly elevated growth rates, the films contained comparable C, O and H levels.

The infrared measurements revealed the reaction products of the precursor step, the change in surface groups during both half-cycles and the composition of the deposited films. In the ALD process, part of the ligands were liberated as t-Butylamine(NH$_2$C(CH$_3$)$_3$) during precursor adsorption, as confirmed by gas phase infrared measurements. Surface measurements revealed that CH groups were present in the precursor half-cycle, indicating that part of the ligands of the precursor molecule remained attached to the Si atom upon precursor adsorption. These ligands were removed by the N$_2$ plasma, of which fragments, such as CN, could redeposit on the surface. At low deposition temperatures, these fragments were incorporated into the film, resulting in films with a high carbon content. At high deposition temperatures, fewer fragments were incorporated in the film. Hence, FTIR spectroscopy yielded important insight in how the carbon is incorporated in the film in this ALD process, a problem which may be resolved by the choice of a precursor molecule with a different molecular structure.
# Contents

1 Introduction .................................................. 5
   1.1 The history of Fourier transform infrared spectroscopy .......... 6
   1.2 Silicon nitride thin films ............................................. 7
   1.3 Goal of this work ................................................... 8
   1.4 Outline of the thesis ............................................... 10

2 Experimental setup ............................................ 11
   2.1 ALD-I and FlexAL deposition tools ..................................... 12
   2.2 Manipulator ................................................................. 13
   2.3 Heating ................................................................. 15
       2.3.1 Transparency of the silicon substrate upon heating .......... 17
   2.4 FTIR setup .............................................................. 18
   2.5 Conclusion .............................................................. 20

3 FTIR data acquisition and processing .......................... 21
   3.1 Performing FTIR measurements ....................................... 22
   3.2 Signal-to-noise ratio ................................................ 22
   3.3 Averaging the spectra .................................................. 24
   3.4 Baseline corrections .................................................. 26
   3.5 Interpreting surface FTIR spectra ................................... 27
   3.6 Conclusion .............................................................. 29

4 SiNₓ ALD process on ALD-I ...................................... 31
   4.1 ALD cycle for SiNₓ ..................................................... 32
   4.2 Saturation curves and standard recipe ................................ 33
   4.3 Material properties ................................................... 34
   4.4 Comparison .............................................................. 36
       4.4.1 Table heating: FlexAL vs. ALD-I .............................. 36
       4.4.2 ALD-I: table heating vs resistive heating ..................... 37
   4.5 Altering the recipe for FTIR measurements ......................... 39
   4.6 Conclusion .............................................................. 42
1

Introduction
1. Introduction

1.1 The history of Fourier transform infrared spectroscopy

A thousand years ago, Ibn Al-Haytham, considered as the father of modern optics, wrote the first literature on the understanding of vision, optics and light. To celebrate its 1000th anniversary, the year 2015 is denoted the international year of light. The history of modern spectroscopy goes back less far, to the 17th century, where in 1666, Isaac Newton carried out his famous experiment with sunlight and prisms [1]. In this experiment he showed that sunlight can be separated in many colors, a phenomenon that is encountered often on a rainy day.

This was the beginning of dispersive spectroscopy, where materials and gasses are investigated by studying the absorption of light. The intensity of light at all frequencies of a spectrum is measured by scanning the wavelength range using gratings or slits. To probe the vibrational states of a molecule, a large wavelength range in the infrared part of the spectrum (400 - 6000 cm\(^{-1}\)) has to be scanned. Due to this scanning, dispersive infrared spectroscopy methods are slow. The introduction of the non-dispersive FTIR spectroscopy solved this issue, by scanning all frequencies of the spectrum simultaneously. As a result, the time needed to complete and combine multiple scans of a spectrum using FTIR is short compared to the scan time of only one scan performed with a dispersive instrument. On top of that, FTIR does not suffer from losses of intensity of the light after passing through a slit, resulting in a better signal-to-noise ratio. The crucial component of a FTIR setup that allows for these advantages is the Michelson interferometer, invented in 1880 by Albert Abraham Michelson, who was awarded the Nobel prize in physics in 1907 [2]. Back in those days, spectra had to be constructed manually, which was very time consuming. Only until the Fast Fourier Transform algorithm was introduced by Cooley and Tukey in 1965 [3] and computers with enough computational power emerged, it was possible to speed up the measurement. It took until the late 1960s before the first commercial FTIRs were available.

Infrared spectroscopy is nowadays used in a wide variety of fields. Interaction of proteins with surfaces is studied in biochemistry for the development and design of biomaterials, biopharmaceuticals and biomedical devices. Even human cells are studied for the detection of cancerous cells[4, 5]. In the environmental field, infrared spectroscopy is used to determine air pollution caused by individual cars [2], for analysis of agricultural soil, for waste management [6] and even for food science and processing [5, 7].

In this work, in situ transmission FTIR spectroscopy has been used to study silicon nitride thin films, deposited using plasma-assisted atomic layer deposition (ALD). The vibrational modes of molecules incorporated in the films were measured, as well as reaction products and surface species during the deposition process.
1.2. Silicon nitride thin films

The first silicon nitride (SiN$_x$) thin films used in microelectronics emerged in the mid 1960’s, when chemical vapor deposition (CVD) was used as a preparation technique [8]. Due to the material’s excellent optical, electrical, chemical and mechanical properties [9], the demand for (SiN$_x$) films increased and various deposition methods of the material have been explored. Nowadays, SiN$_x$ is used for a wide variety of applications, ranging from anti-reflective coatings and passivation layers of solar cells to gate dielectrics, stress liners and spacer layers in transistors[9, 10]. In spacer layers, SiN$_x$ serves as a barrier film and masking material.

Although the deposition process of SiN$_x$ has been studied extensively, there is still demand for new methods because of new requirements emerging from semiconductor industry, such as precise thickness control, optimal conformality and depositions at a low thermal budget[9]. For many years, low pressure chemical vapor deposition (LPCVD) and plasma-enhanced chemical vapor deposition (PECVD) have been the main deposition methods for SiN$_x$[11, 12, 13], both known for their fast deposition rates of high quality material. However, neither LPCVD nor PECVD are good candidates to meet the requirements of thickness control, conformality and low thermal budget [13]. Therefore, the possibilities of deposition of SiN$_x$ using atomic layer deposition (ALD) have been explored recently.

ALD, a deposition technique known for conformal deposition and sub-nm thickness control, uses two or more sequentially dosed reactants, separated by purge or pump steps. The reaction steps are illustrated in Figure 1.1. The two reaction steps, referred to as
half-cycles, are self-limiting. Once the precursor reactant has fully covered the surface, the reaction stops and the excess reactant is purged out of the reactor. The surface sites created by reactant 1 serve as reactive sites for reactant 2 and vice versa. In this way, after two half-cycles, a sub-monolayer of material is deposited. The process can be repeated until the target thickness is reached. In Figure 1.2, typical ALD growth as observed in this work is shown, for depositions at three temperatures. The linear film growth illustrates the excellent thickness control.

For ALD of SiN$_x$, a wide variety of precursors and reactants have been tested. However, the growth of nitrides with ALD is challenging [10]. For thermal ALD, the material can be deposited conformally, but films suffer from low film density, high impurity content and the deposition temperatures are too high [9]. Plasma-assisted ALD, however, is known to deposit films at a lower thermal budget because the plasma species enhance the chemical reactivity [14, 15]. This enhanced chemical reactivity also results in films that contain less contamination than films deposited using the thermal counterpart.

The most used processes for SiN$_x$ ALD use silicon-halide precursors with NH$_3$ gas or plasma as reactants [16, 17, 18, 9]. Other used precursors are silicon hydrides [13], aminosilanes [12] and organosilanes [19]. Halide-free precursors are preferred for applications in industry, because reaction products damage the reactor. Unfortunately, these processes suffer from low growth rates and carbon contamination in the films.

This work was performed in collaboration with Air Products [20]. This international company was founded in 1940 for the production of industrial gases, but nowadays develops precursors for ALD processes as well. For the development of ALD processes, the understanding of surface chemistry is crucial. Once is understood how precursor molecules adsorb and how the surface is reactivated by the co-reactant, improvement of the used reactants and process parameters can be achieved. The studied ALD process uses BTBAS (SiH$_2$(NH(C$_4$H$_9$)$_2$)$_2$), shown in Figure 1.3, as a precursor. It is an organosilane, which consists of a silicon atom with H atoms attached to it and two side groups (NH(CH$_3$)$_3$), which will be referred to as ‘ligand’ in the rest of this work. The used co-reactant in the ALD process is N$_2$ plasma.

### 1.3 Goal of this work

The SiN$_x$ ALD process using BTBAS and N$_2$ plasma was developed in the Plasma and Materials Processing research group in 2013 [21]. During this development stage, diagnostics were used to study the process, such as optical emission spectroscopy (OES), quadrupole mass spectrometry (QMS) and spectroscopy ellipsometry (SE). These diagnostics revealed growth rates and material properties of the deposited films, as well as some of the created reaction products during the ALD process. However, the reaction chemistry of the ALD process was not fully understood. To be able to construct a more detailed picture of the reaction mechanism, not only the reaction products of both half-
1.3. **Goal of this work**

Figure 1.2: SiN<sub>x</sub> ALD growth for different deposition temperatures. The cyclic ALD process can be repeated until the target thickness is reached, providing excellent thickness control.

Figure 1.3: The BTBAS precursor molecule (SiH<sub>2</sub>[NH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>]) consists of a silicon atom (orange) and two side groups, which are referred to as ligands.
cycles, but also the reactive groups on the surface during the ALD half-cycles should be known.

In this work, *in situ* FTIR spectroscopy is used to determine the reaction product of the precursor step, the surface groups during both half-cycles and the composition of the deposited films. Information obtained with the infrared measurements will be used to answer the central research question:

**What is the reaction mechanism of plasma-assisted ALD of SiN$_x$, when using BTBAS as a precursor and N$_2$ plasma as a co-reactant?**

To be able to study the ALD process with *in situ* infrared spectroscopy, the process was transferred from the Oxford Instruments FlexAL deposition tool (which was used previously) to a home-built ALD tool. The ALD process was established and a novel substrate heating method was introduced. The material properties of the deposited films were determined, to investigate the effect of the process transfer, as well as the effect of altering the ALD process to allow for infrared measurements.

After establishing the ALD process on the home-built ALD tool, *in situ* transmission FTIR spectroscopy was used as a diagnostic to detect the surface groups that were present during both ALD half-cycles. Temperature series were performed to study differences in the surface chemistry of the process within the ALD temperature window (85-350°C)[21]. The infrared measurements were used to propose a reaction mechanism of SiN$_x$ ALD, using BTBAS and N$_2$ plasma.

### 1.4 Outline of the thesis

Description of the used deposition tools and experimental setup for infrared spectroscopy can be found in Chapter 2. Information on FTIR data acquisition and interpretation can be found in Chapter 3. The establishment of the ALD process on the home-built ALD-I reactor is discussed in Chapter 4, as well as a comparison with the ALD process on the FlexAL reactor. This chapter also treats the influence of changing the ALD recipe to allow time for infrared measurements on the material properties of the deposited films. All *in situ* infrared results will be discussed in Chapter 5. Focus lies on the observed surface groups during both half-cycles, which will be discussed in great detail. The information gained from gas phase, surface and film measurements will be combined to formulate a hypothesis on the reaction mechanism. In Chapter 6, a conclusion and outlook will be given, which focuses not only on the SiN ALD process, but also on the use of *in situ* FTIR as a diagnostic for ALD processes in general.
2

Experimental setup
The complete setup used in this work consists of an ALD deposition tool, an interferometer setup with detector and a sample manipulator. All three elements of the setup, including the used heating method, will be discussed in detail in this chapter.

2. Experimental setup

2.1 ALD-I and FlexAL deposition tools

Depositions were performed on a home-built ALD tool (ALD-I [22]) and compared to depositions performed in previous work on an Oxford Instruments FlexAL reactor [21]. Both reactors will be discussed in this section.

The ALD-I reactor and the Oxford Instruments FlexAL reactor are similar in design. In Figure 2.1 a schematic drawing of the ALD-I reactor is shown. It consists of a stainless steel vacuum vessel which serves as the reaction chamber, a turbo-molecular pump and an inductively coupled plasma (ICP) source. The vacuum vessel has an effective volume of 9 L (14 L for FlexAL) [23, 24]. On top of the vacuum vessel, the ICP source has been mounted. It consists of a quartz (alumina for FlexAL) tube and a copper coil, and is connected to a RF power supply that operates at 13.56 MHz. An automated matching network ensures efficient coupling of the RF power into the plasma. At the top of the ICP source, a gas inlet is present to supply the N\textsubscript{2} gas for the plasma.

The precursor is supplied from the back of the reactor and is vapor drawn. Precursor condensation on the walls and lines is prevented by heating these to 100 °C (150 °C for FlexAL) and 70 °C respectively. The precursor bubbler is kept at a constant temperature of 50 °C. In FlexAL, a constant Ar flow from the top of the reactor prevents precursor condensation near the plasma source. In ALD-I this is prevented by closing the valve between the ICP and the reactor vessel.

At the bottom of the vessel, the turbo pump, backed up by a rotary vane pump, keeps the system at a vacuum with a base pressure of \( \sim 10^{-6} \) mbar. When reactants or co-reactants have to be contained within the vessel, a bottom valve can be closed to isolate the reactants from the pump and to prevent the species from being pumped away. The FlexAL system has a butterfly valve instead of a bottom valve, that cannot be closed completely.

Samples in ALD-I reactor are loaded by opening the reactor, allowing direct contact between the lab environment and the inside of the reactor. FlexAL uses a loadlock to load the samples. For heating and mounting of the sample, either the sample manipulator (ALD-I), which is discussed in the next section, or the substrate table (FlexAL, ALD-I) were used.

The substrate temperature in FlexAL systems is determined by the table temperature and the pressure. During the process pressures in the chamber fluctuate, which causes a fluctuating thermal contact between the heated table and the substrate. At base pressure, the substrate temperature can be up to over 100 °C lower than the set temperature [25]. When the sample manipulator is used in ALD-I, the heat is delivered to the substrate via
2.2. Manipulator

Figure 2.1: The deposition setup consists of a stainless steel reaction chamber, a turbo-
molecular pump and an inductively coupled plasma (ICP) source. On the reactor, diagnostics can be mounted, such as in situ SE and FTIR.

resistive heating as described in Section 2.3. The substrate temperature is measured and controlled actively and therefore less fluctuations of the temperature during the process are expected.

Two in situ diagnostic tools are used on ALD-I; a FTIR setup and a spectroscopic ellipsometer (SE). The temperature of the sample is measured with SE when the substrate table is used. When the sample manipulator is used, temperature is measured directly with a thermocouple.

In the ALD-I system, the residence time of the N\textsubscript{2} gas is set when the gas pressure is set. A plasma can only be ignited when the pumping is maximal. This means that it is not possible to independently vary the chamber pressure and residence time of the plasma species in the chamber. In the FlexAL system the residence time can be varied, by changing the position of the butterfly valve. There is no one-to-one relation between the plasma power set on ALD-I and FlexAL system. Therefore the most often used plasma power of 100 W was set (600 W in FlexAL).

2.2 Manipulator

To be able to perform infrared measurements in transmission mode, the sample has to be positioned in the ALD-I reactor in a vertical orientation. Therefore, instead of using a
2. Experimental setup

Figure 2.2: The sample manipulator is used to clamp the sample and move it in situ. It is attached to the reactor with a mount (A). The flange (B) can be opened to move the sample out of the reactor. The rod with sample mount (C) can be moved inside the reactor with the micrometer handwheels (D).

substrate table for mounting of the sample, the samples were mounted and handled by a Prevac manipulator[26]. The manipulator is a dedicated high precision tool for placement and handling of Si or GaAs samples in vacuum systems. Movements are along any of the three orthogonal X Y and Z axes, or rotation $\theta$ around the Z axis. The X, Y and Z motions are operated manually by using a handwheel, the $\theta$ motion is motorized. In Figure 2.2, the manipulator is depicted. The outer left half-circle (A) is attached to the reactor permanently. The smaller flange (B) can be opened to remove the sample out of the reactor. The rod with sample mount at the end (C) is moved inside the reactor by adjustment of the micrometer handwheels (D). The sample is heated resistively. Correct clamping of the sample using the u-grips is essential to close the electrical circuit which is used for heating of the sample. In Figure 2.5 a schematic of the sample mount is shown.
2.3. Heating

Previously, when *in situ* FTIR measurements were performed in the PMP research group, the substrates were not actively heated because of a lack of suitable heating method [22, 27]. To be able to study the SiN$_x$ ALD process at temperatures over 150 °C, resistive heating was introduced as a heating method. In this section, the implementation of resistive heating is discussed, as well as the infrared transparency of the heated substrates. Note that the resistive heating is discussed for the SiN$_x$ process, but can be applied to other ALD processes as well.

When the manipulator is used, the sample is mounted with contacts at the outermost parts of the sample, which are also used for heating. The sample is heated resistively, making use of ohmic dissipation by the silicon substrate. A current is run through the sample, which leads to power dissipation via

$$P = I^2R,$$

with $P$ the delivered power in W, $I$ the current and $R$ the resistance of the substrate. In principle, the set current will be the only factor determining the delivered power to a substrate with constant resistance $R$ and will heat it to the target temperature. For quick heating, the resistance of the substrate should be sufficiently high. However, the resistance of the silicon wafer is not constant over the entire temperature range. It depends on the substrate temperature, but also on the deposited material on the wafer. In Figure 2.4, the resistance of three double-sided polished Si(100) wafers (*n*-type, 30-50 Ωcm) is shown: one with native oxide, one with small and one with large deposited platinum particles. At 175 °C, the resistance of the wafer significantly drops, caused by the increase of free carriers in the semiconductor material. Increasingly high currents are needed to reach the target temperature. For the samples with Pt particles, the resistance of the sample is
2. Experimental setup

Figure 2.4: Resistance of the silicon wafer upon heating. When platinum particles were deposited on the wafers, heating became less efficient. The resistance of the wafers significantly drops at high temperatures.

very low, which causes ineffective heating. As the deposition advances, the resistance will become smaller. Therefore, resistive heating is not suitable for ALD of metals. For the deposition of SiN$_x$ this is not a problem, because of the dielectric nature of SiN$_x$. Depending on the resistive behavior of substrate and deposited materials, resistive heating can be used for other ALD processes as well.

Electrical circuit

The schematic representation of the electrical circuit used for heating is depicted in Figure 2.5. An Eurotherm temperature controller (type 2132) is used to obtain the correct temperature. It controls a solid-state relay, to connect the sample to the AC power supply and start the heating. Temperature is measured with a thermocouple, attached to the sample.

To prevent runaway currents when the resistance of the substrate drops, positive temperature coefficient resistors (PTC) are added to the circuit to serve as a current limiter. The resistance of these PTCs is low compared to the substrate resistance at low temperatures, when the current in the circuit is low. When the resistance of the substrate drops and the current running in the circuit quickly rises, the temperature of the PTC increases and its resistance becomes high, hence limiting the current. The use of a PTC resistance instead of a resistor with a constant value is beneficial for the temperature control of the
2.3. Heating

Figure 2.5: The resistive heating circuit consists of an AC power supply, Eurotherm temperature controller, solid state relay and two PTC’s which serve as current limiters. Optionally, the sample can be grounded in between heating pulses.

substrate, as the resistance over the full temperature range remains more constant when a PTC is used.

In the first design of the heating, used for the described infrared measurements in this work, the heating was connected in such a way that there was always a 230 V potential on the sample, even in between heating pulses. Interaction of the plasma with this biased sample caused problems with the uniformity of the deposition, which will be discussed in Section 4.4.2. When these problems were encountered, the circuit was equipped with an additional network to provide two configurations:

- Floating: The substrate is disconnected from the heating circuit and has a floating potential.
- Grounded: The substrate is disconnected from the heating circuit and grounded.

An extended description of the heating circuit can be found in Appendix B.

2.3.1 Transparency of the silicon substrate upon heating

In this section, the transmittance of the wafer upon heating is discussed. The heating of the substrate causes a change in optical properties of the silicon wafers. Therefore, fluctuations in temperature cause fluctuations in the measured intensity. Since the intensity of the transmitted light influences signal and noise levels in the measured FTIR spectra, it is important to get a qualitative feel of the influences of temperature on the measured infrared spectra, such that can be distinguished between spectral features emerging from the ALD deposition process and spectral features emerging from temperature fluctuations of the wafer.

For increasing temperature, as shown in Figure 2.6, the transmittance decreases. At the low wavenumbers, resonances in the absorbance are visible. Also, a curved baseline
2. Experimental setup

2.4 FTIR setup

The infrared absorption spectrum of a sample is measured by directing a broad band infrared beam via an interferometer through the sample. In this way, the absorptions of all frequencies can be measured simultaneously.

The FTIR setup, shown in Figure 2.7 consists of a Bruker Optics Vector 22 interferometer, the reactor chamber and a purge box where an off axis parabolic mirror is used to focus the beam on a detector. The Vector 22 consists of a mid-infrared source (Globar, 10000-50 cm$^{-1}$) and a Michelson interferometer. The detector is a liquid N$_2$ cooled Mercury Cadmium Telluride (MCT) detector (Bruker D316, 10000-550 cm$^{-1}$).

Figure 2.6: Transparency of the heated substrate upon infrared illumination. At high temperatures, free carrier Drude absorption causes a baseline and less light is transmitted by the substrate.

is visible, related to Drude absorption caused by free-carriers[28]. Since heating a semiconductor results in more electrons in the conduction band, more free-carrier absorption is expected upon heating. Hence, for heated samples the intensity of the signal will be lower than for cold samples. Furthermore, fluctuations in temperature will yield spectral features in the region below 1500 cm$^{-1}$. Therefore, excellent temperature control of the sample is crucial when studying an ALD process with \textit{in situ} FTIR.
2.4. FTIR setup

Figure 2.7: The infrared setup consists of a Bruker Optics Vector 22 interferometer, the reactor chamber and a purge box where an off axis parabolic mirror is used to focus the signal on a detector.

The Michelson interferometer consists of two arms with mirrors at either end. When the beam enters the interferometer, a beam splitter is used so that half of the light passes on to the fixed mirror, and the other half is reflected towards movable mirror. By moving this mirror over a distance \( x \), a length difference of the two arms can be introduced. After passing through the arms, the two beams recombine at the beam splitter and have traveled over a path difference of \( 2x \). The beams are spatially coherent. However, they have a relative phase difference and therefore interference will occur upon recombination. The recombined beam passes through the reactor and sample and is focused on the detector. The detector measures the intensity of the beam as a function of the mirror displacement \( x \), a so-called interferogram. The interferogram contains all spectral information. The main information about the sample is in the side wings of the interferogram, which are very small compared to the main peak. This is why the detector is equipped with ADCs with a high dynamic range. Upon Fourier transformation, the interferogram is transformed from the displacement domain to the frequency domain and an intensity spectrum \( I \) is created. To precisely be able to determine the path difference, a HeNe laser with known wavelength and hence known interferogram is used. The accuracy of the spacing \( \Delta x \) is determined by the precision of the laser itself. The error in wavelength, \( \Delta \nu \), is very small and is of the same order as the error in \( \Delta x \). This is the reason why FTIR spectrometers have a very high spectral resolution.

Before data acquisition, some hardware settings have to be chosen such as the aperture of the diaphragm (normally open), the moving velocity of the mirror and the magnitude of the mirror displacement itself. The latter determines the resolution of the obtained spectrum. A high resolution (large mirror displacement) can be changed afterwards to a low resolution (small mirror displacement) by truncating the interferogram, but the other way around is not possible. Before the data acquisition is started, a careful decision on
2. Experimental setup

The resolution has to be made because a larger mirror displacement increases the duration of a scan significantly. Finally, one has to determine the amount of scans used for averaging. Optionally, if the Bruker software is used to perform the Fourier transform, data processing parameters such as apodization to prevent leakage, and zero filling factor for interpolation of the spectrum have to be set. How a Fourier transform is performed and what the result are of different data processing parameters is described in great detail elsewhere [2, 28, 29]. In this work, 3-term Blackman-Harris apodization, Mertz phase correction and a zero filling factor of 2 are used.

2.5 Conclusion

The introduction of the sample manipulator enables in situ handling of the sample and the possibility of changing the orientation of the sample.

Resistive heating was introduced as a heating method, enabling excellent control of the substrate temperature during the process. In the first design, used for experiments that are discussed in this work, the substrate was biased between the heating pulses. When problems with the uniformity of the deposition were encountered, an additional option, to ground the substrate in between heating pulses, was introduced. The transmitted IR intensity of a heated sample is lower than that of a sample at low temperature. Finally, in the case of fluctuations of substrate temperature during measurements, it is expected that resonances of the silicon substrate will be observed in the region below 1000 cm$^{-1}$. 
3

FTIR data acquisition and processing
Figure 3.1: The FTIR measurement scheme during a deposition. The absorbance of a film is obtained by performing a measurement before and after deposition (left). Performing a measurement before and after the precursor half-cycle yields the absorbance of surface species formed during the precursor step (right).

In this chapter, the method for performing in situ FTIR measurements is discussed. Not only are the used schemes for gas phase, film and surface measurements treated, but also some discussion on data processing and interpretation of the spectra will be presented.

3.1 Performing FTIR measurements

The data is collected using the setup described in Section 2.4. After data collection, the Bruker software automatically performs the Fourier transform to create an intensity spectrum. FTIR measurements are set up as difference measurements: the infrared absorbance \( A \) is defined as the difference between the logarithms of the intensity of the light transmitted by the sample \( I \) and the intensity of the light entering the sample \( I_0 \):

\[
A = -\log\left(\frac{I}{I_0}\right),
\]  

(3.1)

In film measurements, the sample is a film deposited with \( n \) cycles of ALD (Figure 3.1, left), where the reference measurement \( I_0 \) is a spectrum of the substrate without the SiN_x film, and \( I \) a spectrum of the substrate with an SiN_x film. In surface measurements, the sample is a half-cycle of ALD. There, \( I_0 \) is the recorded spectrum before the half-cycle is started, \( I \) the spectrum recorded after the half-cycle (Figure 3.1, right). In gas phase measurements, the sample is the reactor filled with volatile species. The reference measurement is performed before the reactor is filled with gas species. A gas phase measurement is treated extensively in Appendix A.

3.2 Signal-to-noise ratio

If noise levels prevent the observation of certain vibrational modes, averaging multiple scans can enable resolving the peak. The signal increases with the number of scans \( N \),
3.2. Signal-to-noise ratio

whereas the noise level scales with $\sqrt{N}$. Therefore the signal to noise ratio (SNR) will increase with the number of scans $N$, via $\text{SNR} \sim \sqrt{N}$ [2]. This means that increasingly long acquisition times are needed to improve the SNR. Spectroscopic features are typically judged to be real when the magnitude of the signal exceeds the noise level by a factor of 3 [2]. In Figure 3.2, the peak-to-peak noise level as function of the performed number of scans is plotted. On the used FTIR setup, the noise levels get to the asymptotic value of about $10^{-5}$. This implies that, assuming real features have a SNR of over 3, the smallest detectable feature has an absorbance of $3 \cdot 10^{-5}$, for which 12,000 to 25,000 scans are needed. This corresponds to a measurement time of 6 to 12 hours. In surface measurements, spectral features can have absorbances of this magnitude. In film or gas phase measurements, however, the magnitude of the spectral features is generally much larger. There, typically 256 to 1024 scans are sufficient for a SNR of over 3, corresponding to a measurement time of 5 to 10 minutes.

![Figure 3.2](image.png)

**Figure 3.2:** Increasingly long acquisition times are needed to reduce the peak-to-peak noise level, which scales with $\frac{1}{\sqrt{N}}$, the number of scans.
3. FTIR data acquisition and processing

3.3 Averaging the spectra

After one half-cycle, the surface is covered with specific surface groups. To increase the SNR, multiple scans of these surfaces have to be made to be able to distinguish the surface groups. However, the (thermal) stability of these surface groups is not infinite. Over time, surface groups can reconstruct or react with small amounts of reactants that are present in the reactor. This implies that within one measurement, the maximal scan time is limited as the signal vanishes over time. An example of this effect was observed for thermal ALD of Al\(_2\)O\(_3\), where surface groups after precursor exposure react with background H\(_2\)O in the reactor, causing the signal to vanish. Dillon and Frank [30, 31] reported this can be solved by dosing a constant supply of precursor during the infrared measurements, to replenish the surface groups. Another way of solving this problem is to decrease the scan time within one measurement, but use multiple ALD half-cycles for averaging. The cyclic nature of ALD enables this averaging, as every half-cycle the same surface groups are present.

For an ALD process, it is expected that the deposited film is homogeneous throughout the full deposition, implying that the surface chemistry does not change during the deposition. To test this, surface spectra were recorded after 100, 500 and 1000 complete ALD cycles. The result, for a deposition at 85\(^\circ\)C is shown in Figure 3.3. Both the precursor half-cycle spectra (left) and plasma half-cycle spectra (right) look similar at each probing moment during the deposition. Because of these similarities, in the rest of this work, spectra recorded after 100, 500 and 1000 cycles will be used for averaging.

The total half cycle spectra are given by

$$A_{\text{plasma,precursor}} = \frac{A_{100} + A_{500} + A_{1000}}{3}$$  \hspace{1cm} (3.2)

To calculate the absorbance after one complete ALD cycle, the averaged precursor half-cycle spectrum and plasma half-cycle spectrum are added.

In Table 3.1 the number of scans performed in this work to measure film, gas phase and surface spectra are listed.
3.3. Averaging the spectra

Figure 3.3: The surface vibrational spectra of the deposition process at 85°C. The spectrum of the precursor half-cycle (left) is similar after 100, 500 and 1000 cycles. The same holds for the plasma half-cycle (right).

Table 3.1: Gas phase, film and surface measurements were all performed at the same spectral resolution. The number of scans per measurement, and the total amount of measurements that were averaged, differs for all measurement types.

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature (°C)</th>
<th># Scans</th>
<th>Resolution (cm⁻¹)</th>
<th># Cycles used for averaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase</td>
<td>85</td>
<td>256</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Film</td>
<td>85,155,275</td>
<td>1024</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Surface</td>
<td>85</td>
<td>1024</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>155</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td></td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>
3. FTIR data acquisition and processing

3.4 Baseline corrections

Between measurement $I$ and $I_0$, fluctuations of the detector and sample can cause baseline shifts in the absorbance spectra. Due to the scale of the surface spectra, even very small baseline shifts are visible. Baselines cause an offset in the absorbance levels, but also change the overall shape of the spectra. To be able to average multiple spectra, the baseline has to be the same for each spectrum. Therefore all spectra were baseline corrected. This was done manually, by fitting a B-spline trough 10 to 20 points in featureless regions. An example of a spectrum before and after baseline correction is shown in Figure 3.4. For the region below 1500 cm$^{-1}$ and close to the H$_2$O absorption regions (1250-1750 cm$^{-1}$ and 3500-4000 cm$^{-1}$), no clear baseline can be assigned. Therefore, the magnitude of the absorbance of the NH (3400 cm$^{-1}$) and SiN$_x$ (below 1000 cm$^{-1}$) modes cannot be determined accurately and changes in these frequency regions cannot be related directly to the ALD process.

Figure 3.4: Typical baseline correction using B-spline. Regions close to H$_2$O vibrational modes (1250-1750 cm$^{-1}$ and 3500-4000 cm$^{-1}$) and close to the edge of the detection window (< 1000 cm$^{-1}$) are subject to errors in baseline correction.
Table 3.2: Typical infrared peak position and relative peak strength of vibrational modes observed in this work. The relative peak strength is as observed in surface measurements and is not normalized to amount of molecules contributing to the signal.

<table>
<thead>
<tr>
<th>Molecular bond</th>
<th>Frequency (cm⁻¹)</th>
<th>Relative strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH</td>
<td>2180</td>
<td>1</td>
</tr>
<tr>
<td>SiN</td>
<td>900</td>
<td>1.1</td>
</tr>
<tr>
<td>CH</td>
<td>2940</td>
<td>0.42</td>
</tr>
<tr>
<td>NH</td>
<td>3340</td>
<td>0.33</td>
</tr>
<tr>
<td>CN</td>
<td>2080</td>
<td>1.2</td>
</tr>
</tbody>
</table>

3.5   Interpreting surface FTIR spectra

When matter interacts with IR light, chemical bonds in the material can start to vibrate when certain selection rules are met. There is a correlation between the structure of molecules and the frequency at which the infrared light is absorbed. IR light can only be absorbed by a molecule if the electric dipole moment of the molecule changes during the vibration. This means that diatomic molecules consisting of two different atoms are generally infrared active, whereas homo-nuclear molecules are infrared inactive. For poly-nuclear molecules with a center of symmetry, like CO₂, only asymmetric vibrations are infrared active.

Different types of vibrational modes can be distinguished. There are stretching and bending vibrations. Stretching can be either symmetric or asymmetric. Within the bending modes; deformation, rocking, wagging and twisting modes can be distinguished. Examples of these movements are illustrated in Figure 3.5. Generally, a combination of vibrational modes is excited. For the CH₃ molecule, both stretching modes at 3000-2800 and bending modes at 1250-1100 cm⁻¹ are expected to be visible in a spectrum [32]. However, depending on the oscillator strength or overlap with other infrared bands, not all vibrational modes of a molecule are clearly visible in the spectrum. In Table 3.2, the most important vibrational bands and their relative intensity, as typically observed in surface measurements in this work, are listed.

The oscillator strength of a vibrational mode, together with the amount of bonds that are probed, determine the strength of the absorbance. In surface FTIR, only a sub-monolayer (<Å) is probed, containing < 10¹⁵ atoms/cm². This causes the magnitude of the signal to be low and the spectrum to be sensitive to noise, fluctuations in background species (i.e. H₂O, CO₂) and fluctuations in substrate temperature.

When interpreting surface FTIR spectra, one has to keep in mind that only changes on the surface are measured. These changes can occur in multiple ways, as illustrated by Figure 3.6:

- Formation and removal of surface species.
Formation and breaking of vibrational bonds during a half-cycle will give positive and negative peaks in the differential spectrum, respectively. Groups that are present on the surface during both half-cycles can not be distinguished.

- **Shifts caused by change in chemical structure.**
  Changed vibrational modes after treating the surface imply that certain molecular bonds are changed. It does not necessarily imply removal of atoms, nor the incorporation of atoms. For example, when species that are deposited in one half-cycle as triple bonded C change during the second half-cycle to double bonded C, a shift from $\sim 2200 \text{ cm}^{-1}$ to $\sim 1650 \text{ cm}^{-1}$ is expected [33]. In the spectrum this is visible as a negative peak at $2200 \text{ cm}^{-1}$, and a positive peak at $1550 \text{ cm}^{-1}$. Thus, the C atom is not removed, even though a negative peak is observed.

- **Shifts caused by changed environment/back-bonding.**
  The position of a vibrational mode can shift depending on the environment of the mode. This shift is caused by a change in electro-negativity of the dipole moment, which changes the force constant of the bonds between the atoms. Since the force constant determines the vibrational frequency of the bond [34], a change in dipole moment results in a different absorption frequency. For SiH in SiN$_x$ films, Bustarret et al. [35] studied the SiH peak position as a function of the back-bonding of the silicon atom. When the back-bonding changes from three silicon atoms to three nitrogen atoms, a shift in peak position from $2005 \text{ cm}^{-1}$ to $2220 \text{ cm}^{-1}$ has been observed. The cross section of shifted bonds is usually not the same [35].

Shifts in peak positions can also occur on a sub-surface level, as observed for crystalline silicon, where the phonon modes of the crystal influence the dipole moment.
of the molecular bond [36]. Since a sub-surface change will also be visible in the surface spectrum, no distinction between surface and sub-surface contributions can be made.

### 3.6 Conclusion

FTIR measurements are set up as difference measurements, where the absorbance spectrum is created by measuring the intensity spectrum before, and after deposition of the layer of interest. For surface infrared measurements, spectra obtained prior, and after a half-cycle are used.

To enhance the signal-to-noise ratio in surface measurements, spectra obtained in multiple half-cycles are averaged. Three probing moments in the ALD process were used, after 100, 500 and 1000 cycles. The half-cycle spectra look similar for each of these probing moments. Every spectrum is baseline-corrected. Since the baseline correction can intro-
duce errors close to the H₂O absorption regions (1250-1750 cm⁻¹ and 3500-4000 cm⁻¹) and close to the edge of the detection window (< 1000 cm⁻¹), the NH absorption and SiN, which lie in the regions, can not be quantified.

The interpretation of infrared surface spectra is not trivial. Formation of a bond results in a positive peak, breaking of a bond in a negative peak. When species are present and unchanged during both half-cycles, no absorption band is visible. Peaks can shift due to back-bonding or change in environment of the corresponding bond. The cross section of the shifted bonds is usually not the same. Finally, changed vibrational modes do not necessarily imply removal of atoms, nor the incorporation of atoms.
SiN$_x$ ALD process on ALD-I
The infrared measurements were performed on the ALD-I setup. The ALD process was established on this deposition tool and compared to depositions performed on the FlexAL setup. In this way, it was verified that the studied ALD process resembled the developed SiN$_x$ process. In this chapter, the SiN$_x$ ALD cycle will be discussed, saturation curves and the standard recipe for both reactors will be compared and the material properties of films grown by ALD-I and FlexAL will be analyzed with ex situ SE, RBS, ERD and FTIR. Finally, the effect of performing FTIR measurements during depositions on the film composition will be discussed.

4.1 ALD cycle for SiN$_x$

The SiN$_x$ deposition process in the ALD-I reactor consists of two half-cycles and is shown in Figure 4.1. In the first half-cycle, the BTBAS precursor molecule is dosed into the reactor, while the bottom valve is closed, hence containing the precursor molecules in the reactor. Some time is allowed for the precursor to react with the surface. Afterwards, the bottom valve is opened and excess precursor and reaction products are pumped out of the reactor. In the second half-cycle, the bottom valve remains open as the nitrogen plasma is ignited. After the plasma is stopped, the reaction products are purged out of the reactor and a new cycle can be started. This recipe is repeated until after $n$ cycles the desired SiN$_x$ film thickness is deposited. An extensive description of the SiN$_x$ ALD process can be found in the work of Braeken and De Peuter [21, 25].
4.2 Saturation curves and standard recipe

A well-developed ALD recipe operates in the saturated regime of the process parameters. This means that the process parameters are chosen such to obtain the self-limiting behavior of ALD. Therefore, there should not be much deviation in terms of material properties and growth rates when an ALD process is transferred to another reactor that operates under the same conditions (i.e., from one FlexAL system to another FlexAL system). However, when depositing in sub-optimal conditions (e.g. when a reaction step is not yet saturated), growth rates can deviate from previously found values and saturation curves can show different saturation values. Since the saturation curves are dependent on the geometry and deposition parameters of the reactor, deviations in material properties and growth rates can be expected when depositing with the ALD-I reactor instead of the FlexAL reactor.

A saturation curve for plasma exposure time was constructed using in situ spectroscopic ellipsometry (SE). The curve has beens constructed for two deposition temperatures and is shown in Figure 4.2. The solid and dashed lines are data from the FlexAL deposition tool. Similar trends and growth per cycle (GPC) values were observed for both reactors. Also, the precursor exposure time and purge times were checked to be well in saturation.

Figure 4.2: Saturation curves for the plasma exposure time for two deposition temperatures obtained by in situ SE.
4. SiN<sub>x</sub> ALD process on ALD-I

Table 4.1: Deposition parameters for the standard recipe in FlexAL and ALD-I.

<table>
<thead>
<tr>
<th>Deposition parameter</th>
<th>FlexAL</th>
<th>ALD-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTBAS dosing time (ms)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Precursor reaction time (s)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Precursor purge time (s)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Plasma exposure time (s)</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Plasma pressure (10&lt;sup&gt;-2&lt;/sup&gt; mbar)</td>
<td>5.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Plasma power (W)</td>
<td>600</td>
<td>100</td>
</tr>
<tr>
<td>Plasma purge time (s)</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The deposition parameters for the standard recipe are listed in Table 4.1. The parameters for the ALD-I reactor were chosen to imitate the FlexAL process. The lower plasma pressure and power were chosen since most known processes on ALD-I use similar plasma pressures and powers [22, 23].

4.3 Material properties

Using the ALD-I reactor, two types of deposition runs were performed using the standard recipe described in Table 4.1. These depositions were compared to FlexAL data. These three processes will be referred to as FlexAL, ALD-I T (substrate table) and ALD-I M (manipulator) process. Between the depositions, there were differences in used reactor/heating method, as well as process temperatures. The process temperatures were measured with <i>in situ</i> SE (FlexAL, ALD-I T) or with a thermocouple (ALD-I M), during the deposition. The relevant temperatures of the depositions can be found in Table 4.2.

The film properties were analyzed with <i>ex situ</i> spectroscopic ellipsometry (SE)[37], Rutherford back scattering (RBS)[38], elastic recoil detection (ERD)[38] and FTIR. SE was used to obtain the thickness, growth per cycle and refractive index of the films, RBS, ERD and FTIR were used to compare the composition of the films. Differences between the two reactors and between heating methods were observed, which will be discussed in Section 4.4.

In Table C.1 the material properties as determined by SE, RBS and ERD are listed. Impurity levels and N/Si ratio differed for all films, but the refractive index of the films was independent of deposition tool or heating method. The GPC and refractive index were however temperature dependent. An extended table, containing all SE, RBS and ERD results, can be found in Appendix C.

The RBS and ERD measurements were performed by AccTec B.V., the results are shown in Figure 4.3. From the measured atomic percentages, the N/Si ratio of the film
### 4.3. Material properties

Table 4.2: Set temperatures of the heating method (substrate table, T, or resistive heating using the sample manipulator, M) as compared to actual temperature at base pressure ($\sim 10^{-6}$ mbar) and during the process.

<table>
<thead>
<tr>
<th>Heating</th>
<th>FlexAL $T_{set}$ (°C)</th>
<th>ALD-I T $T_{set}$ (°C)</th>
<th>ALD-I M $T_{set}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate table</td>
<td>200, 400</td>
<td>200, 400</td>
<td>155, 275</td>
</tr>
<tr>
<td>Resistive, manipulator</td>
<td>155, 275</td>
<td>-,-</td>
<td>155, 275</td>
</tr>
<tr>
<td>$T_{base}$ (°C)</td>
<td>155, 275</td>
<td>146, 230</td>
<td>155, 275</td>
</tr>
<tr>
<td>$T_{process,SE}$ (°C)</td>
<td>180, 310</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>$T_{walls}$ (°C)</td>
<td>150</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$T_{precursorlines}$ (°C)</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>$T_{bubbler}$ (°C)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 4.3: Material properties as determined by SE, RBS and ERD.

<table>
<thead>
<tr>
<th></th>
<th>155°C</th>
<th>275°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FlexAL</td>
<td>ALD-I T</td>
</tr>
<tr>
<td>GPC (Å)</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>$n$ (@ 2 eV)</td>
<td>1.83</td>
<td>1.88</td>
</tr>
<tr>
<td>At% H</td>
<td>11</td>
<td>9.5</td>
</tr>
<tr>
<td>At% O</td>
<td>3</td>
<td>8.5</td>
</tr>
<tr>
<td>At% C</td>
<td>12</td>
<td>7.6</td>
</tr>
<tr>
<td>N/Si</td>
<td>2</td>
<td>1.4</td>
</tr>
<tr>
<td>GPC (Si atoms/nm$^2$)</td>
<td>0.65</td>
<td>0.93</td>
</tr>
</tbody>
</table>
was determined. All the films were nitrogen rich, where ALD-I T depositions have a N/Si ratio close to stoichiometric Si$_3$N$_4$.

From the measured atomic densities per surface area and the total amount of cycles used for deposition of the film, the amount of adsorbed Si atoms per cycle per nm$^2$ was calculated. As every BTBAS molecule contains one Si atom, this is a measure for the amount of adsorbed precursor molecules each cycle. The precursor adsorption is higher for the ALD-I deposition tool than for the FlexAL tool. For the 155°C depositions, the increase is 43% for the Table heating and 100% for the Manipulator heating. For the 275°C depositions the trend is similar, with 56% and 106%, respectively. Whether a high precursor adsorption leads to a high growth rate, depends also on the amount of impurities that are incorporated in the films. A more extended discussion on this topic can be found in the thesis of Van Drunen [39].

Assuming the mass density of stoichiometric Si$_3$N$_4$ to be 3.1 g/cm$^3$ [40], one monolayer of silicon nitride contains roughly 3.2 silicon atoms per nm$^2$. Based on the RBS GPC of approximately 1 Si atom deposited per nm$^2$, each cycle only $\frac{1}{3}$ monolayer of SiN$_x$ is deposited.

High temperature depositions contained fewer contaminations than low temperature depositions. The hydrogen content was similar for the ALD-I T and FlexAL depositions. However, when the resistive heating was used, films with elevated carbon and hydrogen levels were obtained.

### 4.4 Comparison

For depositions performed on the ALD-I reactor, differences in the material properties of the films were observed. In this section, a comparison between the ALD-I depositions and the FlexAL depositions will be made. First, a comparison between the two reactors, using table heating, will be made. Second, the influence of the resistive heating on the depositions is discussed. Here, depositions performed on ALD-I with resistive heating and table heating are compared.

#### 4.4.1 Table heating: FlexAL vs. ALD-I

As stated in Table 4.2, the process temperature for the two deposition tools differed. During depositions, the substrate table temperature was controlled actively. The temperature of the sample fluctuates during the process due to variations in thermal contact between the table and the sample. This thermal contact is mainly determined by pressure in the reactor[21], and is different for FlexAL and ALD-I. The difference in process temperature

---

$^1$The surface density in atoms per cm$^2$ can be calculated via $(\frac{3}{2} \rho \frac{N_A}{\mu})^{2/3}$, where $\rho$ is the mass density, $\mu$ the molecular mass of Si$_3$N$_4$ and $N_A$ Avogadros number
4.4. Comparison

Figure 4.3: Atomic content of the depositions as measured by RBS and ERD (top). The left graph is a deposition at 155°C, the right at 275°C. The bottom left graph shows the N/Si ratio for all depositions. The dashed line is the ratio of Si₃N₄. The bottom right figure shows the GPC in terms of number of deposited Si atoms per nm². The uncertainty in these measurements is about 4%.

can explain the elevated oxygen content for the ALD-I T deposition, as a low process temperature generally yields more oxygen rich films. Also the elevated GPC for the 275°C sample can be related to this, since the adsorption of BTBAS precursor is promoted for low process temperatures [21]. The hydrogen content is independent of deposition tool.

4.4.2 ALD-I: table heating vs resistive heating

By using resistive heating via the manipulator, the process temperature was well controlled and stable during deposition. The samples were heated using the heating scheme described in Section 2.3. The samples had a poor uniformity compared to the table heated samples. The error in the SE model was large, and the RBS and ERD measurements were performed on the thickest part of the deposition. Growth was promoted on some parts of the sample and inhibited on other parts. Because the samples were resistively heated but not grounded, charge could build up during the process, probably leading to biasing of the
Figure 4.4: Part of samples deposited at 275°C, 1750 ALD cycles. The left sample was deposited before grounding was introduced and showed a very inhomogeneous deposition. The uniformity of the deposition increased with the introduction of grounding (right sample). The difference in color is caused by thickness differences. The left sample has locally thicknesses of over 70 nm, whereas the right sample was about 40 nm.

Figure 4.5: Two depositions at 275°C, resistively heated by the manipulator. The grounded sample shows less active vibrational modes in the carbon and hydrogen regions around 1600 cm$^{-1}$ and 2200 cm$^{-1}$. Both depositions consisted of 1750 ALD cycles, but due to the inhomogeneity of the deposition (Figure 4.4), the spectra were scaled to the SiN peak height to compare them.
4.5 Altering the recipe for FTIR measurements

Figure 4.6: To allow time for FTIR measurements, the deposition scheme of Figure 4.1 is altered. When gas phase measurements are performed, a long reaction time of the precursor is allowed before the pump step starts. For surface measurements, both pump steps are lengthened.

substrate. When grounding was introduced, the depositions were uniform and the GPC decreased from 0.45 Å to 0.22 Å for the 275°C deposition. In Figure 4.4, photos of depositions performed at 275°C, without and with grounding are shown. A clear improvement of the uniformity of the deposition was observed when grounding was introduced. In Figure 4.5, the vibrational spectra of the grounded and the ungrounded sample are shown. There, a clear discrepancy in absorbances around 1600 cm\(^{-1}\) and 2200 cm\(^{-1}\) can be seen, related to vibrational modes of carbon and hydrogen species, respectively. It is therefore expected that the incorporation of additional H and C can indeed be related to charge effects during the resistive heating of the substrate.

4.5 Altering the recipe for FTIR measurements

During in situ FTIR measurements, the normal ALD process of SiN\(_x\) had to be altered in order to allow time for the infrared measurements. Depending on the type of measurement, a FTIR measurement adds between 100 s (gas phase) and 15 minutes (surface) to a half-cycle of the ALD process. In this section, the influence of altering the process for FTIR measurements on the deposited films is discussed. This is done by comparing the films deposited using ALD recipes that include time for infrared measurements with films deposited using the normal ALD recipe.

In gas phase measurements, interest lies in the BTBAS precursor molecule and reaction products of the precursor half-cycle. Therefore an infrared spectrum was recorded after the precursor dose, during the reaction time step, while the bottom valve was closed. The standard deposition scheme of Figure 4.1 is hence altered to Figure 4.6, with a reaction time step of 100 s. This deposition scheme is referred to as long reaction time scheme.
4. SiN$_x$ ALD process on ALD-I

Table 4.4: Material properties as measured by ex situ SE. GPC differed for each scheme, while the refractive index was similar for the normal and long purge deposition scheme.

<table>
<thead>
<tr>
<th></th>
<th>GPC (Å)</th>
<th>refractive index</th>
<th>base T (°C)</th>
<th>process T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.77</td>
<td>1.69</td>
<td>86</td>
<td>94</td>
</tr>
<tr>
<td>Long reaction time</td>
<td>2.2</td>
<td>1.57</td>
<td>86</td>
<td>86</td>
</tr>
<tr>
<td>Long purge time</td>
<td>0.59</td>
<td>1.67</td>
<td>86</td>
<td>86</td>
</tr>
</tbody>
</table>

In surface infrared measurements, every half-cycle, the bottom valve was kept open during the measurement. There, the pump/purge-step in the recipe was lengthened. The deposition scheme was hence altered to Figure 4.6, with purge times of 100 s. The purge times of 100 s instead of 15 minutes were chosen for practical reasons. This deposition scheme is referred to as long purge time scheme.

Table 4.4 shows the different GPCs and refractive indices as measured by ex situ SE, for depositions at 86°C, heated by wall heating, a heating method described in Appendix C. The long reaction time scheme had a very high growth rate of 2.2 Å per cycle. The refractive index of the film was low. For the long purge scheme, the GPC was significantly lower than for the normal scheme. The refractive indices were comparable. Ex situ FTIR measurements of these three films are shown in Figure 4.7. The spectra of the normal and long purge schemes are shown in blue and black, and look very similar. However, the long reaction time scheme (in red) shows a different spectrum, containing large features around 1100 cm$^{-1}$, 1500 cm$^{-1}$ and 3400 cm$^{-1}$. These peaks are assigned to SiO$_2$, CN and NH vibrational modes, respectively. The SiN$_x$ peaks 950 and 800 cm$^{-1}$, and SiH at 2200 cm$^{-1}$ are present in all films.

Long reaction time: incorporation of contaminiations

Based on the FTIR spectra it is concluded that the composition of the film deposited with the long reaction time scheme was different than the normal film. The carbon, oxygen and hydrogen bonds were more abundant. In the normal recipe, BTBAS absorbs on the surface and excess precursor molecules are removed out of the reactor by the purging step. When the reaction time is increased, the excess BTBAS is not removed, which might explain the difference in film composition. The excess BTBAS could react in a CVD-like reaction with oxygen and H$_2$O that was leaks into the reactor. This causes the surface to become partially oxidized, creating new reactive sites for BTBAS. Altering the process to a long reaction time yields a porous structure (high GPC) with a lot of contaminants.

Long purge time: low GPC

Based on the FTIR spectra it is concluded that the composition of the long purge time film is similar to the normal films. The process temperature was lower than in the normal case.
4.5. Altering the recipe for FTIR measurements

Figure 4.7: The film spectra for the different deposition schemes. The spectra are scaled to the amount of cycles used for deposition, and hence show the average incorporation of species per cycle. The features at 1100 cm\(^{-1}\), 1500 cm\(^{-1}\) and 3400 cm\(^{-1}\) are assigned to SiO\(_2\), carbon and NH vibrational modes, respectively.

(Table 4.4), but this could not explain the difference in GPC, as the GPC should rise for decreasing temperatures [21]. The observed decreased GPC in this reaction scheme was probably due to deactivation of the surface after the plasma step. As reported by Ande et al. [41] there are indications that the BTBAS precursor adsorbs on an under-coordinated N covered surface (dangling bonds on N atoms). However, when the time between the end of the plasma and the start of BTBAS dose is lengthened, chances are that the dangling N bonds are passivated with H, leading to less reactive sites for the BTBAS to adsorb onto[42]. This then leads to a decrease in GPC. Another explanation could be that not surface passivation by hydrogen, but restructuring of the SiN\(_x\) network over time leads to the decrease in precursor adsorption.

Altering the process to a long purge time does not change the film composition. There are however indications that reactive surface species disappear over time. Since a surface FTIR measurement takes 15 minutes instead of 100 s, it is expected that the growth is even more inhibited when normal measurements are performed. This could have consequences for the presence of detectable surface groups.
4.6 Conclusion

The SiN$_x$ ALD process was transferred successfully from the FlexAL to the ALD-I deposition tool. The deposited films were nitrogen rich with comparable levels of H, O and C contamination. Using manipulator heating without grounding caused both the carbon and hydrogen levels in the film and the amount of deposited silicon atoms each cycle to increase. The introduction of grounding reduced this contamination, and improved the uniformity of the deposition. When the reaction time step in the recipe was altered to allow for gas phase infrared measurements, a porous film with elevated GPC and high levels of H, C and O impurities was obtained. Increasing the purge time steps to allow for surface measurements did not change the contamination content of the film, but reduced the GPC, indicating that reactive sites are passivated because of the long time between the cycles.
5

FTIR to unravel the reaction mechanism of SiN$_x$
5. FTIR to unravel the reaction mechanism of SiN

In this chapter, the results of the *in situ* FTIR measurements are discussed. First, the data is presented. Next, an extended discussion on the data can be found. This discussion mainly focuses on the surface measurements and serves to put the observations into perspective. At the end of the chapter, a possible reaction mechanism is proposed.

5.1 In situ infrared results

This section treats the *in situ* FTIR data. Gas phase measurements of the precursor half-cycle at 85 °C are presented, together with DFT simulations of the vibrational fingerprints of the gas phase species. Next, the film and surface spectra of the ALD process at deposition temperatures of 85, 155 and 275 °C are presented.

5.1.1 Gas phase species

In Figure 5.1 the vibrational spectra of the gas phase species are shown. The top figure shows the species that were present in the reactor during the precursor half-cycle, measured after dosage of a high concentration (above-saturation) of BTBAS molecules. The bottom figure is the vibrational fingerprint of the reaction product, measured for an under-saturated dose of BTBAS. The center figure, containing the vibrational fingerprint of BTBAS, is deducted from the other two. Details on the experiment can be found in Appendix A.

The vibrational fingerprint of the reaction product corresponds to the experimental NIST spectrum of t-Butylamine (NH$_2$C(CH$_3$)$_3$) [43]. This spectrum contained NH$_2$ bending and wagging modes at 1629 cm$^{-1}$ and 810 cm$^{-1}$, respectively. The absence of a SiN stretching mode at 931 cm$^{-1}$ in the reaction product spectrum indicates that the SiN bond was broken upon precursor adsorption. In the spectrum of the precursor molecule, the SiH stretching mode around 2144 cm$^{-1}$ and the NH$_2$ bending mode at 1629 cm$^{-1}$ are visible, as well as the SiNC stretching mode at 1025 cm$^{-1}$ and the SiN stretching mode at 931 cm$^{-1}$. Vibrations in the region 1370-1480 cm$^{-1}$ and 2875-2975 cm$^{-1}$ were assigned to the CH bending and stretching modes, respectively [44, 5, 43] and were present in both fingerprints. The overall spectrum of gas species is a combination of both vibrational fingerprints.

The vibrational fingerprints of the BTBAS and t-Butylamine molecule were calculated [42] using first-principles based density functional theory (DFT). In these calculations, the molecules were represented as a group of oscillators. Using the position of the atoms and the force constant of the bonds between the atoms in harmonic approximation, the vibrational frequencies of the bonds were determined. Generally, computed frequencies are within 5% of the experimental value [42]. The computed and measured vibrational fingerprints are shown in Figure 5.2, and are in good agreement. In figure 5.3, a graphical representation of the gas phase molecules can be found. There, the SiH stretching mode at 2144 cm$^{-1}$ and the NH$_2$ bending mode at 1629 cm$^{-1}$ are illustrated.
5.1. In situ infrared results

Figure 5.1: Vibrational fingerprints of (top) the gas species present in the reactor during the precursor dosing step of the ALD process, (center) the BTBAS precursor molecule and (bottom) the reaction product. The latter was determined to be t-Butylamine (NH₂C(CH₃)₃).
Figure 5.2: The calculated and measured vibrational fingerprints of BTBAS and t-Butylamine. Calculations were performed using first-principles based DFT calculations[42].
5.1. *In situ* infrared results

Figure 5.3: The SiH stretching mode of the BTBAS molecule (top, middle) and the NH$_2$ bending mode of the t-Butylamine molecule (bottom) as modeled using first principle DFT calculations. The molecules consist of Si (orange), H (white), C (grey), and N (blue) atoms.
5. FTIR to unravel the reaction mechanism of SiN<sub>x</sub>

5.1.2 Film species

The vibrational spectra of deposited films at a substrate temperature of 85 °C, 155 °C and 275 °C were measured and are shown in Figure 5.4. The spectra were normalized to the number of cycles used for deposition of the films. In that way, the average incorporation of species in one cycle is visualized. The absorptions in the 800-1000 cm<sup>-1</sup> region are related to the SiN stretching modes with different configuration and hydrogen bonding [35, 45, 46, 47]. Hydrogen stretching modes are visible in the spectrum; the SiH<sub>2</sub> stretching mode at 2175 cm<sup>-1</sup> and the NH stretching mode at 3340 cm<sup>-1</sup>. The peaks at 1180 cm<sup>-1</sup> and 1560 cm<sup>-1</sup> were assigned to NH wag-rock and NH<sub>2</sub> bending modes, respectively [35]. The NH absorbances were small compared to the SiH band. The relative oscillator strength of the SiH and NH stretching mode is reported to be similar [45, 35]. This shows that in this ALD process, the majority of the H was incorporated as SiH groups. The absorbance of the SiH stretching modes decreased when the deposition temperature was increased from 85 °C to 275 °C. The same trend was observed for the 1400-1650 cm<sup>-1</sup> region, where besides the NH also the CN stretching modes were observed [33, 48]. This indicates that less hydrogen and carbon was incorporated into the SiN<sub>x</sub> films at higher deposition temperatures.

5.1.3 Surface species

The surface infrared spectra look similar for all deposition temperatures. Therefore, only the deposition at 155 °C will be discussed here. The corresponding surface spectra are shown in Figure 5.5. The complete set of measurements, including surface spectra of depositions at 85 °C and 275 °C can be found in Appendix C.

In the spectrum of a single complete ALD cycle, peaks were observed that correspond to vibrational modes of bonds of molecules that were incorporated in the film after one cycle. The peaks at 3400 cm<sup>-1</sup>, 2180 cm<sup>-1</sup> and 900 cm<sup>-1</sup> were related to the formation of NH, SiH<sub>x</sub> and SiN respectively. In the precursor half-cycle spectrum, the appearance of the SiH<sub>x</sub> vibrational mode at 2180 cm<sup>-1</sup> indicates precursor adsorption in this half-cycle. This SiH was not removed in the plasma half-cycle and was incorporated into the film.

In all spectra, the signature of H<sub>2</sub>O and CO<sub>2</sub> is visible, around 3700 cm<sup>-1</sup>, 1600 cm<sup>-1</sup> and 2300 cm<sup>-1</sup>. These species were not incorporated in the film, but are gas phase species that were present in very small amounts in the reactor and detector purge box. The CO<sub>2</sub> and H<sub>2</sub>O peaks are formed in the plasma half-cycle, indicating the interaction with carbon and hydrogen containing fragments of precursor ligands in the plasma with background oxygen. The species were pumped out of the reactor over time, showing negative peaks in the precursor half-cycle. Their signature was not visible in the gas phase spectra of Figure 5.1 because their absorbances differ an order of magnitude with the absorbances of the other gas phase species.

In contrast to peaks related to incorporation of species in the film, there were also
5.1. *In situ infrared results*

Figure 5.4: The vibrational spectra of deposited films at 85°C, 155°C and 275°C. The absorbances have been normalized to the number of cycles used for deposition, hence visualizing the incorporation of species each cycle.
Figure 5.5: Vibrational spectra of the surface species during an ALD cycle. The bottom figure in black shows the surface species during the precursor half-cycle. In red, the plasma half-cycle is shown and the blue figure shows the addition of the two. By adding the two half-cycles, the species that were incorporated in the material during one complete ALD cycle can be visualized.
5.1. *In situ* infrared results

peaks visible of species that are related to the ALD process chemistry, which were not incorporated in the film. These molecular bonds were formed or removed during either other half-cycle and their vibrational modes were not visible in the spectrum of a full cycle. The band at 2080 cm\(^{-1}\) is related to such an intermediate state in the ALD process. It was formed in the plasma step and was assigned to formation/deposition of nitride-like (-CN) species \cite{33}. During the precursor step, the bond was changed and hence not incorporated in the film.

The other process related peak visible in the spectrum is the contribution at 2940 cm\(^{-1}\), assigned to the stretching mode of the CH molecule. This bond was formed at the surface during the precursor half-cycle, and was removed in the plasma half-cycle. Even though this peak was very small compared to the noise levels, it appeared consistently throughout the data. In Figure 5.6, the CH stretching peak is shown for all temperatures, the dashed line indicating its position. The absorbances were 1.9 \cdot 10^{-5} and 1.7 \cdot 10^{-5} for the 85 and 155°C spectra, respectively. The 275°C spectrum consisted of less averages than the other spectra, which resulted in a larger peak-to-peak noise of 1.5 \cdot 10^{-5}. Taking the amplitude of the CH absorbances at the lower temperature spectra into account, it is plausible that the CH stretching mode of the 275°C sample had a similar amplitude as the noise levels in this spectrum, which made it impossible to distinguish between the two.

![Figure 5.6: The CH stretching mode at 2940 cm\(^{-1}\) is visible in half-cycle spectra of the depositions at 85 and 155°C. For the 275°C deposition, the CH stretching mode can not be distinguished from the noise levels in the spectra.](image-url)
5.2 Interpretation of the data

In this section, a discussion on the infrared data is provided. This discussion serves to place the infrared measurements in the framework of the ALD process. Comparisons with other ALD processes, and observations of this work are combined to obtain more insight in the ALD process of Si$N_x$.

5.2.1 The nature of the SiN band

The properties of Si$N_x$ films depend on their composition, such as N/Si-ratio and contamination content [49]. In literature, the asymmetric SiN stretching mode in the 800-1000 cm$^{-1}$ region is generally deconvoluted into three Gaussian components which correspond to different chemical configuration of the Si$N_x$ film [46, 49]. There is still controversy about the exact nature of the chemical structure, but generally the lower wavenumbers are assigned to SiN bonding in Si rich films and the high wavenumbers to SiN bonding in N rich films. A deconvolution of peaks observed in the 600-1200 cm$^{-1}$ region of Figure 5.4 is shown in Figure 5.7. In this deconvolution also the SiH bending mode at 700 cm$^{-1}$ and the NH wagging mode at 1170 cm$^{-1}$ are included to obtain a correct fit.

The peak assignments are listed in Table 5.1. Three Si$N_x$ stretching modes can be distinguished: 982-1041 cm$^{-1}$, assigned to N$_3$–Si–N [47], 914-931 cm$^{-1}$, assigned to Si–N–Si[50] and 794-823 cm$^{-1}$, assigned to Si$_3$–Si–N[51]. At all deposition temperatures the three contributions are present. No exclusive trends in peak area (absorption strength) are present. A shift of peak position towards higher wavenumbers for lower deposition temperature can be observed.

Table 5.1: Peak assignment of the Gaussian contributions to the band in the 600-1200 cm$^{-1}$ and their relative absorbances.

<table>
<thead>
<tr>
<th>Assigned band</th>
<th>85°C Frequency (cm$^{-1}$)</th>
<th>155°C Frequency (cm$^{-1}$)</th>
<th>275°C Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_3$–Si–N</td>
<td>1041</td>
<td>988</td>
<td>982</td>
</tr>
<tr>
<td>Si–N–Si</td>
<td>931</td>
<td>918</td>
<td>914</td>
</tr>
<tr>
<td>Si$_3$–Si–N</td>
<td>794</td>
<td>810</td>
<td>823</td>
</tr>
<tr>
<td>SiH</td>
<td>711</td>
<td>691</td>
<td>696</td>
</tr>
<tr>
<td>NH</td>
<td>1183</td>
<td>1169</td>
<td>1148</td>
</tr>
</tbody>
</table>
5.2. Interpretation of the data

Figure 5.7: The peaks observed in the 600-1200 cm$^{-1}$ deconvoluted in Gaussian contributions. The main bands are assigned to asymmetric SiN$_x$ stretching modes. The peaks at 700 cm$^{-1}$ and 1170 cm$^{-1}$ are assigned to SiH bend and NH wag mode, respectively.
5.2.2 Surface groups

Below, the most important observations in the surface FTIR spectra are listed and discussed. Based on the observations, a schematic graphical representation of the surface during an ALD cycle is constructed. This representation does not reflect the actual molecular structure at the surface, but is based on the observed surface groups. Afterwards, the discussed observations are used to construct a reaction mechanism.

1. **CH stretching mode is observed after precursor adsorption.**
   This implies that upon precursor adsorption, one of the ligands, or fragments hereof, remain at the surface. Whether this is exactly one ligand per deposited Si atom cannot be determined, since the cross section of this mode on SiN surfaces is not known. Hence, the magnitude of the absorbance cannot directly be related to the amount of CH molecules. However, some comparison can be made with the TMA Al$_2$O$_3$ process, when the same oscillator strength is assumed for CH on Al$_2$O$_3$ and SiN$_x$.
   To make this comparison, one has to take into account that only changes on the surface are observed using FTIR. If we assume that the BTBAS molecule keeps one ligand upon precursor adsorption, which is removed completely in the plasma, the observed change consists of the 3 CH$_3$ molecules per adsorbed precursor molecule. As found by RBS, about one silicon atom per nm$^2$ is deposited each cycle, corresponding to one BTBAS molecule per nm$^2$. Each cycle, hence a measurable change of 3 CH$_3$ groups per nm$^2$ is expected. Taking the magnitude of the absorbance of $1.8 \times 10^{-5}$, this results in an absorbance of $0.6 \times 10^{-5}$ per CH$_3$ group.
   For TMA, a precursor adsorption of 4 Al atoms/nm$^2$ is reported for the plasma ALD process at 150 °C [52]. The corresponding absorbance is $5 \times 10^{-5}$ [53]. Assuming a change of CH surface coverage of 1.5 methyl groups per adsorbed Al atom [54], this leads to an absorbance per methyl group of $0.8 \times 10^{-5}$.
   This shows that, under these assumptions, it is plausible that BTBAS keeps one ligand upon adsorption and a surface as depicted in Figure 5.8b is assumed.

2. **The CH stretching mode disappeared in the plasma step.**
   This implies that at least part of the remaining ligand (CH groups) is removed in the plasma half-cycle. This is also confirmed in previous experiments, where fragments of ligands and CN emission were observed in the plasma step [21]. Therefore, after the plasma half-cycle the surface is expected to look like Figure 5.8c.

3. **No removal of SiH stretching mode is observed in the plasma half-cycle.**
   This implies that all SiH that is on the surface after precursor adsorption, will eventually be incorporated in the film. However, not all SiH of the precursor molecule can be incorporated in the film, as the hydrogen content of the films is too low. RBS and ERD measurements revealed a Si:H ratio of between 5:1 to 2:1 (Section 4.3).
5.2. Interpretation of the data

Figure 5.8: The schematic representation of the surface during an ALD cycle. a.) starting surface of an ALD cycle. b.) surface after precursor adsorption and c.) surface after plasma exposure. In an ALD cycle, c=a. The surface after plasma exposure can be covered with species created by the plasma, like nitriles (c.1), physisorbed N and CN species (c.2) or partly removed precursor ligands (c.3).
for the deposited films. The precursor molecule has a much higher Si:H ratio of 1:2. In the ALD process, some hydrogen leaves the surface. Whether the hydrogen leaves the surface directly upon precursor adsorption or after multiple ALD cycles can not be concluded from this data. Either could be the case, as every ALD cycle only a sub-monolayer material is deposited.

4. The NH vibrational mode is absent in the surface spectra.
The absence of the peak implies that either the NH bonds do not change during the process, or the infrared signal of this change is too small to be observed. DFT simulations showed that NH\(_x\) (0 ≤ x ≤ 2) species play a crucial role in the surface chemistry of this ALD process [41]. Therefore it was expected that NH modes were visible in the surface spectra. To understand the absence of the NH modes, below, some mechanisms that can contribute to a NH peak are discussed, and an estimation on the magnitude of their absorbances is made. The change in NH vibrational mode is expected to have at least three different causes:

- The incorporation of NH molecules in the film.
  From the film spectra it is known that NH is incorporated in the film. Per cycle, the NH peak height due to this incorporation is on average 0.54 · 10\(^{-5}\) per cycle, which is well below the sensitivity of the used IR detector.

- Precursor adsorption on a NH site.
  When the precursor adsorbs on a NH site, it would imply the removal of one NH bond per adsorbed Si atom. However, the precursor molecule with attached ligand (Figure 5.8 b), also contains one NH molecule. Therefore, no change in NH modes is expected upon precursor adsorption if the reactive site would be NH.
  If the adsorption occurs on a dangling bond (N-), a positive peak caused by the NH of the precursor is expected. By taking the relative oscillator strength of the SiH and NH stretching mode (SiH/NH = 1.4 [45]), and the magnitude of the SiH band, the expected half-cycle absorbance of the NH stretching mode can be calculated. Assuming that upon precursor adsorption two SiH bonds and one NH bond are added, the magnitude of the NH absorbance should be about 2 · 10\(^{-5}\) if the adsorption occurs on a dangling bond, which is below the sensitivity of the detector.
  If the adsorption occurs on a NH\(_2\) site, a negative contribution of this magnitude is expected.

- Creation of dangling bonds.
  After the plasma half cycle, the surface is expected to contain under-coordinated nitrogen (dangling bonds)[41]. If it is assumed that these dangling bonds are created out of NH sites, the change from a NH passivated surface to a surface with dangling bonds in the plasma half-cycle would cause a negative
5.2. Interpretation of the data

Figure 5.9: Multiple species have absorptions in the 2000-2200 cm\(^{-1}\) range. The SiH vibrational mode can shift over 200 cm\(^{-1}\), depending on the backbonding. Also double and triple bonded C and N species, which are expected after interaction of the nitrogen plasma with the BTBAS ligand, have absorptions in this region.

absorbance peak in the spectrum. However, as discussed in Section 4.5, it is expected that part of the reactive sites created by the plasma vanish over the duration of an infrared measurement. Therefore, these changes are likely to be invisible in the half-cycle spectra.

The discussed contributions could add constructively, or cause the full NH signal to vanish when both mechanism resulting in positive and negative peaks occur. Even if contributions do not vanish, their absorbances are small with respect to the detection threshold of the FTIR setup of \(3 \cdot 10^{-5}\). Furthermore, as discussed in Section 3.4, the NH region is subject to errors in baseline correction. Therefore, we assume that infrared signal of the change in NH modes is too small to be observed and the role of NH species can not be determined from the infrared measurements. Therefore, based on simulations, the surface after plasma exposure is expected to be NH covered with NH\(_x\) \((0 \leq x \leq 2)\), as depicted in Figure 5.8c.

5. The positive peak at 2080 cm\(^{-1}\) in the plasma half-cycle is assigned to CN related species.
There is however discussion about the nature of the peak, as multiple double and triple bonded species have vibrational modes in this region. Also the SiH molecule
5. FTIR to unravel the reaction mechanism of $\text{SiN}_x$

has absorptions in the $2080 \text{ cm}^{-1}$ region, depending on the back-bonding, as was already discussed in Section 3.5. An example of species with absorbances in the $2000-2200 \text{ cm}^{-1}$ range are listed in Figure 5.9 [35, 33]. In this case, the assignment of the peak to $\text{SiHNSi}_2$ is not very likely, for two reasons. Firstly, the peak appears in the plasma step, whereas, since the films are N rich, it is expected that nitrogen atoms are incorporated in the film in this half cycle. That means that it is not likely that the SiH mode shifts to lower wavenumbers, as more N backbonding would result in higher wavenumbers. Secondly, a shift of the SiH peak would result in the disappearance of the $\text{SiH}_2\text{N}_2$ peak at $2180 \text{ cm}^{-1}$, visible as a negative peak in the spectrum. As no negative absorbance is seen at this peak position, a shift of SiH peak can not be the case.

Assignment to any of the double and triple bonded species is more likely. In an infrared study on the adsorption of TEMAZ (tetraethylmethylamine-zirconium) on silica powder, in an ALD process using ammonia as a reactant, a band at $2048 \text{ cm}^{-1}$ was observed, assigned to triple bonded CN ($-\text{N}≡\text{C}$) on the surface[48]. In the ALD process described in this work, the remaining precursor ligand is removed and dissociated (fragmented) by the plasma species, resulting in a variety of reactive N and CN species in the gas phase during the plasma half-cycle. These species could redeposit on the surface, as indicated by Figure 5.8c.2. Other options would be the formation of nitrogen chains, as also observed in simulations [41] (Figure 5.8c.1.) or only partial removal of the remaining precursor ligand, resulting in NCH on the surface (Figure 5.8c.3.).

5.2.3 Redeposition

The effect of redeposition, as described above, is the continuous effect of removing and addition of species to the exposed surface. These species can for example be parts of ligands that are removed from the substrate, fragmented and excited by the plasma. The species will keep redepositing on the surface until they are flushed out of the reactor. Knoops et al. showed that this redeposition effect is dependent on the residence time of the species in the reactor [10]. Its influence is visible in saturation curves for the plasma exposure. For long plasma exposures, the redeposited species are removed again after redeposition and flushed out of the reactor. For short plasma exposures, the redeposited species remain at the surface and are incorporated in the film. This results in elevated growth rates at short plasma exposure times. At low deposition temperatures, the effect is more prominent and a steady saturation is reached only after a long plasma exposure time; once the fragmented precursor ligands are flushed out of the reactor after redeposition.

Although we think that the formation of the CN band at $2080 \text{ cm}^{-1}$ is related to the redeposition effect, it has a similar absorbance for all temperatures, indicating that it is independent of temperature and incorporation of carbon. The removal of this peak, is
5.3. Proposed reaction mechanism

However slightly temperature dependent, with more removal at higher temperatures. This indicates that at high deposition temperature, less triple bonded CN is incorporated in the film. As RBS and ERD analysis of the films showed that also less nitrogen and hydrogen is incorporated in the film at high deposition temperature, it seems that some temperature driven desorption of H, C and N atoms take place. This desorption could be in the form of stable gases such as HCN, NH$_3$ or H$_2$ gas. Thermal desorption is not investigated in this work, but in the ALD process of Al$_2$O$_3$ a similar effect is observed as described by Puurunen et al. [55]. There, OH groups created in the co-reactant half-cycle leave the surface over time due to thermal recombination to H$_2$O.

At low temperature, more CN is incorporated in the film. Van Drunen[39] observed a correlation between the incorporated carbon and the amount of precursor adsorption, where the precursor adsorption per cycle increased for films with higher carbon contents. This could imply that CN could even serve as a reactive site for precursor adsorption, which would explain the removal of the peak at 2080 cm$^{-1}$ in the precursor half-cycle.

5.3 Proposed reaction mechanism

Using the infrared results and bearing in mind the discussed observations, we propose a reaction mechanism for the plasma-assisted ALD process of SiN$_x$ films using BTBAS and N$_2$ plasma. The reaction mechanism is shown in Figure 5.10. Note that this is a schematic representation. The exact molecular structure at the surface during the process is unknown.

The ALD cycle starts at step 1 with a dose of BTBAS (SiH$_2$(NH$_2$tBu)$_2$) precursor, which adsorbs mono-functionally on the surface. The Si-N bond between the silicon atom and part of the ligands is broken, liberating the ligand as t-Butylamine(NH$_2$tBu), as confirmed by infrared gas phase measurements.

The observation of CH groups in the precursor half-cycle (a positive peak at 2940 cm$^{-1}$) and CN emission in the plasma [21] shows that some ligands remain attached to the silicon upon precursor adsorption. Some hydrogen of the precursor also remains attached to the silicon upon adsorption, observed as a positive peak in SiH at 2180 cm$^{-1}$.

At step 2, the N$_2$ plasma is ignited. CN emission indicates the removal of (parts of) the remaining ligand, which is confirmed by the surface infrared measurement: the CH peak at 2940 cm$^{-1}$ disappeared. A positive peak at 2080 cm$^{-1}$, assigned to triple bonded CN, indicates that parts of the ligands, fragmented and excited by the plasma, can stay or redeposit on the surface (blue). Also, N-N bonds are formed and the films become nitrogen rich. Based on simulations, it is assumed that the surface is NH covered (NH$_x$ ($0 \leq x \leq 2$)), where under-coordinated nitrogen serves as reactive site for precursor adsorption.

At step 3, the next cycle starts with a precursor dose. Hydrogen could leave the surface as H$_2$, HCN or NH$_3$ to create films with low hydrogen content. For depositions at high
temperature, the majority of the CN bonds is removed. For low temperature deposition, large amounts of carbon and hydrogen are incorporated in the film. Each cycle, about $\frac{1}{3}$ of a monolayer of SiN$_x$ is deposited (155 and 275 °C).
Conclusion & outlook
6. Conclusion & outlook

6.1 Conclusion

For the development of ALD processes, the understanding of surface chemistry is crucial. Once is understood how precursor molecules adsorb and how the surface is reactivated by the co-reactant, improvements of the used reactants, process parameters and film properties can be achieved. In this work, in situ FTIR spectroscopy was used to determine the reaction mechanism of SiN$_x$ film growth by plasma-assisted ALD. The infrared measurements revealed information about gas phase species, film composition and surface species during the process. Before the infrared measurements were performed, the ALD process was established on the ALD-I reactor and the in situ setup for infrared spectroscopy experiments was improved.

**In situ FTIR setup**

This work showed that in situ Fourier transform infrared spectroscopy is a versatile tool to study ALD processes. The cyclic behavior of ALD enabled averaging of consecutive ALD cycles to increase the signal-to-noise ratio, which allowed for the detection of absorbances down to $3 \cdot 10^{-5}$, corresponding to sub-nm film thicknesses. Qualitative analysis of film composition could be performed in situ, eliminating the effects of oxidation after exposure to air. Also, volatile species could be measured, to determine which by-products are generated in the precursor half-cycle. The complete identification of surface groups, film species and reaction products enabled to hypothesize on the ALD reaction mechanisms.

In the used deposition setup, a sample manipulator was introduced to enable infrared measurements in transmission mode. A circuit for resistive heating of the sample was designed to allow depositions in the full ALD temperature window (85-350$^\circ$C). The circuit was set up such to actively control the substrate temperature, which was essential for the successful performance of surface infrared measurements. Using the resistive heating without grounding caused the C and H levels in the films as well as the growth rates of the films to increase. It was shown that grounding of the substrate was essential to avoid charging effects which lead to non-uniform depositions and high contamination levels. The introduction of grounding reduced the contamination levels and improved the uniformity of the deposition.

**SiN$_x$ film growth on ALD-I**

The ALD process, using BTBAS and N$_2$ plasma, was developed in 2013 in the PMP research group using an Oxford Instruments FlexAL reactor. In this work, the process was transferred to the home-built ALD-I setup to enable in situ infrared measurements.

The SiN$_x$ film composition was studied using FTIR, SE, RBS and ERD. The films were nitrogen rich and the levels of H, O and C contamination were comparable to the previously performed depositions on the FlexAL. The vibrational spectra of the deposited
films at low temperature depositions showed elevated densities of SiH and CN molecular bonds, which was in agreement with the elevated H, C and N content as measured by RBS and ERD. The film measurements also indicated that in this ALD process, the hydrogen in the films is mainly bonded as SiH, originating from the BTBAS precursor molecule.

**Reaction mechanism**

Every SiN\textsubscript{x} ALD cycle starts with a BTBAS dose. There, part of the precursor ligands were liberated as t-Butylamine, as confirmed by gas phase infrared measurements. Surface measurements revealed that CH groups were present in the precursor half-cycle, indicating that part of the ligands of the precursor molecule remained attached to the Si atom upon precursor adsorption. These ligands were removed by the N\textsubscript{2} plasma, activating the surface for the next ALD cycle.

In this reaction mechanism, the exact role of the plasma remains unknown. Besides removal of the remaining ligand, the plasma also fragments ligand species when they are liberated into the plasma. These carbon-containing fragments (e.g. CN) can presumably redeposit on the surface, as is suggested by a peak in the surface measurements. The magnitude of this redeposition effect was the same over the ALD temperature range. However, the removal of the redeposited species in the precursor step was less efficient for depositions at 85°C, yielding a film with high C, H and N content.

Overall, it is shown that BTBAS is suitable for plasma-assisted ALD of SiN\textsubscript{x}, but it remains challenging to obtain the highest quality films with low contaminant levels due to the design of the precursor molecule.

**6.2 Outlook**

Although it is shown that in situ infrared measurements yield insight in surface chemistry and we were able to refine the view on the reaction mechanism of SiN\textsubscript{x}, some questions remain and recommendations can be made for future research. The recommendations involve further investigation of the BTBAS ALD process, the change to another precursor (DSBAS), improvement of the infrared setup and exploration of the functionality of the sample manipulator.

- **BTBAS ALD process**
  Although a reaction mechanism of the ALD process is proposed, the influence of the plasma on the incorporation of carbon in the films remains unclear. The appearance and disappearance of the band at 2080 cm\textsuperscript{-1} was assigned to CN species and could imply that the carbon can serve as a reactive site in the process. It was also suggested that HCN might leave the surface in a thermally driven process. Furthermore, it is not yet clear how the hydrogen leaves the surface. This could also be
6. Conclusion & outlook

Figure 6.1: The DSBAS molecule (SiH$_3$N(C$_4$H$_9$)$_2$) is similar to the BTBAS molecule, but has only one carbon-containing ligand instead of two.

thermal desorption. An experiment to observe the thermal desorption of HCN, H$_2$ and NH$_3$ is to deposit SiN on a sample, and ramp the temperature. By performing consecutive FTIR gas phase measurements (as described in Appendix A), the desorption of HCN and NH$_3$ as a function of temperature can be studied. For the detection of H$_2$, quadropole mass spectrometry (QMS) can be used.

• Change of precursor: DSBAS

One of the key observations of the SiN work with BTBAS is that at least some ligands remain after precursor adsorption, which are fragmentend by the plasma and can redeposit on the surface. This redeposition leads to films with high carbon content, especially at low temperatures. This could be reduced when a precursor is used that adsorbs in such a way that after precursor adsorption no carbon-containing ligands are present on the surface. For the DSBAS precursor (SiH$_3$N(C$_4$H$_9$)$_2$), which contains only one ligand (Figure 6.1), it is expected that the ligand leaves the surface upon precursor adsorption. Work of Van Drunen showed that films deposited in a similar ALD process using the DSBAS precursor yielded high quality films [39] containing less carbon contaminations than the BTBAS precursor. It is expected, that when infrared spectroscopy is used to study the DSBAS process, no CH peak will be observed at 2940 cm$^{-1}$. Also, the peak at 2080 cm$^{-1}$ should be less apparent. The absence of these two bands for the DSBAS process would confirm that the redeposition effect does not occur for this precursor.

• Improve the infrared setup

In this work, it was discussed that purge times of the ALD process have to be lengthened to allow time for infrared measurements. It was suggested that the used
6.2. Outlook

scan times inhibited the ALD growth. Therefore, it is advised to decrease the scan time per ALD cycle when the surface chemistry is studied. When the scan time per measurement is reduced (to for example 128 scans instead of 1024), it is expected that surface sites created during the half-cycles remain visible. However, to still be able to obtain a good signal-to-noise ratio, more consecutive cycles have to be measured. In this work, all half-cycles and all infrared measurement were started manually. The automation of the measurement and data processing is advised when large amount of cycles are used to obtain the surface spectra.

For in situ infrared measurements of ALD processes in general, it is advised that before a decision is made on the amount of used scans per cycle, the stability of the surface groups is investigated. This can be done in a simple in situ SE measurement, where the effect of increasing the purge times can be investigated.

- **Explore the functionality of the sample manipulator**

In this work, the sample manipulator was used to perform measurements in transmission mode and as a tool to provide the resistive heating. However, the opportunities of rotation of the substrate in the reactor were not explored. Performing infrared measurements under Brewster angle to optimize the in-coupled light can be investigated. Also, the influence of the orientation of the sample on the deposited films can be explored.
Dankwoord

Dat elk probleem op verschillende niveaus van complexiteit te beschrijven is, vind ik fascinerend. Daarom heb ik met ontzettend veel plezier colleges gevolgd van inspirerende docenten, die met passie vertelden over hun vakgebied. Maar zelf onderzoek doen, dat is een vak apart! Zonder de hulp en aanmoediging van de mensen om me heen was ik denk ik voor altijd weggekropen in mijn lab-baal-trui. Een woordje van dank is daarom wel op zijn plek.

Erwin, ik vind het bewonderenswaardig hoe enthousiast je kon worden van een berg met ruis, waarmee je mijn scepsis aan de kant veegde. Dat de dataset het verhaal compleet maakte kon ik toen pas zien. Hoe je zo scherp en op de hoogte kon blijven met de kleine beetjes informatie temidden van alle andere projecten die je begeleidt is me een raadsel. Ontzettend bedankt voor al je hulp!

Roger, jou wil ik graag bedanken voor al je hulp gedurende het jaar. Niet alleen was je een goede trouble-shooter als de ALD-I weer eens dienst weigerde, maar ook heb je me top geholpen met het herformuleren van moeilijke secties uit mijn thesis.

Chai, I’d like to thank you for performing the IR calculations which were essential for the peak assignment of the gas phase spectra and provided nice visual input. You may want to ask Maarten to do the ‘BTBAS dance’; a by-product of your calculations.

Janneke, Joris, Cristian en Caspar, jullie wil ik graag bedanken voor alle technische support en het oplappen van de reactor. Caspar, als het lab gevuld is met serieuze, geconcentreerde mensen, zijn jouw flauwe opmerkingen een verademing, bedankt daarvoor!

In het bijzonder wil ik Vincent bedanken. Meer dan je misschien in de gaten had hebben je peptalks me geholpen als ik er even klaar mee was. Je enthousiasme werkt aanstekelijk, of je het nou hebt over lasers, schorpioenen in de woestijn of paarden wassen.

Joris, Martijn en Maarten, ik zal jullie gaan missen. Bij gebrek aan bedankwoorden, laat ik het voorlopig hierbij.


Gillis, je verzette je hevig tegen mijn pogingen tot workaholic-schap, waarvoor ik je niet genoeg kan bedanken. Elke dag maak je me bewust van wat belangrijk is in het leven, bij jou kom ik tot rust en in balans. Laten we samen op reis gaan, naar de paadjes, Norbert mag mee.

Ik voel me ozo heppie
zo heppie deze dag.
en als je vraagt: wat heppie
als ik eens vragen mag,
dan zeg ik: hoe wat heppie,
wat heppik aan die vraag,
heppie nooit dat heppieje
dat ik hep vandaag?

– Joke van Leeuwen, Ozo heppie
6.2. Outlook
6. Conclusion & outlook
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Appendix A

Stability of gas phase species
Appendix A: Gas phase species

Gas phase measurements show volatile species that are not incorporated in the film, such as reaction products and excess precursors and reactants that remain after the surface is saturated. For gas phase measurements, the process is operated without a mounted substrate in the IR beam path. The walls are kept at a constant temperature of 80-100 °C and serve as a substrate for the deposition. This large reactive surface results in a high concentration of volatile by-products, which can be measured with FTIR. To confine the gas phase species in the reactor, the bottom valve is closed during dosing of the reactant. Note that because the plasma cannot be operated without a nitrogen flow and maximal pumping, gas phase reaction products of the plasma half-cycle cannot be measured.

For the precursor step, the measurement scheme is illustrated in Figure A.1. First, a nitrogen plasma was run to activate the walls of the reactor. To assure optimal activation, this plasma was run for 150 seconds. When the base pressure of $\sim 6 \cdot 10^{-6}$ was reached, the bottom valve was closed after which the reference spectrum $I_0$ was recorded. Then, a high concentration of BTBAS was dosed, to ensure the presence of both precursor and reaction product volatile species during the measurement. Directly after this dose, eight consecutive FTIR measurements were started, to create a time resolved evolution of the gas phase species. Each measurement consisted of 256 scans at resolution 6 cm$^{-1}$, lasting for 1 minute and 40 seconds.

Figure A.2 shows a schematic of this evolution. At $t = 0$, on the left, BTBAS is dosed and the chamber is filled with both precursor and reaction products. However, as time proceeds, all of the precursor molecules react with the wall and the reaction chamber is filled with reaction products.

In figure A.3, the FTIR spectra of the measurement are shown. Over time, peaks around 2140 cm$^{-1}$ and 931 cm$^{-1}$ are disappearing, whereas a peak at 811 cm$^{-1}$ appears. These bands are associated with the SiH$_2$ stretching, SiN stretching and NH$_2$ bending modes, respectively. As BTBAS is the donor of silicon atoms in the ALD process, all bands assigned to silicon modes belong to precursor volatile species. Disappearance of these modes over time show that indeed all BTBAS molecules have reacted at the end of the experiment.

It is remarkable that all precursor molecules react over the full duration of the exper-
Figure A.2: Over time, the BTBAS molecule reacts with the reactor walls and the vessel is filled with reactive species.

Figure A.3: The evolution of the volatile species in the reactor over time. Bands associated with the BTBAS molecule (SiH (2140 cm$^{-1}$) and SiN (931 cm$^{-1}$) disappeared, whereas a band at 811 cm$^{-1}$, assigned to the NH$_2$ bending mode of the reaction product, appeared.
iment (12 minutes). The self-limiting character of the ALD processes should imply that reaction stops after saturation. This result either shows that BTBAS is not self-limiting (within the time scales of an ALD cycle)[19], or that in this experiment, due to the long time scale, new reactive sites are created for precursor adsorption.
Appendix B

Resistive heating
The heating electrical circuit consists of an Eurotherm controller, a 24V DC power supply, a 230V AC power supply, the sample in the manipulator (M) and three relays, as shown in Figure B.1. The Eurotherm controller, with output of 12V DC, switches the NEC relay. When this relay is switched, the 24 DC power supply is connected to two relays which switch simultaneously. The large Crydon relay has three switches, of which two are used to connect the sample in the manipulator (M) to the 230V AC power supply. The third switch is not connected.

The Siemens relay switches the grounding of the substrate. This relay is normally closed, such that when the heating is turned off, the sample is grounded. When the Eurotherm gives a heating pulse, the grounding is disconnected. The 500Ω resistor between the sample and the grounding is introduced to dissipate any electrical current when the grounding is connected. Finally, the switch between the Siemens relay and ground is a manual switch which can be used to operate the heating in floating or grounded configuration.

The current through the sample is limited with two PTC’s. As a cost-efficient PTC resistor equivalent with a fast electrical response, two light bulbs of 100 W are used.
Appendix C

RBS and infrared results for all measurements
This appendix provides all infrared surface spectra, as well as the RBS and SE data.

For the depositions at 85°C, the standard recipe was used, with a precursor dose of 300 ms and a plasma exposure time of 15 s, to ensure saturated ALD growth. The sample was heated passively using wall heating. The walls of the reactor vessel were set to 100°C. During the ALD process, the thermal contact increased and the sample was heated further. When the infrared measurements were performed, the temperature was at the base level of 85°C. The advantage of using wall heating instead of manipulator heating is that effects of the heating method on the detectable surface groups can be excluded. The sample is grounded, such that interaction with the plasma does not cause buildup of charge.

The infrared measurements after 100, 500 and 1000 cycles for depositions at 85, 155 and 275°C can be found in Figure C.1. The RBS and SE data of the depositions can be found in Table C.1.
Appendix C. RBS and infrared results for all measurements

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{155°C, 100 cycles}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig2.png}
\caption{155°C, 500 cycles}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{155°C, 1000 cycles}
\end{figure}
Figure C.1: The infrared measurements after 100, 500 and 1000 cycles for depositions at 85, 155 and 275°C
Table C.1: Material properties as determined by SE, RBS and ERD.

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