Master

Cavity-ringdown spectroscopy on methyl and silyl radicals: examining expanding plasmas

Bocker, P.J.

Award date: 1999

Disclaimer
This document contains a student thesis (bachelor’s or master’s), as authored by a student at Eindhoven University of Technology. Student theses are made available in the TU/e repository upon obtaining the required degree. The grade received is not published on the document as presented in the repository. The required complexity or quality of research of student theses may vary by program, and the required minimum study period may vary in duration.

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
Cavity-Ringdown Spectroscopy on Methyl and Silyl Radicals

Examining expanding plasmas

Master's Thesis

Paul J. Böcker

October 1999, VDF/NT 99-20

Under the supervision of

dr. M.G.H. Boogaarts
dr.ir. M.C.M. van de Sanden
prof.dr.ir. D.C. Schram

This report describes the work done within the framework of a graduation project from November 1998 to September 1999. The project is part of the research programme of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)".
**SUMMARY**

The Cavity-Ringdown Spectroscopy (CRDS) technique has been applied for the determination of absolute radical densities in expanding thermal plasmas, generated by a cascaded arc. With this plasma source, it is possible to deposit a-C:H and a-Si:H thin film layers with high growth rates (several nm/s).

First, spectral identification of methyl (CH₃) generated in a remote Ar/CH₄-plasma is accomplished. For various settings of the cascaded arc current and the CH₄ gas flow, absorptions have been measured on the B → X electronic transition around 216 nm, which is broad due to the pre-dissociative character of the upper state B. This has been done for two spectral positions. A comparison between these measurements revealed a temperature dependence of the absorption cross-section at 215.9 nm: the cross-section decreases with increasing temperature. Furthermore, evidence has been found that for this type of plasma interferences of absorption by acetylene (C₂H₂) occur. Methyl densities from 0.5 - 3.2·10¹⁹ m⁻³ have been found, which could confirm the expectation that CH₃ is the most abundant radical present in an Ar/CH₄-plasma. The observed densities have been linked to a-C:H growth rates obtained in the expanding Ar/CH₄-plasma. Having used the reported loss-probability of CH₃, it is concluded from these calculations that methyl does not significantly contribute to film growth. This is confirmed by the observed non-correlation between CH₃-density and growth-rate. Consequently, other radicals present in the Ar/CH₄-plasma have to be responsible for the observed growth. One of the candidates could be the main dissociation product of acetylene, C₂H. However, this is not confirmed yet.

Second, CRDS has been successfully installed and applied for the detection of gas-phase silyl (SiH₃) radical densities in an expanding Ar/H₂/SiH₄-plasma. The spectrum of the A → X electronic transition shows a very broad structureless absorption extending from beyond 213 to 226 nm with a peak absorption at 215 nm. Absorptions have been measured for various SiH₄ and H₂ gas flows. The observed trends directly confirm expected plasma-chemical processes. In the plasma, for which the best a-Si:H quality has been obtained at a growth rate of 10 nm/s, SiH₃ densities of 1.4·10¹⁹ m⁻³ have been found. However, having compared this density to calculated densities that should be responsible for the observed growth rate, it is suggested that the reported absorption cross-section of SiH₃ at 215.0 nm is too low. This is also confirmed by a comparison with and between other reported SiH₃ densities, as measured using other techniques. It is believed that the cross-section should be higher by a factor (3.0 ± 0.3): \( \sigma = 6 - 8\times10^{-21} \text{m}^2 \) instead of 2.4·10⁻²¹ m². It should be noted that there is also some uncertainty in the absorbing path length and the density profile is assumed to be more or less homogeneous. Furthermore, the linear correlation between SiH₃ density and growth rate has been corroborated for 0.2 to 10 nm/s.

To conclude with, it has been shown that CRDS provides a useful tool for in-situ measurements of broad-band absorbing radical densities in plasmas.
It's almost October now and I have nearly finished the report of my graduation project. Therefore, I think this is a nice opportunity to look back on this final period of my studies at the university.

It started last year in November, when I was introduced to the SiH₃ detection project by Richard and Maarten. The match between my desires with respect to the content of my graduation and the possibilities within the proposal was excellent. So I started reading Arno's report on Cavity-Ringdown Spectroscopy, a quite new diagnostic tool. Then, having seen the way Karine was working with CRD computer programs (no further details authorised...) and how it could be done graphically with LabVIEW, I even didn't object to developing a set of new CRD computer programs.

When these were more or less finished and tested by Richard( e) and Karine (who insisted upon being the first – happy – users), Maarten and I prepared the set-up for detection of the methyl radical. After a quick class on How To Use DEPO I by Ariel, we indeed could identify CH₃ and started collecting data during long days without any substantial setbacks (which, according to Maarten, was quite unusual...). At this point, I'd like to thank Alexandre for his help during the three months he worked with ETP for his traineeship.

In the mean time, preparations were made for the removal of the set-up to DEPO II. After the Socrates Summer Course, a short holiday, arrival of the new laser and indispensable help of Ries and Jo, we started measuring in silane plasmas together with Erwin. And we did it again! Now also SiH₃ was detected, to our knowledge for the first time with CRD. And since everything went quite well, we could finish our intended measurement series.

This would not have been possible without help of all the people involved. I'd like to take this opportunity to thank Arno, Karine and Richard( e), for your practical knowledge of CRD and your help with plasma-chemical processes. Also Ariel and Erwin, for your explanations concerning the deposition set-ups and the controls of them. And Erwin, for the co-operation during the measurements and the interpretation of course. Furthermore, many thanks to Ries, Herman and Bertus for the technical assistance and useful solutions; Jeanne for dealing with all the organisational concerns. And everyone else with ETP for pleasant coffee breaks and a nice atmosphere ... (and Harm, thanks for letting me occupy your desk!).

Maarten, many thanks for your day-to-day supervision and for your patient explications about all kinds of things I asked you (or even didn't)! I presume our contribution in Lake Tahoe was quite smashing?!

Thanks, Richard, for your overall enthusiasm and ideas (even though a one-minute idea might take several days!). Thanks also for critically reading this report. I'm afraid I can't really help you guys with the filling of your vacancy!

And, last but not least, thank you, Daan, for letting me participate in your group and for walking in regularly!

Finally, a (refreshing) cheers! to everyone, family and friends, I was allowed to bother with status reports and, I have to say this, especially Hanneke for her understanding and her patience... I owe you a Grand Day Out!
# Table of Contents

**SUMMARY** .................................................................................................................. i  
**PREFACE** .................................................................................................................. iii  

## 1. INTRODUCTION  
1.1 TECHNOLOGY ASSESSMENT .................................................................................. 1  
1.2 MOTIVATION ........................................................................................................ 2  
1.3 OUTLINE OF THE REPORT ...................................................................................... 2  

## 2. CAVITY-RINGDOWN SPECTROSCOPY  
2.1 INTRODUCTION TO SPECTROSCOPY ....................................................................... 5  
2.2 ABSORPTION SPECTROSCOPY ................................................................................ 5  
  2.2.1 Absorption theory ............................................................................................... 5  
  2.2.2 Predissociation process ...................................................................................... 7  
  2.2.3 P, Q, and R branches ........................................................................................ 8  
2.3 FUNDAMENTALS OF CAVITY-RINGDOWN SPECTROSCOPY .................................... 9  
  2.3.1 Basic considerations .......................................................................................... 9  
  2.3.2 Theoretical assessment ..................................................................................... 10  
2.4 CAVITY-RINGDOWN AND BROAD-BAND ABSORPTION ........................................ 11  

## 3. EXPERIMENTAL CAVITY-RINGDOWN SPECTROSCOPY SET-UP  
3.1 INTRODUCTION ................................................................................................... 13  
3.2 CAVITY-RINGDOWN SPECTROSCOPY ON AN EXPANDING PLASMA ...................... 13  
  3.2.1 Ringdown cavity on deposition set-up ................................................................ 13  
  3.2.2 Optical layout ................................................................................................... 14  
3.3 CRDS COMPUTER CODE ..................................................................................... 16  
  3.3.1 Fitting procedure .............................................................................................. 17  
  3.3.2 Main CRDS programs ..................................................................................... 18  

## 4. CAVITY-RINGDOWN DETECTION OF CH₃ IN AN EXPANDING AR/CH₄ PLASMA  
4.1 INTRODUCTION ........................................................................................................ 21  
4.2 PLASMA CHEMISTRY IN AN EXPANDING AR/CH₄ PLASMA ................................... 21  
  4.2.1 Plasma processes .............................................................................................. 21  
  4.2.2 Chemical reactions with methyl ...................................................................... 22  
4.3 SPECTROSCOPY OF CH₃ ............................................................... 22  
4.4 CAVITY-RINGDOWN MEASUREMENTS .................................................................. 23  
  4.4.1. Reflectivity of mirrors .................................................................................. 23  
  4.4.2. Spectral scan .................................................................................................. 24  
  4.4.3. Acetylene absorption ................................................................................. 26  
  4.4.4. Flow and current series ............................................................................... 28  
4.5 CONTRIBUTION OF CH₃ TO FILM GROWTH ........................................................ 32  
  4.5.1 Density, sticking probability and growth rate ................................................. 32  
  4.5.2 Conclusion ...................................................................................................... 34
5. CAVITY-RINGDOWN DETECTION OF SIH₃ IN AN EXPANDING AR/H₂/SIH₄ PLASMA

5.1 INTRODUCTION ........................................................................................................... 35
5.2 PLASMA CHEMISTRY IN AN EXPANDING AR/H₂/SIH₄ PLASMA .................................. 35
  5.2.1 Plasma processes .................................................................................................... 35
  5.2.2 Surface reactions .................................................................................................. 36
5.3 SPECTROSCOPY OF SIH₃ ...................................................................................... 37
5.4 CAVITY-RINGDOWN MEASUREMENTS ........................................................................ 37
  5.4.1 Spectral scan ......................................................................................................... 37
  5.4.2 Dependence of SiH₃-density on SiH₄-flow ............................................................ 39
  5.4.3 Dependence of SiH₃-density on H₂-flow .............................................................. 42
5.5 VALIDATION OF THE ABSORPTION CROSS-SECTION ............................................. 44
  5.5.1 Density and growth rate ....................................................................................... 44
  5.5.2 Comparison with reported densities ................................................................... 46

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CAVITY-RINGDOWN SPECTROSCOPY ON BROAD-BAND ABSORBING MOLECULES 49
6.2 CRD DETECTION OF METHYL (CH₃) ..................................................................... 50
6.3 CRD DETECTION OF SILYL (SIH₃) ....................................................................... 50

ACKNOWLEDGMENTS ........................................................................................................ 53

REFERENCES .......................................................................................................................... 55

APPENDICES .......................................................................................................................... 59

I. DERIVATION OF GROWTH RATE AS FUNCTION OF DENSITY ....................................... 59
II. OTHER TECHNIQUES THAT CAN BE USED FOR THE DETECTION OF SIH₃ .................. 62
  1. Threshold ionisation mass spectrometry ................................................................... 62
  2. Infrared absorption spectroscopy ............................................................................. 63
  3. Ultraviolet absorption / transmission spectroscopy .................................................. 65
  4. Other techniques ....................................................................................................... 66
  5. Summary .................................................................................................................... 67
Chapter 1

INTRODUCTION

In this chapter an introduction to the project, presented in this report, will be given. After a general assessment in the first section, some questions and indefinite aspects will be raised to motivate this project in the second section. To conclude with, the outline of this report will be clarified (1.3).

1.1 Technology assessment

The technique of growing thin film layers by plasma-enhanced chemical vapour deposition (PECVD) has become a promising method and is being investigated for various scientific and industrial applications. With this method, various types of films can be produced. Due to their extra-ordinary material properties, diamond-like films and hydrogenated amorphous carbon films (a-C:H) for instance, are widely used in technology, for instance as protective coatings for tools and optical devices (currently even in nuclear fusion devices). Another important type of film is hydrogenated amorphous silicon (a-Si:H). This is considered to be the basic material for the next generation thin film solar cells and thin film transistors.

One of the main problems and limiting factor for the commercialisation of this production technique and hence the large scale introduction of as well the diamond-like coatings as the new solar cells, are the relatively high production costs owing to their low growth rate. Using the conventional technique of RF capacitively coupled plasmas, a deposition rate of usually some Å/s can be achieved. At the Eindhoven University of Technology (Department of Applied Physics, Equilibrium and Transport in Plasmas) an expanding thermal plasma, generated by a cascaded arc, is used for deposition.

For growth of a-C:H layers, carbon containing precursor gases are injected in an argon (Ar) plasma emanating from the cascaded arc plasma channel. This precursor (in this case methane, CH₄) is dissociated and certain dissociation products subsequently deposit on a surface. Using this technique, growth rates of up to 14 nm/s have been obtained.

The precursor gas used to deposit a-Si:H films is silane (SiH₄), which is injected in an argon-hydrogen plasma (Ar/H₂). Deposition rates around 10 nm/s yield cells with up to now 4% efficiency. Higher rates can be achieved, however, until now only at the expense of the opto-electronic properties, which of course are essential for a-Si based layers.

Despite intensive research, both deposition processes are not completely understood and substantiated. To be able to increase the deposition rate while upholding optimal quality, i.e. mechanical and/or electronic properties, it is of great importance to fundamentally understand the deposition mechanisms of these films.
1.2 Motivation

In order to better understand the deposition processes, many experiments have been carried out by various scientific groups. From the gained knowledge, it is concluded, that for a-Si:H layers the silyl radical SiH$_3$ is the dominant contributor to film growth. In short, the deposition process is thought to take place according to the next phases. In the first step towards deposition, the radical physisorbs to the hydrogenated amorphous silicon surface in a weakly bound state. Given by a high mobility, the absorbed radical then diffuses to a surface site (second step) where it chemisorbs onto a dangling bond (a vacancy or free location in the top layer; last step). To quantitatively validate this model, measurements of the gas-phase densities of silyl close to the surface and determination of the corresponding fluxes towards the surface should be carried out as a first step. This will be done by direct absorption spectroscopy. The promising Cavity-RingDown Spectroscopy technique (CRDS) - developed a decade ago - is used because of the fact that it is a straight-forward, remote, and non-disturbing method that allows direct, sensitive in-situ absorption measurements. It is capable of performing fast measurements under the arduous circumstances during plasma operation. Besides, with some additional techniques, it is possible to detect broad-band absorptions. To the best of our knowledge, no results of CRDS on SiH$_3$-radicals have been reported in literature up to this moment.

For the growth of amorphous carbon containing films, a more or less analogue mechanism is assumed, which explains the film growth with surface adsorption of the methyl radical (CH$_3$). However, presently a discussion is going on whether CH$_3$ is capable of sticking to a surface and whether the assumed analogy with the contribution of SiH$_3$ to a-Si:H layers is valid, or not. Density measurements and subsequent calculations of fluxes, combined with observed growth rates, can provide a clear answer to this question.

Apart from these studies, density measurements could provide empirical verification (or falsification) of several plasma-chemical processes, which are expected to take place in Ar/CH$_4$- or Ar/SiH$_4$/H$_2$)-plasmas.

1.3 Outline of the report

This report consists of six chapters. After the Introduction, the basic mechanism of absorption as a powerful spectroscopic tool will be recalled in chapter 2, as well as some important features of molecular spectroscopy. With this in mind, the fundamentals of the used technique, Cavity-RingDown Spectroscopy (CRDS), will be explained. Also some comments will be made concerning the difficulties when the experimentalist is engaging in molecular spectroscopy. Then, in chapter 3, the instrumental details of the used CRD technique will be explained. The used experimental set-up will be presented, together with some details of the new CRD computer program, which was developed to facilitate the experiments. Subsequently in chapter 4, the experimental results of the CRD measurements on the methyl radical CH$_3$ in an expanding argon-methane (Ar/CH$_4$) plasma will be presented. These include spectroscopic details, calculations of densities as function of
CRDS ON CH₃ AND SiH₃ RADICALS

gas flows and arc currents, and the discussion concerning the contribution of this radical to the growth of a-C:H thin films. Some conclusions about plasma-chemical processes with regard to CH₃ and its importance for the growth process will be drawn. With chapter 5 the report proceeds with CRD results on the other radical, silyl (SiH₃). These are obtained in an expanding argon-hydrogen-silane (Ar/H₂/SiH₄) plasma. Again, spectroscopic identification of the silyl radical is presented, together with density measurements upon various gas flows. These will be compared to densities reported in literature to be able to make a new estimation for the absorption cross-section of SiH₃. Also some plasma-chemical processes will be characterised. Finally, in chapter 6 the main conclusions are drawn from these results. Also some recommendations for future experiments or work will be made.
In this chapter cavity-ringdown spectroscopy (CRDS) will be introduced (2.3), after a description of general spectroscopy (2.1) and more in particular absorption spectroscopy (2.2). In preparation for understanding experimental results, some features of broad-band absorption will also be considered. Afterwards, the principle set-up and theory of CRDS will be explained, together with some techniques to measure broad-band profiles.

2.1 Introduction to spectroscopy

Since the first spectroscopic measurement of the 589-nm line in a sodium flame in 1752, spectroscopy is a well-known and widely used diagnostic technique. It is based on the existence of discrete energy levels in atoms and molecules, as proposed by Planck. The electrons of an atom not only occupy these various levels; they are also able to make transitions between two levels. When going to a level with a lower energy as the initial one, the energy difference $\Delta E$ is released by emitting a photon with the same amount of energy. Then the frequency $\omega$ of this electromagnetic radiation is given by the well-known Planck formula

$$\Delta E = h\omega,$$

where $h = h \cdot 2\pi$ is Planck’s constant. These frequencies, which can be measured, are unique to every atom or molecule and can be used to identify specific species. This technique is called emission spectroscopy. The opposite process, in which radiation of the specific frequency is taken up by the atom or molecule, giving rise to the occupation of a higher energy level, is called absorption. The light after passing the absorbing medium now has a lower intensity compared to the initial radiation intensity and also the spectrum will be altered. These differences, the amount of attenuation as a function of its frequency, can be used to characterise the particular species sampled, e.g. with regard to concentration, temperature, etc. This is called absorption spectroscopy.

2.2 Absorption spectroscopy

2.2.1 Absorption theory

Consider a plane electro-magnetic wave of intensity $I_0$, passing in the $z$-direction through an absorbing sample with energy levels $i$ (lower) and $k$ (upper level). Then the decrease in intensity $dI$ of the wave as a result of absorption in the $k \leftarrow i$ transition, in a distance $dz$ is given by
The absorption coefficient $\alpha$ for the given transition depends on the absolute population densities $N_i$ and $N_k$ of the lower and upper level, as well as on the optical absorption cross section $\sigma$ (which is a function of frequency) for each absorbing atom:

$$\alpha(\omega) = \sigma(\omega) \left[ N_i - \left( \frac{g_i}{g_k} \right) N_k \right], \quad (2.3)$$

where $g_i$ and $g_k$ are the statistical weights of the corresponding levels (see section 2.3 in [1] for more details). In the case $N_k << N_i$ (thus $N_i = N_m = n$, where $n$ is the absolute number density) Eq. (2.3) reduces to

$$\alpha(\omega) = \sigma(\omega) n, \quad (2.4)$$

If the incident radiation intensity is sufficiently small, the induced absorption rate is small compared to the refilling rate of the lower level $i$. Then the population density $N_i$ does not depend on the light intensity and remains constant. This means, that $\alpha$ is also constant and, according to Eq. (2.2), $dI$ correlates linearly with $I$: this is called linear absorption. If this is the case, it is possible to integrate Eq. (2.2) over the full size $l$ of the sample in direction $z$, which yields Lambert-Beer's law for linear absorption

$$I_t = I_0 \exp(-\alpha(\omega)l), \quad (2.5)$$

where $I_t$ is the transmitted intensity at given frequency $\omega$ (or wavelength $\lambda = 2\pi c / \omega$, in which $c$ is the speed of light).

The absorption profile $\alpha(\omega)$, i.e. the spectrum, has a Lorentzian line profile with a full width at half maximum which equals the natural line width, which is the result of the existence of a probability of radiative transfer into lower states (remember the uncertainty principle). However, in practice this profile is broadened by a Doppler width due to the thermal motion of the absorbing molecules at a given temperature, which gives rise to a Gaussian line profile.

Now two difficulties appear: first, in the resulting spectrum the separate absorption lines should be distinguishable, and second, the (small) intensity change due to a weak energy absorption should be visible. To overcome the first problem, a (tuneable) laser can be used, providing a light source with a narrow spectral bandwidth. But, the output intensity should be very stable to prevent a weak absorption from being masked by an intensity variation, e.g. with a pulsed laser. For the second difficulty, a long path length could be useful: the absorption is directly dependent on the absorbing length, Eq. (2.5). This can be achieved by a multipass cell, which consists of two plano-concave mirrors. Then the incoming light is reflected many times in the cell and absorption can take place during every pass. It is evident that the maximum achievable path length is determined by the reflectivity of the mirrors. Nevertheless, lengths of up to several hundred metres can be obtained.
Before explaining the cavity-ringdown absorption method, which makes use of a sensitive multipass cell (absorbing lengths of several kilometres are achievable), we first consider two processes which are essential for understanding molecular spectroscopy: predissociation and the formation of branches.

### 2.2.2 Predissociation process

Consider a molecular system of electronic states $A$ which has discrete energy levels and another system $B$ that has a continuous range of levels on top of discrete states. See Fig. 2.1.

![Energy level diagram.](image.png)

**FIG. 2.1**: Energy level diagram. Electronic states of system $A$ (discrete) and $B$ (both discrete and continuous) are shown. To the left, the theoretical spectrum resulting from absorbing $A$-states is depicted.

If some of the levels in $A$ have the same energy as the continuous part of system $B$, then the former (levels $a$, $b$, and $c$) mix with the continuous part of $B$. To a small extent they take over the properties of the latter, provided that certain selection rules are obeyed. As a result, the absorption lines, belonging to the discrete energy levels in $A$, adapt to the continuum in $B$ and become wider: a diffuse absorption profile, consisting of broad spectral lines, will appear. Furthermore, when the continuum of $B$ represents a molecular system flying apart (i.e. dissociates) with various amounts of kinetic energy, also an occupied state in the discrete system $A$ will after some time find itself in the continuous energy range of $B$ and dissociates with matching kinetic energy $E_k$. This radiationless decomposition process is referred to as an Auger process and the discrete levels $a$, $b$, and $c$ of $A$ are called predissociative. Because the broadening can be related to a time interval, this is also called predissociative lifetime broadening.
2.2.3 P, Q and R branches

For molecules, there exist large numbers of vibrational (quantum number $v$) and rotational states (quantum number $J$), with accompanying energy levels. Between these levels in different electronic states transitions are possible, if the selection rules

$$\Delta v = 0, \pm 1, \pm 2, ...$$
$$\Delta J = 0, \pm 1$$

are obeyed. The latter rule leads to separate branches in the rotational structure of a vibrational (or vibronic) band (given $\Delta v$):

$$\Delta J = -1 \quad P - \text{branch}$$
$$\Delta J = 0 \quad Q - \text{branch}$$
$$\Delta J = +1 \quad R - \text{branch}$$

These branches usually appear as (sets of) different lines in a spectrum, see Fig. 2.2.

![Energy level diagram showing the origin of rotational branches and the resulting rotational structure in the spectrum.](image)

The $P$- and $R$-branches are usually well separated due to the energy differences between the allowed transitions. The $Q$-branch lines often cannot be resolved: the energy differences for each transition are nearly equal. In reality, the separate lines are broadened by the Doppler width, or even by predissociative life-time broadening as discussed before. As a result, the different branches can coincide and form one wide absorption profile.
2.3 Fundamentals of Cavity-Ringdown spectroscopy

2.3.1 Basic considerations

A recently developed, sensitive laser absorption technique is Cavity-Ringdown Spectroscopy (CRDS). The basic concept originates from the early 1980's, when it was necessary to improve the reflectivity of highly reflective mirrors in an optical ring gyroscope for the use in both civilian and military aviation. In 1984, Anderson et al. [2] presented a method to measure the reflectivity of a mirror pair in an optical cavity. In 1988, O'Keefe and Deacon [3] first demonstrated the use of the CRD technique as a spectroscopic instrument. It is based on the measurement of the rate of absorption of a monochromatic light pulse (e.g. from a pulsed laser) confined in a high-finesse optical cavity containing the sample. The cavity (Fig. 2.3) consists of two highly reflective plano-concave mirrors with reflectivity $R$, which are separated by a distance $d$.

![Cavity Diagram](image)

**FIG. 2.3: Schematic diagram of ringdown cavity and detector signal.**

In between, the absorbing sample medium is situated. It has an absorption length $l$, a density $n$ and an absorption cross-section $\sigma$. A pulsed laser is coupled in from the left and a detector (in this case a photomultiplier tube, PMT) is placed on the right side. The injected laser pulse then travels through the cavity and the sample and will be reflected almost completely at the second mirror. It then crosses the medium again, and in this way the pulse travels back and forth within the cavity many times. During this process, energy is lost in two ways:

1. Energy is absorbed by the sample (we assume a frequency for which the absorption coefficient is greater than 0).
2. Energy leaks out of the cavity at the mirrors. When reflected at a mirror, a small part of the pulse will be transmitted (transmittivity $T$). Also diffraction losses and Rayleigh scattering by the gaseous sample occur and can be included in the mirror loss coefficient $L$. Conservation of energy yields Kirchhoff's law $R + T + L = 1$.

As a result of this the intensity inside the cavity gradually decreases with time. The characteristic decay time can be calculated and is called the cavity-ringdown time. The derivation will be given in the next section.
2.3.2 Theoretical assessment

Consider the set-up given in Fig. 2.3, with initial laser intensity $I_m$. After the first pass through the cell, the intensity is attenuated to

$$I_0 = T^2 \exp(-\alpha l) \cdot I_m,$$

(2.6)

according to Eq. (2.5). During each additional round trip, the intensity decreases by the same factor $R^2 \exp(-2\alpha l)$. Then, after $n$ round trips, the intensity at the detector is

$$I_n = [R \exp(-\alpha l)]^n \cdot I_0,$$

(2.7)

which can be written as

$$I_n = I_0 \cdot \exp[2n(\ln R - \alpha l)] \equiv I_0 \cdot \exp[-2n((1-R)+\alpha l)].$$

(2.8)

if we assume $R = 1$ ($T, L<<1$; if typically $R = 0.999$ or higher, the introduced error is 0.05% or less). Furthermore, if we use a PMT, which has a time constant large enough to give only the intensity envelope of the pulse train, we can use the continuous time variable $t=2nd/c$ (the time for $n$ round trips) instead of the discrete $n$:

$$I(t) = I_0 \exp\left(-\frac{tc((1-R)+\alpha l)}{d}\right).$$

(2.9)

To determine the characteristic decay time, we calculate when $I(t) = I_0 \exp(-1)$. The (wavelength dependent) ringdown time $\tau$ is then given by

$$\tau(\lambda) = \frac{d/c}{(1-R(\lambda)) + \alpha(\lambda) l}.$$

(2.10)

The absorption coefficient $\alpha(\lambda)$ can be replaced by $n\sigma(\lambda)$ according to Eq. (2.4). The reflectivity of the mirrors is wavelength-dependent as a result of the used reflective coating materials. Now consider the cavity without any absorbers inside: in Eq. (2.10), the second term in the denominator will be zero. Then, a measurement of the ringdown time (in this case called $\tau_0$) yields directly the reflectivity of the mirrors, possibly as a function of wavelength when a tunable laser is used to produce a spectral scan.

In experiments, we are interested in the absolute absorption per pass $A(\lambda)$ by the sample in the cell, which can be calculated by

$$A(\lambda) = \frac{d}{c} \left( \frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} \right).$$

(2.11)

From this equation, it will be clear that CRDS is independent of the initial light intensity. This is a big advantage, because then we do not have to use a highly stable
light source to be able to detect weak absorptions (see section 2.2.1). Nevertheless, sensitivity is limited: the smallest measurable absorption is in the first order given by

\[ A_{\text{min}} = (1 - R) \frac{\tau - \tau_0}{\tau_0} . \]  

(2.12)

For a more detailed description of the sensitivity and accuracy refer to [4] and [5].

Up to now, the behaviour of the optical cavity, i.e. a volume of space with boundary conditions, has not been discussed. It turns out that the cavity is not stable for every frequency of the incoming light: the cavity is only resonant for frequencies that match the eigenmodes of the cavity. However, if certain conditions (see [5], [6]) are met, it is possible to use the cavity with a quasi-continuum eigenmode distribution. For more background on optical cavities, mode formation and implications for CRDS, refer to [7], [8] and [9].

2.4 Cavity-Ringdown and broad-band absorption

In order to be able to measure wide absorption profiles as explained in section 2.2.2 and 2.2.3, some additional techniques have to be used. Contrary to a narrow-band absorption, where the cavity loss \( \tau_0 \) baseline is automatically recorded as the ringdown time \( \tau \) at a non-absorbing (or off-peak) wavelength, it is for broad-band absorptions necessary to perform additional measurements to determine the baseline cavity loss. In addition, some instrumental effects that significantly alter the ringdown time have to be considered:

1. The reflectivity of the mirrors is wavelength-dependent and can decrease dramatically at the wings of the scan due to the necessity to measure over a large range of wavelengths.
2. The influence of hostile particles on the mirrors: hydrogen is expected to diffuse into the reflective coating during plasma operation and decreases the reflectivity. See [10].
3. Contamination from reactive radicals sticking to the mirror surfaces during plasma operation decreases the mirror's reflectivity.
4. Experimental conditions as pressure or temperature can change the alignment and thus the ringdown time.

This makes it indispensable to continuously keep track of the value of \( \tau_0 \), needed to calculate the absolute absorption (Eq. 2.11). In order to do this, measurements of the ringdown time have to be made for every wavelength also in the absence of absorbing species in the vessel. This implies two measurements at each wavelength step during the spectral scan: one with \( \tau \) and one without \( \tau_0 \) absorbers, or plasma. This can practically be achieved in several ways:

1. Switching on and off the plasma: this might not be preferable due to the desired plasma stability and system performance: before the measurement can take place, a stable plasma situation should be reached. For some plasmas this is even not a
realistic option, especially when large powers are involved: fast switching between zero and full power is difficult.

2. Switching the precursor gas flow, responsible for the production of the absorbing species, on and off. The main advantage is a continuously operating and thus stable plasma. In practice, the flow-controlling unit should respond quickly upon user commands to limit the overall measurement time (since time should be allowed for full mixing of the particles, created from the injected gas – or for the absorbing particles to be lost by reactions or to get pumped away).

3. Modulating the plasma. If an amplitude modulation (AM) of the plasma current can be imposed, and the CRD-laser can be triggered externally, it is possible to measure either in or out of phase with the plasma. Switching between these conditions is possible by changing the Nd:YAG trigger delay time. This AM-method, in which a quasi-stationary state is reached, can be useful for small-sized plasmas where the currents are not too large. For larger installations, an RF biasing field can be applied near the substrate holder for local modulation of the plasma. A more detailed description will be given in section 3.3.2. Moreover, by scanning the time at which the laser pulse arrives over the on and off period of the pulsed plasma, it is possible to study the time-evolution of the plasma particles.

Given the deposition set-up (large vessel, high currents; discussed in the next chapter) with easy-to-regulate flow controllers, the second method is the most suitable one for this project. A method in which the wavelength scan is performed twice (first time with plasma including precursor, second time without precursor) proved to fail: the asynchronously recorded ringdown time fluctuations completely masked the absorption features. However, for experiments in the near future the third method is recommended, because of the fact that in this way a quasi-stationary plasma can be achieved, in which parameters as temperature and pressure do not change anymore and the influence of these parameters on the measurement is excluded. Moreover, it would be recommendable to use a fast data-acquisition system to be able to analyse each single pulse. In this way, less time would be available for the baseline to change during one measurement (instead of during 64 averaged measurements). Such a new acquisition system is currently being designed. See section 6.1.
Chapter 3

EXPERIMENTAL CAVITY-RINGDOWN SPECTROSCOPY SET-UP

In this chapter the CRDS set-up used for measurements on expanding plasmas is presented (3.2). In section 3.3 the computer code, which is used for the CRD measurements, is summarised.

3.1 Introduction

The CRD measurements on the methyl radical (in an Ar/CH₄-plasma) and on the silyl radical (in an Ar/H₂/SiH₄-plasma) are performed in two separate plasma deposition reactors. It would be beyond the scope of this report to explain both deposition systems in detail. However, the principles of the two reactors are very similar and will be outlined below. In addition, two optical set-ups will be presented.

3.2 Cavity-Ringdown Spectroscopy on an expanding plasma

3.2.1 Ringdown cavity on deposition set-up

The experimental set-up for the CRD measurements in an expanding plasma beam is given in Fig. 3.1.

![Fig. 3.1: Schematic drawing of the CRD set-up for measurements on an expanding plasma, originating from a cascaded arc plasma source.](image-url)
Pure argon (Ar) gas flows through a cascaded arc channel where the plasma is generated from a DC current. This source has already been described many times, e.g. in [11], and therefore will not be discussed here. The plasma expands with supersonic velocity from a nozzle into a low-pressure (sub-mbar) vessel. After a stationary shock front the plasma flows subsonically towards the substrate, mounted on a holder. Additional gases (precursors) can be injected into the plasma in the arc channel, or through a symmetrical injection ring, which is mounted a few cm downstream from the nozzle. The ringdown cavity is situated in such way, that the radicals in the expanding plasma beam are sampled 6 cm above the substrate.

The optical cavity consists of two highly reflective plano-concave mirrors (Laser Optik GmbH). They have a diameter of 2.54 cm and a specified maximum reflectivity of 0.998 around 218 nm. Mirrors with different radii of curvature are used, at different distances: see Table 3.1.

<table>
<thead>
<tr>
<th>Deposited Film type</th>
<th>Studied radical</th>
<th>Radius of curvature (mm)</th>
<th>Cavity length d (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C:H</td>
<td>Methyl (CH₃)</td>
<td>-500</td>
<td>78</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>Silyl (SiH₃)</td>
<td>-1000</td>
<td>102</td>
</tr>
</tbody>
</table>

The mirrors themselves also act as the vacuum seals for the low-pressure vessel: they are mounted on flexible bellows, allowing accurate alignment. To prevent the mirrors from getting polluted by the depositing plasma, they are protected by a non-optimised Ar-gas flow, which continuously flows from the mirrors to the plasma vessel at some 30 scc/s.

At the right side of the cavity, the detector is situated. In this case a photomultiplier tube (PMT, Hamamatsu R928) connected to a high-voltage power supply, operating around 520 V. Between the second cavity mirror and the PMT, a bandpass filter with a maximum transmittivity close to the laser light pulse wavelength is placed to shield the PMT from the continuous plasma and background light. This filter has a central transmission wavelength of 210 nm and a width of 20 nm. A digital 1 Gs/s, 100 MHz oscilloscope (Tektronix TDS340a) is used to monitor the PMT signal. This oscilloscope performs a running average over several light pulses. The resulting transient is transferred to a PC via a GPIB connection (IEEE 488.2 standard) and processed by a computer code written in LabVIEW to compute the ringdown time. This new program is introduced in section 3.3.

At the left side of the cavity, the laser light pulse is generated (which is discussed next) and coupled into the cavity.

### 3.2.2 Optical layout

Two optical set-ups are used to produce a suitable light pulse. First, the one used for CRDS on CH₃ will be given. Second, the optical layout for measurements on SiH₃ will be presented.
a. Optical CRD set-up for the a-C:H film deposition set-up

In order to perform the desired CRD measurements, a tuneable monochromatic light pulse around 215 nm should be generated. This is done by the optical set-up depicted in Fig. 3.2 (top view).

![Diagram of optical set-up](image)

**FIG. 3.2: Optical set-up to generate UV laser pulses around 215 nm with Spectra Physics / Quanta Ray PDL-2 dye-laser.**

The output of a Nd:YAG-laser (Spectra-Physics / Quanta Ray DCR-11) with a repetition rate of 10 Hz at 1064 nm, is frequency-tripled to 355 nm with KDP (Potassium di-Hydrogen Phosphate) crystals. The different wavelengths are separated by two dichroic mirrors and the 355 nm pulses are used to pump a tuneable dye-laser (Spectra-Physics / Quanta Ray PDL-2) operating on a Coumarine 440 (Exciton) dye solution. The dye-laser output has a bandwidth of 0.4 cm$^{-1}$. This laser light is frequency-doubled by a BBO ($\beta$-BaB$_2$O$_4$, Barium Borate) crystal. To separate the original and doubled frequencies, two mirrors with a high reflectivity around 218 nm are used as an UV-filter$^1$ (these mirrors are also manufactured by Laser Optik, in the same coating run as the cavity mirrors). Another bandpass filter, just in front of the first cavity mirror, is used to assure a low light intensity level in the ringdown cavity. The resulting light has a tuning range of 213 to 227 nm and a bandwidth of 0.7 cm$^{-1}$. The pulse energy after frequency doubling amounts to several tenths of mJ. Diaphragms are used to select the part of the laser spot to be used and to align the laser beam.

The Nd:YAG triggers and thus synchronises the measurements of the oscilloscope. The dye-laser is connected to the PC, which allows automated scanning of

---

$^1$ Initially, a Pellin-Broca prism was used to split the two beams. However, while scanning the wavelength, the optical alignment significantly altered due to the wavelength-dependant refraction of the prism. A second Pellin-Broca prism could also be used to partly correct for this effect. (Complete correction is only possible with four Pellin-Broca prisms. Though, this is not beneficial to the intensity of the transmitted light).
wavelength. Nevertheless, the BBO crystal angle still has to be adjusted manually for each wavelength.

b. Optical CRD set-up for the a-Si:H film deposition set-up

At the Si-depositing reactor, another dye-laser is used. Consequently, the optical path changes. This can be seen in Fig. 3.3 (top view). Notice the non-horizontal part: in this case, the plasma is sampled vertically.

![Optical set-up to generate UV laser pulses around 215 nm with Sirah PrecisionScan-D dye-laser.](image)

Instead of the PDL-2 dye-laser, a Sirah PrecisionScan-D (Sirah Laser- und Plasmatechnik GmbH) dye-laser is used, also operating on Coumarine 440 dye. This dye-laser is equipped with an optional BBO crystal, of which the angle is automatically tuned to the wavelength. Also two Pellin-Broca prisms are installed to select the desired wavelength, which means that the 218 nm mirrors in Fig. 3.2 can be left out. Depending on the laser energy (or wavelength) a bandpass filter is placed between dye-laser and cavity. The resulting laser light has a tuning range of 213 to 228 nm and an estimated bandwidth of 0.2 cm\(^{-1}\). Again, the wavelength scanning of the dye-laser is controlled by PC.

3.3 CRDS computer code

A new computer program is developed to control the CRDS set-up including both dye-lasers and the oscilloscope and to calculate the CRD-time. The LabVIEW (National Instruments, Version 4.1, Full Development System) graphical programming language is used. This language is chosen because of its capability to conveniently build so-called Virtual Instruments (VI) with a high level of graphical interfacing. In this section the most important part, the calculation of the ringdown time, will be discussed, after which some general functions will be presented.
3.3.1 Fitting procedure

A CRD measurement produces a transient, which is an exponential decaying function, Eq. (2.9), from which the exponential factor has to be calculated. The most convenient way to do this is to fit a linear function to the logarithm of the transient $Y_k$ (after subtraction of the baseline $Y_0$). This is done by the General Least Squares Linear (GLSL) Fit algorithm, which is available in the Analysis Library of LabVIEW (see page 44.4 in [12]). It performs a multiple regression analysis based on the observables $y_k$, i.e. the logarithm of the measured values, and the fitting function, which in our case is

$$y_k = \ln(Y_k - Y_0) = \ln(A\exp(-Bt_k))$$

$$\equiv b_0 + b_1t_k$$

(3.1)

where $A$ is the amplitude and $B$ is $1/\tau$ (furthermore, $b_0 = \ln(A)$ and $b_1 = -B$). In the GLSL algorithm, this can be represented in matrix notation as

$$Y = HB,$$

(3.2)

in which $Y$ is the observables matrix, $B$ the fitting coefficients and $H$ contains the basis functions in (3.1), evaluated at each data point (for $n$ observables). In this case, the first function is simply $f_0(t_k)=1$ and the second $f_1(t_k)=t_k$.

Then the least chi-squared method (minimising the sum of squared deviations between the observed data and the predicted value) is used to calculate the coefficients $B$. For more information see for instance [13].

To include standard deviations due to noise and photon statistics (see [5]), the observables are weighted by

$$\sigma_{y_k} = \frac{1}{\sqrt{Y_k - Y_0}} \cdot \sqrt{1 + \frac{\sigma_{\text{noise}}^2}{Y_k - Y_0}},$$

(3.4)

where $\sigma_{\text{noise}}$ results from a calculation of the mean value of the baseline.

The above-discussed fitting procedure is inserted into a LabVIEW program to process the CRD signals. This VI, CALCULATE CRD-TIME is the core of every CRD measurement program and is depicted on the next page in Fig. 3.4 to give an impression of a LabVIEW program.
FIG. 3.4: CALCULATE CRD-TIME program, which calculates the ringdown time.

Input (at the left side) is the **Time base** of the oscilloscope, necessary to build the time axis, and the transient itself, called **Ydata**. Before a fit can be made, the so-called gates should be set, *i.e.* the user has to determine the fitting range for calculation of the mean baseline value and the ringdown time. This can be done with use of another program, discussed in the next section.

The main output is the CRD-time and the mean squared error (*mse*)

\[
 mse = \frac{1}{n} \sum_{k=0}^{n-1} \left( y_k - \frac{b_0 + b_1 t_k}{\sigma_k} \right)^2, \quad (3.5)
\]

representing the quality of the fit. Also an array containing the best fit curve can be used.

### 3.3.2 Main CRDS programs

Additional low-levels programs are (re-)written to control both dye-lasers (**PDL CONTROLLER** and **SIRAH CONTROLLER**) and to communicate with the oscilloscope (several **TKTDS-files**). These are used to build various CRDS measurement programs. The most important vi's are described next.

**SET-UP UTILITIES**

This program incorporates some useful tools when preparing CRD experiments.

The first option provides the user a continuous read-out of the oscilloscope. The transient signal is displayed on screen. Furthermore, for each transient, the ringdown time is calculated. This value is presented in large figures, useful during alignment of the set-up and optimisation of the ringdown signal at some distance of the pc or the oscilloscope. Also a history chart of these values is displayed, in which the time evolution of $\tau$ can be followed.

The second option stores a transient signal to disk.
With the third option the gates to be used for fitting of the baseline and the transient can be set. Baseline gates are set with the transient signal, the gates needed for the linear fit to determine the ringdown time, \( \text{i.e.} \) a linear fit to the logarithm of the signal, can be set using the logarithm of the data \( (\ln[Y_k-Y_0]) \). This is beneficial to the accuracy. The values set with this option will be used in further measurement programs.

**SCAN TIME**

This program records the ringdown time continuously for a given number of points. By doing this, the stability of the signal can be measured, or the influence of certain changes in the experimental environment (such as gas flow on, plasma on or off, \textit{etc.}) on the ringdown time can be established.

**SCAN WAVELENGTH**

Several versions of this program exist: the main feature is the possibility to perform a wavelength scan with given starting and ending value and the number of points to be set. The dye-laser (either PDL-2 or Precision Scan-D) is then automatically set to each spectral position, after which a measurement resulting in the ringdown time for this specific wavelength is initiated.

To be able to measure broad-band absorptions as discussed in section 2.4, it should be possible to determine \( \tau_0 \) for every wavelength value. This is done by performing two measurements of the ringdown time at each spectral position. In between, the user is given the opportunity to change the experimental conditions. In most cases, the precursor flow was switched on and off. By doing this, both \( \tau \) and \( \tau_0 \) are recorded. Then the next wavelength step is made.

A third version is built, which can be used to modulate the plasma (option 3 in section 2.4). For this, a digital delay / pulse generator (Stanford Research Instruments, DG535) is used. The generator is connected to the PC by GPIB and triggers the CRD-laser system. It can be synchronised with for instance an RF-plasma via a common pulse generator, which modulates the plasma. See Fig. 3.5 below.

![FIG. 3.5: Schematic diagram of a CRD-set-up with plasma-modulation. An RF plasma source is used as an example to clarify the set-up.](image-url)

Controlling of the timing of the measurement is possible by changing the delay time for the YAG-laser pulse with respect to the starting time of the RF-plasma. Then also the scope is triggered and measurements are performed in one interval of the modulated RF-plasma, \textit{e.g.} "plasma off". When finished (normally after 64 laser
shots), the delay time is changed to measure in the other interval of the RF-plasma, e.g. "plasma on". Subsequently, the laser can be moved to the next spectral position.

**SCAN USER-DEFINED**

With this program, it is possible to perform a number of CRD-measurements as function of any user-defined variable as for instance arc current, (precursor) gas flow or pressure. Before the first measurement will take place, the user is asked to set the first desired parameter value, after which determination of $\tau$ can be initiated. When this is completed, the parameter can be adjusted to the next value. To complete with, also two measurements can be taken for each user-defined step to allow determination of both $\tau$ and $\tau_0$. 
In this chapter the CRD measurements to detect methyl radicals (CH₃) are presented. First, the plasma processes are explained (4.2), then the spectroscopy of the methyl radical is discussed. The results are presented in section 4.4, after which some discussion about these and earlier results is entered in section 4.5.

4.1 Introduction

In expanding Ar/CH₄-plasmas, which are used in expanding thermal plasma deposition of hydrogenated amorphous carbon (a-C:H) layers, the role of the methyl radical CH₃ in the deposition process is not completely understood. The radical is expected to be dominantly present in the plasma, as concluded from both modelling [14] and experiments [15]. Direct CH₃ density measurements should confirm this for the cascaded arc set-up as used at the Eindhoven University of Technology. However, some authors conclude from their models and experiments that CH₃ radicals contribute significantly to the deposition of a-C:H films, e.g. [16] and [17], whereas others suggest that higher polymers, produced in the Ar/CH₄-plasma, are responsible for film growth [18]. In order to better understand these processes and to clarify the present discussion, the study of the methyl radical is imperative. Here, this study is performed by measuring absolute absorptions with the sensitive cavity-ringdown technique.

4.2 Plasma chemistry in an expanding Ar/CH₄ plasma

4.2.1 Plasma processes

To produce an expanding Ar/CH₄-plasma, methane (CH₄) is injected as the precursor gas in the Ar-plasma through the injection ring (see Fig. 3.1). The CH₄ molecules are then ionised by Ar⁺-ions (charge exchange, [19]; the superscripts \( r \) and \( v \) denote certain rotational and / or vibrational excitations, * indicates excited Rydberg states):

\[
\begin{align*}
\text{Ar}^+ + \text{CH}_4 & \rightarrow \text{Ar} + \text{CH}_4^{+,r,v} & k = 1 \cdot 10^{-16} \, \text{m}^3/\text{s} \\
& \rightarrow \text{Ar} + \text{CH}_3^{+,r,v} + \text{H} & k = 1 \cdot 10^{-15} \, \text{m}^3/\text{s} \\
& \rightarrow \text{Ar} + \text{CH}_2^{+,r,v} + \text{H}_2 & k = 3 \cdot 10^{-16} \, \text{m}^3/\text{s}
\end{align*}
\]

(it should be noted that the given rates are indicative). The first channel is important for the creation of methyl (CH₃), which is then formed by dissociative recombination:

\[
\text{CH}_4^{*} + \text{e}^- \rightarrow \text{CH}_3^{*,r,v} + \text{H}^* \\
k = 2 \cdot 10^{-13} \, \text{m}^3/\text{s}
\]
The methyl radical may stick to the wall or react at the wall or in the gas phase. This will be discussed in the next section.

4.2.2 Chemical reactions with methyl

When the methyl radical is formed, higher order reactions can take place, at the surface or in the gas phase. Processes, in which radicals are destroyed by surface reactions, are characterised by the loss probability $\beta$. This coefficient includes two different mechanisms. The first is the probability that stable species are desorbed back to the gas phase after a surface reaction of the radicals. This is referred to as the recombination probability $\gamma$. The second is the sticking probability $s$, which represents the likelihood that radicals, chemisorbed on the surface, are incorporated into the growing film. Hence, $\beta = s + \gamma$. For CH$_3$ the reported loss probability is very low: $0.001 < \beta_{\text{CH}_3} < 0.01$, [14] and [20]. Preliminary experiments by Von Keudell [21] indicate even $s \approx 10^{-5}$. This low loss probability is one of the key points in the current discussion concerning the contribution of CH$_3$ to the growth of a-C:H films.

In the gas phase, methyl radicals may react with other radicals such as CH$_2$, CH$_3$ or with CH$_4$ molecules, by which two-carbon molecules are produced such as C$_2$H$_2$ (acetylene), C$_2$H$_4$ (ethylene) and C$_2$H$_6$ (ethane), or even higher polymers. For polymerisation reactions see [22] and [18].

4.3 Spectroscopy of CH$_3$

First spectroscopic descriptions of methyl have been given by Herzberg [23]. He observed the $B \leftarrow X$ electronic transition at 216 nm, which consists of two diffuse maxima. The continuous absorption profile, i.e. broad band absorption, is a result of predissociation (for CH$_3$: p.465, [23]), a process which is discussed in section 2.2.2. Also see the schematic potential energy curves in Fig. 4.1.

![Fig. 4.1: Schematic potential energy diagram with the predissociation process of CH$_3$ upon an electronic X- to B-state transition.](image-url)
After transition to certain levels in the excited $B$-state that have their classical turning point close to a crossing of the stable ($B$-)state with a dissociative state (in Fig. 4.1 level $v=1$), the molecule will after some time find itself on the unstable potential curve that leads to a high molecular distance, i.e. the molecule dissociates. (The time constant involved depends, classically, on the position of the crossing point: a position very close to the classical turning point means a short lifetime of the $B$-state. Levels $v=2$ and higher, which are also pre-dissociative (see Fig. 4.1), will have a longer lifetime). In analogy with pre-dissociation of SiH$_3$ (discussed in the next chapter), the dissociation products are expected to be CH$_2$ and H, possibly in an excited state (this is unknown).

In this project, the methyl radical is measured on the $\tilde{B} \, ^2A'_1 \leftarrow \tilde{X} \, ^2A'_2$ transition around 216 nm (called the $\beta_1$(0-0) band by Herzberg). It consists (at room temperature) of two maxima: an $R$-band centred at 215.7 nm and a $P+Q$-band centred at 216.4 nm. The full width at half maximum of the combined absorption peaks ($R$ and $P+Q$) is several nm (cf. section 2.2.3 for more details about these branches). The molecule is thought to be planar due to the absence of the $^2E' \leftarrow ^2A_2^+$ transition, which in this case is an electronically forbidden transition (cf. Table 65 in [23] for more information).

The absorption cross-sections for the $B \leftarrow X$ transition are not very well known. In this report, we make use of values given in Table 4.1.

**TABLE 4.1 Absorption cross-sections of methyl (CH$_3$) for the $B \leftarrow X$ transition.**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Cross-section (m$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>213.9</td>
<td>3.89 · 10$^{-22}$</td>
<td>Hwang et al. [24]</td>
</tr>
<tr>
<td>216.6</td>
<td>8 · 10$^{-22}$</td>
<td>Zalicki et al. [25]</td>
</tr>
</tbody>
</table>

Hwang and co-workers found the cross-section to be constant within the range of gas temperatures between 1250 and 2000 K. However, both wavelength and cross section for the peak absorptions are expected to vary significantly with temperature as reported by other authors [26].

### 4.4 Cavity-ringdown measurements

With the CRD set-up as given in Fig. 3.2, absorption measurements of CH$_3$ on the previously mentioned electronic transition are made. Results of spectral scans and flow- and current series are given in the sections below. In these experiments, due to the broad-band character of the methyl absorption, ringdown time measurements of both an empty and a filled cavity are made. This is accomplished by switching the precursor flow on and off. This is the second method as mentioned in section 2.4. After switching, a delay of some seconds was introduced to allow the plasma to reach a stationary state.

**4.4.1. Reflectivity of mirrors**

From the measurements without absorbance, the reflectivity $R$ of the coated mirrors is derived. Ringdown times of typically 80 to 90 ns have been measured at 215 to 218 nm (see Fig. 4.2), which yield a reflectivity $R = 97\%$. Specified is a
minimum transmittivity $T = 0.2\%$ around 218 nm, which would give a higher reflectivity $R = 99.8\%$. However, also refractional losses in the mirror should be taken into account if the specified $R$ is calculated ($R = 1 - T - L$, where $L$ includes additional losses), so the maximum reflectivity will always be somewhat lower. Nevertheless, if the mirrors were mounted on the vessel and the vessel itself remained at low pressure (order $10^{-6}$ mbar) for a prolonged time (up to several days), reflectivity was found to improve. A maximum ringdown time of 180 ns was observed at 217 nm, which gives $R \approx 98.5\%$. This suggests an effect on the reflective coating if the mirrors are placed in an atmospheric surrounding, probably due to inward hydrogen diffusion as reported by Boogaarts et al. in [10].

For the 78 cm long cavity, a time of 85 ns means that during one ringdown time the light pulse travels 26 m, equivalent to 34 passes or 17 roundtrips. (A ringdown time of 180 ns yields 71 passes, which is already difficult to obtain using straightforward multipass techniques).

**4.4.2. Spectral scan**

In Fig. 4.2 the CRD-measurement of CH$_3$ on the $B \leftrightarrow X$ transition around 216 nm is presented. The plasma parameters are: arc current $I_{\text{arc}} = 56.8$ A, flow of argon $\phi_{\text{Ar}} = 100.0$ scc/s and flow of methane $\phi_{\text{CH}_4} = 36.0$ scc/s. This combination represents a typical plasma setting during a-C:H deposition. For each wavelength value, first the measurement without CH$_4$ gas flow was taken, then the ringdown time with CH$_4$ gas flow was obtained, after which a wavelength step was made. After switching the flow controller, some time was allowed for the plasma to adapt to the new conditions and to stabilise. Each data point was obtained from an average over 64 laser shots.

![FIG. 4.2: CRD-measurement in an Ar-plasma ($\tau_0$) and in an Ar/CH$_4$-plasma ($\tau$). Plasma conditions are: $I_{\text{arc}}=56.8$ A, $\phi_{\text{Ar}}=100.0$ scc/s and $\phi_{\text{CH}_4}=36.0$ scc/s.](image)

The absorption profile is obtained from the difference in ringdown time with and without absorber using Eq. (2.11).
The corresponding absorption spectrum is shown in Fig. 4.3 (square data markers; also given is the spectrum as reported in literature).

![Absorption spectrum of CH₃ (B→X transition) for different conditions of the expanding Ar/CH₄ plasma](image)

Insert: spectrum as reported in literature by Zalicki et al. [25].

The spectrum measured at the plasma conditions $I_{\text{arc}} = 56.8$ A and $\varphi_{\text{CH}_4} = 36.0$ scc/s is reproduced (square data markers, dotted line) and clearly shows the two broad absorption peaks that result from the underlying $P$, $Q$ and $R$ branches. The first peak at 215.8 nm covers the $R$ lines, the second one at 216.3 nm the combined $Q+P$ lines of this vibronic band, which are all broadened by the predissociative life-time. The peak wavelengths are slightly shifted with respect to the theoretical values: the $R$ peak 0.1 nm to the red, the $Q+P$ peak 0.1 nm to the blue side of the spectrum. This is probably a coincidental result of the chosen stepsize, being also 0.1 nm. A structureless absorption extends to lower wavelengths. This could be allocated to a secondary absorption band at 212.5 nm, which extends from 216 nm to below 210 nm as a very broad absorption feature, as reported by Callear and Metcalfe, [27]. Or, as mentioned by Zalicki and Wahl and co-workers ([25] and [28]) who studied CH₃ by CRDS in a hot-filament reactor at 213.9 nm, the methyl spectrum could be interfered by acetylene (C₂H₂) absorptions. This possibility will be discussed later.

The estimated concentration of CH₃ in the vessel is $1.9 \cdot 10^{19}$ m⁻³, based on the measured absorption at 213.9 nm, an absorption path length² of 0.7 m and the absorption cross section at this wavelength of $3.89 \cdot 10^{-22}$ m². This is consistent with a determination of the density from the absorption at 216.6 nm ($\sigma = 8 \cdot 10^{-22}$ m²), which yields $n = 1.7 \cdot 10^{19}$ m⁻³.

---

² The methyl radicals are expected to be uniformly present in the entire vessel due to their low loss probability. As a result, the complete cavity length should be taken as the absorption path length. It would be explicatory to measure the density as function of the radial position to verify this. This will be discussed later.
In Fig. 4.3, also spectra measured at different plasma conditions are plotted. The combinations $I_{\text{arc}} = 36.7 \, \text{A}$, $\varphi_{\text{CH}_4} = 44.5 \, \text{scc/s}$ and $I_{\text{arc}} = 89.2 \, \text{A}$, $\varphi_{\text{CH}_4} = 15.2 \, \text{scc/s}$ are chosen because they represent extreme cases of low and high temperatures in the plasma, respectively. The different shapes of the absorption profiles for the various plasma conditions can be clearly seen.

First, differences between the peak structures are visible: in the case of a high temperature (round data markers), the absorption peaks are more flat. This considerable effect is apparently caused by the difference in temperature and confirms the consideration that the absorption spectrum and thus the wavelength dependent cross section is significantly temperature dependent. This is also affirmatively reported by Davidson et al. in [26] for the cross section at 216.615 nm. Also, in the tails of the double peak structure the absorption decreases less rapidly for higher temperatures, resulting in a wider profile. These effects can not be explained by Doppler broadening: this is only in the order of $\Delta \lambda / \lambda = 10^{-6}$.

Second, at the blue side of the spectrum the absorption significantly increases for higher temperatures. This effect might be caused by acetylene absorption as mentioned before and is not necessarily interpreted as a contribution from CH$_3$. The C$_2$H$_2$ absorption will be discussed next.

### 4.4.3. Acetylene absorption

As already mentioned before, the CH$_3$ absorption spectra could be influenced by absorption from C$_2$H$_2$ molecules, that are also generated in a Ar/CH$_4$-plasma (see reactions (4.1) and [29]):

\[
\begin{align*}
\text{CH}_3^+ + e^- &\rightarrow \text{CH}_2^+ + \text{H}^+ & k = 2\cdot10^{-13} \, \text{m}^3/\text{s} \\
\text{CH}_2 + \text{CH}_2 &\rightarrow \text{C}_2\text{H}_2 + \text{H}_2 & k = 5\cdot10^{-17} \, \text{m}^3/\text{s}
\end{align*}
\]

Another process is given by Dagel et al. [18], who identify CH$_3$ recombination as the principle loss mechanism:

\[
\begin{align*}
\text{CH}_3 + \text{CH}_3 + \text{(M)} &\rightarrow \text{C}_2\text{H}_6 + \text{(M)} & k = 8\cdot10^{-17} \, \text{m}^3/\text{s} \\
\text{CH}_2 + \text{CH}_3 &\rightarrow \text{C}_2\text{H}_4 + \text{H} & k = 1\cdot10^{-16} \, \text{m}^3/\text{s}
\end{align*}
\]

The products C$_2$H$_6$ and C$_2$H$_4$, which can also be created by desorption from the surface after radical impact, can give C$_2$H$_2$ by H$_2$-abstraction. The C$_2$H$_2$ transition of interest is the $\tilde{A} \, ^1\Sigma_u^+ \leftrightarrow \tilde{X} \, ^1\Sigma_g^+$ electronic transition from 210 to 237 nm consisting of several narrow absorption lines. Refer to Table 66 in [23].

To establish the influence of acetylene absorption on the methyl absorption measurements, several parts of the CH$_3$ spectrum have been measured again under plasma conditions in which the C$_2$H$_2$ production is mostly favoured (high arc current,
This is done at the highest possible resolution (which is limited by the laser bandwidth): $1.5 \cdot 10^{-3}$ nm (0.4 cm$^{-1}$). The measurements always showed a structureless, continuous absorption, not allowing identification of the absorbing species by its spectral fingerprint. See an example in Fig. 4.4 (upper trace).

![Absorption spectra around 214.5 nm in the expanding Ar/CH$_4$-plasma](image)

**Fig. 4.4:** Absorption spectra around 214.5 nm in the expanding Ar/CH$_4$-plasma ($I_{\text{arc}}=89.2$ A, $\phi_{\text{CH}_4}=11.0$ scc/s; upper trace) and in pure C$_2$H$_2$ gas at room temperature (0.313 mbar; lower trace).

However, a measurement with pure C$_2$H$_2$ gas at room temperature and at the same pressure as the Ar/CH$_4$-plasma revealed a dense line spectrum (Fig. 4.4, lower trace). At higher temperatures in the case of the plasma state, two effects occur: first, the lines are broadened as a result of the Doppler broadening. Second, at elevated temperatures the distribution of occupied states changes to higher levels: more energy levels become occupied, which results in an increase in probable transitions at various wavelengths. More different absorption peaks appear and the spectrum becomes denser. This is in literature often referred to as a congested spectrum. As a result, the line profiles broaden and the overall absorption increases, resulting in the structureless steady absorption as obtained in the plasma (round data markers). Around 213.9 nm, a similar structure was found in the Ar/CH$_4$-plasma.

Considering this, the observed absorption on the blue side of the CH$_3$ spectrum in Fig. 4.3 could very well originate from acetylene absorption on the $A \leftarrow X$ transition. Also note in Fig. 4.3 the arc current dependence of absorption below 215 nm: in case of the highest arc current ($I_{\text{arc}}=89.2$ A) the absorption is the highest (compared to the absorption at lower currents). This is in accordance with the expected dependence of C$_2$H$_2$ production on plasma conditions (increasing production with growing current).

---

Production of C$_2$H$_2$ in a methane plasma increases with increasing arc current. The CH$_4$ flow is of minor importance above some 8 scc/s. The acetylene production saturates around 25 scc/s CH$_4$. Refer to [22].
Another spectral measurement is made in the C₂H₂ gas at room temperature to assure that there is no interference of acetylene absorption at 215.9 nm, where methyl absorptions for varying CH₄ flow and arc current are measured (which are presented in the next section). Again, a high spectral resolution is used and the pressure was held constant at 0.312 mbar (with Q_C2H2=14.5 scc/s). See for the resulting spectrum Fig. 4.5.

\[
\text{Gaussian fit}
\]

![Absorption spectrum of C₂H₂ gas at room temperature (p=0.312 mbar) around 215.9 nm (two measurement series). Also shown is a Gaussian peak fit at 215.92 nm (see text).}

The reproducible spectrum in Fig. 4.5 suggests that there is no significant absorption of acetylene at 215.90 nm, at least at room temperature. Apart from this, narrow absorption lines appear around 215.92 nm and higher wavelengths. Identification of these individual lines however failed (also for the lines in Fig. 4.4.) because no extensive spectroscopic database concerning C₂H₂ was available.

A Gaussian profile is fitted to the absorption peak at 215.92 nm. Accounting for the Doppler line width (at T=300 K), the width at half maximum of the peak yields the line width of the laser, which is 0.9 cm⁻¹ (0.004 nm) assuming the considered peak represents a single rovibronic transition. This is a few tenths of a wavenumber higher than the optimal value of 0.7 cm⁻¹ (0.003 nm) as mentioned in section 3.2.1.

4.4.4. Flow and current series

The absorption of CH₃ radicals in the Ar/CH₄ plasma is also measured for different CH₄ flows. In addition, these flow scans are determined for various arc currents. The arc currents are chosen such that comparison with earlier measurements is possible. See Fig. 4.6 on the next page for the series measured at 213.9 nm. Measurements were initially performed at this wavelength because of the fact that it is reported that the corresponding absorption cross-section of methyl does not strongly depend on temperature (see Table 4.1) and the comment of Zalicki et al. [30] that they did not observe any absorption of acetylene at this wavelength. This last comment
contradicts with our results described above. Despite this, the measurements could provide information on the temperature dependence of the absorption cross-section. This will be discussed later.

![Graph of absorption and density of CH₃ as a function of CH₄ flow for various arc currents. Series are taken at 213.9 nm.](image)

**FIG. 4.6:** Absorption and density of CH₃ as a function of CH₄ flow for various arc currents. Series are taken at 213.9 nm.

The measurements show an increase of absorption by CH₃ with increasing arc current: this is evidently a result of the fact that at higher currents more Ar-ions are produced which leads to more charge-exchange reactions (4.1) and thus a higher number of dissociatively recombinative processes, producing CH₃ radicals. Densities up to $3.2 \times 10^{19}$ m⁻³ are found.

Also an increase in density appears with increasing methane flow, although this effect is not visible for the lower currents (probably due to a low signal-to-noise ratio and the influence of C₂H₃ on the absorption). This means that more CH₃-radicals are produced when the CH₄-flow increases, which is trivial. However, the increase is not linear, as would be expected considering constant reaction rates for reactions (4.1), but less than proportional. At around 25 scc/s of methane flow, the absorption saturates in the case of $I_{\text{arc}}=56.9$ A (up triangles), whereas for $I_{\text{arc}}=89.2$ A this does not occur below 40 scc/s. This suggests that the CH₃ production is Ar⁺-limited: the availability of Ar⁺ decreases as more CH₄ is injected, consequently less CH₃ radicals are formed. The flow for which this decrease starts, is determined by the amount of Ar⁺-ions present and hence by the arc current. This might also be a reason why the expected increase in density is not visible for the lower currents.

In previous publications, e.g. [31], a decrease of the CH₄ depletion (or dissociation degree$^5$) was reported for increasing methane flow, which means that relatively less CH₄ molecules are able to form CH₃. This could explain the less than proportional increase in CH₃ absorption. Also the polymerisation to C₂Hₙ polymers with use of methyl becomes more efficiently at higher CH₄ flow, which would lead to a less increasing CH₃ density or even a stabilisation of the density.

$^5$ Defined as the amount of consumed precursor gas divided by the injected amount of precursor gas.
Because of the higher absorption cross-section of methyl radicals near 216 nm (with accompanying better signals) and moreover, the probably smaller interference of acetylene, another set of methane flow scans is measured. This could be done at $\lambda = 215.90$ nm due to the absence of C$_2$H$_2$ absorptions at this wavelength as noticed before. See Fig. 4.7 for the results. Same arc currents and methane flows are used.

**Fig. 4.7:** Absorption of CH$_3$ as a function of CH$_4$-flow for various arc currents. Series are taken at 215.9 nm.

In general, the same trends are visible as in Fig. 4.6. The curves are smoother now due to a better signal-to-noise ratio. The crossing between the lines corresponding to $I_{\text{arc}} = 89.2$ and 56.8 A (down- and up triangles, respectively) is an artificial result of the measurement. In this graph, the absorption curves do not seem to saturate: this will be discussed in the next chapter. The calculated densities are consistent with the values in the previous flow scan. Also the levels of absorption match the absorptions at equivalent conditions in the spectral scan in Fig. 4.3.

To estimate the contribution of acetylene to the measured absorption at 213.9 nm, Fig. 4.4 is used to extrapolate the lower trace to 213.9 nm (as mentioned before, a structure, similar to the upper trace in Fig. 4.4, is measured in the Ar/CH$_4$-plasma around 213.9 nm). If we assume a broadening of the spectral lines for elevated temperatures and a corresponding estimated absorption of $2.5 \times 10^{-3}$ per pass, the accompanying density can be calculated with the ideal gas law (pressure and temperature are known). This results in $n_{\text{C}_2\text{H}_2} = 7.5 \times 10^{21}$ m$^{-3}$. In the Ar/CH$_4$-plasma ($I_{\text{arc}} = 89$ A, $\phi_{\text{CH}_4} = 31.6$ scc/s) an estimated C$_2$H$_2$-flow of 4 scc/s is produced cf. [22]. This is the upper limit. Then, assuming partial pressures$^6$ for Ar (100 scc/s), CH$_4$ and C$_2$H$_2$, we are able to calculate the accompanying density (temperature $T = 1500$ K, pressure $p = 30$ Pa): $n_{\text{C}_2\text{H}_2} = \frac{4}{131.6} \cdot \frac{p}{k_B T} = 4.4 \times 10^{19}$ m$^{-3}$, which is two orders of

$^6$ The pumping speed is independent of the species in the vessel. This means that the individual residence times of the particles are equal. Furthermore, it is known that the particles are fully mixed. This validates the assumption of partial pressures.
magnitude lower. The matching absorption for acetylene then is $1.5 \cdot 10^{-5}$ per pass. This should be compared to the detected absorption in Fig. 4.6, i.e. $8 \cdot 10^{-3}$ per pass. Hence, the contribution of acetylene is only 0.2% at 213.9 nm. It will be clear from Fig. 4.5 that there is no interference of acetylene absorption at 215.9 nm, since there is no absorption detected from C$_2$H$_2$ at 215.90 nm.

At this point, a comparison between methyl and methane densities should be made. For CH$_4$, an estimated density of $n_{\text{CH}_4} = \frac{32}{152} \cdot \frac{p}{k_B T} = 2 \cdot 10^{21}$ m$^{-3}$ can be found at a flow of 52 scc/s ($p = 20$ Pa, $T = 1500$ K and an Ar-flow of 100 scc/s). Given the 60% depletion of CH$_4$ at $I_{\text{arc}} = 89$ A for this flow (cf. Fig. 1 in [31]) and $n_{\text{CH}_3} = 3.2 \cdot 10^{19}$ m$^{-3}$, it follows that $n_{\text{CH}_3}/n_{\text{CH}_4} = 2$% of the injected methane is transformed into methyl. According to the rate constants for reactions (4.1), 7% of the consumed CH$_4$ would be used to form CH$_3$. However, there exist several reactions in which CH$_3$ is subsequently consumed, e.g. reactions (4.4). This would account for the lower percentage.

To confirm the influence of temperature on the absorption cross-section as already deduced from Fig. 4.3, the absorptions measured in the flow- and current series for 213.9 (A$^{213.9}$) and 215.9 nm (A$^{215.9}$) should be compared to each other. This is done in Fig. 4.8. The horizontal axis represents measurements of absorption at 215.9 nm, the vertical at 213.9 nm.

**Fig. 4.8:** Comparison between detected absorptions at 213.9 and 215.9 nm (see Fig.'s 4.6 and 4.7). The slope of the line is given by $\sigma^{(213.9)}/\sigma^{(215.9)}$. The methane flow increases from left to right (see arrow).

Taking into consideration that for each data point the same density of CH$_3$ is present (same plasma conditions) and that path length $l$ is constant, the absorptions at 213.9 and 215.9 nm should coincide with the ratio of absorption cross-sections, i.e. $A^{(213.9)} = (\sigma^{(213.9)}/\sigma^{(215.9)}) \cdot A^{(215.9)}$. This ratio is characterised by the line in Fig. 4.8. Except for the flow scans at $I = 89.2$ A, the data points are located around the line.
representing the cross-section ratio for low CH₄-flows. When the methane flow is increased (above 23 scc/s), the data start to deviate from this line to the right side. This means, that the cross-section ratio decreases as the slope of the line declines in order to fit to these points. A higher flow means a lower temperature (due to more cooling capacity). Hence, if we assume that \( \sigma^{(213.9)} \) remains constant within the used temperature range cf. [24], it can be concluded that \( \sigma^{(215.9)} \) becomes higher when decreasing the temperature. This inverse dependency is also reported by Davidson and co-workers [26].

The fact that the data points for 89.2 Å can be found somewhat higher than the cross-section ratio can be explained by the influence of acetylene absorption. As argued before, the production of C₂H₂ is favoured by a high current. Thus, at wavelengths where absorption by acetylene occurs, i.e. at 213.9 nm, the measured absorptions will be higher than predicted by the ratio of cross-sections. The fact that the difference is 4·10⁻⁴ per pass, which is higher than the estimated C₂H₂ contribution (see before), suggests that also the temperature dependency of the cross-section at 215.9 nm causes the points to be more to the left (a lower flow gives rise to a higher temperature). Subsequently, at higher flows (also around 23 scc/s), the points move to the right side, revealing the same behaviour as discussed before.

The found dependence of the cross-section on temperature confirms the suggestions mentioned in section 4.4.2 concerning the differences in the CH₃ spectra.

4.5 Contribution of CH₃ to film growth

At this point, the question whether methyl contributes significantly to the growth of a-C:H films, raised in the introduction of this chapter, should be answered if possible. To be able to do this, several experimental facts should be set side by side to construct arguments pro or contra. This is done in the following sections.

4.5.1 Density, sticking probability and growth rate

From absorption measurements on CH₃ it can be concluded that the methyl radical is significantly present in the entire reactor during Ar/CH₄-plasma operation. Densities up to 3.2·10¹⁹ m⁻³ have been found. Beside this, density is increasing with increasing methane precursor flow, although not linearly. However, from this high density and by the assumed analogy with deposition from SiH₃ radicals forming a-Si:H films, it can not be concluded that CH₃ is the dominant film growth precursor: contrary to silyl (SiH₃), methyl has a reported very low loss probability \( \beta \) and thus a low sticking probability (or 'growth efficiency') \( s \), which is in the order of 10⁻³. This also suggests that gas-phase reactions are more probable to occur.

With this number and the particle density \( n \), the theoretical growth rate for deposition of a-C:H films by CH₃ radicals can be deduced. This deposition rate \( R_g \) resulting from a diffusive flow is given by (for the derivation see Appendix I):
\[ R_g = \frac{1}{4} n \nu_\text{th} \frac{m}{\rho} \frac{s}{1 - \frac{1}{2} \beta}, \quad (4.5) \]

in which \( \nu_\text{th} \) is the thermal velocity (500 m/s), \( m \) represents the mass of a carbon atom \((2.0 \cdot 10^{-23} \text{ g})\), and \( \rho \) denotes the volumetric density of an a-C:H film \((2.0 \cdot 10^6 \text{ g/m}^3)\).

First we insert a sticking probability for CH\(_3\) of 0.001 (assuming that \( s = \beta \)), and the highest measured CH\(_3\) density \((3 \cdot 10^{19} \text{ m}^{-3})\), which then yields a growing rate \( R_g = 0.04 \text{ nm/s} \) \(^7\). This is much lower than the observed growth rates ranging to 14 nm/s, which has been obtained in an Ar/CH\(_4\)-plasma using the cascaded arc source [31] with the same gas flows and arc currents (the substrate temperature was held constant at \( T_{\text{substrate}} = 50 \degree\text{C} \)).

However, some authors suggest an enhancement of \( s \) during discharges. Refer to [16] (RF plasma) and [17] (electron cyclotron resonance plasma) for experimental arguments and [32], [33] for models. During RF and ECR plasma operation, the growth surface is exposed to an ion bombardment, which could create active sites to which radicals can chemisorb. This way, the surface becomes more reactive and thus the sticking of methyl radicals gets more effective. Assuming the reported [16] upper bound \( \beta = 0.011 \) as a result of this process, the maximum achievable growth rate is ten times higher, 0.4 nm/s, which still is less than 3% of the maximum observed growth rate. (Eventually, assuming that the CH\(_3\)-radical is fully responsible for the observed growth, a sticking probability of 0.3 should be achieved if \( n_{\text{gas phase}} (6 \text{ cm}) = n_{\text{surface}} \)). These arguments lead to the conclusion that CH\(_3\) radicals do not contribute significantly to the growth of a-C:H films in an expanding Ar/CH\(_4\)-plasma and can not be seen as the dominant growth radical.

Furthermore, as already reported in section 4.4.4, the CH\(_3\) density increases with increasing methane flow and no density maximum appears. If the presence of CH\(_3\) would directly lead to a-C:H growth, the same trend should be observed for the growth rate as function of methane flow (which means that methyl density and growth rate are correlated). For the growth rate vs. injected methane flow refer to [31]. In Fig. 4.9 on the next page the growth rate is plotted as function of CH\(_3\) density.

\(^7\) It should be noted that the CH\(_3\)-density inserted in Eq. (4.5) is the gas phase density at 6 cm from the surface whereas \( n \) refers to the density near the surface. Since the first density is higher than the latter radical density (radicals are lost at the surface), the growth rate is overestimated. This error becomes smaller for lower values of \( \beta \).
It is evident that the growth rate does not vary linearly with respect to or even correlate with the CH$_3$ density present in the plasma as would be predicted from Eq. (4.5). This implies that growth does not originate from methyl radicals and deposition has to be caused by other species.

4.5.2 Conclusion

The reasoning in the previous sections a clear answer for the debate whether methyl radicals provide significant deposition to a-C:H films in a first order reaction in the expanding Ar/CH$_4$-plasma. It can be concluded that CH$_3$ radicals do not deposit and as a consequence of the long residence time high densities are built up.

Furthermore, De Graaf and co-workers [31] report polymerisation from the radicals produced in the dissociation of the injected methane. The first polymer to appear is C$_2$H$_2$, which is also found in the experiments carried out in this work. The main dissociative channel of acetylene leads to C$_2$H radicals, which have a relatively high loss probability. Given the reported linear correlation between the C$_2$H$_2$ production in methane and the growth rate [31], it is suggested that C$_2$H may become the dominant growth precursor for a-C:H films in Ar/CH$_4$-plasmas. This is also affirmatively suggested by [18] and, more recently, by [34]. However, recent modelling of the relative C$_2$H$_2$-production in an Ar/CH$_4$-plasma does not (yet) confirm the observed trend in growth rate in this plasma. Other candidates could be CH and / or CH$_2$ radicals, which is also being investigated.
Chapter 5

CAVITY-RINGDOWN DETECTION OF SiH₃ IN AN EXPANDING Ar/H₂/SiH₄ PLASMA

In this chapter the first results of CRD-measurements on silyl radicals (SiH₃) in an expanding Ar/H₂/SiH₄-plasma are presented. After a short introduction, the relevant processes in the plasma are described (5.2). Then in section 5.3 the spectroscopic details of the silyl radical are given, after which the CRDS results are presented in section 5.4. In section 5.5 a comparison will be made to other experimental results.

5.1 Introduction

At the Eindhoven University of Technology, a remote silane plasma generated by a cascaded arc is used for deposition of a-Si:H, by which films with good solar grade properties can be obtained at a growth rate of 10 nm/s [35]. As already mentioned in the Introduction (chapter 1), silyl (SiH₃) is expected to be the most dominantly contributing radical during growth of a-Si:H thin films. To verify this hypothesis and to corroborate the expected behaviour of SiH₃ upon external plasma parameters like gas flows, in-situ measurements of gas phase SiH₃ densities should be carried out. This is established with the sensitive cavity-ringdown technique.

5.2 Plasma chemistry in an expanding Ar/H₂/SiH₄ plasma

5.2.1 Plasma processes

A mixture of Ar and H₂ is injected into the cascaded arc (see section 3.2.1), where the thermal Ar/H₂-plasma is generated. The arc runs at 45 A (180 V). The Ar-flow is 55 scc/s and the H₂-flow can be varied between 0 and 15 scc/s. Pure silane gas (SiH₄) is injected as the precursor into the low-pressure (0.2 mbar) deposition chamber by means of an injection ring.

Due to the low downstream electron temperature (0.1 to 0.3 eV), mainly reactive heavy particles, emanating from the plasma source, interact with SiH₄. When the hydrogen flow is low, these are essentially Ar⁺-ions, whereas in the case of higher H₂-flows H⁺-ions dominate. Even more, when admixing of H₂ is increased, the plasma source acts primarily as an atomic hydrogen source [35], [36]. Distinguishing between these two regimes, SiH₄ is dissociated according to the following reactions:

- For no or low H₂-flow the reactivity of the expanding plasma is dominated by Ar⁺. Consequently, mainly ion-molecule dissociative charge-exchange reactions occur (for which the reaction rates are in the order of $10^{-16} - 10^{-17}$ m³/s):

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

\[ (5.1) \]
which are almost immediately followed either by fast dissociative recombination reactions (rate $10^{-13}$ m$^3$/s) provided the electron density is high, $n_e > 10^{17}$ m$^{-3}$:

$$\text{SiH}_4^+ + e^- \rightarrow \text{SiH}_m + p \text{H}_2 + q \text{H} \quad (m \leq 2), \quad (5.2)$$

or by reactions with silane gas:

$$\text{SiH}_2^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{SiH}_3 \quad k = 1.1 \cdot 10^{-15} \text{ m}^3/\text{s}. \quad (5.3)$$

In this way, radicals as SiH, SiH$_2$ and SiH$_3$ are created, which are very reactive with both SiH$_4$ (apart from SiH$_3$) and the surfaces. When the electron density is decreased, reactions can take place in which large cationic clusters are produced with up to ten silicon atoms, forming eventually dust particles (see [37]):

$$\text{Si}_n \text{H}_m^+ + \text{SiH}_4 \rightarrow \text{Si}_{n+1} \text{H}_p^+ + q \text{H}_2 \quad (m + 4 = p + 2q). \quad (5.4)$$

- In case of a high H$_2$-flow (several scc/s), hydrogen abstraction dominates the silane dissociation due to a high density of atomic hydrogen:

$$\text{H} + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}_2 \quad k \approx 10^{-17} \text{ m}^3/\text{s}, \quad (5.5)$$

by which a large amount of silyl is produced.

The produced SiH$_3$ is known to be less reactive with silane or other radicals and hence capable of reaching the substrate relatively easy. For more information the reader is referred to work reported by [38] and [39]. For a comprehensive review concerning chemical reactions in which silane and related products are involved, see [40].

### 5.2.2 Surface reactions

In analogy with the hypothesis of CH$_3$ being the dominant growth precursor for a-C:H thin films (treated in the previous chapter), the surface reaction probabilities $\beta$ for the various radicals present in the Ar/H$_2$/SiH$_4$-plasma should be investigated to identify the main growth precursor. This has already been done extensively by various experimental groups, of which a summary can be found in [41]. Under plasma- and substrate conditions that yield optimal film quality (i.e. $I_{arc} = 45$ A, gas flows Ar: 55, H$_2$: 10 and SiH$_4$: 10 scc/s), a surface reaction probability $\beta$ of $0.33 \pm 0.05$ is measured for SiH$_3$, [41], which is in good agreement with other results on different reactors. This surface reaction probability is significantly higher than the value for CH$_3$ radicals (which is in order of $10^{-3}$) as mentioned in the previous chapter. It is suggested by Perrin et al. [20] that this difference results from the radical structures: the CH$_3$ radical is planar, as already deduced by Herzberg [23], whereas the SiH$_3$ radical has a tetrahedral structure (see [45] and references therein). For a more detailed discussion the reader is referred to [20].
5.3 Spectroscopy of SiH₃

First observations of the silyl radical were made in cryogenic matrices with ESR spectroscopy in 1966. Then in 1986 Olbrich [42] predicted the excited states of SiH₃ by extensive MRD CI⁸ molecular orbital calculations. These revealed the first excited (Rydberg) state at 238.9 nm, which is dissociative with respect to SiH₂ and H [43]. The short life-time of the excited state suggests a structureless absorption band as a result of the $\tilde{A} \, ^2A_i \leftarrow \tilde{X} \, ^2A_g$ electronic transition, which then is pre-dissociative. A detailed spectroscopic description of SiH₃ is given in [44] and [45]. The absorption cross-section which is used in this report is determined experimentally by Lightfoot et al. [43]: $\sigma = 2.4 \cdot 10^{-21}$ m² at 215 nm, where the maximum absorption was found.

5.4 Cavity-ringdown measurements

In this section the first cavity-ringdown measurements on SiH₃ in the Ar/H₂/SiH₄-plasma are presented. The set-up as explained in section 3.2.2 is used. The gas phase is sampled at 11 cm in front of the sample holder. First, a wavelength scan revealing the spectrum of silyl is presented. Next, absorption (or density) measurements as function of different gas flows are shown.

In advance, no significant change of the ringdown time is observed in the case of a SiH₄- and / or Ar/H₂-gas flow and an Ar/H₂-plasma, indicating that there is no direct interfering absorption when trying to measure SiH₃-absorption. This is in contrast with work done by Boogaarts and co-workers [10], who noticed that the reflectivity of the mirrors and thus the ringdown time significantly altered in presence of a hydrogen containing plasma. For the experiments described now, another set of cavity mirrors is used with a different reflective coating, which might explain this discrepancy. Nonetheless, interference could arise from other plasma-produced radicals, as in the case of CH₃.

5.4.1 Spectral scan

Due to the expected broad absorption profile as indicated in section 5.3, CRD-measurements have been performed using the second measuring method as mentioned in section 2.4. Furthermore, because of the length of the scan, the determination of the spectrum was split into several parts, for which the CRD-signal was optimised individually. These sub-scans were all reproducible. Plasma conditions were $I_{\text{arc}} = 45$ A, $\varphi_{\text{Ar}} = 55$ scc/s, $\varphi_{\text{H₂}} = 10$ scc/s, and $\varphi_{\text{SiH₄}} = 5$ scc/s. These settings (except the silane flow, which normally is 10 scc/s) represent standard experimental conditions for a-Si:H deposition. The overall spectrum over the full range of the optical set-up is given in Fig. 5.1 on the next page.

⁸ MRD CI stands for multi-reference double-excitation configuration interaction.
FIG. 5.1: Absorption spectrum of SiH$_3$ ($A \leftarrow X$ transition) in an expanding Ar/H$_2$/SiH$_4$-plasma ($I_{arc} = 45$ A, $\varphi_{Ar} = 55$, $\varphi_{H_2} = 10$, and $\varphi_{SiH_4} = 5$ scc/s). Inset: spectrum as reported in literature by Lightfoot and co-workers [43] together with the measurements from this work.

The spectral scan shows only a part (14 nm wide) of a very broad structure, in which the maximum absorption (0.005 per pass) seems to appear at 215 nm. Given the reported cross-section and an absorbing length of 0.2 m, this yields a density of $1.0 \times 10^{19}$ m$^{-3}$ for the SiH$_3$ radicals. The relative decrease of absorption at 226 nm (approximately 0.0035 per pass) with respect to the peak value is 30%. The decrease from 215 nm to lower wavelengths seems to be steeper. Lightfoot et al. reported a similar spectrum, see the inset in Fig. 5.1 [43]; their UV-absorption measurements extended from 205 to 260 nm and a maximum absorption was found at 215 nm. Also, a faster decrease was recorded into the blue range than to higher wavelengths. At 226 nm, they found an absorption decrease of only 10%.

Toyoda and co-workers [46] detected SiH$_3$ with UV transmission spectroscopy and found a minimum transmission at 215 nm with a broader absorption tail to the region of higher wavelengths as compared to lower wavelengths. This is in accordance with the in Fig. 5.1 depicted spectrum. However, their results show a 66% decrease at 226 nm. These differences are not yet understood. A possible explanation could be the influence of dust particles in their work: according to reaction (5.4), large Si$_{x}$H$_{y}$ clusters can grow. And, as known from theory, the amount of light that scatters at particles with dimension $d$ increases towards shorter wavelengths. As a result, UV measurements can be influenced, as is demonstrated in [46]. Apart from this, the absorbing features of Si$_{x}$H$_{y}$ clusters are not known and the SiH$_3$ spectrum might be interfered by absorption from these particles.
To ensure that there is no change of the measured spectral features of silyl when H\textsubscript{2}-gas is admixed, the spectrum is measured again for conditions with and without H\textsubscript{2} gas flow. See Fig. 5.2 below.

![Absorption spectra of SiH\textsubscript{3}](image)

**Fig. 5.2**: Absorption spectra of SiH\textsubscript{3} (A ← X transition) for two plasma conditions (I\textsubscript{arc} = 45 A, $q_{Ar} = 55$ scc/s, $q_{H2} = 0$ scc/s (upper trace and line (scaled)) and 10 scc/s (lower trace), and $q_{SiH4} = 5$ scc/s).

The spectra in Fig. 5.2 suggest no change of the measured spectroscopic features under the influence of the admixing of H\textsubscript{2} (the scaled and averaged signal for 0 scc/s coincides with the trace for 10 scc/s H\textsubscript{2}-flow). The only difference is the value of the absorption itself: this is higher in the case of no hydrogen flow (square data markers). This indicates higher SiH\textsubscript{3}-densities in the absence of H\textsubscript{2}. This will be discussed in more detail in the next section. The absolute absorption in Fig. 5.2 for the lower trace (10 scc/s H\textsubscript{2}) is higher than in Fig. 5.1, obtained under identically set conditions. This can be subscribed to a shift of the calibration of the silane flow controller (around 7 scc/s SiH\textsubscript{4} is injected instead of 5 scc/s, which results in higher SiH\textsubscript{3}-densities).

5.4.2 Dependence of SiH\textsubscript{3}-density on SiH\textsubscript{4}-flow

To be able to assign the measured spectrum uniquely to SiH\textsubscript{3} and to record silyl densities as function of gas flows, absorption measurements are performed at the peak wavelength, *i.e.* 215 nm, for various SiH\textsubscript{4} precursor gas flows. Plasma conditions are $I_{arc} = 45$ A and $q_{Ar} = 55$ scc/s. No H\textsubscript{2}-gas was injected. For calculating the density, the absorption cross-section reported in section 5.3 is used. The result is given in Fig. 5.3 on the next page.
Fig. 5.3 shows a twofold linear behaviour: from 0 to 4 scc/s and from 4 scc/s to higher flows of silane. For low flows the measurement is noisier owing to a lower signal-to-noise ratio. The linear correlation between SiH$_3$-density and the SiH$_4$-flow confirms the expected behaviour of a linearly increasing silyl density with increasing silane precursor flow. However, the transition of the slope around 4 scc/s is striking: this is a result of the limited number of Ar$^+$ ions emanating from the source (which amounts to 3 to 4 scc/s at $\phi_{Ar} = 55$ scc/s according to Kessels and co-workers [35]). Consequently, another chemical reaction starts to compete, in which either silane or the silyl radical is consumed. Reaction (5.4), by which large clusters consuming SiH$_4$ are produced, and which is initiated when the electron density is low enough, could be a candidate. (As more silane is injected, more SiH$_4$ is dissociated and immediately recombined with an electron: consequently, the electron density decreases). This would lead to a less increasing silyl density, as observed. The fact that the production of SiH$_3$ does not saturate around 4 scc/s SiH$_4$, can be explained by the fact that there are enough H-atoms present from reactions (5.2) and (5.4) to create SiH$_3$ by H-abstraction. This will be discussed in more detail later.

Densities up to 6.5·10$^{19}$ m$^{-3}$ are reached at the highest silane flow, i.e. 15 scc/s. This is higher than the observed CH$_3$-densities at comparable conditions (1.0·10$^{19}$ m$^{-3}$), even though the loss of SiH$_3$ at surfaces is higher. This means that the production of SiH$_3$ has to be much larger than of CH$_3$. Also the density profiles will be different: for CH$_3$ we expect a homogeneous profile, whereas for SiH$_3$ the highest density will be in the centre of the plasma bundle. This is accounted for in the absorption path length $l$ (see section 2.3).

In Fig. 5.4, another measurement of SiH$_3$-density as function of silane gas flow is presented. This time however, hydrogen gas is admixed in the arc at a rate of 10 scc/s.
FIG. 5.4: SiH3-density as function of SiH4 precursor gas flow in an expanding Ar/H2/SiH4-plasma (I_{arc} = 45 A, \varphi_{Ar} = 55 scc/s, and \varphi_{H2} = 10 scc/s). Measurements are performed at 215.0 nm.

The first measurements (round data markers) are reproduced and extended to higher flows (square data markers). These curves have more or less the same behaviour as in Fig. 5.3, but this time the transition from a higher to a lower slope around 4 scc/s is less visible because of the fact that the silyl production is not fully Ar+-dominated: there is a gradual decrease of the slope. With these plasma conditions, SiH3-densities up to almost 2.0·10^{19} m^{-3} are measured (at a silane flow of 23 scc/s). At 5 scc/s, the absorption corresponds to the value as determined in the spectrum, i.e. 0.005 per pass.

At \varphi_{SiH4}=15 scc/s, the density is now 1.6·10^{19} m^{-3}, which is only 25 \% of the density achieved without H2-gas (Fig. 5.3). This is considerably lower and seems to contradict with the reactions in section 5.2.1, where in the case of H2-injection reaction (5.5) was expected to yield higher silyl densities. In this case SiH3 is already created in the primary reaction and no successive secondary or higher reactions are required as in the case of dissociation by Ar+-ions. If we consider a 'reaction length' or 'interaction length' \lambda_{r}, defined as

$$\lambda_{r} = \frac{v_{th}}{n_{SiH4} \cdot k},$$

we can estimate the average distance, after which a reaction in which SiH4 is consumed with rate \( k \) has taken place. \( v_{th} \) denotes the thermal velocity. Experimental conditions yield a gas temperature \( T \) of 1500 K, a pressure \( p = 20 \) Pa and gas flows 55, 10 and 10 scc/s for Ar, H2 and SiH4, respectively. This results in

\[ n_{SiH4} = \frac{10}{75} \cdot \frac{p \cdot T}{k_B} = 1.3 \cdot 10^{20} \text{ m}^{-3} \]

(ideal gas law; \( k_B \) is Boltzmann's constant) and

\[ v_{th} = 10^3 \text{ m/s}. \]

This can be inserted in Eq. (5.6) to give the reaction length. See Table 5.1 for the results.
TABLE 5.1 Reaction lengths for SiH₃-production from SiH₄-dissociation by Ar⁺ and from H-abstraction by H.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate constant (m³/s)</th>
<th>λₑ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁺ dissociation, (5.1,3)⁹</td>
<td>10⁻¹⁶</td>
<td>0.08</td>
</tr>
<tr>
<td>H-abstraction, (5.5)</td>
<td>10⁻¹⁷</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The first process, Ar⁺-induced dissociation, is fast enough and will take place a few cm from the injection ring. The second process (H-abstraction) however, has a reaction length in the order of 1 m, which extends to regions out of the central plasma beam. Here the densities are lower, hence less reactions will take place. Consequently, less SiH₃ is formed and the density of silyl will be lower for this dissociation process. (It should be mentioned that the distance between the injection ring and the substrate is around 30 cm.) This is in agreement with the observed behaviour and also explains the fact that the SiH₃-production does not saturate at a given silane flow. If the silane flow is increased, λₑ will decrease, see Eq. (5.6). This means that silyl creation by H-abstraction becomes more important and eventually takes over from the Ar⁺-dissociation of silane. Hence, also in Ar/SiH₄-plasmas the SiH₃ production does not saturate, review Fig. 5.3. A similar process occurs for CH₃ production as seen before.

5.4.3 Dependence of SiH₃-density on H₂-flow

For determining the tendencies in SiH₃-density as function of H₂ gas flow, the following plasma conditions are taken: \(I_{\text{arc}} = 45\ \text{A}\), \(\varphi_{\text{Ar}} = 55\ \text{scc/s}\), and \(\varphi_{\text{SiH₄}} = 10\ \text{scc/s}\). For the result, see Fig. 5.5.

![Graph](image)

**FIG. 5.5:** SiH₃-density as function of H₂ gas flow in an expanding Ar/H₂/SiH₄-plasma \((I_{\text{arc}} = 45\ \text{A}, \varphi_{\text{Ar}} = 55\ \text{scc/s}, \text{and } \varphi_{\text{SiH₄}} = 10\ \text{scc/s})\). The line is merely a guide to the eye. Measurements are performed at 215.0 nm.

⁹ The higher limit for the rate constant of reaction (5.1) is taken because of the high SiH₃-densities found in Fig. 5.3. This would suggest an efficient dissociation process (which can be interpreted as a high reaction rate). The secondary reaction with a rate of \(10^{-15}\ \text{m}^3/\text{s}\) has a negligible path length.
The measurements show a distinct non-proportional behaviour. Minimum SiH$_3$-density is found around 5 scc/s of H$_2$. The dependence of the density on H$_2$-flow can be explained by the influence of H on the formation processes of SiH$_3$. As the amount of H$_2$ increases, less silyl is formed according to the reactions (5.1) and (5.3), and reaction (5.5) takes over because of a growing density of H-atoms. This means, the creation of SiH$_3$-radicals becomes less efficient, as is discussed in the previous section. Consequently, the density decreases. At some point, mainly H is produced in the arc (see section 5.2) and creation of silyl by H-abstraction (reaction [5.5]) dominates. The SiH$_3$-density is then at its minimum. According to Fig. 5.5, this occurs at $\varphi_{\text{H}_2} = 5$ scc/s. Then, when the H$_2$-flow is increased, the formation of SiH$_3$ just increases proportionally according to chemical reaction (5.5).

It is interesting to compare the measured absorption to the consumption of SiH$_4$, both as function of H$_2$-flow. This is done in Fig. 5.6 below. The values for depletion or consumption are taken from [36] and have been measured with quadrupole appearance potential mass spectrometry (see also Appendix II).

At 0 scc/s H$_2$, the Ar$^+$-dominated dissociation of silane (reaction [5.1,3]) is responsible for the SiH$_4$-depletion. Because it could be argued that the measured silyl absorption should be linearly dependent on the silane depletion if only reactions with H and Ar$^+$ are taken into account, a line can be drawn from this data point to the origin. (It is evident, that without silane consumption no silyl radicals can be detected). This is the dotted line in Fig. 5.6 having a slope for absorption vs. depletion of 0.035. In analogy to this, a line can be drawn from the measured absorption at 15 scc/s H$_2$, where the H-abstraction by H-atoms dominates the silane consumption. This process is represented by the dashed line (slope 0.064). Given the difference in slope (steeper for H-abstraction), it can be concluded that for the same silane consumption the SiH$_3$-production by H-abstraction is more efficient by a factor of 1.8.
This trend is as expected from the given chemical reactions in section 5.2.1. However, owing to the difference in reaction lengths $\lambda_r$ for the two considered processes (discussed in the previous section), far more H atoms are needed to supply a certain SiH$_3$ density. The silyl production from around 4 scc/s Ar$^+$-ions (which results from 55 scc/s input of Ar) is still much larger than from 30 scc/s H (emanating from the cascaded arc when 15 scc/s H$_2$ is injected).

The difference in the maximum achieved depletion for the two processes (for Ar$^+$-dominated: 0.70; H-dominated: 0.14) confirms the discussion in section 5.4.3 concerning the lower absorption in the case of H$_2$-inlet: owing to the higher reaction length for H-abstraction, less SiH$_4$ is dissociated. Hence, the depletion is lower.

To conclude with, it is noted that the density at $\phi_{\text{H}2} = 0$ scc/s (Fig. 5.5) is comparable to the density at 10 scc/s SiH$_4$ flow in Fig. 5.3, being around $5 \times 10^{19}$ m$^{-3}$, which means that the independent measurements are consistent.

The importance of the presence of H-atoms might also explain the behaviour of the absorption as function of SiH$_4$-flows near 4 to 5 scc/s. Review Fig. 5.3. According to reaction (5.1), dissociation of SiH$_4$ also results in production of H and H$_2$. As seen before, if the amount of H-atoms present is high enough, reaction (5.5) becomes important, which has a different behaviour concerning SiH$_3$-formation. As this is less efficient, the slope of absorption as function of flow decreases. This explains the observed trend in Fig. 5.3.

### 5.5 Validation of the absorption cross-section

In this section some of the results presented in the last section will be linked to earlier reported measurements concerning growth rate, densities and depletion rates. From this, conclusions will be drawn concerning the used absorption cross-section of SiH$_3$ as reported in literature.

#### 5.5.1 Density and growth rate

As mentioned before, silyl is assumed to be the most dominant particle contributing to the growth of a-Si:H thin films. To link the observed densities to the reported growth rates, as also done for CH$_3$ in chapter 4, a calculation of the depositing density of SiH$_3$ should be made. For this, Eq. (4.5) is used. In section 5.1 a growth rate of 10 nm/s was mentioned. This was obtained for the conditions: $I_{\text{arc}} = 45$ A, $\phi_{\text{Ar}} = 55$ scc/s, $\phi_{\text{H}2} = 10$ scc/s, and $\phi_{\text{SiH}4} = 10$ scc/s with a substrate temperature of 400 °C as presented in [35]. Also known from experiments (see section 5.2.2) is a value for the loss probability $f_3$ of 0.33. Furthermore, at 1500 K we use the thermal velocity $v = 10^3$ m/s, a mass $m_{\text{Si}} = 4.6 \times 10^{-23}$ g and a volumetric density $\rho = 2.3$ g/cm$^3$ for films with a Si-concentration [Si] = $5 \times 10^{28}$ m$^{-3}$. Inserting this under the assumption $s = f_3$ in Eq. (4.5), a density of $5.1 \times 10^{18}$ m$^{-3}$ for SiH$_3$-radicals is

---

10 As discussed in section 4.2.2, the loss probability $\beta$ is defined as the sum of the sticking probability $s$ and the surface recombination probability $\gamma$ (also see Appendix I). The assumption $s = \beta$ implies that all radicals, reacting with the surface, stick to it and form a film. This corresponds to the upper limit for achievable growth rate.
required to fully account for the 10 nm/s film growth. This should be compared to the observed densities at the same plasma conditions. In Fig. 5.4, a SiH₃-density of $1.3 \times 10^{19}$ m⁻³ is found, and in Fig. 5.5 a silyl radical density $n = 1.4 \times 10^{19}$ m⁻³ (both at 11 cm from the substrate). These observed densities are higher than the calculated one, by a factor of 2.7 (review footnote 6 on page 33, where it is noted that the density at a larger distance from the surface will be somewhat higher).

At this point, it should be noted that growth of a-Si:H layers does not completely originate from SiH₃-radicals. Also SiH and SiH₂ might contribute, albeit not more than 10% according to [47] for an RF glow-discharge plasma. According to Kessels et al. [37] also cationic silicon clusters might contribute to film growth. This means, that the calculated densities according to Eq. (4.5) can be interpreted as the upper limit for the SiH₃-density. The real silyl flux towards the surface and thus the density will be lower. This suggests that the densities, derived from the measured absorption, are too high. Even more, determination of the ratio $n_{\text{SiH}3} / n_{\text{SiH}4}$ yields a factor of 0.1 for the measured densities. This seems somewhat high in comparison to the reported depletion of SiH₄ at these conditions [36], which is around 11%. Although it is known that SiH₃ is less reactive with other silane molecules, full conversion of SiH₄ into SiH₃ by H-abstraction without any secondary reactions is not expected.

Therefore, it is likely that the SiH₃-density is overestimated, presumably because the absorption cross-section for SiH₃ at 215.0 nm (2.4·10⁻²¹ m²), used to calculate the density, is too low. Of course, the length over which absorption takes place (l in Eq. [2.10]) is not exactly known: however, a change of this value would have only minor influence on the calculation of the densities from the observed absorptions as the uncertainty is not too large. More important might be the profile of the silyl density in the vessel. If the radicals are significantly non-homogeneously distributed, the used straightforward correlation between growth rate and observed density might not be valid anymore since local densities should be considered. However, because of the fact that CRDS provides line-of-sight measurements and the data are obtained at some distance to surfaces, a more or less flat profile (at least inside the plasma beam, which is assumed to be around 20 cm) is postulated. More experiments are needed to determine the concentration profile: measurements at various spatial positions should be performed, as well as closer to the substrate surface.

A comparison to densities reported by other groups should be made to be able to verify the correctness of the used cross-section. This is done in the next section.

However, being the dominant contributor to film growth, there should be a correlation between the observed densities of SiH₃ and the growth rate (assuming a more or less linear profile). To prove this, absorptions are measured for various plasma conditions, for which the growth rates have been established in earlier experiments. At these conditions the film growth is dominated by SiH₃-surface adsorption [21]. See Table 5.2 below for the corresponding plasma conditions.

<table>
<thead>
<tr>
<th>Table 5.2 Plasma conditions corresponding to observed growth rates.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_g$ (nm/s)</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>11</td>
</tr>
</tbody>
</table>
Absorptions are measured at 215.0 nm using these conditions, shown in Fig. 5.7. The error bars originate from the standard deviations of the averaged densities (a number of CRD-measurements are performed for each condition, for which the average density values are determined).

![Graph showing correlation between a-Si:H growth rate and measured SiH3 densities.](image)

**Fig. 5.7:** Correlation between a-Si:H growth rate and measured SiH3 densities. For the used plasma conditions refer to Table 5.2.

A linear correlation is found between the observed SiH3-densities and the growth rate of a-Si:H films under these conditions, which confirms the expectation. The fitting parameters for the log-log plot are: slope \( \ln(R)/\ln(n) = 0.97 \pm 0.09 \), which is obvious, and an intersection point \( 27.2 \pm 0.9 \), which results in \( R/n = 6.3 \cdot 10^{-28} \text{ s}^{-1} \text{m}^2 \). This value can be inserted in Eq. (4.5) to verify the correctness of the inserted density \( n \). If we also insert the numbers for \( m \) and \( \rho \) as given before, and assume \( \beta = s \) (where \( \beta = 0.33 \)), a thermal velocity \( v \) of \( 3.2 \cdot 10^2 \text{ m/s} \) is obtained. This should be compared to the calculated \( 1.0 \cdot 10^3 \text{ m/s} \) which is a factor of 3.3 larger. If \( s = \frac{1}{2} \beta \), we obtain \( v = 6.2 \cdot 10^2 \text{ m/s} \), which consequently is a factor of 1.7 smaller. To correct this discrepancy, the used densities in Fig. 5.7 should be decreased by these same factors. Therefore, it is believed that the SiH3 absorption cross-section, used to calculate the densities, should be increased and the cross-section is estimated to \( \sigma \approx 6 - 8 \cdot 10^{-21} \text{ m}^2 \) as an indication.

5.5.2 Comparison with reported densities

To facilitate the discussion, various densities reported in literature are summarised in Table 5.3 on the next page. The reader is also referred to Appendix II, where the spectroscopic techniques, used in the references as given in Table 5.3, are described in more detail.
TABLE 5.3 Overview of reported SiH₃-densities using various techniques. See the text for a more detailed description.

<table>
<thead>
<tr>
<th>Reference</th>
<th>SiH₃-density (m⁻³)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work (Fig. 5.4)</td>
<td>1.3·10¹⁹</td>
<td>cascaded arc, CRDS</td>
</tr>
<tr>
<td>Calculated (Eq. [4.5])</td>
<td>5.1·10¹⁸</td>
<td>( s = \beta, 100% ) contrib.</td>
</tr>
<tr>
<td>Toyoda et al. [46]</td>
<td>9.3·10¹⁸</td>
<td>RF (80 W), UVTS(^a)</td>
</tr>
<tr>
<td>Kae-Nune et al. [48]</td>
<td>3·10¹⁷</td>
<td>RF (80 W), TIMS(^b)</td>
</tr>
<tr>
<td>Itabashi et al. [49]</td>
<td>7.5·10¹⁷</td>
<td>RF (125 W), IRLAS(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Ultraviolet transmission spectroscopy: see also Appendix II.
\(^b\) Threshold ionisation mass spectrometry.
\(^c\) Infrared laser absorption spectroscopy.

Toyoda et al. [46] used an H₂/SiH₄ RF-plasma\(^{11}\) and detected SiH₃ by ultraviolet transmission spectroscopy. The plasma conditions were as follows: a pressure of 20 Pa and an H₂:SiH₄ mixture of 1:1 at an RF power of 80 W. Combined with the presented electrodes configuration, this yields a power density of 0.016 W/cm². They reported an absorption of 0.012 in a 49 cm path length, but did not calculate the density. If we use the SiH₃ cross-section, this would give a density of 9.3·10¹⁸ m⁻³. Though, when comparing this value to densities reported by Perrin and co-workers in [48], lower values should be expected. At the equivalent power density for their RF configuration (8 Pa, pure silane discharge), they found a SiH₃-density of 3·10¹⁷ m⁻³ (detected with mass-spectrometry). This also leads to the suggestion that the used value for the absorption cross-section is too low.

In work reported by Itabashi et al. [49] (also an H₂/SiH₄ RF-plasma, 0.13 W/cm², partial SiH₄-pressure is 7 Pa) SiH₃-densities up to 7.5·10¹⁷ m⁻³ were found, as detected with infrared absorption spectroscopy. Again, this value is much lower than the observed \( n_{\text{SiH}} = 1.3·10¹⁹ \) m⁻³. A general SiH₃-density for steady-state plasmas as given by Matsuda [47] is 10¹⁸ m⁻³. This confirms the impression that the used absorption cross-section is too low.

If we use the in section 5.5.1 calculated density (corresponding to a growth rate of 10 nm/s) \( n_{\text{SiH}} = 5.1·10¹⁸ \) m⁻³, corrected for a 90 % contribution of SiH₃, an estimation can be given for the SiH₃-absorption cross-section at 215 nm, which then is 8·10⁻²¹ m².

\(^{11}\) When using RF plasmas for deposition, growth rates of typically 1 – 3 Å/s can be obtained.
Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

In this last chapter the main conclusions will be presented together with some recommendations for future scientific research concerning the use of CRDS on radicals as CH$_3$, SiH$_3$ or other species that are important during plasma deposition of a-C:H and a-Si:H thin films.

6.1 Cavity-ringdown spectroscopy on broad-band absorbing molecules

First, a recapitulation concerning the cavity-ringdown spectroscopy set-up will be made, after which some recommendations will be given for further use of CRDS.

Experiments have proven that Cavity-ringdown spectroscopy is capable of measuring broad-band absorptions at wavelengths in the UV region. However, to perform these measurements successfully, a dedicated measuring technique is indispensable. Owing to the necessity of determining absorptions over a wide spectral range and the limited range of action of the cavity mirrors, it is essential to keep track of the baseline signal, i.e. the ringdown time during absence of the absorbing medium. The method used in this project, switching on and off the precursor gas flow, provided reliable data, from which broad-band absorption features could be calculated.

The used cavity mirrors have a maximum reflectivity of 97.0 to 98.5%, which is less than specified. Striking detail is the fact that the reflectivity increased when the mirrors were mounted on the vessel and the plasma chamber retained at low pressures for several days. Furthermore, a new and user-friendly computer program is developed. Apart from providing some useful cavity alignment tools, various measurement schemes can be executed, allowing real-time interpretation of the data. A new dye-laser, which features an automatic tuning of the frequency doubling crystal, is introduced for the detection of SiH$_3$ radicals.

In the near future, a new data acquisition system will be introduced to replace the oscilloscope. A PHYSDAS (Physics Data Acquisition) system, consisting of a state-of-the-art 100 MHz, 12 bit ADC (Analogue-Digital Converter) and a fast DSP (Digital Signal Processor) is currently being designed. This allows real-time calculation of the ringdown-time for each transient signal. In this way, 'bad transients' can be filtered out, resulting in more accurate measurements. Also the measurement time will decrease, which is beneficial for the use of plasma modulation (the measurement time is no longer the limiting factor).

After successful use of CRDS on atoms (H), ions (H$^-$) and molecules (SO$_2$, CH), it is demonstrated that CRDS is also capable of identifying broad absorption profiles as featured in methyl (CH$_3$) and silyl (SiH$_3$) radicals.
6.2 CRD detection of methyl (CH₃)

In the expanding Ar/CH₄-plasma, in-situ measurements of CH₃ densities upon various plasma conditions have been successfully performed with the CRD set-up.

As a first step, the methyl radical is identified at the $B \leftarrow X$ electronic transition around 216 nm by its specific spectrum, revealing the pre-dissociative character of the upper state $B$. Next, methyl densities are measured as function of precursor flow and arc current: the production of CH₃ increases for higher arc currents due to the fact that more Ar⁺-ions emerge from the cascaded arc plasma source and hence more methane is dissociated. Also, the density increases when the methane flux is enlarged, however, this increase becomes smaller for higher flows. The observed effect is a result of the fact that for higher precursor flows the depletion (or relative consumption) decreases. This is a direct confirmation of earlier experiments. A comparison between densities measured at 213.9 and 215.9 nm reveals a temperature dependence of the absorption cross-section: the cross-section at 215.9 nm varies inversely with the temperature. Beside methyl absorption, also absorption originating from acetylene is observed, confirming that also C₂H₂ is produced in the Ar/CH₄-plasma. As expected, the production is most favoured with high current and low methane flow. It is concluded that the suggestion from literature to measure CH₃ at 213.9 nm is not useful in the case of the expanding Ar/CH₄-plasma.

The observed densities have been linked to a-C:H growth rates obtained in the expanding Ar/CH₄-plasma. Using the reported loss-probability of CH₃ it can be concluded from these calculations that methyl does not significantly contribute to film growth. Consequently, other radicals present in the Ar/CH₄-plasma have to be responsible for the observed growth. One of the candidates could be the main dissociation product of acetylene, C₂H. However, this is not confirmed yet.

In order to allocate the observed growth to a certain radical, the C₂H presence – as the main candidate – in the Ar/CH₄-plasma should be investigated. This could also be done by CRDS, however, up to now this unfortunately failed. More efforts have to be put in to be able to better understand the deposition process in expanding Ar/CH₄-plasmas.

6.3 CRD detection of silyl (SiH₃)

To the best of our knowledge, these are the first reported CRD measurements on the silyl radical. SiH₃ is produced in an expanding Ar/H₂/SiH₄ plasma. The spectrum, obtained at the $A \leftarrow X$ electronic transition, revealed a broad profile, extending beyond 213 to 226 nm with a peak absorption at 215 nm.

In-situ density measurements for various gas flows are performed to obtain a positive identification of SiH₃ and to confirm directly some plasma-chemical processes concerning Ar, H₂, SiH₄ and SiH₃. These measurements validate the expected dependence of SiH₃ production on both SiH₄ flow and / or H₂ gas flow. Silyl
production from silane dissociation by Ar⁺ ions is more efficient than from H-abstraction by H, the process that dominates for H₂ gas flows of 5 scc/s and higher. This is a result of the reaction length, which is longer for the H-abstraction process by a factor of 10. However, the H-abstraction process is more efficient with regard to the SiH₄ depletion (or consumption): at the same SiH₄ depletion, more SiH₃ is produced in the case of H-abstraction. The absence of a saturation of the silyl production with increasing silane flow in an Ar/SiH₄-plasma can also be explained by the H-abstraction process and its decreasing reactive length.

In the plasma, for which the best a-Si:H quality is obtained at a growth rate of 10 nm/s ($l_{\text{arc}} = 45$ A, $\varphi_{\text{Ar}} = 55$ scc/s, $\varphi_{\text{H₂}} = 10$ scc/s, and $\varphi_{\text{SiH₄}} = 10$ scc/s), SiH₃ densities of $n = 1.4 \cdot 10^{19}$ m⁻³ are found. A comparison with calculated densities that should be responsible for the observed growth rate suggests that the observed density is too high. This is also confirmed by a comparison with and between other reported SiH₃ densities, as measured using other techniques. An explanation can be found in an uncertainty for the absorption path length and, moreover, in the used value of the absorption cross-section at 215 nm. It is believed that this cross-section should be higher by a factor of $(3.0 \pm 0.3)$: $\sigma = 6 - 8 \cdot 10^{-21}$ m² instead of $2.4 \cdot 10^{-21}$ m².

Furthermore, the linear correlation between SiH₃ density and growth rate is corroborated for 0.2 to 10 nm/s. To conclude with, it has been shown that CRDS provides a useful tool for in-situ measurements of SiH₃ radical densities.

As these density measurements are performed at some distance of the substrate (at 11 cm), it would be preferable to also detect SiH₃ radicals more in the vicinity of the surface. In this way, more information can be gained about the dependence of the density on the spatial position. Also a radial profile could be composed. At this moment, work is being done in which these measurements will be performed.

Also, an extension to higher and lower wavelengths could be made to obtain the full spectral fingerprint of silyl. For this, another set of highly reflective cavity mirrors together with another laser dye is required to be able to measure from 226 to 260, for instance. This could, given the observed densities, also be done with classical (multipass) UV absorption techniques (UVAS).

Furthermore, CRDS could be used to detect other radicals present in the plasma. This could lead to an even better understanding of the relevant chemical processes that play an important role in the Ar/H₂/SiH₄ plasma.

In the second phase of the project to obtain experimental evidence of the expected a-Si:H growth process, the aim is to measure the SiH₃ density on the surface itself. In this way, the weakly bound surface adsorbed radicals could be studied (for a short description of the growth process, see chapter 1). For this, a new cavity that is no longer one-dimensional has to be constructed now that CRDS has proven to be a successful diagnostic technique.

Beside CRDS, also infrared absorption spectroscopy could be used to detect gas phase SiH₃ densities. It could be worthwhile to investigate the possibilities to introduce this technique. However, for detection of surface bound radicals the sensitive CRDS should be used as a result of the low expected densities ($10^{17}$ to $10^{15}$ m⁻²).
ACKNOWLEDGMENTS

The author would like to thank A. Bes (Université d'Orléans, Ecole Supérieure des Procédés Electronique et Optiques) for his useful contribution to the measurements, and the group Elementary Processes in Gas-Discharges (EPG) at the Eindhoven University of Technology for using their BBO doubling crystal. M.J.F van de Sande, H.M.M. de Jong, and A.B.M. Hüskin are gratefully acknowledged for their skilful technical assistance.

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the "Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)".
REFERENCES


APPENDICES

I. Derivation of growth rate as function of density

A derivation of the growth rate resulting from a certain density of radicals responsible for the growth of a thin film is given below.

Consider, in two dimensions, two fluxes of radicals $\phi^+$ and $\phi^-$ in the $z$-direction towards an imaginary surface $z_0$, extending to infinity perpendicular to $z$. See Fig. A.1 below.

**Fig. A.1: Radical fluxes towards an imaginary plane at coordinate $z = z_0$.**

The distance $\lambda_z$ should be considered to be small. The total flux at $z_0$ is the sum of the two radical fluxes $\phi^+$ and $\phi^-$ originating from a position at distance $\lambda_z$ of $z_0$:

$$\phi(z_0) = \phi^+(z_0 - \lambda_z) - \phi^-(z_0 + \lambda_z), \quad (A.1)$$

where

$$\phi^+(z_0 - \lambda_z) = \phi^+(z_0) - \lambda_z \frac{d\phi^+}{dz} |_{z_0}, \quad (A.2)$$
$$\phi^-(z_0 + \lambda_z) = \phi^-(z_0) + \lambda_z \frac{d\phi^-}{dz} |_{z_0}.$$ 

These functions can be inserted in (A.1). Given by symmetry, we assume $\phi^+(z_0) = \phi^-(z_0)$. Then we are left with:

$$\phi(z_0) = -2\lambda_z \left. \frac{d\phi^+}{dz} \right|_{z_0} = -2\lambda_z \frac{d\left( \frac{1}{2} \nu n \right)}{dz}, \quad (A.3)$$
$$= - \frac{1}{2} \lambda_m \nu \frac{dn}{dz}.$$
if we assume a constant thermal velocity $v$ and a density $n$. Furthermore, we introduced a diffusion mean free path $\lambda_m = \frac{3}{2} \lambda_z$, cf. [50] and, according to standard kinetic theory, substituted the particle flux $\phi^+$ to a surface (in a vessel) with $nv/4$. From (A.3) follows that there is no diffusion $\phi(z_0)$ if $dn/dz = 0$.

Now we introduce a wall at $z = z_0$ where the incoming radicals reflect with a coefficient for reflection $R$. This links the incoming flux $\phi^+(z_0 - \lambda_z)$ and outward flux $\phi^-(z_0 + \lambda_z)$ together by the following equation:

$$\phi^-(z_0 + \lambda_z) = R \cdot \phi^+(z_0 - \lambda_z). \quad (A.4)$$

Eq. (A.4) is valid for small $\lambda_z$ and can be inserted in Eq. (A.1) to give

$$\phi(z_0) = (1 - R) \cdot \phi^+(z_0 - \lambda_z). \quad (A.5)$$

Combined with (A.2):

$$\phi(z_0) = (1 - R) \cdot \phi^+(z_0) - (1 - R) \lambda_z \frac{d \phi^+}{dz} \bigg|_{z_0}. \quad (A.6)$$

This is equal to Eq. (A.3), which can also be written as $\left( -D \frac{d n}{dz} \right)$ if we insert the diffusion coefficient $D = \frac{1}{3} v \lambda_m$. Proceeding with $\phi^+ = nv/4$, Eq. (A.6) can be written as

$$\left(1 - R\right) \cdot \frac{1}{4} nv = -\frac{1}{3} \lambda_m v \left(\frac{1}{2} + \frac{1}{2} R\right) \frac{d n}{d z}. \quad (A.7)$$

This results in

$$-\frac{1}{3} \lambda_m v \frac{d n}{d z} = \frac{2}{3} nv \cdot \frac{(1 - R)}{(1 + R)}. \quad (A.8)$$

To conclude, we define the fraction of particles that is not reflected as $\beta = 1 - R$:

$$-\frac{1}{3} \lambda_m v \frac{d n}{d z} = -D \frac{d n}{d z} = \frac{1}{4} nv \cdot \frac{\beta}{(1 - \frac{1}{2} \beta)}. \quad (A.9)$$

Now two possibilities are given for a fraction $\beta$ of incoming particles: the particles might stick to the surface (fraction $s$) or react with the surface and desorb back into the gas phase as another particle (fraction $\gamma$). These processes are illustrated by Fig. A.2 on the next page.
The net contribution to growth of the film is a fraction $s/\beta$ of the total lost flux, given by Eq. (A.9). We can convert this flux to a growth rate $R_g$ by using $-D \frac{dn}{dz} = R_g \frac{\rho}{m}$ (where $\rho$ denotes the volumetric density of the film and $m$ is the mass of the depositing atom). Inserting this, we obtain the expression for the growth rate resulting from a density of radicals having a given loss probability:

$$R_g = \frac{1}{4} nv \cdot \frac{s}{1 - \frac{1}{2} \beta} \frac{m}{\rho} .$$  \hspace{1cm} (A.10)
II. Other techniques that can be used for the detection of SiH₃

In this section, a comparison will be made between Cavity-Ringdown as a spectroscopic tool and other techniques, which are capable of detecting SiH₃ in SiH₄ discharge gas phases. These methods will be presented and assessed, after which some general remarks will be made.

1. Threshold ionisation mass spectrometry

Since the construction of the first mass spectrometer by Aston in 1919, this instrument has been developed into a commercially available tool with diverse applications. The method that can be used for detection of silyl radicals in plasmas is the so-called threshold ionisation mass spectrometry (TIMS).

As mass spectrometers are only able to detect ions, it should be possible to detect only certain neutral species if only these neutrals are ionised. The threshold ionisation technique (also called appearance potential mass spectrometry) is based on the principle of selective ionisation of neutral species. This is achieved by means of applying a well-defined ionisation energy \( E \).

An extraction pinhole is located somewhere in the plasma, preferably on the position of the substrate. Several kinds of neutrals can enter the mass spectrometer head, leading to the ion source. Now the radical of interest is \( \text{SiH}_3 \cdot \). To detect this radical, it has to be ionised in the ionisation chamber by electron impact. Now two mechanisms are important:

\[
\text{SiH}_3 + e^- \rightarrow \text{SiH}_3^+ + 2e^- \quad \text{for } E > E_i = 8.0 \text{eV} \\
\text{SiH}_4 + e^- \rightarrow \text{SiH}_3^+ + \text{H} + 2e^- \quad \text{for } E > E_{di} = 12.0 \text{eV}
\]

where \( E_i \) and \( E_{di} \) are the ionisation and the dissociative ionisation potentials, respectively [48]. The first process is direct ionisation, the second is called dissociative ionisation from the parent neutral \( \text{SiH}_4 \). It will be evident that the second process should be avoided as this would lead to the detection of \( \text{SiH}_4 \) instead of \( \text{SiH}_3 \): this is possible by applying an electron energy \( E \) with \( E_i < E < E_{di} \), since \( E_i < E_{di} \) (the difference is typically the binding energy between the molecule and the released atom). In this way, only the \( \text{SiH}_3 \) radicals are ionised. Plasma ions can be repelled at the entrance slit by applying a positive potential.

The created positive ions are then accelerated to a mass filter, for instance a quadrupole mass filter. Here the different ions are separated from each other according to their mass-to-charge ratio. By applying appropriate voltages to the poles of the filter, the desired \( \text{SiH}_3^+ \) ions can be extracted from the filter and eventually detected, e.g. with an electron multiplier.

However, some problems occur when trying to measure \( \text{SiH}_3 \) radicals in plasmas: for instance, the radical signal is even present for the plasma off situation, when there should be no radicals available to ionise. This is owing to pyrolysis of \( \text{SiH}_4 \) on the hot filament which produces the electrons in the ionisation chamber. Furthermore, background impurities and contamination in the mass spectrometer
might cause interfering signals. The resulting net plasma radical contribution to the ion signal is given by the following relation:

\[ \Delta I_{\text{SiH}_3} = (I_{\text{plasma on}} - I_{\text{background}}) - (I_{\text{plasma off}} - I_{\text{background}}) \cdot \frac{I_{\text{plasma on}}}{I_{\text{plasma off}}} \]  

(A.12)

where \( I_x \) are the measured intensities for the plasma on or off period and the background signal. The ratio of intensities (the last term) is important for the case \( E > E_{di} \) when a correction should be made for the depletion (consumption) of SiH\(_4\).

The procedure for obtaining absolute densities (at the extraction position) from the measured intensities is quite complicated. It involves the signal due to dissociative ionisation, the net radical signal, the (dissociative) ionisation cross-sections for Eq. (A.11), and a correction factor that depends on the experimental configuration. See [51]. For this method, Kae-Nune and co-workers [48] quote a density detectivity limit of several \( 10^{15} \) m\(^{-3}\) (however, this seems to be questionable for SiH\(_3\)) and an estimated accuracy of 30% on absolute densities.

Aside of these remarks, a more fundamental problem rises: the composition of the extracted gas might change during entrance through the pinhole extractor and the motion to the ionisation chamber as a result of the reactivity of the species. Moreover, as SiH\(_3\) is very reactive with respect to surfaces, it can stick inside the mass spectrometer head, form a film and consequently will not be detected. Also film growth occurs in the close vicinity of the pinhole, causing a reduction of the diameter which affects the above-mentioned calculation of the correction factor. Eventually, the extractor might even become congested. This makes absolute density measurements less reliable.

Another issue could be the fact that the introduction of the extractor head significantly influences the plasma (or even replaces the substrate itself): therefore, TIMS is not suited for being used for in-situ and real-time plasma monitoring during deposition of a-Si:H layers.

To conclude with, TIMS is a useful complementary tool for ex-situ plasma monitoring using mass spectrometers. It can also be used for detection of positive and negative plasma ions. However, accuracy on absolute densities is limited for reactive gases (which of course are present in depositing plasmas).

2. Infrared absorption spectroscopy

Apart from measuring silyl densities on the electronic transition from the ground (\(X\)) to the first excited state (\(A\)), it is also possible to use the vibrational transitions in the \(v_2\) frequency band. This band reaches into the infrared region of the spectrum and hence IR spectroscopic methods can be used.

As for all spectroscopic absorption techniques, a density \((n)\) measurement with infrared absorption is also governed by Lambert-Beer's law with respect to the frequency-dependent absorption coefficient \(k_\nu\). The absorption \(A\) (assuming a homogeneous density profile) is thus given by
\[ A = -\log \left( \frac{I_v(x)}{I_{v,0}} \right) = k_v x, \quad (A.13) \]

where \( I_{v,0} \) and \( I_v(x) \) are the laser intensities entering the absorbing medium and emerging from the absorber after a distance \( x \), respectively. The light source can be a globar or an Ar, Xe or Hg light source, e.g. a cascaded arc running on Ar or Xe. Before detection, the various frequencies emitted by and from the plasma have to be split by a monochromator (in practice, most visible / UV grating monochromators can easily be converted into IR instruments by exchanging the grating and the mirrors). The type of detector depends on the wavelength, e.g. Ge or CuGe photodiodes can be used, or an MCT (mercury cadmium tellure) crystal, which is cooled by liquid nitrogen.

It will be evident that this method is not capable of measuring small absorptions: the difference between \( I_{v,0} \) and \( I_v(x) \) has to be significant with respect to the noise of a measurement while sensitivity is limited by the stability of the light source and the IR detector. However, as discussed before, multipass absorption increases the sensitivity. For this, a White-cell can be used, where up to 50 passes can be achieved with three mirrors.

### 2.1 Infrared diode-laser absorption spectroscopy

Moreover, the use of a tuneable diode laser provides more flexibility and better sensitivity. This technique then is called IRLAS. (This semi-conductor laser consists for instance of a lead-salt pn-junction where the conduction band \( n \) is filled with electrons.) If the laser wavelength is modulated by a time-dependence \( \lambda(t) = \lambda(0) + \Lambda \sin \omega t \), \( \Lambda \) denotes the strength of the modulation), it is possible to detect absorption via three detection schemes: plane intensity measurement, the first derivative of the intensity signal with use of a lock-in amplifier, and the second derivative (lock-in detection also). This follows immediately from a Taylor expansion of \( I(\lambda) \) to \( \Lambda \sin \omega t \). The lock-in detection reduces the intensity variations of the laser and the detector and hence yields a better signal-to-noise ratio. Furthermore, depending of the type of experiments, it might be useful to use a 3-path calibration technique for calibration of the wavelength of the laser. This is done by simultaneously recording of the intensity emanating from the plasma, the intensity through a gas reference cell with known rovibrational transitions, and through an etalon, which provides a relative scale.

Practical difficulties lie in the availability of IR-transparent windows that are vacuum-compatible and in optical components (expensive gold platted concave mirrors give best performance). Also the used set-up is quite complex.

### 2.2 Fourier transform infrared spectroscopy

Another method that can be used for IR-absorption measurements is the Fourier transform technique, or FTIR. Essentially, FTIR consists of a Michelson interferometer. It would be beyond the scope of this appendix to explain the interferometer in detail. For more information see for instance [52], p. 266. In short, the intensity measured by the detector depends on the length difference \( \Delta l \) between
the two interferometer arms (one mirror can be moved). If \( I(\Delta l) \) is measured, a simple Fourier transform operation has to be applied to obtain \( I(\nu) \):

\[
I(\nu) = \frac{1}{2\pi} \int_0^\infty I(\Delta l) \exp(2\pi i \nu \Delta l) d\Delta l. \tag{A.14}
\]

In practice, a HeNe laser is used for calibration of the (moving) mirror position.

In comparison to the dispersive technique, the level of noise is lower for FTIR detection (the detector sees the complete spectrum, not only a small portion as is the case when a monochromator is used). Also, FTIR is less time consuming (the stepper motors in a monochromator are slow in comparison to the movement of one single mirror and a Fourier transformation calculated by a computer). Furthermore, the resolution of FTIR is generally ten times better, also with a higher frequency precision.

An IR-absorption measurement yields intensities for various rotational transition. From this data, the rotational temperature can be determined. Then, using (complex) rotational and vibrational partition functions, the total radical density in the ground state \((X^2A_1)\) can be calculated. See [53] and references therein for more details. This makes interpretation of data somewhat difficult when absolute densities are required, for instance when a comparison to other measurements should be made.

### 3. Ultraviolet absorption / transmission spectroscopy

If the expected densities are high enough, also normal absorption (or transmission) spectroscopy can be used on the transition between the ground state and the first electronically excited state, *i.e.* in the ultraviolet spectral region. This is known as UVAS (or UVTS for transmission measurements). Since the availability of sensitive multi-channel optical detectors as CCD cameras equipped with a UV scintillator, the sensitivity is good enough to detect small absorptions and to minimise the effect of lamp intensity fluctuations. Absolute absorptions in the range of several \(10^{-3}\) can be readily observed.

UV light can be obtained from the spectrum emitted by a stable arc lamp, *e.g.* with Xe gas, via dispersion by a quartz prism\(^\text{12}\). The light transmitted through the reactor can be analysed with a monochromator and detected with the earlier mentioned (cooled) CCD camera. To correct for background light and dark counts, the spectra can be acquired in four modes:

- intensity recorded when plasma and lamp are on \((L_p)\);
- when plasma is off, and lamp is on \((L_0)\);
- when plasma is on, and lamp is off \((P)\): this accounts for light emitted by the plasma;

\(^{12}\) Of course, also the laser set-up which is described in section 3.2.2 produces UV light: however, as this makes use of a pulsed laser, the intensity fluctuations would be too large owing to large pulse-to-pulse fluctuations.
when both plasma and lamp are off (B): this gives the background and dark count signals.

In this way, the absorption $A$ (and thus density $n$) can be calculated from:

$$\frac{I_T}{I_0} = \frac{L_p(\lambda) - P(\lambda)}{L_0(\lambda) - B(\lambda)} = \exp(-A(\lambda)),$$

where $I_T$ is the transmitted UV intensity and $I_0$ the incident intensity. See for instance UV measurements by Booth et al. [54]. With this method, Booth and co-workers report a minimum detectable absorption of several $10^{-4}$ for a 18 cm path length (or minimum density $10^{17}$ m$^{-3}$), having a signal-to-noise ratio $S/N = 5/1$. This is limited by the uncertainty of the zero absorption baseline. The fact that this value slowly varies across the spectrum as a result of alignment and thermal effects makes determinations of broad-band absorption less accurate. In UV measurements done by Loh [55] (ultrastable deuterium discharge lamp, monochromator with CCD-array) a minimum absorption of $10^{-3}$ was found, limited by observed bleaching of the CCD's UV scintillator coating. This limits the useful lamp intensity range and hence the achievable signal-to-noise ratio. Both Booth and Loh give an uncertainty in the density of 30 to 50%.

4. Other techniques

4.1 Laser-induced fluorescence

Another sensitive and powerful technique for detecting molecules and measuring densities, is laser-induced fluorescence spectroscopy (LIF). In this method, molecules are typically excited from the ground electronic level to an excited electronic level by absorption of laser radiation. Once excited, the molecules can decay back to the ground electronic level by spontaneous emission of a photon: the intensity of the spontaneous emission, i.e. fluorescence, is proportional to the number density in the excited state of the species. From this, ground-state population densities can be calculated. However, for SiH$_3$, the first excited state is pre-dissociative, hence no spontaneous emission will occur. The molecule decomposes and the pumped laser energy is converted into kinetic energy and can not be detected as fluorescence. Of course it is possible to excite other electronic levels by laser. However, this requires higher frequencies, i.e. shorter wavelengths, and is therefore difficult to carry out.

4.2 Resonance-enhanced multi-photon ionisation mass spectroscopy

This technique, REMPI (+ MS), makes use of subsequent absorption of photons, eventually leading to ionisation. The ionised radicals can be detected with a mass spectrometer as described before. As a result of the short life-time of the first electronic state owing to the pre-dissociative character, this method is also not suited for excitation around 215 nm. REMPI+MS has been applied between 310 and 430 nm by Johnson and co-workers [45], who identified various vibronic states.
5. Summary

In Table A.1 below the main features of the discussed diagnostic tools are summarised.

**TABLE A.1: Overview of the main aspects of the discussed diagnostics.**

*Numbers are indications as given in references (see table header and text).*

<table>
<thead>
<tr>
<th></th>
<th>CRDS</th>
<th>TIMS ref. [48]</th>
<th>IRLAS / FTIR ref. [49]</th>
<th>UVAS ref. [43]</th>
</tr>
</thead>
<tbody>
<tr>
<td>detection limit</td>
<td>(1 \times 10^{17}) m(^{-3}) (for non-optimal mirrors)</td>
<td>few (10^{15}) m(^{-3}) (\dagger)</td>
<td>(10^{17}) m(^{-3})</td>
<td>several (10^{17}) m(^{-3})</td>
</tr>
<tr>
<td>accuracy</td>
<td>few – 30 %</td>
<td>20 – 50 %</td>
<td>30 %</td>
<td>30 – 50 %</td>
</tr>
<tr>
<td>negative aspects</td>
<td>- exact cavity alignment needed</td>
<td>- not very suitable with reactive species</td>
<td>- complex set-up and calculations needed</td>
<td>- stability UV source and detector important</td>
</tr>
<tr>
<td></td>
<td>- clean mirrors important</td>
<td>- not real-time during growth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>positive aspects</td>
<td>- high time-resolution</td>
<td>- easy to use once installed</td>
<td>- high spectral resolution</td>
<td>- simple set-up</td>
</tr>
<tr>
<td></td>
<td>- fast interpretation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\dagger\) This value, quoted by Kae-Nune et al., is thought to be too low, especially for SiH\(_3\). The origin of this value is unknown.

One comment concerning CRDS should be made: the above mentioned detection limit is found for the mirrors currently used. As their reflectivity is found to be limited to 98.5% under the best circumstances, the detection is clearly limited. Best mirror reflectivities between 300 and 200 nm are in the range of 99.5% to 99%, as discussed by the group of Meijer in [6] and [56]. This would yield a detection limit of \(A_{\text{min}} = 10^{-5}\) per pass, or \(n_{\text{min}} = 10^{16}\) for an absorption path length of 0.2 m. Even more, the data-acquisition system currently in development will provide better accuracy since then transient selection is possible.

It will be evident that every single of the discussed diagnostics has its own (dis-)advantages. Depending on the needs and which arguments are important (accuracy, time-resolution or even costs), a selection can be made, where it should also be noted that these techniques are in some way complementary to each other.