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Modulated beam threshold ionization mass spectrometry radical detection in the NH₃/Ar and NH₃/SiH₄/Ar plasma

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Modulated Beam Threshold Ionization Mass Spectrometry:
Radical detection in the \( \text{NH}_3/\text{Ar} \) and \( \text{NH}_3/\text{SiH}_4/\text{Ar} \) plasma

J.L. van Hemmen
Summary

Threshold Ionization Mass Spectrometry (TIMS), together with a triple stage differentially pumped sampling system, was used in this study to measure absolute particle densities in the NH3/Ar and NH3/SiH4/Ar Expanding Thermal Plasma (ETP). The setup and the sampling system were studied to obtain deeper insight into the relation between the TIMS signal and the density of a certain species in the plasma.

In the differentially pumped stages a molecular beam is formed which is subsequently detected by a mass spectrometer, located in the third stage and in line-of-sight with the plasma. Particles build up background densities in the three stages of the sampling system and the third stage background density will also be detected by the mass spectrometer. The background densities were calculated, assuming molecular flow, to obtain a theoretical relation for the beam-to-background ratio. The calculated densities and the beam-to-background relation were verified by pressure measurements in two of the three stages and mass dependent beam-to-background ratios measured, ranging from approximately 0.1 for H2 and 1 for Ar. Furthermore, beam attenuation effects could be explained by collisions between beam and background particles in the first stage of the sampling system.

Important aspects of the QMS are investigated in order to obtain a calibration procedure for determining absolute densities of radicals and stable gases. An important improvement to the setup was a chopper implemented to modulate the molecular beam. This made it possible to determine the background contribution to the signal. Chopping also led to background modulation of the ionizer density and it was found that the modulation frequency should be at least 50Hz and preferably be as high as 100Hz in order to do a correct background measurement.

The insights into the TIMS setup and the triple stage sampling system were used to perform measurements on the NH3/Ar and NH3/SiH4/Ar plasmas. First the feasibility of detecting NHx and SiHx radicals was investigated, using beam modulation. N, NH2, Si, SiH, and SiH2 were successfully detected. The signals were analyzed and ionization potentials of the detected radicals, as well as the appearance potentials of dissociative ionization processes, were determined.

Absolute N radical densities were measured in the NH3/Ar and NH3/SiH4/Ar plasma at different reactor conditions to supplement previous Cavity Ringdown Spectroscopy data. The N density was found to be in the order of $3 \cdot 10^{18}$ m$^{-3}$ in the NH3/Ar and $5 \cdot 10^{18}$ m$^{-3}$ in the NH3/SiH4/Ar plasma, whereas the total gas density is approximately $5 \cdot 10^{21}$ m$^{-3}$. Trend and densities of the N radicals were compared with NH and NH2 radicals and possible reaction mechanisms in the plasma were suggested. It was found that the N radical density depends on surface conditions. Further analysis showed that an a-SiNx:H surface had approximately 1% recombination probability of N, three times smaller than the estimated surface recombination probability for N on a stainless steel surface. Furthermore the sticking probability for N, during a-SiNx:H growth, was estimated to be approximately 1%, equal to the recombination probability of N on an a-SiNx:H surface. This sticking coefficient of 1% leads to the conclusion that approximately 6% of the N atoms, incorporated in an a-SiNx:H film, is due to incorporation of N radicals.

Finally, to obtain further insight into the plasma, absolute densities of NH3, N2, and H2 as well as the depletion of the precursors were determined in the NH3/Ar and NH3/SiH4/Ar plasma for different flow settings. The results were discussed and we found that in the NH3/Ar plasma, H2 and especially the N2 production can be related to the consumption of NH3, while production of other stable gasses was not observed.
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1 Introduction

1.1 Technology assessment

Plasmas are frequently used as a tool in various industrial production processes and have a vast amount of applications. NH₃ plasmas for instance are used for surface nitridation [Lai2002] [Wan2003], passivation [Ayd1993] [Yu2003] and modification, changing properties like, wetability and biocompatibility [Kle1991] [Kur2002]. Other examples are modification of the catalyst surface for the production of carbon nanotubes [Cho2003] and ligand abstraction and nitridation in atomic layer deposition [Lee2004] [Sim2004] [Kwo2004].

If SiH₄ is added to the NH₃/Ar plasma deposition of a-SiNₓ:H occurs at surfaces containing the plasma. a-SiNₓ:H has a wide range of tunable properties depending on their chemical composition, e.g. band gap, refractive index, dielectric constant and stress. Therefore, a-SiNₓ:H is suitable for very diverse applications. For example, in the semiconductor device technology a-SiNₓ:H is used for insulation, mechanical protection, device passivation, as a dielectric [Gup1991] and as etch stop for both wet etching and plasma etching [Gha2004]. In solar cell technology his material can be used as an antireflection coating [Hab1994]. Furthermore, because of the diffusion-limiting properties of a-SiNₓ:H, it can be used as an encapsulating film that protects materials against oxidation and diffusion [Has1986] [Ose1988] [Str2002].

It is in general very useful to know what densities species have because one can relate them to production and loss processes, thus obtaining deeper insight into the plasma. Radicals are very reactive particles and therefore very important in plasma processes, which makes it even more relevant to know their densities. However, the reactivity of radicals results in high loss rates, which leads to relatively low densities. Therefore sensitive techniques have to be used to determine their densities. Cavity Ringdown Spectroscopy (CRDS) [Eng1999] [Bus1999] [Kes2001] is one of the possible techniques that can be used. However some radicals like N cannot be detected easily, because to electronically excite the N radical, one would need high energy photons (VUV), which (if practically realizable at all) leads to very high demands on the setup. To determine N radical densities Two-photon Absorption Laser Induced Fluorescence (TALIF) spectroscopy could be used [Ada1998]. However, this technique needs a large and complicated laser and detection system as is the case for CRDS. In this study molecular beam sampling and Threshold Ionization Mass Spectrometry (TIMS) is used. TIMS is based on mass spectrometry and is able to detect radicals [Sin1999] [Kae1995] [Ben2005] [Ar2003] [Kes2000]. With a proper calibration, radical densities can be determined absolutely with TIMS. Furthermore, this technique is very versatile in the sense that a lot of different particles can be detected without changing the setup to large extent. This makes TIMS a very powerful diagnostic to get deeper insight into plasmas, in this study the NH₃/Ar and SiH₄/NH₃/Ar plasma Expanding Thermal Plasma.
1.2 ETP plasma

The Expanding Thermal Plasma was used in this study with precursors NH$_3$/Ar and NH$_3$/SiH$_4$/Ar. The main characteristics of the ETP will be given here and more information can be found in previous publications [San1994] [Gie1997] [San1998]. The ETP consists of a cascaded arc, where an Ar discharge is induced by applying a DC current between anode and cathode, creating a plasma with 3-10% ionization degree. The plasma expands supersonically through a nozzle into a reactor vessel, see Figure 1.1. This makes it a remote plasma because the source, located outside the reactor and far from the substrate, is not influenced by downstream properties. After a stationary shock, the beam continues subsonically. The electron temperature in the plasma decreases due to the expansion from roughly 1 eV to 0.3 eV. Due to this low electron temperature, there is only a low plasma sheath voltage and low ion bombardment of the substrate. The NH$_3$ is added in the nozzle and SiH$_4$ is added through a ring approximately 7 cm after the nozzle exit. Typical flows used in this study are 55 sccs Ar, 0 to 16.67 sccs NH$_3$ and 0 to 5 sccs SiH$_4$. The arc current was usually set to 45 A or 75 A and the typical reactor pressure was 0.2 mbar.

![Figure 1.1 Schematic of the depo 2 reactor with substrate holder](image)

1.3 TIMS

To understand the principle of Threshold ionization Mass Spectrometry (TIMS), N radicals created in a N$_2$/Ar plasma are used as an example. The heart of this technique is a Mass Spectrometer (MS). In the MS ionizer first ions are created by ionization of the neutral particles from the reactor. The flux of ions enters the MS mass filter which selects ions, with the desired mass-to-charge ratio $m/e$ (=14 amu in the case of N$^+$). The selected ions are subsequently detected. In the case of a N$_2$/Ar plasma there are two processes that can lead to ions with $m/e$=14 amu: Direct ionization of N radicals leading to $N^+$:

$$N + e^- \rightarrow N^+ + 2e^- \quad E > E_1,$$

(1.1)
and dissociative ionization of \( \text{N}_2 \) leading to \( \text{N}^{**} \):

\[
\text{N}_2 + e^- \rightarrow \text{N}^+ + \text{N} + 2e^- \quad E > E_2.
\]

(1.2)

\( E_1 \) and \( E_2 \) are the electron energies \( E \) required for the reaction to take place. In the case of dissociative ionization, Reaction (1.2), an N-N bond needs to be broken. This means that dissociative ionization of \( \text{N}_2 \) will need electrons with a higher energy \( E_2 \) than the energy \( E_1 \) needed for direct ionization of \( \text{N} \), Equation (1.1). The amount of ionizations taking place will depend linearly on the density of the particles in the MS ionizer. Usually, in mass spectrometry, electron energies of approximately 70 eV are used to obtain a high signal (typically the electron impact ionization cross section has a maximum near this electron energy). However, both direct ionization of \( \text{N} \) radicals as well as dissociative ionization of \( \text{N}_2 \) occur at 70 eV and it is not possible to determine which detected ion is produced due to \( \text{N} \) radicals and which due to \( \text{N}_2 \). Furthermore, the density of \( \text{N} \) radicals is usually considerably smaller than the density of stable \( \text{N}_2 \) molecules and the signal due to dissociative ionization can overshadow the signal due to direct ionization completely.

TIMS can be used to measure radicals because it uses the fact that direct and dissociative ionization occur at different energies. The electron energy is increased in small increments, see Figure 1.2. When the electron energy becomes high enough for direct ionization, at the threshold \( E_1 = 15.2 \) eV, a signal starts to appear. However, dissociative ionization is not observed at energies lower than \( E_2 < 25 \) eV. The signal measured between the threshold \( E_1 \) and \( E_2 \) is therefore due to ionization of radicals, in this case \( \text{N} \).

![Figure 1.2 Electron energy scan of the m/e=14amu signal of a \( \text{N}_2/\text{Ar} \) plasma. Direct ionization of \( \text{N} \) occurs when the plasma is on and the electron energy is higher than the threshold energy of 15.2 eV. The plasma-off signal is zero up to approximately 25 eV indicating that no \( \text{N} \) radicals are detected. After reaching 25 eV, both the plasma-on as the plasma-off signal show an additional signal due to dissociative ionization of \( \text{N}_2 \).](image)

*Note that double ionization of \( \text{N}_2 \) leading to \( \text{N}_2^{**} \) \( (m/e=14 \text{ amu}) \) is not taken into consideration because it is an unlikely process and only occurs at high electron energies \( (>27.2 \text{ eV}) \).
1.4 Current status

Usually, in mass spectrometry the plasma is sampled from a volume that is connected to the reactor chamber. As mentioned before, radicals are low in density and very reactive at surfaces and sometimes also in the volume. This means that the particles need to be detected in line of sight from the plasma and the background densities needs to be reduced. Therefore, the mass spectrometer (MS) used for TIMS is placed in a triple stage differentially pumped housing that creates a molecular beam, which is sampled by the MS, and reduces the background density in the MS ionizer. This triple stage sampling system was designed previously by Jan Benedikt [Ben2004], based on an earlier single stage setup [Kes2000] and a triple stage differentially pumped setup designed by Agarwal [Arg2003]. Benedikt used the setup to detect reactive species in a C_2H_4/Ar ETP [Ben2005].

A chopper was located in the setup to correct the MS signal for background density contributions to the signal by subtracting the signal measured when the chopper was in its blocking position from the signal measured when the chopper was in its open position. However because the chopper was not located in the same stage as the MS, background modulation occurred, i.e. the net beam component of the signal could not directly be obtained by subtracting the chopper blocking from the chopper open signal because the background changed between these two measurements. To correct for this the measured background signal was scaled with a residual gas analyzer (RGA), connected to the same stage as where the MS was located.

1.5 Goal of the project

The purpose of this study is twofold. First of all, the goal is to get deeper insight into the characteristics of the TIMS setup. This knowledge is then used to obtain better understanding of the NH_3/Ar and NH_3/SiH_4/Ar plasma volume and surface processes. Focus will be on the following research questions, which are divided into a TIMS and a plasma related part:

**Questions related to TIMS:**
1. What is the relation between the measured signal in relation to particle densities in the reactor and what are the background contributions to the signal?
2. How can beam chopping, used to correct for background signals, be implemented in the setup and what are important aspects that need to be considered?
3. What modifications can be made in the calibration procedure to better determine absolute (radical) densities?

**Questions related to the NH_3/Ar and NH_3/SiH_4/Ar plasmas:**
4. Is NH_x and SiH_x radical detection possible in the NH_3/Ar and NH_3/SiH_4/Ar plasma with TIMS and the chopping procedure? What might be possible causes when detection is not possible?
5. What are the absolute N radical densities in the NH_3/Ar and NH_3/SiH_4/Ar plasma and can the data be used to get insight into questions like: What is the wall reaction probability of radicals, at different conditions?
6. What are the absolute densities of stable gases produced in the NH_3/Ar and NH_3/SiH_4/Ar plasma? Can these densities be related to the consumption of the precursors?
1.6 Outline

In Chapter 2 the experimental setup of the triple stage pumped TIMS system is given. Important properties of the Quadrupole Mass Spectrometer will be discussed resulting in a relation between signal and ionizer density. The chopping procedure will be discussed to get a better insight and to see what is necessary to use this procedure correctly. Chapter 3 discusses the molecular beam formation and the densities in the three differentially pumped stages. A relation is derived between the ionizer density and the reactor density, assuming molecular flow. Beam attenuation effects and the error due to the molecular flow assumption will be discussed qualitatively. In Chapter 4, to show the versatility and possibilities of TIMS setup, radical detection on the plasmas under investigation is performed. The feasibility of detecting different radicals in the NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasma is checked. Furthermore, the calibration procedure for absolute density determination is presented, using N as an example. The insights given by Chapter 2 to 4 will be used to determine absolute N radical densities in the NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasmas in Chapter 5. In Chapter 5 also stable gas measurements will be presented. Data will be discussed together with previous NH and NH$_2$ measurements to answer some concrete questions about the NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasma and to get insight into e.g. surface reaction probabilities. Finally in Chapter 6 the general conclusions will be given.
2 Experimental setup

The Threshold Ionization Mass Spectrometry (TIMS) setup will be discussed resulting in a relation between the Mass spectrometer signal and ionizer density. Furthermore, a procedure will be presented that will make it possible to determine background contributions to the signal with a chopper. Figure 2.1 shows a schematic of the experimental setup.

Figure 2.1 Schematic of the TIMS setup and the reactor Depo 2

An Expanding Thermal Plasma (ETP) is created in a reactor vessel as described in Chapter 1. For deposition usually a substrate holder is located 38 cm from the (ETP) source, but in this study it is exchanged for the TIMS setup. The Expanding Thermal Plasma (ETP) is sampled through a 0.8 mm diameter orifice. The position of the sampling orifice is 45 mm off the centerline axis at a distance of 51 cm from the ETP source. A triple stage differentially pumped system, see Figure 2.1 and Figure 2.2, creates a high

Figure 2.2 Detailed schematic of the mass spectrometer triple stage housing.
intensity molecular beam stage while maintaining a low \((10^{-7}\) mbar\) pressure in the third stage. The molecular beam is sampled in the third stage with a line-of-sight Quadruple Mass Spectrometer (QMS, Hiden Analytical EPIC 300 PSM upgrade with Bessel box analyzer). The second and third pumping stages are equipped with two Penning ionization pressure gauges.

This configuration was designed and used earlier by Benedikt on a different reactor [Ben2004]. As explained in Chapter 1, a chopper (Caburn SM32MC9-UHV) was located in the second stage to determine, together with third stage residual gas analysis, the background contribution to the QMS signal. Benedikt found that if chopping could be performed fast enough, i.e. fast beam modulation, no third stage residual gas analysis was necessary because the background would not be modulated. A new chopper blade design and mounting have been implemented to increase the chop frequency at similar rotation speeds of the motor. In the following sections the setup will be investigated further. First the principles of the mass spectrometer will be explained.

2.1 Hiden QMS probe

The QMS is used to separate and detect the particles sampled from the reactor vessel. It consists of a probe containing an ionizer, a Bessel Box energy filter, a quadrupole mass analyzer and a channeltron detector, see Figure 2.3. An Amplifier head connects the probe to the Mass Spectrometer Interface Unit (MSIU). This interface unit is connected to a computer. The QMS is controlled with MASsoft, software provided by Hiden Analytical. The so called environment in MASsoft is used to set the environment variables. The environment variables are uploaded to the MSIU at the beginning of each experiment and determine the acquisition modes and parameters of the QMS. These variables will be denoted italic throughout this report.

To mass-separate neutral particles with electromagnetic fields in the quadrupole, first electron impact ionization (EII) takes place in the ionizer cage, which was replaced at the beginning of this study. The new ionizer has a finer metal grid to increase the number of particles entering the ionizer and it has larger openings to decrease the residence time. A filament is heated, generating an electron emission current \(I_{e}(s^{-1})\) (emission). The filament

\[
\text{Figure 2.3 QMS probe consisting, from right to left, of the ionizer, the Bessel box, the mass filter and the detector.}
\]
Experimental setup

The experimental setup 13 temperature and subsequently the electron emission current are controlled by a feedback loop in the Amplifier Head. To prevent nonlinear effects due to build up of space charge the emission current is never set higher than 80 μA (Appendix A). The electrons are accelerated into the ionizer cage by an electric field determined by the electron energy potential. The resulting electron energy distribution has a full width half mean of approximately 0.5 eV. The ion current generated from species $i$ in the ionizer depends on the electron energy because the electron impact ionization cross section $\sigma$ is energy dependent. The amount of ions produced is linear dependent on the ionizer cage length $l_{\text{ionizer}}$, the electron emission current $I_{e}$ (s$^{-1}$) and the density of the species in the ionizer cage $n_{i,\text{ionizer}}$. The ions produced in the ionizer are extracted with extraction efficiency $\beta$. The ionizer cage and the filament are at a 3 V cage potential above ground to increase the extraction efficiency, i.e. to increase the number of positive ions entering the Bessel Box energy filter by keeping them from hitting the ionizer cage.

The Bessel Box energy filter acts as a photon shield thereby eliminating signal due to high energy photons hitting the detector. It consists of a cylinder at a certain cylinder potential, which is closed by two caps at certain endcap potential. Ions and photons move through a hole in the cap closest to the ionizer cage. In the middle of the ionizer there is a grid with a small center plate. Photons hit the plate and do not pass the analyzer while ions are deflected from the plate and focused on a hole in the second endcap. The Bessel Box has a certain mass-to-charge ratio dependent transmission efficiency $T_{B}(m/e)$.

After passing the Bessel box, the ions enter the quadrupole mass filter. The quadrupole has a pre and post filter to decrease the influence of fringing fields. By setting certain RF and DC voltages onto the rods of the mass filter [Lee1998], only a species with certain charge-to-mass ratio are selected. The quadrupole mass filter has a transport efficiency $T_{Q}(m/e)$.

Finally the ions are accelerated into the Secondary Electron Multiplier (SEM) channeltron detector by an electric field determined by the 1st-dynode voltage. The multiplier voltage across the channeltron determines the number of secondary electrons created. The channeltron has a mass-to-charge ratio dependent sensitivity $\theta(m/e)$. The SEM output current is amplified at the amplifier head and the signal is fed to a discriminator. The discriminator level is a percentage that determines the minimum current that is associated to an actual ion count. At the Mass Spectrometer interface Unit (MSIU) the discriminator signal is translated to a TTL (Transistor-Transistor-Logic) pulse and processed by pulse counting logics. The result can be read out by a computer.

Other environment variables mentioned here for completeness are 1) the extractor potential of a set of lenses located before the ionizer cage, which is set to a positive value in the present study to ensure that only neutrals enter the QMS, 2) the lens potential of a lens located before the Bessel box to increase the extraction efficiency, 3) the focus voltage of a lens that focuses the ions into the quadrupole mass filter and 4) the suppressor voltage of a lens located between the mass filter and the channeltron. Finally there are two sets of lenses located before and after the mass filter, one set is at ground potential and the other at a certain energy potential [Hid01].

We will take the Bessel box transmission efficiency $T_{B}(m/e)$ and the quadrupole mass filter efficiency $T_{Q}(m/e)$ into one transmission variable $T(m/e)$. Furthermore we will look only at single ionized species and the signal due to specie with density $n_{i}$ in the ionizer becomes [Sin2000]:

$$S_{i} = \beta T(m_{i})\theta(m_{i})l_{\text{ionizer}}I_{e}(E)n_{i,\text{ionizer}}$$

This equation will be used in Chapter 4 where the calibration procedure, that is used for absolute density measurements, is described.
2.2 Background Correction

In the triple stage differentially pumped QMS housing a molecular beam is formed from the particles present in the reactor vessel. Beam particles of species \(i\) have a certain density in the ionizer \(n_{i,\text{beam}}\). These particles will reside in the third stage for a certain time and also contribute to the background density in the ionizer. The total background density \(n_{i,\text{bg}}\) in the ionizer will also be due to species \(i\) diffusing from the second into the third stage and species \(i\) created in the third stage e.g. by pyrolysis at the hot filament. In Chapter 3 the relation between \(n_{i,\text{beam}}\) and \(n_{i,\text{bg}}\) and the density in the reactor \(n_{i,\text{o}}\) is given. For now it is important to note that only the beam density is linearly related to the density of particles in the reaction vessel, furthermore this relation is species and temperature independent. The background density in the ionizer depends on all kind of factors, e.g. temperature, species dependent pumping capacities and fluxes, wall absorption, conductance limitations and the amount of species \(i\) created due to pyrolysis of molecules at the emission filament. It is therefore necessary to correct for this background density if we want to determine absolute (radical) densities. A beam-to-background ratio can be used to obtain the beam contribution to the signal. However it is not always possible to determine this beam-to-background ratio and even if it is, the ratio might not be constant. Another way to correct for background contributions is by modulating the molecular beam. The background density then can be measured during the time the beam density is zero. In order to modulate the molecular beam a chopper driven by a stepper motor is implemented in the setup, see Figure 2.4. Due to geometrical constraints this chopper is not located in the third stage but in the second stage. The disadvantage of this location is that the background density will be modulated in time because the influx into the third stage is modulated. Quantitatively one can understand that if the residence time in the third differentially pumped stage is long compared to the modulation or chop time \(1/f_{\text{chop}}\) the background can be assumed constant. This means that at high shop frequencies a correct background measurement is done during the time the chopper is closed. However if the chop time is long compared to the residence time the background varies during a chopping period. The measurement done during the time the chopper blocks the beam will give an underestimation of the background signal and the measurement during the time the chopper is open will give an overestimation of the beam density because the background increases when the chopper is opened, this is further explained in subsection 2.2.2.

Figure 2.4 The chopper blade and motor are mounted on the third stage housing. The ceramic support for the IR LED and detector is located under the chopper blade.
2.2.1 Gating of the input signal

The MSIU HA 061-303/Q Analyser Control Board was upgraded with new EPROMs that made gating of the pulse counting logics possible. The pulse counting logics consists of two counters. When gating is off \((gating=0)\) only one counter is active and only the SEM detector can be selected in MASsoft. When gating is on \((gating=1)\) both counters are activated, one counter \((on\_ct)\) is used to count pulses when the chopper is open and the other \((off\_ct)\) is used to count when the chopper is blocking the beam. The on\_ct is addressed by the SEM detector and off\_ct is addressed by the background detector in MASsoft. The foreground detector gives the difference between both counters \((on\_ct-off\_ct)\). Depending on the integration time \((dwell)\) that is used, the MSIU will calculate the signal in units of counts per second and this signal can be monitored on the computer. The MSIU counters need to be gated with a TTL signal so that the on\_ct is activated when the chopper is open and the off\_ct is activated when the chopper is blocking the beam. This gating signal is generated by a Stanford DG535 delay generator. The delay generator is triggered when the aluminum chopper reflects the light of an infrared (IR) LED (Honeywell LED55C) into an IR detector (Honeywell SD5620). The LED and detector are placed in a non conducting ceramic holder, see Figure 2.4. Figure 2.5 shows the electric scheme of the IR LED and detector.

The stepper motor speed is set by a certain step frequency \(f_{\text{step}}\). By dividing \(f_{\text{step}}\) by the number of steps per revolution \((200)\) and multiplying by the number of holes in the chopper blade \((8)\), one obtains the chop frequency \(f_{\text{chop}}\). One wants to measure only when the chopper is either fully open or fully closed and discard the signal when the chopper blade is partially intercepting the molecular beam of nonzero width. By measuring the signal at different stepper motor positions, while maintaining a constant Ar pressure in the reactor, the delays \(A\) (start off\_ct), \(B\) (stop off\_ct), \(C\) (start on\_ct) and \(D\) (stop on\_ct) were determined to be 3, 10, 15 and 22 steps respectively. By multiplying these values with the time it takes the motor to make one step \((=1/f_{\text{step}})\) one obtains the equivalent delay times that can be entered into the delay generator; see Figure 2.6 for a visualization of the triggering procedure.

![Electric circuit of the IR LED and detector](image)

**Figure 2.5 Electric circuit of the IR LED and detector. The detector will generate a TTL high (5V) signal when the IR light of the LED is reflected by the chopper blade and illuminates the detector.**

* At the 24 pin D type connector at the back of the MSIU there is an analogue output. This output was previously used to measure the signal when chopping. However it was found that this output is a convolution of analogue unit pulses. Each unit pulse is generated when approximately 9 ion detections have taken place. The unit pulse has an amplitude of 2.3V and decays exponentially with a decay time of 0.43 ms. This analogue signal is therefore not suitable to use for fast chopping because it has bad time resolution, especially when the count rate is low.
2.2.2 Determination of the necessary chop frequency

As mentioned in the beginning of this section, the chop frequency has to be high enough to prevent any background modulation. The background density in the third stage \( n_{\text{bg}, i} \) of species \( i \) is determined by the effective pumping speed of the third stage \( S \), the volume \( V \) and the time dependent influx \( \Phi(t) \):

\[
\frac{dn_{\text{bg}, i}(t)}{dt} = -\frac{S}{V} n_{\text{bg}, i}(t) + \frac{\Phi(t)}{V}.
\]  

(2.2)

To get an insight in how the background density behaves when chopping at different chop frequencies \( f_{\text{chop}} \), the on\_ct, off\_ct and on\_ct-off\_ct signal due to a 0.2 mbar Ar gas in the reactor were measured as function of chop frequency, see Figure 2.7. The average influx (particles per second) is constant over one chop period and independent of \( f_{\text{chop}} \). This fact was used to correct for scatter due to pressure deviations in the reactor, by normalizing to the average number of counts in one period (on\_ct/2+off\_ct/2).

Figure 2.7 shows that at very low chopping frequencies the on\_ct signal has a maximum and the off\_ct signal has a minimum. Because of the low frequency, the background density in the third stage can be described by the steady state situation of Equation (2.2) for the duration that the chopper is either open or closed. The minimum value of the off\_ct can be explained by the fact that, when measuring during the time that the chopper blocks the beam, the influx of particles into the third stage is lowest, the density reached steady state and the molecular beam is absent in the ionizer. When the chopper is in its open position the beam is present in the ionizer. The background density however will be higher than is the case if the chopper is closed. The influx is at a maximum creating a maximum steady state background density; this explains that the on\_ct signal is highest for very low chop frequencies. By subtracting the off\_ct from the on\_ct one obtains the sum of the signal due to the beam density and the signal due to the density difference between the chopper open and chopper closed measurement. Therefore, the beam contribution to the signal is not measured correctly because the off\_ct will not represent a correct background measurement (despite the fact that off\_ct is addressed by background in MASsoft).

The off\_ct signal increases with chop frequency because the duration that the
Figure 2.7 Count rates of the on_ct (SEM), the off_ct (background) and the on_ct-off_ct (foreground) at different chop frequencies for Ar (filled points) and H₂ (open points)

chopper is closed becomes smaller compared to the time it takes to reach a steady state after closing the chopper. The on_ct signal decreases because the background density decreases. The chopper is only opened for a relatively short period of time compared to the time it takes the larger influx to increase the density throughout the volume of the third stage.

Finally a state is reached where the high chop frequency results in a more or less constant background density. The residence time $\tau = V/S$ has become large compared to the time it takes to complete a full chopping period. There will still be a fluctuation in the background density but this fluctuation is small or even negligible compared to the constant background that results from the average fluxes.

In Figure 2.7 also equivalent measurements on a H₂ gas (open points) are plotted and similar trends for the different detector signals can be observed. It is interesting to see that the background of H₂ is larger than the foreground signal. The main reason for this is that H₂ has a higher thermal velocity, resulting in higher fluxes and background densities; this will be further explained in Chapter 3.

The Ar foreground data points are fitted with a model derived in Appendix B. The model assumes an influx into the third stage described by a block function and subtracts the average density when the chopper is closed from the average density when the chopper is open. From this fit a residence time $\tau = 7.7 \pm 0.7$ ms is obtained, which is lower than expected if one assumes a pumping capacity of 30 ls⁻¹ and a volume of 1.7 l for the third stage, resulting in a residence time of 57 ms. However, if one uses effective pumping capacity of 20 ls⁻¹ (estimated lower due to third stage conductance limitations) and looks at the volume occupied by the first 10cm of the third stage (which is where the ionizer is located and which is the most narrow part of the third stage) a residence of 6 ms is estimated, which is in closer agreement with the measurement. Therefore, the difference in residence times can be explained by density gradients in the third stage due to conductance limitations. If the influx in the third stage is stopped the volume in the first 10cm of the third stage is vacated quicker then expected on basis of the total third stage volume and
pumping capacity, because of diffusion due to the density gradients.

In conclusion, if the chop frequency is high enough the chopper open signal, SEM, consist of a beam and a background contribution. The signal measured when the chopper is in the closed position, background, will consist of the same background contribution and the difference between the two, foreground, is the signal solely due to the beam component of the ionizer density. Looking at Figure 2.7 one can conclude that, at chopping frequency of approximately 50Hz, there is practically no contribution of background to the foreground signal anymore. Higher frequencies are preferred if the modulated background density is relatively high compared to the beam density, which might be the case if pyrolysis of a very abundant parent molecule occurs.

2.3 Mass transport efficiency

As mentioned in the beginning of Section 2.1, the Bessel box analyzer, the quadrupole and the detector have a certain mass-to-charge ratio dependent transmission efficiency. Together with the extraction efficiency these factors are collected into a single mass dependent mass discrimination factor $F(m)$:

$$F(m) = \beta T(m) \theta(m)$$  \hspace{1cm} (2.3)

It is important to know the relative mass discrimination factor to do a correct calibration for detection of radicals, which will be done Chapter 4. Therefore, the foreground signals of $\text{H}_2$, $\text{He}$, $\text{NH}_3$, $\text{N}_2$, $\text{O}_2$, $\text{Ar}$ and $\text{CF}_4$ were measured at 100Hz chopping frequency. The beam density and foreground signal are linearly related to the reactor density. This means that if the foreground signal is normalized to the cross section, the electron emission current and the density in the reactor vessel one has a relative measurement of the mass discrimination factor according to Equation (2.1), see Figure 2.8. The scatter in data can be explained by the error in the cross section data, references can be found in Table 2.1.

Note that $\text{CF}_4^+$ ($m=88$) is not a stable particle and therefore the dissociative ionization product $\text{CF}_3^+$ ($m=69$) was monitored. It is known that the extraction efficiency of dissociatively produced ions can be much lower than for ions produced by direct ionization. This is due to excess kinetic energy of dissociatively produced ions and the fact

![Figure 2.8 Mass discrimination factor determined for $\text{H}_2$, $\text{He}$, $\text{NH}_3$, $\text{N}_2$, $\text{O}_2$, $\text{Ar}$ and $\text{CF}_4$. Data of Benedikt is normalized to $\text{H}_2$.](image-url)
that the ion energy distribution is nonisotropic near the threshold. For this effect the CF$_4$ signal was corrected with experimental data of Singh et al. [Sin2000].

Before the Bessel box was installed Leewis measured the mass transport efficiency of the currently used QMS. Experimentally, he came to the conclusion that the mass discrimination factor should be proportional to the inverse of mass [Lee1998]. In Figure 2.8 the currently obtained data is fitted with a function inversely proportional to mass. As can be seen this inverse dependence does not predict the behavior of the mass discrimination factor well, this is most likely due to the implementation of the Bessel box. The behavior of the mass discrimination factor as function of mass is proposed to be of the form:

$$F(m) \propto \frac{1}{M^\alpha}.$$  \hspace{1cm} (2.4)

The factor $\alpha$ is determined to be $(0.29\pm0.06)$ by fitting the recently obtained data. The CF$_4$ measurement is discarded because there might be a large additional error in this data point due to the correction for low extraction efficiency.

Benedikt [Ben2004] also measured mass discrimination factors for H$_2$, He, CH$_4$, C$_2$H$_2$, O$_2$ and Kr at 0.29 mbar and 0.13 mbar when the Bessel box was already installed. His data was normalized to the H$_2$ value of the currently determined mass discrimination factor, to make comparison possible (we are not interested in the absolute discrimination factor). By fitting Benedikt's data up to 40 amu a value of $(0.33\pm0.03)$ is obtained for $\alpha$. These values are in agreement within their margin of error. The mass discrimination factor for CF$_4$ and Kr deviate from the fit, for CF$_4$ this can be explained by the additional error from correction for lower extraction efficiency. However, Kr$^+$ is created by direct ionization and no error due to correction of the extraction efficiency was necessary. It might be that a large error is present in the electron impact ionization cross section data of Kr. It might also be that the proposed form of Equation (2.4) does not hold at high masses, while it is in good agreement with masses up to 40 amu.

### Table 2.1 References of EII cross section data

<table>
<thead>
<tr>
<th>Gas</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>[NISTcs]</td>
</tr>
<tr>
<td>N$_2$</td>
<td>[Rap1965]</td>
</tr>
<tr>
<td>O$_2$</td>
<td>[Rap1965]</td>
</tr>
<tr>
<td>Ar</td>
<td>[Rap1965]</td>
</tr>
<tr>
<td>He</td>
<td>[Rap1965]</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>[Tar1997_2]</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>[Tor2002]</td>
</tr>
</tbody>
</table>

---

$^1$ Measurements of the signal of dissociative ionization of SiH$_4$ into SiH$_2^+$ and comparison with data in the graph showed an extraction efficiency equal to that of direct ionization products within the margin of error.
3 Molecular beam sampling

3.1 Molecular beam formation

In this chapter the ionizer density $n_{i, \text{ionizer}}$ of species $i$, which consists of a beam density $n_{i, \text{beam}}$ and a third stage background density $n_{i, \text{bg3}}$, will be related to the density of species $i$ in the reactor $n_{i, 0}$ by assuming molecular flow through the sampling orifice and in the differentially pumped stages. The densities in the differentially pumped stages will be calculated and a relation for the beam-to-background ratio is derived and evaluated. Beam sampling distortion that might cause deviation from the derived density relationship will be discussed and the relation between the ionizer density and reactor density will be modified to a relation that is valid if there are particle losses at the wall. Finally, errors due to the molecular flow approximation will be discussed.

![Figure 3.1 Dimensions of the pumping stages with pumping capacities for $N_2$.](image)

Figure 3.1 shows a schematic with the dimensions and pumping capacities of the differentially pumped stages in the beam sampling system. Particles enter the first stage through a sampling orifice with radius $R_1$. At the second orifice this particle flux is sampled, creating a molecular beam. The intensity of the molecular beam depends on the acceptance angle determined by the second orifice radius $R_2$ and the distance between the first and second stage $a$. This beam passes freely through the second stage and third orifice into the ionizer of the mass spectrometer. Besides beam formation the triple stage configuration also increases the beam-to-background ratio in the ionizer of the mass spectrometer. In order to determine a relationship between $n_{i, \text{ionizer}}$ and $n_{i, 0}$ free molecular flow is assumed at the sampling orifice. The main reason for this assumption is that the flow is closer to the free molecular flow regime than to the viscous regime, explained next.

The Knudsen number ($Kn$), the dimensionless ratio of the mean free path $\lambda$ of particles divided by the typical length scale of the setup, characterizes the flow. According to the kinetic gas theory, $\lambda$ is determined by the density $n$ and the collision diameter of particles $d_{\text{coll}}$. The Knudsen number can be calculated by using the orifice diameter $d$ as a typical length scale.

* Note that the density $n_{i, 0}$ is the density that is effectively sampled. This is the density just before the sampling orifice within approximately a mean free path distance and this density is equal to the reactor density if there is no considerable surface production or loss and the gas density is constant throughout the volume of the reactor.
Molecular beam sampling

\[ \lambda = \frac{1}{\sqrt{2\pi d_{\text{coll}}^2 n}} \quad ; \quad Kn = \frac{\lambda}{d} \]

\begin{align*}
\text{Table 3.1 Hard sphere diameters and mean free paths of different gases at } \rho &= 0.2 \text{ mbar and } T = 298 \text{ K} \\
\text{gas} & & \lambda [\text{mm}] & & Kn \\
\text{Ar} & 3.58 & 0.35 & 0.43 \\
\text{H}_2 & 2.71 & 0.62 & 0.78 \\
\text{NH}_3 & 4.32 & 0.24 & 0.30 \\
\text{N}_2 & 3.70 & 0.33 & 0.41
\end{align*}

For \( Kn < 0.01 \), the flow is viscous and if \( Kn > 1 \) the flow can be assumed molecular. If \( 0.01 < Kn < 1 \) the flow is neither molecular nor viscous and this regime is called transitional. In Table 3, the collision cross sections and mean free path lengths are shown for a number of gases at typical plasma-off reactor conditions (\( \rho = 0.2 \) mbar and \( T = 298 \text{ K} \)). The extraction orifice used in the current setup has a diameter of 0.8 mm and the corresponding \( Kn \) numbers are also shown in Table 3. It is clear that the flow will be neither fully molecular nor fully viscous but the Knudsen numbers indicate that the flow is indeed closer to the molecular regime. Note that if the gas temperature increases, the density will decrease resulting in higher \( Kn \) numbers (this happens when the plasma is turned on and the pressure is kept constant).

Looking at the mean free paths in Table 3.1, a small extraction orifice with a diameter of approximately 0.2 mm or smaller would result in a molecular flow for all gases because then \( Kn > 1 \) for all gases. If one uses these very small orifices not enough flow through the sampling orifice is obtained to detect low density particles from the reactor. A trade off between being able to assume molecular flow and wanting sufficient flow was made by choosing the currently used orifice diameter of 0.8 mm.

We will find that all gas in the three stages will behave molecular, except in the first stage when beam modulation occurs, which is discussed later. Because in the remainder of this chapter molecular flow is assumed, it is possible to derive a more general density relationship, whereas in the viscous flow regime one should take into account quite a number of (species dependent) beam composition distortion effects [Knu1995]. This is because, in a free molecular flow, sampled particles have no interaction with each other or with surfaces.

3.1.1 Derivation of orifice flux (\( Kn > 1 \))

A molecular flow through a small orifice is determined by collisionless effusion if the density on one side of the orifice is negligible compared to the density on the other side. The number of particles of species \( i \) in a volume element in the sampled volume is \( dV \) is \( n_0 dV \), where \( n_0 \) is the density in front of the orifice. The particles have a certain distance \( r \) to the center of the sampling orifice which is assumed to have infinitively small area \( dS \). All particles that have a velocity \( v \) reach

\[ \text{Figure 3.2 Schematic of effusion through area } dS. \]

\(^1\) In the ideal situation, the diameter is preferably even smaller; according to measurements by Stickney et al. [Sti1966] the flow through an orifice will be completely molecular if \( Kn = 20 \).

\(^2\) Beam distortion effect mainly occur in a supersonic free jet, which will be formed in the first stage if one is dealing with viscous flow and with a reactor pressure versus first stage pressure ratio that exceeds 2.1 [Sco1988]. This ratio is easily exceeded in sampling systems like the one used in this study.
the area $dS$ in time interval $[t, t+dt]$ when their distance is within $r=[vt, vt+vdt]$. If one assumes an isotropic velocity distribution, the fraction $dS \cos(\theta)/4\pi r^2$ (the solid angle) of total particle flow from the element $dV$ reaches area $dS$, see Figure 3.2. The number of particles $N$ passing through $dS$ in time interval $[t, t+dt]$ is obtained by integrating over the total volume sampled in this time interval. The sampled volume is the volume between a hemisphere with radius $v(t+dt)$ and a hemisphere with radius $vt$.

$$
dN = n_{i,0} \int_0^{2\pi} d\varphi \int_0^{\pi/2} dr \int_0^{r^2 \sin \theta \frac{dS}{4\pi r^2}} \cos \theta \frac{d\theta}{2} = \frac{1}{4} n_{i,0} v dS dt$$  

(3.2)

Dividing $dN$ by the area $dS$ and interval $dt$ results in the particle flux $\Phi$ at the origin. This evaluation is for one certain velocity and integrating over the velocity distribution $f(v)$, assuming isotropic and Maxwellian, will give the commonly known result [Woo1993]:

$$
\Phi = \int_0^\infty v f(v) \frac{dN}{dS dt} dv = \frac{1}{4} n_{i,0} \bar{v} ; \quad \bar{v} = \sqrt{\frac{8k_b T}{\pi m}},
$$  

(3.3)

where $\bar{v}$ is the average velocity of an Maxwellian velocity distribution, $k_b$ is the Boltzmann constant, $m$ is the mass of the particles under investigation and $T$ is the temperature.

### 3.1.2 Derivation of centerline flux ($Kn>1$)

To obtain the centerline flux at a certain distance $x$ from an orifice with radius $R$, the same approach can be used as above. The difference is that the integration is not done over a volume between two complete hemispheres but over a volume between two hemispheres with radii $vt$ and $v(t+dt)$ confined by angle $\theta'$, see Equation (3.4) and Figure 3.3. This is again for one particular velocity. And integration over the velocity distribution $f(v)$ will give the real flux [Cob1971].

$$
\Phi(x) = \frac{n_{i,0}}{\partial x} \int_0^\infty v f(v) \int_0^{2\pi} d\varphi \int_0^{\pi/2} dr \int_0^{r^2 \sin \theta \frac{1}{4\pi r^2}} \cos \theta \frac{d\theta}{2} = \frac{1}{4} n_{i,0} \bar{v} \frac{R^2}{R^2 + x^2}
$$  

(3.4)

### 3.1.3 Density related to flux

Per definition, density is related to flux by the local velocity distribution of particles. For example if one needs to know the centerline density immediately after the orifice ($0 \leq x << R$) the gas will have an isotropic velocity distribution, with the exception that no particles have a velocity directed into the high gas density regime. The relation between the centerline density and flux in this case is given by Equation (3.5) and result in a position independent density directly after the sampling orifice ($0 \leq x << R$).

$$
\frac{1}{2} n_i(x) \bar{v} = \Phi(x) \Rightarrow n_i(x) = \frac{n_{i,0}}{2} ; \quad 0 \leq x << R
$$  

(3.5)

At the centerline of the effusive flux further away from the sampling orifice ($x >> R$) however, the relation between density and flux is different. The particle velocity at will be approximately parallel to the centerline and when sampling the molecular beam through a small area perpendicular to the centerline the flux equals the velocity times the density resulting in a centerline density given by Equation (3.6).
Molecular beam sampling

\[ n_i(x) \Phi = \Phi(x) \Rightarrow n_i(x) = \frac{n_{i,0} R^2}{4 x^2} \quad x \gg R \]  

(3.6)

As one can see, the centerline beam density is independent of the kind of particles sampled and linearly related to the density \( n_{i,0} \) of the sampled volume. This centerline density will be used in the following sections.

3.2 Densities evaluated in different stages

In the following section we will analyze the density in the different stages. First it is verified that, if molecular flow is assumed, we are dealing with an effusive flow, i.e. the background density of species \( i \) in the first pumping stage \( n_{i, bg1} \) is low compared to the density in the reactor. Figure 3.1 shows that the second orifice is at a distance \( a=40 \text{mm} \) from the first orifice. The radius \( R_2 \) of the second orifice is much smaller than the distance \( a \) (\( R_2 \ll a \)). Due to this small acceptance angle most of the flow emanating from the first orifice will end up in the first pumping stage. The total flow through the first orifice is given by Equation (3.3) and together with the fact that the first stage pumping capacity \( S_1 \), \( n_{bg, 1} \) is given by:

\[ n_{i, bg1} = \frac{\Phi A_i}{S_1} = \frac{1}{4} n_{i,0} \frac{A_i}{S_1} = \frac{n_{i,0} \pi R^2}{4 S_1} \sqrt{\frac{8 k_B T}{\pi m}} \quad 0 < x < a. \]  

(3.7)

The effusive flow through the second orifice is neglected in this calculation because it is insignificant compared to the inflow. For a typical gas densities used or created in the reactor and even for temperatures up to 1500K the ratio \( n_{i, bg1} / n_{i,0} \) is below 1%. Therefore, we will assume effusive flow.

A small portion of the effusive flux through the sampling orifice moves through the first stage directly into the second stage and this flux will pass through the second stage and the third orifice into the ionizer cage. The density of this flux is the beam density \( n_{i, beam}(x) \). Because the radius \( R_1 \) of the second orifice is much smaller than the distance \( a \) (\( R_2 \ll a \)) a centerline approximation of the effusive flux may be used. After the second stage orifice, the distance \( x \) is much larger than the sampling orifice radius \( R_2 \) (\( x \gg R_2 \)) and the centerline density relation of Equation (3.6) can be used to determine the beam density \( n_{i, beam}(x) \) at position \( x \). The radius of the second orifice \( R_2 \) and the distance \( a \) determines the acceptance angle of the beam (\( R_2 / a < R_2 / h \)) and the beam area \( A_{beam}(x) \):

\[ n_{i, beam}(x) = \frac{n_{i,0} R^2}{4 x^2} \quad A_{beam}(x) = \pi \left( \frac{x R_2}{a} \right)^2. \]  

(3.8)

The area and density of the beam can now be determined in the ionizer, located at \( x=c \).

The background densities in the second and third stage (where the ionizer is located) will be calculated next. First stage background particles will effuse into the second stage, generating a background \( n_{i, bg2} \). Second stage background particles effuse again to the third stage creating a background pressure \( n_{i, bg3} \). Both these densities \( n_{i, bg2} \) and \( n_{i, bg3} \) can be calculated with Equation (3.7) by substituting \( n_{i,0} \) by the appropriate density, \( n_{i, bg1} \) and \( n_{i, bg2} \), pumping capacity \( S_1 \) by \( S_2 \) and \( S_3 \) and orifice radius \( R_1 \) by \( R_2 \) and \( R_3 \) respectively. A more general description of the \( m^{th} \) stage background is given by Singh et al.[Sin1999]:

\[ n_{i, bgm} = n_{i,0} \prod_{k=1}^{m} \frac{C_k}{S_k} \quad C_k = \frac{1}{4} \pi R_k^2 \sqrt{\frac{8 k_B T}{\pi m_i}}, \]  

(3.9)

where \( C_k \) is the conductance of the \( k^{th} \) orifice. Note that effusion of first and second stage background particles will increase the centerline density in the second and third stage,
which can be calculated with Equation (3.6) by substituting \( n_{i,0} \) with \( n_{i,bg1} \) and \( n_{i,bg2} \) respectively. However this additional centerline density is only significant in the very near proximity of the second and third orifice and can be neglected at the location of the ionizer.

Besides the calculated background densities, beam particles will end up in the third stage and introduce an additional beam background \( n_{i,beambg} \). This \( n_{i,beambg} \) is determined by the particle flow into the third stage at \( x=b \) and the third stage pumping capacity \( S_3 \):

\[
n_{i,beambg} = \frac{A_{beam}(b)n_{i,beam}(b)\bar{v}}{S_3}.
\] (3.10)

Figure 3.4 shows the sampling beam density \( n_{Ar, beam} \), the background density \( n_{Ar, bg} \) and the beam background \( n_{Ar, beambg} \) calculated for an Ar gas with a typical 0.2 mbar reactor pressure \( n_{Ar,0} \) of 0.2 mbar at \( T=293 \) K. (In Figure 3.4 the additional densities due to effusion at the second and third stage, which are neglected in the calculations, are added to the constant background densities \( n_{Ar,bg2} \) and \( n_{Ar,bg3} \) for completeness.) The pumping capacities are estimated to be 30 ls\(^{-1}\), 120 ls\(^{-1}\) and 20 ls\(^{-1}\) for the first, second and third stage respectively. These estimated effective pumping capacities are lower than the values specified in Figure 3.1 because of conductance limitations of the pumping system. The unit on the y-axis is in mbar, where 1 mbar corresponds to a density of \( 2.47 \times 10^{22} \) m\(^{-3}\) at room temperature (293K). The calculated second stage background pressure of \( n_{Ar,bg2}=6 \times 10^{-7} \) mbar is in fair agreement with Penning ionization gauge background pressure measurements \( (4 \times 10^{-7} \text{ mbar}) \) done when 0.2 mbar of Ar gas was present in the reactor vessel. The sum of the calculated third stage background \( n_{Ar,bg3} \) and beam background \( n_{Ar,beambg} \) pressure is \( 3 \times 10^{-7} \) mbar. This is in the same order of magnitude as the pressure measured \( (1 \times 10^{-7} \) mbar\). The differences in calculated and measured pressures can most likely be explained by density gradients (because especially the third stage pressure gauge is located close to the pump), errors in the pressure measurement and errors in the estimated pumping capacities.

![Figure 3.4 Centerline beam density, densities due to effusive fluxes out of the preceding stage and the additional beam density as function of distance x from the sampling orifice.](image)

\(^6\) Note that pressure readings of Penning ionization gauges need to be corrected depending on the gas that is present in the gauge. For Ar the measured pressure was multiplied by a factor of 0.8.
3.3 Beam-to-background ratio

To obtain a theoretical beam-to-background ratio $R$ one has to take into account that background particles will be present throughout the whole ionizer volume $V_{\text{ionizer}}$. The beam particles however fill a volume smaller than $V_{\text{ionizer}}$ and will therefore have a relative smaller contribution to the QMS signal. To correct for this fact, the beam density averaged over the whole of the ionizer volume and the theoretical beam-to-background ratio $R$, is given by:

$$R = \frac{V_{\text{beam}} \cdot n_{i,\text{beam}}}{V_{\text{ionizer}} \cdot n_{i,\text{bg}} + n_{i,\text{beambg}}} = \frac{A_{\text{beam}} (c) \cdot n_{i,\text{beam}}}{A_{\text{ionizer}} \cdot n_{i,\text{bg}} + n_{i,\text{beambg}}},$$

where the ionizer area $A_{\text{ionizer}} = 3.8 \cdot 10^{-5}$ m$^2$ and $c$ is the distance between sampling orifice and the center of the ionizer. Together with Equations (3.8), (3.9) and (3.10), given in the previous section, this leads to the following beam-to-background ratio $R$:

$$R = \frac{1}{A_{\text{ionizer}} \left[ \pi^2 a^2 R_s^2 \left( \frac{v}{v_s} \right)^{1} \right]},$$

where the first part between brackets is due to effusive background and the second part is due to the beam background. The average velocity is related to the inverse square of the mass of the particle, see Equation (3.9). $R$ will therefore depend on the mass of the particles. To verify this result, signals of a 0.2 mbar H$_2$, He, NH$_3$, N$_2$, SiH$_4$, O$_2$, Ar and CF$_4$ gas were measured at 100 Hz chop frequency. The foreground signal was divided by the background signal resulting in a beam-to-background ratio. Equation (3.12) is derived without taking into account chopping, thus taking the flow into the third stage to be not modulated. Therefore, to obtain the beam-to-background ratio from the measured beam-to-background ratios, the measured beam-to-background ratios are divided by a factor of two. This factor of two can be explained by assuming the influx when the chopper is closed to be negligible compared to the influx when the chopper is in its open position. The average influx when the chopper is open position, is then twice as large as the average influx when the beam is modulated with the chopper. Figure 3.5 shows the corrected beam-to-background ratios as well as a simulation of Equation (3.12).

The experimental data shows a general increase of the beam-to-background ratio with increasing masses up to 40 g/mol. However the increase seems not to continue at higher masses. The scatter in the data points might be explained by the fact that the pumping capacities depend on other factors than mass alone. The predicted beam-to-background ratios are mostly larger than the experimental data, which might be partially due to error in the estimated pumping capacities. Another source for error might be the fact that the measured beam-to-background ratios were reduced by a factor of two to obtain the beam-to-background ratio when no chopping is applied. The flux might not be completely stopped when the beam is blocked by the chopper, in which case the measured beam-to-background ratio should be divided by a number slightly less than two, leading to higher experimental data in better agreement with the predicted values. This however might be the case for low mass particles like H$_2$ and He because a large part of their background density is due to particles effusing from the second into the third stage. However, the reduction of the beam-to-background ratio by a factor of two will probably be correct for particles with high mass, because the background density of these species is mostly determined by beam influx.

The main reason for the over-prediction of beam-to-background ratios is thought to

**The definition of foreground and background signal have been explained in Chapter 2**
Figure 3.5 Beam-to-background measurements performed on H₂, He, NH₃, N₂, SiH₄, O₂, Ar and CF₄. The data is corrected for the fact that the average third stage influx is twice as high when no chopping is used. The solid line represents the
be due to the fact that the third stage pumping capacity is mass dependent, which will be
discussed next.

The beam-to-background relation of Equation (3.12) is mainly determined by the beam background \( n_{i,\text{beambg}} \), because effusive fluxes through the different stages become smaller due to the lower thermal velocity of particles of higher mass and \( n_{i,\text{bg}} \) becomes relatively small compared to \( n_{i,\text{beambg}} \). Neglecting the effusive background, Equation (3.12) becomes [Ben2004]:

\[
R = \frac{S_3}{A_{\text{ionizer}} V} 
\]  

The third stage pumping capacity \( S_3 \) can be approximated by assuming a pump with nominal pumping capacity \( S=56 \text{ l/s} \). The third stage conductance \( C \) between the pump and the ionizer can be estimated by taking a pipe with diameter \( d \) and length \( l \) that connects the pump to the third stage. The pipe has a certain conductance \( C \) [Han1989] and \( S_3 \) can be determined:

\[
S_3 = \frac{SC}{C+S}, \text{ with } C = \frac{\pi}{12} \frac{V}{l} d^2 \]  

Therefore, for particles with high masses and low thermal velocities, the pumping gets less efficient because the conductance is smaller. The mass dependent pumping capacity leads to a constant mass independent beam-to-background ratio in the limiting case where \( C<S \) (\( C \) is estimated to be 30 l/s for Ar) and \( S_3 \) is proportional to \( V \). This explains the fact that the beam-to-background is relatively low and constant for particles of large mass, e.g. \( R(\text{CF}_4 \text{ M}=88 \text{ g/mol}) \approx R(\text{Ar M}=40 \text{ g/mol}) \).

Finally, there can be another effect taking place that decreases the beam-to-background ratio and that is beam attenuation due to first stage particle collisions. This effect is discussed next and will be found to be of minor importance in explaining the deviation between data and model.
3.4 Beam attenuation

Beam particles in the first stage can collide with each other or with background particles if the mean free path is smaller than the distance a particles need to travel before reaching the second stage. Collisions can lead to scattering of beam particles into the first stage background resulting in beam attenuation. Indications for such a beam sampling effect became apparent when measuring the Ar signal and H$_2$ signals by changing their partial pressures but keeping the total pressure constant at 0.15 mbar, see Figure 3.6. (Note that in this experiment the beam was not modulated with the chopper.) The Ar signal does not depend linearly on its partial density and it decreases faster than what one might expect if the partial density of H$_2$ is increased. The same measurement with the Residual Gas Analyser connected to the reactor, which does not use a molecular beam to probe reactor densities, did give a linear behavior of signal versus partial pressure for Ar and H$_2$. This means that the effect cannot be explained by pumping velocity changes of the Depo2 reactor leading to specie enrichment. Therefore the most likely explanation is that beam attenuation occurs. Measurements with a shutter placed in front of the extraction orifice and measurements at different pressures, exclude the possibility that this effect is due to the Depo 2 gas expansion. To get an insight in what is the cause of this effect, the average number of collisions in the first stage is calculated.

The mean free path $\lambda_a$ of particles of species $a$ traveling in gas of species $b$ is given by Equation (3.15) [Hanl 1989]. Note that this equation is derived for an isotropic Maxwellian velocity distribution.

$$\lambda_a = \sqrt{2\pi n_a d_{\text{coll},a}^2 + \left(1 + \frac{v_b^2}{v_a^2}\right)n_b \frac{1}{4} (d_{\text{coll},a} + d_{\text{coll},b})^2}$$  (3.15)

Because $\lambda_a$ depends on the density, which in turn depends on the distance $x$ from the sampling orifice, the average number of collisions $\alpha_x$ can be calculated:

$\text{Figure 3.6 Signal versus partial pressure of an Ar/H}_2\text{ mixture, the total density is constant. The H}_2\text{ signal is linearly related to its partial density. The Ar signal is fitted exponentially, see text.}$
Evaluation of Equation (3.15) and (3.16), with typical particle densities in the second and third stage, leads to the conclusion that the mean free path is much larger than the traveled particle distance. This means that indeed only the first stage collisions need to be evaluated. The 0.15 mbar gas mixture at room temperature that consists of a fraction $X$ of H$_2$ and (1-$X$) Ar. The first stage pumping capacity is taken to be 30 l/s for both H$_2$ and Ar. Numerical calculation of the average number $\alpha_{H_2}$ of collisions of a H$_2$ molecule and the average number of collisions $\alpha_{Ar}$ of an Ar atom was done using the collision diameters of Table 3.1 and Equations (3.15) and (3.16), which leads to:

$$\alpha_{H_2} = 0.36 - 0.28(1-X)$$
$$\alpha_{Ar} = 0.14 + 1.4X. \tag{3.17}$$

From Equations (3.17) one can conclude that when increasing the partial density of H$_2$ (X), the number of collisions of Ar particles in the beam increases rapidly whereas the number of H$_2$ beam particles colliding with other particles decreases (less rapidly) when the partial density of Ar (1-X) increases. The main reason for this is the high thermal velocity of H$_2$, creating a high first stage background, and the velocity dependence of Equation (3.15). For H$_2$ a linear signal-density relationship is observed because nearly 93% of the H$_2$ signal is due to collision independent background density $n_{H_2, bg}$, see Figure 3.5. Furthermore, the average number of collisions is less dependent on $X$.

The Ar signal depends for 50% on the beam density $n_{Ar, beam}$ and its background contribution is mostly due to the beam influx in the third stage. Therefore the beam attenuation of Ar is clearly seen in this measurement. To understand the trend of Ar observed in Figure 3.6 one can take $\delta$ to be the number of collisions necessary for an Ar particle to be scattered from the beam into the background. When traveling a distance $dx'$ the decrease in the argon beam density $dn_{Ar, beam}$ is:

$$dn_{beam, Ar}(x') = -n_{Ar, beam}(x') \frac{dx'}{\lambda(x')} \Rightarrow \frac{dn_{Ar, beam}(x')}{n_{Ar, beam}(x')} = -\frac{dx'}{\lambda(x')} \delta.$$

Integration on both sides of the equation gives:

$$n_{beam, Ar}(a) = n_{beam, Ar}(0) \exp\left[-\frac{\alpha_{Ar}}{\delta}\right]. \tag{3.19}$$

Equation (3.19) was used to fit the Ar signal-density behavior in Figure 3.6. The fit shows that the trend of the data can be explained well by Equation (3.19). Note that in this section the particle velocity distribution was assumed isotropic and Maxwellian, which is not the case for beam particles colliding with other beam particles. It might also be that beam attenuation depends on if we are dealing with Ar-Ar collisions or Ar-H$_2$ collisions. Therefore the determined variables $\alpha_{Ar}$ and $\alpha_{Ar}$ probably are not very realistic ($\alpha_{Ar}/\delta$ determined by fitting was not in agreement with Equation (3.17)) but still useful for qualitative understanding.

Beam attenuation was only observed when working with H$_2$. This is, as explained, due to the high velocity of H$_2$ resulting in high first stage background and the velocity dependence in Equation (3.15). In early measurements, without chopper, the density of Ar and N$_2$ were measured with a calibrated baratron pressure gauge connected to a temporary vessel in front of the sampling orifice. The signals were found to be linear with partial density up to 0.2 mbar indicating that the beam intensity is linear with the density in the sampled volume and no beam distortion occurred. Therefore, to prevent such distortion effects, measurements and calibrations are best done with a majority gas of relatively high
mass like Ar, especially when working with H₂. Note that significant beam attenuation when measuring pure gases is expected to occur only for low mass particles like H₂ and He, so it does not, as suggested previously, explain the overestimation of the calculated beam-to-background ratio for high mass particles.

### 3.5 Relation ionizer versus wall density

Up to now the wall was silently assumed to reflect all particles. This resulted in zero density gradients at the surface where the orifice was located. The density \( n_{i,0} \) close (<\( \lambda \)) to the surface which actually determines the influx into the sampling orifice, was assumed to be equal to the reactor density. If particle loss takes place at the surface, there will be a deviation from the isotropic velocity distribution of particles near the surface. The centerline density of Equation (3.8) at distances \( x \) relatively far away from the sampling orifice needs to be modified. The flux to a surface, where a fraction \( \beta \) is lost of the incoming flux, is determined by Moth [Mot1960]†:

\[
\Phi_i = \frac{1}{4} n_{i,0} v \frac{1}{1 - \beta / 2}
\]

(3.20)

The factor \( 1/(1-\beta/2) \) is a result of the fact that because part of the particles are lost at the wall, relatively more particles are moving toward the surface. This means that to obtain the density relation when particle losses at the surface occur, the factor \( 1/(1-\beta/2) \) needs to be added in the beam density relationship:

\[
n_{i,\text{beam}}(x) = \frac{n_{i,0}}{4} \frac{R_i^2}{x^2} \frac{1}{1 - \beta / 2}
\]

(3.21)

In this study we will find that the reaction probability is very small at the surface (≤3%) which means that this effect can be neglected but it is presented here to complete the beam density relationship.

### 3.6 Transitional flow

The assumption of molecular flow can lead to errors in the analysis in this chapter. First of all, using a sampling orifice smaller than the mean free path will result in a surface density measurement. If the orifice is larger than the mean free path, there might be a partial convective flux into the orifice, which can lead to a density measurement above the surface. If the particles that need to be measured, e.g. radicals, are lost quickly at the surface, or in the volume just in front of the surface, this will lead to an overestimated density due to density gradients [Ben2005].

The flow through an orifice with the inverse Knudsen number [Sha2003], see Equation (3.18). \( W \) is the ratio between the transitional flow and molecular flow, \( n_i \) is the densities on the low pressure side of the orifice and \( n_o \) is the density on the high pressure side of the orifice, the constant \( A \approx 0.12 \) [Sha2003].

† To understand this relation assume the total surface density \( n_{i,0} \) to be build up out of a density \( n_i \) related to the incoming flux \( \Phi_{\text{in}} \) and a density \( n_{r} \) related to the outgoing flux \( \Phi_{\text{out}} \). Because the incoming flux \( \Phi_{\text{in}} \) has no velocity component directed away from the surface but is, besides that fact, isotropic the relation between density and flux is: \( \Phi_{\text{in}} = 1/2 n_i v \), where \( v \) is the average velocity. Similarly, the outgoing flux has no velocity component directed to the surface so \( \Phi_{\text{out}} = 1/2 n_r v \). A fraction \( \beta \) of the incoming flux is consumed so that means \( \Phi_{\text{out}} = (1-\beta) \Phi_{\text{in}} \). Adding up the two density components and using the relation between \( \Phi_{\text{in}} \) and \( \Phi_{\text{out}} \) result in \( n_{i,0} = n_i + n_r = 4 \Phi_{\text{in}} (1-\beta/2) v \rightarrow \Phi_{\text{in}} = 4n_{i,0} v (1-\beta/2) \)
\[ W = \left(1 - \frac{n_i}{n_0}\right) \left(1 + \frac{A}{Kn}\right) \approx \left(1 + \frac{A}{Kn}\right) \] (3.23)

The beam centerline density will also be higher in the transitional regime according to an equation similar to Equation (3.23). The dependence on the \( Kn \) number is however larger with values of \( A \) ranging from 0.23 to 0.45 [Sti1966]. Therefore, we would expect a density overestimate when using the molecular flow assumption. The increased flow into the first stage leads to additional background compared to the molecular model. The number of collisions of beam particles with background particles therefore probably will increase. Additional beam attenuation might decrease the centerline density, decreasing the amount of overestimation.

As noticed in the previous section, measurements of the density of Ar and N\(_2\) showed a linear signal-density relation up to reactor pressures of 0.2 mbar. It is also interesting to note that the QMS mass discrimination factors determined in Chapter 2 were measurements on pure gases. The presented data is consistent with that of Benedikt [Ben2004], who used an Ar majority gas and measured at two different pressures (Kn=0.28 and 0.63). This confirms that beam attenuation is probably not significant (except when dealing with large partial densities of low mass particles as explained in the previous section) and that there are no indications that transitional flow through the first stage orifice leads to density overestimations. The beam density can be assumed to be linearly related to the reactor density as given by the specie independent relation given in Equation (3.6)\(^\text{\dag}\).

\(^\text{\dag}\) An explanation for the fact that there is a larger flow when sampling in the transitional region might due to an additional velocity component directed into the low pressure side of the orifice. The signal will then not increase as much as expected because of the inverse velocity dependence of the residence time of beam particles in the ionizer [Don1996].
4 Radical detection and calibration procedure

4.1 \(NH_x(x \leq 2)\) detection in the Ar/NH\(_3\) plasma

In order to show the versatility of TIMS and the fast chopping method, the feasibility of measuring the radicals N, NH and NH\(_2\) in the Ar/NH\(_3\) plasma was investigated. These measurements were done on a plasma with 55 sccs Ar and 10 sccs NH\(_3\) plasma at constant pressure of 0.2 mbar and a high arc current of 75A. The settings are based on earlier CRDS measurements and are used to create sufficiently high radical densities so that the expected count rates will be high enough for detection [Oever]. Electron energy scans were carried out at the different mass-over-charge \((m/e)\) ratios. To correct for background contributions fast chopping was used and the SEM, background and foreground signals were all recorded. The electron energy step size was set to its minimum value of 0.1 eV to get the maximal energy resolution and the integration time (or dwell time) was set as high as possible to decrease noise. The used dwell times were limited by the chopper motor performance and will be noted in each experiment. The foreground signal of the plasma-on as well as plasma-off conditions will be presented, unless noted otherwise. The contributions of various species will be distinguished, the ionization and appearance potentials will be determined and any background contributions leading to noise in the foreground signal are investigated.

\(N\) \((m/e=14)\) Figure 4.1 shows the plasma-off and plasma-on foreground signal at \(m/e=14\). At low energies the plasma-on signal starts to increase whereas the plasma-off signal stays zero. The initial increase of the plasma-on signal can be attributed to the

![Figure 4.1 m/e=14, dwell time = 1000ms](image)

*These signals have been discussed in detail in Chapter 2. In short: The SEM signal is the signal measured when the sampling beam is not blocked by the chopper blade, background is the signal measured when the beam is intercepted and foreground is the difference between the two signals.*
ionization of ground state N radicals and starts at the ionization potential (IP) of 15.2±0.2 eV, which is determined by linear extrapolation of the near threshold regime. This ionization potential (IP) is in agreement with values from literature, see Appendix C, which shows that N radicals are detection successfully. The plasma-off signal remains zero up to an energy of 30±1 eV because N radicals are only created in the reactor when the plasma is on. The increase in signal after 30±1 eV is due to N+ created by dissociative ionization (DI) of NH3 under formation of 3H. The appearance potential (AP) at 30 eV is in agreement with the literature value of Märk (29.5±0.5 eV) within the margin of error. The plasma-off signal shows no increase of signal at 22.5 eV, the AP for DI of NH3 into N+, H2 and H (note that this AP is expected to be lower than DI of NH3 into N, H and H2 by at least 4.53 eV, the H-H binding energy) so apparently this process is unlikely to occur. At 25±1 eV an additional signal appears in the plasma-on signal. This cannot be due to DI of NH3 otherwise the plasma-off signal would also show an AP at this energy. The AP of 25±1 eV corresponds to literature values for DI of N2 into N+ and N, therefore this additional component to the plasma-on signal is most likely due to N2 molecules created when the plasma is on. DI of NH3 into N+ cannot be distinguished in the plasma-on signal because of low NH3 density due to consumption\textsuperscript{1}.

\[ \text{NH (m/e=15)} \]

Figure 4.2a shows an electron energy scan made at m/e=15 amu. DI of NH3 into NH and H2 is distinguished in the plasma-off signal at 21±1 eV and DI of NH3 into NH and 2H is visible at 26±2 eV for both plasma-on as well as plasma-off. These values agree with literature and the difference between the two measured AP's can be explained by the binding energy of an H-H bond (4.53 eV). A signal due NH radical can not be distinguished at energies higher than its ionization energy of 13 eV because of scatter in the data points. In general the scatter can be attributed to third stage background particles, in this case either NH created by pyrolysis of NH3 at the hot electron emitting filament, or other species with the same mass-to-charge ratio m/e=15 amu when ionized. The background measurement (not shown) at this m/e indicated that there was indeed a background species and reducing the NH3 flow to zero also showed that the signal was not due to ionization of NH present in the background.

In Figure 4.2b a scan at m/e=15 amu and lower electron energies is shown. The measurement was done without the use of the chopper which made longer integration times possible (5000 ms). Although slightly different plasma settings were used, still this measurement can be used to detect and identify the particle responsible for the background signal. The scan clearly shows a signal with an AP of 9.7±0.4 eV. This energy corresponds to the ionization energy of the CH3 radical. It is therefore thought that pyrolysis of hydrocarbon molecules (e.g. generated from oil of the turbo pumps) occurs at the hot electron emitting filament. If CH3 is created and detected, other fractions of hydrocarbons are likely to be created too. Dissociative ionization of these fragments into CH3+ possibly explains the AP’s of 13.7±0.4 eV and 16.2±0.4 eV. At the latter energy the small super linear increase might also be due to the ionization cross sections versus energy behavior. The fact that the plasma-on signal is higher is not completely understood and a possible explanation might be an increased amount of hydrocarbon molecules desorbed from the third stage walls and components when the gas temperature increases. Note that the signal of CH3+ is in the order of 4000 cs\textsuperscript{1} at 18 eV. The chopper procedure effectively reduces this background contribution to the signal to zero with a scatter of less than 250 cs\textsuperscript{1}.

\textsuperscript{1} The partial ionization cross-section of N2 into N+ is high compared to the partial ionization cross-section of NH3 into N+ (≈4·10\textsuperscript{-2} Å\textsuperscript{2} [Strl1996] and ~1·10\textsuperscript{-3} Å\textsuperscript{2} [Mär1977] at 33 eV respectively). This makes it even more difficult to distinguish the appearance of DI of NH3 into N+. 
**Radical detection and calibration procedure**

4.5x10

• plasma off

2.5x10

• plasma on

- plasma on

1.5x10

- plasma off

1.0x10

- (b)

0.0

Figure 4.2 m/e=15 a) The plasma-off foreground signal at a dwell time of 1000 ms shows two AP due to DI of NH₃ into NH. Ionization of NH cannot be distinguished from the scatter in the plasma-on data points b) Both the plasma-on SEM signal and the plasma-off SEM signal, measured when the beam was not modulated with a dwell time of 5000 ms, indicate that ionization of CH₃ created by pyrolysis causes the scatter in the foreground signal.

NH₂ (m/e=16) Figure 4.3a shows a plot of an electron energy scan made at m/e=16 amu. Dissociative ionization of NH₃ into NH₂⁺ is visible at electron energies higher than the AP 17.0±0.3 eV. This AP is up to 0.7 eV higher than values from literature within the combined margin of errors. This can be explained by the fact that linear extrapolation can lead to an over-estimate of the AP if the behavior of the partial ionization cross section is super linear in the near threshold regime. This super linear behavior of NH₂ can also be found in partial ionization cross section data on ND₃ by Rejoub [Rej2001]. Note that the plasma-on signal is lower due consumption of NH₃. The depletion was determined by dividing the signal decrease when the plasma was turned on by the plasma-off signal at 24 eV and found to be 65%. In Figure 4.3b the low count rate signal is shown before dissociative ionization of NH₃ sets in. Ionization of NH₂ radicals is successfully observed and an IP of 11.5±0.5 eV is determined, in agreement with literature.

The scatter in the low NH₂ count rate might indicate that a background species contributes to the SEM signal. Investigation of the background signal and measurement with zero NH₃ flow revealed a third stage background contribution to the signal, which explains the scatter. These measurements showed that the background signal increased continuously by approximately a factor of ten during a period of 20 minutes. The long measurement times probably lead to heating of the third stage because of the hot ionizer filament. This heating leads in turn to wall desorption of primarily water. The background signal observed can be explained by ionization of O radicals created by pyrolysis of H₂O.

---

1 The relative consumption, i.e. the ratio between decrease in density due to consumption and the plasma-off density.
Radical detection and calibration procedure

1.0 \times 10^{-5}

• plasma off

150 • plasma on

8.0 \times 10^{-4}

6.0 \times 10^{-4}

4.0 \times 10^{-4}

2.0 \times 10^{-4}

10
12
14
16
18
20
22
24

electron energy [eV]

1.2 \times 10^{5}

1.0 \times 10^{5}

8.0 \times 10^{4}

6.0 \times 10^{4}

4.0 \times 10^{4}

2.0 \times 10^{4}

0.0

signal [s^{-1}]

17.0 \ eV

Figure 4.3 m/e=16, dwell time = 1000 ms

(a)

10
12
14
16
18
20
22
24

electron energy [eV]

11.5 \ eV

(b)

10
12
14
16
18

10
11
12
13
14
15
16
17

10
11
12
13
14
15
16
17

10
11
12
13
14
15
16
17

electron energy [eV]

electron energy [eV]

The fact that indeed O radicals are responsible for the background in the m/e=16 signal is confirmed in Figure 4.4 where a background measurement is shown. The determined IP of 13.7±0.2 eV corresponds to the literature values of O. Pyrolysis of O$_2$ and subsequent ionization of O radicals is not a likely explanation for this signal because the density of O$_2$ was measured to be constant before and after measurements of long duration. The fact that the plasma-off signal somewhat higher than the plasma-on signal can be explained by the fact that the plasma-off measurement was done after the plasma-on measurement and the walls were heated in the meantime.

Figure 4.4 m/e=16 The plasma-off and plasma-on background signals measured at a dwell time of 1000 ms shows a signal that can be associated to O radicals.
4.2 $\text{SiH}_x$ ($x \leq 3$) detection in the $\text{SiH}_4$/NH$_3$/Ar plasma

Similar to the previous section, here the feasibility of $\text{SiH}_x$ radical detection in the Ar/NH$_3$/SiH$_4$ plasma is checked. In earlier measurements Kessels et al. demonstrated the detection of SiH$_3$ and SiH$_2$ radicals in the Ar/H$_2$/SiH$_4$ plasma with TIMS (comparable setup was used only without the triple stage pumping) [Kes2000]. The used gas flows are 2.5 sccs SiH$_4$, 55 sccs Ar and 10 sccs NH$_3$. The arc current was set to 75A to maximize the radical densities in the plasma. These settings were used in all measurements in this section unless noted otherwise.

$\text{Si}$ ($m/e=28$) In Figure 4.5a an electron energy scan is shown for $m/e=28$ amu. Again the foreground signal is shown which is corrected for background contributions by means of chopping. In the plasma-off signal dissociative ionization of SiH$_4$ molecules into Si$^+$ can be seen at 13.6±0.2 eV. No other APs are visible in the plasma-off signal. The plasma-on signal shows a number of interesting features. The signal increases early in the energy scan and a close up of this region is shown in Figure 4.5b. An AP of 8.4±0.3 eV can be determined and this value is in agreement with literature values for ionization of Si radicals within the margin of error, so we can conclude that Si radicals are detected successfully. Figure 4.5a the plasma-on signal also shows an AP at 15.4±0.4 eV which is in agreement with literature values of ionization of N$_2$, which is created in the Ar/NH$_3$ plasma. DI of SiH$_4$ into Si$^+$ cannot be distinguished in the plasma-on scan, which is due to the fact that SiH$_4$ is almost completely consumed in the plasma. Therefore, the signal is too low to discern from the signal due to ionization of N$_2$.

$\text{SiH}$ ($m/e=29$) In Figure 4.6 one can see that the ionization of SiH start to occur at 8.1±0.3 eV when the plasma is on. Again only when the plasma is off DI of SiH$_4$ into SiH, H and H$_2$ is visible with threshold energy of 14.9±0.4 eV. Both the ionization potential of SiH as the AP of dissociative ionization corresponds to literature values. The statistical error is relatively large due to the low count rate (<100 s$^{-1}$) of the SiH signal.
Radical detection and calibration procedure

Figure 4.6 $m/e=29$ dwell time = 200ms The plasma-on foreground signal shows ionization of SiH and the plasma-off foreground signal shows DI of SiH$_4$.

$\text{SiH}_2$ ($m/e=30$) In Figure 4.7a, dissociation of SiH$_4$ into SiH$_2^+$ and H$_2$ can be seen and the AP is determined to be 11.8±0.2 eV. The plasma-on signal is lower than the plasma-off signal due to consumption of SiH$_4$ in the plasma. From the signal due to DI of SiH$_4$ into SiH$^+$, the depletion of SiH$_4$ is calculated to be approximately 96%.

Figure 4.7b shows a low energy close-up of the foreground signal, where no increase in signal can be distinguished at the expected IP of SiH$_2$ (8.5 to 8.9 eV, see appendix C). The reason for this is that the density and resulting count rate are too low to be distinguished from the background signal with the short integration time used (200 ms).

Figure 4.7 $m/e=30$ dwell time = 200ms a) The signals show SiH$_2^+$ created by DI of SiH$_4$ b) Close-up shows that no SiH$_2$ component can be resolved due to noise c) Background analysis shows SiH$_2$ created by pyrolysis of SiH$_4$ at the filament
Measurements without the background correction, i.e. the SEM signal, were used to determine which background species was responsible for the scatter in the measured signal, see Figure 4.7c. From this picture an IP of 8.8±0.3 eV was determined for ionization of SiH₂. The presence of SiH₂ in the third stage background can be explained by pyrolysis of SiH₄ at the filament. The plasma-on signal is lower and this is due to the fact that SiH₄ is consumed resulting in less SiH₂ is created at the filament. It is interesting to note that no other background particles were detected, in contrast with when the triple stage pumping was not used (NO was possibly detected) [Kes2000].

SiH₃ (m/e=31) In Figure 4.8a dissociation of SiH₄ into SiH₃⁺ is visible and an AP of 11.9±0.2 eV is determined, in agreement with literature within the combined errors. Also here the depletion was determined and was found to be approximately 99%. This value is slightly higher than obtained previously, which can be explained by the experimental error. No SiH₃ signal could be distinguished in the foreground signal due to scatter. Detection of SiH₃ without using fast chopping (slightly different plasma settings were used), made longer integration time possible (1000 ms) and shows an IP of 7.9±0.3 eV (see Figure 4.8b), which is in agreement with literature values of ionization of SiH₃.

\[ SiH₄ \text{ (m/e=32) Ionization of SiH₄ was not observed, as the unstable ion SiH₄⁺ decays very fast into SiH₂⁺ and H₂ [Bas1997].} \]
4.3 Calibration and measurement procedure

In Section 2.1 a linear relation is derived between the signal $S_i$ of a certain species $i$ and its density $n_{i,\text{ionizer}}$ in the ionizer, see Equation (2.1). Also the mass discrimination factor $F(m)$, Equation (2.4), was introduced and together with Equation (2.1) a relation of signal versus ionizer $n_{i,\text{ionizer}}$ density is obtained:

$$S_i(E) = F(m_i)I_{\text{ionizer}}I_e\sigma_i(E)n_{i,\text{ionizer}}.$$  \hfill (4.1)

The quantity of interest is the density in the reactor, $n_{i,0}$. To determine absolute densities directly it is in principle possible to use Equation (4.1) and the relation between $n_{i,\text{ionizer}}$ and $n_{i,0}$ given in Chapter 3. $F(m_i)$, $I_{\text{ionizer}}$, $I_e$ and $\sigma_i$ can be measured or are determined by the QMS settings. This method results in large statistical errors in the ionizer versus reactor density relation and the mass discrimination factor due to assumptions that have to be made to determine the beam density. It was also found that properties of the QMS like transport efficiencies and channeltron efficiencies changed from day to day. Figure 4.9 summarizes the problems leading to the need of a calibration procedure. Therefore, in order to determine the absolute density of radicals and stable gasses in the Ar/NH$_3$ and Ar/SiH$_4$/NH$_3$ plasmas (Chapter 5) a calibration and measurement procedure is necessary, which will be explained in this section. As noted before, due to problems with the chopper motor, proper background measurements were not always possible and the calibration procedure will be adapted to correct for this fact.

![Figure 4.9 Assumptions made and QMS properties lead to the need for a calibration procedure.](image)

In Chapter 3 a species independent linear relation between the beam density $n_{i,\text{beam}}$ in the ionizer and the reactor density $n_{i,0}$ was derived. The foreground signal $S_i$ will be solely due to the beam density in the ionizer, if the beam is modulated with at least 50Hz to ensure that the background density is not modulated, as was described in Chapter 2. Knowing this, the signal due to reactor density $n_{i,0}$ can be described by the proportionality:

$$S_i(E) = cF(m_i)I_{\text{ionizer}}I_e\sigma_i(E)n_{i,0},$$  \hfill (4.2)

where $c$ is a species independent constant. In order to determine the density of radical $A$, a stable calibration gas $B$ is used. The signal $S_B$ at known density $n_B$ in the reactor is measured and the signal $S_A$ of radical $A$ with density $n_A$ can be related to this calibration measurement:
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\[ S_A(E) = \frac{cF(m_A)I_{\text{ionizer}} f_{e,A} \sigma_A(E)n_A}{S_B(E) = \frac{cF(m_B)I_{\text{ionizer}} f_{e,B} \sigma_B(E)n_B}. \]  

(4.3)

The constant \( c \) and ionizer cage length \( I_{\text{ionizer}} \) cancel out and Equation (4.3) can be rewritten to give the density of radical A:

\[ n_A = \frac{F(m_B)I_{e,B} \sigma_B(E)}{F(m_A)I_{e,A} \sigma_A(E)} \frac{n_B}{S_A(E)}. \]  

(4.4)

Equation (4.4) can be used for a signal that is measured at certain known electron energy \( E \). Normally the energy scale offset, i.e. the difference between set acceleration potential and actual electron energy, is determined with a calibration procedure. However, it is has been found that during a measurement the offset also can change quite a lot and one would like to correct for the change in the electron energy offset. A better approach is therefore to use the offset independent slope \( S' \) of signal versus electron energy in stead of the count signal \( S(E) \) at energy \( E \). The linear slope \( S'_A \) near the appearance thresholds and the equivalent slope \( S'_B \) are used in Equation (4.4) for radical A and calibration gas B. Equation (4.4) changes into:

\[ n_A = \frac{F(m_B)I_{e,B} \sigma'_B}{F(m_A)I_{e,A} \sigma'_A} \frac{n_B}{S'_A} \cdot S'_A = C_A \cdot S'_A, \]  

(4.5)

where \( C_A \) is the calibration factor that gives the relation between the radical density \( n_A \) and the slope of the energy scan \( S'_A \). To be able to determine \( n_A \) when the calibration gas is different from the detected species, one needs to know the emission currents \( I_{e,A} \) and \( I_{e,B} \), the ratio of the mass discrimination factors \( F(m_B)/F(m_A) \) and the slopes of the EII cross sections, \( \sigma'_A \) and \( \sigma'_B \). \( I_{e,A} \) and \( I_{e,B} \), are known values determined by the QMS settings. \( F(m_B)/F(m_A) \) can be determined from figure 2.8 and Equation (2.5). Note that in Chapter 2 a maximal electron emission current of 80 \( \mu \)A was determined to prevent build up of space charge at electron energies higher than 8 eV. Also noted was the fact that dissociative ionized products can have lower extraction efficiencies than direct ionized products and therefore only direct ionization processes are suitable for calibration. These problems and the procedures used to circumvent them are summarized in Figure 4.10.

![Figure 4.10 Problems related to absolute density measurements and procedures used to circumvent them.](image)

\( ^6 \) If stable gas density needs to be determined, the same gas and mass spectrometer settings as used in the experiment can be used in the calibration procedure. The mass discrimination factor, ionization cross section and emission current all cancel from equation (4.5). Besides this simplification of the calibration factor, the procedure of stable gasses is the same as for radicals.
4.3.1 Calibration procedure for N radicals

The calibration procedure of \( A \) will be explained for \( N \) (\( m/e=14 \)) radicals and with \( \text{NH}_3 \) (\( m/e=17 \)) the calibration gas \( B \). The \( N \) radical densities were measured in a \( \text{N}_2/\text{Ar} \) plasma and compared values obtained by Kessels et al. [Kes2004]. In order to determine the calibration factor \( C_N \) the variables in Equation (4.5) need to be determined as mentioned previously. The ratio of the mass discrimination factors was determined to be \( F(\text{mNH}_3)/F(\text{mN}) = 0.94 \) from Figure 2.8 in Chapter 2. During the calibration measurements the emission current for \( \text{NH}_3 \) was 10 \( \mu \text{A} \) and for \( N \) the emission was set to 80\( \mu \text{A} \) so the ratio \( I_{e,\text{NH}_3}/I_{e,N} \) is equal to 0.125. The calibration gas was injected in the reactor together with a constant \( \text{Ar} \) flow (20 sccs). The reactor pressure is kept constant at 0.2 mbar (corresponding to a particle density of \( 4.94 \times 10^{21} \text{ m}^{-3} \) at room temperature). The density \( n_{\text{NH}_3} \) can be calculated by multiplying the total particle density with the partial \( \text{NH}_3 \) flow. The slope of the signal versus electron energy \( S'_{\text{NH}_3} \) is determined while a known density \( n_{\text{NH}_3} \) is present in the reactor, see Figure 4.11a. This procedure is repeated for different densities and collected in Figure 4.11b. Now the calibration factor \( C_{\text{NH}_3} = n_{\text{NH}_3}/S'_{\text{NH}_3} \) can be determined to be \( (1.16 \pm 0.02) \times 10^{17} \text{ m}^{-3} \cdot \text{s} \cdot \text{eV} \) by a linear data fit forced through zero, note that this value is the calibration \( C_{\text{NH}_3} \) factor for \( \text{NH}_3 \).

![Figure 4.11](image_url)

Figure 4.11 \( m/e=17 \) a) Determination of \( S'_{\text{NH}_3} \) at certain calculated density \( n_{\text{NH}_3} \) b) A linear fit of slopes determined at different densities is used to determine \( n_{\text{NH}_3}/S'_{\text{NH}_3} \)

The only unknowns left in Equation (4.5) are the electron impact ionization cross sections \( \sigma'_{N} \) and \( \sigma'_{\text{NH}_3} \). In literature several studies can be found into the EII for direct ionization of \( N \). Experimental data by Brook [Bro1978], a model based on Brooks data by Bell [Bel1983] and theoretical values deduced from a model called Binary Encounter Bethe (BEB) [Kim2002] are plotted in Figure 4.12. The BEB theory takes into account all possible electronic transitions and only uses simple theoretical data for the ground state of the target molecule.

When the experimental data of Brook was used to determine the near onset slope of \( N \) radicals, a value of \( (0.053 \pm 0.002) \text{ A}^2 \text{eV}^{-1} \) was found. This value is slightly above the value \( (0.048 \pm 0.004) \text{ A}^2 \text{eV}^{-1} \) determined with the data from the BEB model. Brooks data is
higher than the BEB data, while the latter is an upper overestimate because it takes into account all possible electronic transitions. Furthermore, the appearance potential found by Brook is lower than the ground state ionization energy of N (14.5 eV). A likely explanation for this is that Brook measured radicals in long lived exited and metastable states. Therefore \( \sigma'_{\nu} \) determined with data from the BEB model, is used for calibration. The theoretical data obtained from Bell is based on Brooks experiments and is also discarded.

![Figure 4.12](image1.png)

**Figure 4.12** The electron impact ionization cross section of N plotted against the electron energy. The solid line is a near threshold linearization of the data, the slope is used for calibration of N.

In Figure 4.13 total and partial EII cross section data for NH\(_3\) is plotted. The total ionization cross section is the sum of all partial cross sections, i.e. the cross section for direct ionization plus the partial cross sections related to dissociative ionization. Whenever total ionization cross section data is used, only data points at energies lower than the smallest dissociative ionization energy are evaluated, i.e. energies lower than 16 eV corresponding to the dissociative ionization of NH\(_3\) into NH\(_2^+\). The data of Rejoub *et al.* [Rej2001] was used to determine a slope of \((0.077 \pm 0.007) \text{Å}^2 \text{eV}^{-1}\) for NH\(_3\). The less recent

![Figure 4.13](image2.png)

**Figure 4.13** The electron impact ionization cross section of NH\(_3\) plotted against the electron energy. The solid line is a near threshold linearization of the data of Tarnovsky, the slope is used for calibration of NH\(_3\) and N.
data of Rao et al. [Rao1992] only has two points in the region of interest and is mainly focused on higher electron energy and is therefore discarded. Tarnovskly et al. [Tar1997] and Märk et al. [Mär1977] obtained absolute cross section by calibrating with the ELI cross section of Argon and their data agree quite well in the low energy part. According to Rejoub the discrepancy between his data and data of Tarnovskly and Märk is explained by incomplete collection of their particles (especially of low mass) resulting in lower cross sections. Tarnovskly's and Märk's data is used to determine \( \sigma'_{NH_3} = (0.043 \pm 0.004) \mu^2eV^{-1} \) and this value is used for calibration. The use of this value is supported by the fact that measurement of the mass discrimination factor \( F \) with use of Rejoub’s cross section data leads to a large deviation from the empirical relation of \( F \) versus mass in Equation (2.5). 

And secondly: Rejoubs data is in agreement with the BEB model [Kim1997], which means that this data possibly is overestimated.

Now all the ingredients are there to calculate the calibration coefficient \( C_N \) with Equation (4.5). However, because the currently used stepper motor does not function over long periods of time it was necessary to make an additional adaptation to the calibration procedure. N radicals have a high sticking probability in the third stage **, which means that the N signal will consist of only a beam component and has no background component, in contrast to NH$_3$. The beam to background ratio \( R \) for NH$_3$ was measured at 100 Hz chopping and was determined to be 0.62. If no beam modulation is used, as is the case for the N radical measurements in this chapter, the background will be higher (due to a two times higher average influx because the beam is not blocked half the time as is the case when the beam is modulated). Assuming a two times higher NH$_3$ background without chopping, gives a beam to background ratio of \( R=0.31 \). By dividing the beam contribution to the density by the total density (beam plus background) one can conclude that a fraction \( R/(1+R)=0.24 \) of the NH$_3$ signal is due to the beam density. This value is used to correct the calibration factor \( C_N \) for the fact that N radicals do not have a background contribution while NH$_3$ molecules do:

\[
C_N = \frac{F(m_{NH_3}) I_{e,NH_3} \sigma'_{NH_3} n_{NH_3} 1+R}{F(m_N) I_{e,N} \sigma'_{N} S_{NH_3} R} = 4.8 \cdot 10^{16}
\] (4.6)

The N radical densities were determined in a N$_2$/Ar plasma (10 sccs N$_2$ and 55 sccs Ar) at a reactor pressure of 0.2 mbar and the arc current of 45A. The signal \( S_N \) was measured to be 1121 s$^2$/eV$^1$. Using calibration factor \( C_N \) leads to a density of $5.4 \cdot 10^{19}$m$^{-3}$ which is in fair agreement with the literature value of $4.9 \cdot 10^{19}$m$^{-3}$ by Kessels [Kes2004].

The main cause of errors in the determination of N radical density are 1) Cross section data: Using Rejoub’s data as an upper limit for \( \sigma'_{NH_3} \) we obtain an 54% higher value for \( C_N \) and \( n_N \). 2) If there is a N radical background density, unlike the assumption made, this results in at most a 40% lower value for \( C_N \) and \( n_N \). (Measurements showed that pyrolysis can make up 40% of the signal at maximum NH$_3$ flow, at lower NH$_3$ flows the contribution of N created by pyrolysis will be smaller because there will be less parent molecules.)

** The partial pressure of N$_2$ is very low in the third stage and therefore the stainless steel surface is barely covered with N$_2$. This results in a high sticking coefficient for N radicals [Ada2000], [Sin2000].

†† Kessels, using the same setup however without the triple stage configuration, used an empirical relation for the mass discrimination factor that scales linearly with \( (m/e)^{1} \) and Ar was used as a calibration gas. In Chapter 2 the relation was determined to be \( (m/e)^{0.33} \) and the reported value was corrected for this.
5 Measurements

In Chapter 4 different radicals were successfully detected and the goal of this chapter is to further show the versatility and possibilities of the triple stage pumped TIMS setup. As an example the NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasmas, based on the Expanding Thermal Plasma (ETP) technique, will be investigated. An important question that we want to answer is what the absolute N radical densities are at different reactor conditions in the NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasmas. Therefore the TIMS setup was used to determine the N radical densities with use of the calibration procedure described in Chapter 4. (Note that because the chopper motor malfunctioned, the molecular beam was not modulated when performing the measurements presented in this chapter.) The determined N densities will be discussed and related to wall reaction probabilities and the importance of N in a-SiH$_4$ film deposition is investigated. The trends and densities of N will be compared to NH and NH$_2$ densities, which were determined previously with Cavity Ringdown Spectroscopy [Oever]. Chemical reactions that might explain the observed trends are presented to get deeper insight into plasma processes, without going deep into plasma-chemical detail. Furthermore absolute densities of stable gases, produced in the plasma, are determined with the calibration procedure of Chapter 4. These densities are used to compare production of particles in the plasma and consumption of NH$_3$ and SiH$_4$.

The NH$_3$/SiH$_4$/Ar plasma is very complex. First of all it has two precursors, NH$_3$ and SiH$_4$. Secondly, deposition occurs at the surfaces that contain the plasma, leading to additional loss processes. The NH$_3$/Ar plasma is an easier system because no wall deposition occurs and there are less precursors and possible reaction products. Furthermore, information on the NH$_3$/Ar plasma can be used to understand the more complex SiH$_4$/NH$_3$/Ar plasma, which makes the NH$_3$/Ar plasma a good starting point.

5.1 NH$_3$/Ar plasma

5.1.1 Current status

In the ETP source Ar gas flows through a cascaded arc where in the order of 3-10% of the atoms is ionized by applying a DC current through the Ar. These Ar ions supply the energy to start the chemistry. The Ar atoms and ions expand supersonically through a nozzle where NH$_3$ is injected. The beam then enters the reactor where, after a stationary shock, the beam continues subsonically.

In the case of the NH$_3$/Ar plasma the most important processes that create reactive particles are charge transfer:

\[ \text{NH}_3 + \text{Ar}^+ \rightarrow \text{NH}_3^+ + \text{Ar}. \quad (5.1) \]

and subsequently dissociative recombination:

\[ \text{NH}_3^+ + e^- \rightarrow \text{NH}_x + (3-x)\text{H}. \quad (5.2) \]

Other reactions with NH$_3^+$ can occur also, e.g.

\[ \text{NH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_x^+ + \text{NH}_x. \quad (5.3) \]

Radicals and ions created in the plasma can take part in volume reactions, e.g. hydrogen abstraction by hydrogen:

\[ \text{H} + \text{NH}_x \rightarrow \text{H}_2 + \text{NH}_{x-1} \quad x = 1, 2, 3 \quad (5.4) \]

or surface reactions like recombination of N at the reactor wall.

\[ \text{N} + \text{N}_{\text{surface}} \rightarrow \text{N}_2. \quad (5.5) \]
Figure 5.1 CRDS measurements of the NH (a) and NH$_2$ (b) radical density in the Ar/NH$_3$ plasma by Oever et al., lines serve as guides to the eye.

Figure 5.1a and b show CRDS measurements [Oever] of the NH and NH$_2$ densities in the NH$_3$/Ar plasma as function of the NH$_3$ flow. The arc current was 45 A, the Ar flow 55 sccs and the reactor pressure was 0.2 mbar, maintained by changing the pump valve settings. These settings are used for all experiments in this chapter, unless noted otherwise. A sharp increase of NH radical density up to $2.7 \cdot 10^{18} \text{m}^{-3}$ is observed within the low NH$_3$ flow regime ($\leq 3$ sccs). The NH$_2$ density increases more or less linearly up to $2.5 \cdot 10^{18} \text{m}^{-3}$ for a NH$_3$ flow of 15 sccs. NH is most likely produced by dissociative recombination, Reaction (5.2), because the density saturates after an initial increase, which corresponds to the limited amount of Ar$^+$ fluence (2-3 sccs [Kes1999]) emanating from the plasma source. The fact that the NH density saturates also indicates that loss processes with NH$_3$ are not significant; otherwise a decrease in density would be expected with increasing NH$_3$ flow. The NH$_2$ increases linearly in density with increasing NH$_3$ flow; this indicates that NH$_2$ is not produced by dissociative recombination reactions of NH$_3$. Secondary reactions might explain the linear trend of NH$_2$ like the reaction of NH$_3$ with NH$^+$, Equation (5.3), and hydrogen abstraction of NH$_3$, Equation (5.4).

5.1.2 TIMS measurements

Figure 5.2 shows the absolute N radical density versus NH$_3$ flow, successfully measured with TIMS and complementing the CRDS data. The trend of the N radical density versus NH$_3$ flow shows an increase in the low flow range ($\leq 3$ sccs NH$_3$) up to a value of approximately $3.0 \cdot 10^{18} \text{m}^{-3}$. The trend is similar to the trend observed for NH and the density of N is approximately 10% higher than the density of NH. Similar trends indicate that the production of N radicals may be determined by dissociative recombination as it was for NH discussed above.

NH$_3$ density measurements were performed with TIMS and the net consumption of NH$_3$ is determined by subtracting the plasma-on density $n_{\text{NH}_3(\text{plasma-on})}$ from the plasma-off density $n_{\text{NH}_3(\text{plasma-off})}$. The depletion or relative consumption $D_{\text{NH}_3}$ can be calculated by dividing the consumption by the initial plasma-off density and is plotted in Figure 5.3a.

$$D_{\text{NH}_3} = \frac{n_{\text{NH}_3(\text{plasma-off})} - n_{\text{NH}_3(\text{plasma-on})}}{n_{\text{NH}_3(\text{plasma-off})}}$$ (5.6)
Figure 5.2 Absolute N radical densities in an NH$_3$/Ar plasma as a function of the NH$_3$ flow determined with TIMS. The solid line acts as guide to the eye.

Figure 5.3a shows that the depletion decreases almost linearly with increasing flow. At low NH$_3$ flows approximately 75% of the NH$_3$ injected is consumed, whereas only 20% is consumed at 16.67 sccs NH$_3$. The depletion likely decreases with increasing NH$_3$ flow because of the limited amount of NH$_3$ that can be dissociated by the finite Ar$^+$ flow. Figure 5.3b shows the density decrease (consumption) of NH$_3$ when the plasma is turned on. The density decrease of NH$_3$ reaches values of approximately 2.5·10$^{20}$ m$^{-3}$. The total density increase of NH$_x$ radicals (<10$^{19}$ m$^{-3}$) due to production can not account for this large density decrease of NH$_3$. A possible explanation for this is that also stable gases are produced in the plasma, which might account for a larger part of the NH$_3$ consumption. In Chapter 4 it was already seen that N$_2$ is produced in the NH$_3$/Ar plasma, because it appeared in the electron energy scan of m/e=28 amu. Mass scans also showed production H$_2$ while no other stable gases were detected up to 80 amu.

Figure 5.3b also shows the density increase (production) of N$_2$ and H$_2$ when the plasma is turned on as well as the NH$_3$ consumption. All trends look similar, increasing up to approximately 10 sccs NH$_3$ and reaching saturation values of approximately 2.5·10$^{20}$ m$^{-3}$ for the consumption of NH$_3$ (mentioned before) and production of H$_2$ and 1.1·10$^{20}$ m$^{-3}$ for N$_2$. Stable gas densities of N$_2$ and H$_2$ are in the same order of magnitude as the NH$_3$ consumption. Langmuir probe measurements have shown that at the extraction orifice, 51 cm downstream of the expansion, most ions have recombined and the ion density is low. Therefore we expect that consumed NH$_3$ mainly results in production of N$_2$ and H$_2$.

The average measured ratio of N$_2$ produced and NH$_3$ consumed, the N$_2$/NH$_3$$_{\text{cons}}$ ratio, is 0.43±0.03, which is in fair agreement with the expected N$_2$/NH$_3$$_{\text{cons}}$ ratio of 0.5 if it is assumed that consumed NH$_3$ leads to production of N$_2$ and H$_2$ only. The ratio of H$_2$ production and NH$_3$ consumption, the H$_2$/NH$_3$$_{\text{cons}}$ ratio, is approximately 1, which is lower than the expected H$_2$/NH$_3$$_{\text{cons}}$ ratio of 1.5. The measured N$_2$/H$_2$ ratio is 0.43±0.03 which is also higher than the expected ratio of 1/3. The estimated measurement error of ±10% can partially explain the deviation between measured and expected density ratios. It is also possible that the assumption, that no other H containing particles with considerable densities are formed, might be incorrect. For instance, assuming an additional H density with a similar trend as the stable gases, reaching a density of 2.5·10$^{20}$ m$^{-3}$ would lead to an theoretical H$_2$/NH$_3$$_{\text{cons}}$ ratio that is more in agreement with the measured ratio. Such a high density however is not very realistic because H is a reactive radical and its density is
expected to be in the same order of magnitude as the other radical densities. Furthermore, the expected \( N_2/H_2 \) ratio becomes too large if such an H density is assumed.

A more likely explanation for the low \( H_2/NH_3,\text{cons} \) ratio is an overestimation of the consumption. The consumption is calculated by subtracting the \( n_{NH_3(\text{plasma-off})} \) from \( n_{NH_3(\text{plasma-on})} \) and it is assumed that a decrease in \( NH_3 \) density is totally due to reactions leading to other products. However, an increased particle temperature due to plasma also leads to a particle density decrease, if the pressure is kept constant. This will lead to an overestimate of the consumption (the density decrease due to temperature is mistaken for the density decrease due to chemical reactions). Measurements of the Ar density (not shown) indicated a 10% decrease in signal when the plasma was turned on, which can be attributed to a temperature increase of 30 K. If this effect is taken into account, the consumption was overestimated by approximately 20%. Recalculation of the \( N_2/NH_3,\text{cons} \) ratio leads to a value \( (0.53 \pm 0.03) \) in agreement with the expected value of 0.5 within the margin of error. Recalculation of the \( H_2/NH_3,\text{cons} \) ratio leads to a value of 1.2, which is in better agreement with the theoretical value of 1.5. However, the consumption overestimation does not explain the high \( N_2/H_2 \) ratio.

In conclusion, the \( NH_3 \) consumption can be related to the production of \( N_2 \). \( H_2 \) densities are somewhat lower than expected, even when taking into account that \( NH_3 \) consumption is overestimated. Because the molecular beam was not modulated when performing these measurements, the signal of \( H_2 \) is for a large part due to the background density of \( H_2 \) in the ionizer. Therefore, the calibration procedure of \( H_2 \) possibly leads to an underestimation of \( H_2 \) because the beam-to-background ratio is higher when the plasma is on.

** The creation of \( N_2 \) and \( H_2 \) might be underestimated because they are calculated by subtracting the plasma-off density from the plasma-on density. However, the resulting error is very small because the plasma-off signal is relatively low.

\(^1\) 30K is small compared to the typical gas temperature of the plasma expansion (1000K). This can be explained by the fact that most stable particles measured come from the relatively cold background of the reactor. Furthermore the cooling plate in front of the mass spectrometer housing cools the gases.
5.2 NH₃/SiH₄/Ar plasma

5.2.1 Current status

The NH₃/Ar plasma will be discussed here on the basis of the discussion in the previous section. The effects of adding SiH₄ to the plasma will be shown. Figure 5.4a and b show NH₂ and NH densities in the Ar/SiH₄/NH₃ plasma determined by CRDS [Oever]. The NH₃/Ar data is also shown for comparison.

The standard flow setting for SiH₄ is 2.5 sccs, injected through the ring approximately 7 cm downstream of the nozzle exit. The NH density increases with increasing NH₃ flow up to a value of 3.0·10¹⁸ m⁻³, which is 10% higher compared to the NH₃/Ar plasma (2.7·10¹⁸ m⁻³). The density also increases less steeply and reaches a saturation value at NH₃ flows higher than 10 sccs, whereas saturation in the NH₃/Ar plasma occurs at approximately 3 sccs. In the previous section it was found that NH probably is produced by charge transfer and subsequent dissociative recombination of NH₃, Reactions (5.1) and (5.2). The less pronounced density increase might be explained by charge transfer of Ar⁺ to SiH₄ which:

\[
\text{Ar}^+ + \text{SiH}_4 \rightarrow \text{Ar} + \text{SiH}_3^+ + \text{H},
\]

and subsequent dissociative recombination of SiH₃⁺

\[
\text{SiH}_3^+ + e^- \rightarrow \text{SiH}_x + (3-x)\text{H},
\]

which leaves less Ar ions for charge transfer with NH₃. Incorporation of NH in the depositing a-SiNx:H layer might also explain the less pronounced increase. The higher NH density for large NH₃ flows compared to the NH₃/Ar plasma can possibly be explained by the measurement error.

The NH₂ density increases linearly up to value of approximately 1.5·10¹⁸ m⁻³, which is 40% lower than the maximum density in the NH₃/Ar measurement (2.5·10¹⁸ m⁻³). The slope of the density increase is less steep (20% decrease) and furthermore the density is zero for NH₃ flows smaller than 4 sccs. The lower densities and less pronounced density
Measurements

increase with increasing NH₃ flow might be due to hydrogen abstraction of SiH₄ by H:

\[
\text{SiH}_4 + H \rightarrow \text{SiH}_3 + H_2
\]  

(5.9)

competing with the hydrogen abstraction of NH₃, Reaction (5.4). This might also explain that no NH₂ is created when the NH₃ flow is smaller than 4 sccs. A second explanation for the lower density and no initial NH₂ density might be that NH₂ is preferentially incorporated in the a-SiNx:H film.

5.2.2 TIMS measurements

Figure 5.5 shows the N radical density, successfully determined with TIMS as a function of NH₃ flow. Again the trend of N looks similar to that of NH. Comparing with the NH₃/Ar plasma, the density increase is less abrupt for low NH₃ flows and keeps on increasing with NH₃ flow up to a value of approximately \(5.3 \times 10^{18} \text{ m}^{-3}\), which is almost a factor of two higher than the density of N in the NH₃/Ar plasma. The less pronounced increase of N at low NH₃ flows might be explained by competing charge transfer reactions with SiH₄, Reaction (5.7). Furthermore, N radicals might also be incorporated in the film, further discussed in Section 5.3. It is remarkable that the N density in the NH₃/SiH₄/Ar plasma increases to values significantly above those measured in the NH₃/Ar plasma at high NH₃ flows (> 5.5 sccs), while one would expect lower radical densities at all times due to competing reactions and film incorporation. The high N densities are thought to be due to a lower recombination probability of N at the reactor walls, which also will be further discussed in Section 5.3.

Figure 5.6a shows the depletion of NH₃ which is approximately 90% at very low NH₃ flows and decreases to 40% for 15 sccs NH₃. The depletion of NH₃ in the SiH₄/NH₃/Ar plasma is approximately 15-20% higher compared to the depletion of NH₃ measured in the NH₃/Ar plasma, see Figure 5.3a. Measurements of the NH₃ depletion (at a NH₃ flow of 16.67 sccs) as function of SiH₄ flow showed that the depletion of NH₃ was

\[ \text{Figure 5.5 Absolute N radical density as function of NH}_3 \text{ flow in the Ar/SiH}_4/\text{NH}_3 \text{ plasma, determined with TIMS. Solid lines serve as a guide to the eye.} \]

\(^1\) Hydrogen abstraction was also found to be important for SiH₃ production in the Ar/H₂/SiH₄ plasma [Kes2000].
independent on the SiH₄ flow. This means that loss of NH₃ due to reactions with SiH₄ can not explain the increased depletion of NH₃ when adding SiH₄ to the NH₃/Ar plasma. A possible explanation for the higher depletion of NH₃ in the SiH₄/NH₃/Ar plasma might be that after initial dissociation, NH₃ is reproduced at the surface due to recombination. Because a-SiNx:H film is deposited on the stainless steel reactor wall one might expect less reproduction of NH₃ due to lower wall recombination probabilities.

Figure 5.6b shows that the depletion of SiH₄ starts out to be almost 100% in the limit of zero NH₃ flow and decreases to approximately 80% when the NH₃ flow is higher than 4 sccs. The SiH₄ depletion becomes constant at a value of 80%, which is when the NH₂ radicals start to appear in the CRDS measurements. The decrease in SiH₄ depletion might be explained by competing reactions with NH₃, Reaction (5.1), decreasing Ar⁺ charge transfer to SiH₄ and subsequent dissociative recombination, Equations (5.7) and (5.8).

Consumption of NH₃ and SiH₄ and creation of N₂ and H₂ are plotted in Figure 5.6c. The N₂ production reaches similar densities as in the NH₃/Ar plasma but the increase of production with NH₃ flow is less pronounced. The ratio between N₂ production and NH₃ consumption N₂/NH₃,cons ratio is determined to be 0.32±0.01, which is lower than the expected ratio of 0.5. (Again NH₄ radical densities are too low to explain consumption) This low ratio can be partially explained by the fact that the temperature increases leading to an overestimate of the consumption. N will also be incorporated in the film, which is thought to be the main explanation for the low N₂/NH₃,cons ratio.

H₂ has a density of 2.6×10²⁰ at zero NH₃ flow and follows a similar trend as N₂ with increasing NH₃ flow. At zero NH₃ flow, the amount of H₂ created is solely due to SiH₄ consumed and the fact that H₂ production is approximately the same as SiH₄ consumption means that, on average, approximately two out of 4 H atoms of a consumed SiH₄ molecule contribute to creation of H₂. The production of H₂ is thought to be due to Reactions (5.7), (5.8) and (5.9), which create atomic H that recombines to H₂ at the reactor walls. At high NH₃ flows the ratio between the H₂ density and the density decrease of NH₃ flows reaches a value of approximately 1, the same ratio as obtained in the NH₃/Ar plasma, which can be

![Figure 5.6 NH₃ flow series of a) Depletion of NH₃ b) Depletion of SiH₄ c) The production (density increase) of N₂, H₂, and the consumption (absolute density decrease) of NH₃ as well as SiH₄. Solid lines serve as guide to the eye.](image-url)
explained by the fact that the production of $H_2$ due to the large NH$_3$ flow is large compared to the production of $H_2$ due to the relatively small 2.5 sccs SiH$_4$ flow.

The $H_2$ density is again lower than one would expect on the basis the consumption of SiH$_4$ and NH$_3$. Incorporation of H into the a-SiN$_x$:H film can only partially explain the low $H_2$ density, because the incorporation flux of H is expected to be in the same order of magnitude as the incorporation flux of N. The SiH$_4$ radical densities are expected to be low compared to stable gas densities, as is the case for NH$_x$ radical densities. Therefore, temperature increase leading to overestimated consumption of NH$_3$ and SiH$_4$ as well as measurement errors, explained in Section 3.1, lead to a lower than expected $H_2$ density.

5.3 Further analysis of surface processes.

In the discussion on N radical detection it was mentioned that N densities in the NH$_3$/SiH$_4$/Ar plasma where higher than in the NH$_3$/Ar plasma, while one would expect lower densities due to film incorporation and competing reactions with SiH$_4$. Decreased recombination of N at the a-SiN$_x$:H surface, Reaction (5.5), might explain the high N radical densities measured in the NH$_3$/SiH$_4$/Ar plasma. Measurements where done to investigate these surface loss changes. The recombination loss rate and sticking coefficient of N on a a-SiN$_x$:H surface will be determined with use of an estimated value of the recombination coefficient of N on stainless steel. The contribution of N radicals to the total number of N atoms in a film will be estimated.

To see if indeed surface recombination can explain the high N radical densities in an NH$_3$/SiH$_4$/Ar plasma, the N radical density was determined as function of NH$_3$ flow in an Ar/NH$_3$ plasma after 1m30 of deposition time with a Ar/SiH$_4$/NH$_3$ plasma. This data is compared with N radical densities out of Figure 5.7, where a clean stainless steel vessel was used. A factor of 3.0±0.2 density increase is observed when the surface was covered with an a-SiN$_x$:H film. Therefore, Figure 5.7 shows that the surface recombination indeed can have a large influence on radical densities.

![Figure 5.7 The N radical density versus NH$_3$ flow in a NH$_3$/Ar plasma was measured. In the clean stainless steel reactor vessel lower N densities were observed compared to measurement done when an a-SiN$_x$ layer was deposited on the reactor wall. Solid lines serve as guides to the eye.](image-url)
In general, particles can be lost at a surface either by recombination with a probability $\gamma$ or by surface incorporation with a probability $s$ (also called the sticking coefficient). According to Chantry [Mot1960] [Cha1987], the recombination $\Phi_{\text{rec}}$ and growth flux $\Phi_{\text{growth}}$ is given by:

$$
\Phi_{\text{rec}} = \frac{1}{4} n v \frac{\gamma}{1 - \beta/2}, \quad \Phi_{\text{growth}} = \frac{1}{4} n v \frac{s}{1 - \beta/2},
$$

(5.10)

where $\beta = \gamma + s$ is the total fraction of incident particles lost, $n$ is the wall density and $v$ is the thermal velocity of the particles. Because the NH$_3$/Ar plasma does not deposit, the sticking coefficient $s$ will be zero and Equation (5.10) becomes:

$$
\Phi_{\text{rec}} = \frac{1}{4} n v \frac{\gamma}{1 - \gamma/2}, \quad \Phi_{\text{growth}} = 0.
$$

(5.11)

Because the flow and current settings were unchanged in the measurements of Figure 5.7, large differences in production of N radicals are not expected between the NH$_3$/Ar plasmas and the change in density is expected to be solely due to surface recombination probability of N into N$_2$. The production of N radicals might be assumed constant and if one also assumes that volume losses of N can be neglected compared to loss at surfaces one will obtain a steady state density if the flow of production into the volume will equal the flow of recombination at the wall. This will lead to the following density relation:

$$
P = \Phi_{\text{rec},0} = \Phi_{\text{rec},D} \Rightarrow \frac{n_D}{n_0} = \frac{\gamma_0}{1 - \beta_0/2} \times \frac{1 - \beta_D/2}{\gamma_D},
$$

(5.12)

where $n_0$ ($\gamma_0$) and $n_D$ ($\gamma_D$) are the wall density (recombination probability) for a clean surface, in this case stainless steel, and an a-SiNx:H surface respectively. The recombination probability of N on stainless steel was estimated to be $\gamma_0 = 3\%$ Together with Equation (5.12) and the density ratio determined** $n_D/n_0 = 3.0 \pm 0.2$ a value for the recombination probability of N on SiNx:H of $\gamma_D = (1 \pm 0.1)\%$ was found.

Figure 5.8 shows N radical densities measured at different SiH$_4$ flows, a constant NH$_3$ flow of 16.67 sccs was used. The N radical density is $10^{19}$ m$^{-3}$ at zero SiH$_4$ flow and decreases to a density of approximately $2 \times 10^{18}$ m$^{-3}$ for 5 sccs SiH$_4$. The N radical density was also determined directly after a CF$_4$ plasma clean. The latter showed a lower N density, in agreement with a higher recombination probability of N at an a-SiNx:H surface, as discussed previously. The N density decrease as function of SiH$_4$ flow might be explained by competing reactions with SiH$_4$. However the NH$_3$ flow is large compared to the SiH$_4$ flow and therefore the volumetric production of N radicals is assumed constant. Increasing the SiH$_4$ flow will also result in film deposition and incorporation of N in the film is therefore assumed to determine its decrease in density.

In the case of zero sccs SiH$_4$ flow the sticking coefficient will be zero because no deposition occurs and the surface density $n_D$ will generate a flux ($\Phi_{\text{rec}}$) to the surface

---

§ Studies on surface recombination probability of N in N$_2$/Ar plasmas showed that N reacts easily at stainless steel surfaces unless a "protective" N$_2$ layer is formed over a saturated N layer adsorbed at the stainless steel [Kes2004][Ada200][Sin200_2]. This N$_2$ layer has a higher fractional surface coverage at higher pressures. A probability $\gamma_0$ of 3% was determined by interpolation of data and using a typical gas pressure of 0.1 mbar, half the reacto density is used because Ar is expected to interact less with the surface.

** Note that the densities measured in principle be corrected for the fact that relatively fewer particles are moving toward the surface if $\beta$ is reduced, see Equation (3.21). The change in $\beta$ due to deposition is however so small that this was neglected, see Section 3.5.
completely determined by recombination. Recombination also occurs at for example 1 sccs SiH₄ flow, however the sticking coefficient s will be nonzero, this leads to a surface density \( n_G \) and flux \( \Phi_{\text{rec + growth}} \) determined by recombination and growth. Because the production of N is assumed constant and there is a steady state situation in both cases, the N flux to the surface at zero SiH₄ flow has to be equal to the N flux to the surface at 1 sccs SiH₄ flow:

\[
P = \Phi_{\text{rec}} = \Phi_{\text{rec + growth}} \Rightarrow \frac{n_D}{n_G} = \frac{\gamma_D + s}{1 - (\gamma_D + s)/2} \times \frac{1 - \gamma_D/2}{\gamma_D} \quad (5.13)
\]

Figure 5.8 shows a N radical density of \( n_0 = 5 \cdot 10^{18} \) m\(^{-3}\) at 1 sccs SiH₄ flow, compared to \( n_D = 1 \cdot 10^{19} \) m\(^{-3}\) at zero SiH₄ flow, at this point previous depositions covered the wall with SiNx:H. the recombination coefficient \( \gamma_D \) previously obtained was 1%. Using these values makes it possible to determine a sticking probability s of 1%. Note that this is a rough estimate because there might be a large error in the estimated recombination probability for stainless steel \( \gamma_0 \), which leads to subsequent errors in \( \gamma_D \) and s. Furthermore, the production of N is probably lower when SiH₄ is present in the plasma. This leads to the conclusion that s is an overestimate. (s \( \approx \gamma_D \))

The value of s=1% will be used to calculate the importance of incorporation of N in the film. A typical sample, grown at a rate of 6nm/s with 1 sccs SiH₄ and further similar plasma conditions as used in this study, has a N density of \( 3.8 \cdot 10^{28} \) m\(^{-3}\) and a growth rate of 6 nm/s. The incorporation flux of a species can be determined by:

\[
\text{growth flux} = \text{density} \times \text{deposition rate}, \quad (5.14)
\]

which results in a growth rate for N of \( 2.28 \cdot 10^{20} \) m\(^2\)s\(^{-1}\). The incorporation flux was calculated to be \( 1.3 \cdot 10^{19} \) m\(^2\)s\(^{-1}\) with Equation (5.10), a thermal speed of 1000 ms\(^{-1}\) and the values obtained for s and \( \gamma_D \). This would mean that approximately 6% of the N atoms in the film can be attributed to incorporation of N radicals. Other radicals like NH and NH₂ possibly are responsible for the other 94% of N atoms incorporated in the \( \alpha \)-SiNx film.

Figure 5.8 The N radical density in the NH₃/SiH₄/Ar plasma is plotted as function of the SiH₄ flow. The NH₃ flow was set to 16.67 sccs. Before starting the flow series the N radical density was measured, at that time the reactor walls were cleaned with a CF₄/Ar plasma, solid line serves as guide to the eye.
6 Conclusions and recommendations

During the course of this study the Threshold Ionization Mass Spectrometry setup was upgraded and analyzed. Subsequently this setup was used for measurements on the NH₃/Ar and NH₃/SiH₄/Ar plasma. The main conclusions and recommendations will be divided into a MS related part and a plasma related part. Finally, possible future modifications to increase the setup’s performance and versatility are discussed.

6.1 TIMS related

A new chopper design was successfully implemented into the second stage of the triple stage differentially pumped sampling system. The Hiden QMS interface (MSIU) was upgraded and a gating procedure, triggered by a delay generator and IR detection circuit, is presented. It is now possible to correct signals for background contributions directly, without any assumptions or additional measurements. Background modulation of the third stage did occur, as expected, because the chopper is located in the second pumping stage and the third stage influx changes when modulating the beam. This background modulation was investigated, which lead to a recommended minimal beam modulation frequency of 50 Hz.

Analysis of the beam and background densities in the pumping stages resulted in a beam-to-background relation in agreement with measurements, within the margin of error. It was found that light particles, with high thermal velocities, can cause beam attenuation effects because they build up a higher first stage background density and because the collision frequency increases. When however the majority of the gas consists of heavy, relatively slow, species like Ar it was found that beam attenuation is minimal in the currently used setup at a reactor pressure of 0.2 mbar.

During testing it was found that the offset between the actual and the set electron energy changes not only from day to day but also during measurements. To prevent errors due to this change in offset, the calibration procedure was altered to measure the slope of the signal versus electron energy in stead of the signal at certain constant electron energy. The calibration procedure was described, using N radicals as example. Because it was not always possible to use beam modulation due to malfunction of the chopper, an additional adaptation was made to the calibration procedure to be able to determine absolute radical densities without beam modulation. This was done with use of the beam-to-background ratio and the assumption that the amount of N created by pyrolysis relatively small.

6.2 Plasma related

NH₃ and SiH₄ radicals were investigated, in the NH₃/Ar and NH₃/SiH₄/Ar expanding thermal plasma respectively, with use of the chopping procedure and beam modulation. N, NH₃, Si, SiH and SiH₂ radicals were successfully detected and the ionization potentials were determined to be 15.2 eV, 11.5 eV, 8.4 eV, 8.1 eV, and 7.9 eV respectively. NH could not be detected because of background contributions to the signal at the mass-over-charge ratio of m/e=15 amu, thought to be due to CH₃ created at the hot electron emission filament. At m/e=16 O radicals created at the hot filament by pyrolysis of H₂O, were found to be responsible for increasing the noise in the NH₂ signal. SiH₂ could not be detected because its density was too small compared to the background density created due to pyrolysis of SiH₄ at the hot filament; however from the signal due to pyrolysis an ionization potential of 8.8 eV could be determined. Measurement integration times (typically 1s for NH₃ radicals and 0.2s for SiH₄ radicals) were limited by the duration the
chopper could operate without malfunction. This limited the detection sensitivity because of noise in the (for background contributions corrected) signal.

Absolute N radical densities were determined in a NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasma at different conditions keeping the arc current constant at 45A, the pressure at 0.2 mbar and the Ar flow at 55 sccs. The N density as function of NH$_3$ flow was found to have similar trends as NH radicals measured in previous Cavity Ringdown studies. In the NH$_3$/Ar plasma the N density increased rapidly with increasing NH$_3$ flow and saturates at approximately 3·10$^{18}$ m$^{-3}$ when the NH$_3$ flow is increased to values above 3 sccs. This could indicate that N is mainly produced by charge exchange and subsequent dissociative recombination. In the NH$_3$/SiH$_4$/Ar plasma it was found that the saturation is less prominent and that there is a more gradual increase of N density, indicating competing reactions with SiH$_4$. The N density increases up to a value of approximately 5·10$^{18}$ m$^{-3}$ when increasing the NH$_3$ flow to 16.67 sccs. Further analysis showed that, assuming a stainless steel surface has a 3% recombination probability of N, an a-SiN$_x$:H surface has a 1% recombination probability of N. Furthermore the sticking probability of N, during a-SiN$_x$:H growth, was estimated to be approximately 1%, just as large as the recombination probability of N on an a-SiN$_x$:H surface. The relatively low sticking coefficient of 1% results in the conclusion that approximately 6% of N incorporated in the film, is due to incorporation of N radicals.

Absolute densities of NH$_3$, N$_2$, and H$_2$ in the NH$_3$/Ar and NH$_3$/SiH$_4$/Ar plasma were determined and discussed for different flow settings. It was found that, in the NH$_3$/Ar plasma, H$_2$ and especially the N$_2$ production can be related to the consumption of NH$_3$, while production of other stable gasses was not observed. Depletion of NH$_3$ (decreasing from 75% to 20% almost linear with the NH$_3$ flow, ranging from 0 to 16.67 sccs) was found to be higher when SiH$_4$ was added (decreasing from 100% to 35%). The depletion of SiH$_4$ was found to be almost 100% at very low NH$_3$ flows and the depletion dropped to 80% when increasing the NH$_3$ flow up to 4 sccs. After 4 sccs, SiH$_4$ depletion was constant when the NH$_3$ flow was increased.
6.3 Recommendation for future use of the TIMS setup

Fast beam modulation was successful, however the stepper motor used for modulation was able to function properly only for a few hours of continuous use. A new (stepper) motor that can operate at 500-800 rpm continuously and for long periods will increase the fast modulation procedure considerably. Few motors that are Ultra High Vacuum compatible and can operate at the necessary rotation frequency can be found (currently the Tectra B14.1, which can be operated with currently used AML SMD2 controller, is a possible candidate). As suggested by Jan Benedikt [Ben2004] the removal of the third stage will lead to less beam modulation because the chopper is then located in the same stage as the mass spectrometer. However one has to be aware of the fact that the background density increases. Furthermore, conduction limitations of the ionizer might still result in background modulation.

A lock in amplifier might be used in combination with a D/A converter to measure the TTL output signal of the Mass Spectrometer Interface Unit. This will result in less statistical error than is the case when the chopper closed signal is subtracted from the chopper open signal to obtain the net beam signal.

Time resolved TIMS might be possible if the TTL output is of the MSIU is connected to a multiscaler*. Radical plasma densities can be modulated with an additional pulsed RF voltage. By measuring the decay time of the signal immediately after the RF pulse one can obtain the radical loss time in the plasma and relate this to volume losses and to surface reaction probabilities [Hoe2005].

* Note that the TTL output was found to give pulses of approximately 50ns wide, which limits the time resolution. The pulse does not have a well defined block shape and the width was found to depend on the multiplier voltage. Currently, the cause of the ill defined TTL pulse shape is unknown.
Dankwoord

Allereerst wil ik mijn ouders bedanken voor de steun en het vertrouwen dat ze me gedurende mijn studietijd hebben gegeven, ook al was ik vaak met zaken buiten mijn studie bezig. Zij hebben mogelijk gemaakt dat ik de dingen kon doen waar ik mijn tijd in wilde steken.

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References


References

[9] Eldon L. Knuth, Combustion and flame, **103**: p171 (1995) and references therein
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http://physics.nist.gov/PhysRefData/Ionization/Xsection.html
Appendix A  Maximal emission current

A filament in the ionizer is heated with an electric current controlled by a feedback loop which measures the actual emission current. The demanded emission current can be increased and the feedback loop than will increase the voltage over the filament. The filament current subsequently increases resulting in a higher filament temperature and emission current [Lee1998]. Electrons emitted are accelerated to the positively biased ionizer cage. This potential also determines the electron energy and is set by the environment variable electron energy in MassSoft. At low potentials and high emission currents electrons are not removed quick enough and space charge between the filament and ionizer cage builds up. This space charge limits the number of electrons that can be extracted from the filament. There is therefore a certain maximal emission current \( I_{CL} \) depending on the bias potential between the ionizer cage and filament given by the Child-Langmuir law [Lee1998]:

\[
I_{CL} = pV^{3/2}
\]

(A1)

Where \( p \) is a geometrical factor and \( V \) is the electron energy. If one measures the signal at different electron energies and demanded emission currents, the signal is expected to increase linearly with the increasing demanded emission current. After reaching the electron energy dependent \( I_{CL} \), the current is expected to stop increasing, even if the demanded current is increased, resulting in a plateau.

In Figure A1 one can see a selection of measurements, where the signal of Argon is plotted as function of the demanded emission current at different electron energies, [Lee1998]. All signals deviate from linear behavior before reaching a maximum, the expected plateau is not observed. The deviation from linear behavior might be partially explained by charge build-up and the Child Langmuir law of Equation (A1). However one would expect the maximum to occur at increasing demanded emission currents when increasing the electron energy, this is not the case for energies higher than 30 eV. The plateau is observed neither, for electron energies higher than 30 eV especially, the signal decreases quickly with increasing demanded emission current.

![Figure A1 Signal versus demanded emission current at different electron energies](image-url)
The demanded emission current at maximum signal were determined as function of the electron energy and plotted in Figure A2. The electron energy is plotted in as \( (eV)^{3/2} \) to verify the Child Langmuir law of formula (A1). As one can see this law is only valid in the low electron energy range because the curve is only linear for electron energies lower than 20 eV (90 eV). A value for \( p \) was obtained of \((5.2\pm1.2)\mu A eV^{3/2}\) which is comparable to earlier geometrical factors measured by Leewis: \(6.2\mu A eV^{3/2}\) and \(4.2\mu A eV^{3/2}\). Deviations in the geometrical factors can be explained by the fact that different methods of determining \( I_{CL} \) were used.

The fact that the Child Langmuir law does not hold anymore at electron energies higher than 20 eV is might be due to another process that decreases the electron impact ionization probability, leading to lower signals. In that case one might expect that the space charge decreases the number of electrons entering the ionizer by deflecting the electrons, increasing the number of collisions with the ionizer. The maximum emission current might also be lower than expected because the extraction efficiency is influenced by space charge. The deviation from the Child Langmuir law however was not observed by Leewis [Lee1998]. He used a small plate to prevent photons from reaching the detector. Currently the QMS is fitted with a Bessel Box energy analyzer to block photons and the Bessel box might also explain the maximal signal occurring at smaller emission currents than predicted by the Child Langmuir law, hence this possibility was investigated. In Figure A3 emission current scans are plotted while maintaining an electron energy of 50 eV. The Bessel Box environment variables cylinder and endcap were varied. The maximum of the signal occurs at higher emissions when the cylinder and endcap are optimized. Optimization of the Bessel box variables however does not influence the signal-emission behavior for small emission currents. Maybe the electron emission current has an influence on the kinetic energy off ions created. The transmission efficiency of the Bessel box energy filter might then change. The deviation from the Child Langmuir law was not further investigated.

The most important conclusion that has to be drawn from these experiments is the maximal emission current that can be used when determining radical densities. A linear behavior of the signal versus demanded emission current emission is assumed in the calibration procedure. Therefore, the emission current is set to 80\(\mu A\) to guarantee this
linear behavior for the electron energy range of 8 to 30 eV. However, if the count rate exceeds approximately $2 \times 10^5$ s$^{-1}$ lower emission currents are used. This count rate has to be taken into account to be sure that also the channeltron detection is linear with the number of incident ions. Count rates of $3.5 \times 10^6$ s$^{-1}$ should always be prevented to avoid destruction of the channeltron, lower count rates are preferred to increase lifetime.

Figure A3 Signal versus demanded emission at 50 eV electron energy and variable endcap and cylinder voltages.
Appendix B: Model of relation between chopper frequency and background modulation

It is assumed that the modulated molecular beam causes an influx that is described by a periodic block function $g(t)$ with period $T = 1/f_{chop}$:

$$g(t) = \begin{cases} \Phi, & n/f_{chop} < t < (n+1/2)/f_{chop} \\ 0 & (n+1/2)/f_{chop} < t < (n+1)/f_{chop} \end{cases} \quad n = \ldots, -1, 0, 1, \ldots . \quad (B1)$$

This signal can be expanded into a Fourier integral:

$$g(t) = \Phi \left( 1 + \sum_{k} \frac{1}{2\pi} \sin[2(2k+1)\pi f t] \right) ; k = 0, 1, 2, \ldots \quad (B2)$$

Now the differential equation for the background density $n_{bg}$ can be solved:

$$\frac{dn_{bg}(t)}{dt} = -\frac{S}{V} n_{bg}(t) + \frac{g(t)}{V} \quad (B3)$$

Note that this differential equation is linear. The solution to the differential equation is:

$$n_{bg}(t) = \frac{\Phi}{2S} + Ce^{-S/\sqrt{V}} + \frac{4\Phi}{\pi} \sum_{k} \left[ \frac{S \sin((4k+2)\pi f t) - \pi fV(4k+2)\cos((4k+2)\pi f t)}{(4k+2)(S^2+(4k+2)\pi^2 f^2 V^2)} \right] \quad (B4)$$

The $C$ can be assumed zero if we wait for the density $n_{bg}(t)$ to settle after a time $t > V/S$.

Chopper open (SEM) consist out of a signal due to a beam density $n_{beam}$ and average background density $n_{bg,open}$. The chopper closed (background) signal consist only out of an average background density contribution $n_{bg,closed}$. The foreground measurement of the signal is obtained by subtracting the chopper closed measurement from the chopper open measurement.

$$S_{foreground} \propto n_{beam} + n_{bg,open} - n_{bg,closed} = n_{beam} + 2f \int_0^{1/2f} n_{bg}(t) - 2f \int_{1/2f}^{1f} n_{bg}(t) \quad (B5)$$

The factor $2f$ is introduced to the average density measured. During integration only the constant factor ($\Phi/2S$) and the asymmetrical functions (the sines) will contribute to the integral. Finally when subtracting the two integrals, the constant contribution will cancel leaving only a contribution of the sine. Combining formula (B4) and (B5) results in an expression for the foreground signal as function of the chop frequency $f_{chop}$:

$$S_{foreground} \propto n_{beam} + C \sum_{k} \left( \frac{1}{(2k+1)^4} \right) \left( \frac{1}{f^2 + \frac{B}{(2k+1)^2}} \right) \quad (B6)$$

Note that the contributions of higher order signal decrease rapidly. This is due to the fact that higher order terms get smaller in the Fourier expansion and it is due to the fact that there contribution to the integral gets smaller. Note that for $f=0$ the expression becomes:
$$S_{\text{foreground}} \propto n_{\text{beam}} + \frac{C}{B} \sum_{k} \frac{1}{(2k+1)^2} = n_{\text{beam}} + \frac{C}{B} \frac{\pi^2}{8} = n_{\text{beam}} + \Phi$$  \hspace{1cm} (B7)

This means that when chopping very slowly, the background created by the influx ($\Phi/S$) is only measured when the chopper is open and the signal measured when the chopper is closed is zero because there is no influx. In practice there will still be an influx when the chopper is closed which leads to a nonzero but very small "chopper closed" signal.

In Chapter 2 the foreground signal is measured as function of the chop frequency. With an expansion up to $k=4$ and parameters $P1$, $P2$, and $P3$ the data is fitted with the following formula:

$$S = P1 + P2 \sum_{k=0}^{k=4} \frac{1/(2k+1)^4}{f^2 + \left(\frac{P3}{(2k+1)^2}\right)}$$  \hspace{1cm} (B8)

$P3$ is equal to the constant $B$ in formula (B6) and is used in chapter 2 to determine the residence time $\tau$ of the third stage.
### Appendix C Literature values of IP and AP

<table>
<thead>
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<td>O⁺</td>
<td>O₂</td>
<td></td>
<td>18.9(^{4})</td>
</tr>
<tr>
<td></td>
<td>O⁺</td>
<td>H₂O</td>
<td>H₂</td>
<td>19(^{4}), 18(^{4})</td>
</tr>
<tr>
<td>17</td>
<td>NH₃⁺</td>
<td>NH₃</td>
<td></td>
<td>10.3(^{1}), 10.07(^{3}), 10.16(^{4}), 10.4(^{2})</td>
</tr>
<tr>
<td>28</td>
<td>N₂⁺</td>
<td>N₂</td>
<td></td>
<td>15.58(^{4,3})</td>
</tr>
<tr>
<td></td>
<td>Si⁺</td>
<td>Si</td>
<td></td>
<td>8.15(^{4,3})</td>
</tr>
<tr>
<td></td>
<td>Si⁺</td>
<td>SiH</td>
<td>H</td>
<td>11.3(^{10})</td>
</tr>
<tr>
<td></td>
<td>Si⁺</td>
<td>SiH₄</td>
<td></td>
<td>13.5(^{1}), 13.56(^{4}), 13.6(^{9,11})</td>
</tr>
<tr>
<td>29</td>
<td>SiH⁺</td>
<td>SiH</td>
<td>H</td>
<td>7.89(^{3}), 8.0(^{4}), 7.6(^{10})</td>
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<tr>
<td></td>
<td>SiH⁺</td>
<td>SiH₂</td>
<td>H + H₂</td>
<td>12.2(^{10})</td>
</tr>
<tr>
<td></td>
<td>SiH⁺</td>
<td>SiH₄</td>
<td></td>
<td>15.0(^{1}), 15.1(^{11}), 16.1(^{4}), 15.3(^{4,9})</td>
</tr>
<tr>
<td>30</td>
<td>SiH₂⁺</td>
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<td>H</td>
<td>8.92(^{2}), 8.5(^{10})</td>
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<tr>
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<td>SiH₃</td>
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<td>11.3(^{10})</td>
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<tr>
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<td>SiH₂⁺</td>
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<td>H₂</td>
<td>11.6(^{7,11}), 12.1(^{4}), 11.90(^{4,9})</td>
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<td>31</td>
<td>SiH₃⁺</td>
<td>SiH₃</td>
<td>H</td>
<td>8.14(^{2}), 8.0(^{10})</td>
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<tr>
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<td>SiH₃⁺</td>
<td>SiH₄</td>
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<td>12.2(^{7,11}), 11.8(^{4}), 12.30(^{4,9})</td>
</tr>
</tbody>
</table>

References:
1. [Rao1992] Reported error ± 0.2 eV. If DI of NH₃ into N⁺ gave either 3H or H+H₂ as products was not investigated in this reference. This can explain why the AP is lower than the value recorded for DI under formation of 3H and higher than the value recorded corresponding to the formation of H₂+H. For NH₂.
2. [Mär1977] Error ±0.5 eV.
3. [NIST.2] Theoretical ionization energies
4. [Ros1979]
Appendix C

5. [Arg2003] Also used a Hiden QMS with PSM upgrade
6. [Kes2004] Same QMS as used here
7. [Cha1984] error ±0.4 eV except for SiH⁺(±1 eV) and Si (±2 eV)
8. [Rej2001] Linear extrapolation of data
9. [Pot1969]
10. [Tar1996]
11. [Bas1997] error ±0.5-0.6 eV, ±1 eV for Si⁺
12. [Kim2002] Linear extrapolation of cross section data
13. [Tar1996] Linear extrapolation of cross section data error ±0.5 eV

In general, if literature IP and AP are lower than measured an explanation can be that linear extrapolation of the data leads to a higher than theoretical IP. For example the measured IP of N is 0.7 higher than the theoretical IP but extrapolation of the electron impact ionization cross sections of N determined with the (theoretical) BEB model [Kim2002] does leads to a value that does correspond to the measurement within the margin of error.