Deposition of CNH Materials:
Plasma and Film Characterization

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Chapter 1

General Introduction

1.1 CNH materials

Compounds consisting of carbon, nitrogen and/or hydrogen atoms, hereafter called CNH materials, are very important constituents in the chemistry of everyday, and may be found in various forms. The application of CNH materials in solid thin films, however, only started in the last decades, driven by industrial demands for tribological coatings with one or more useful properties like high hardness, low friction coefficient, chemical inertness, biocompatibility, high thermal conductivity and/or optical transparency.

One of the CNH materials which appeared to be very useful for coating purposes is hydrogenated amorphous carbon (a-C:H). The properties of the a-C:H compound are adjustable from soft polymer-like to hard diamond-like carbon (DLC). Despite the amorphous structure and the incorporation of hydrogen, the material is relatively hard and possesses diamond-like features, which makes it suitable for use as a protective coating on optical devices, e.g. bar-code laser scanners and flat panel displays, and as a wear resistant coating [1,2]. Moreover, in contrast to diamond, a-C:H has a low friction coefficient against most materials and thus may be used as a solid lubricant.

The interest in carbon nitride materials was initiated by predictions of Liu and Cohen that the hypothetical compound $\beta$-C$_3$N$_4$, with a structure similar to $\beta$-Si$_3$N$_4$, would have a bulk modulus comparable to or even greater than that of diamond (443 GPa) [3]. In the same article Liu and Cohen found empirical ‘evidence’ for the relation between the hardness and the bulk modulus and came to the conclusion that $\beta$-C$_3$N$_4$ might be harder than diamond. Their *ab initio* calculations furthermore showed that the $\beta$-C$_3$N$_4$ structure would have a good chance of being (at least) metastable under normal conditions. Soon four other viable C$_3$N$_4$ structures, shown in Figure 1.1, were discovered [4,5,6]. All proposed structures, except the graphite phase, were found to have a bulk modulus approaching that of diamond [5]. Other investigated CN stoichiometries (1:1) showed a considerably lower bulk modulus [7]. Moreover, Teter pointed out that the aggregate shear modulus (the resistance to reversible deformation upon shear), which for the proposed C$_3$N$_4$ structures is only 60 % that of diamond, was a better measure for the hardness than the bulk modulus used by Liu and Cohen [8]. Teter therefore suggested refocusing on materials more *useful* than diamond, rather than *harder* than diamond.

The hypothetical C$_3$N$_4$ compounds have not only attracted attention for their hardness, but also for the predicted optical properties. Calculations suggested that the bandgaps of the various C$_3$N$_4$ polymorphs might be as high as 6.4 eV [9], and that the films might therefore be transparent for visible and/or UV light.

* The bulk modulus $B$ is defined as the pressure change $\delta p$ over the volume change $\delta V$ during compression, i.e. $B = -V \frac{\partial p}{\partial V} = V \frac{\partial^2 E}{\partial V^2}$, where $\delta E$ is the energy required for the compression.
Needless to say that the predictions of a possibly superhard carbon nitride material with good optical properties stimulated an extensive worldwide effort to synthesize this crystalline compound and that almost any deposition technique has been used for this purpose. These attempts are nicely reviewed in references [10,11,12]. In most cases amorphous nitrogen-deficient material was obtained. In numerous publications the authors claim, based on electron or x-ray diffraction data, to have synthesized grains of crystalline C$_3$N$_4$. However, in most cases the nitrogen content of the films was very small (less than 30 at.%) so that one has to assume that the C$_3$N$_4$ grains are embedded in an otherwise nitrogen-deficient carbon matrix. Furthermore, the usually reported size of the crystallites (a few nm) seems too small for tribological applications. Therefore, at present it is well agreed upon that the synthesis of a crystalline C$_3$N$_4$ compound with the predicted favorable properties is extremely difficult, if not impossible.

Nevertheless, C$_{N_{x}}$ films in a stoichiometry other than C$_3$N$_4$ or a-C:H:N$^\dagger$ films have their own virtue. For instance, a few years ago a so-called “fullerene-like” phase has been discovered in magnetron sputtered C$_{N_{x}}$ ($x = 0.1 - 0.2$) films which combines a high hardness (~ 40 - 60 GPa) with an extreme elasticity (60 – 90 % recovery) [14]. Other experiments also report on a-C:H:N and C$_{N_{x}}$ films with properties comparable to a-C:H films, i.e. a relatively high hardness and elasticity [15,16], low friction coefficient [17], infrared and visible light transparency [18,19,20], chemical inertness [19] and tunable optical constants (like refractive index and bandgap) depending on the nitrogen content of the film [20,21,22].

The most promising use of carbon nitride materials, however, seems to be in the field of either “nanocomposites” or multilayer structures (also called “superlattices”) [23].

$^\dagger$ Amorphous films consisting of carbon, hydrogen and nitrogen, sometimes referred to as nitrogen-doped a-C:H films.

**Figure 1.1:** The five hypothetical C$_3$N$_4$ structures. The larger atoms represent nitrogen. Adapted from reference [13].
Nanocomposites are nanocrystalline materials composed of a mixture of hard compounds. Superlattices are artificial, man-made periodic arrangements of thin (several nanometers), epitaxial layers of two different materials. With such heterostructures, consisting of CN_x/TiN [24] and CN_x/ZrN [25], hardness values of 45 – 55 GPa and elastic moduli of ~ 400 GPa could be reached.

1.2 Deposition from expanding thermal plasmas

For industrial applications of thin film coatings high growth rates are desirable. In previous work it has been shown that with an expanding thermal argon plasma into which acetylene (C_2H_2) is injected downstream a-C:H films can be deposited at rates as high as 70 nm·s^{-1} [26]. This is about 100 times faster than reported for other deposition techniques. Moreover, it was demonstrated that the quality in terms of hardness and infrared refractive index increases with increasing growth rate without the need of an additional ion bombardment [26].

In the past years the deposition from expanding plasmas created in a DC arc source has been extensively studied. Besides a-C:H films also hydrogenated amorphous silicon (a-Si:H) for application in solar cells has been synthesized using this technique [27]. A detailed description of the deposition set-up is given in section 2.2. The very efficient dissociation and ionization of gases in the high-density arc plasma allows a high throughput (typically 100 sccs‡), which results in high fluxes of active species and hence, as mentioned above, in high growth rates. Another big advantage of this type of deposition set-up is the fact that the high-pressure (typically 3-5 \times 10^4 Pa) arc plasma is expanding supersonically into the low-pressure (typically 30 Pa) vessel. Due to this supersonic expansion the plasma production (arc) and downstream (or deposition) region are decoupled, i.e. the downstream plasma is remote. This means that plasma settings and substrate conditions can be optimized separately, in contrast to most other non-remote (or direct) plasmas where both parameters are mutually connected. Furthermore, in the downstream plasma the electron temperature will be low (typically 0.2 eV) [28]. The dissociation of precursor gases injected into the downstream plasma beam is therefore suggested to proceed via charge exchange of the ions with the molecules followed by dissociative recombination of the newly formed molecular ions, i.e.:

\[ \text{Ar}^+ + \text{AB} \rightarrow \text{Ar} + \text{AB}^+ \quad (1.2.1) \]
\[ \text{AB}^+ + e^- \rightarrow \text{A} + \text{B} \quad (1.2.2) \]

where AB represents a molecule which is dissociated into A and B. In section 3.2 of this thesis more evidence for this ion-induced dissociation will be found and it will be shown that the process is very efficient. This means that a major part of the ions will be consumed on their way to the substrate. The relatively low electron temperature (\(T_e \sim 0.3 \text{ eV}\)) and ion density at the substrate lead to a negligible substrate bias (typically a few V), which is advantageous, since ion bombardment may damage the growing film.

In some cases RF bias may actually be necessary for obtaining a certain film structure which without the additional ion bombardment would be energetically not favorable. The deposition set-up used in this work is equipped with an RF power supply with which an adjustable DC bias voltage can be generated at the substrate and hence the energy of the incoming ions may be controlled.

‡ sccs = standard (\(T = 298 \text{ K}, p = 1 \text{ atm}\)) cm³ per second; 1 sccs is equivalent to 2.69\times10^{19} particles/s.
Chapter 1

Notwithstanding the great amount of work that has been devoted to understanding the expanding plasma and the deposition process, still some mysteries remain to be solved. One of them, which will also be dealt with in this thesis, is the interaction of the plasma beam with the background gas. The picture of the expansion as conceived at present is schematically shown in Figure 1.2. In this picture the time-scale on which the dissociation of injected precursor gases occurs, i.e. the primary chemistry, is short and the transport of the dissociation products towards the substrate is fast (~ 1000 m·s⁻¹). On the way to the substrate reactive species may be lost by diffusion of the plasma towards the walls or by volume reactions. However, the diffusion process is about ten times slower than the forward transport, and as long as enough ions are available the loss rate by volume reactions will be dominated by the charge exchange and not by radical–radical reactions. At the substrate the reactive species may either stick (and contribute to deposition) or abstract species from the film to form new molecules which leave into the gas phase.

The steady-state composition of the mixture in the reactor, which will be established in the typical residence time needed to pump the total vessel volume (~ 0.4 s), will thus depend on the volume chemistry, the surface chemistry⁸ and the typical time-scales outlined above. For a good understanding of the relation between the plasma species and the quality of the deposited material, we first have to know what species are responsible for the film growth. In that respect it is important to determine to what extent molecules in the recirculating background gas may contribute to the deposition.

As has been shown by Gielen et al. [29] and Brussaard et al. [30] for a-C:H deposition respectively N₂ and Ar/N₂ plasmas, a substantial part of the background gas may re-enter the plasma beam. In this thesis we will find more evidence that species created at the vessel walls may enter the plasma beam again and affect the chemistry. The consequences for the deposition process are also examined by considering two deposition models: one in which only the primary chemistry in the

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⁸ The importance of the sticking probability, for instance, for the plasma chemistry, e.g. polymerization, is demonstrated in sections 3.2.4 and 3.2.5.
beam is taken into account, and a second in which the composition of the plasma beam is determining the background gas composition and vice versa.

1.3 Hydrogen-free carbon precursors

From the study presented in section 5.1 and work of others [21,31,32] it was concluded that for obtaining hard carbon nitride films incorporation of hydrogen should be avoided. One way of introducing hydrogen-free carbon precursors into the plasma is by means of a graphite nozzle through which an Ar/N₂ is expanding. The characteristics of this carbon source and of the CNₓ films deposited from it will be thoroughly discussed in this thesis.

Two other sources of hydrogen-free carbon that have been investigated during this thesis work are the C₆₀ evaporator and biased graphite ring. A detailed description of the C₆₀ evaporator is given elsewhere [33]. It has been shown that when C₆₀ vapor is injected into the argon plasma, C₂ emission bands appear and that deposition ** takes place at a reasonable rate (0.5 – 2 nm·s⁻¹). For the occurring C₂ emission the following process has been suggested††:

\[
\text{Ar}^+ + \text{C}_6\text{O} \rightarrow \text{Ar} + \text{C}_6\text{O}^+, \quad (1.3.1)
\]

after which the fullerene ion either decays spontaneously [34] or due to dissociative recombination with an electron [35] by the following cascade of reactions, in which also excited C₂ molecules are formed:

\[
\begin{align*}
\text{C}_6\text{O}^+ (+ e^-) &\rightarrow \text{C}_{58} \left(\text{C}_{58}^+\right) + \text{C}_2^* \\
\text{C}_{58}^+ (+ e^-) &\rightarrow \text{C}_{56} \left(\text{C}_{56}^+\right) + \text{C}_2^*, \text{ etc.}
\end{align*}
\]

Photodissociation studies of the C₆₀ molecule have shown that fragmentation may occur through the loss of carbon dimers and subsequent cage reclosure down to a cluster size of C₃₂ [36]. The clusters C₅₈, C₅₆…C₃₄ are all metastable, and hence the fragmentation process may easily via inelastic collisions. Yet another mechanism could involve an electron attachment reaction, for which only 0.26 eV is needed [37], followed by dissociative recombination with an argon ion:

\[
\begin{align*}
\text{C}_6\text{O} + e^- &\rightarrow \text{C}_6\text{O}^- \\
\text{C}_6\text{O}^- + \text{Ar}^+ &\rightarrow \text{C}_2^* + \text{C}_{58} + \text{Ar}
\end{align*}
\]

The experiments with the C₆₀ evaporator were however aborted because of the high costs of the fullerenes at that time. Moreover, it appeared to be very difficult to obtain stable and well-defined plasma conditions with the home-built evaporator. However, considering reports on the successful preparation of (nanocrystalline) diamond films by C₆₀ vapor injection into an argon beam [35] and the reduced costs of the fullerenes it may be worthwhile to design a new evaporator.

**From XPS measurements of one film prepared from an Ar/N₂/C₆₀ plasma the composition was determined to be 50 % carbon, 36 % nitrogen and 14 % oxygen. Furthermore, from comparison of the Auger spectrum of this film with the spectra of diamond and graphite, it was estimated that ~ 90 % of the carbon atoms was sp³ hybridized [38].

††The C₆₀ molecule has an ionization potential of 7.6 eV and therefore both charge exchange collisions with Ar⁺ (ionization energy 15.76 eV) and Penning ionization from Ar metastables (11.6 eV) are energetically allowed process by which to produce C₆₀⁺.
1.4 Plasma and film characterization

For a good understanding of the correlation between the material properties and the operating conditions, i.e. plasma settings and substrate conditions, one has to study the plasma-film interaction. One way to do this is by characterizing the plasma and film separately, but when one wants to unravel the growth mechanism, time-resolved in situ measurements are indispensable.

To follow the evolution of the different bonding types in the film in time, an infrared reflection absorption spectroscopy set-up was designed and implemented (section 2.7). The type of bonds in the film determines to a great extent its properties, as has been shown for a-C:H films [26]. This is also evident from the difference between graphite and diamond which both consist of carbon atoms only. However, the correlation between the type of bonds and the material properties is not straightforward. For a-C:H materials the correlation between the relative fraction of bonding types, e.g. $sp^2/sp^3$ ratio, and the material properties like hardness and refractive index is more or less understood [26]. In the case of CNH materials, despite the vast amount of work, still no clear overall trends have been derived. This is probably due to the larger diversity of possible structures in comparison to a-C:H materials. The study undertaken in this thesis on the relation between the different film properties and bonding types should therefore be considered as explorative.

1.5 Aim of the work

The aim of the project has been in the first place to investigate the possibilities of the expanding thermal plasma deposition technique for the synthesis of hard carbon nitride thin films. From literature it was concluded that hydrogen incorporation in the films should be avoided. A main task was therefore to find new hydrogen-free precursors that could be introduced into the expanding plasma.

A second goal has been to gain more insight in the correlation between the plasma parameters and the material properties and the influence of the substrate conditions on the quality of the films. For this purpose several new diagnostic techniques needed to be implemented both for studying the plasma phase and the film surface in situ.

An additional objective of our work has been to shed some light on the influence of hydrogen on the structure and composition of carbon nitride films. This has been achieved by analyzing the depositions from hydrogen-containing and hydrogen-free precursors.

Finally, a more general goal has been to understand the plasma chemistry and the role of the recirculating background gas in the deposition process. For this purpose the deposition and polymerization in a-C:H deposition plasmas have been scrutinized.

1.6 Outline of the thesis

In Chapter 2 the deposition set-up used in this work is extensively discussed and the diagnostic techniques are presented. Emphasis is put on the diagnostics that have been implemented during this thesis: mass spectrometry, infrared gas phase absorption spectroscopy and infrared reflection absorption spectroscopy.

Chapter 3 deals with the plasma characterization of the plasmas used for etching and deposition. First in section 3.2 the argon/acetylene ($Ar/C_2H_2$) and argon/methane ($Ar/CH_4$) plasmas are scrutinized. Because the deposition from $Ar/C_2H_2$ plasmas has been extensively studied in the past [29], in this thesis only the plasma characteristics
are treated. The consequences of the ion-induced C$_2$H$_2$ dissociation, as suggested in earlier work [26] are investigated and confirmed. Furthermore, the difference in plasma chemistry between the Ar/CH$_4$ and Ar/C$_2$H$_2$ plasmas is discussed, and an attempt is made to determine the dominant growth precursors in both plasmas by means of two simple models (see section 1.2).

The Ar/N$_2$ plasmas are treated in section 3.3, since these plasmas are used for the etching experiments and are forming the basis for the two other deposition plasmas. The characteristics of the Ar/N$_2$ plasmas are compared with those of the Ar/N$_2$/C$_2$H$_2$ plasma (section 3.4) and of the Ar/N$_2$ plasma expanding through a graphite nozzle (section 3.5).

In Chapter 4 the etching of a-C:H (section 4.2), a-C:H:N (section 4.3) and CN$_x$ films (section 4.4) by Ar/N$_2$ plasmas is investigated as function of plasma and substrate conditions. The results of these experiments are used in Chapter 5 to determine the importance of etching to the deposition and material properties.

The deposition of a-C:H:N films from Ar/N$_2$/C$_2$H$_2$ plasmas (section 5.1) and the deposition of CN$_x$ films from Ar/N$_2$ plasmas expanding through a graphite nozzle (section 5.2) are then examined. The influence of both the plasma settings and the substrate conditions (temperature and bias) are scrutinized. Finally, in Chapter 6 the general conclusions are summarized.

References


Chapter 2

Experimental Details

2.1 Introduction
In this chapter the main diagnostic tools that have been used to characterize the plasma and the film during and after deposition will be presented. Furthermore, details on the deposition setup will be discussed. Emphasis is put on the techniques and data analysis methods that have been introduced during the thesis work, i.e. the deconvolution of mass spectrometry data (section 2.4) and the infrared gas phase (section 2.5) and reflection (section 2.6) absorption spectroscopy. The other diagnostics are treated very briefly and according to their relevance to the work presented in this thesis. A more detailed description of these diagnostics may be found in the references supplied in the text.

2.2 Deposition setup
The plasma deposition set up has been extensively described elsewhere [1]. It consists of a wall-stabilized cascaded arc [2], depicted in Figure 2.1, in which a thermal plasma is generated between the three cathodes and the nozzle at a typical pressure of 0.3 - 0.5 bar. Argon gas is injected at the cathodes position into the arc and, depending on the application, nitrogen may be added half-way in the arc channel. Typical parameters in the arc are a pressure of 40-60 kPa, an arc current $I_{arc}$ of 30-90 A (1-5 kW), and a carrier gas flow of 100 sccs. The argon or argon/nitrogen plasma expands into a cylindrical vacuumed vessel (diameter 36 cm, length 65 cm) at a typical pressure of 25 - 30 Pa. Due to the large pressure difference between the arc source and the vessel, the plasma expansion will become supersonic. At a few

![Figure 2.1: Schematic of the cascaded arc.](image-url)
centimeters from the nozzle a stationary shock occurs, after which the plasma continues at subsonic speed [3].

The characteristics of the cascaded arc plasma source have been studied quite extensively in the past years for argon [3,4], hydrogen [5], argon/hydrogen [6], nitrogen [7] and argon/nitrogen [8] plasmas. The investigations revealed that the electron temperature inside the arc is typically 1 eV and that the ionization degree is around 10 %, resulting in electron densities in the order of $10^{21} - 10^{23} \text{ m}^{-3}$ depending on the argon flow. The dissociation degree in case nitrogen or hydrogen are admixed is high (50 – 100 % [9]). Moreover, due to the high electron temperature and density only electrons and atomic ions, i.e. $\text{Ar}^+$, $\text{H}^+$ and $\text{N}^+$, will emanate from the arc.

In this work different precursor ‘injection’ methods have been applied. In the case of the hydrocarbon (section 3.2) and Ar/N₂/C₂H₂ (section 3.4) plasmas the gaseous CₓHy precursors are injected into the expanding argon, respectively, argon/nitrogen plasma by means of an injection ring. The injection ring is positioned at 5 cm below the arc exit. In the case of the graphite nozzle plasma (section 3.5) the normal copper nozzle is replaced by a graphite nozzle (cf. Figure 2.2) and the gaseous precursors are created by interaction of the argon/nitrogen plasma with the solid graphite surface.

The reactive species, either created in the nozzle or by dissociation of the precursor gases, are transported at a high velocity ($\sim 1000 \text{ m} \cdot \text{s}^{-1}$ [4]) with the flowing plasma towards the temperature-controlled substrate holder, which is usually positioned at 60 cm from the arc outlet. The arc is mounted on a moveable holder, and hence the distance between the arc and the substrate can be varied.

The films are deposited on c-Si <100/111> samples or glass microscope slides which are cleaned following the procedure described in reference [10]. The substrate temperature can be varied from $-25 \text{ °C}$ to $400 \text{ °C}$, and is controlled within $5 \text{ °C}$ [11]. When no additional substrate biasing is applied, the self-bias is typically a few volts, which means that no energetic ion bombardment is present. With an RF unit (RF Power Products RF-5S) consisting of an RF power supply and an LC matching network additional RF bias (0 – 300 W) can be applied to the substrate. The bias voltage is measured with a high-voltage probe (Fluke PM910).

Recently a load-lock system has been implemented which allows sample handling under vacuum conditions.
2.3 Various diagnostics

Ellipsometry

Ellipsometry is a diagnostic technique that is used to determine the complex refractive index and the thickness of a film during deposition. It is an optical technique which is based on the principle that the reflection coefficient of light polarized parallel to the plane of incidence (p-direction) differs from the reflection coefficient of the light polarized perpendicular to the plane of incidence (s-direction). This means that at reflection the polarization of the incident light will change. This change will depend on the optical properties and thickness of both film and substrate.

In this work a specially designed in situ rotating compensator ellipsometer has been used (cf. Figure 2.3). Light from a He-Ne laser (\(\lambda = 632.8\) nm) is transformed into circularly polarized light by a retarder (\(\lambda/4\) plate) after which a polarizer transforms the light into linearly polarized light. The linearly polarized light passes through another \(\lambda/4\) plate coated with a non-polarizing anti-reflection coating (compensator) which is rotating and thus introduces a time-dependent polarization change. The light will then enter the reactor, where it is reflected at the sample. At this reflection the polarization is altered depending on the optical properties of the system. The reflected light leaves the vessel and passes through another polarizer (analyzer), after which it is focused onto a photodiode detector by a lens. An AD converter converts the signal from the detector into a digital signal that is fed to a computer. From the data obtained as function of the compensator position, registered by the encoder connected to the compensator, the values of the ellipsometric parameters \(\Psi\) and \(\Delta\) can be calculated.

The ellipsometric parameters \(\Psi\) and \(\Delta\) are related to the parallel and the perpendicular reflection coefficients \((r_p\) and \(r_s)\) as [12]:

\[
\rho = \frac{r_p}{r_s} = \tan(\Psi) \exp(i\Delta) \tag{2.3.1}
\]

As can be seen from this equation, \(\tan(\Psi)\) is equal to the ratio of the amplitude of the reflected light in the parallel and perpendicular direction, whereas \(\Delta\) is the difference in phase shift between these two directions at reflection.

With the help of an optical model for the multi-layer system [13] the complex refractive index and the thickness of the film as function of time can be derived from the \(\Psi\) and \(\Delta\) values recorded during deposition.

Figure 2.3: Schematic representation of the in situ rotating compensator ellipsometer with \(\lambda/4\): retarder (\(\lambda/4\) plate), \(P\): polarizer, \(E\): encoder, \(C\): rotating compensator (\(\lambda/4\) plate), \(A\): analyzer and \(L\): lens.
Infrared transmission absorption spectroscopy

The vibrational bonding frequencies of most molecules are observed in the infrared part of the electromagnetic spectrum. Therefore, infrared spectroscopy is a powerful tool in the identification of molecular bonds present in the film, provided that the bonding frequencies are known.

In the case of a-C:H materials these frequencies are well known [14,15]. For CN_x and a-C:H:N films however, in literature no real consensus has been reached on the exact positions of the different C-N absorptions in the infrared spectrum (see also section 5.2). This is probably due to the larger diversity of possible bonding structures and the relatively short time that these materials have been studied in comparison with e.g. a-C:H films. To date the only indisputable evidence for the presence of C-N bonds is the stretching vibration of the nitrile (-C≡N) group at ~ 2200 cm^{-1}. However, a common feature which is observed in most infrared spectra of CN_x and a-C:H:N films, is a broad absorption in the 1100 - 1700 cm^{-1} region. This absorption is often ascribed to the Raman-active $G$ (graphitic) and $D$ (disordered) bands at ~ 1584 cm^{-1} and ~ 1360 cm^{-1} respectively, which become infrared active due to the symmetry breaking in the sp^2 domains with nitrogen incorporation [16]. The intensity of the $D$ peak is quite sensitive to the average size of the graphitic domains [16], and therefore the $G$ to $D$ peak ratio is commonly used as a measure of the order in the system. However, at the same time incorporation of nitrogen may lead to a broadening of the $G$ and $D$ peaks and/or to a different film structure, which makes a good quantitative analysis questionable.

At the risk of giving erroneous assignments, we have compiled a list of average vibrational frequencies from the values that have been reported in literature for the different bonds in CN_x and a-C:H:N films (cf. Table 2.1). This list is far from exhaustive, especially in the 1000 - 1700 cm^{-1} region where numerous absorptions resulting from CH_x and NH_x bending vibrations may be observed [36], but it already shows the complexity of the spectral identification of the CN_x and a-C:H:N materials.

The infrared spectrum of the deposited films is obtained from the spectrum of the film plus substrate divided by the spectrum of the bare substrate. Both spectra are

![Figure 2.4: Top view of the Bruker Vector 22 Fourier transform infrared spectrometer.](image)
Experimental Details

measured with a Fourier transform infrared (FTIR) spectrometer (Bruker, Vector 22), schematically shown in Figure 2.4. The absorptions in the resulting spectrum are superimposed on an interference background (see e.g. Figure 5.2) that is caused by multiple reflections in the deposited films. From this background the refractive index and thickness of the film can be derived, using an analytical expression given in [17]*.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) [37] is a commonly used technique for the characterization of carbon nitride and a-C:H:N films [38]. It is a surface sensitive technique (the maximum depth sampled is about 4 nm) which is based on the ejection of an electron from the core level of an atom by an X-ray photon. From the kinetic energy of the ejected electrons and the energy of the incoming photons the binding energy of the core electrons is determined. The energy distribution of the emitted core-level electrons reveals the chemical environment of the atoms and -only under specific circumstances- the bonding structure.

As is the case for the interpretation of the infrared spectra, the various assignments given in literature for the different XPS features observed in CNx and a-C:H:N materials diverge to a large extent. This may again be explained by the large variety of deposition methods that have been applied and that may result in different structures, or the different analysis conditions, i.e. photon energy, spectral resolution, take-off angle etc., under which the XPS spectra were recorded. Furthermore, the sputter cleaning which is usually performed to remove surface contamination may change the film structure due to preferential sputtering, as has been observed in our films [39] and also by others [38].

In the search for the predicted β-C$_3$N$_4$ compound, which should have a tetrahedral (sp$^3$-bonded) structure resulting in C1s and N1s XPS peaks with only one feature at a position defined by the electronegativity of four C-N bonds, for identification of the carbon sp$^3$-bonds hexamethylenetetramine (C$_6$H$_{12}$N$_4$) is often used [40,41]. However,

\* In this expression the Kramers-Kronig (KK) relation [80], which connects the imaginary and real part of the refractive index close to and in the absorption band, is not included. In those parts of the spectrum that are free from molecular absorption bands, this KK relation will not influence the result (for the real part of the refractive index). Moreover, for a-C:H films it has been shown that the influence of the KK relation on the absorption is negligible [81]. However, for C-N vibrations the oscillator strengths are larger as compared to C-H vibrations, and the influence of the absorption band on the real part of the refractive may be important.

\† See for instance the review by Ronning et al. [38].

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250 – 1440</td>
<td>disordered carbon or C – N</td>
<td>[16,18,19,20,21,22,23]</td>
</tr>
<tr>
<td></td>
<td>Raman D peak</td>
<td></td>
</tr>
<tr>
<td>1500 – 1650</td>
<td>graphite, C=C, C≡N</td>
<td>[16,24,25,26,27,28,29]</td>
</tr>
<tr>
<td></td>
<td>Raman G peak</td>
<td></td>
</tr>
<tr>
<td>2150 – 2260</td>
<td>C≡N stretching</td>
<td>[16,30,31,32,33,34,35]</td>
</tr>
<tr>
<td>2850 – 3045</td>
<td>sp$^2$ and sp$^3$ CH$_x$ stretching</td>
<td>[14,15]</td>
</tr>
<tr>
<td>3200 – 3500</td>
<td>&gt;N-H, -NH$_2$ stretching</td>
<td>[36]</td>
</tr>
<tr>
<td>3300</td>
<td>sp$^1$ CH stretching</td>
<td>[14,15]</td>
</tr>
</tbody>
</table>

Table 2.1: Compilation of the vibrational frequencies of the most important features reported for CN$_x$ and a-C:H:N films.
because the carbon atoms in this compound have only two single bonds with nitrogen and two single bonds with hydrogen, we have proposed a different compound, melamine (C$_3$N$_6$H$_6$), as a more suitable XPS reference for the β-C$_3$N$_4$ phase [42]. The binding energy of the C1s and N1s XPS peaks in melamine have been determined to be equal to 287.9 and 398.8 eV, respectively. In our films the contribution of this “β-C$_3$N$_4$” phase was large [39]. However, the assignments of the other peak components in the XPS spectra is, as mentioned above, still under discussion, and therefore in this thesis the spectral identification has not been undertaken.

From the area of the different XPS peaks, i.e. C1s, N1s and O1s, the relative concentration of carbon, nitrogen and oxygen in the films could be derived using known sensitivity factors [43]. In this way it was found that approximately 8 % of oxygen is incorporated in the CNx and a-C:H:N films.

The XPS data were obtained using a MK II VG Scientific spectrometer with an Al K$\alpha$ X-ray source (photon energy: 1486.6 eV) in the analyzer constant energy mode. The C1s and N1s and O1s XPS spectra were acquired with a 0.1 or 0.05 eV step size.

**Optical emission spectroscopy**

The light emitted by the plasma in the visible range of the electromagnetic spectrum can be recorded by an optical emission spectroscopy (OES) setup that has been described elsewhere [44]. The plasma emission is collected by a focusing lens, and directed via a quartz optical fiber to the entrance slit (50 – 250 µm) of a monochromator (Jobin Yvon THR 1000, 1 m focal length). A Peltier cooled photomultiplier (Hamamatsu R 268) is used in the photon-counting mode to detect the incoming light. The lens can be moved, so that spectra can be collected at different axial and radial positions in the expansion.

In some cases from a comparison of computer simulated spectra with the recorded spectra the rotational and vibrational temperatures of the emitting species can be determined [45]. The procedure, which includes the influence of self-absorption on the simulated spectra, also provides an estimate of the ground state density of these molecules.

**Other diagnostics**

For the Langmuir probe measurements performed in the Ar/N$_2$ plasmas (see section 3.3) and in a pure Ar plasma (see section 3.2) a single cylindrical tungsten probe is used with a radius of 0.1 mm and a length of 5 mm. The radius is smaller than the mean free path for electrons and ions (typically 10$^{-1}$ – 10$^{-3}$ m), but much larger than the Debye length (typically 10$^{-6}$ m) at an electron density $n_e$ ~ 10$^{18}$ m$^{-3}$ and electron temperature $T_e$ ~ 0.3 eV. In this regime the electron temperature and density can be easily derived from the probe current versus voltage characteristic by a method described in reference [46].

The stoichiometry of some films was determined with elastic recoil detection analysis (ERDA) in combination with Rutherford back scattering (RBS). Of these nuclear analysis techniques a detailed description is given elsewhere [47,48].

For the evaluation of the microhardness and Young’s modulus two different nano-indenters were used: a depth-sensing nano-indenter (NanoTest 500, Berkovich) and a home-built (Berkovich) nano-indenter at the Department of Mechanical Engineering. The indentation data are analyzed using a method described in reference [49], and are
regularly calibrated against the values measured on c-Si <111>, which according to literature should yield 12 GPa and 170 GPa respectively [49]. The topography of the films has been measured by means of atomic force microscopy (AFM, Nanoscope 111a, working in the tapping mode). As a measure for the corrugation of the films the root mean square value of the surface roughness over an area of 1 µm x 1 µm has been determined for films of comparable thickness (~ 1 µm).

2.4 Mass spectrometry

2.4.1 Residual Gas Analyzer

In order to unravel the chemistry in the different deposition plasmas, the stable products are sampled with a mass spectrometer. The measured products and their abundance tell us more about the reaction pathways in the plasma. In this way not only information on the depletion of the precursor(s) may be obtained, but also on the stable monomers in the background which may contribute to film growth.

A residual gas analyzer (RGA) is a type of mass spectrometer with which only stable molecules, i.e. no ions or radicals, can be discriminated according to their molecular mass. The RGA consists of three main parts: the ionizer, the quadrupole mass filter (QMS) and detector (cf. Figure 2.5). In the ionizer a heating filament produces electrons with a typical energy of 70 eV. These electrons will ionize neutral species entering the ionizer by electron impact ionization. The ionized particles are redirected towards the entrance of the QMS, where they are separated according to their charge to mass ratio. The species that pass through the QMS are collected in the detector, which in our RGA (AccuQuad™ 200 D, Kurt Lesker Co.) can either be a Faraday cup or an electron multiplier. In this work we have only used the electron multiplier, since much higher sensitivity can be reached with this type of detector. A disadvantage of the electron multiplier however is the fact that the gain decreases with increasing mass \( M \) (roughly as \( 1/M \)).

2.4.2 Deconvolution of Mass Spectra

The molecules entering the RGA may not only get ionized on electron impact, but also fragmented. Moreover, due to the high electron energy used (~ 70 eV) molecules

\[ \text{Figure 2.5: The residual gas analyzer (RGA) and the connection to the vessel.} \]
may get doubly ionized, halving their mass to charge ratio. Each molecule has a typical ionization and fragmentation pattern, also called ‘cracking pattern’, which depends on the electron energy. The cracking pattern of an Ar/C2H2 mixture is shown in Figure 2.6. As can be seen, the signal of C2H2 does not only show up at mass 26, but also at 25, 24, etc. due to the fragmentation. And the signal of Ar, which can not be dissociated, does not only show up at mass 40, but also at mass 20 due to doubly ionized Ar2+. Furthermore, at masses 27 and 28 a signal appears due to isotopes of the carbon and/or hydrogen atoms in acetylene.

In a mixture of gases, e.g. as described in section 3.2 for the hydrocarbon plasmas, it is therefore very likely that parts of the mass spectra of the individual species are superimposed, which makes quantitative identification difficult if not impossible. This problem may be solved when the cracking patterns of all the gases present in the mixture are known by deconvolution of the mass spectrum. For the deconvolution first the cracking pattern of each gas is measured as function of the gas flow to account for the change in efficiency of the RGA with the amount of gas sampled. This gas flow dependence may be caused by a change in conductivity of the pinhole, pumping capacity, ionization efficiency or detector efficiency.

Each constituent of the cracking pattern is then fitted by an expression like

\[ I_x = A + B \cdot (\phi_{\text{gas}})^C \]  

where \( I_x \) is the mass spectrometer intensity at mass \( x \), \( \phi_{\text{gas}} \) the gas flow and \( A, B, \text{ and } C \) constants. \( A \) is typically close to 0 and \( C \) close to 1. The flow dependence of each mass in the cracking pattern will thus be characterized by the values of \( A, B, \text{ and } C \) which are unique for that specific gas.

When a mixture of calibrated gases is sampled, the unique set of constants for each gas allows the determination of the gas flow of the individual gases by means of a simple fitting procedure, as has been verified for mixtures of C\text{\textsubscript{x}}H\text{\textsubscript{y}} gases [52]. The maximum error in the calculated gas flows is approximately 5 % of the real gas flow. When the plasma is switched on the temperature of the gas sampled may change and thereby the conductivity of the gas extraction pinhole. One should therefore verify that the plasma on and plasma off signals of the sampled species are the same. This has been done for both an argon and argon/nitrogen plasma for which a maximum

![Figure 2.6: Mass spectrum of an Ar (100 sccs) / C\text{\textsubscript{2}}H\text{\textsubscript{2}} (19 sccs) mixture at 30 Pa.](image-url)
difference of 5% was found. For argon/hydrocarbon plasmas the background gas
temperature, as obtained from infrared gas phase absorption measurements (cf. next
section), was found to be close to room temperature. We can therefore assume that it
is safe to compare the plasma on and plasma off signal in this plasma.

2.5 Infrared gas phase absorption spectroscopy

2.5.1 Molecular Absorption
Infrared gas phase absorption spectroscopy (FTIRAS) is used in combination with
mass spectrometry (MS) to probe the gas phase. The advantage of FTIRAS over MS
is that species are readily identified by their absorption spectrum, which appears at
specific positions and has a shape characteristic for that specific molecule. The
tedious calibration and deconvolution of the MS data is thus circumvented. Moreover,
as will be shown in this section, from the infrared spectra information on the gas
temperature may be obtained. The disadvantage of FTIRAS is that it is a line-of-sight
technique, meaning that for a quantitative analysis the density and temperature profile
over the line-of-sight should be known. For plasma conditions these profiles are only
roughly known.

For non-homonuclear molecules in the infrared specific absorptions exist which
correspond to transitions between the vibrational and rotational states. Since for a
great number of molecules the energies of the allowed rotational or vibrational
transitions are exactly known, the infrared absorption spectrum is a good fingerprint
of a molecule. Depending on the number of atoms and the structure of the molecule
the spectrum will consist of several absorption bands, each associated with a certain
vibrational mode of the molecule [50].

From quantum mechanical considerations it is known that the rotational and
vibrational energy values of a diatomic molecule are not continuous and that only
those transitions are allowed which obey the following selection rules [51]:

\[ \Delta J = \pm 1 \text{ and, depending on the symmetry of the molecule, also } \Delta J = 0 \]
\[ \Delta n = \pm 1, 2, ... \]

where \( J \) is the rotational quantum number and \( n \) the vibrational quantum number. The
transitions for which \( \Delta J = 0, \pm 1 \) holds, result in two branches (P and R) of almost
equidistant absorption lines (see Figure 2.7) and one branch (Q) where the absorption
lines are almost at the same position. This is due to the transition energy of the lines
which is given by:

\[ \Delta E = h c ( \alpha \Delta n + 2B(J+1) - 4D(J+1)^3) \quad \Delta J = +1 \quad R-branch \]
\[ \Delta E = h c (\alpha \Delta n) \quad \Delta J = 0 \quad Q-branch \quad (2.5.1) \]
\[ \Delta E = h c (\alpha \Delta n - 2B + 4DJ^3) \quad \Delta J = -1 \quad P-branch \]

where \( J \) indicates the quantum number of the initial rotational level, \( B \) is the rotational
constant and \( D \) a constant which accounts for the non-rigidity of the molecule. The
fact that the lines in the Q-branch are not completely coinciding is due to the small
difference between the value of \( B \) for the upper and lower vibrational level (\( B'' \) and \( B' \)
respectively), which depends on the exact form of the potential energy curve and
which results in an energy shift of \((B''-B')J(J+1))\)
According to Boltzmann’s distribution law, at room temperature the number of molecules in the \( n = 1 \) level will be almost negligible. For the thermal particle distribution of the rotational energy levels we find:

\[
N_J = (2J + 1)N_0 e^{-\frac{B(J+1)}{kT}} = (2J + 1)N_{0r} \frac{B}{kT} e^{-\frac{B(J+1)}{kT}}
\] (2.5.2)

where \( J \) is the quantum number of rotation, \( N_J \) the number of particles in state \( J \), \( N_0 \) the number of particles in the ground state \( J = 0 \), \( k \) Boltzmann’s constant, \( T \) the temperature and \( N_{0r} \) the total number of particles.

When the temperature of the absorbing medium is changed, not only the spectrum itself will change due to the altered rotational and vibrational level distribution (see above), but also the width of each individual absorption line in the spectrum. The natural line width of an absorption line is usually determined by the Doppler line width (\( \Delta v_d \)). Pressure broadening can be neglected, because this mechanism only occurs at pressures much higher than used in this work. The Doppler line width (full width at half maximum (FWHM)) is given by:

\[
\Delta v_d = v_0 \sqrt{\frac{8kT \ln 2}{mc^2}}
\] (2.5.3)

Here \( v_0 \) is the wavenumber of the absorption line, \( k \) Boltzmann’s constant, \( m \) the mass of the molecule, and \( c \) the speed of light. From this equation it can be seen that the line width is proportional to \( \sqrt{T} \).

With these equations it is in principle possible, provided that the required constants, e.g. \( B \), \( D \) and \( \omega \), are known, to simulate the spectrum and to derive the temperature of a gas or plasma from it. But before we can do that, we first have to know the influence of the measuring device on the appearance of the spectrum. This issue will be discussed in the next section.

**Figure 2.7:** Energy level diagram for simple rotational-vibrational spectra (left) and the infrared absorption spectrum of CH\(_4\) (right).
2.5.2 Non-Linearity

In general the transmission through a medium obeys the Lambert-Beer law, which can be written in differential form as:

\[
\frac{dI}{dx} = -k_v I \quad (2.5.4)
\]

Here \( I \) is the intensity of the transmitted light, \( dx \) a certain displacement through the medium in the propagation direction of the light and \( k_v \) the frequency-dependent absorption coefficient of the medium. When the medium is assumed to be homogeneous, the solution of the differential equation is given by:

\[
I_v(x) = I_{v0} e^{-k_v x}
\]

where \( I_{v0} \) is the intensity of the light at frequency \( v \) before it enters the absorbing medium and \( I_v(x) \) the intensity of the light at frequency \( v \) after a distance \( x \) through the medium. The frequency-dependent absorption coefficient \( k_v \) is given by

\[
k_v = \frac{h}{c} v_{qp} B_{qp} N_q P(v - v_{qp}) \quad (2.5.5)
\]

with \( v_{qp} \) the transition frequency for the transition from state \( J = q \) to \( J = p \), \( N_q \) the density of the particles in the state \( J = q \), \( B_{qp} \) the Einstein coefficient for absorption for the transition from \( J = q \) to \( J = p \), and \( P(v - v_{qp}) \) is the absorption line profile. The absorption can be derived from the transmission \( T_r \), and is defined as:

\[
A = -\log(T_r) = -\log \left( \frac{I_v(x)}{I_{v0}} \right) \propto k_v x \quad (2.5.6)
\]

According to equation (2.5.6), for small absorptions the absorption would be linear with the density of the medium if one could measure the absorption with infinitesimal resolution in frequency \( v \). In reality however, the absorption is measured over a frequency interval that is determined by the apparatus profile (\( \Delta v_a \)), i.e. resolution of

![Graph](image)

**Figure 2.8:** The measured and simulated Q-branch bandhead absorption intensity (at 729 cm\(^{-1}\), resolution: 1 cm\(^{-1}\)) as function of the injected C\(_2\)H\(_2\) flow.
the spectrometer. Since the maximum resolution of the spectrometer (1 cm\(^{-1}\)) is many times greater than the natural (i.e. Doppler) linewidth (\(\Delta v_l \approx 0.01\) cm\(^{-1}\)), the measured absorption will be a convolution of the apparatus profile \(\Delta v_a\) and the real absorption at each specific frequency. This leads to a non-linear behaviour of the measured absorption as function of particle density (cf. Figure 2.8). This effect will become more pronounced as the ratio between \(\Delta v_a\) and \(\Delta v_l\) increases. As was shown by van Hest et al. [52], when the right settings for the Fourier transform infrared spectrometer are chosen, the apparatus profile can be considered as Gaussian, and the non-linear behaviour may be approximated by (see Appendix):

\[
A_{\text{meas}}(\tilde{\nu}') = -\log \left[ 1 + \sum_{J} \frac{\Delta v_l}{\Delta v_a} \exp \left[ -\frac{(\tilde{\nu}' - \tilde{\nu}_{qp})^2}{2\Delta v_a^2} \right] \cdot \sum_{n=1}^{\infty} \frac{1}{n! \sqrt{n}} \left( -\frac{\alpha}{\Delta v_l \sqrt{\pi}} \right)^n \right] \tag{2.5.7}
\]

where \(\tilde{\nu}_{qp}\) is the absorption frequency for a single line, the sum over \(J\) is over all absorption lines, and

\[
\alpha = \frac{c^2}{8\pi \tilde{\nu}_{qp}^2} A_{qp} N_q L \tag{2.5.8}
\]

in which \(A_{qp}\) is the transition probability for a transition from state \(p\) to state \(q\), \(L\) is the absorption path length, and \(N_q\) is the density of the particles in state \(q\).

As can be seen in Figure 2.8, the measured absorption can be very nicely described with the expression given in equation (2.5.7). This opens the way to derive the real spectrum, which contains information on the temperature and particle densities, from the measured one.

2.5.3 Gas cell measurements

From all the available information on the infrared spectrum an infrared spectrum simulation program has been compiled in Borland Pascal 7.0. For the molecular data the Hitran 1996 molecular database [53] has been used. This database contains all absorption line positions and intensities at 296 K for various molecules in the 0 - 17900 cm\(^{-1}\) range. With the transition probabilities and the quantum numbers, which are specified for each line, it is possible to calculate the thermal distribution of

![Figure 2.9:](image)

**Figure 2.9:** Left picture shows the normalized Q-band absorption intensity for three different temperatures as derived from C\(_2\)H\(_2\) spectrum simulation at a resolution of 1 cm\(^{-1}\). Right picture shows the measured (■) and simulated (solid line) spectrum for C\(_2\)H\(_2\) at a pressure of 0.875 mbar and a gas cell set temperature of 425 K.
the rotational energy levels (equation (2.5.2)) and to make also a spectrum simulation at a different temperature. To make the simulated spectra comparable with the measured spectra obtained by Fourier transform infrared spectroscopy the non-linearity theorem presented in section 2.5.2 has also been implemented.

The simulation results for three different temperatures are presented in Figure 2.9 for the Q-branch, the only feature of the spectrum that will be clearly resolved under plasma conditions. As can be seen, the width of the Q-branch is a good measure for the temperature and can, provide the simulation is correct, thus be used for determination of the plasma temperature.

To verify the validity of the simulation program a temperature-controlled gas cell has been constructed. The experimental setup has been extensively described elsewhere [52]. The temperature of the gas cell, which is measured by means of a thermocouple, is controlled manually between 300 and 725 K and can be kept constant within 1 K.

To obtain the temperature and density of the C2H2 molecules that corresponds best to the measured spectrum, a numerical fitting procedure which is based on the Levenberg-Marquardt least mean square routine [54] has been added to the spectrum simulation program. An example of such a fitting result is shown in Figure 2.9. The fit gives also a nice match with the measured P- and R-branch, not shown here, and is a good indication that the spectrum simulation works well. The measured spectrum shows two bands at ~ 720 cm⁻¹ and ~ 725 cm⁻¹ which are so-called ‘hot bands’, i.e. transitions from vibrationally excited states. From the ratio between these ‘hot bands’ the vibrational temperature might also be derived [55]. However, to our knowledge the exact assignment of the transitions involved is not known, and hence the determination of the temperature by this method is not possible.

In Figure 2.10 the results from a series of gas cell measurements are shown. As can be seen, there is a slight discrepancy between the set temperature and the fitted temperature, which may be explained by the construction of the gas cell which introduces some uncertainties in the temperature and/or density profile in the cell [52]. However, the results show that it is possible to obtain the temperature from a simulation of the measured infrared spectrum with an accuracy of ~ 100 K.

**Figure 2.10:** The temperature $T_{\text{fit}}$, as obtained from simulation of the Q-band absorption intensity, as function of the gas cell temperature $T_{\text{set}}$ for C2H2 at 0.85 mbar.
2.5.4 Infrared gas phase absorption setup

With the FTIR spectrometer (Bruker, Vector 22) measurements can be performed either internally or externally. In the internal sample chamber (see Figure 2.4) infrared spectra can be obtained from e.g. films deposited on a substrate. For these measurements an internal detector is used (DTGS) which has a detection range from 370 to 7500 cm\(^{-1}\) (1.33 to 27 \(\mu\)m). For external measurements the infrared light can be directed through an exit port (see Figure 2.4). The light is focused with a Sodium Chloride (NaCl) lens (\(f = 35\) cm) onto the first KBr window and is directed through the plasma towards the exit window (also from KBr). The light is then focused onto the nitrogen-cooled infrared detector (Graseby MCT D315) with the help of a spherical mirror (\(f = 5\) cm) (see Figure 2.11).

Since the infrared light is passing through both the (hot) plasma beam and the (cold) background gas, the absorption will depend on the temperature and density profile in the plasma reactor. Therefore, quantification of the infrared absorption data is not feasible without \textit{a priori} assumptions on the temperature and density profiles. However, simulations of the acetylene absorption spectrum under different plasma conditions reveal that the average rotational gas temperature is independent of the precursor flow and within 100 K also independent of the arc current [52]. This is an indication that especially the (colder) background gas is sampled due to the higher density. It also means that in the mass spectrometer, which is sampling the background gas, no correction for a change in temperature on ignition of the plasma has to be taken into account.

\[ A \text{ preliminary study into the use of the arc as an alternative infrared light source clearly demonstrated that with an arc a considerable improvement of the intensity and divergence of the light can be achieved while maintaining a stability comparable to that of the globar (\sim 10^{-5}) [52]. Notwithstanding these advantages, for further experiments we have chosen to work with the globar, because it is more easy to work with and less expensive. Moreover, at that time the power supply of the arc and the thickness of the infrared transparent window were not capable of sustaining the high powers and pressures which would be required for a really profitable intensity increase by a factor of 10 (Xenon, 6 bar, 60 A). ]"
2.6 Infrared reflection absorption spectroscopy

2.6.1 Introduction

Infrared (IR) spectroscopy is a widely used technique for studying the chemical nature, bonding configuration and orientation of bonds in adsorbates on surfaces [56,57,58,59]. The application of infrared reflection absorption spectroscopy to (sub)monolayer films, though, has always been troubled by the limited sensitivity of the method. As long as the adsorbates are static, a good sensitivity can be obtained by increasing the number of scans [60]. For real-time investigation of film growth, however, special requirements are needed to enhance the signal above the typical detection limit of most Fourier transform infrared (FTIR) spectrometers (~5×10^{-4} for an integration time of 1 s in our case).

Single crystal substrates have been successfully used for this purpose [57,59], as well as metal substrates [61,62]. These two types of substrates are sensitive to vibrational modes on the surface, but much less to those in the bulk. Furthermore, the enhancement does only occur for a specific polarization, viz. p polarization (electric field component parallel to the plane of incidence §), which means that only IR-active vibrational modes with a dipole oscillation normal to the surface are observable. Hence, bond orientation information cannot be obtained using these substrates.

The use of multiple internal reflection (MIR) [63,64] or attenuated total reflection (ATR) [65] crystals, which have only a small and constant dependence of the signal enhancement on the polarization state, allows one to study the alignment of molecules on the surface [66]. Drawbacks are the relatively high costs of the crystals and the limitation of the spectral range due to the cut-off frequency below which the crystals become opaque, e.g. Si below 1400 cm^{-1}.

A substrate that was developed by Maley et al. [67] to enhance the signal from vibrational modes both on the surface and in the bulk is the so-called optical cavity substrate (OCS). The substrate structure is shown in Figure 2.12 (b). It is designed to maximize the electric field in the absorbing film by constructive interference of backward- and forward-going beams across the SiO_{2} layer including incoherent beams from the back of the c-Si substrate. The OCS has been successfully used in the time-resolved study of amorphous and polycrystalline carbon and silicon film growth [68,69].

Investigations on the applicability of the OCS for analysis of the CN_{x} film deposition led to the conclusion that the enhancement of the OCS could be optimized even further by removal of the thick c-Si substrate (typically 500 μm) [70]. The substrate system that arises in this way, a so-called SIM substrate, is depicted in Figure 2.12 (c). It shows some resemblance with the “buried metal structure” (BML) introduced by Bermudez et al. [71] to probe adsorbates on dielectric materials. However, in the case of a BML a thin dielectric layer (typically 50 nm) covers the optically thick metal layer, whereas in the case of a SIM substrate a thick SiO_{2} layer (typically 1 μm) is used. As a consequence, the BML system displays the same IR optical properties, i.e. enhancement and polarization dependence, as a metal. The optical response of the SIM substrate is a function of the thickness of the SiO_{2} layer, the angle of incidence and the polarization. The optical constants of the metal, SiO_{2} and film have of course also a great influence on the ultimate enhancement of the absorption signal. The

§ The plane of incidence is defined as the plane perpendicular to the surface and the propagation vector of the electric field of the light.
performance of the SIM substrate in comparison with the two other substrate types depicted in Figure 2.12 will be evaluated in the next section with the help of an optical model. To elucidate the advantages of the different enhancement systems, the following characteristics will be discussed:

− the sensitivity in the two polarization states (perpendicular (s) and parallel (p) to the plane of incidence), i.e. to what extent may one determine the bond orientation?
− the influence of the optical constants of the film (refractive index \( n \), and extinction coefficient \( k \)) on the enhancement, i.e. can one study a range of films without \textit{a priori} knowledge of \( n \) and \( k \)?
− the dependence of the absorption on the thickness of the film, i.e. does one obtain good sensitivity for both surface and bulk vibrational modes?
− the optimum angle of incidence, i.e. what freedom does one have in the choice of the experimental geometry?
− the enhancement as function of the wavelength of the IR light.

### 2.6.2 Substrates for signal enhancement

#### Optical model and simulations

The absorption of IR light in a thin film depends on the interaction of the electric field \( E \) of the light (electromagnetic wave) within the film with the dynamic dipole moments \( \mu \) associated with the specific vibrational mode. With other words, for maximum absorption in the film, the electric field \( E \) should be maximum in the direction of the dipole oscillations. To calculate the electric field \( E \) at the film surface for a given system of layers (see Figure 2.13), we make use of the recurrence relations derived from Maxwell’s equations which connect the electric and magnetic field components in adjacent layers [72]. For an assembly of non-magnetic layers with smooth interfaces, like depicted in Figure 2.13, the optical response in the limit of coherent interference can be calculated from the characteristic matrix \( M \) defined as:

\[
M = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = \prod_{j=1}^{N} \begin{bmatrix} \cos(\delta_j) & i \cdot \sin(\delta_j) / g_j \\ i \cdot g_j \cdot \sin(\delta_j) & \cos(\delta_j) \end{bmatrix}
\]

with the following definitions of \( g_j \) and \( \delta \):
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$$g_j = \cos(\theta_j) \cdot \tilde{n}_j$$ (for s-polarization\textsuperscript{**})

$$g_j = \cos(\theta_j) / \tilde{n}_j$$ (for p-polarization) (2.6.2)

$$\delta_j = 2\pi \cdot v \cdot d_j \cdot \tilde{n}_j \cdot \cos(\theta_j)$$

$$\tilde{n}_j = n_j - i \cdot k_j$$

Here $v$ is the wavenumber (reciprocal wavelength) in vacuum and $d_j$, $n_j$ and $k_j$ respectively the thickness, refractive index and absorption (or extinction) coefficient of layer $j$. The angle of incidence in each layer ($\theta_j$) is determined by Snell’s law:

$$\tilde{n}_j \cdot \sin(\theta_{j+1}) = \tilde{n}_j \cdot \sin(\theta_j)$$ (2.6.3)

When the refractive index $\tilde{n}_j$ is complex, the angle $\theta_j$ will also be complex. From this characteristic matrix $M$ the total reflectance and transmission coefficients for the electric field can be simply calculated:

$$r = \frac{E_r}{E_0} = \frac{g_0 (m_{11} + g_s \cdot m_{12}) - (m_{21} + g_s \cdot m_{22})}{g_0 (m_{11} + g_s \cdot m_{12}) + (m_{21} + g_s \cdot m_{22})}$$ (2.6.4)

$$t = \frac{E_t}{E_0} = \frac{2 \cdot g_0}{g_0 (m_{11} + g_s \cdot m_{12}) + (m_{21} + g_s \cdot m_{22})}$$ (2.6.5)

where $g_0$ (vacuum) and $g_s$ (substrate) are given by equation 2.6.2. The total reflectance $R$ and transmission $T$ are given by:

\textbf{Figure 2.13:} Schematic drawing of a multilayer system of $N$ layers and a semi-infinite substrate. Each layer $j$ is defined by a certain imaginary refractive index $\tilde{n}_j = n_j - i \cdot k_j$ with $n_j$ and $k_j$ the refractive index and absorption (or extinction) coefficient respectively. thickness $d_j$ and angle of incidence $\theta_j$. The total electric fields of the incident, reflected and transmitted waves are denoted by $E_0$, $E_r$ and $E_t$ respectively.

\textsuperscript{**} For s-polarised light ($s = \text{senkrecht}$) the component of the electric field is perpendicular to the plane of incidence. Light that is p-polarised ($p = \text{parallel}$) has the electric field component in the plane of incidence.
The absorption ($A$) in the thin film can then be calculated from the generally used definition:

$$ A = (R_0 - R)/R_0 $$

(2.6.8)

Actually the absorption obtained in this way can not be directly related to a measurable quantity. Even when there is no absorption in the thin film, the reflectance is less than unity. It is therefore more convenient to use the definition proposed by Greenler [73] for the depth of an absorption band in the infrared spectrum of the film:

$$ A' = 1 - R - T $$

(2.6.9)

where $R_0$ is the value of the reflectance for a non-absorbing film and $v_0$ is the wavenumber (in cm$^{-1}$) at which the absorption occurs. This is clarified in Figure 2.14.

The value of $R_0$ can not be measured directly, but can often be estimated from extrapolation of the reflectance $R$ in the non-absorbing parts of the spectrum (cf. Figure 2.14)††.

The matrix method that was introduced above to calculate the optical response of an assembly of layers is based upon a relation between the electric fields at two adjacent layer boundaries. This relation can only be used when the light interference on both sides of the boundary is coherent, i.e. when the phase relation between the interacting light waves is well determined. For layers with a thickness in the order of the

†† The reflectance $R$ close to or in the absorption band is connected with the absorption via the Kramers-Kronig relation [80] (see also footnote on page 13). For strong absorptions this effect has to be included for a good interpretation of the spectrum.
wavelength (1.5-20 µm) the beams which interact after the reflection from two interfaces can be considered coherent. When the layer thickness is much larger than the wavelength (\(d_j \gg n_j \cdot \lambda_0\)) the phase coherence will be lost and hence the intensities of the interfering waves simply add up [74]. The total reflection of a thick layer as depicted in Figure 2.15 is given by [75]:

\[
R = \frac{R_a^+ + R_b^+ T_s^2 (T_a^2 - R_a^+ R_a^-)}{1 - R_a^- R_b^+ T_s^2} \tag{2.6.10}
\]

Here \(R_a^+, R_a^-, R_b^+, R_b^-\), \(T_a\) and \(T_b\) are the reflection and transmission coefficients at the layer interfaces as shown in Figure 2.15. The transmission coefficient \(T_s\) of the thick layer is given by:

\[
T_s = \exp\left(-\frac{4\pi \cdot n_s \cdot k_s \cdot d_s}{\lambda_0 \cos(\theta_s)}\right) \tag{2.6.11}
\]

with \(n_s\) and \(k_s\) the refractive index and absorption coefficient respectively, \(\theta_s\) the angle of incidence and \(d_s\) the thickness of the layer. The case in which both coherent and incoherent interference occur in a multilayer system, e.g. OCS, is calculated by a combination of the matrix method and the equations for the incoherent situation. The multilayer system is first separated into two systems as shown in Figure 2.15. The assembly of layers at the left side of interface a is considered as a multilayer system with a semi-infinite bottom layer to calculate the coefficients \(R_a^+, R_a^-\) and \(T_a\) with help of the coherent matrix method. This is also done for the system on the right of interface b to obtain the values for \(R_b^+, R_b^-\) and \(T_b\). Next, the total reflection of the multilayer system is calculated according to the incoherent equations given above.

The several expressions presented in the optical model are evaluated with help of the mathematical software package Maple®, release 5 [70]. In the model the real (\(n_{film}\)) and imaginary (\(k_{film}\)) part of the refractive index and the film thickness (\(d_{film}\)) characterize the deposited film. The absorption as shown in Figure 2.14 and defined in equation (2.6.9) is computed as follows:
For comparison of the enhancement properties of the substrates under different film conditions, i.e. different $n_{\text{film}}$, $k_{\text{film}}$ and $d_{\text{film}}$, it is convenient to introduce an enhancement factor $M$ defined as \[ M = \frac{n_{\text{film}}}{n_{\text{film}} - i \cdot k_{\text{film}}}. \] (2.6.12)

In order to study a range of films without a priori knowledge of $n_{\text{film}}$ and $k_{\text{film}}$, $M$ should be in first approximation independent of $n_{\text{film}}$ and $k_{\text{film}}$. Furthermore, when films with different thickness are studied, e.g. during film growth, it is desirable to have a more or less constant enhancement factor $M$. In the following, the characteristics of $M$ for the three substrate types will be compared. In order to have a feeling of the significance of $M$, in Table 2.3 the minimum enhancement factor needed for detection of a monolayer (3 Å) film is shown for several refractive indices and a detection limit of $5 \cdot 10^{-4}$.

<table>
<thead>
<tr>
<th>Layer</th>
<th>$n$</th>
<th>$k$</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>1 – (4.5; ) fixed: 1.5</td>
<td>0 – 0.5; fixed: 0.05</td>
<td>0 – 500 nm; fixed: 2.5 nm</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1.41</td>
<td>0</td>
<td>0.5 – 5 (\mu)m; fixed: 1.08 (\mu)m</td>
</tr>
<tr>
<td>c-Si</td>
<td>3.42</td>
<td>0</td>
<td>350 (\mu)m</td>
</tr>
<tr>
<td>Aluminium</td>
<td>7</td>
<td>32</td>
<td>semi-infinite; 300 nm (OCS)</td>
</tr>
<tr>
<td>Spectral range</td>
<td>500 – 5000 cm(^{-1}); fixed: 2200 cm(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Angle of incidence</td>
<td>0 – 90°; fixed: 70°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Parameters used for the simulations of film on top of OCS, SIM and metal substrates.

\[^{11}\text{ When } d_{\text{film}} \text{ is given in } \mu\text{m}, M \text{ will have the unit } \mu\text{m}^{-1}.\]
that for films of a few monolayers the refractive index will probably be lower than measured for bulk material due to roughness on the surface and/or the incorporation of voids [76]. For the absorption coefficient also a slightly smaller value than obtained in the bulk material is taken to account for the fact that for (sub)monolayer films the density of the film and hence of the dipole oscillators will be smaller.

In Figure 2.16 the simulated absorption is shown as a function of the angle of incidence, as defined in Figure 2.13, on the three substrates. The dependence of the absorption in the two polarization states on a metal substrate is quite distinct from that of the OCS and SIM substrates. On a metal substrate only \(p\)-polarized light is significantly enhanced. The sensitivity for \(s\)-polarized light is far below the detection limit, and hence molecular vibrations of which the change in electric dipole is parallel to the surface will not be probed. Thus, a metal substrate can not be used to study bond orientation. The strong enhancement of \(p\)-polarized light on a metal at nearly grazing incidence has been explained by Greenler [73]. It is attributed to the phase shift on reflection, which at large angles of incidence approaches 90° for \(p\)-polarized light and 180° for \(s\)-polarized light. Due to this phase shift the reflected and incident light will either combine to produce a nonzero electric field vector normal to the substrate in the case of \(p\)-polarized light or cancel in the case of \(s\)-polarized light. The principle is shown in Figure 2.17.

The enhancement from the OCS and SIM substrates relies on constructive

\[
\frac{\Delta R}{R_0} = \begin{cases} \approx 0 & \text{for } s\text{-polarized} \\ E \neq 0 & \text{for } p\text{-polarized} \end{cases}
\]

**Figure 2.16:** Absorption at 2200 cm\(^{-1}\) in a 2.5 nm film (1.5 - i\(0.05\)) on top of a metal substrate (left), a SIM substrate (right, solid line) and OCS (right, dashed line) as function of angle of incidence.

**Figure 2.17:** Reflection of \(s\)- and \(p\)-polarized light on a metal substrate at large angle of incidence. In the case of \(p\)-polarized light the incident and reflected light form a standing wave, whereas in the case of \(s\)-polarized light they cancel.
interference of incident and reflected light across the SiO\textsubscript{2} layer(s), and is therefore dependent on both the wavelength of the light and the thickness of the SiO\textsubscript{2} layer(s). A relation between the optimum SiO\textsubscript{2} layer thickness and wavelength can be obtained by considering the phase difference between two reflected beams, as depicted in Figure 2.18. The difference in optical path length ($\Delta$OPL) between the reflected beams r1 and r2 is given by \cite{72}:

$$\Delta\text{OPL} = 2d_2 - d_1 = 2d\sqrt{n_{\text{SiO}_2}^2 - \sin^2(\theta_i)}$$  \hspace{1cm} (2.6.14)

An extra phase shift $\Delta\phi$ has to be taken into account for the reflection at the boundary. The interference of beam r1 and r2 will only be constructive when the following condition is satisfied:

$$k_0\Delta\text{OPL} + \Delta\phi = k_0m\lambda_0, \ m = 1, 2, 3...$$  \hspace{1cm} (2.6.15)

Here $k_0 (2\pi/\lambda_0)$ is the propagation wave vector and $\lambda_0$ is the wavelength in vacuum. For s-polarised light a phase shift of nearly 180$^\circ$ occurs upon internal reflection at the interface between the SiO\textsubscript{2} layer and the metal (in the case of a SIM substrate) or c-Si layer (in the case of an OCS). From these two equations it follows that the optimum SiO\textsubscript{2} thickness $d_{\text{SiO}_2}$ at wavelength $\lambda_0$ is given by:

$$d_{\text{SiO}_2} = \frac{1}{4\sqrt{n_{\text{SiO}_2}^2 - \sin^2(\theta_i)}}\lambda_0$$  \hspace{1cm} (2.6.16)

For an angle of incidence of 70$^\circ$, a wavelength of 4.55 $\mu$m (2200 cm$^{-1}$) and a SiO\textsubscript{2} refractive index of 1.41 - $i$0 an optimum SiO\textsubscript{2} thickness of 1.08 $\mu$m is obtained. This layer thickness was used for all simulations performed at 2200 cm$^{-1}$.

Opposite to the metal substrate, for the OCS and SIM substrate the largest enhancement is obtained for s-polarized light. However, the sensitivity of the other polarization component, i.e. p-polarization, is not negligible in this case. From Figure 2.16 even an enhancement factor for p-polarized light of ~2.7 can be deduced. This means that both the OCS and SIM substrates can also be used to study bonds that are oriented perpendicular to the surface. Furthermore, the signal enhancement is not only restricted to large angles of incidence as in the case of a metal substrate. Even at small angles of incidence the signal is above the typical detection limit of $5\times10^{-4}$, which allows us to choose the most convenient experimental geometry. In our case the trade-off between signal enhancement and experimental degrees of freedom resulted in an

![Figure 2.18: Phase difference between directly (r1) and indirectly (r2) reflected beam.](image-url)
angle of incidence of ~70°. In the following simulations, therefore, this angle will be kept fixed. As can be seen in Figure 2.16, at an angle of incidence of 70° and the used film parameters the enhancement of the SIM substrate is superior to that of the OCS. To see what the influence of the film parameters is on the enhancement, simulations have been performed as function of $n_{\text{film}}$, $k_{\text{film}}$ and $d_{\text{film}}$ for the polarization state in which the enhancement is maximum, i.e. $p$-polarization for a metal substrate and $s$-polarization for an OCS and SIM substrate. In Figure 2.19 the simulated enhancement factor $M$ is shown as function of the refractive index and absorption coefficient of the film. It is evident from these simulations that the SIM and OCS are very well suited for studying films without a priori knowledge of the optical constants of the films. The metal substrate on the other hand shows a very strong dependence on the refractive index and a rather strong change with the extinction coefficient. Over the whole range of optical constants the SIM substrate shows about two times stronger enhancement than the OCS.

The influence of the film thickness on the IR light absorption is shown in Figure 2.21 for the three substrates. As can be seen, the changes are quite dramatic, indicating that the three substrate types can not be used for the quantitative analysis of both monolayer films and thick films without good knowledge, i.e. by modelling, of the enhancement. This complicates especially the real-time study of film growth where the film thickness (or growth rate) is not a priori known. For a good analysis, therefore, information from additional in situ diagnostics, e.g. ellipsometry, is indispensable. Fortunately, in our case the IR reflection absorption experiments could usually be supported by in situ ellipsometry measurements performed simultaneously. For the study of initial growth (from 0 up to a few nm) a constant enhancement factor can be assumed, as shown in the inset of Figure 2.21. Again, the SIM substrate seems the best choice for this purpose, although it shows the largest dependence on the thickness of the film (14.3 % over 50 nm).

**Figure 2.19:** Enhancement factor $M$ as function of the refractive index (left) and absorption coefficient (right) of the film on top of a SIM (solid line), metal (dashed line) and OCS (dash dotted line). Left picture: $k_{\text{film}} = 0.05$; right picture: $n_{\text{film}} = 1.5$. Angle of incidence: 70° at 2200 cm$^{-1}$, $d_{\text{film}} = 2.5$ nm. The percentages indicate the relative change over the entire range.
Schreur has shown that for larger wavelengths (smaller wavenumbers) the linear relation between absorption and film thickness is preserved up to larger film thickness in comparison to smaller wavelengths (larger wavenumbers) [70]. The dependence of $M$ on $n_{film}$ and $k_{film}$ also becomes more pronounced at larger wavenumbers. This is attributed to the dependence of the absorption signal on the wavelength of the light. As can be seen in Figure 2.20, for larger wavenumbers the enhancement factor or absorption signal increases and will hence be more sensitive to changes in the film properties. For the OCS and SIM substrate the requirement of constructive interference at the film surface results in a strong resonance-like dependence on the

![Figure 2.21: The enhancement factor $M$ as function of the film thickness on top of a SIM (solid line), metal (dashed line) and OCS (dash dotted line). Angle of incidence: 70° at 2200 cm$^{-1}$, $k_{film} = 0.05$, $n_{film} = 1.5$. The insert shows a magnification of the 0 – 50 nm range with percentages indicating the relative change over this range.](image)

![Figure 2.20: The absorption of a film ($n_{film} = 1.5$, $k_{film} = 0.05$, $d_{film} = 2.5$ nm) on top of SIM substrates optimized for 1200, 1350, 1600 and 2200 cm$^{-1}$ as function of wavenumber (left). The right picture shows the enhancement factor for the same film on top of a SIM, metal and OCS substrate. Both OCS and SIM substrate have been optimized for each specific wavenumber.](image)
wavelength of the IR light (see Figure 2.20, left picture). This is clearly a disadvantage of these types of substrates compared to the metal substrate whose reflectance is just monotonically increasing with wavenumber. On the other hand, the possibility to tune the enhancement at a specific wavelength with the SiO₂ layer thickness gives one more flexibility and allows one to have a reasonable signal enhancement even at very small wavenumbers. The wavelength characteristics of the SIM substrate and OCS are comparable, except that the full width at half maximum (FWHM) is larger for the OCS. Figure 2.20 shows that for a SIM substrate the full width at 90% of the maximum is about ±(200-350) cm⁻¹. For an OCS approximately twice this value is found [70]. This makes an OCS, when the enhancement is not the primary concern, more favorable than the SIM substrate for studying different vibrational modes whose frequencies lie in a small frequency range, e.g. CH band (2850 – 3045 cm⁻¹).

Let us finish this section with some practical remarks about the performed simulations. In the simulations the refractive index for the film, metal, c-Si and SiO₂ layers were assumed to be independent of wavelength, the c-Si and SiO₂ were considered non-absorbing, and the interfaces between the different layers were treated as completely flat. Furthermore, the angle of incidence was taken as a well-defined quantity, and any effects, such as dipole orientation, arising from adsorbate-substrate interaction were omitted. Unfortunately, these simplifications do not always hold in reality, as investigation of the infrared transmission spectrum of a SiOₓ layer evaporated onto a c-Si reveals [70][9]. Therefore, the presented simulations should merely be considered as an indication of the possibilities and most important trends in the three types of substrates. For the exact modeling of the characteristics the optical

\[ \frac{d(A)}{dt} (10^{-3} \text{ s}^{-1}) \]

\[ \text{Wavenumber (cm}^{-1}) \]

Figure 2.22: The rate of increase of the absorption \( A = (R_0-R)/R_0 \) measured during film growth as function of the wavenumber for a SIM (\( s \)-polarized) and a metal substrate (\( p \)-polarized; ▲ unpolarized) under identical deposition conditions. Deposition conditions: Graphite nozzle, 70 sccs Ar, 30 sccs N₂, \( I_{\text{arc}} = 80 \) A and \( T = 275 \) °C

[9] Also in the interpretation of the ellipsometry measurements, which employ light in the visible region of the spectrum (\( \lambda = 632.8 \) nm), the optical response of a metal and SIM substrate can not always be described by the optical constants reported in literature for the metal and SiO₂.
properties of all the layers—as well as their wavelength dependence—should be precisely determined. Moreover, a more complicated problem that remains to be solved is the optical description of the interaction between ‘real’ metal surfaces, i.e. with surface roughness and a possible oxide on top, and adsorbates [77,78]. Notwithstanding these uncertainties in the modeling, experiments reveal that with a SIM substrate about 4 times more signal can be obtained than with a metal substrate (see Figure 2.22).

Conclusions
For detection of submonolayer films by infrared reflection absorption spectroscopy special substrates are needed to enhance the absorption signal in the film. For this purpose three substrates have been investigated: a metal, SiO₂ on top of metal (SIM) and an optical cavity substrate [67] (OCS). The characteristics of the three substrates have been simulated with the help of an optical model. The following issues have been addressed: the dependence of the enhancement on the optical constants (n, k and d) of the film, the angle of incidence, the polarization of the light and the wavelength of the light. The enhancement factor of the SIM substrate is larger as compared to the OCS and metal substrate over the entire range of film properties and angles of incidence. Maximum signal enhancement is achieved for all three substrate types at large angles of incidence (88° – 89°). The signal decrease towards smaller angles is much less pronounced in the case of the SIM and OCS substrate as compared to the metal substrate. Hence, with the SIM and OCS substrates measurements at smaller -and often more convenient- angles of incidence can be performed. Another important difference is that for the OCS and SIM substrate particularly s-polarized light is enhanced, whereas for a metal substrate the p-polarization is favored. Moreover, in the case of a metal substrate the signal from the s component is not detectable, while for the OCS and SIM substrate the ‘weaker’ p component still has a reasonable enhancement. In other words, on a metal substrate only those vibrational modes oriented perpendicular to the surface (p-polarized) will be probed, whereas on a SIM or OCS substrate bonds oriented both parallel (s-polarised) and perpendicular to the surface can be detected. For the SIM and OCS substrate the enhancement factor M changes only slightly over a large range of refractive indices (n_{film}) and extinction coefficients (k_{film}). This makes the OCS and SIM very suitable for measurements in which the optical constants of the film are not a priori known, in contrast to a metal substrate, which shows a strong dependence on both n_{film} and k_{film}. The decrease of M with increasing film thickness is most pronounced for the SIM substrate, but is also clearly observed for the other two substrates. As long as films in a small thickness interval are studied, e.g. during initial growth (0 – 10 nm), the films may be compared without taking into account the influence of the thickness on the enhancement. For the study of initial growth the OCS substrate seems best suited, because of the nearly constant M on the interval 0 – 50 nm. On the other hand, the SIM substrate yields an approximately two times higher signal enhancement. For all three substrates the enhancement increases with increasing wavenumber, i.e. decreasing wavelength of the light. The OCS and SIM substrate show a similar resonance-like dependence on the wavelength of the IR light. However, the value of the full width at 90 % of the maximum for an OCS is about twice the value obtained for a SIM substrate (200-350 cm⁻¹). Therefore, when the enhancement is not the primary concern, an OCS is better suited than the SIM substrate to study absorptions that lie close together in a small frequency range, e.g. CH band (2850 – 3045 cm⁻¹). The experimental comparison
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between film growth on a metal and a SIM substrate shows that, despite some uncertainties in the optical properties used in the models, with a SIM substrate about 4 times more signal is obtained.

2.6.3 Infrared reflection absorption setup

The FTIRAS setup (cf. Figure 2.23) consists of a FTIR spectrometer (Bruker, Vector 22) and a system of lenses and mirrors to focus the infrared beam onto the substrate and, after reflection onto the detector. The infrared light exits the spectrometer through the exit port (cf. Figure 2.4) after which it is focussed by a Sodium Chloride (NaCl) lens \( f = 35 \text{ cm} \) onto a plane mirror. From here the light is directed to an Aluminium off-axis parabolic mirror \( f = 37 \text{ cm} \), angle of incidence: 45\(^\circ\) [79] which focuses the light through an IR transparent Potassium Bromide (KBr) window onto the substrate. The light comes in at an angle of \( \sim 70\^\circ \) to the normal and will exit the vessel again after reflection through a second KBr window. The light then goes through a wire-grid polarizer (Graseby, IGP 228) after which a similar combination of an off-axis parabolic and plane mirror directs it to a spherical mirror which finally focuses it onto the nitrogen-cooled detector (MCT, Graseby D316/6). To reduce the absorption from H\(_2\)O and CO\(_2\) from the ambient air, the whole setup is covered with a plastic foil.

The reflection changes caused by film growth/etching are calculated from the ratio of the spectra measured before and during deposition/etching. As a background spectrum either the bare substrate (in case of deposition) or the film on top of the substrate (in case of etching) is taken. For a good signal-to-noise ratio the background spectrum is averaged over typically 1000 scans. The time-resolved spectra are recorded as fast as possible, but for a good signal-to-noise ratio an average of at least 3 scans is required, which takes about 1 s at a resolution of 8 cm\(^{-1}\). The time per scan will be shorter at a smaller resolution, e.g. 0.18 s per scan at 64 cm\(^{-1}\). The minimum reflection changes that can be measured at 2200 cm\(^{-1}\) are in the order of 1.5\(\times\)10\(^{-4}\) for 1 scan and 4\(\times\)10\(^{-5}\) for 128 scans [70].
References


Experimental Details


Appendix: Non-linearity (derivation of equation (2.5.7))

Transmission is described by the following differential equation:

\[
\frac{dI}{dx} = -\hbar \tilde{\nu}_{qp} B_{qp} N_q P(\tilde{\nu} - \tilde{\nu}_{qp}) \Rightarrow \frac{1}{I} \frac{dI}{dx} = \frac{-\hbar \tilde{\nu}_{qp} B_{qp} N_q P(\tilde{\nu} - \tilde{\nu}_{qp})}{c} dx \quad (A.1)
\]

Here \( \frac{dI}{dx} \) is the change in intensity of the light \( (I) \) in a displacement \( dx \) through the absorbing medium, \( h \) is Planck’s constant, \( \tilde{\nu}_{qp} \) is the frequency of the absorbed light, \( N_q \) the density of the particles in the state \( J = q \), \( P(\tilde{\nu} - \tilde{\nu}_{qp}) \) is the absorption line profile, \( c \) the speed of light, and \( B_{qp} \) the absorption coefficient for absorption from state \( J = q \) to \( J = p \), which is given by:

\[
B_{qp} = \frac{c^3}{8\pi h \tilde{\nu}_{qp}^3} A_{qp} \quad (A.2)
\]

If the absorbing medium is considered homogeneous \((N \text{ and } A_{qp} \text{ constant})\) of length \( L \) and the effect of the apparatus line profile is neglected, the solution of this differential equation is given by:

\[
\ln \frac{I}{I_0} = \frac{-\hbar \tilde{\nu}_{qp}}{c B_{qp} N_q} P(\tilde{\nu} - \tilde{\nu}_{qp}) L = \frac{-c^2 L}{8\pi \tilde{\nu}_{qp}^2} A_{qp} N_q P(\tilde{\nu} - \tilde{\nu}_{qp}) = -\alpha P(\tilde{\nu} - \tilde{\nu}_{qp}) \quad (A.3)
\]

and thus the transmission \( T_r \) becomes:

\[
T_r = \frac{I}{I_0} = \exp[-\alpha P(\tilde{\nu} - \tilde{\nu}_{qp})] \approx 1 - \alpha P(\tilde{\nu} - \tilde{\nu}_{qp}) + \frac{\alpha^2}{2!} P^2(\tilde{\nu} - \tilde{\nu}_{qp}) - \ldots
\]

\[
= 1 + \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{n!} P^n(\tilde{\nu} - \tilde{\nu}_{qp}) \quad (A.4)
\]

When the absorption is being measured, the measured absorption line will be a convolution of the absorption line profile and the apparatus profile. In the case of the Fourier transform infrared spectrometer the apparatus profile width \((\Delta \nu_a)\) is much broader than the absorption line width \((\Delta \nu_l)\). Therefore, individual absorption lines that are close together (within the apparatus profile width) in the spectrum will not be resolved. From the convolution theory it can be derived that the convolution of multiple absorption lines is equal to the sum of the convolutions of the individual absorption lines. The absorption given by \( A = -\log(T_r) \) thus becomes a function of the absorption line profile \( P(\tilde{\nu} - \tilde{\nu}_{qp}) \) and apparatus profile \( W(\tilde{\nu} - \tilde{\nu}^*) \):

\[
A = -\log \left[ 1 + \sum_{J} \int_{0}^{\infty} \left( \frac{I}{I_0} - 1 \right) W(\tilde{\nu} - \tilde{\nu}^*) d\tilde{\nu} \right] = -\log \left[ 1 + \sum_{J} \int_{0}^{\infty} \left( \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{n!} P^n(\tilde{\nu} - \tilde{\nu}_{qp}) \cdot W(\tilde{\nu} - \tilde{\nu}^*) d\tilde{\nu} \right) \right]
\]

\* The exponential is here approximated by its Taylor polynomial to get a manageable expression. However, this expression may also be solved numerically to give a more accurate approximation.
\[ A = -\log \left[ 1 + \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{n!} \left( \frac{1}{\sqrt{\pi} \Delta v_a} \right) \left( \frac{\delta}{\Delta v_a} \right) \exp \left[ \frac{-(\tilde{\nu} - \tilde{\nu}_{qp})^2}{\Delta v_a^2} \right] \right] \]
\[ A \approx -\log \left[ 1 + \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{n!} \frac{1}{\pi^2} \frac{1}{\Delta v_i} \frac{1}{q\sqrt{n}} \exp \left( -\frac{(\bar{\nu} - \bar{\nu}_{qp})^2}{\Delta v_i^2} \right) \right] \]

\[ = -\log \left[ 1 + \sum_{n=1}^{\infty} \frac{1}{q} \exp \left( -\frac{(\bar{\nu} - \bar{\nu}_{qp})^2}{\Delta v_i^2} \right) \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{n!} \frac{1}{\pi^2} \frac{1}{\Delta v_i^2} \right] \tag{A.8} \]

Which finally results in a measured absorption which is given by

\[ A_{\text{meas}} = -\log \left[ 1 + \sum_{n=1}^{\infty} \frac{\Delta v_i}{\Delta v_a} \exp \left( -\frac{(\bar{\nu} - \bar{\nu}_{qp})^2}{\Delta v_i^2} \right) \sum_{n=1}^{\infty} \frac{1}{n!\sqrt{n}} \left( -\frac{\alpha}{\Delta v_i \sqrt{\pi}} \right)^n \right] \tag{A.9} \]

with

\[ \alpha = \frac{c^2}{8\pi \bar{\nu}_{qp}^2} \frac{A_{qp}}{N_q \lambda} \]  

\[ \tag{A.10} \]
Chapter 3

Plasma Characterization

3.1 Introduction
In our endeavor to describe the correlation between the plasma chemistry and the film deposition we will first embark on the plasma characterization. The various types of plasmas that have been used (i.e. argon-hydrocarbon, argon-nitrogen, argon-nitrogen-hydrocarbon plasmas and argon-nitrogen plasmas expanding through a graphite nozzle) will be described. Although each of these plasmas has its own characteristics, it is possible to make a meaningful comparison between them due to the fact that their flow patterns show large similarity and that the characteristic times of the important processes, e.g. transport, chemistry etc., are alike. In section 3.2 the argon-acetylene and argon-methane plasmas will be dealt with. These hydrocarbon plasmas, and the argon-acetylene plasma in particular, have been extensively studied in our group [1,2,3,4] and may serve as a steppingstone to describe the dissociation mechanism and polymerization processes in the other plasmas. In section 3.3 the influence of nitrogen addition to the argon plasma will be discussed and the importance of wall-produced molecular nitrogen to the chemistry will be demonstrated. In this section we will often refer to a recent comprehensive study by Brussaard [5] on cascaded arc generated argon-nitrogen and nitrogen plasmas, under slightly different operating conditions than in our case though. A plasma that has not been investigated in our group before is the argon-nitrogen-acetylene plasma. It will be presented in section 3.3 and will be compared to the argon-nitrogen and argon-acetylene plasmas. The last section of this chapter deals with hydrogen-free carbon plasmas. By the use of a graphite nozzle through which an argon-nitrogen plasma expands, hydrogen-free carbon can be introduced into the plasma. The process of radical formation in the nozzle and the downstream plasma chemistry will be investigated in section 3.4. The knowledge gained in this chapter of the different plasma chemistries lays the foundation for the discussion on the plasma-induced etching and deposition which will be presented in the following two chapters.
3.2 Argon - Hydrocarbon Plasmas

3.2.1 Introduction

Hydrogenated amorphous carbon (a-C:H), diamondlike carbon (DLC) and artificial diamond are well known for their favorable properties like high hardness, chemical inertness and infrared transparency [6,7]. These properties make the material very suitable for use as a protective coating on optical devices, e.g. bar-code laser scanners and flat panel displays, and as a wear resistant coating. For the deposition different plasma-enhanced CVD techniques have been successfully applied in the past.

For industrial applications however, high growth rates are desirable. It was shown in previous work by Gielen et al. that with an expanding thermal argon plasma into which acetylene (C₂H₂) is injected downstream, a-C:H films can be deposited at rates as high as 70 nm s⁻¹ [8]. This is about 100 times faster than the deposition rates reported for most other deposition techniques. Moreover, it was demonstrated that the quality in terms of hardness and infrared refractive index increases with increasing growth rate [8] and that additional ion bombardment is not required. The maximum hardness obtained is approximately 14 GPa [8].

Although it has long been believed that atomic hydrogen plays a crucial role in the quality of the film, recently it was shown that high-quality, smooth (nanocrystalline) diamond films can be deposited from hydrogen-poor or even hydrogen-free plasmas [9]. This raises the question which species are responsible for the film growth and/or quality of the film. For the growth precursors several candidates have been suggested: the methyl radical (CH₃) [10,11], acetylene (C₂H₂) [12,13], both methyl and acetylene [14], CₓHₓ radicals [8,15,16,17], CₓHₓ radicals [17], the CH₂ radical [15,18,19], the C₂ radical [15,18,19], the carbon dimer C₂ [9,20] and the C atom [21,22,23].

To determine which of these species is the most dominant growth precursor not only the particle fluxes towards the substrate, but also the sticking probabilities of the particular species have to be known. The partial fluxes of radicals are often more than an order of magnitude smaller than the partial fluxes of the neutrals. However, the sticking probabilities of radicals are usually at least an order of magnitude larger than the sticking probabilities of neutrals [23]. Moreover, during deposition the sticking probabilities of the radicals may increase drastically due to ion bombardment or the hydrogen-induced etching [26,27]. The sticking probabilities reported for the various radicals are listed in Table 3.1.

In a recent experiment in which the influence of ion bombardment could be excluded the measured surface reaction probability of a methane electron-cyclotron resonance

<table>
<thead>
<tr>
<th>Radical</th>
<th>Sticking probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H</td>
<td>0.13 [23] – 0.65 [28]</td>
</tr>
<tr>
<td>CH₃</td>
<td>0.001 [24] – 0.01 [26]</td>
</tr>
<tr>
<td>CH₂</td>
<td>0.028 [24,25]</td>
</tr>
<tr>
<td>C</td>
<td>0.27 [23]</td>
</tr>
</tbody>
</table>

Table 3.1: The sticking probabilities reported for the various hydrocarbon radicals. The values are either computed for an activated (single dangling bond) diamond (111) terrace at 1250 K [23], either obtained from the temporal density decay during the postdischarge [24-26], either measured directly in the discharge with the help of a cavity [28].
(ECR) plasma led to the conclusion that the CH$_3$ radical is not the dominant growth precursor in the methane discharge [28]. From the comparison with the surface reaction probability obtained in the acetylene discharge it was suggested that the C$_2$H radical is the main growth precursor both in an acetylene and a methane plasma [28]. This would mean that in the case of a methane plasma the deposition process is mainly governed by the polymerization and radicalization rate.

For a good understanding of the relation between the plasma parameters and the film quality therefore a good knowledge of the dissociation (products) is essential. In earlier studies it was argued that the dissociation of acetylene in the expanding thermal plasma is ion-induced since the electron temperature in the expansion is too low (< 0.3 eV) for significant electron-induced dissociation or ionization [8]. Note that this is a main difference with most other plasma deposition techniques in which the dissociation of the precursor gases is by electron impact. Dissociation of the precursor gas may proceed via several fragmentation channels all leading to different products. The branching ratio between these dissociation channels determines the relative abundances of the various products and thereby the plasma chemistry and film quality. Unfortunately, the branching ratios are not always known.

Radicals formed in the dissociation may either react (both in the gas phase and at the wall) or stick to the wall and contribute to deposition. The chance that a radical in contact with the film surface sticks to it is called the sticking probability and it differs from radical to radical. When the sticking probability of a radical is low, the radical will dwell in the vessel for a longer time and thus the chance that it will react in the gas phase will relatively increase. So to understand what the steady-state composition of the mixture in the reactor will be, we have to compare the typical loss-time of a radical with the so-called residence time, the time needed to pump the total vessel volume (typically 0.4 s). The typical loss-time of a radical is given by the reaction loss rate, determined by the reaction rates and the densities of species involved, and wall loss rates, determined by the radical density, the time needed to reach the wall by diffusion (typically 0.01 s) and the sticking probability. Another characteristic time is the transport time within the plasma beam (typically 0.001 s) which is dictated by the drift velocity and the distance between the arc and the substrate.

To find out more about the role of the radical’s reaction and sticking probabilities, the chemistry of expanding argon plasmas into which either methane (CH$_4$) or acetylene (C$_2$H$_2$) is injected are compared. The expanding thermal plasma is very appropriate for this purpose because it assures a high radicalization rate and allows for separate control of the plasma source, transport and deposition parameters [8]. In the two hydrocarbon plasmas different radicals are formed leading to distinct plasma chemistry. The film growth depends not only on the plasma chemistry, but also on the fluxes arriving at the substrate. In order to establish a connection between the plasma chemistry and the deposition process we therefore need knowledge of the flow behavior too. We make use of two simple models to describe the plasma chemistry and deposition for the case the plasma chemistry is restricted to the plasma beam only and for the case the plasma beam has interaction with the background gas. Combination of the model predictions and measurements of the growth rate gives insight into which radicals are the dominant growth precursors in the two remote hydrocarbon plasmas and into the type of radical flow (i.e. beam-like or isotropic) that should be considered for the deposition.
### 3.2.2 Experimental

The expanding thermal plasma deposition set-up has been extensively described in section 2.2 and reference [8]. For the experiments presented in this section an expanding argon plasma is used into which either methane (CH₄) or acetylene (C₂H₂) is injected by means of the injection ring. The typical settings used for the experiments are given in Table 3.2. The plasma is characterized by means of mass spectrometry, Fourier transform infrared gas phase absorption spectroscopy (FTIRAS) and Langmuir probe. The Langmuir probe measurements are performed in a pure argon plasma at approximately 30 cm from the arc exit. The probe can be moved in radial direction to obtain radial profiles of the ion flux passing the plasma beam area. The probe characteristic is analyzed using conventional methods [29]. The film deposition is monitored in situ by an ellipsometer (632.8 nm). Details on these diagnostics may be found in Chapter 2.

From the mass spectrometer data the consumption of the precursor gas can be calculated. The depletion \( D \) of the precursor gas is defined as

\[
D = 1 - \frac{I_{\text{on, deconv.}}}{I_{\text{off, deconv.}}}
\]

with \( I_{\text{on, deconv.}} \) and \( I_{\text{off, deconv.}} \) the contribution of the precursor gas, obtained after deconvolution of the total signal, in plasma on, respectively plasma off situation.

Because the precursor injection is supersonic and the residence time of the gas (~0.4 s) is much longer than the diffusion time from wall to wall (~0.01 s), both in the plasma off and plasma on situation the reactor is expected to be fully mixed. In this case the depletion as defined in equation (3.2.1) is a good measure for the precursor consumption.

The depletion \( D \) measured in this way is of course a measure for the dissociation of the precursor gas. But it also includes possible regeneration of the precursor gas from the dissociation products or species formed from these. Therefore, the depletion will also depend on the loss of the radicals formed in the dissociation. When these radicals have a large sticking probability they will be quickly removed from the gas phase where they might contribute to regeneration of the precursor gas. In this case the measured depletion will reflect more closely the efficiency of the dissociation process. When on the other hand the radicals formed during the dissociation have a small sticking probability they may be lost to the pump or contribute to regeneration of the gas, and the measured depletion will be smaller than one would expect on basis of the dissociation efficiency.

### 3.2.3 Argon ion-induced dissociation

In earlier studies it was argued that the dissociation of acetylene in the expanding thermal plasma is ion-induced, since the electron temperature in the expansion is too

| \( \Phi_{\text{Ar}} \) | 100 sccs |
| \( I_{\text{arc}}, V_{\text{arc}} \) | 20 – 90 A, 50 – 80 V |
| \( \Phi_{\text{CH}_4}, \Phi_{\text{C}_2\text{H}_2} \) | 0 – 50 sccs, 0 – 20 sccs |
| \( T_{\text{substrate}}, p_{\text{vessel}}, d_{\text{arc-substrate}} \) | 50 °C, 25 – 35 Pa, 60 cm |

Table 3.2: Typical settings used for the experiments: Ar flow (\( \Phi_{\text{Ar}} \)), arc current and voltage (\( I_{\text{arc}}, V_{\text{arc}} \)), \( \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \) flow (\( \Phi_{\text{CH}_4}, \Phi_{\text{C}_2\text{H}_2} \)), substrate temperature (\( T_{\text{substrate}} \)), vessel pressure (\( p_{\text{vessel}} \)) and arc to substrate distance (\( d_{\text{arc-substrate}} \)).
low (< 0.3 eV) for significant electron-induced dissociation or ionization (at equal ion and electron density) [8]. The proposed dissociation mechanism consists of a charge exchange reaction of an argon ion with an acetylene molecule directly followed by the dissociative recombination of the (rovibrationally excited) acetylene ion with an electron, i.e.:

\[
\text{Ar}^+ + \text{C}_2\text{H}_2 \rightarrow \text{Ar} + \text{C}_2\text{H}_2^{+,r,v} \quad k \approx 10^{-16} \text{ m}^3\cdot\text{s}^{-1} \quad [30] \quad (R1a)
\]

\[
\text{C}_2\text{H}_2^{+,r,v} + e \rightarrow \text{C}_2\text{H}^* + \text{H}^* \quad k \approx 3 \cdot 10^{-13} \text{ m}^3\cdot\text{s}^{-1} \quad [31] \quad (R1b)
\]

Of the various dissociation channels the one shown was argued to be the most probable at an electron energy of \( \approx 0.3 \) eV [8]. This idea is also supported by results from particle flow rate and arc current studies [32], cavity ringdown spectroscopy and optical emission spectroscopy measurements [33] and measurements by Derkatch et al. [34]. For methane the dissociation may be explained in a similar way, i.e.

\[
\text{Ar}^+ + \text{CH}_4 \rightarrow \text{Ar} + \text{CH}_4^{+,r,v} \quad k \approx 10^{-16} \text{ m}^3\cdot\text{s}^{-1} \quad [35] \quad (R2a)
\]

\[
\text{Ar}^+ + \text{CH}_3 \rightarrow \text{Ar} + \text{CH}_3^{+,r,v} \quad k \approx 10^{-15} \text{ m}^3\cdot\text{s}^{-1} \quad [35] \quad (R2b)
\]

The possible dissociation products in reaction (R2b) are C and H atoms, CH\(_x\) (\( x = 1, 2, 3 \)) radicals and H\(_2\) molecules. Since in the charge exchange reaction most (\( \pm 70\% \)) of the CH\(_4\) is transformed into CH\(_3^+\), the CH\(_2\) and CH radicals are expected to be the dominant species in the plasma. As long as the electron density \( n_e \) is high compared to the density \( n_{\text{CH}_4} \) of the injected hydrocarbon precursors (\( n_e/n_{\text{CH}_4} > 10^{-16}/10^{-13} \)) the dissociative recombination reactions (R1b) and (R2b) are much faster than the charge exchange reactions (R1a) and (R2a), and the dissociation rates will be determined by the reaction rates for the charge exchange reactions. In our argon plasma \( n_e \) is typically \( 10^{18} \) – \( 10^{20} \) m\(^{-3}\) and the precursor density \( 10^{19} \) – \( 10^{21} \), which means that the rate-limiting process will indeed be the charge exchange reaction. When the argon ions are in excess, secondary dissociation of the CH\(_x\) radicals may occur, leading to CH\(_y\) radicals with \( y < x \).

As can be seen in Figure 3.1, where the depletion is shown for methane and acetylene plasmas as function of the injected precursor flow for different arc currents, the depletion increases with decreasing precursor flow and increasing arc current (higher

![Figure 3.1: The methane (left) and acetylene (right) depletion as function of injected precursor flow at different arc currents (▼ 24.6 A, ■ 37.5 A, ▲ 57.1 A, ● 89.3 A, \( \Phi_{\text{Ar}} = 100 \) sccs) as measured by RGA. Solid lines are fits to equation 3.2.8.](image-url)
ion and electron flow). This behavior can be perfectly understood in the picture of ion-induced dissociation. In this picture a higher ion and electron flow results in a higher reactivity of the plasma. Furthermore, because of the remote character of the plasma, at higher precursor seeding more ions will be consumed and the reactivity will diminish.

When we assume that ion-induced dissociation is the only process contributing to the consumption of the precursor gas, and that the dissociation products are not lost to the pump, the consumption rate \( C \) of the molecules can be written as:

\[
C = \int_0^r \int_0^L n_{\text{ion}}(r,z) \cdot n_{\text{mol}}(r,z) \cdot k \cdot 2\pi r dr dz,
\]

with \( n_{\text{ion}}(r,z) \) the ion density, \( n_{\text{mol}}(r,z) \) the molecular density, \( k \) the reaction rate of the dissociation process, and \( r \) and \( z \) the coordinates in radial and axial direction respectively. The model used for the fits presented in Figure 3.1 as solid lines is a 1-dimensional simplification of equation (3.2.2), assuming a cylindrical reaction volume (length \( L \), radius \( R \)) with uniform axial velocity \( v_z \) (\( v_r = 0 \)) and temperature, and densities \( n_{\text{ion}}(r,z) \) and \( n_{\text{mol}}(r,z) \) depending on axial position \( z \) only (see Figure 3.2). It is furthermore assumed that the charge exchange and subsequent dissociative recombination reaction (R1a) and (R1b) is the only loss process for the precursor gas and argon ions. With these assumptions the consumption rate \( C \) can be written as a differential equation at axial position \( z \):

\[
\frac{\partial}{\partial z} n_{\text{mol}}(z) = -\frac{k}{v_z} \cdot n_{\text{mol}}(z) \cdot n_{\text{ion}}(z)
\]

(3.2.3)

Because we assume that both molecules and ions have the same constant beam area \( A \) and forward velocity \( v_z \), and that the gases in the cylindrical reaction volume are homogeneously distributed, the particle flow rate \( \Phi \) can be related to the density \( n \) by the relation:

\[
\Phi \text{ (in number of particles per second)} = n \cdot v_z \cdot A.
\]

(3.2.4)

With this definition equation (3.2.3) can be transformed to:

\[
\frac{\partial}{\partial z} \Phi_{\text{mol}}(z) = -\frac{k}{A \cdot v_z^2} \cdot \Phi_{\text{mol}}(z) \cdot \Phi_{\text{ion}}(z) = -k_\Phi \cdot \Phi_{\text{mol}}(z) \cdot \Phi_{\text{ion}}(z)
\]

(3.2.5)

Which relates the flow reaction probability \( k_\Phi \) to the overall dissociation, i.e. charge exchange, reaction rate \( k \) by:

\[
k_\Phi = \frac{k}{A \cdot v_z^2}
\]

(3.2.6)

The position-dependent solution of equation (3.2.5), which with our assumptions can easily be converted to a time-dependent solution, is expressed in the initial particle flow rates of argon ions \( \Phi_{\text{ion}}(z_0) \) and precursor gas \( \Phi_{\text{mol}}(z_0) \) at the injection point \( z_0 \) [37]∗:

```
* For \( \Phi_{\text{ion}}(z_0) = \Phi_{\text{mol}}(z_0) \) the solution for \( \Phi_{\text{mol}}(z) \) will be \( 1/(k_\Phi z) \).
```
For the depletion $D$, as defined in equation (3.2.1), we then find:

$$D = \frac{\exp((\Phi_{\text{ion}}(z_0) - \Phi_{\text{mol}}(z_0)) \cdot k_\Phi z) - 1}{\exp((\Phi_{\text{ion}}(z_0) - \Phi_{\text{mol}}(z_0)) \cdot k_\Phi z) - \frac{\Phi_{\text{mol}}(z_0)}{\Phi_{\text{ion}}(z_0)}}$$

(3.2.8)

In Figure 3.1 the solid lines represent the fits to the measured depletion of the precursor gas following from equation (3.2.8). The measurement at 89.3 A was fitted using equation (3.2.8), varying $k_\Phi$ and $\Phi_{\text{ion}}(z_0)$. For the other arc current settings only $\Phi_{\text{ion}}(z_0)$ was varied while keeping $k_\Phi$ fixed at the value found at $I_{\text{arc}} = 89.3$ A. The value obtained for $k_\Phi$ is related to the dissociation rate $k$ via the relation given in equation (3.2.6). When we take typical values for the axial velocity of 1000 m·s$^{-1}$ [38], axial position of $z = 0.65$ m (the approximate position of the substrate and

\[†\] In a recent study [41] the drift velocity of argon plasmas (with 5% nitrogen added downstream) was measured to be 300-600 m·s$^{-1}$ depending on the distance from the nozzle and the operating conditions (arc current and background pressure). Since in our case much higher argon flows are used (100 sccs instead of 1 slm) a velocity of 1000 m·s$^{-1}$ seems a reasonable estimate, especially close to the injection point, where most of the chemistry is taking place.
RGA) and a (constant) plasma beam radius of 0.1 m the corresponding rates found for acetylene and methane injection are \(4.3 \times 10^{-16} \text{ m}^3 \cdot \text{s}^{-1}\) and \(3.9 \times 10^{-16} \text{ m}^3 \cdot \text{s}^{-1}\) respectively. The value of \(k\) for acetylene injection is in good agreement with the typical values (\(\approx 10^{-16} \text{ m}^3 \cdot \text{s}^{-1}\) [30]) reported for the charge exchange reaction (R1a) of \(\text{Ar}^+\) and \(\text{C}_2\text{H}_2\) suggesting that the plasma chemistry is indeed dominated by this reaction. For methane injection the rate obtained for the charge exchange reaction is about a factor two smaller than reported values [35].

The expanding thermal plasma is a remote plasma which means that the downstream region is decoupled from the arc source due to the large pressure difference of approximately \(10^4\) Pa [39]. Therefore, the chemical reactivity emanating from the arc can be characterized by measuring the ion flow rate in a pure argon plasma, i.e. without precursor injection. Figure 3.3 shows the ion fluence (expressed in equivalent ion flow rate) as function of the arc current at 30 cm from the arc exit. It was determined from the radially integrated ion density profile measured with a Langmuir probe assuming a directed velocity of approximately \(1000 \text{ m} \cdot \text{s}^{-1}\) for the ions [38]. As can be seen, at 50 A about 10% of the total injected argon particle flow rate is ionized, which is in good agreement with arc modeling [40].

In Figure 3.3 also the results for \(\Phi_{\text{ion}}(z_0)\) obtained from the fits of equation (3.2.8) are shown for acetylene and methane injection. The good agreement found in the case of acetylene injection strongly suggests that the proposed acetylene consumption mechanism is a one-to-one reaction, i.e. each argon ion (plus electron) consumes exactly one acetylene molecule and vice versa. This result is corroborated by recent measurements of Engeln et al. [41] which show that the part of argon ions that is involved in a successive charge exchange reaction with the dissociation products is at maximum 5%. In the case of methane injection a more complicated chemistry has to be considered as was already hinted at by the discrepancy between the dissociation rate obtained from the fits and from literature.

**Figure 3.3:** The ion particle flow emanating from the arc as function of the arc current as obtained from Langmuir probe measurements in a pure argon plasma (□) and from modeling the mass spectrometry results for \(\text{C}_2\text{H}_2\) (▲) and \(\text{CH}_4\) (●) injection. Plasma settings: \(\Phi_{\text{Ar}} = 100 \text{ sccs}, p = 25 \text{ Pa}\).
Because in the case of acetylene injection the measured depletion and ion density are in accordance with the simple 'plug-down' model, i.e. equation (3.2.8), the depleted amount of C$_2$H$_2$ may be directly related to the deposition rate. The growth rate depends of course on the incoming flux, but also on the mass of the growth species, the mass density of the film and the sticking probability of the growth species. As discussed above, the good correspondence between the measured and calculated depletion points to a large sticking probability of the dissociation products in the Ar/C$_2$H$_2$ plasma.

For an acetylene plasma Gielen [32] determined the effective sticking probability of the C$_2$H radical‡ under the assumptions that the incoming flux of radicals is isotropic and that the dissociation degree is independent of the injected precursor flow. The latter assumption, which as the RGA measurements show (see Figure 3.1) is not entirely justified, led to an effective sticking probability which is independent of the acetylene flow, but dependent on the dissociation degree. Using the plug-down model fits to the RGA measurements (equation 3.2.8), the C$_2$H radical density at the substrate level can be calculated. The effective sticking probability that follows from this is depicted in Figure 3.4. The value is in good agreement with the value reported by Perry et al. [23] and with the values estimated by Gielen et al. for a dissociation degree between 40% and 80% [32], but it dissents from the value reported by Hopf et al. [28]. The high values found by Hopf et al. [28] for the effective sticking probability of the radicals in both a methane and an acetylene plasma (in the absence of ion bombardment), suggest that under their deposition conditions the dangling bond density at the surface is high, e.g. due to a small hydrogen density at the surface. When the dangling bond concentration is high, the effective sticking probability will

---

‡ Gielen assumed for his calculation of the effective sticking probability that the C$_2$H radical is the only dissociation product. Recent measurements [41] revealed that at low C$_2$H$_2$ flows and high arc currents a second dissociation step may take place leading to C and CH radicals with a different sticking probability. However, the contribution of these radicals to film growth was shown to be of minor importance.
approach the sticking probability of a radical on a dangling bond, which is assumed to be near one.

As can be seen in Figure 3.1, in the case of acetylene injection the ion-induced dissociation is so efficient that under certain conditions full depletion is reached. Since the rate of the charge exchange with argon ions is ten times higher for methane ($k_{\text{CH}_4} \approx 10^{-15} \text{ m}^3\text{s}^{-1}$ [35]) than for acetylene ($k_{\text{C}_2\text{H}_2} \approx 10^{-16} \text{ m}^3\text{s}^{-1}$ [30]) under equal conditions the methane dissociation is expected to be equally - or even more - efficient. However, in the case of an Ar/CH$_4$ plasma 100% depletion does not occur even under conditions of highest reactivity. This is a clear indication that the measured depletion is not purely reflecting the dissociation of methane.

An explanation could be that methane is regenerated from the dissociation products and/or that the molecular hydrogen formed in the methane dissociation quenches the argon ions. Note that the place where methane regeneration occurs, if so, is significant. Methane formed in the plasma beam may be dissociated again and thus contribute to film growth, but methane produced at the vessel wall will have to reenter the plasma beam first. The reason why quenching of argon ions by hydrogen molecules is thought to be much more important for methane injection is that hydrogen molecules may be formed directly in the methane dissociation ($\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2$) but not in acetylene. Furthermore, in the methane plasma a considerable amount of C$_2$H$_2$ is formed, as will be shown later. In this process also hydrogen molecules are produced.

Other explanations for the incomplete consumption of methane may be sought in its mass, which is almost two times smaller than the mass of acetylene. This smaller mass may result in a broader diffusion profile or in a less efficient (subsonic) injection into the plasma beam. A broader diffusion profile will lead to a smaller overlap with the plasma beam emanating from the arc and this will result in a smaller consumption as can be seen in equation (3.2.2).

The values obtained from the fits of the methane and acetylene depletion shown in Figure 3.1 also support the above-mentioned ideas. In both cases approximately the same $k_\Phi = k / v_z^2 \cdot \pi R^2$ is obtained. Since according to literature [30,35] the dissociation rate $k$ of CH$_4$ is ten times higher than that of C$_2$H$_2$, in the case of CH$_4$ injection either a larger radius $R$ of the reaction volume, regeneration of methane or quenching of argon ions has to be assumed. The approximately two times lower values of $\Phi_{\text{Ar}^+}(t_0)$ obtained for CH$_4$ injection suggest that the loss of argon ions is not by one charge exchange reaction only, but that the quenching by H$_2$ molecules or secondary reactions with the dissociation products contribute to additional loss of argon ions.

This is already an indication that the methane plasma chemistry is not as straightforward as the acetylene plasma chemistry. The difference in plasma chemistry is attributed to the nature of the radicals formed in the dissociation of the two hydrocarbons. This contrast is nicely expressed in the distinct polymerization occurring in both plasmas, and will be analyzed in the next section.

### 3.2.4 Polymerization in remote hydrocarbon plasmas

In Figure 3.5 the difference between the RGA signal in case the plasma is on ($I_{on}$) and in case the plasma is off ($I_{off}$), i.e. the net production in the plasma, is shown for both plasmas. The large peak around mass 40 is due to argon. It is clear that in both plasmas C$_m$H$_n$ polymers are formed with $m \geq 2$. Deconvolution of the mass spectra [42]
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reveals however that the contribution of the polymers is almost negligible in the case of an acetylene plasma (less than 4% of the injected precursor flow), whereas for a methane plasma up to 40% of the injected gas is transformed into polymers (cf. Figure 3.7). This is also confirmed by the FTIR gas phase measurements depicted in Figure 3.6.

The difference in polymerization rate may be explained by the difference in sticking probability of the radicals formed in the two plasmas. For acetylene it is established that the dominant product in the dissociative recombination reaction equation (R1b) is the C2H radical [8,34,41] which has a moderate to large sticking probability (cf. Table 3.1). In the methane plasma the dominant radical is expected to be the CH2 radical having a much smaller sticking probability than the C2H radical (see Table 3.1). Therefore, the lifetime of C2H radicals in the plasma will be much shorter compared to the lifetime of CH2 radicals leading to less polymerization.

We should be careful not to draw any quantitative conclusion from the spectra shown in Figure 3.5, since they were not deconvoluted nor corrected for the (weak) mass-dependency of the RGA. Qualitatively however, Figure 3.5 nicely demonstrates that the plasma polymerization is taking place mainly via reactions with the dominant radicals. In an acetylene plasma where the C2H radical is expected to be the main

Figure 3.5: The difference between the RGA signal for plasma on (I_{on}) and plasma off (I_{off}) (i.e. the net production of C_{m}H_{n} polymers) for a methane (left) and acetylene (right) plasma. I_{arc} = 89.3 A, \Phi_{CH4} = 34 sccs, \Phi_{C2H2} = 19 sccs.

Figure 3.6: Infrared spectra of CH4 (left) and C2H2 (right) in plasma off and plasma on situation. I_{arc} = 89.3 A, \Phi_{Ar} = 100 sccs, \Phi_{CH4} = 34 sccs, \Phi_{C2H2} = 17 sccs. The baseline has been shifted for the sake of clarity.
building block in the polymerization process preferentially $C_{2m}H_n$ polymers are formed, whereas in a methane plasma the abundance of $C_nH_m$ polymers gradually decreases with increasing $m$, as would be expected for addition reactions with $CH_x$ radicals. Moreover, the distribution of $C_mH_n$ polymers formed within one ‘m band’ shows that in the case of methane the polymers are more hydrogen-rich, i.e. extending to higher mass numbers, than in the case of acetylene. In the case of acetylene the $m=4$ and $m=6$ bands point to the dominant production of $C_4H_2$ and $C_6H_2$ respectively. Measurements of Doyle [17] affirm the production of $C_4H_2$ and $C_6H_2$ in $C_2H_2$ plasmas. The relative production of $C_mH_n$ polymers in the methane plasma is depicted in Figure 3.7. As can be seen, an important part of the consumed precursor gas is used for the production of polymers and radicals. Dagel et al. [16] observed that in a methane radio-frequency glow discharge $C_2H_2$ is produced from subsequent reactions of the discharge-produced $C_2H_4$ and $C_2H_6$. In our plasma it seems that first $C_2H_2$ is produced and only at higher methane seedings $C_2H_4$ and $C_2H_6$ are formed. Acetylene ($C_2H_2$) and ethene ($C_2H_4$) may be formed directly in the gas phase from $CH_x$ radicals and/or methane [16,19]:

$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2 \quad k \approx 5.3 \times 10^{-17} \text{ m}^3\text{s}^{-1} [19]$$

$$CH_2 + CH_3 \rightarrow C_2H_4 + H \quad k \approx 7.0 \times 10^{-17} \text{ m}^3\text{s}^{-1} [16] \quad (3.2.9)$$

$$CH + CH_4 \rightarrow C_2H_4 + H \quad k \approx 5.4 \times 10^{-17} \text{ m}^3\text{s}^{-1} [16]$$

Ethane ($C_2H_6$) however, can only be formed in a highly improbable three-body volume reaction or alternatively at the vessel wall covered with $H$ and/or $CH_3$:

$$CH_3 + CH_3 + M / \text{wall} \rightarrow C_2H_6 + M / \text{wall} \quad (3.2.10)$$

Let us now see if we can correlate the growth rate with the measured depletion of acetylene and methane. When the loss probability of the radicals formed is large, their lifetime will be shorter than the residence time and hence the effective carbon deposition flow can be obtained by subtracting the contribution to polymer formation from the consumed precursor flow. When however their loss probability is so small that their lifetime becomes comparable to the residence time, the effective carbon deposition flow will also depend on the part of the radicals which is pumped away.
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For acetylene the polymerization is negligible and the sticking probability of the C\textsubscript{2}H\textsubscript{2} radical is large so the consumed carbon flow (two times the amount of consumed C\textsubscript{2}H\textsubscript{2}) is simply the carbon flow that is available for deposition. For methane an important part of the consumed gas is used for the formation of polymers. Moreover, the sticking probability of the CH\textsubscript{x} radicals is small. So the actual carbon flow that is available for deposition should be corrected for both the production of C\textsubscript{m}H\textsubscript{n} polymers and the loss of CH\textsubscript{x} radicals to the pump. However, the part of the CH\textsubscript{x} radicals that is not transformed into either film or polymers, i.e. the part that is pumped away, is not known and probably depends on the plasma conditions.

In Figure 3.8 the effective carbon particle flow available for deposition (i.e. depletion - polymerization\textsuperscript{§}), is correlated with \textit{in situ} ellipsometry measurements of the growth rate. Actually, the effective carbon deposition flow should be compared to the deposition flux, i.e. the flux of radicals necessary to account for the observed growth rate. The deposition flux is related to the mass of the dominant radical in the deposition, the mass density of the film and the growth rate [4]. In the case of deposition from acetylene it was shown that the mass density $\rho$ depends linearly on the refractive index of the a-C:H films [4]. The refractive index on its turn depends on the growth rate [8]. From the relation between the growth rate and the refractive index [8] we deduce that the refractive index in the case of deposition from acetylene varies from 1.85 to 2.0 in the presented growth rate range. This means that by taking a constant refractive index, or -in other words- a constant mass density, a maximum error of 8 \% will be introduced in the calculated deposition flux. Hence, it is expected that the dependence of the growth rate on the precursor flow is not too much different from that of the deposition flux. Furthermore, since in the case of a methane plasma both the dominant growth precursor and the mass density of the films is not known, a calculation of the deposition flux is not possible. It should be noted here, that the refractive index of films deposited from methane plasmas is substantially lower than of films deposited from acetylene plasmas (cf. Figure 3.18 and reference [8]), indicating that the mass density of the films deposited from methane plasmas is lower. This may be explained by the fact that in a methane plasma much more hydrogen is available to be incorporated in the film than in an acetylene plasma.

\textsuperscript{§} Only the contribution of the C\textsubscript{2}H\textsubscript{n} polymers could be exactly quantified by calibration. Therefore the effective carbon particle flow is not corrected for the contribution of higher polymers (C\textsubscript{x}H\textsubscript{y}).

\textbf{Figure 3.8: Deposition rate and the effective carbon deposition flow (consumption corrected for polymerization) as function of injected precursor flow for an acetylene (left) and methane (right) plasma ($\Phi_{Ar} = 100$ sccs, $I_{arc}=57.1$ A).}
In the methane plasma the dominant growth precursors are thought to be the CH$_x$ radicals. Whether this assumption is true or that other radicals, formed in a second step from the CH$_x$ radicals, also contribute to growth will be discussed in the next section. Compared to the C$_2$H radical, which is presumed to be the dominant precursor in the acetylene plasma \[8\], the CH$_x$ radicals contain much more hydrogen per carbon atom. Moreover, in the dissociation of methane relatively more hydrogen is produced than in the acetylene dissociation.

As can be seen in Figure 3.8, in the case of acetylene the consumed carbon particle flow correlates nicely with the growth rate. This indicates that the loss probability of the C$_2$H radicals is large enough to assure that only a negligible part is not used for deposition. From the proportionality between the consumed carbon particle flow rate and the deposition rate an effective deposition area of approximately 0.3 m$^2$ can be deduced assuming an a-C:H density of 1.6 g·cm$^{-3}$ and a hydrogen content in the film of 40% \[8\]. This is about ten times the beam area suggesting that the largest fraction of the dissociation products ends up at other positions than the substrate. This may be attributed to the radial diffusion. Moreover, recent velocity measurements \[5\] and model calculations \[43\] show a stagnation zone in front of the substrate where the forward velocity becomes equal to the radial velocity. Another explanation could be that the effective sticking probability of the C$_2$H radical is (much) smaller than unity.

For methane, however, the non-proportionality between the consumed carbon particle flow and the deposition rate suggests that a considerable part of the CH$_x$ radicals is lost to other causes than deposition or formation of C$_2$H$_n$ polymers. The radicals might be lost to the pumps owing to their small loss probability, the formation of higher (C$_{x>2}$H$_n$) polymers for which the effective carbon deposition flow was not corrected (see footnote on page 50) and/or to deposition elsewhere. An increase of the effective deposition area with injected methane flow could also account for this non-proportionality. The effective deposition area in the case of methane injection is expected to be larger than in the case of acetylene injection due to the much smaller sticking probability of the radicals formed in the methane plasma compared to those formed in an acetylene plasma. In the next section we will take a closer look at the

Figure 3.9: Growth rate as function of injected methane flow for two different arc currents ($\Phi_{Ar} = 100$ sccs, ■ 89.3 A, ▲ 57.1 A).
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methane plasma chemistry and deposition with the help of two models in order to elucidate the discrepancy between the consumed flow and the deposition rate.

3.2.5 The Ar/CH₄ plasma chemistry and deposition models

In Figure 3.9 the growth rate as function of injected methane flow is shown again for two different arc currents. It is immediately clear from this figure that the growth can not be simply explained like in the acetylene plasma by the dissociation of the precursor gas and the deposition of the radicals formed. It seems that in the methane plasma, due to the much smaller sticking probability of the primary dissociation products, i.e. the CHₓ radicals, a more complicated plasma chemistry is involved. This leads to a growth rate which even decreases with injected precursor flow (57 A and 89 A at higher CH₄ flows). In the case of “simple” dissociation→deposition chemistry, the growth rate is found to increase with the injected precursor flow and finally to saturate (see Figure 3.8). This saturation effect is due to the limited supply of argon ions available for the dissociation of the precursor gas.

Moreover, recent cavity-ringdown spectroscopy measurements of the methyl (CH₃) density in an Ar/CH₄ plasma performed by Böcker et al. [44] on the same deposition set-up show saturation of the CH₃ density at higher methane flows (cf. Figure 3.10). It is evident from the measured CH₃ density that the CH₃ radical can not account for the decrease of growth rate with methane flow**. Hence, the CH₃ radical can not be the dominant –or only- growth precursor in our methane deposition plasma. Our findings are supported by measurements of Hopf et al. [28] which show that also in methane electron-cyclotron resonance (ECR) plasmas the influence of CH₃ radicals on the film growth is negligible. The other CHₓ radicals (i.e. CH₂, CH and C) however, may still

---

**Böcker et al. concluded that due to the extremely low sticking probability of the CH₃ radical (cf. Table 3.1) also on quantitative arguments the measured CH₃ density could not account for the observed growth rate [44].
be good candidates as growth precursor. As said before, the CH₂ and CH radicals are expected to be the dominant products in the dissociation of methane. Because the production of C₂H₂n polymers proceeds mainly via reactions between CHₓ radicals themselves and CHₓ radicals with CH₄, it is expected to find a correlation between the measured C₂H₂n density (Figure 3.7) and the CH₃ density (Figure 3.10). The comparison of both figures is shown in Figure 3.11. The figure reveals that indeed a relation exists between the CH₃ and C₂Hn density. Depending on the arc current (ion and electron flow), at a certain CH₄ flow the production of CH₃ stops while the growth of the C₂Hn density continues. At this point all ions have been consumed and the surplus of CH₄ molecules may get involved in the polymerization reactions. In order to understand the behavior of the growth rate in methane plasmas, we need to know what species is/are the dominant growth precursor(s) in the plasma and what the flow patterns are. Because of the large amount of polymers produced in the methane plasma, the possibility that radicals formed from these polymers in a second dissociation step are contributing to the film growth should also be considered. Therefore in Figure 3.12 the amount of C₂H₂ in the plasma, as measured by RGA, is compared to the growth rate. Note that the measured quantity of C₂H₂ reflects the produced amount of C₂H₂ minus the part that is possibly consumed in the deposition. The absolute amount of C₂H₂ does not show any correlation with the growth rate. The relative amount of C₂H₂ however, shows an almost linear dependence with the growth rate. This striking feature is not easily explained, but it is clear that the radicals responsible for growth are closely related to the relative amount of C₂H₂. If we think of the CHₓ radicals as the main growth precursors, this implies that the production of CHₓ radicals is a direct measure for the relative C₂H₂ production. Figure 3.11 indeed suggests a direct relation between the CH₃ radical density and the C₂H₂ production. However, as explained before, the CH₃ radical can not be the dominant growth radical, and thus for a good correlation with the growth rate we need to assume that another CHₓ radical, with a larger sticking probability, is also involved in the production of C₂H₂. If, on the other hand, we think of the C₂H as the dominant growth
precursor, the production of C\textsubscript{2}H via dissociation of C\textsubscript{2}H\textsubscript{2} in a second dissociation step should be directly linked with the relative amount of C\textsubscript{2}H\textsubscript{2}. In other words, either the production of CH\textsubscript{x} radicals or the destruction of C\textsubscript{2}H\textsubscript{2} is associated with the relative amount of C\textsubscript{2}H\textsubscript{2}. To get more insight into the methane deposition, we will have to rely on models of the plasma chemistry.

### Deposition models

Describing the methane plasma chemistry in detail is rather elaborate and cumbersome and is beyond the scope of this thesis. We will therefore focus on the question whether the observed trend of the growth rate can be explained by first-order or second-order radicals (i.e. radicals either formed directly in the dissociation of methane or in a second dissociation step). The abundance of second-order radicals (e.g. C\textsubscript{2}H) is expected to be smaller than of first-order radicals (e.g. CH\textsubscript{x}). However, the sticking probabilities of the former are at least an order of magnitude higher than the sticking probabilities of the latter (cf. Table 3.1).

For the acetylene plasma the plug-down model presented in section 3.2.3 appeared to describe the plasma chemistry and deposition satisfactorily in terms of first-order (i.e. C\textsubscript{2}H) radicals only. For the methane plasma chemistry it is however necessary, as pointed out above, to include both first-order and second-order radicals. To describe the methane plasma two models are used: a simple plug-down model, equal to the one used before for acetylene, and a self-consistent model which takes into account the influence of the background gas (see further on). In the models the following simplifications, similar to those used earlier for solving the consumption in the case of argon ion-induced dissociation, have been made:

- Only the part after the stationary shock\textsuperscript{††} (see section 2.2) where the particles have a subsonic speed \cite{45,46} is considered.

\textsuperscript{††} As already mentioned in section 2.2, the particles emanating from the arc into the low-pressure vessel will first be accelerated and reach a supersonic velocity. At a certain point in the vessel, depending on the vessel pressure and arc conditions, a stationary shock will occur, after which the particles continue their way at a subsonic speed. The precursor gas is injected in the subsonic part of the expansion, and will have no influence on the upstream supersonic part, as has been explained in section 2.2.
- A cylindrical reaction volume (length $L = 0.65$ m, radius $R = 0.10$ m) is assumed starting at the precursor injection point (at 5 cm from the arc) which is taken as axial position $z = 0$ (see Figure 3.2).
- The temperature is assumed to be constant ($T = 1000$ K) throughout the vessel.
- The species densities $n(r,z)$ are integrated over the radial coordinate $r$ and depend therefore on the axial position $z$ only.
- The drift velocity is assumed to be mainly axial and constant ($v_z = 1000$ m s$^{-1}$).
- Diffusion in the axial ($z$) direction is assumed to be negligible in comparison to the contribution of the drift.
- Radial diffusion of the radicals and ions to the walls, i.e. reaction volume boundaries, is accounted for by introduction of a typical diffusion time $\tau_{\text{diff}}$. The typical diffusion times listed in Table 3.3 (~10 ms) are calculated by taking into account the diffusion coefficient $D$, defined as [49]:

$$D = \frac{2}{3\sqrt{\pi}} \frac{1}{\sigma_0 p} \left(\frac{kT}{m}\right)^{3/2}.$$  \hspace{1cm} (2.11)

At a pressure $p$ of 25 Pa, a temperature $T$ of 1000 K and an approximate total collision cross section for momentum exchange $\sigma_0$ of $10^{-19}$ m$^2$, the diffusion coefficient for C$_2$H is 1.2 m$^2$ s$^{-1}$. With a beam radius $R$ of 0.1 m the diffusion time $\tau_{\text{diff}} (= R^2/D)$ is then calculated to be 8.3 ms. Because the temperature outside the plasma beam is much lower (typically around room temperature) the diffusion will be much slower in this region. In order to take into account the slow diffusion from the plasma periphery towards the walls a slightly longer diffusion time was taken for the modeling, i.e. 10 ms instead of the calculated 8.3 ms.
- To account for the fact that the species arriving at the wall, i.e. reaction volume boundary, have a certain loss probability, which determines how long they may dwell in the gas phase and participate in the chemistry, the sticking (or destruction) probability $P_{\text{loss}}$ is also included in the model. It is assumed that

<table>
<thead>
<tr>
<th>Constants</th>
<th>Chemistry</th>
<th>Species</th>
<th>$\tau_{\text{diff}}$ (s)</th>
<th>$P_{\text{loss}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylindrical reaction volume: $L = 0.65$ m, $R = 0.1$ m</td>
<td>$\text{Ar}^+ + \text{CH}_4 \rightarrow \text{Ar} + \text{CH}_x + a\text{H} + b\text{H}_2$&lt;br&gt;$k = 1.1\times10^{-15}$ m$^3$ s$^{-1}$ [35]</td>
<td>$\text{Ar}^+$</td>
<td>1.25 x 10$^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td>Axial drift velocity: $v_z = 1000$ m s$^{-1}$</td>
<td>$\text{CH}_x + \text{CH}_x \rightarrow \text{C}_2\text{H}_2\text{n} + a\text{H} + b\text{H}_2$&lt;br&gt;$k = 5.25\times10^{-17}$ m$^3$ s$^{-1}$ [19,47]</td>
<td>$\text{CH}_x$</td>
<td>7.85 x 10$^{-3}$</td>
<td>0.01</td>
</tr>
<tr>
<td>Temperature: $T = 1000$ K</td>
<td>$\text{CH}_x + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2\text{n} + a\text{H} + b\text{H}_2$&lt;br&gt;$k = 5\times10^{-17}$ m$^3$ s$^{-1}$ [16]</td>
<td>$\text{C}_2\text{H}$</td>
<td>1.0 x 10$^{-2}$</td>
<td>0.2</td>
</tr>
<tr>
<td>Residence time: $\tau_{\text{res}} = 0.4$ s</td>
<td>$\text{Ar}^+ + \text{C}_2\text{H}_2\text{n} \rightarrow \text{Ar} + \text{C}_2\text{H} + a\text{H} + b\text{H}_2$&lt;br&gt;$k = 1.1\times10^{-16}$ m$^3$ s$^{-1}$ [30]</td>
<td>$\text{CH}_4$</td>
<td>0.4 s ($\tau_{\text{res}}$)</td>
<td>0</td>
</tr>
<tr>
<td>$\text{CH}<em>4$ and $\text{Ar}^+ = f(I</em>{\text{arc}})$ particle flows at $z = 0$</td>
<td>$(\text{Ar}^+ + \text{H}_2 \rightarrow \ldots \rightarrow \text{Ar} + \text{H}^*)$&lt;br&gt;$k = 1.1\times10^{-15}$ m$^3$ s$^{-1}$ [48]</td>
<td>$\text{C}_2\text{H}_2\text{n}$</td>
<td>0.4 s ($\tau_{\text{res}}$)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$(\text{H}_2)$</td>
<td></td>
<td>2.75 x 10$^{-3}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.3: The various parameters used in the model to describe the Ar/CH$_4$ plasma.
neutrals and ions have a loss probability of 0 respectively 1. Therefore, the loss of neutrals is defined by the loss to the pump with the typical residence time $\tau_{\text{res}}$ (0.4 s for all species), and the loss of ions entirely by the diffusion time. For the radicals the averaged sticking probabilities, listed in Table 3.1, are taken.

- The vast number of all possible reactions between the radicals, neutrals and ions has been reduced to the four most dominant reactions. Since we are only interested in explaining the observed trend, we expect that these will suffice. All first and second-order radicals are represented by one species (respectively CH$_x$ and C$_2$H radicals) with ‘averaged’ chemistry. The reactions that are taken into account are listed in Table 3.3.

In Table 3.3 all the assumptions and parameters used in the models are summarized. With the simplifications mentioned above the problem becomes in fact 1-dimensional (in axial position $z$) leaving us with seven differential equations describing the production and destruction of each of the species involved (Ar$^+$, Ar, CH$_4$, CH$_x$, C$_2$H$_{2n}$, C$_2$H and H$_y$). These differential equations are solved numerically within the commercial software package Maple® using a fourth-fifth order Runge-Kutta method with the initial argon ion and methane particle flow as initial conditions.

The quasi one-dimensional modeling of the expanding plasma has been proven to be quite successful in the case of argon [38,46], argon/hydrogen [50] and, as has been shown in the former section, argon/acetylene plasmas.

The constant axial velocity $v_z$ used in the models determines to a great extent the chemistry. A lower $v_z$ will result in more chemistry and thus in a higher production and/or consumption of species. The species densities obtained at $z = 0.65$ m are treated as entries for the background gas composition which should be compared with the RGA data. Notice that in the models production or destruction of species is only taking place in the cylindrical reaction volume. Once a species is in the background it is considered to be non-reactive. This means that creation of species at the vessel walls or volume reactions in the background region are not considered. This is illustrated in Figure 3.13.

![Figure 3.13: Schematic representation of the simplifications used for the modeling. The chemistry is only taking place in the cylindrical reaction volume (plasma beam) and is 'feeding' the background gas.](image-url)
The difference between the plug-down model and the self-consistent model is that in the self-consistent model the effect of the chemistry in the beam on the background gas and vice versa is iteratively calculated. In the plug-down model the background composition is solely determined by the chemistry in the beam and the losses to the walls integrated over the reaction length $L$ (0.65 m in our model). The self-consistent model may therefore be considered as representing a fully-mixed reactor, and the plug-down model a reactor in which the background gas has no effect on the plasma beam. Of course the real situation is somewhere between these two models. Some species are most likely formed at the vessel walls, e.g. H$_2$ by association of H and C$_2$H$_6$ by recombination of CH$_3$ radicals. These species have no directed velocity, unlike the species in the plasma beam. The time needed to re-enter the plasma beam or to diffuse towards the substrate is on average much longer than the transport time of the species created in the beam (0.01 s compared to 0.001 s). In the plasma beam the typical mean free path is a few mm’s, so once a species enters into the beam it has a large probability to get involved in the plasma chemistry.

The models however, do not take into account surface chemistry. The background gas composition is thus entirely determined by the composition of the plasma beam at axial position $z = 0.65$ and the interaction of the background gas with the plasma beam. In the models the interaction of the plasma beam with the background is either completely neglected (in the plug-down model) or is determining the plasma beam composition completely (in the self-consistent model). A more accurate approach, which is recently being investigated in our group [40,43], consists in solving the Navier-Stokes equations (conservation of mass, momentum and energy) coupled with gas phase and surface chemistry in the vessel.

In Figure 3.14 and Figure 3.15 the predictions of both models are compared with the CH$_4$ and C$_2$H$_2$ densities in the background as measured with the RGA‡‡. We see that even with these very simple models it is possible to predict the background densities within a factor of two. The plug-down model seems to be a little more accurate, especially for predicting the precursor consumption.

‡‡ The RGA signal of the different species is obtained after deconvolution in scs (2.69×10$^{19}$ particles per second). To compare this particle flow rate to the densities predicted by the models the same flux area and velocity as in the models (i.e. π×0.01 m$^2$ and 1000 m s$^{-1}$) are used. A flux of 1 sccs corresponds in this picture to a density of 8.96×10$^{17}$ m$^{-3}$.
When we compare Figure 3.14 and Figure 3.15 it is clear that the predictions for the C$_2$H$_{2n}$ density are not as good as for the CH$_4$ density. There may be several explanations for this:

- Contrary to the assumption made in the model that all CH$_x$ radicals formed in the dissociation of CH$_4$ are contributing to the formation of C$_2$H$_{2n}$, in reality a certain –unknown- part of the CH$_x$ radicals may be fragmented even further in a second dissociation step. The model thus presents the upper limit of the C$_2$H$_{2n}$ production.

- The chemistry in which C$_2$H$_{2n}$ is only lost by interaction with argon ions may be over-simplified. Especially at higher methane flows reactions in which the C$_2$H$_{2n}$ polymers are transformed into higher order (C$_{x>2}$H$_y$) polymers become more important (cf. Figure 3.7). Including these reactions in the models will inevitably reduce the calculated values.

- For the sticking probability of the four CH$_x$ ($x = 0, 1, 2, 3$) radicals one value (0.01) was assumed in the models. However, the reported sticking probabilities for the CH$_2$ and C radicals, 0.028 [25] and 0.27 [23] respectively (see Table 3.1), indicate that the generalized sticking probability is a very crude approximation. As a consequence, the dwell time of the CH$_{x<3}$ radicals in the reaction volume and thereby their chemistry will be overestimated in the models, leading to a too high

![Figure 3.15:](image)

*Figure 3.15: The total C$_2$H$_n$ density measured with RGA (symbols) as function of injected methane flow for $I_{arc} = 57$ A (left) and $I_{arc} = 89$ A (right). The solid and dashed lines represent results of the self-consistent and plug-down model respectively.*

When we compare Figure 3.14 and Figure 3.15 it is clear that the predictions for the C$_2$H$_{2n}$ density are not as good as for the CH$_4$ density. There may be several explanations for this:

- Contrary to the assumption made in the model that all CH$_x$ radicals formed in the dissociation of CH$_4$ are contributing to the formation of C$_2$H$_{2n}$, in reality a certain –unknown- part of the CH$_x$ radicals may be fragmented even further in a second dissociation step. The model thus presents the upper limit of the C$_2$H$_{2n}$ production.

- The chemistry in which C$_2$H$_{2n}$ is only lost by interaction with argon ions may be over-simplified. Especially at higher methane flows reactions in which the C$_2$H$_{2n}$ polymers are transformed into higher order (C$_{x>2}$H$_y$) polymers become more important (cf. Figure 3.7). Including these reactions in the models will inevitably reduce the calculated values.

- For the sticking probability of the four CH$_x$ ($x = 0, 1, 2, 3$) radicals one value (0.01) was assumed in the models. However, the reported sticking probabilities for the CH$_2$ and C radicals, 0.028 [25] and 0.27 [23] respectively (see Table 3.1), indicate that the generalized sticking probability is a very crude approximation. As a consequence, the dwell time of the CH$_{x<3}$ radicals in the reaction volume and thereby their chemistry will be overestimated in the models, leading to a too high

![Figure 3.16:](image)

*Figure 3.16: The CH$_4$ (left) and C$_2$H$_2$ (right) densities as predicted by the plug-down model with and without H$_2$ quenching (dashed and solid lines respectively) at $I_{arc} = 89$ A.*
The quenching of argon ions by molecular hydrogen, i.e. $\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}$ followed by $\text{ArH}^+ + e \rightarrow \text{Ar} + \text{H}^*$ [48], was not considered in the models. The effect the quenching has on the model predictions is depicted in Figure 3.16 for the plug-down model. In this example it was assumed that the only dissociation products are CH$_2$ and H$_2$, i.e. that H$_2$ is directly available in the plasma beam. It can be seen that adding the hydrogen quenching reactions would indeed lead to a lower C$_2$H$_{2n}$ production.

After having ascertained that the models describe the plasma chemistry reasonably well, we can try to understand the peculiar dependence of the growth rate on the injected methane flow (see Figure 3.9). Since the plasma chemistry is far from complete to make a detailed pronouncement upon which radical is the dominant growth precursor, we will restrict ourselves to the question whether first-order, i.e. CH$_x$, or second-order, i.e. C$_2$H, radicals can explain the observed trend of the growth rate.

The CH$_x$ and C$_2$H radical densities obtained with the two models are presented in Figure 3.17 together with the growth rate. The densities are arbitrarily scaled only to

\[ \text{Figure 3.17: Measured growth rate (■) as function of injected methane flow for } I_{\text{arc}} = 57 \text{ A (left) and } I_{\text{arc}} = 89 \text{ A (right). The solid respectively dashed lines represent the arbitrarily scaled CH$_x$ respectively C$_2$H density from the self-consistent (top) and plug-down model (bottom).} \]

\[ \text{Notice that this assumption of 100% conversion of CH}_4 \text{ into H}_2 \text{ is a worst-case scenario. In reality a considerable part of the dissociation products will consist of H atoms. Only a part of the H}_2 \text{ formed from these H atoms by reassociation at the walls, may enter the plasma beam again.} \]
show the trends. As expected, in both models the C₂H production starts just after the production of CHₓ radicals begins. However, it is apparent that the two models predict distinct trends for the CHₓ and C₂H densities. In the plug-down model the decrease of the C₂H density is faster and sets in at a lower methane flow in comparison with the CHₓ density, whereas in the self-consistent model the opposite trend is predicted. This is explained by the fact that in the plug-down model the supply of argon ions and electrons for the dissociation of C₂H₂ will be limited, because first methane and ions + electrons need to be consumed before C₂H₂ and finally also C₂H radicals may be formed. In the self-consistent model the argon plasma penetrates into a background mixture of methane and acetylene. Because the dissociation rate used in the model for methane is higher than for acetylene, the production of CHₓ radicals from methane will decrease faster than the production of C₂H radicals.

We will discuss the quantitative implication of the predicted radical densities later. Looking to the trends in Figure 3.17 qualitatively, one can already conclude that in the plug-down model picture the C₂H radical can not be the one and only growth precursor. Also in the picture of the self-consistent model, the C₂H radical alone can not account for the trend over the complete range of precursor flows, although it seems to be a better candidate than the CHₓ radical, especially at higher precursor flows. The CHₓ radical densities predicted by the plug-down model seem to explain the observed behavior of the growth rate for both arc currents the best.

The predictions of the models can also be compared to the cavity-ringdown spectroscopy measurements of the CH₃ density shown in Figure 3.10. Although the trend is not the same, i.e. the CH₃ density saturates at higher methane flows while the model results for the CHₓ radical density show a maximum, the measured CH₃ density has the same order of magnitude as the model calculations. As discussed before, it is evident that the CH₃ radical can not be the dominant –or only- growth precursor in our methane deposition plasma. Therefore, if the picture is adapted that the CHₓ radicals are responsible for growth, the CH₂, CH and C radicals should also have an important contribution to the deposition. Especially since the CH₂ and CH radicals are expected to be the dominant products in the dissociation of methane.

Plasma beam deposition

Maybe it is good at this point to see whether the qualitative agreement with the models can also be quantified to some extent. The number density of the growth precursor can be directly related to the growth rate times the film density if the sticking probability and the deposition area are known. Since both parameters are not exactly known, we will consider two cases: ‘plasma beam deposition’ and ‘isotropic deposition’. The true deposition process is obviously a combination of the two extremes. In the early expansion the plasma still has its ‘directed beam’ characteristics, but as the plasma moves towards the substrate holder the beam either dies away in the background gas or stagnates in front of the substrate holder. This is also illustrated by measurements of the axial velocity, which decreases with increasing distance from the arc [5]. Thus, in the late expansion the ‘directed beam’ properties will be more or less lost.

Let us first consider the case in which the deposition area is equal to the plasma beam area \( A \) (radius 0.1 m) used in the models. Assuming a directed velocity \( v_z \) of 1000 m·s⁻¹ (also used in the models), the incoming flux \( \Gamma_{in} \) of the radicals is simply given by: \( \Gamma_{in} = n \cdot v_z \), with \( n \) the radical density. This flux should be compared to the flux \( \Gamma_{depo} \) needed to account for the deposition rate \( R \): \( \Gamma_{depo} = 6.0 \times 10^{20} \rho R/m \), with \( \rho \)
the film density in g cm$^{-3}$, $R$ the deposition rate in nm s$^{-1}$ and $m$ the mass in atomic mass units (amu) of the radicals ($m = 25, 15, 14$ and 13 amu for C$_2$H, CH$_3$, CH$_2$ and CH respectively). The effective sticking probability $S$ of a radical is defined as the ratio between the actual deposited particle flux and the incident particle flux:

$$S = \frac{\Gamma_{\text{depo}}}{\Gamma_{\text{in}}} = 6.0 \times 10^{17} \rho \cdot R / (n \cdot m)$$

(3.2.12)

It was shown by Gielen et al. [8] that for acetylene as precursor gas the film density $\rho$ depends linearly on the infrared refractive index from 1.1 to 1.7 g cm$^{-3}$. In Figure 3.18 the real and imaginary parts of the refractive index\footnote{In Figure 3.18 the refractive index at 632.8 nm is given and not the infrared refractive index. However, for a-C:H films it has been shown that both increase with increasing film density [8].} are shown for the films deposited at different methane particle flows. If we assume that in this case the film density has also a linear dependence on the refractive index, the maximum error introduced in the value of $S$ by taking a constant $\rho$ will be 15%. However, since the exact value of $\rho$ has not been determined, a much larger uncertainty is introduced by assuming a constant density of $1.4 \pm 0.3$ g cm$^{-3}$. Because in the models no distinction between the CH$_x$ radicals is made, the average mass (14 amu) of the three CH$_x$ radicals will be used for the calculation. In Figure 3.19 the results of these calculations are shown. We see in Figure 3.19 that for some settings the models predict sticking probabilities which are exceeding 1. It is obvious that the sticking probability can not exceed 1, otherwise the deposition flux would be larger than the incoming particle flux\footnote{Due to the uncertainty in the forward drift velocity (see section 3.2.3) the incoming particle flux could in reality be much smaller. This would lead to even larger values of the effective sticking probabilities of the radicals, which in the picture of the self-consistent model exceed unity by several orders of magnitude.}. We have chosen to display those “unphysical” points with effective sticking probability $>1$ anyway, in order to indicate where the radical densities predicted by the models are becoming insufficient to explain the growth rate. It seems that the CH$_x$ radical densities as predicted by the plug-down model can account for the growth rate both qualitatively (cf. Figure 3.17) and quantitatively. However, the relatively large effective sticking probability (see Table 3.1) suggests that either the incoming flux is consisting predominantly from CH$_2$, CH or C radicals or that the flux is underestimated in the calculations. As argued before, the CH$_2$ radical will be the dominant dissociation product. The sticking probabilities obtained

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Real ($n$) and imaginary ($k$) part of the refractive index ($n - i \cdot k$) of the films as function of injected methane particle flow at $I_{\text{arc}} = 57$ A (left) and 89 A (right).}
\end{figure}
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in the plug-down model are about 2-3 times larger than reported for the CH$_2$ radical (see Table 3.1). This may be accounted for by the contribution of the other dissociation products, i.e. the CH and C radicals, which have a larger sticking probability. When the ions are in excess, i.e. at small methane flows, the CH and C radicals may also be formed in a secondary dissociation reaction from the CH$_3$ and CH$_2$ radicals. This reaction is not included in the models, and hence the production of high-sticking radicals is underestimated. In the plug-down model picture the involvement of C$_2$H radicals in the deposition is out of the question, since the “sticking probability” exceeds 1 for all CH$_4$ flows. Moreover, the sticking probability depends on the CH$_4$ flow, which is illogical. In contrast, the sticking probability obtained for the CH$_x$ radicals remains fairly constant.

In the self-consistent model the C$_2$H production is larger than in the plug-down model, because not only the secondary dissociation of the C$_2$H$_2$ that is produced in the forward kinetics is taken into account, as is the case in the plug-down model, but also that of the recirculating C$_2$H$_2$. Therefore, the sticking probability obtained for the C$_2$H radical with the self-consistent model is smaller. In fact, at large methane flows the values indicate that the C$_3$H radicals can account for the growth rate. At small methane flows the C$_2$H$_2$ production will be small, and the use of a recirculation, i.e. self-consistent, model becomes questionable. The CH$_x$ densities predicted by the self-

Figure 3.19: The effective sticking probabilities for CH$_x$ (■) and C$_2$H (●) radicals calculated from the growth rate and the densities predicted by the plug-down (top) and self-consistent (bottom) model assuming a directed velocity of 1000 m·s$^{-1}$ for I$_{arc}$ = 57 A (left) and I$_{arc}$ = 89 A (right). The values exceeding 1 indicate that the densities predicted by the models are insufficient to account for the observed growth rate.
consistent model are definitely insufficient to account for the deposition rate at large precursor flows. At small flows the effective sticking probability of the CHₙ radicals is also rather large in comparison with reported values (cf. Table 3.1), but this may be explained by the fact that in the small-flow regime the self-consistent model is not an appropriate model, as said before.

In conclusion, the models predict that in a plug-down picture the CHₙ radicals will be the dominant growth precursors, whereas in a self-consistent picture at larger precursor flows the C₂H radicals become dominant. However, due to the uncertainty in the forward velocity, beam and/or deposition area, reaction rates, etc., used in the models, the possibility that a combination of C₂H and CHₙ radicals is contributing to the film growth can not be excluded. An argument in favor of this scenario is the trend observed in Figure 3.18 for the refractive index and absorption coefficient. A decrease of the refractive index and absorption coefficient is usually attributed to an increase in the hydrogen content of the a-C:H film [51]. The trend observed in Figure 3.18 therefore suggests that at larger CH₄ flows more hydrogen is incorporated in the film. Since in our plasma hydrogen-abstraction reactions are of minor importance, we may conclude that the higher hydrogen content in the film is due to the incorporation of more hydrogen-rich radicals in the growing film. This means that at larger methane flows either the C₂H/CHₙ flux ratio at the substrate is lower, or that at smaller flows the radicals become hydrogen-poor, e.g. by secondary dissociation reactions. Qualitatively, in the self-consistent representation the only possibility that both CHₙ and C₂H radicals contribute to the deposition, is that the former contributes at lower and the latter at higher CH₄ flows (cf. Figure 3.17). This can not be reconciled with the observed decrease of the refractive index at higher flows. In the plug-down model, on the other hand, a combination of C₂H radicals at low methane flows and CHₙ radicals at higher flows, which does fit with the observed trend of the refractive index, may be feasible. After all the possibility exists that both models predict a too small radical density or that the contribution of heavier species, e.g. Cₓ>2Hᵧ radicals, to the deposition flux is not negligible.

**Isotropic deposition**

In the case the directed beam properties are lost completely at the substrate level, the incoming flux is isotropic. When we assume that the incoming particles do not react with the surface to desorb back into the gas phase, i.e. they only stick to the surface, the growth rate \( R_g \) will be given by [44]:

\[
R_g = \frac{1}{4} n_x \bar{v}_x \cdot \frac{s}{1 - \frac{1}{2} s} \cdot \frac{m_x}{\rho} = \frac{1}{4} \frac{p_x}{k T_x} \frac{8kT_x}{\pi m_x} \cdot \frac{s}{1 - \frac{1}{2} s} \cdot \frac{m_x}{\rho}
\]

(3.2.13)

with \( n_x \) the density, \( \bar{v}_x \) the mean thermal velocity, \( s \) the effective sticking probability, \( p_x \) the partial pressure, \( m_x \) the mass, \( \rho \) the volumetric density of the film and \( T_x \) the temperature of species \( x \) and \( k \) Boltzmann’s constant. At \( T_x = 1000 \) K, the constant temperature used in the models, the mean thermal velocity \( \bar{v}_x \) will be 920 m·s⁻¹ for C₂H and 1230 m·s⁻¹ for the CHₙ radicals. In both cases we obtain even larger values for the effective sticking probability \( s \) than calculated for the ‘plasma beam deposition’.
3.2.6 Conclusions
In previous work it was shown that for deposition from an Ar/C\textsubscript{2}H\textsubscript{2} plasma the best material is obtained at high growth rates or under conditions where the ion particle flow rate emanating from the arc is approximately equal to the injected acetylene particle flow rate (so-called critical loading) [8]. This suggestion which was based on indirect particle flow rate and arc current variations can now be confirmed considering the measured consumption of acetylene.

The measurements clearly demonstrate that in an expanding Ar/C\textsubscript{2}H\textsubscript{2} plasma the argon ions and electrons emanating from the arc are responsible for the consumption of acetylene. Furthermore, the good agreement found between a simple model describing the consumption of acetylene and independent measurements with a Langmuir probe points to a one-to-one reaction between argon ions and acetylene molecules.

Under certain conditions a dissociation degree of 100\% is reached, indicating that the ion-induced dissociation is more efficient than dissociation by electron impact, for which full dissociation has never been reported. The fact that the growth rate is proportional to the depletion shows that the dissociation products are also very efficiently used in the deposition.

The chemistry of an Ar/CH\textsubscript{4} plasma however, is more complicated. The comparison of an Ar/C\textsubscript{2}H\textsubscript{2} and an Ar/CH\textsubscript{4} plasma reveals the importance of the loss probability of the radicals formed during dissociation of the precursor gas to the plasma chemistry. In an Ar/CH\textsubscript{4} plasma under certain conditions up to 40\% of the injected CH\textsubscript{4} flow is transformed into C\textsubscript{m}H\textsubscript{n} (m>1) polymers, while in an Ar/C\textsubscript{2}H\textsubscript{2} plasma the polymerization is much less (maximum 4\%) and preferentially C\textsubscript{2m}H\textsubscript{n} polymers are formed. This is attributed to the small sticking probability of the CH\textsubscript{x} radicals formed in the methane plasma as compared to the C\textsubscript{2}H radicals formed in the acetylene dissociation. The small sticking probability leads to a build-up of the radicals during the residence time resulting in more polymerization.

Another consequence of the difference in sticking probability is that in the case of acetylene injection the growth rate is proportional to the depletion of the precursor gas, whereas for methane injection this does not hold even when the polymerization (of C\textsubscript{2}H\textsubscript{n} polymers only) is taken into account. This may either be explained by a loss of CH\textsubscript{x} radicals to the pump, a non-negligible contribution of C\textsubscript{x}H\textsubscript{n} polymers to the consumption or a flow-dependent effective deposition area.

In order to describe the plasma chemistry two simple models were introduced: a self-consistent and a plug-down model. The self-consistent model treats the plasma as a plasma beam penetrating into the background. The plasma beam and background gas composition are thus linked in this model. In the plug-down model the plasma is treated as a plasma beam, allowing for diffusion outwards only.

For the acetylene discharge the plug-down model seems to be in good agreement with the measurements (see Figure 3.3 and Figure 3.4). The good agreement is attributed to the large sticking probability of the C\textsubscript{2}H radical and its small reaction probability in the gas phase. In the methane plasma a more complicated plasma chemistry is needed to explain the peculiar behavior of the growth rate with injected precursor flow. The CH\textsubscript{x} radical densities as predicted by the plug-down model can very well account for the observed growth rate qualitatively and quantitatively. In the self-consistent picture the CH\textsubscript{x} and C\textsubscript{2}H radical densities are both not sufficient to describe the growth rate qualitatively. In this picture a combination of the two radicals should be considered.

It seems that a plug-down model can describe the plasma chemistry and deposition more adequate than a self-consistent model. As long as the sticking probability of the
radicals produced in the dissociation is large and their reaction probability small, as is the case in e.g. the acetylene plasma, the plasma behaves more or less like a ‘plasma beam’. Even when the sticking probability of the dissociation products is so small that a considerable part is transformed into polymers, still the plug-down model appears to predict the plasma chemistry reasonably well. For a good quantitative description of the deposition it is however important to deduce which species are the main growth precursors and to model the plasma chemistry and flow behavior in more detail.
3.3 Argon - Nitrogen Plasmas

3.3.1 Introduction
Nitrogen plasmas find their use in a variety of industrial applications [52]. They are not only being employed in the synthesis of CNH materials (e.g. this thesis), but also in the nitridization of materials e.g. steel and titanium [53,54]. Because nitrogen is the most abundant constituent of air, it plays an important role in many open, atmospheric plasmas and processes in the Earth’s atmosphere. The aurora phenomenon and the re-entry of spacecrafts into the atmosphere, for instance, have led to an extensive study of the nitrogen excitation and the plasma-surface interaction [55,56]. Moreover, in the last few years, the kinetic modeling of nitrogen discharges has provided more detailed insight in the plasma processes [57,58]. Recently, Brussaard has published an extensive study on pure expanding nitrogen plasmas [5]. Because in this thesis a similar type of plasma has been used, this work will serve as reference material for our results on the expanding Ar/N₂ plasmas presented in this section.

In this thesis expanding Ar/N₂ plasmas are not only used for the deposition of CNH materials, but also for etching purposes. Because the reactivity of the plasma is an important parameter in the dissociation of the precursor and the downstream plasma chemistry, a thorough investigation of the argon-nitrogen plasmas is indispensable. In this section experimental results on these argon-nitrogen plasmas are presented. The argon-nitrogen plasmas are created in three different ways: by arc injection of Ar/N₂ mixtures, by ring injection of N₂ into an expanding argon plasma and by background injection of N₂. The plasmas are investigated with a Langmuir probe and by optical emission spectroscopy (OES). With the help of this model not only the electron density can be predicted, but also the density of other species that may be important during deposition or etching, e.g. N atoms and N₂⁺ ions. The electron temperature in the Ar/N₂ plasma appears to be (much) higher than in a pure argon plasma. The origin of the higher electron temperature is investigated by considering the dissociative recombination of the molecular ion. The study on the formation of this molecular ion reveals the importance of energetic (metastable) species in the argon-nitrogen plasma as had already been pointed out by Brussaard et al. [59]. In the emission of the Ar/N₂ plasma more evidence is found for the existence of energetic nitrogen species in the downstream plasma.

3.3.2 Model for argon-nitrogen plasmas
A theoretical model, which has been developed by Brussaard et al. [59] to describe low-flow (100-500 sccm Ar, 0-400 sccm N₂) argon-nitrogen plasmas, has been used to calculate the electron and ion densities in the downstream part at a given axial position. The densities are calculated as a function of the nitrogen concentration and arc current and are compared to the experimental values obtained with a Langmuir probe.
To calculate the densities at a given position, the densities of the different particles emanating from the arc (position $z = 0$) have to be known. Due to the high electron density ($n_e \approx 10^{22} \text{ m}^{-3}$) and high temperatures ($T_h \approx T_e \approx 1.1 \text{ eV}$) inside the arc the conditions for partial local thermodynamic equilibrium (pLTE) are met, and the nitrogen will be fully dissociated. The relative abundance of the ions, which will be atomic ions only, can therefore be approximated by the Saha equilibrium equation:

$$\frac{n_{N^+}}{n_{Ar^+}} = \frac{2g(N^+)g(Ar)\Phi_{N_2}}{g(N)g(Ar^+)\Phi_{Ar}} \exp\left(\frac{(E_{Ar^+} - E_{N^+})}{T_e}\right)$$  \hspace{1cm} (3.3.1)

with $n_{N^+}$, $n_{Ar^+}$ the density of $N^+$ respectively $Ar^+$, $g(Ar)$, $g(Ar^+)$, $g(N)$ and $g(N^+)$ the statistical weights (including other ground states) of the argon atom, argon ion, nitrogen atom and nitrogen ion respectively (at 1 eV respectively 1, 5.7, 5.1 and 9.8 [60]), $E_{Ar^+}$ and $E_{N^+}$ the ionization energy for argon (15.76 eV) and nitrogen (14.53 eV) respectively, $\Phi_{N_2}$ and $\Phi_{Ar}$ the injected nitrogen respectively argon flow, and $T_e$ the electron temperature in the arc.

In Figure 3.20 the relative density of $Ar^+$ and $N^+$ as calculated from equation (3.3.1) at an electron temperature of 1 eV and 1.2 eV inside the arc, is given as a function of the nitrogen seeding in the arc. It is assumed for simplicity that the relative densities given by equation (3.3.1) still hold after the stationary shock*. Van de Sanden et al. showed for a pure argon plasma that the ion density is not so much influenced by the stationary shock (a maximum ion density jump of four was found [45]), so this assumption seems justified.

The plasma emanating from the arc expands into a vessel, where neutral argon and nitrogen molecules, which are formed at the walls, are present. As was shown by Brussaard et al., a considerable part of the nitrogen molecules may be in the excited $N_2(A^3\Sigma_u^+)$ metastable state [61]. In the model the excited molecules are introduced as

* Due to the decrease in temperature over the shock region the relative amount of nitrogen ions may actually increase.
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a fraction $\chi$ of the non-excited molecules. The total particle density $n$ in the vessel is taken as initial condition and is estimated from the relation $p = n \cdot k \cdot T$, with $p$ the pressure in the vessel (25 Pa), $k$ Boltzmann’s constant and $T$ the temperature of the neutrals (500 - 2000 K). The argon neutral and molecular nitrogen densities are given by their relative flows times the total particle density and are assumed to be homogeneously distributed in the vessel.

This plasma chemistry model is thus based on a fully mixed reactor and may in that sense be compared with the self-consistent model that has been used to describe the hydrocarbon deposition plasmas (cf. section 3.2). However, in the hydrocarbon self-consistent model the plasma chemistry is restricted to a cylindrical reaction volume, whereas in this model the reaction volume is not relevant, and the chemistry is entirely determined by the partial pressures of the species involved. The reason that we choose a fully mixed reactor model for our simulations is that, when the nitrogen is completely dissociated in the arc, the only way to form nitrogen molecules is by reassociation at the wall. Therefore, the vessel as a whole needs to be considered as reaction volume.

The three different injection methods presented here, i.e. arc, ring and background injection, are accounted for by changing the initial conditions in the model. In the case of arc injection at $z = 0$ only atomic argon and nitrogen ions are present, their ratio being dictated by equation (3.3.2). For ring injection at $z = 0$ only argon ions are present and at $z = 5$ cm (the ring position) molecular nitrogen is introduced. In the background injection experiments a nitrogen flow of 5 sccs was added to the total flow in the arc and the argon flow in the arc was adjusted to maintain a total flow including the variable nitrogen flow injected in the vessel- of 100 sccs. This was modeled by introduction of an atomic argon/nitrogen mixture at $z = 0$ and an additional injection of molecular nitrogen at $z = 0$.

In the expansion the reactions between the different species influence the composition. The three reactions considered in this model are:

$$\text{Ar}^+ + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+ \quad k_1 \approx 7 \times 10^{-17} \text{ m}^3 \cdot \text{s}^{-1} \text{ at } 0.2 \text{ eV} \ [62] \quad (3.3.2)$$

$$\text{N}^+ + \text{N}_2^* \rightarrow \text{N} + \text{N}_2^+ \quad k_2 \approx 1 \times 10^{-16} \text{ m}^3 \cdot \text{s}^{-1} \text{ at } 0.2 \text{ eV} \ [63] \quad (3.3.3)$$

$$\text{N}_2^+ + e^- \rightarrow \text{N}^* + \text{N} \quad k_3 \approx 1 \times 10^{-13} \text{ m}^3 \cdot \text{s}^{-1} \text{ at } 0.5 \text{ eV} \ [64] \quad (3.3.4)$$

Reactions (3.3.2) and (3.3.3) lead to a reduction of $\text{Ar}^+$ and $\text{N}^+$ ions and to the production of $\text{N}_2^+$ ions. Reaction (3.3.4) is the main source of loss of electrons and $\text{N}_2^+$ ions. The reaction rates $k_1$ and $k_2$ depend on the gas temperature, whereas $k_3$ depends on the electron temperature. For reactions (3.3.2) and (3.3.3) the rate increases with increasing temperature, for reaction (3.3.4) it decreases. In the model the temperature is assumed to be independent of the position in the plasma, so the three reaction rates will be considered constant during the expansion. As we will show later, both the gas and electron temperature are constant within 20%, so this assumption is justified. Due to the fast loss of $\text{N}_2^+$ ions by reaction (3.3.4) the $\text{N}_2^+$ density is low and the backward reactions, i.e. $\text{N}_2^+ + \text{Ar} \rightarrow \text{N}_2 + \text{Ar}^+$ and $\text{N}_2^+ + \text{N} \rightarrow \text{N}_2 + \text{N}^+$, which have 10-100 times smaller rates than the forward reactions [62], can be neglected.

For the low-flow argon-nitrogen plasma it was demonstrated that the three reactions (3.3.2) - (3.3.4) plus loss of species by diffusion towards the wall at electron densities

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*Species denoted with * stand for excited (metastable) species.*
below $10^{17}$ m$^{-3}$ (i.e. nitrogen seedings above 10 %) can account for the measured electron density [59]. In the case of higher total flow the ion densities will be higher and therefore it is expected that the diffusion outwards will be negligible compared to the losses due to reaction (3.3.4). Three-body reactions can be neglected at the typical densities of $10^{19}$-10$^{20}$ m$^{-3}$ due to the low rates in the order of $10^{-43}$ m$^6$ s$^{-1}$ [65]. Reactions (3.3.2) and (3.3.4) are exothermal, reaction (3.3.3) only becomes exothermal when the excitation energy of N$^*_2$ exceeds 1 eV (the difference in ionization energy between N$^+$ and N$^+_2$). This means that either vibrationally excited ground state molecules N$^*_2$(X$^1\Sigma_g^+$, $v > 3$) are required or molecules in one of the excited electronic states. In the case of a Maxwellian electron energy distribution with an average of 0.5 eV, only 13.5 % of the nitrogen will be excited to a level with a total energy larger than 1 eV. To account for the fact that the N$^*_2$ concentration is lower than the total N$^+_2$ concentration, in the model the N$^*_2$ density is introduced as the N$^+_2$ density times a fraction $\chi < 1$. Neglecting the diffusion and assuming a uniform axial velocity $v$, the mass balance in steady state can be written as a set of 1-dimensional rate equations to axial position $z$:

$$
v \frac{\partial n_{Ar^+}}{\partial z} = -k_1 n_{Ar^+} n_{N^+_2} \quad (3.3.5)
$$

$$
v \frac{\partial n_{N^+_2}}{\partial z} = -k_2 n_{N^+_2} (\chi \cdot n_{N^+_2}) \quad (3.3.6)
$$

$$
v \frac{\partial n_{N^*_2}}{\partial z} = k_1 n_{Ar^+} n_{N^+_2} + k_2 n_{N^+_2} (\chi \cdot n_{N^+_2}) - k_3 n_e n_{N^*_2} \quad (3.3.7)
$$

where $n_{Ar^+}$, $n_{N^+_2}$, $n_{N^+_2}$ and $n_{N^*_2}$ are the densities of Ar$^+$, N$^+_2$, N$^+_2$ and N$^*_2$ respectively.

The electron density $n_e$, which follows from quasi-neutrality, is given by $n_e = n_{Ar^+} + n_{N^+_2} + n_{N^*_2}$. These equations are solved numerically yielding the densities of the different species at every desired axial position.

### 3.3.3 Electron densities

As the plasma travels towards the substrate, the electron density will decrease with increasing distance from the arc. In Figure 3.21 the electron density\(^1\) as a function of the distance from the nozzle is shown for a nitrogen percentage of 10 % in the arc. An exponential decrease is observed, as expected for a constant loss rate along the axis. Due to the decrease of the electron and N$^+_2$ density with distance the loss of electrons downstream will become less for larger axial position. The values used for the model are in agreement with reported values. However, in order to obtain a good fit, we have to assume that only a fraction $\chi$ of 0.1 of the neutral nitrogen molecules is participating in reaction (3.3.3). This fraction is in agreement with recent findings [5].

The neutral density used in the model corresponds to a gas temperature of $1.8 \times 10^3$ K (0.16 eV). This temperature is close to the temperature of 0.2 eV at which the values

---

\(^1\) The error bars give an indication of the uncertainty in the measured electron density. In Figures where the error bars have been omitted for the sake of clarity, typical uncertainties of 20 % and 30 % in the electron density respectively temperature have to be taken into account.
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of reaction rates $k_1$ and $k_2$ were determined. By calculating the gas temperature $T$ from the relation $p = n \cdot k \cdot T$ it is assumed that the neutrals are homogeneously distributed in the vessel. However, as was pointed out by Brussaard et al. [61], the neutrals that are contributing to reaction (3.3.3) are in the periphery of the plasma, leading to a non-homogeneous radial distribution.

This assumption is supported by emission measurements of the so-called First Negative System (N$_2$$^+$ $(B^3\Sigma_u^+)$ $\rightarrow$ N$_2$$^+$ $(X^2\Sigma_g^+)$ $+$ hv) as a function of the radial position (see Figure 3.22). At low electron temperatures ($< 0.5$ eV) the FNS emission is predominantly produced from reactions (3.3.2) and (3.3.3) with chemically excited nitrogen [61], and is therefore a measure for the number of these excited species. In Figure 3.22 one can see that the emission is much smaller in the center of the plasma than at the outside. Since the Langmuir probe measurements have been performed at the expansion axis, the neutral density, which was adjusted in the model to fit to the

Figure 3.21: Electron density as a function of the distance from the nozzle for 10 % nitrogen seeding in the arc at $I_{arc} = 48$ A. Dashed line represents model results with $k_1 = 7 \times 10^{17}$ m$^3$s$^{-1}$, $k_2 = 1 \times 10^{16}$ m$^3$s$^{-1}$, $k_3 = 1 \times 10^{13}$ m$^3$s$^{-1}$, $\chi = 0.1$, $v = 1000$ m$s^{-1}$ and $n_{N_2} + n_A = 1 \times 10^{21}$ m$^{-3}$.

Figure 3.22: The intensity of the N$_2$$^+$ First Negative System (0,0) bandhead at 391.4 nm measured at 55 cm from the nozzle as function of radial position obtained from Abel inverted [66] lateral scans. $\Phi_{Ar} = 85$ sccs, $\Phi_{N_2} = 15$ sccs, $I_{arc} = 89$ A.
data, may in fact be underestimated. The gas temperature may thus be overestimated. The electron density as a function of the concentration of nitrogen in the arc is shown in Figure 3.23 together with the model results. The higher electron density at higher arc currents is explained, as has been done for a pure argon plasma, by the increase of the ionization degree with arc power \cite{45}.

In Figure 3.24 the electron density as a function of the concentration of nitrogen is shown for arc injection, ring injection and background injection. Surprisingly enough the injection method does not seem to have a large influence on the electron density. If one assumes that the only loss mechanism for electrons in the expansion is by recombination with $N_2^+$ (reaction (3.3.4)) and that the electron diffusion profile and density is not dependent on the injection method, one has to conclude that the production of $N_2^+$ is almost independent of the injection method used. This is also

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure323}
\caption{Electron density at 20 cm from the nozzle as a function of the nitrogen concentration in the arc for $I_{arc} = 48 \, A$ (■), 75 A (●) and 87 A (▲). Solid lines are model results with the same parameters as used in Figure 3.21.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure324}
\caption{Electron density at 20 cm from the nozzle as a function of nitrogen concentration for arc (■), ring (●) and background (▲) injection at $I_{arc} = 48 \, A$. The solid, dashed and dotted lines represent the model results for respectively arc, ring and background injection.}
\end{figure}
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supported by optical emission spectroscopy measurements, which show almost no difference between ring and arc injection. This would mean that the production by charge exchange with argon ions (reaction (3.3.2)) in the case of ring injection equals the production by charge exchange with both argon and nitrogen ions in the case of arc injection. Yet another explanation could be that in the early supersonic expansion all argon ions are transformed into nitrogen ions in the presence of N₂.

The model predictions for background and ring injection, shown as lines in Figure 3.24, appear to overestimate the loss of electrons when the same values for the different parameters are used as for arc injection (cf. Figure 3.21). This may be explained by the fact that in reality in these two cases the mixing is less efficient or that the production of energetic N₂ molecules, which -as said before- are thought to be formed at the walls by recombination of nitrogen atoms, is lower. The influence of the electron temperature on the reaction rate $k_3$ could also contribute to an overestimation of the electron consumption. As will be shown in the next section, the electron temperature is higher for background and ring injection (especially at higher nitrogen seedings) than for arc injection. Therefore, the dissociative recombination is expected to be less fast in the two vessel injection cases. However, the dependence of reaction rate $k_3$ on the electron temperature is rather small.

3.3.4 Electron temperatures

From the Langmuir probe data also the electron temperatures of the Ar/N₂ plasmas have been determined. The electron temperature as a function of the nitrogen seeding is shown in Figure 3.25 for arc injection at three different arc currents and in Figure 3.26 for the different injection methods at $I_{\text{arc}} = 48$ A. We see that the electron temperature, which was assumed constant in the model, is in fact not independent of the nitrogen seeding. The effect of the electron temperature on the reaction rates is however almost negligible. Assuming an average electron temperature of 0.5 eV leads to a maximum error of 20 % in reaction rate $k_3$. The electron temperature of pure argon plasmas (i.e. 0 % N₂ seeding) lies between 0.28 and 0.41 eV, depending on the arc current. This increase of electron temperature with increasing arc current in a pure argon plasma has also been observed by others, and has been attributed to an increase in the number of three-particle recombination reactions [67].

![Figure 3.25: Electron temperature at 20 cm from the nozzle as a function of nitrogen concentration in the arc for $I_{\text{arc}} = 48$ A (■), 75 A (●) and 87 A (▲).](image)

Figure 3.25: Electron temperature at 20 cm from the nozzle as a function of nitrogen concentration in the arc for $I_{\text{arc}} = 48$ A (■), 75 A (●) and 87 A (▲).
of the maximum in the electron temperature with nitrogen seeding depends on the arc current and injection method, as can be seen in Figure 3.25 and Figure 3.26. A higher arc current leads to a higher electron temperature and also to a shift of the maximum to a higher nitrogen concentration. This observation is exactly opposite to Langmuir probe measurements in a pure expanding nitrogen plasma [5], operated at a different pressure (225 Pa) and with a nitrogen flow of 1 slm (16.7 sccs), which show a decrease of electron temperature with increasing arc current.

The different injection methods result in almost the same electron temperature at low nitrogen seedings (up to 5 %). At higher nitrogen percentages the electron temperature shows distinct differences between arc injection and vessel (i.e. ring or background) injection. Measurements of the electron temperature in a pure nitrogen plasma [5] reveal that the electron temperature is higher than in a pure argon plasma. This may explain the initial increase of the electron temperature with nitrogen addition. Two possible mechanisms for the electron heating are proposed: ‘super-elastic’ collisions with excited nitrogen species and recombination of the molecular ion (reaction (3.3.4)). In the case of ‘super-elastic’ collisions the excited nitrogen species transfer their excitation energy to the electrons:

\[
M^* + e^- (\text{cold}) \rightarrow M + e^- (\text{hot}) \quad (3.3.8)
\]

Especially the metastable species, e.g. \( \text{N}_2(A^3\Sigma_u^+) \), \( \text{N}(^2\text{D}) \) and \( \text{N}(^2\text{P}) \) have a radiative lifetime which is long enough (1-3 seconds) for these collisions to occur. As mentioned before, \( \text{N}_2(A^3\Sigma_u^+) \) may be formed by recombination of nitrogen atoms at the vessel walls or by radiative decay from higher lying levels. \( \text{N}(^2\text{D}) \) and \( \text{N}(^2\text{P}) \) are formed in the dissociative recombination of the molecular ion (reaction (3.3.4)). The other mechanism proposed for the electron heating, i.e. dissociative recombination of the molecular ion, is based on the fact that reaction (3.3.4) is more favorable for low-energy electrons:

\[
\text{N}_2^+ + e^- (\text{cold}) \rightarrow \text{N}^* + \text{N} \quad (3.3.9)
\]

for which the rate has a reported \( T_e^{-1/2} \) dependence [64]. This reaction mainly leads to the loss of low-energy electrons, leaving behind the electrons with a higher energy. This will eventually result in an increase of the average electron temperature due to electron-electron collisions. Furthermore, in this reaction the electron energy is

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**Figure 3.26:** Electron temperature at 20 cm from the nozzle as a function of nitrogen seeding for arc (■), ring (●) and background (▲) injection at \( I_{arc} = 48 \, \text{A} \).
efficiently transferred to the heavy particles. The two nitrogen atoms produced in this reaction have a relatively high kinetic energy, which may act as a significant heat source (for the heavy particles) [68]. The excited nitrogen atoms may also contribute to electron heating via reaction (3.3.8).

In both cases, i.e. heating of the electrons by ‘super-elastic’ collisions and the dissociative recombination, the heating of the electron temperature is related to the convolution of the electron density $n_e$ and the $N_2^+$ density. Since the electron density decreases monotonically with the nitrogen percentage (see Figure 3.23), we have to review the production of $N_2^+$ in order to explain the observed maximum in the case of arc injection.

Admixture of nitrogen in the arc causes an increase of the $N^+$ and $N_2$ density and a decrease of the $Ar^+$ density. The increase of the $N_2$ and $N^+$ density contributes to the increase of $N_2^+$ by reactions (3.3.2) and (3.3.3). At a certain nitrogen seeding the amount of $Ar^+$, which decreases with increasing nitrogen concentration, becomes the limiting factor in reaction (3.3.2). Increasing the nitrogen concentration even further then leads to a decrease of the $N_2^+$ formed by reaction (3.3.2). This decrease may only partially be compensated by the increase of $N_2^+$ formed by reaction (3.3.3), because this reaction depends also on the amount of $N_2^*$ which may be small on the expansion axis, as was discussed before. The amount of $N_2^+$ thus first increases with increasing nitrogen concentration, reaches a maximum and then decreases with increasing nitrogen concentration.

This effect is also observed in the model calculations presented in Figure 3.27. The values predicted by the model for the $N_2^+$ density are in good agreement with a recent study of Brussaard et al. [5]. When the calculated destruction of $N_2^+$ and electrons due to the dissociative recombination (reaction (3.3.4)), shown in Figure 3.28, is compared to the measured electron temperatures (Figure 3.24), we see that the trends can be reasonably well described by assuming this heating mechanism.

Note that for a meaningful comparison with the model the heating should be a local effect, i.e. the characteristic interaction length of the heating process should be small compared to the length scale at which reactions (3.3.2) and (3.3.3) take place. For a process like $A + B \rightarrow \text{products}$ with reaction rate $k_{AB}$, the interaction length $L_A$ of

![Figure 3.27: Model predictions for the $N_2^+$ density at 20 cm from the nozzle as a function of the nitrogen concentration for arc, ring and background injection (solid, dashed and dotted line respectively) at $I_{arc} = 48 A.$](image-url)
species \( A \) can be approximated by: \( L_A = \frac{v}{k_{AB} n_B} \), where \( v \) is the plasma flow velocity and \( n_B \) the density of species \( B \). The reaction rates reported for dissociative recombination and ‘super elastic’ collisions (\( 10^{-13} \text{ m}^3 \text{s}^{-1} \) \cite{64} and \( 10^{-14} \text{ m}^3 \text{s}^{-1} \) \cite{69} respectively) are both 100-1000 times higher than the rates for the production of \( \text{N}_2^+ \).

Thus, at an electron density of \( 10^{19} \text{ m}^{-3} \) and nitrogen neutral density of \( 10^{20} \text{ m}^{-3} \), the interaction length of \( \text{N}_2 \) or \( \text{N}_2^+ \) for the heating process will be at least 10 times shorter than the characteristic length at which \( \text{N}_2^+ \) is formed. This means that we can treat the heating as a local effect.

The fact that higher arc currents lead to a shift of the maximum of the electron temperature towards higher nitrogen concentrations (cf. Figure 3.25), can also be explained by the convolution of \( n_e \) and the \( \text{N}_2^+ \) density. This heating mechanism could also account for the observation of Brussaard et al. that the electron temperature

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**Figure 3.28:** Model calculations of the electron and \( \text{N}_2^+ \) destruction as function of the nitrogen seeding for arc, ring and background injection (solid, dashed and dotted line respectively) at 20 cm from the nozzle and \( I_{arc} = 48 \text{ A} \).

**Figure 3.29:** Electron temperature as a function of the distance from the nozzle for arc (■) and ring (●) injection at a nitrogen seeding of 10 % and a pure argon plasma (●) at \( I_{arc} = 48 \text{ A} \).
increases with radial distance from the expansion axis [5]. The N₂ molecules, which are formed at the vessel walls, will be predominantly at the edges of the plasma. Therefore, it is expected that both the ‘super-elastic’ collisions between N₂⁺ and electrons and the formation and subsequent dissociation of N₂⁺ will take primarily place at the plasma periphery.

As a final ‘proof’ for the heating by background species, the electron temperature as function of the distance from the nozzle is presented in Figure 3.29. Contrary to a pure argon plasma for which the electron temperature decreases when moving away from the plasma source, the electron temperature in the Ar/N₂ plasma increases. This is an indication that in an argon-nitrogen plasma the chemistry with the background gas itself provides a heating mechanism for the electrons (and neutrals). The N₂(A³Σ⁺) density as deduced by Brussaard et al. [5] shows a similar increase with increasing distance from the nozzle, giving further support to the idea that the heating occurs via energetic nitrogen molecules.

3.3.5 Emission spectroscopy

The emission from an Ar/N₂ expanding plasma is shown in Figure 3.30 for two axial positions. On addition of nitrogen in the arc, a strong quenching of the plasma emission compared to the pure argon plasma is observed. Nevertheless the spectrum close to the arc nozzle is still dominated by the Ar lines, the nitrogen giving its signature by the presence of N₂⁺-FNS (N₂⁺(B³Σ⁺) → N₂⁺(X²Σ⁺)) and N₂-SPS (N₂(C¹Π) → N₂(B¹Π)) spectral system bands [70] in the observed range. The Ar lines are due to the decay of highly excited Ar** atoms produced in the three particle recombination reaction

\[
\text{Ar}^+ + e^- + e^- \rightarrow \text{Ar}^{**} + e^- \quad (3.3.10)
\]

Although the effect of this reaction on the plasma chemistry is negligible, the resulting emission is dominant close to the arc. The Ar** decays primarily to the 4s manifold (two resonant and two metastable levels) at about 11.5 eV above the ground state.

![Emission spectra from an expanding Ar/N₂ plasma](Figure 3.30)

Figure 3.30: Emission spectra from an expanding Ar/N₂ plasma (95 sccs Ar, 5 sccs N₂, I_{arc} = 75 A) at 7 cm (left) and 62 cm (right) below the arc nozzle.

[1] Unfortunately Brussaard et al. did not discuss the origin of this radial increase, which they ascribed to an experimental inaccuracy.

[2] A simplified potential energy diagram of N₂ and N₂⁺ is shown in Figure 3.31.
state [71]. The Ar metastables may cause excitation of the N$_2$-SPS (threshold energy 11.1 eV [72]) by means of an excitation exchange reaction:

$$\text{Ar}_{\text{metastable}} + \text{N}_2(X^1\Sigma_g^+) \rightarrow \text{Ar} + \text{N}_2(C^3\Pi_u) \quad k = 3.6 \times 10^{-17} \text{ m}^3 \cdot \text{s}^{-1} \quad \text{(3.3.11)}$$

This reaction has almost perfect energy resonance, and thus it will be very effective and much faster than excitation by electrons. But, as was shown by Buuron [3], the fraction of argon metastables is small -especially at larger axial position-, so this reaction will only have significance close to the arc. This is also reflected in Figure 3.30: the emission signal of the N$_2$-SPS is already quite small close to the arc, and is almost absent near the substrate. Another possible way of exciting the N$_2$-SPS is by pooling reactions between N$_2(A^3\Sigma_u^+)$ metastables:

$$\text{N}_2(A^3\Sigma_u^+) + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{N}_2(C^3\Pi_u) + \text{N}_2(X^1\Sigma_g^+) \quad k = 1.5 \times 10^{-16} \text{ m}^3 \cdot \text{s}^{-1} \quad \text{(3.3.12)}$$

As has been indirectly shown by Brussaard et al. [5], a considerable part of the N$_2$ molecules is in the metastable N$_2(A^3\Sigma_u^+)$ state. The N$_2$ molecules need to be formed first at the vessel walls by association of two N(4S) atoms. In the association process at the wall the molecules may gain a large amount of internal energy when rovibrationally excited N$_2(X, v>0,1)$ and/or metastable N$_2(A^3\Sigma_u^+)$ molecules are formed. The rovibrationally excited N$_2(X, v>0,1)$ could also be formed in the plasma by stepwise V-V energy transfer [69].

Because of the high temperatures inside the arc ($T_\text{h} = T_\text{e} \approx 1 \text{ eV}$) and the high electron density ($n_\text{e} \approx 10^{22} \text{ m}^{-3}$), only Ar$^+$ ions and atomic nitrogen ions will survive [59]. Only in the very early (supersonic) expansion N$_2^+(B^2\Sigma_u^+)$ may be produced by three-particle association reactions and/or electron excitation. Production of N$_2^+$ in the expansion zone, where $T_\text{e}$ is about 0.5 eV (see Figure 3.29), can be explained by the charge exchange reactions (3.3.2) and (3.3.3) with molecular nitrogen formed on the vessel walls. Electronic excitation of the N$_2^+$-FNS from the N$_2^+$ ground state is insignificant, since it requires an energy of 3.1 eV [72], which is substantially higher than $T_\text{e}$. Another possibility would be to get N$_2^+$ excited via reactions (3.3.2) or (3.3.3), but the maximum amount of energy transferred in this way is only 15.76 eV (the argon ionization energy [71]). Excitation of the N$_2^+$-FNS from the N$_2$ ground state requires an energy of 18.7 eV [72]. So to excite the N$_2^+$-FNS band directly from the N$_2$ ground state by charge exchange with an argon ion an extra energy of about 1.9 eV is needed, taking into account the 1.03 eV difference in the dissociation energies of N$_2$ and N$_2^+$ [74].

There are several possible explanations for this extra 1.9 eV. The electron temperature in the expansion is substantially higher than the 0.2 eV which was observed in a pure argon plasma [45]. At these higher temperatures, excitation by electrons gets more probable. However, the fact that the FNS emission does not decrease with increasing distance from the nozzle (cf. Figure 3.30), whereas the electron density does (see Figure 3.21), does not seem to be consistent with that picture. Another mechanism that may account for the FNS emission involves excitation exchange reactions with rovibrationally excited and/or metastable N$_2$ molecules or N$_2^+$ ions. It was shown by Brussaard et al. [61] that in a pure nitrogen plasma part of the N$_2^+$-FNS emission can be explained by charge exchange of a nitrogen atomic ion with a metastable N$_2(A^3\Sigma_u^+)$ molecule. Due to its extremely long radiative lifetime of 1 to 3 seconds [69], which exceeds the residence time of the gas in the vessel, the metastable
molecule can enter the plasma again with an “extra” energy of about 6 eV. Due to collisional quenching of this metastable state (highest rate for electrons: $10^{14} \text{m}^3\text{s}^{-1}$ [69]) only 10% will actually succeed in returning to the center of the plasma [5]. But since the OES measurement is a line-of-sight measurement, this effect can only be observed after Abel inversion of lateral scans at different radial positions (see Figure 3.22).

At the substrate position the $\text{N}_2^+$-FNS molecular bands dominate the spectrum. The $\text{N}_2$-SPS bands are almost absent and the Ar lines have disappeared completely. As long as the electron density is high enough ($>10^{17} \text{m}^{-3}$) the $\text{N}_2^+$ loss will be mainly due to the dissociative recombination reaction (3.3.4). The electron density downstream is in the order of $5 \times 10^{18} \text{m}^{-3}$. At these densities the dissociative recombination (reaction (3.3.4)) which destroys $\text{N}_2^+$ is still important, so the observation of the $\text{N}_2^+$-FNS bands at the substrate position is an indication that production of excited $\text{N}_2^+$ is also taking place in the late expansion. This means that even close to the substrate a mechanism as argued before should apply which delivers extra energy for the excitation of the FNS. This is a clear indication that the energetic nitrogen species (rovibrationally excited $\text{N}_2$, $\text{N}_2^+$ and/or metastable $\text{N}_2 (A^3\Sigma^+_u)$) are not only produced close to or in the arc, but also in the late expansion. This is also supported by the observation that injection of nitrogen in the ring, i.e. without energetic nitrogen species emanating from the arc, similar spectra are obtained. This proves that, at least in this case, the

![Figure 3.31](image-url): Simplified potential energy diagram of $\text{N}_2$ and $\text{N}_2^+$. The numbers indicate the vibrational levels.
excitation of the $N_2^+$-FNS band cannot be explained by rovibrationally excited $N_2$ or $N_2^+$ ions produced in the arc, and must therefore involve either electron excitation or formation of energetic nitrogen species by association at the wall. It also shows that the argon species is very effective in excitation of ionic and neutral nitrogen. The intensities of the $N_2^+$-FNS ($N_2^+ (B^2Σ_u^+ → N_2^+ (X^2Σ_g^+))$ bandhead at 391.44 nm, the $N_2$-SPS ($N_2 (C^3Π_u → N_2 (B^3Π_g))$ bandhead at 375.54 nm and the atomic N emission line ($N(3p) → N(3s)$) at 409.99 nm are shown in Figure 3.32 as a function of the nitrogen concentration. A maximum, similar to the one observed for the electron temperature (Figure 3.26) or for the $N_2^+$ density (Figure 3.27), occurs at nitrogen seedings between 5 % and 10 %. This resemblance may support the assumption that the emission, especially the $N_2^+$-FNS, originates from electron excitation or reactions with energetic (metastable) nitrogen molecules of which the density is being determined by the dissociative recombination reaction. As argued before, the fact that the FNS emission does not decrease with increasing distance from the nozzle (cf. Figure 3.30), whereas the electron density does (see Figure 3.21), seems to favor the latter excitation mechanism.

### 3.3.6 Rotational and vibrational temperatures

For a pure nitrogen plasma Brussaard et al. calculated the density of vibrationally excited ground state molecules $N_2 (X^1Σ_g^+, v > 3)$ needed to account for the charge exchange with atomic ions [5]. From this density a vibrational temperature of the ground state molecules of 3000 K was deduced. Moreover, since the electron temperature was found to be lower, it was concluded that a slight overpopulation of the vibrational distribution with respect to thermal equilibrium must exist [5]. In the present Ar/N$_2$ plasma the vibrational and rotational temperature of the $N_2^+$-FNS ($Δv = 0$) band have been determined from the measured spectra with a computer.
simulation procedure developed by Aldea et al. A typical fitting result is shown in Figure 3.33. The rotational temperature of the different plasmas varies between 0.16 eV and 0.34 eV and has no clear relationship with the composition of the plasma. The average rotational temperature is 0.25 eV. Usually the exchange between the rotational energy and the translational energy of the neutrals is efficient so that the rotational temperature is a good measure for the gas temperature. In this case it would mean that the gas temperature is around 0.25 eV.

The vibrational temperature varies between 0.22 eV and 0.60 eV. It reaches a maximum around a nitrogen concentration of 10 %. If we compare the vibrational temperature (not shown) with the electron temperature (Figure 3.25), we see that they have a similar dependence on the nitrogen concentration and more or less the same values. Apparently the energy exchange between the electrons and the vibrational levels is rather good. It seems however that the coupling between the electron or vibrational temperatures and the rotational energy is very weak. The aforementioned overpopulation of the vibrational distribution with respect to thermal equilibrium as predicted by Brussaard et al. does indeed exist, at least for the $N_2^+$-FNS ($\Delta v = 0$) band.

The degree of non-equilibrium of the vibrational ($T_{\text{vib}}$) and rotational ($T_{\text{rot}}$) temperature increases with the distance from the arc from $T_{\text{vib}}/T_{\text{rot}} \approx 2$ near the nozzle to $T_{\text{vib}}/T_{\text{rot}} \approx 4$ in the deposition zone. This is due to the huge increase of $T_{\text{vib}}$ downstream ($T_{\text{rot}}$ even slightly decreases at larger distances from the arc). The electron temperature increases at the same time only by 20 % with increasing distance. This indicates that either the electron and vibrational energy are not linked at all, or that more downstream the coupling between the electrons and the vibrational energy levels of the $N_2^+$-FNS ($\Delta v = 0$) band is lost.

**The Boltzmann distribution of the rotational levels in the ground state will be preserved as long as the reaction is not highly exothermic.**

---

**Figure 3.33:** A typical fitting result of the $N_2^+$-FNS ($\Delta v = 0$) band recorded at 7 cm below the arc nozzle in an expanding Ar/N$_2$ plasma (90 sccs Ar, 10 sccs N$_2$, $I_{\text{arc}} = 75$ A). The fitting results are: $T_{\text{rot}} = 3271 \pm 31$ K and $T_{\text{vib}} = 5429 \pm 117$ K.
3.3.7 Conclusions
It has been shown that in Ar/N₂ plasmas the dominant loss mechanism for ions and electrons is the charge exchange between ions and N₂ formed at the vessel walls followed by dissociative recombination. The dissociative recombination is also an important mechanism for the production of nitrogen atoms in the downstream plasma. In the downstream region the dominant ion will be the molecular nitrogen ion. This may have important consequences for the application of RF bias on the substrate, where a N₂⁺ ion may dissociate on impact.
Furthermore, it has been shown that a substantial part of the nitrogen formed at the vessel walls is in an excited or metastable state and can penetrate into the plasma beam. With these energetic nitrogen species not only the N₂⁺-FNS emission can be explained, but also partially the relatively high electron temperature (~ 0.5 eV instead of ~ 0.3 eV in a pure argon plasma). The dissociative recombination has been found to be the main heating mechanism for the electrons. The higher electron temperature and large abundance of excited nitrogen molecules may have a large influence on the excitation and/or dissociation in the plasmas that will be discussed in the following sections. Moreover, the presence of energetic nitrogen molecules in the downstream plasmas may have important consequences for the dissociation of the precursor gas due to their excess energy and even for the deposition and/or etching process.
3.4 Argon - Nitrogen - Hydrocarbon Plasmas

3.4.1 Introduction

In the past years several studies have been devoted to plasmas of hydrocarbon-nitrogen mixtures. The interest in these type of plasmas has been provoked by interest in, among others, the chemistry of particular interstellar clouds [76,77]. The use of plasmas for toxic agent purification purposes [78] and hydrocarbon gas trace detection [79] has also led to investigation of the interaction of nitrogen and hydrocarbon in a plasma environment. Furthermore, some research has been dedicated to surface treatment, e.g. nitridization [53], deposition of polymeric material with specific functional groups [80] and -closely related- the deposition of a-C:H:N films [81,82].

The possibility to deposit hydrogenated carbon nitride materials with the use of an Expanding Thermal Plasma (ETP) generated by a cascaded arc has been previously shown [82]. In this section the Ar/N$_2$/C$_2$H$_2$ plasma which has been employed for that purpose will be scrutinized. To elucidate the role of plasma species and of their physical state in the deposition process optical emission spectroscopy and mass spectrometry will be used. Moreover, the effect of nitrogen seeding on the acetylene dissociation will be discussed.

3.4.2 Experimental

The experimental set-up has been described in detail elsewhere [83] and in section 2.2. Argon gas is injected at the cathodes position into the arc, and nitrogen is added half-way in the arc channel. The Ar/N$_2$ plasma expands into a vacuum vessel at a typical pressure of 25 Pa. In order to gain more insight in the processes taking place along the plasma flow, the plasma emission has been collected at 7 cm below the arc nozzle, i.e. 2 cm downstream the injection point and at 62 cm from the arc nozzle, i.e. 3 cm above the substrate. The spectral features have been studied as function of the gas mixture, gas particle flow rate, background pressure and arc current. Comparison of computer simulated spectra with the recorded spectra has been used for the determination of the rotational and vibrational temperatures of the CN and CH radical emission [75]. The procedure, which includes the influence of self-absorption on the simulated spectra, also provides an estimate of the ground state density of these molecules.

The background gas composition is sampled with a residual gas analyzer (RGA) positioned approximately at the position of the substrate holder. Exact calculation of the precursor consumption or production of new species is troubled by the fact that the possible products sampled are not a priori known, as well as their cracking patterns. This problem can be circumvented by considering all known cracking pattern components of one species (e.g. C$_2$H$_2$) simultaneously in order to discern the interference of other species. When two or more cracking pattern components yield the same depletion $D$, defined as $D = (I_{\text{off}} - I_{\text{on}})/I_{\text{off}}$, with $I_{\text{off}}$ and $I_{\text{on}}$ the signal in the plasma-off respectively plasma-on situation, it is reasonable to assume that for these components no interference with other species has occurred. In this case the calculated depletion should therefore be equal to the real depletion.
3.4.3 Emission spectroscopy

In order to discern the differences in the precursor dissociation and excitation mechanisms on addition of N\textsubscript{2} to the Ar/C\textsubscript{2}H\textsubscript{2} plasma -or differently- of C\textsubscript{2}H\textsubscript{2} to the Ar/N\textsubscript{2} plasma, it may be instructive to compare the emission spectra of Ar/N\textsubscript{2}, Ar/N\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} and Ar/C\textsubscript{2}H\textsubscript{2} plasmas. The emission characteristics of Ar/N\textsubscript{2} plasmas have been thoroughly discussed in the previous section. The emission features as encountered by Gielen \textit{et al.} in pure Ar/C\textsubscript{2}H\textsubscript{2} plasmas [84] will first be reviewed briefly. The spectrum of an Ar/C\textsubscript{2}H\textsubscript{2} plasma exhibits the emission of Ar and H lines, CH bands and C\textsubscript{2} radicals (see Figure 3.34, left picture). The emission of the argon lines is explained by the decay of highly excited Ar** atoms produced in the three-particle recombination reaction

\[ \text{Ar}^+ + e^- + M \rightarrow \text{Ar}^{**} + M \]  

(3.4.1)

This process will only be significant close to the arc. The emission of the CH and C\textsubscript{2} radicals and -for a part- also of the hydrogen atoms arises from the argon ion-induced dissociation of the acetylene molecule. As was shown in section 3.2, in a pure argon plasma decomposition of acetylene will take place in two steps. First a (probably rovibrationally excited) acetylene ion is formed via a charge exchange reaction with an argon ion*:

\[ \text{Ar}^+ + \text{C}_2\text{H}_2 \rightarrow \text{Ar} + \text{C}_2\text{H}_2^{+}\nu \]  

(3.4.2)

This ion then rapidly recombines dissociatively with an electron forming electronically and rovibrationally excited molecules:

\[ \text{C}_2\text{H}_2^{+}\nu + e^- \rightarrow \text{C}_2\text{H}^* + \text{H}^* \]  

\[ \rightarrow \text{CH}^* + \text{CH}^* \]  

\[ \rightarrow \text{C}_2^* + \text{H}_2 \]  

\[ \rightarrow \text{C}^* + \text{CH}_2^* \]  

(3.4.3)

The various dissociation channels are displayed in decreasing order of probability [84]. It has recently been shown by Engeln \textit{et al.} that it is even more probable to form

\[ \text{Ar}^+ + e^- + M \rightarrow \text{Ar}^{**} + M \]  

* In the vicinity of the arc the argon metastables (with energies of 11.55 eV (3P2) and 11.72 eV (3P0)) could also contribute to the ionization of the C2H2 molecule (ionization threshold: 11.6eV), or of its dissociation products, via Penning ionization. However, their influence will be of minor importance in comparison to the argon ion-induced dissociation.

Figure 3.34: Emission spectra of an Ar (100 sccs) / C\textsubscript{2}H\textsubscript{2} (2 sccs) plasma (left) and an Ar (95 sccs) / N\textsubscript{2} (5 sccs) / C\textsubscript{2}H\textsubscript{2} (2 sccs) plasma (right) at I\textsubscript{arc} = 48 A, recorded at 7 cm below the arc nozzle.
CH radicals in a second charge exchange/dissociative recombination step, starting from the C$_2$H radical, than directly in the dissociation of C$_2$H$_2$ [41]. Such a second dissociation reaction may also result in excited C$_2$ radicals and H atoms:

\[ \text{Ar}^+ + \text{C}_2\text{H} \rightarrow \text{Ar} + \text{C}_2\text{H}^+ \]  \hspace{1cm} (3.4.4)

\[ \text{C}_2\text{H}^+ + \text{e}^- \rightarrow \text{CH}^* + \text{C}^* \]  \hspace{1cm} (3.4.5)

Yet another way to form CH and/or C$_2$, excluding three-particle volume reactions which are improbable at the low pressures used, is re-association of two atoms at the wall:

\[ \text{C} + \text{C}, \text{H} + \text{wall} \rightarrow \text{C}_2^*, \text{CH}^* + \text{wall} \]  \hspace{1cm} (3.4.6)

However, the reported sticking probability of the C atom is rather high (0.27 [23]), and its abundance is expected to be small regarding the branching ratios of the various dissociation channels. Furthermore, we expect that especially at low temperatures (the wall is approximately at room temperature) only stable molecules will desorb from the surface. Therefore this reaction will only be of minor importance for the C$_2$ production. The excitation of H atoms to the p=2 state (at 10.2 eV) may result from the dissociative recombination reaction of the C$_2$H$_2^+$ ion (reaction (3.4.3)), in which about 10 eV is released. In order to explain the (Balmer series) emission from the higher-lying H levels, the following excitation scheme, which involves hydrogen formed at the vessel walls, should also be considered:

\[ \text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \]  \hspace{1cm} (3.4.7)

\[ \text{ArH}^+ + \text{e}^- \rightarrow \text{Ar} + \text{H}^* \]  \hspace{1cm} (3.4.8)

When C$_2$H$_2$ is injected into the expanding Ar/N$_2$ plasma the spectra reveal a new feature (cf. Figure 3.34, right picture, and Figure 3.35). Next to the bands and lines observed in a pure Ar/C$_2$H$_2$ plasma additional CN(B$^2\Sigma^{-}X^2\Sigma^{-}$) violet system bands appear. The N$_2$-SPS and N$_2^+\text{-FNS}$ bands observed in pure Ar/N$_2$ plasmas (see Figure 3.30) have completely disappeared from the spectrum. This may indicate that nitrogen species are directly involved in the dissociation of acetylene and/or in reactions with the dissociation products. On the other hand, it may also point to a mechanism that prohibits the excitation of the nitrogen species. We know for instance from the arguments in the former section that the N$_2^+$-FNS emission is likely to arise from

![Figure 3.35: Emission spectra of an Ar/N$_2$/C$_2$H$_2$ plasma (95 sccs Ar, 5 sccs N$_2$, 2 sccs C$_2$H$_2$, I$_\text{arc} = 75$ A) at 7 cm (left) and 62 cm (right) below the arc nozzle.](image-url)
charge transfer reactions between ions and ro-vibrationally excited or metastable nitrogen molecules formed at the vessel walls. If in the presence of acetylene this association at the wall is prohibited, e.g. by coverage with hydrogen or carbon species, the \( \text{N}_2^+\text{-FNS} \) band will not be observed. Since the metastable nitrogen species have enough energy to dissociate the acetylene molecule, yet another explanation could be that the nitrogen is actually formed at the vessel walls, but is consumed by reactions with \( \text{C}_2\text{H}_2 \) molecules before it can react with the ions. Nevertheless, the apparent CN emission shows that at least a part of the nitrogen is used in chemical reactions with carbon species.

The plasma emission decreases along the plasma flow as can be seen in Figure 3.35. However, the emission of the CH and C\(_2\) bands and of the Ar and H lines is declining much more than the CN band emission, which is prevailing at the substrate position. Also at the substrate position the Ar/N\(_2\)/C\(_2\)H\(_2\) spectrum does not exhibit the dominant bands observed in the Ar/N\(_2\) spectrum (the \( \text{N}_2^+\text{-FNS} \) bands).

There are many reactions that can occur in the plasma leading to excited CH and CN bands \[85,\]. First of all, and most important, the \( \text{N}^+ \) ions emanating from the arc possess enough energy (14.53 eV) to produce \( \text{C}_2\text{H}_2^+ \) ions (11.4 eV) in a similar charge transfer reaction as presented earlier for the argon ion †. The difference in ionization energy (3.13 eV) is released as kinetic energy or as internal energy of the formed acetylene ion and/or nitrogen atom which can be formed in the N(S) or N(D) metastable state:

\[
\text{N}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2^{+,v,r} + \text{N(S,D)} \quad (3.4.9)
\]

The \( \text{C}_2\text{H}_2^{+,v,r} \) ion may follow the same dissociative recombination reactions as in Ar/C\(_2\)H\(_2\) plasmas. Recent flow tube studies have shown that the \( \text{C}_2\text{H}_2^+ \) ion is unreactive with N\(_2\), but exhibits a moderately fast (2.4×10\(^{-16}\) m\(^3\)⋅s\(^{-1}\)) reaction with N atoms \[86\]:

\[
\begin{align*}
\text{C}_2\text{H}_2^+ + \text{N} & \rightarrow \text{HCCN}^+ + \text{H}, & 60 \%, \Delta E = -0.52 \text{ eV} \quad (3.4.10) \\
& \rightarrow \text{HCNH}^+ + \text{C}, & 25 \%, \Delta E = -1.39 \text{ eV} \\
& \rightarrow \text{C}_2\text{N}^+ + \text{H}_2, & 10 \%, \Delta E = -0.85 \text{ eV} \\
& \rightarrow \text{CH}^+ + \text{HCN}, & 5 \%, \Delta E = -0.43 \text{ eV}
\end{align*}
\]

However, the dissociative recombination with an electron is so fast (~10\(^{-13}\) m\(^3\)⋅s\(^{-1}\)), that this reaction will hardly take place. A reaction sequence that has tentatively been proposed by Platzner et al. \[85\] would provide an additional dissociation path for the acetylene molecule‡:

\[
\begin{align*}
\text{N} + \text{C}_2\text{H}_2 & \rightarrow \text{HCN} + \text{CH}, & \Delta E \approx -0.6 \text{ eV} \quad (3.4.11) \\
& \rightarrow \text{CN} + \text{CH}_2, & \Delta E \approx -0.6 \text{ eV} \\
\text{C}_2\text{H}_2 + \text{CN} & \rightarrow \text{H-C≡C-CN} + \text{H}, & \Delta E \approx 0 \text{ eV} \quad (3.4.12)
\end{align*}
\]

The nitrogen-containing products formed during the acetylene dissociation or by abstraction reactions at the vessel walls, may be another important source of CN and CH emission when they are involved in a secondary dissociation reaction, e.g.:

\[
\text{Ar}^+ + \text{HCN} \rightarrow \text{Ar} + \text{HCN}^+, \text{ followed by} \quad (3.4.13)
\]

---

† The possibility that a molecular \( \text{N}_2^+ \) ion is involved in the charge exchange with acetylene can be excluded, since the dissociative recombination with an electron is many times faster as long as the electron density is above 10\(^{17}\) m\(^{-3}\).

‡ The reaction enthalpies have been estimated from the binding enthalpies.
Chapter 3

HCN$^+ + e^- \rightarrow H + CN^*$  \hspace{1cm} (3.4.14)

More downstream such secondary dissociation reactions will become less important. The N atoms will also be consumed by reactions with the dissociation products. For the reaction(s) of nitrogen species with the C$_2$H radical, which is probably the main dissociation product of acetylene [83], no data in literature was available. Hence, we tentatively propose the following reactions$^8$:

\[
\begin{align*}
N + C_2H & \rightarrow C + HCN, \quad \Delta E \approx -0.6 \text{ eV} \quad (3.4.15) \\
& \rightarrow CN + CH, \quad \Delta E \approx -0.6 \text{ eV}
\end{align*}
\]

However, further work is necessary to elucidate the true mechanism. When the ions are in excess, the C$_2$H radicals formed in the first dissociation step may be involved in a second charge exchange reaction leading to a C$_2$H$^+$ ion (reaction (3.4.4)). This ion is found to undergo slow association with N$_2$ [86], but again a more rapid ($\sim 10^{16} \text{ m}^3 \cdot \text{s}^{-1}$) reaction with N atoms [87,88]. For the CH radical the following exothermic reactions with nitrogen are reported:

\[
\begin{align*}
N(4S) + CH(X) & \rightarrow CN(B) + H, \quad \Delta E = -1.09 \text{ eV} \quad (3.4.16) \\
& \rightarrow CN(A) + H, \quad \Delta E = -3.16 \text{ eV} \\
& \rightarrow CN(X) + H, \quad \Delta E = -4.31 \text{ eV} \\
& \rightarrow HCN^*, \quad \Delta E = -9.6 \text{ eV}
\end{align*}
\]

having an overall rate of $\approx 10^{-17} \text{ m}^3 \cdot \text{s}^{-1}$ [89]. The metastables N(2D) and N(2P) will have the same reaction paths, only a larger amount of energy is released in the corresponding reactions, giving rise to CN in highly excited rotational and vibrational states. Finally, the C$_2$ radicals may also contribute to the consumption of N atoms by the following exothermic reaction:

\[
N(4S) + C_2(X) / C_2(a) \rightarrow CN + C, \quad \Delta E = -1.3 \text{ eV} \quad (3.4.17)
\]

All the above mentioned reactions lead to a general shift from C$_x$H$_y$ species towards CN and C, which could explain the observed dominance of the CN emission in the downstream part of the plasma. Furthermore, the diffusion of CH radicals towards the walls is expected to be faster than that of the CN radicals due to the smaller mass. If the sticking probability of the CH radicals is also larger, a higher concentration of CN radicals in the deposition zone will be found. Another argument for the prevalence of the CN bands over the CH bands along the plasma flow is the larger stability of the CN radical. This is indicated by the dissociation energy of the CH radical (3.47 eV) which is much lower than that of the CN radical (7.55 eV).

The destruction of the formed CN radicals may proceed via reactions like:

\[
\begin{align*}
N + CN & \rightarrow C + N_2, \quad \Delta E = -0.55 \text{ eV}, \ k \approx 10^{17} - 10^{16} \text{ m}^3 \cdot \text{s}^{-1} \quad [90] \quad (3.4.18) \\
CN + H_2 & \rightarrow HCN^* + H, \quad \Delta E = -3.92 \text{ eV}, \ k \approx 3 \times 10^{18} - 4.5 \times 10^{17} \text{ m}^3 \cdot \text{s}^{-1} \quad [91] \quad (3.4.19)
\end{align*}
\]

At CN densities of $10^{17}$-$10^{18} \text{ m}^{-3}$ these destruction mechanisms may not be very relevant, although H$_2$, being a stable molecule, can dwell in the gas phase for as long as the residence time ($\sim 0.4$ s).

It is clear from the reactions presented above that not many nitrogen atoms will reach the vessel walls where they can re-associate to form N$_2$ molecules. Moreover, in contrast to pure Ar/N$_2$ plasmas, in the Ar/N$_2$/C$_2$H$_2$ deposition plasmas the vessel surface is covered with a carbon-containing layer. The few nitrogen atoms that

$^8$ The reaction enthalpies have been estimated from the binding enthalpies.
succeed to reach the wall will therefore encounter a surface condition that differs from the stainless steel wall in the case of pure Ar/N\textsubscript{2} plasmas. Consequently, the re-association at the wall will be controlled by an altered association probability, which is probably different from that on stainless steel [92]. In fact, as will be shown in the next section, the N atoms can easily react with (hydro)carbon surfaces to produce volatile - and sometimes electronically excited [93,94] - CN radicals or HCN and C\textsubscript{2}N\textsubscript{2} molecules, which are released in the plasma volume. We therefore expect that virtually no N\textsubscript{2} molecules are formed at the vessel walls, and that those that are formed will be consumed in the background before they can reach the ions in the plasma beam. As a consequence, the emission of the N\textsubscript{2}-SPS and N\textsubscript{2}\textsuperscript{+}-FNS bands is absent.

For excitation of the CN(B), CH(A) and CH(B) levels an energy of approximately 3 eV is needed. In the recombining Ar/N\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} plasma the mean electron temperature is rather low (~ 0.3 eV), which makes excitation of these levels by electrons improbable. As has been mentioned above, excitation by secondary dissociation of the nitrogen-containing dissociation and/or wall-produced products, e.g. HCN, will only be important in the upstream region. Therefore, in the late expansion excitation of the CH and CN radicals may either result from the radical formation itself** or from excitation transfer from rovibrationally excited and/or metastable molecules, e.g. the long-lived vibrational metastable states of the N\textsubscript{2}(X) and C\textsubscript{2}(X) molecules and the electronically metastable N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsuperscript{+}) state. However, since these energetic species are not so abundant, as argued before, they are expected to have only a small contribution to the excitation.

The consequence of excitation by chemical processes is that the energy involved in the reactions is only distributed to specific states that comply with the physical conservation laws. This induces a non-equilibrium distribution over the energy levels of the nascent species population, which will evolve towards thermal equilibrium, i.e. a Boltzmann distribution, due to collisional relaxation. At low pressures the relaxation of the energy levels towards an equilibrium distribution will be slower than at higher pressures and the non-equilibrium situation may persist for a longer time. In such cases physical quantities, e.g. molecular rotational and vibrational temperatures, which are well defined for equilibrium conditions could become meaningless and must be used with care. In that respect, the rotational and vibrational temperature values that have been derived from simulations of the optical emission spectroscopy data [75], and which will be presented hereafter, should not be confused with the true thermodynamic temperatures. As a matter of fact, when certain levels are selectively populated by chemical reactions, it is expected to find temperatures that are higher than the true thermodynamic (gas) temperature, since the emission intensity coming from selectively populated levels is averaged over all the energy levels in the simulation procedure. The rotational and vibrational temperatures obtained from the simulation can thus still give valuable information on the existence of such selective excitation processes and the degree of non-equilibrium in the system. In some situations where the selective population process can be hypothesized, its effect can be introduced into the simulation procedure [61]. Otherwise, the non-equilibrium energy distribution manifests itself by different apparent temperatures for the different plasma species and a large difference in rotational and vibrational temperatures for one and the same species.

** This type of excitation is also referred to as ‘chemiluminescence’.
The rotational and vibrational temperatures of the CH(A-X), CH(B-X) and CN(B-X) bands have been calculated for both Ar/C2H2 and Ar/N2/C2H2 plasmas. An example of an experimental and fitted spectrum of the CH(B-X) band is given in Figure 3.36.

When we compare the ro-vibrational temperatures obtained in both plasmas (see Table I) we can draw three important conclusions. First, the very disparate and rather high rotational and vibrational temperatures of the two CH radical states point to a strong non-equilibrium effect due to different excitation channels. The observed values are in good agreement with the values found earlier by Beulens et al. in an expanding Ar/CH4 plasma [2], but are 2-3 times higher than the temperatures reported for the same states in an arcjet plume of Ar/H2/CH4 [95]. This is not at all surprising considering the approximately 100 times higher pressure used in that experiment (25 mbar compared to 0.25 mbar in our case) which strongly enhances the collisional relaxation, and the difference in excitation mechanism which in that case is mainly governed by electron collisions. A second striking feature is that the CH radical temperatures measured in Ar/C2H2 and Ar/N2/C2H2 plasmas are almost equal (within 10%) indicating that in both plasmas the CH radicals are excited via similar excitation reactions. It seems that the presence of N2 does not alter the excitation channel of the CH radical. For the CN radical even higher ro-vibrational temperatures are found indicating that the reactions in which it is produced have a high degree of exothermicity.

<table>
<thead>
<tr>
<th></th>
<th>CH(A-X)</th>
<th>CH(B-X)</th>
<th>CN(B-X)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trot (K)</td>
<td>Tvib (K)</td>
<td>Trot (K)</td>
</tr>
<tr>
<td>Ar/C2H2</td>
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<td>3010</td>
<td>8780</td>
</tr>
<tr>
<td>Ar/N2/C2H2</td>
<td>4025</td>
<td>2955</td>
<td>8230</td>
</tr>
</tbody>
</table>

**Table 3.4:** Rotational and vibrational temperatures of the CH and CN radical bands in an Ar (100 sccs) / C2H2 (2 sccs) and Ar (95 sccs) / N2 (5 sccs) / C2H2 (2 sccs) plasma at $I_{arc} = 48A$, $p=0.25$ mbar.
The simulations can also provide an estimation of the ground state densities of the species concerned by taking into account the self-absorption of radiation in the plasma. In Figure 3.37 the calculated ground state densities of the CN and CH radicals are shown as a function of the admixed nitrogen flow and as function of the arc current. As can be seen, the CN density increases on addition of nitrogen to the plasma, whereas the CH density decreases. This is in accordance with what we have discussed earlier about the chemistry: the introduction of nitrogen into Ar/C₂H₂ plasmas leads to a shift from CₓHy species towards CN and C. The increase of both the CH and CN density with increasing arc current is also very logical considering that both radicals can only be produced in the dissociation of acetylene or from its dissociation products. Since the arc current controls the ion density emanating from the arc and thereby the dissociation capacity, a higher arc current will lead to more production of the two radicals. From the calculated densities it can be concluded that in the plasma phase the CN radical is about one order of magnitude more abundant than the CH radical. The value of the CH density deduced from the emission spectrum at the substrate position ($\sim 10^{17}$ m$^{-3}$) agrees well with recent Cavity Ring Down absorption spectroscopy measurements performed in the same Ar/C₂H₂ plasma under the same conditions [41]. This gives us confidence that the results of the simulation are reliable.

### 3.4.4 Mass spectrometry

With the help of mass spectrometry data we can try to address the question whether nitrogen species are really involved in the dissociation of acetylene or are just reacting with the dissociation products. Moreover, the data may reveal whether the addition of nitrogen leads to a more effective depletion of the precursor gas or not. The analysis of the mass spectra is however troubled by the large number of species that might possibly enter the gas analyzer and of which in most cases the cracking patterns are not known. With other words, a good deconvolution of the spectrum is
This not only prohibits us to make a quantitative statement with certainty, but could also conceal the presence of less abundant species in the spectrum. These difficulties notwithstanding, a great deal of information may be obtained by comparing the spectra of Ar/N₂, Ar/C₂H₂ and Ar/N₂/C₂H₂ plasmas. The predicted and measured cracking patterns for the three species are depicted in Table 3.5. Apparently, only for masses 28 and 14 amu an unambiguous assignment can not be given due to interference of N₂ and C₂H₂. However, the contribution of the C₂H₂ signal to the N₂ signal is so small (0.3 % C₂H₂ on 100 % respectively 9.1 % N₂ for mass 28 and 14 amu) that it appears to be negligible in comparison with the uncertainty of the measurement.

<table>
<thead>
<tr>
<th>Species</th>
<th>M/z (amu)</th>
<th>Predicted††</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>40</td>
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<td>100 %</td>
</tr>
<tr>
<td></td>
<td>38</td>
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<td>0.1 %</td>
</tr>
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</tr>
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<td>10 %</td>
</tr>
<tr>
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</tr>
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</tr>
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<tr>
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</tr>
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<td>C₂H₂</td>
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<td>0.3 %</td>
</tr>
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<td></td>
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<td>3.0 %</td>
<td>3.0 %</td>
</tr>
</tbody>
</table>

Table 3.5: Predicted [96] and measured cracking patterns of the investigated species in the gas phase (plasma off). All spectra have been recorded with a 30 µm pinhole and at the same electron-multiplier settings (gain: 198, voltage: 1190 V).

infeasible. This not only prohibits us to make a quantitative statement with certainty, but could also conceal the presence of less abundant species in the spectrum. These difficulties notwithstanding, a great deal of information may be obtained by comparing the spectra of Ar/N₂, Ar/C₂H₂ and Ar/N₂/C₂H₂ plasmas. The predicted and measured cracking patterns for the three species are depicted in Table 3.5. Apparently, only for masses 28 and 14 amu an unambiguous assignment can not be given due to interference of N₂ and C₂H₂. However, the contribution of the C₂H₂ signal to the N₂ signal is so small (0.3 % C₂H₂ on 100 % respectively 9.1 % N₂ for mass 28 and 14 amu) that it appears to be negligible in comparison with the uncertainty of the measurement.

Figure 3.38: The production (plasma on - plasma off signal) of new species in an Ar (80 sccs) / N₂ (20 sccs) / C₂H₂ (18.7 sccs) plasma (left) and an Ar (100 sccs) / C₂H₂ (18.7 sccs) plasma (right) at I_{arc} = 57 A.

†† The cracking pattern is strongly dependent on the settings of the mass spectrometer and on the way the gas is extracted. Therefore, the predicted values should be considered merely as an indication.
In Figure 3.38 the production (plasma on – plasma off signal) of new species in an Ar/N$_2$/C$_2$H$_2$ plasma is shown along with the production in an Ar/C$_2$H$_2$ plasma. On first sight, in the Ar/N$_2$/C$_2$H$_2$ plasma the only new species created is HCN at 27 amu. The molecules H$_2$ (2 amu), C$_3$H$_n$ (36-44 amu), C$_4$H$_n$ (48-58 amu) and C$_6$H$_n$ (72-86 amu) are also produced in the Ar/C$_2$H$_2$ plasmas. A closer look however reveals that the distribution of the peaks in the 48-58 amu and the 72-86 amu range is different from the Ar/C$_2$H$_2$ case (see Figure 3.39). The maximum signal is obtained for a mass of 51 amu instead of 50 amu, respectively 75 amu instead of 74 amu. This may be an indication that H-(C≡C)$_n$-C≡N polymers with $n = 0$, 1 and 2 are formed, as has been proposed by Platzner et al. [85], or C$_2$N$_2$ (52 amu), but could also mean that the presence of nitrogen leads to the dominance of other hydrocarbon polymers with a different cracking pattern.

For the acetylene plasma the maximum signal at 50 amu has been tentatively ascribed to C$_4$H$_2$. In order to explain a shift of the maximum signal due to C$_4$H$_n$ polymers, we have to assume that in addition of nitrogen more hydrogen-rich polymers, i.e. C$_4$H$_4$ - C$_4$H$_{10}$, are formed. Further investigation of the spectrum shows that at 17 amu a new feature arises when the plasma is switched on. This very small (<10$^{-13}$ A) contribution which appears in both spectra (cf. Figure 3.38) as well as in the

**Figure 3.39:** Mass spectra of an Ar (100 sccs) / C$_2$H$_2$ (18.7 sccs) (solid line) and an Ar (80 sccs) / N$_2$ (20 sccs) / C$_2$H$_2$ (18.7 sccs) plasma (dotted line) at $I_{arc} = 57$ A

In Figure 3.38 the production (plasma on – plasma off signal) of new species in an Ar/N$_2$/C$_2$H$_2$ plasma is shown along with the production in an Ar/C$_2$H$_2$ plasma. On first sight, in the Ar/N$_2$/C$_2$H$_2$ plasma the only new species created is HCN at 27 amu. The molecules H$_2$ (2 amu), C$_3$H$_n$ (36-44 amu), C$_4$H$_n$ (48-58 amu) and C$_6$H$_n$ (72-86 amu) are also produced in the Ar/C$_2$H$_2$ plasmas. A closer look however reveals that the distribution of the peaks in the 48-58 amu and the 72-86 amu range is different from the Ar/C$_2$H$_2$ case (see Figure 3.39). The maximum signal is obtained for a mass of 51 amu instead of 50 amu, respectively 75 amu instead of 74 amu. This may be an indication that H-(C≡C)$_n$-C≡N polymers with $n = 0$, 1 and 2 are formed, as has been proposed by Platzner et al. [85], or C$_2$N$_2$ (52 amu), but could also mean that the presence of nitrogen leads to the dominance of other hydrocarbon polymers with a different cracking pattern.

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**Figure 3.40:** Left: Consumption (plasma off - plasma on signal) in an Ar (80 sccs) / N$_2$ (20 sccs) / C$_2$H$_2$ (18.7 sccs) plasma. Right: Average depletion of masses 24, 25 and 26 amu as function of the injected acetylene flow in a 100 sccs Ar plasma (■) and an Ar (90 sccs) / N$_2$ (10 sccs) plasma (○) at $I_{arc} = 57$ A.
background spectrum is attributed to interference of the H₂O (18 amu) cracking pattern. It is probably not due to the production of NH₃. Creation of NH₃, if any, should therefore be negligible.

It is clear from Figure 3.40, where the consumption in the Ar/N₂/C₂H₂ plasma is shown that both acetylene and nitrogen are consumed. The nitrogen consumption is much more dramatic (up to 40 %) than in the case of an Ar/N₂ plasma, where no nitrogen is depleted. This clearly demonstrates the involvement of nitrogen species in the plasma chemistry and the deposition.

To clarify the effect of nitrogen on the dissociation of acetylene, the depletion of acetylene must be calculated in an unambiguous way. Since we do not know what possible species may enter the gas analyzer, and how their cracking patterns may influence the C₂H₂ signal, we have decided to calculate the acetylene depletion from the three components at 24, 25 and 26 amu. It is very unlikely that the signal of an interfering species will contribute to the three signals with exactly the same amount. Hence, if the three depletions calculated are consistent with each other, these values should with great certainty represent the real acetylene consumption. The average depletion of the three components, which agree within 10 %, is shown in Figure 3.40. Since addition of nitrogen to the main flow in the arc will lead to replacement of argon ions by atomic nitrogen ions, this result suggests that the nitrogen ions are more effective in the dissociation of acetylene and/or that the N atoms also contribute to the dissociation.

### 3.4.5 Conclusions

Comparison of Ar/N₂, Ar/C₂H₂ and Ar/N₂/C₂H₂ plasmas reveals very distinct chemistries, leading to different products and excitation mechanisms. In Ar/N₂/C₂H₂ plasmas the emission observed in Ar/N₂ plasmas is absent, indicating that formation of (metastable and/or excited) N₂ is prohibited in the presence of C₂H₂. This may be explained by a coverage of the wall with C, H or CₘHₙ species which prevents association of N atoms and/or promotes incorporation of nitrogen in the wall. Another explanation might be the loss of N atoms or wall-produced N₂ species by volume reactions. It is evident from the observed CN emission and mass spectrometry data that a part of the nitrogen species is indeed consumed. The mass spectrometry data also suggest that in comparison with a pure Ar/C₂H₂ plasma new, nitrogen-containing products, e.g. HCN (27 amu), H-C≡C-C≡N (51 amu), C₂N₂ (52 amu), are formed. The outlined chemistry predicts a shift from CH species towards CN and C. This is reflected in the emission of the CN radical, which becomes increasingly dominant over the CH and C₂ emission along the plasma flow, and in the estimated ground state densities of the CH and CN radicals, which decrease respectively increase with nitrogen seeding. From the unexpectedly high ro-vibrational temperatures obtained for both the CH and CN radical it is concluded that excitation of these radicals must occur either during their formation or by excitation transfer from chemically excited N₂ or C₂ molecules. Since the ro-vibrational temperatures of the CH radicals in pure Ar/C₂H₂ and in Ar/N₂/C₂H₂ plasmas are within 10 %, the excitation and -consequently- production pathway must be unaffected by the addition of N₂. The admixture of nitrogen leads to an even more efficient depletion of the acetylene molecules, probably due to a higher charge exchange efficiency of nitrogen ions compared to that of argon ions and/or involvement of N atoms in the dissociation process.
3.5 Graphite Nozzle Plasmas

3.5.1 Introduction

Many different techniques have been used for the synthesis of carbon nitride films. Attempts to produce carbon nitride from hydrocarbon precursor gases [82,97] proved that for the realization of hard films incorporation of hydrogen should be avoided. Therefore, new hydrogen-free carbon precursors have to be sought. In this thesis we introduce a graphite nozzle through which an Ar/N₂ plasma is expanding as a hydrogen-free carbon source.

The combination of an Ar/N₂ arc plasma with graphite has been used before for deposition of CNₓ films [98,99]. However, in these two cases the arc was used to evaporate the graphite anode, in contrast to our (water-cooled) graphite nozzle which remains at temperatures well below the evaporation temperature. Most other techniques employing graphite in combination with either nitrogen gas or nitrogen plasmas, e.g. laser ablation of a graphite target in a nitrogen environment [100], DC magnetron sputtering of graphite in Ar/N₂ discharge [101], involve physical sputtering of the graphite. In our case however, physical sputtering of the graphite nozzle can not occur, as will be shown hereafter. The etching of the nozzle must therefore be chemically induced.

In this section the deposition plasmas created with the graphite nozzle are investigated by means of optical emission spectroscopy and mass spectrometry to elucidate the creation of the growth precursors and the downstream plasma chemistry. From simulation of the emission spectra we obtain an estimation of the density of the CN radicals, which we propose as the depositing species, close to the substrate. The temperature of the graphite nozzle as determined by pyrometry is used as a measure for the power dissipated in the arc. In this way we can reveal the influence of the arc power on the production of growth precursors and the influence of the nozzle diameter, which increases during deposition, on the production of precursors. Moreover, in this section a mechanism for the graphite etching and precursor generation will be proposed.

3.5.2 Experimental

The deposition set-up, which has been described in detail in section 2.2 and elsewhere [83], is depicted in Figure 3.41 along with the arc and the graphite nozzle. The arc generates a subatmospheric (≈0.40 kPa) thermal Ar/N₂ plasma which expands into the low pressure vessel (≈30 Pa) through a graphite nozzle. For some experiments the exit diameter of the nozzle is kept fixed by means of a molybdenum (Mo) piece with variable diameter.

Argon and nitrogen are introduced in the arc with a total flow of 100 sccs. The amount of nitrogen is varied (0-30% of the total flow) as well as the current through the arc (30-89 A). The temperature at the outside of the graphite nozzle is determined at three positions with a pyrometer (Chino, Comet 1000) using an emissivity of 0.80 for graphite. The temperature averaged over the three positions has a typical uncertainty of ±10 K. The optical emission spectra of the N₂⁺-FNS (B²Σ→X²Σ) band and the B²Σ→A²Π CN-band are simulated, using a method described elsewhere [100], to obtain the vibrational and rotational temperatures and the ground state densities including the self-absorption of the plasma.
3.5.3 Results

The emission spectra from a pure Ar plasma and Ar/N\textsubscript{2} plasmas expanding through the graphite nozzle are presented in Figure 3.42. In the case of an Ar plasma only Ar emission lines are observed\textsuperscript{*}. No noticeable differences with an Ar plasma operated with a copper nozzle are observed. Moreover, no excited carbon or C\textsubscript{2} is detected, which may be explained by the fact that the excitation energies (7.95 and 2.45 eV respectively) are relatively high compared to the average electron energy in the expansion (≈0.3 eV), but is most likely due to the absence of carbon species. When nitrogen is added, again no C and C\textsubscript{2} emission is observed, however, the B\textsuperscript{2}\Sigma→A\textsuperscript{2}\Pi CN-bands clearly appear in the emission spectrum. Since the electron

\textsuperscript{*} The very small CN emission features observed in the spectrum are probably due to contamination of the vessel walls.
energy is too low for significant excitation of the $B^2\Sigma$ level (3.2 eV required), this points to an excitation mechanism which involves a chemical reaction. But more importantly, in the case of an Ar/N₂ plasma deposition takes place, whereas in a pure Ar plasma no deposition is observed after one hour of operation, as testified by in situ ellipsometry, a technique with Å sensitivity.

Since graphite has a much higher temperature of evaporation than copper and Ar/N₂ plasmas do not affect the copper nozzle, the evaporation of graphite can be excluded. Also physical sputtering of the graphite can be excluded, since the sputtering efficiency of nitrogen ions is lower than that of argon ions. Moreover, the maximum ion energy in the arc (~1 eV) is much lower than the energies usually reported for ion sputtering (several tens of Volts [101]). We therefore postulate that nitrogen is needed to induce a chemical etching, e.g. via the weakly exothermic (0.17 eV for N($^3S$) [102]) reaction:

$$\text{C(solid)} + \text{N} \rightarrow \text{CN(gas)} \ [103] \quad (3.5.1)$$

The nitrogen ions (atomic or molecular) should be in small amounts near the nozzle, because it is the anodic part of the discharge and thus the ions will be repelled. The process cannot be based on nitrogen molecules either, because the reaction of nitrogen molecules with the carbon surface:

$$\text{C(solid)} + \frac{1}{2} \text{N}_2(gas) \rightarrow \text{CN} \quad (3.5.2)$$

is strongly endothermic (4.7 eV at 298 K [103]). Moreover, due to the high dissociation degree in the arc the concentration of molecular species will be small at the nozzle.

Hellgren et al., who explained the decrease in growth rate of their magnetron sputtered CNₓ films with increasing nitrogen seeding by nitrogen-induced chemical sputtering, suggested that, since the C≡N dimer is not a stable saturated molecule, it is more reasonable to assume that cyanogen (C₂N₂) molecules are emitted [104]. As a possible mechanism for the formation of the C₂N₂ molecule they proposed a reaction between two C≡N radicals which diffuse on the surface until they desorb.

In this picture the CN radicals formed at the graphite nozzle may only desorb into the gas phase when they meet another CN radical to form a volatile C₂N₂ molecule. However, because this process occurs in the nozzle where the ion density is high, the C₂N₂ will be almost immediately dissociated again via the following mechanism:

$$\text{Ar}^+ / \text{N}^+ + \text{C}_2\text{N}_2 \rightarrow \text{Ar} / \text{N} + \text{C}_2\text{N}_2^+, \text{followed by} \quad (3.5.3)$$

$$\text{C}_2\text{N}_2^+ + \text{e}^- \rightarrow \text{CN}^* + \text{CN}^* \quad (3.5.4)$$

In this reaction again CN radicals are formed which may be in an excited state. The CN radicals formed in reaction (3.5.1) may also be excited to the $B^2\Sigma$ level (at 3.2 eV) when the metastable N($^3P$) state at 3.6 eV is involved. So, when we assume that the CN radicals can immediately desorb from the graphite surface, we have two processes (reactions (3.5.1) and (3.5.3)) to explain the CN emission in the vicinity of the nozzle†. However, the fact that the CN emission is also observed at the substrate position (≈1 ms after the excitation) while the radiative lifetime is only about 65 ns, proves that (also) another excitation mechanism is present.

† The excitation transfer from argon metastables, which are in considerable amounts close to the arc, is not possible, since the excitation energy of ~11.5 eV surpasses the dissociation energy of the CN molecule (7.55 eV).
A possible mechanism for CN excitation in the late expansion is the atomic recombination of C and N atoms in the presence of a third body:

\[ C + N + M \rightarrow \text{CN}(B^2\Sigma, v' = 7) + M \]  

with \( k = 9.4 \times 10^{-45} \text{ m}^6\text{s}^{-1} \). The recombination process should produce CN\((B^2\Sigma)\) molecules with overpopulation of level \( v = 7 \) as has been previously reported \([77,105]\). However, at the low pressure in our system these three-particle reactions are highly improbable unless they occur at the vessel wall, which then serves as a third body.

The electron temperature measured in Ar/N\(_2\) plasmas operated with a copper nozzle is in the range of 0.4-0.6 eV (see section 3.3.4). It is expected that the presence of a graphite nozzle will not influence this value much, but probably the electron density will be lower due to the extreme electronegativity of the CN radical \((2.55 \text{ eV for CN}(X) \text{ and } 5.75 \text{ eV for CN}(B^2\Sigma) \text{ [106])}. \) Under these conditions population of the CN\((B^2\Sigma)\) state by electron collisions will be negligible as well.

As has been aforementioned in section 3.3, the Ar/N\(_2\) plasma is an important source of vibrationally excited ground state nitrogen molecules \( \text{N}_2(X,v>0) \) which are metastable species and of metastable \( \text{N}_2(A) \) molecules. These are most likely formed by re-association at the wall. The re-association should be small for carbon covered walls as has been discussed in the section before. However, the emission of the \( \text{N}_2^+\)-FNS is still present in the spectra indicating that the energetic nitrogen species, which are necessary for excitation of the \( \text{N}_2^+\)-FNS bands are available in the plasma. The energy of the roto-vibrational \( \text{N}_2(X,v>0) \) states and/or metastable \( \text{N}_2(A) \) could also be transferred to the CN molecule thereby populating the \( \text{CN}(B^2\Sigma) \) state. In the late expansion this is probably the most important excitation mechanism for the CN radical.

As a last possibility for CN emission in the downstream plasma the mechanism proposed in reaction (3.5.3) should be considered. The \( \text{C}_2\text{N}_2 \) molecules formed at the nozzle surface will not survive in the late expansion. However, association of two CN radicals at the wall may lead to the formation of a cyanogen molecule:

\[ \text{CN} + \text{CN} + (\text{wall}) \rightarrow \text{C}_2\text{N}_2 + (\text{wall}), \Delta E = -4.1 - -5.4 \text{ eV} \]  

(3.5.6)

Figure 3.43: The consumption (plasma off – plasma on signal) and production (plasma on – plasma off signal) in an Ar \((70 \text{ sccs}) / N_2 \((30 \text{ sccs}) \) plasma at \( I_{\text{arc}} = 89 \text{ A} \) expanding through a graphite nozzle.
The presence of C$_2$N$_2$ is testified by mass spectrometry data shown in Figure 3.43. However, its contribution is very small, suggesting that the CN emission in the downstream part is predominantly established via reactions with energetic nitrogen species produced at the vessel walls. In fact, C$_2$N$_2$ is the only species that is produced in the plasma. At the same time N$_2$ is consumed, as can be deduced from the signal at masses 28, 29 and 14. Assuming a linear dependence for the mass spectrometry signal, it can be concluded that about 5.8 – 7.5 % of the nitrogen is consumed under the conditions presented in Figure 3.43. If all the nitrogen is used for the formation of CN radicals, this means that about 1.7 – 2.3 sccs of CN radicals should emanate from the arc.

The CN bandhead emission intensity ($I_{CN}$) increases with increasing arc current and decreases with increasing distance from the nozzle. The increase and decrease are more pronounced for higher respectively lower N$_2$ flows. The increase of $I_{CN}$ with increasing arc current is explained by the increased dissociation degree at higher arc currents. At the same time, admixture of nitrogen in the arc will lead to a higher arc voltage when the arc current is kept constant. Thus, the power put into the plasma will also increase with nitrogen seeding and so will the CN production. This explains why the increase of $I_{CN}$ with increasing arc current is more prominent for higher N$_2$ flows. The decrease of $I_{CN}$ with increasing distance from the nozzle is related to radiative decay of the excited state and loss processes of the CN radicals, e.g. chemistry, diffusion and deposition on the walls. If the nitrogen atoms are in excess, the CN radicals are destroyed by the following reaction:

$$N + CN \rightarrow C + N_2, \quad k \approx 10^{-17} - 10^{-16} \text{ m}^3\text{s}^{-1} \text{ at room temperature} \quad [107] \quad (3.5.7)$$

The N atoms, on the other hand, are also responsible for creation of the CN radicals and are necessary for formation of energetic nitrogen molecules which could lead to excitation of CN in the late expansion. This complex interplay between creation, destruction and excitation of the CN radicals is reflected in the dependence of $I_{CN}$ on the nitrogen seeding. At larger distances (the higher the arc current the larger the distance) from the nozzle $I_{CN}$ increases with increasing N$_2$ flow, whereas close to the nozzle almost no dependence is observed. This example shows that far away from the nozzle the excitation and formation of CN are two separate processes. Therefore, it is not surprising that the densities of the CN ground state (CN(X)) derived from the emission spectrum calculations have no correlation with $I_{CN}$. The CN(X) density was

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**Figure 3.44:** The nozzle temperature measured with a pyrometer for (■) Ar (100 sccs) and (●) Ar (70 sccs) / N$_2$ (30 sccs) plasmas as function of arc current (left) and as function of nitrogen seeding at $I_{arc} = 89$ A (right).
Chapter 3

estimated to be $7 \times 10^{17} \text{ m}^{-3}$ at 5 cm from the arc, i.e. $\sim 2.4 \text{ cm}$ from the nozzle exit, and $\sim 8 \times 10^{16} \text{ m}^{-3}$ at 62 cm from the arc.‡ When we assume that the CN radical is the main growth precursor, as suggested by the measurements presented in section 5.2, with these high densities the observed growth rate (several nm’s per second) can be explained.

A good measure for the power put into the plasma is the temperature of the graphite nozzle. The temperatures as measured with a pyrometer are depicted in Figure 3.44 as function of the arc current and nitrogen seeding. As can be seen, the temperature of the graphite increases with both the arc current and nitrogen seeding. This is attributed to the arc power which, as has been explained before, increases on increase of both parameters. The relatively small difference in nozzle temperature between pure argon plasmas and argon/nitrogen plasmas (±100 K) shows that the nozzle is not considerably heated by the etching reaction. Moreover, it shows that it is not the graphite temperature which is the limiting parameter for etching, but the presence of nitrogen.

Due to the erosion of the nozzle, the diameter of the nozzle increases in time. This leads to a lower growth rate, and is accompanied by a change in the quality of the deposited material (see section 5.2). To understand this decrease in growth rate with increasing nozzle diameter, experiments have been conducted on nozzles with variable diameter. As an additional option a molybdenum piece with a fixed diameter could be mounted on the nozzle outlet (cf. Figure 3.41). The influence of the nozzle diameter and/or exit conditions on the arc characteristics is clearly demonstrated in Figure 3.45. Apparently, the nozzle may be considered as a prolongation of the arc channel, imposing by its diameter the pressure inside the arc and thereby the arc voltage. The decrease of growth rate with time, i.e. with increasing nozzle diameter, thus boils down to a decrease of arc power, which affects the production of CN radicals negatively. The consequences of the reduced growth rate for the film properties will be dealt with in section 5.2.

‡ In the calculation of the ground state densities from the self-absorption of the plasma a constant plasma beam radius is taken into account.
3.5.4 Conclusions
The Ar/N$_2$ arc plasma expanding through a graphite nozzle, which is used to deposit CN$_x$ films, has been investigated. In the absence of nitrogen no graphite is sputtered. This indicates that the sputtering is a chemical rather than physical process. We propose that CN radicals are formed at the graphite surface via a reaction of nitrogen atoms with carbon atoms in the solid. In this process excited CN radicals may be formed. During the late expansion, where, despite the low electron temperature, the CN emission is still observed, the excitation is probably realized by excitation transfer reactions with metastable energetic nitrogen species, e.g. N$_2$(X,$\nu>0$) and N$_2$(A). The excitation and formation of CN seem to be two separate mechanisms, and therefore no correlation between the CN emission and deposition rate is expected. The high densities obtained from simulation of the emission spectrum for the CN(X) ground state close to the substrate could account for the observed growth rate. This makes the CN radical a very plausible candidate as the dominant growth precursor in this type of plasma. From measurements of the nozzle temperature it is concluded that the highest production of CN radicals is achieved at high arc currents and nitrogen seedings. A study on the influence of nozzle diameter on the arc characteristics reveals that the observed decrease of growth rate in time (see section 5.2) can be reduced to an increase of the nozzle diameter accompanied by a decrease of arc power.
References


Plasma Characterization

[96] The predicted cracking patterns were taken from the library supplied with the AccuQuad Residual Gas Analyzer software of the Kurt J. Lesker Company.
Chapter 4

Plasma-induced Etching

4.1 Introduction

Before we can proceed to the discussion of the deposition of a-C:H:N and CN_x materials in Chapter 5 we first have to deal with a subject which could be of major importance for the quality of the deposited films: the etching and film modification by the plasma.

During deposition the particle flux towards the substrate will not only consist of depositing species, but also of species, e.g. H or N atoms, capable of abstracting atoms or molecules which are chemisorbed at the surface. Some precursors may even be capable of contributing to deposition and abstraction depending on the surface conditions [1]. In the abstraction or chemisorption process the type of bonds in the film may also be modified [1,2]. For instance, in the deposition of diamond films the conversion of graphite-like $sp^2$ to diamond-like $sp^3$ C-C bonds is suggested to be the result of modification of the weaker $sp^2$ groups by hydrogen atoms [3]. In this way the erosion may determine the final quality of the material.

For a good understanding of the deposition of CNH materials it is therefore important to elucidate the etching role of nitrogen and to determine whether the nitrogen can take over the modifying role of the hydrogen when hydrogen-free carbon precursors are used. The erosion may not only lead to a change in the film quality, but may also influence the growth rate. Since the net growth rate is determined by the deposition rate minus the etch rate, a different dependence of the two components on the process parameters, e.g. substrate temperature, will result in a growth rate that depends on that particular parameter.

Von Keudell et al., for example, showed that in an ECR-plasma deposition set-up the decrease of the growth rate with increasing substrate temperature can be fully ascribed to a thermally activated hydrogen-induced erosion of the a-C:H film [2]. However, Gielen et al. demonstrated that in the case of a-C:H film deposition with the expanding plasma beam deposition set-up, also used in this thesis, hydrogen etching only can not explain the decrease of the growth rate with increasing substrate temperature [1].

The same study revealed that for Ar/N_2 plasmas on a-C:H films the etch rate decreases with increasing ‘quality’ of the film [1]. The ‘quality’ of the films was in this case inferred from the infrared refractive index which for the a-C:H films shows a positive correlation with both hardness and $sp^2/sp^3$ ratio [4,5]. The hydrogen-induced erosion of carbon is assumed to occur via the formation of CH_3 groups that desorb from the surface [2,6]. Therefore, the smaller erosion rate for higher quality films was explained by the increased number of $sp^2$ C=C bonds which first need to be transformed into $sp^3$ C-C bonds before CH_3 can be formed.

From the results presented in Chapter 3 it is clear that an Ar/N_2 plasma is able to chemically etch a graphite nozzle. Therefore, we expect that the Ar/N_2 plasma can also attack the deposited film. However, the precise mechanism for formation of the volatile products during etching of carbon-containing films has still to be elucidated.
By studying the etching of a-C:H, a-C:H:N and CN_x films by Ar/N_2 plasmas under various conditions and by comparing it to the etching characteristics of Ar/H_2 and Ar/O_2 plasmas, we hope to learn more about the processes involved and their relevance to deposition. Especially the influence of the substrate conditions on the etching and their correlation with the film structure has to be determined first to be able to estimate their importance in the deposition process.

### 4.2 Etching of a-C:H films

For the study of the etching characteristics of Ar/N_2 plasmas on a-C:H films, films of different quality have been prepared with an expanding argon plasma into which acetylene (C_2H_2) is injected. The various deposition conditions used for preparation of the films are listed in Table 4.1. The settings were chosen on the basis of an earlier study which revealed that the quality of the film in terms of hardness is closely related to the refractive index and growth rate [5]. The films are deposited on c-Si (100) samples held at a fixed temperature (50 °C). From the infrared transmission spectra of the films the refractive index and thickness of the films was derived [7]. The average values found for the infrared refractive index and growth rate of the films are shown in Table 4.2 along with the values reported in a previous study for films deposited under the same conditions, but at floating substrate temperature [5]. As can be seen, the refractive indices, but also the growth rates differ about 10 % in the two cases, bringing to light the influence of the substrate temperature on the deposition process [1]. Since the refractive index is a measure for the hardness and sp^2/sp^3 ratio in the film [4,5], the quality, and hence ‘etching resistance’ [1], of the films deposited under the same conditions is also expected to be different for the two studies.

For a-C:H films deposited at 250 °C the etch rate for an Ar/H_2 plasma was found to decrease with increasing refractive index in the range of 1.89 to 2.00 [1]. The etch rate obtained for Ar/N_2 plasmas is shown in Figure 4.1 for different etching conditions as

<table>
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<tr>
<th>I_{arc} (A)</th>
<th>Φ_{C2H2} (sccs)</th>
<th>Present study</th>
<th>Previous study [5]</th>
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<td>n</td>
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<td>49 ± 2</td>
</tr>
</tbody>
</table>

**Table 4.1:** The various deposition conditions used to prepare a-C:H films of varying quality.

**Table 4.2:** Average values of the infrared refractive index n and growth rate R of the a-C:H films deposited under various conditions as obtained in the present study (T_{substrate} = 50 °C) and in a previous one (T_{substrate, floating}).
function of the refractive index of the films. In the same figure the etch rate of the Ar/N₂ plasma is compared to that of Ar/H₂ and Ar/O₂ plasmas. The various etching conditions used in this study are summarized in Table 4.3.

As already suspected, the nitrogen plasma is capable of etching the a-C:H films. The role of nitrogen as etching agent is also clearly demonstrated in Figure 4.1. When the nitrogen seeding is lowered from 20 sccs to 5 sccs the etch rate is reduced. The fact that the decrease in the erosion rate is much less than a factor 4 shows that the plasma chemistry, i.e. the creation of chemically reactive species, is not straightforward, as has already been shown in Chapter 3. From Figure 4.1 we can also conclude that not only the plasma chemistry is important, i.e. the radical/ion composition, but also the type of film that the plasma etches. The dependence of the etching rate on the refractive index is, although different, apparent for all experimental conditions. Under the two conditions which yield the highest etch rates, a maximum etch rate is found for films with a refractive index of around 1.61. For the two other conditions the etch rate decreases gradually with increasing refractive index. This discrepancy suggests that the chemistry between the incoming etching species and the volatile products

<table>
<thead>
<tr>
<th>I_{arc}</th>
<th>75 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Φ_{Ar}</td>
<td>100 sccs</td>
</tr>
<tr>
<td>Φ_{N₂}</td>
<td>5 sccs / 20 sccs (arc injection)</td>
</tr>
<tr>
<td>Φ_{H₂}</td>
<td>5 sccs (arc injection)</td>
</tr>
<tr>
<td>Φ_{O₂}</td>
<td>5 sccs (ring injection)</td>
</tr>
<tr>
<td>T_{sub}</td>
<td>0 °C – 275 °C</td>
</tr>
<tr>
<td>distance to substrate (d)</td>
<td>15 cm – 65 cm</td>
</tr>
</tbody>
</table>

Table 4.3: The various etching conditions employed in this study.
formed at the surface should also be considered for a good description of the etching mechanism. The overall trend for all four etching conditions, though, is a decreasing etch rate towards higher refractive index, indicating that the ‘etching resistance’ or the density of the films increases with increasing refractive index.

Comparison with Ar/H2 or Ar/O2 plasmas shows that the etch rate for Ar/N2 plasmas is much lower.* This is an indication that either the formation of volatile products is more difficult in the case of nitrogen or that in the nitrogen plasma less etching agents are produced. The etch rate obtained for etching of the a-C:H films with an Ar/O2 plasma is in good agreement with the etch rate observed in the stripping of photoresist [8], another hydrocarbon material. All three plasmas show a dependence on the refractive index of the film that is being etched. The characteristics are distinct, however, which is not so surprising since for each plasma the etching involves a different volatile product. In the case of an Ar/H2 plasma it is suggested that first a CH3 group has to be formed [2,6], which makes a material with a large number of sp2 C=C bonds, which first need to be transformed into sp3 C-C bonds, harder to etch [1].

However, for an Ar/O2 plasma in which both CO and CO2 may be formed during etching, or for an Ar/N2 plasma in which C≡N, HCN or C2N2 as volatile products may be expected, just another bond configuration at the surface may be more favourable for etching. Note in this connection also the behaviour of the etch rate for an Ar/H2 plasma which does not show a monotonic decrease with increasing refractive index, as has been observed for films with a refractive index in the range 1.89 to 2.00 [1].

In Figure 4.1 it is apparent that both the substrate temperature and the distance between the arc and the substrate are important parameters which determine the etch rate. To investigate their influence on the etching in more detail, a series of similar films has been etched under constant plasma conditions, but with variable substrate

---

* Because oxygen is injected in the ring and the diffusion profile of hydrogen is broader than that of nitrogen, the oxygen and hydrogen atom fluxes at the surface will not be the same as the nitrogen flux at the same precursor flow. The oxygen and hydrogen atom fluxes will probably be smaller than the nitrogen flux, which reinforces our argument that nitrogen-induced etching is less efficient.
temperature respectively distance to the substrate. The results are shown in Figure 4.2. At a fixed film composition the etch rate depends mainly on the flux of etching species towards the substrate and the etching reaction rate. We can safely assume that the substrate temperature, which was varied over only a small range (0 – 275 °C), does not influence the plasma composition much. Therefore, the increase of etch rate with increasing substrate temperature should be attributed to the temperature-dependence of the etching reaction rate. If linear kinetics are assumed for the reaction at the substrate, the etch rate \( R_{\text{etch}} \) will be governed by an Arrhenius type of behaviour [9]:

\[
R_{\text{etch}} = R_{\text{etch},0} \exp(-E_{\text{act}}/kT_{\text{sub}}) \tag{4.1}
\]

with \( R_{\text{etch},0} \) a weakly temperature-dependent prefactor which depends on film quality and flux of etching species, \( E_{\text{act}} \) the activation energy and \( k \) Boltzmann’s constant. The best fit of this relation to the data is shown in Figure 4.2 as the solid line, and yields a \( R_{\text{etch},0} \) of 2.3 ± 1.2 nm·s\(^{-1}\) and an activation energy \( E_{\text{act}} \) of 25 ± 5 meV (equivalent to 290 ± 60 K). The value of the activation energy is much smaller than reported in experiments on hydrogen etching of a-C:H films (0.43 eV [1], 0.5 eV [2] and 0.2 - 0.35 eV [6]), but is comparable to that found in the stripping of photoresist with Ar/O\(_2\) plasmas (250 ± 100 K [8]). However, if the temperature dependence of the etch rate is assumed to be composed of two contributions, as follows

\[
R_{\text{etch}} = R_{\text{etch}(0)} + R_{\text{etch},0} \exp(-E_{\text{act}}/kT_{\text{sub}}), \tag{4.2}
\]

an activation energy of 0.11 ± 0.04 eV is found with \( R_{\text{etch},0} = 5.3 \pm 2.3 \) nm·s\(^{-1}\) and \( R_{\text{etch}(0)} = 0.88 \pm 0.01 \) nm·s\(^{-1}\). The value of \( R_{\text{etch}(0)} \) seems too high for a process which is not thermally activated. However, the value of \( E_{\text{act}} \) approaches the values found for hydrogen etching.

The most dramatic change in etch rate however, is observed for the change of the arc to substrate distance. A very simple explanation for this effect is the decreasing ratio of projected beam area, which determines the flux of etching species at the substrate, to substrate area \( O \) with increasing distance \( d \) to the substrate (cf. Figure 4.3). When the influence of \( d \) on the plasma chemistry is neglected, the incoming etching flux will thus decrease with increasing \( d \). In this simple picture the etch rate will be fully determined by the expansion profile, i.e. the dependence of the radial component on \( d \).

In other words:

\[
R_{\text{etch}} \propto \frac{O}{\pi \cdot d^{2/\alpha}} \tag{4.3}
\]

with \( O \) the substrate area, \( \pi \cdot d^{2/\alpha} \) the projected beam area which depends on the expansion profile described by \( \alpha \). In Figure 4.3 the significance of \( \alpha \) for the expansion profile is explained. The results presented in Figure 4.2 are best described by an expansion profile with \( \alpha = 0.86 \pm 0.08 \). This means that in this picture the plasma profile can not be described by a parabolic or Gaussian profile, as has been observed in other experiments [10,11] and calculations [8]. The observed dependence implies even a more than linear expansion, which, considering the limited radius of the vessel (17 cm), is not a realistic solution.

It seems that the simple picture presented above in which the influence of the distance on the Ar/N\(_2\) plasma chemistry was neglected, is not sufficient to explain the large decrease of etch rate with increasing distance. The plasma chemistry does indeed depend on axial position, as has been shown in Chapter 3. The loss of nitrogen atoms,
which are thought to be the etching agents, to the walls will be larger at larger separations from the substrate. Moreover, as explained in Chapter 3, at larger distances from the arc the production of N atoms will be predominantly due to dissociative recombination of N$_2^+$ at the plasma periphery. This leads to an inhomogeneous radial distribution of etching species, which results in an effectively broader etching profile. However, the broad etching profile may also be accounted for by a stagnation of the beam in front of the substrate, as observed in modeling of the flow patterns. The stagnation leads to a decrease of axial velocity at the expense of an increase in radial velocity, and hence to a broader plasma beam.

In order to reveal the nature of the volatile products formed during etching of the a-C:H films, optical emission spectroscopy (OES) and mass spectrometry (MS) have been employed. The OES experiments have been performed on the deposition set-up itself, whereas the MS measurements have been carried out with a spectrometer (Prisma, Balzers) attached to a similar set-up which is mainly used for a-Si:H deposition. The emission spectra recorded at the same position for a pure argon plasma and an argon/nitrogen plasma in contact with an a-C:H film are shown in Figure 4.4. In situ ellipsometry measurements demonstrate that in the case of an argon plasma nor etching nor modification is taking place. Correspondingly, in the emission spectrum only Ar lines are observed, and no signs of carbon or hydrocarbons. In the case of an Ar/N$_2$ plasma the CN emission is clearly observed, indicating that CN is either directly formed as (one of) the volatile product(s) or indirectly from other...
volatile etching products. From these results it can be concluded that, similar to the case of a graphite nozzle described in Chapter 3, the etching is not due to physical sputtering but rather chemical in nature. However, in the mass spectrometer attached to the carbon-free set-up no new products were detected during etching. This suggests that the density of etching products from the film is very small and hence can only have a minor contribution to the CN emission observed in Figure 4.4. The main contribution should then come from the carbon contamination on the vessel walls. In any case, the appearance of CN emission during Ar/N₂ operation can thus be ascribed to the presence of a hydrocarbon film.

The effect of the carbon contamination is clearly demonstrated with in situ ellipsometry measurements of the Ar/N₂ plasma treatment of a clean c-Si substrate, shown in Figure 4.5. As long as the vessel walls are clean the plasma treatment will only lead to a minor change in the ellipsometric angle, probably due to a slight change in substrate temperature or the removal or creation of an oxide and/or nitride layer. When the walls are covered with an a-C:H film however, on ignition of the Ar/N₂ plasma Δ first decreases and then increases again after some given time. The decrease in Δ as well as the time at which Δ starts to increase again seem to be dependent on the degree of contamination: the longer the preceding deposition takes, the more Δ will decrease and the later it will start to increase again. The decrease respectively increase of Δ is associated with deposition respectively etching of a film on top of the c-Si substrate. At the point where Δ starts to increase again the deposition rate, determined by the flux of volatile products coming off the walls and their sticking probability, equals the etch rate. Apparently, after a given time the formation of volatile species at the walls diminishes, as the etching flux stays constant in time.

Optical modelling of the curve after 2'00” deposition shown in Figure 4.5 shows that the treatment with an Ar/N₂ plasma results in a film of approximately 6 ± 2 nm with a refractive index in the range (1.7±0.3 – i0.1±0.1). This corresponds to a ‘deposition’ rate of 0.04 ± 0.01 nm·s⁻¹, and hence the deposition from etching products will have a negligible effect on the deposition rate which is typically several tens of nm·s⁻¹.
Nevertheless, the fact that the volatile products formed at the vessel walls can reach the substrate, where they are deposited, demonstrates that the species recirculating in the background can actually enter the plasma beam and contribute to the chemistry. This implies that the vessel conditions, i.e. type of material, degree of coverage, temperature etc., may have an influence on the outcome of etching experiments as well as of depositions. Moreover, in the light of these findings species formed in the background gas, e.g. C2Hn polymers in an Ar/CH4 plasma (see Chapter 3), may also contribute to growth.

Operation of hydrogen plasmas in a ‘dirty’ vessel covered with a-C:H material will also lead to deposition, as can be seen in Figure 4.5. Oxygen plasmas however do not bring about deposition, although from Figure 4.1 it is clear that in comparison to hydrogen and nitrogen plasmas the production rate of volatile species should be the highest. The reason is simple: the volatile products formed in an oxygen plasma, e.g. CO, CO2 and H2O, have sticking probabilities close to 0.

The etching experiments shown in Figure 4.1 and Figure 4.2 have been conducted on a-C:H films that had been taken out into the open air from the vacuum vessel for ex situ analysis. In order to investigate the influence of the ambient air on the etching behavior of the films, three films have been deposited and subsequently etched without breaking the vacuum. The comparison between the films that were exposed and not exposed to the atmosphere is shown in Figure 4.6. As can be seen, the contact with the ambient air results in films with a remarkably lower ‘etching resistance’. This suggests that a kind of ‘annealing’ is taking place either in the film or in the a-C:H film covering the vessel walls when the film and vessel are brought in contact with the atmosphere¹, e.g. by uptake of oxygen, water or nitrogen from the ambient air, which has a catalytic effect on the surface chemistry. The ‘annealing’ of the film may also be caused by the change in substrate temperature on removal from the vessel, although the difference between the deposition temperature (50 °C) and room temperature is rather small. In any case, the results show that in situ diagnostics are

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¹ These experiments have been performed in the time that the load-lock, with which nowadays the vacuum of the vessel and substrate can be controlled separately, was not operational yet.
indispensable for an accurate study of film deposition and that one can not solely rely on ex situ analysis of the films.

Apart from OES, which revealed that during etching CN radicals are formed, two other in situ techniques are at our disposal for investigation of the etching products: infrared reflection absorption spectroscopy (IRRAS) and ellipsometry. Both techniques unveil that a typical etching experiment (cf. Figure 4.7) actually consists of an initial deposition trajectory followed by etching. From the ellipsometry curve it can be estimated that the initial deposition rate is approximately 2 times higher than the etch rate (at \( d = 65 \) cm) and that it decreases towards 0 at the point where the etching takes over. The deposition at the beginning of the etching experiment is, as was explained above, attributed to the volatile species formed at the vessel walls. At a certain point the flux of wall-produced species towards the substrate will not be sufficient anymore to compete with the flux of etching agents, and the actual etching of the film will start. Figure 4.7 shows that the initial deposition involves also CHx radicals, with vibrational modes in the 2800 - 3050 cm\(^{-1}\) region. Thus, the interaction of an Ar/N\(_2\) plasma with a-C:H material leads to the formation of CHx radicals and CN radicals.

In Figure 4.8 we compare the spectrum of a partially etched film with that of the original film. As can be seen, the Ar/N\(_2\) plasma treatment not only induces changes in the CH bonds (in the 2800 - 3050 cm\(^{-1}\) region), but also brings up the absorptions around 2200 cm\(^{-1}\) (C≡N), 1600 cm\(^{-1}\) (C=N) and 1400 cm\(^{-1}\) (C-N) which are typical for CN bonds. From the small absorption values of the CN bonds one can deduce that the incorporation of CN bonds occurs only in the 30 - 60 uppermost layers of the film, i.e. the first 10 - 20 nm. This explains why in transmission mode, where the bulk and top layers are probed with equal sensitivity, these changes could not be observed, and shows again the power of the in situ IRRAS diagnostic. Since the first top layers mainly determine the wear resistance of a material, for tribological applications the plasma nitridization of the uppermost carbon layers, as described above, may offer the possibility to combine the favorable bulk characteristics of carbon, e.g. high hardness, with the wear properties of carbon nitride.

The typical deposition rates during deposition of a-C:H:N films are in the range 10 - 40 nm\(\cdot\)s\(^{-1}\). Therefore, the influence of nitrogen- or hydrogen-induced etching, with typical rates (at \( d = 65 \) cm) in the range 0.05 - 1 nm\(\cdot\)s\(^{-1}\), on the effective
deposition rate will be negligible. Nevertheless, the modification of the film by nitrogen or hydrogen may still be an important factor in the deposition process, e.g. in the creation of available sites.

4.3 Etching of a-C:H:N films

The etching behavior of a-C:H:N films is expected to be similar to that of the a-C:H films. This is supported by the values found for the etch rates of both materials which are indeed comparable. To complete our investigation on the influence of the substrate conditions on the deposition, we will have to address one more issue: the substrate bias.

By applying a radio-frequency (RF) voltage to the substrate a negative DC bias voltage, which depends on the applied power, can be generated (cf. Chapter 2). This negative potential will accelerate positive ions towards the substrate and result in an additional ion bombardment during deposition. It can be calculated that the thickness of the ion sheath in front of the substrate is at most 1 mm, whereas the mean free path of the ions for ion-neutral collisions is several millimeters [12]. Therefore, the ions will have no collisions in the sheath and they will gain an energy corresponding to the difference between the plasma potential and the bias potential, which is practically equal to the bias potential.

Gielen et al. showed that in the deposition of a-C:H films from an expanding thermal plasma the influence of an energetic ion bombardment is negligible [1]. This was on one hand attributed to the negligibly small ion flux at the substrate in comparison with the growth flux and on the other hand to the limited penetration depth of the Ar ions which prohibits sub-surface reorganization reactions [1]. We therefore expect similarly to find no dependence on the applied substrate bias in the deposition of a-C:H:N films from Ar/N₂/C₂H₂ plasmas.

However, as will be shown in Chapter 5 and also in this section, despite the fact that the refractive index of the material seems independent on the applied bias voltage, the
growth rate and ‘etching resistance’ are not. An explanation may be the distinct surface chemistry in the a-C:H:N films which, in contrast to the pure a-C:H film chemistry, does benefit from the additional ion energy. The difference between a-C:H:N films deposited with and without additional bias is demonstrated in Figure 4.9. As can be seen, the film that has been deposited at a substrate bias of –230 V displays a much better ‘resistance’ to etching than the film deposited without additional bias. Note that at low bias voltages the etching can not compete with the deposition of wall-produced species and the deposition prevails‡.

The influence of the bias voltage applied during etching on the etch rate is also clearly observed in Figure 4.9. The additional ion energy contributes to a faster etching. Note that in an Ar/N2/C2H2 plasma the effect of the etching will be smaller as compared to the Ar/N2 plasma due to a smaller ion density.

From Chapter 3 it follows that the ion density in an Ar/N2 plasma (90 sccs Ar, 10 sccs N2, 48 A) halfway the expansion (z = 30 cm) has decreased to about 3×10¹⁸ m⁻³. At the substrate level the ion density will have decreased even further. When C2H2 is injected into the Ar/N2 plasma the ion density will become lower due to the ion-induced dissociation of acetylene (cf. Chapter 3). We therefore take, in analogy with the Ar/C2H2 plasma (100 sccs Ar, 10 sccs C2H2, 48 A) [1], an ion density of 2×10¹⁸ m⁻³ as an upper limit for the density at the substrate level. As was shown by Gielen et al. §, at an average ion temperature of 0.3 eV the calculated upper limit of the ion flux towards the substrate (~3×10²¹ m⁻²s⁻¹) is about 30 times smaller than the flux of C2H radicals [1].

In the case of Ar/N2/C2H2 plasmas it is very likely to find a ratio of comparable magnitude between the ion and growth flux. However, in Ar/N2/C2H2 plasmas, in

‡ Both biased and unbiased films have been etched under similar conditions, i.e. comparable vessel coverage, and therefore the deposition rate from volatile species produced at the wall should be comparable in the two cases.

§ The dissociation degree of 70 % which was assumed by Gielen et al. in their calculation of the C2H flux under these particular conditions has been confirmed by the measurements and modeling presented in Chapter 3.
Plasma-induced Etching

contrast to Ar/C₂H₂ plasmas, besides the argon ions also chemically active nitrogen ions are available. Argon ions can improve the film structure by energy transfer, but nitrogen ions on the other hand may also contribute to growth by chemical reactions. Therefore, in the case of Ar/N₂/C₂H₂ plasmas despite the small ion flux to growth flux ratio the additional bias may have a beneficial effect on the film.

The ellipsometry curves of the deposition and consecutive etching steps, shown in Figure 4.9, provide not only information on the etch rate, but also on the modification of the film. Namely, the ellipsometry curve describing the etching of a film during which no considerable changes occur to the film structure, reflected in its optical properties, should follow more or less the same trajectory as the deposition, however in the opposite direction. From simulation of the deposition it follows that the deposition of etching products which occurs at low bias voltages (trajectory I in Figure 4.9) does not proceed along the extrapolated deposition track. This means that the material deposited during etching differs from the material deposited during normal a-C:H:N deposition. This is not at all surprising, since the particle fluxes towards the substrate in the deposition from etching products are quite distinct from those encountered during normal deposition.

When the bias voltage is increased (in absolute sense) the etch rate increases and starts to compete with the deposition (trajectory M in Figure 4.9). Unfortunately, optical simulation of this state of transition often fails or is rather dubious, and no clear statements can be made on whether deposition or etching is prevailing and on the rate with which this happens. It is clear though that the transition trajectory is not at all related to the earlier depositions, both from etching products as from the injected precursors. This suggests that the film properties are modified either due to the changing flux of wall-produced species or due to the ion bombardment. It is known that ion bombardment can lead to a decrease in surface roughness [13], which would induce a shift of the ellipsometry curve. In order to elucidate which of the two processes is responsible for the film modification, more research is however needed.

At even higher bias voltages the etching curve (trajectory II) will come back to the ellipsometry deposition track after some time, probably the time needed to remove the (modified) top layer of deposited etching products.

The bias-induced etch rates presented for pure Ar/N₂ plasmas, which -as explained above- are a gross overestimation of the actual etch rates expected in Ar/N₂/C₂H₂ plasmas, are usually 10 – 50 times smaller than the deposition rate (typically 10 – 40 nm·s⁻¹). We therefore expect that the influence of the bias voltage on the net growth rate of a-C:H:N films will be minimal, just as the influence from nitrogen- or hydrogen-induced etching. However, as was demonstrated in this section, the bias voltage does affect the ‘etching resistance’ of the films. This suggests that the ion bombardment is inducing a transformation in the material either by the enhanced interaction with nitrogen ions and/or by the creation of active sites.

4.4 Etching of CNₓ films

In the deposition of CNₓ films from a graphite nozzle (cf. Chapter 3 and 5) the influence of the substrate conditions is perhaps expected to be the most prominent. This is suggested by the observation that under certain ‘deposition’ conditions, i.e. with the graphite nozzle at the arc exit, a net etching occurs, indicating that the flux of etching species towards the substrate is comparable to or is surpassing the growth flux. The typical growth rates (0.5 – 5 nm·s⁻¹) are indeed comparable to the values of the etch rate. Hence, the dependence of the etch rate on the substrate conditions
Chapter 4

should be reflected in the growth rate, provided that the growth rate itself does not depend strongly on the particular parameter. Since the density of CN radicals, which in Chapter 3 have been postulated as the growth precursors, is of the same order of magnitude (~$10^{17}$ m$^{-3}$) at the substrate as the ion density (~$10^{17} - 10^{18}$ m$^{-3}$), the influence of the substrate bias is also predicted to be large. Therefore, in this section we will take a closer look at the etching, both for ‘deposition’ and etching conditions and under influence of substrate bias.

In Figure 4.10 the changes, as measured by infrared reflection absorption spectroscopy (IRRAS), of the different C-N bonds in the CN$_x$ film when exposed to a pure Ar/N$_2$ plasma are shown as function of time*. The absorption from $sp^2$ and $sp^3$ C-N bonds decreases gradually in time as expected for a film being etched away. The absorption of the $sp^1$ hybridized C≡N bond however shows an initial increase that extends over almost 200 seconds before the expected decrease sets in. At first glance this may be attributed to the deposition resulting from the wall contamination, as has been shown to be the case in the etching of a-C:H and a-C:H:N films. But, in contrast to both aforementioned cases, the ellipsometry measurements do not display any sign of initial deposition or material modification. This means that deposition of wall-produced species can not explain the observed behavior. Moreover, treatment of the CN$_x$ films with an Ar/O$_2$ plasma shows a similar increase of the C≡N bonds in the initial stage, which in this case extends only over 10 - 20 seconds. As has been discussed before, in an Ar/O$_2$ plasma deposition of etching products is not observed because of the low sticking probability of CO, NO, CO$_2$ and NO$_2$.

An explanation that fits to both ellipsometry and IRRAS observations is the simultaneous etching and transformation of (part of the) C-N and C≡N bonds into C≡N bonds. This would explain the decrease of the $sp^3$ and $sp^2$ C-N bonds and the initial increase of $sp^1$ bonds. From a bonding enthalpy point of view the breaking of the C≡N bonds (~8.9 eV [14]) is less probable than breaking of the C≡N and C-N bonds (~6.2 eV and ~2.8 eV respectively [14]). However, since other bonds in the film are available to form new bonds as soon as one is broken, it is difficult to predict which bond (configuration) will in fact be energetically less stable.

At a certain point the etch rate of $sp^1$ bonds, which at a constant etching flux is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_4.10}
\caption{Relative absorption changes of the C-N bonds during etching with a pure Ar/N$_2$ plasma (70 sccs Ar, 30 sccs N$_2$, 75 A, 50 °C) on a metal substrate.}
\end{figure}

* In order to exchange the graphite nozzle for a copper one the vacuum in the vessel had to be broken, and the film has therefore been exposed to atmospheric pressure prior to etching. As has been shown in section 4.2, the exposure to the ambient may result in distinct etching behavior.
determined by the bond density times the reaction rate of the etching process, will become comparable to the production rate of \( sp^1 \) bonds from \( sp^2 \) and \( sp^3 \) bonds. At this point the removal of \( C≡N \) bonds will start.

The ejection of \( C≡N \) containing groups may proceed via direct abstraction by plasma species or by relaxation of the bonds in the film. In the latter case one may for instance think of the formation of volatile \( C_2N_2 \) (\( N≡C-C≡N \)) molecules from two \( C≡N \) bonds inside the film. The IRRAS measurements show in any case that the \( C≡N \) containing groups are accumulated in the film till they can form a volatile species.

The etching thus results in a different response of the three \( C-N \) bonds. It is therefore expected that the film structure will change during the process and thereby also the optical properties of the film. This prediction is confirmed by ellipsometry measurements (cf. Figure 4.11) which show a deviation from the deposition trajectory for the etching curve. Optical simulation reveals that the deposition and etching curves can be reasonably well described by a complex refractive index of 1.90 – \( i\cdot 0.078 \) and 1.71 - \( i\cdot 0.057 \) respectively. The real part of the refractive index is usually associated with the volume density of oscillators in the film [15]. The imaginary part is a measure for the absorption (at 632.8 nm in this case) in the film [15]. The fact that both real and imaginary parts of the refractive index decrease during etching is an indication that a less dense material is formed. From the IRRAS results it is deduced that this material should have an increased number of \( C≡N \) groups in comparison with the deposited film. This may be explained by the fact that the \( -C≡N \) group is a so-called endgroup, which terminates the polymeric chain and which is not capable of cross-linking like the \( C-N \) and \( C≡N \) bonds. Cross-linking will result in a denser material, whereas the incorporation of \( -C≡N \) groups leads to creation of so-called microvoids.

As said before, even at certain ‘deposition’ conditions, i.e. with the Ar/N2 plasma expanding through a graphite nozzle, etching may occur. A major difference with the ‘normal’ etching process presented above is that in this case next to a flux of etching species also a flux of depositing species is arriving at the substrate. Of course the
effect of the etching flux is larger than that of the deposition flux, otherwise no net etching would be observed, but the fluxes are expected to be comparable in size. We see immediately that the etch rate in this case must be smaller than in the case of ‘normal’ etching under equivalent conditions. This is indeed confirmed by ellipsometry measurements.

The ellipsometry measurements also show that the ‘etching’ induces a change in the film structure like observed in the ‘normal’ etching (see Figure 4.11). The IRRAS measurements (cf. Figure 4.12) however reveal that the absorption of the different C-N bonds behaves differently as compared to ‘normal’ etching. Figure 4.12 shows that the absorption of all C-N bonds increases in the first 20 – 40 seconds after which the absorption of the C≡N bonds keeps on growing and that of the C-N and C=N bonds starts to decrease. Apparently, during the first seconds minor film growth takes place.

Unfortunately this observation cannot be corroborated by ellipsometry measurements due to considerable scatter on the data. The fact that the possible growth occurs only in the first 40 seconds suggests that the balance between deposition and etching is changing in this short time towards etching. A process that manifests itself on this time scale is the heating of the substrate by the plasma. From the decrease of the baseline intensity Schreur estimated that, during the 120 s that the plasma is on, the temperature increases by almost 40 °C [16]. Hence the etch rate, which in section 4.2 was shown to increase with increasing substrate temperature, is expected to increase during the first seconds. Maybe this (small) increase in etch rate is just enough to make the balance between deposition and etching shift towards etching. However, more work is needed to elucidate the exact nature of the deposition-etching dynamics.

It seems that the \( sp^1 \) bonds behave in a similar way as during ‘normal’ etching, although due to the limited measuring time the point at which the etching of the bonds sets in cannot be observed. One may argue that the removal of C≡N bonds will start at a later time than during ‘normal’ etching because of the additional deposition flux, which as proposed in Chapter 3 consists mainly of \( sp^1 \)-hybridized CN radicals. The CN radicals on the other hand may also contribute to etching and/or of the C≡N containing groups by formation of volatile \( C_2 N_2 (N≡C-C≡N) \) molecules, as has been suggested by Hellgren et al. [17].
Bias-induced etching

The influence of the bias voltage on the etch rate of CN$_x$ films deposited with and without RF bias is shown in Figure 4.13. Similar to the etching of a-C:H:N films an increase of the etch rate is observed for increasing ion bombardment. However, the effect of the bias voltage on the etch rate seems to be larger than for etching of a-C:H:N films (cf. Figure 4.9). Since in both cases the same arc current and substrate temperature (50 A and 50 °C respectively) were employed, this difference may be ascribed either to the different Ar/N$_2$ flow ratios (90/10 vs. 70/30) used or to a difference in ‘etching resistance’ of the CN$_x$ and a-C:H:N films. In this case probably a combination of the two effects should be considered.

Figure 4.13 also shows that for both type of films after a fast initial increase of the etch rate with increasing bias voltage at a bias voltage of ~60 V the etch rate starts to saturate††. This suggests that the ion bombardment can be divided into a low and a high voltage regime where distinct processes take place. According to literature [18,19], at low ion energies (< 100 eV) mainly local reorganization of the film structure occurs, whereas at high ion energies physical sputtering of the material is prevailing.

The application of RF bias during deposition seems furthermore to improve the ‘etching resistance’ of the CN$_x$ films, equivalent to a-C:H:N films. The etch rates obtained with a bias voltage on the substrate are in some cases much larger than the typical deposition rate, and therefore under certain ‘deposition’ conditions the application of RF bias will certainly result in etching. The ellipsometry measurements shown in Figure 4.14 clearly demonstrate that under certain conditions the film structure is modified under influence of the ion bombardment: the etching curve strongly deviates from the deposition curve. The corresponding IRRAS measurements however do not display a clear change of the C-N bonds on RF treatment (cf. Figure

††A similar behavior is more or less observed in the etching of a-C:H:N films at bias voltages of ~150 - 200 V.
4.14). This may indicate that the divergence between the etching and deposition curves is caused by a structural change only, e.g. decrease of surface roughness, which is not accompanied by an alteration of the bond distribution. The improved ‘etching resistance’ of films deposited with additional RF bias should then be attributed to structural differences, e.g. higher compactness, rather than to a different bond composition.

4.5 Conclusions

During the deposition of CNH materials next to the flux of depositing species also etching species, e.g. H or N atoms, will reach the substrate. In order to estimate the importance of the etching component to the net growth rate and the film quality the etching behavior of a-C:H, a-C:H:N and CN\(_x\) films has been scrutinized. All films appear to get eroded by Ar/N\(_2\) plasmas. This is particularly interesting in the case of deposition from hydrogen-free carbon precursors (CN\(_x\) films), where the nitrogen thus may take over the modifying role sometimes imputed to hydrogen atoms in the deposition of diamond-like material [3].

Etching of a-C:H films with an Ar/N\(_2\) plasma reveals that the etch rate is dependent on the substrate temperature, the nitrogen seeding, the distance from the plasma source to the substrate, the exposure to ambient pressure and on the deposition conditions, i.e. the type of material. The increase of etch rate with increasing substrate temperature can be described by an Arrhenius-type of reaction rate with an activation energy of 25 ± 5 meV. This value is much smaller than reported in experiments on hydrogen etching of a-C:H films [1,2,6], but is comparable to that found in the stripping of photoresist with Ar/O\(_2\) plasmas [8]. The etch rate of Ar/O\(_2\) plasmas is found to be ~5 times higher than the etch rate of Ar/H\(_2\) plasmas under similar conditions and about 15-20 times higher than the etch rate of Ar/N\(_2\) plasmas.

The erosion does not only take place at the substrate, but also at the vessel walls. The volatile products formed during the etching lead to CN band emission and may be
Plasma-induced Etching

redeposited on the substrate, as ellipsometry measurements on a clean substrate reveal. Furthermore, the flux of volatile etching products towards the substrate is decreasing in time and at some point the redeposited etching products will be etched away again. This behavior is observed for both Ar/N\textsubscript{2} and Ar/H\textsubscript{2} plasmas, but not for Ar/O\textsubscript{2} plasmas for which probably the volatile species (CO, CO\textsubscript{2}, H\textsubscript{2}O, NO\textsubscript{2}) have a too low sticking probability. However, this ‘deposition’ at a rate of \(\sim 0.04 \pm 0.01 \text{ nm s}^{-1}\) will have only a minor effect on the deposition rate.

The influence of the nitrogen seeding on the etch rate and the fact that a pure Ar plasma does not lead to erosion of the film demonstrates that the etching is due to a chemical process rather than due to physical sputtering. The importance of the chemistry is also observed in the dependence of the etch rate on the distance between the plasma source and the substrate. To explain the increase of the erosion rate with decreasing distance to the substrate, it is not enough to consider the increase in the ratio between the substrate area and the forward projected beam area, but one also needs to include a distance-dependent chemistry as described in Chapter 3 and/or flow dynamics.

Finally, the deposition conditions under which the films have been produced turn out to have a large influence on the etching behavior. Although the dependence on the material is quite distinct for the Ar/H\textsubscript{2}, Ar/O\textsubscript{2} and Ar/N\textsubscript{2} plasmas, the overall trend seems to be that films with a higher refractive index possess a better resistance to etching. Exposure to air appears to have a large effect on the ‘etching resistance’ of the films: unexposed films show a remarkably lower etch rate. This is explained by a possible uptake of oxygen, water or nitrogen from the ambient air, or by a change of temperature, which takes place either in the film or in the a-C:H film covering the vessel walls when the film and vessel are brought in contact with the atmosphere. The results show that in situ diagnostics are indispensable for an accurate study of film deposition and that great attention should be paid to the (vacuum) handling of samples before, during and after deposition and/or etching.

IRRAS measurements reveal that the treatment of a-C:H films with an Ar/N\textsubscript{2} plasma leads to a permanent change of the C-H bonds and introduction of C-N bonds in the uppermost 10 – 20 nm of the film. This ‘nitridization’ offers the possibility to combine the favorable bulk characteristics of carbon, e.g. high hardness, with the wear properties of carbon nitride.

For a-C:H:N films the influence of RF bias on the etching behavior was studied. It is found that the etch rate of a pure Ar/N\textsubscript{2} plasma increases with applied bias voltage and that films that have been deposited with additional ion bombardment possess an improved ‘etching resistance’. This latter observation is remarkable, since in the deposition of a-C:H films with the same set-up the influence of the bias voltage on the film quality was found to be negligible [1]. However, in that study the film quality was inferred from the infrared refractive index only and the ‘etching resistance’ was not investigated. On the other hand, the presence of N\textsuperscript{+} and N\textsubscript{2}\textsuperscript{+} ions in the Ar/N\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} plasma may introduce additional chemistry during the ion bombardment, in contrast to the Ar/C\textsubscript{2}H\textsubscript{2} plasma where the ‘inert’ argon ions can only influence the growth by energy transfer.

The etch rates found for nitrogen- or hydrogen-induced etching and for the RF bias-induced etching are very small compared to the typical growth rates encountered in the deposition of a-C:H:N films. Therefore, their influence on the net deposition rate is expected to be negligible. However, these processes may still contribute to
modification of the film properties, e.g. by etching of ‘weaker’ bonds or creation of active sites.

During deposition of CNₙ films from a graphite nozzle the growth rate is moderate and the effect of nitrogen- and bias-induced etching on the net growth rate will be more prominent. The experiments reveal that the different C-N bonds in the film respond differently during etching with both Ar/N₂ and Ar/O₂ plasmas: the sp³ and sp² bonds (C-N and C≡N respectively) decrease whereas the sp¹ bonds (C≡N) first increase and then decrease. The initial increase of the C≡N bonds can not be ascribed to deposition of etching products, and is tentatively attributed to a transformation of part of the sp³ and sp² bonds into sp¹ bonds. The different response of the C-N bonds will lead to a modification of the material during etching, as corroborated by ellipsometry measurements. The etching leads to a material with a lower refractive index and absorption coefficient, indicating that the modification results in a less dense film.

The erosion rates are so high that under certain ‘deposition’ conditions a net etching occurs. This type of etching results in an initial increase of the absorption of all three C-N bonds, probably due to a heating-up of the substrate by the plasma which makes the etching flux become more dominant than the deposition flux. The initial increase of the absorption is followed by a decrease of the sp³ and sp² bonds while the sp¹ bonds keep increasing. Eventually the sp¹ bonds will also decrease. The selective etching of the different hybridizations is accompanied by a change in film properties, similar to that observed during ‘normal’ etching, as ellipsometry measurements show. The etch rate of CNₓ films increases dramatically when the bias voltage at the substrate is increased. Furthermore, the application of ion bombardment during deposition appears to improve the ‘etching resistance’ of the CNₓ films, equivalent to a-C:H:N films. The change in the material’s optical properties, as inferred from ellipsometry, is not corroborated by the IRRAS measurements, which show no clear differences in the C-N bond configuration. This may indicate that the RF bias induces a structural change only, e.g. decrease of surface roughness, which is not accompanied by an alteration of the bond distribution. The improved ‘etching resistance’ of films deposited with additional ion bombardment should then be attributed to structural differences, e.g. higher compactness, rather than to a different bond composition. The influence of the ion bombardment on the etch rate seems to be divided into a low and a high voltage regime where different processes take place. This suggests that, as proposed in literature [18,19], at low ion energies (< 100 eV) mainly local reorganization of the film structure occurs, whereas at high ion energies physical sputtering of the material is prevailing.

References
Chapter 5
Deposition of a-C:H:N and CN\textsubscript{x} films

5.1 Deposition of a-C:H:N films

5.1.1 Introduction
Following the predictions by Liu and Cohen, a large number of deposition techniques has been used to synthesize the possibly superhard crystalline compound $\beta$-C$_3$N$_4$. Most attempts have yielded amorphous material until now. However, as was pointed out in Chapter 1, the amorphous CN\textsubscript{x} and a-C:H:N materials have their own virtues. In this section we investigate the possibilities of the deposition of hydrogenated amorphous CN\textsubscript{x} (a-C:H:N) films from an expanding thermal plasma and the properties of the deposited films.
Most studies on a-C:H:N films report the weakening of the CH bond due to nitrogen incorporation, resulting in either a loss of hydrogen [1,2,3,4,5,6] or a loss of carbon [7,8]. Furthermore, an increase in the degree of disorder is observed, leading to a reduction of the internal stress [2,6,9]. While Freire et al. report a maximum hardness of about 21 GPa for both their a-C:H:N films and their hydrogenated amorphous carbon (a-C:H) films [7,9], the hardness of the a-C:H:N films investigated by De Martino et al. even exceeds that of their a-C:H films [4]. The hardness found by others is substantially lower than that of a-C:H films [5,10]. Schwan et al. [5] attribute this to the increasing content of nitrile (C≡N) network terminating groups with increasing nitrogen partial pressure.
Until now, to our knowledge, only non-remote plasmas have been used for the deposition of a-C:H:N films. The cascaded arc set-up used in our experiments is a remote plasma source, i.e. the plasma production, the plasma transport towards the substrate and the deposition of the films are geometrically separated. This allows for individual optimization of each of the deposition parameters, and thus for a better insight into the processes which take place in the plasma and at the substrate surface, and which finally determine the quality of the deposited film. In this chapter the mechanical, chemical as well as optical properties of the films deposited under various conditions are discussed in relation to each other, and in relation to the plasma composition and chemistry.
For practical technological applications high growth rates are desirable. In contrast to most common deposition techniques, for which growth rates between 0.1 and 1 nm s$^{-1}$ have been reported, with the deposition method presented in this chapter good quality a-Si:H and a-C:H films can be deposited at high growth rates (for a-C:H films as high as 70 nm s$^{-1}$) [11]. Furthermore, for the deposition of nitrogen-rich CN\textsubscript{x} films the large amount of nitrogen ions produced in the cascaded arc may be advantageous. This deposition technique has a further advantage above most others: no external bias needs to be applied for good quality a-C:H [12]. A recent study also revealed that quality in terms of hardness improves with growth rate, accompanied by an increase of the refractive index [13].
5.1.2 Experimental

Hydrogenated amorphous carbon nitride (a-C:H:N) films are deposited on glass and crystalline silicon substrates. The deposition setup has been described in detail elsewhere [12,14] and in section 2.2. Argon and nitrogen gas are introduced in the arc with a total flow of 100 sccs. The amount of nitrogen injected in the arc is varied (1, 2, 5 and 10% of the total flow) as well as the current through the arc ($I_{\text{arc}}$: 48, 75 and 87 A). The arc generates a sub-atmospheric (typically 30-50 kPa) thermal Ar/N2 plasma, which expands into the vacuum chamber (pressure typically 25 Pa) where acetylene is admixed via an injection ring, at about 5 cm from the arc exit. Three different acetylene flows are used: 2, 4.7 and 10 sccs.

On the temperature-controlled substrate holder, which is positioned 65 cm from the arc exit an additional RF bias can be applied. The dependence of the bias voltage on the applied RF power is displayed in Figure 5.1 for one of the plasma settings. As can be seen, the bias potential increases (in absolute sense) with increasing power, but flattens off for high powers. The fact that the RF bias is not linearly dependent on the RF power indicates that not all RF power is used in the creation of the bias potential over the ion sheath and thus affects the plasma over a distance larger than the sheath thickness*. Moreover, especially at higher RF powers the RF voltage is not a perfect sinusoidal, but includes higher harmonics and/or frequencies that are superposed on it. This is a clear evidence of the non-linear behavior of the sheath.

* The maximum distance over which the RF field can penetrate the plasma is given by the skin depth $\delta$, defined by: $\delta = c / \omega_{\text{pe}}$ with $c$ the velocity of light and $\omega_{\text{pe}}$ the electron plasma frequency [55]. For typical electron densities of $10^{17}$-$10^{18}$ m$^{-3}$ we find a skin depth of 5-15 mm.
5.1.3 Influence of plasma settings on material properties

As has been shown in section 3.4, the dissociation of acetylene will predominantly proceed via ion-induced reactions with argon and/or nitrogen ions emanating from the arc. Moreover, nitrogen atoms may also be involved in the dissociation. During and after the dissociation of the acetylene molecule a large variety of radical-neutral, neutral-neutral and radical-radical reactions may occur [15,16], leading to (excited) CH, CN and C₂ radicals and stable molecules, e.g. HCN, H-C≡C≡N and C₃N₂. At the substrate we therefore expect to find a mixture of nitrogen- and hydrogen-containing radicals and molecules which may contribute either to deposition or etching. The implications of this complex surface chemistry for the deposited films are discussed below.

In Figure 5.2 the FTIR spectra of two a-C:H:N films, deposited under different conditions, are shown together with the FTIR spectrum of an a-C:H film [13]. The C≡N absorption at 2216 cm⁻¹, corresponding to the stretching mode of triple bonded (sp¹) C≡N [17,18,19,20,21,22,23,24], is the most reliable ‘fingerprint’ for the bonding of nitrogen with carbon. This absorption is not observed for the a-C:H film, and is much stronger for film B deposited at a high N₂ flow leading to a higher N incorporation, than for film A which has a lower N content due to the lower N₂ flow used. In the assignment of absorption peaks due to the other bonding states of carbon and nitrogen (sp² and sp³) literature is rather divided [17-25]. The sp² and sp³ CN bands should appear somewhere in the region 1100-1700 cm⁻¹ where the identification of the distinct bands is complicated by the large amount of other bands (like NH₂, C≡C, CHₓ etc.) situated in that region. In this region also the Raman-active G (graphitic) and D (disordered) bands could become infrared active due to the symmetry breaking in sp² domains [25]. The broad absorption region 2700-3100 cm⁻¹ which is clearly observed for film A, is attributed to CH bonds and the broad absorption region 3200-3500 cm⁻¹ which is clearly observed for film B, is attributed to NH bonds [1-3,5,6,17,26].

Figure 5.2: Infrared absorption spectra of two a-C:H:N films deposited under different conditions and of an a-C:H film. Film A: Iₐrc = 75 A, 10 sccs C₂H₂, 99 sccs Ar, 1 sccs N₂; Film B: Iₐrc = 75 A, 2 sccs C₂H₂, 90 sccs Ar, 10 sccs N₂; a-C:H film [13]: Iₐrc = 49 A, 10 sccs C₂H₂, 100 sccs Ar.
When the N₂/C₂H₂ ratio in the plasma is gradually increased from 0.1 (film A) to 5 (film B) in the infrared spectrum four distinct features become clear:

1. The C≡N absorption at 2216 cm⁻¹ increases. This feature is absolutely absent in infrared spectra of a-C:H films deposited under the same conditions (i.e. with a pure 100 sccs Ar plasma instead of an 100 sccs Ar/N₂ plasma).

2. The absorption of CHₓ groups in the region 2700-3100 cm⁻¹ decreases.

3. A broad absorption band attributed to NH appears in the region 3200-3500 cm⁻¹.

4. The absorption in the region 1475-1800 cm⁻¹ becomes more pronounced. As discussed before, the assignment of absorption peaks in this region is very questionable. The increase of the absorption in this region might be attributed to an increase in either C-N and C≡N groups, graphitization (i.e. C=C groups) or NH₂, or to the Raman-active G and D bands becoming IR active [25].

The simultaneous increase of C≡N absorption, decrease of CHₓ absorption, increase of NH absorption and increase of absorption in the 1475-1800 cm⁻¹ region on nitrogen incorporation is also reported by Schwan et al. [5]. Further support for one or more of the observed features is found in other publications [1-3,5,6,17]. The overall conclusion that can be drawn from the infrared spectrum is that the incorporation of nitrogen is leading to a polymeric structure of the film [17,26] in which hydrogen is preferentially bonded to nitrogen [1,5,6,26]. Moreover, the increased absorption in the 1475-1800 cm⁻¹ region might indicate an increase in the number and/or size of graphitic clusters as a consequence of the incorporation of nitrogen [5-10].

The refractive index and thickness of the films can be determined from the interference pattern in the non-absorbing parts of the spectrum [27]. The refractive index as determined by FTIR ranges from 1.45 to 1.84 and is about 10% lower than the refractive index as determined by ellipsometry (at 632.8 nm). In contrast to earlier observations in the deposition of a-C:H films with the same method [13] the refractive index does not display a clear correlation with the growth rate. The growth rate shows an evident increase from 12.4 to 36.6 nm s⁻¹ with increasing C₂H₂ flow (see Figure 5.3), but no distinct dependence on the N₂ flow in the arc.

**Figure 5.3:** Growth rate, as determined from ellipsometry measurements, as function of the injected C₂H₂ flow for a-C:H:N films (I_{arc} = 48 A, 95 sccs Ar, 5 sccs N₂) and for a-C:H films (I_{arc} = 48 A, 100 sccs Ar) [13].
From a comparison with a-C:H films deposited under the same conditions, but without N₂ addition in the main flow (i.e. a pure 100 sccs Ar plasma with different C₂H₂ flows) [13], two important conclusions can be drawn. First, that the growth rates of a-C:H:N films are higher than those of a-C:H films, and secondly that the refractive index of a-C:H films is higher than that of a-C:H:N films. The growth rates for acetylene in an Ar/N₂ plasma are expected to be higher than for acetylene in a pure Ar plasma, since Ar species do not contribute to deposition whereas nitrogen species do. Moreover, in Chapter 3 it was demonstrated that the dissociation of C₂H₂ on addition of nitrogen is more efficient which may also contribute to a higher deposition rate. The lowering of the refractive index on incorporation of nitrogen has also been observed by others [28,29] and may be attributed to the fact that the films become more polymer-like (with less cross-linking) due to the incorporation of terminated sites in the amorphous network (as discussed above). It may also arise from the role of N as a weak dopant, as suggested by Silva et al. [29].

From ERDA and RBS measurements the chemical composition is determined. The results, which are presented in Figure 5.4, show no clear dependence on the depth. The amount of hydrogen in the film proves to decrease with increasing nitrogen content in the film, while the amount of carbon remains fairly constant. As said before, the dehydrogenation of the films on incorporation of nitrogen is also observed by others [1,3-6], and is also supported by our findings from the infrared absorption measurements. The relation between the hydrogen and the nitrogen incorporation is clearly seen in Figure 5.4, as well as the dependence of the nitrogen incorporation on the acetylene flow. Exactly as suggested, a C₂H₂ flow of 2 sccs (having a N/H ratio 5 times larger than at a flow of 10 sccs) leads to a substantially higher incorporation of nitrogen. Note that a 5 times larger N/H ratio does not lead to a 5 times higher nitrogen incorporation.

The XPS measurements support the observation that the films deposited from the hydrogen-containing Ar/N₂/C₂H₂ have less nitrogen incorporated in the film than films deposited from hydrogen-free precursors (see next section).

The hardness and elastic (Young’s) modulus of the films are derived from nano-

![Figure 5.4: The hydrogen concentration in the deposited a-C:H:N films as function of the nitrogen concentration, as determined by ERDA and RBS measurements, for two different C₂H₂ flows (2 and 10 sccs) in a 90 sccs Ar, 10 sccs N₂ plasma.](image-url)
indentation results, and are shown in Table 5.1. The hardness lies in the range 1.95-9.41 GPa, while the Young’s modulus varies from 54.2 to 94.0 GPa. The hardness shows a strong increase with increasing acetylene flow, and the Young’s modulus shows -apart from two points- the same tendency. The addition of N₂ appears to produce a softer material. For comparison: the above mentioned a-C:H films reached a maximum hardness and Young’s modulus of 13 and 120 GPa respectively [30]. We explain the decrease in hardness on incorporation of nitrogen, analogous to Schwan et al. [5], by the increase of nitrogen-containing network terminating groups (i.e. C≡N and NH) as observed in the infrared absorption measurements. The earlier reported correlation between the hardness or Young’s modulus and the refractive index for a-C:H films [13] could not be confirmed for the a-C:H:N films. This may indicate that a-C:H:N films possess a richer chemistry than a-C:H films. Namely, a chemistry which obscures the straightforward distinction between soft polymer-like films (with corresponding low refractive index) and hard diamond-like films (with corresponding high refractive index) as in the case of a-C:H films [13].

5.1.4 Influence of substrate conditions
In an attempt to improve the a-C:H:N film quality and to clarify the role of the surface chemistry, the substrate conditions, i.e. substrate temperature and additional bias voltage, have been varied. The chemistry in the growing film will in the first place depend on the particle fluxes arriving at the substrate. However, the equilibrium film structure that will evolve from the growth species may depend on the substrate temperature and/or ion bombardment conditions. Evidence for this change in film structure with substrate conditions is found in Chapter 4, where it was demonstrated that an additional ion bombardment improves the resistance of a-C:H:N films to nitrogen-induced etching. Moreover, in this same Chapter 4 it was shown that the substrate conditions also influence the nitrogen- and hydrogen-induced etching of the film. Since during a-C:H:N deposition always some nitrogen and hydrogen will be present at the substrate, this dependence on the substrate conditions may be important.

<table>
<thead>
<tr>
<th>N₂/(Ar+N₂) (%)</th>
<th>C₂H₂ (sccs)</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>3.2 ± 0.1</td>
<td>61 ± 2</td>
</tr>
<tr>
<td>1</td>
<td>4.7</td>
<td>5.1 ± 0.3</td>
<td>79 ± 5</td>
</tr>
<tr>
<td>1</td>
<td>10.0</td>
<td>9.4 ± 0.4</td>
<td>91 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>2.7 ± 0.1</td>
<td>56 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>4.7</td>
<td>4.2 ± 0.1</td>
<td>94 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>10.0</td>
<td>9.4 ± 0.4</td>
<td>88 ± 1</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>1.95 ± 0.06</td>
<td>50 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>4.7</td>
<td>3.5 ± 0.1</td>
<td>61 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>2.03 ± 0.06</td>
<td>64 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>4.7</td>
<td>3.17 ± 0.07</td>
<td>54 ± 1</td>
</tr>
<tr>
<td>a-C:H [30]:</td>
<td>20.0</td>
<td>13 ± 1</td>
<td>120 ± 7</td>
</tr>
</tbody>
</table>

Table 5.1: Hardness H and Young’s modulus E of the deposited a-C:H:N films and of an a-C:H film [30] for different N₂ seeding in the arc and injected C₂H₂ flows. Iₐrc = 75 A.
for the final structure of the film. With our remote plasma deposition set-up the substrate and plasma conditions may be varied independently in first order† and thus a good study into the effects of the substrate temperature and bias voltage can be undertaken.

**Substrate temperature**

The influence of the substrate temperature on the growth rate and the infrared refractive index is shown in Figure 5.5. As can be seen, the growth rate shows a dramatic decrease with increasing substrate temperature. The decrease cannot be ascribed to an increased etch rate only, since the maximum difference in etch rate, as was shown in Chapter 4, is only a few nm s⁻¹, whereas the observed decrease in growth rate is about 30 nm s⁻¹. Furthermore, the etching experiments have been performed with pure Ar/N₂ or Ar/H₂ plasmas where the flux of nitrogen and hydrogen atoms towards the substrate is much higher than in the deposition plasma into which acetylene is admixed. Therefore, another temperature-induced process has to be considered as well.

In the deposition of a-C:H films with the same deposition set-up Gielen *et al.* also observed a decrease in the growth rate with increasing substrate temperature [14]. This decrease is however much less pronounced than in our a-C:H:N films. This may be explained by the fact that the refractive index of the a-C:H:N material is much smaller. For comparison, at 275 K a refractive index of ~1.35 is found for the a-C:H:N film and of ~1.9 for the a-C:H film. The refractive index reported by Gielen *et al.* for their a-C:H films ranges from ~1.55 to ~2.1, and was attributed to a material ranging from soft polymer-like to hard diamond-like [13]. The refractive index of ~1.35 obtained by addition of nitrogen either reflects an even more polymer-like material, i.e. with a higher bandgap, or a material in which the relation between refractive index and structure is not as straightforward as for a-C:H films. In any case, the range over which the refractive index of the a-C:H:N films can vary is substantially larger than for a-C:H films. The more pronounced increase of the a-C:H:N refractive index with substrate temperature may on the other hand also be

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† There are some clues [39] that in the vicinity of the substrate the substrate conditions do actually influence the plasma chemistry. See also section 5.1.2.
linked with the more prominent dependence of the growth rate, as will be explained later.

In the case of a-C:H deposition Gielen et al. succeeded to explain both observations, i.e. the increase of the infrared refractive index and the decrease of the growth rate with increasing temperature, qualitatively with the help of a simple growth model in which the only temperature-dependent quantity is the sticking probability of the C$_2$H radical [14]. In this model the only particles participating in the deposition process were assumed to be the C$_2$H radical and the H atom, and the sticking probability of the C$_2$H radical was proposed to decrease with temperature. When nitrogen is added to the plasma things get of course more complicated. First of all, the assumption that the C$_2$H radical is the only growth precursor becomes questionable. As was shown in Chapter 3, the involvement of CN radicals or other nitrogen containing species in the deposition process is very likely. Second, in the presence of nitrogen the dangling bonds at the surface will be passivated by both hydrogen and nitrogen atoms. The passivated surface will thus consist of C-H and C-N bonds. It goes without saying that these bonds possess distinct chemistry with respect to incoming species, e.g. C$_2$H, H or N.

The altered chemistry together with the presence of other possible growth precursors next to the C$_2$H radical asks for a more complicated model than used for describing the a-C:H deposition. However, the similar trends observed for the growth rate and refractive index in the a-C:H and a-C:H:N deposition suggest that despite the increased complexity of the a-C:H:N system, the deposition can be more or less be described as “a-C:H like”. With other words, we propose that nitrogen is embedded in an a-C:H matrix which is formed in as much as the same way as in pure argon plasmas, i.e. with the C$_2$H radical as main growth precursor. In this picture the incorporation of nitrogen does not “hinder” the formation of the a-C:H matrix too much, but only leads to a material with a more polymer-like structure and lower refractive index. This picture is supported by findings of Freire et al. which show that the concentration of voids/micropores increases with the amount of incorporated nitrogen [9]. We realise that the proposed model for the a-C:H:N structure is highly speculative and that much more work is needed to clear up the complex chemistry at the surface, but it may be a good starting point for interpreting the results.

The observed increase of the infrared refractive index of the a-C:H:N films with increasing substrate temperature, as depicted in Figure 5.5, is an indication that a denser material is formed at elevated temperatures. The increase of the film density may for a large part account for the decrease of the growth rate. To understand the change in film density we will take a closer look at the infrared spectra of the films.

In Figure 5.6 the absorption of the C≡N and C-H bonds (around 2200 cm$^{-1}$ and 2900 cm$^{-1}$ respectively) is shown for films deposited at different substrate temperatures after correction for the film thickness. As can be seen, the infrared spectra of the films deposited at different temperatures show distinct features. For increasing substrate temperature the contribution of the C≡N bonds decreases while that of the C-H bonds increases. This observation suggests that at higher substrate temperatures preferentially nitrogen is removed from C≡N bonds in the film and that the carbon is used to form C-H bonds. That is, at elevated temperatures the a-C:H:N films become more “a-C:H like”.

There may be two reasons for the decreased amount of nitrogen at higher substrate temperatures: an increased out-diffusion of nitrogen species during growth and/or a change in surface chemistry which promotes the incorporation of hydrogen-containing groups at the expense of nitrogen-containing groups. The latter may also be translated
to a decreased etching probability of hydrogen-containing groups relative to that of nitrogen-containing groups.

The diffusion of nitrogen out of the film is consistent with the picture that part of the nitrogen is embedded as voids in the a-C:H matrix. These voids may, as suggested by Freire et al., form an interconnected network which facilitates the out-diffusion of molecular species [7], e.g. N$_2$ and NH$_3$. Since in the voids the nitrogen will be the most abundant species, an increased diffusion will probably lead to a relative reduction of the N concentration in the film. Moreover, the decrease of the nitrogen concentration in the film at higher substrate temperatures has also been observed in annealing experiments [7,31].

There are two arguments that support the idea that at elevated substrate temperatures the plasma-surface chemistry is favoring the incorporation of hydrogen-containing groups over that of nitrogen-containing groups. First, the growth rate of a-C:H:N films, as depicted in Figure 5.5, shows a stronger dependence on the substrate temperature than reported for a-C:H films [14]. This might indicate that the sticking probability of the nitrogen-containing growth precursor(s) is decreasing faster with temperature than the sticking probability of the nitrogen-free growth precursor(s). Furthermore, as has been suggested by Hellgren et al. [32] and Bohr et al. [33], the

![Figure 5.6: The normalized infrared absorption of the C≡N (left) and C-H (right) bonds for a-C:H:N films deposited at different substrate temperatures.](image)

![Figure 5.7: Atomic force microscopy images (1 μm × 1 μm) of a-C:H:N films deposited at different substrate temperatures. I$_{arc}$ = 48 A, 90 sccs Ar, 10 sccs N$_2$ and 10 sccs C$_2$H$_2$.](image)

273 K 373 K 568 K
Deposition of a-C:H:N and CNx films

-C≡N groups in the film may be etched by other CN radicals, H atoms and HCN molecules.

The effect of the substrate temperature on the surface morphology and the material properties is shown in Figure 5.7 respectively Table 5.2. The results show that it is indeed possible to improve the quality of a-C:H:N films, i.e. higher hardness, higher Young’s modulus (elasticity) and lower surface roughness, by increasing the substrate temperature. Note that in this case the higher hardness and elasticity are apparently linked with a higher refractive index, in contrast with the findings of section 5.1.3. Although this correlation is based on three points only, it fits well into the picture that we have of the a-C:H:N structure.

As mentioned before, we believe that the substrate temperature is mainly controlling the incorporation of nitrogen into the a-C:H matrix, and that its increase leads to a more “a-C:H like” material. Following this reasoning, when the plasma settings are kept fixed, the observed increase in refractive index at elevated substrate temperatures only reflects a decrease in the amount of nitrogen in the film. From section 5.1.3 it is concluded that incorporation of nitrogen results in a smaller hardness and elasticity of the film, independently of the plasma settings. Therefore, the suggested correlation between the refractive index and the hardness and/or elasticity of the film can be understood as arising from the changing degree of “a-C:H likeness”: from a polymer-like a-C:H:N film with poor hardness and elasticity at low substrate temperatures (and hence high nitrogen concentration) to a hard diamond-like a-C:H film at high substrate temperatures (and small nitrogen incorporation). The hardness of 7.0 ± 0.6 GPa obtained at 568 K for the a-C:H:N film with infrared refractive index of 1.86 (cf. Table 5.2) is indeed comparable to the value found in pure a-C:H films at this refractive index value [13]. Only the value for the Young’s modulus seems approximately 10% higher than observed in this specific a-C:H film.

The fact that a similar relation between the refractive index and the hardness has not been obtained in the study on the influence of the plasma settings (section 5.1.3) shows that the material properties are to a large extent also governed by the plasma chemistry. Moreover, it manifests the complex a-C:H:N chemistry which blurs the distinction observed for a-C:H films [13] between hard diamond-like films, with high refractive index, and soft polymer-like films, with low refractive index.

### Substrate bias voltage

It has been proven by Gielen et al. that with the deposition method employed in this study for deposition of a-C:H:N films diamond-like a-C:H films with a hardness of 13 - 14 GPa can be deposited without additional bias voltage [12]. This result is remarkable, since most other deposition techniques require additional ion energies of

<table>
<thead>
<tr>
<th>T (K)</th>
<th>n</th>
<th>H (GPa)</th>
<th>E (GPa)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>1.33</td>
<td>5.3 ± 0.6</td>
<td>88 ± 10</td>
<td>3.83</td>
</tr>
<tr>
<td>323</td>
<td>1.36</td>
<td>6.5 ± 0.5</td>
<td>94 ± 12</td>
<td>-</td>
</tr>
<tr>
<td>373</td>
<td>1.48</td>
<td>-</td>
<td>-</td>
<td>3.07</td>
</tr>
<tr>
<td>568</td>
<td>1.86</td>
<td>7.0 ± 0.6</td>
<td>117 ± 11</td>
<td>2.66</td>
</tr>
</tbody>
</table>

**Table 5.2:** The refractive index n, hardness H, elasticity E and root mean square (RMS) value of the surface roughness of a-C:H:N films as function of substrate temperature T. I_{arc} = 48 A, 90 sccs Ar, 10 sccs N2 and 10 sccs C2H2.
at least 100 eV per deposited carbon atom for good quality a-C:H [34,35,36,37].

Because in our deposition set-up under certain conditions the ions are fully consumed (see section 3.2) and thus can not play an important role in the deposition process, Gielen et al. concluded that for the formation of good quality films both ion dominated and radical dominated flows can be used. Recently von Keudell et al. managed to produce a C₂H radical source and to prove that indeed a flow of high sticking probability (0.65) radicals is sufficient to produce hard diamond-like a-C:H films [38]. In a tentative study on the influence of an additional ion bombardment on the quality of a-C:H films Gielen et al. found that the influence is negligible [14]. This was attributed to the small number of ions in the case of critical loading and to the limited penetration depth of the argon ions, which prohibits subsurface reorganization reactions, in the underloaded case.

When also nitrogen ions are available, as in the deposition of a-C:H:N films, the situation may be different. Nitrogen is unlike argon a reactive species that can contribute to the surface chemistry on impact. Especially the effect of molecular ions, which can dissociatively recombine at the surface thereby releasing the N₂ binding energy, may be large. The fact that a-C:H:N films deposited with additional RF bias possess an improved etching resistance to Ar/N₂ plasmas, as has been demonstrated in section 4.3, already shows that in the a-C:H:N deposition the ion bombardment must have some influence on the film properties.

The additional bias voltage applied to the substrate during deposition results in a higher growth rate, as can be seen in Figure 5.8. At first sight this seems contradictory with the observation in section 4.3 that the nitrogen-induced etching is increasing with applied bias voltage. On that basis the growth rate is expected to decrease due to the increased erosion. However, the measurements presented in section 4.3 have been performed in pure Ar/N₂ plasmas, i.e. in the absence of hydrocarbon radicals. When hydrocarbon radicals are present, the creation of active sites (dangling bonds) due to the nitrogen-induced etching may induce a faster growth. Furthermore, when acetylene is injected into the Ar/N₂ plasma the electron density will diminish considerably and hence the ion flux towards the substrate will be smaller. The higher

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\[ \text{Critical loading} \] is defined as the point at which the ion particle flow rate equals the injected precursor gas flow rate. In the underloaded case the injected precursor gas flow rate is smaller than the ion particle flow rate.
bias voltage obtained for an Ar/N2/C2H2 plasma in comparison with an Ar/N2 plasma at the same RF power (see Figure 5.1) is an indication for this.

Another explanation for the increased growth rate may be found in the fact that not all RF power is used for sustaining the bias (see section 5.1.2) [39]. In the vicinity of the substrate, actually within the skin depth of the RF plasma (5 – 15 mm), part of the RF power is thus used for plasma creation (increase of $n_e$) and/or heating (increase of $T_e$). Both effects may lead to extra dissociation of the precursor gases or of the dissociation products very close to the substrate and to a faster growth. The deposition rate measured in the absence of an arc plasma, i.e. for an Ar (90 sccs) / N2 (10 sccs) / C2H2 (10 sccs) RF plasma, increases from 0.21±0.01 nm s$^{-1}$ at 25 W RF power ($V_{\text{bias}} = -124$ V) to 1.16±0.09 nm s$^{-1}$ at 100 W ($V_{\text{bias}} = -260$ V). The RF-induced growth rate has the same order of magnitude as the increase observed in Figure 5.8, and could hence account for it. However, if such a supplementary dissociation is occurring, its effect on the overall plasma chemistry will be very small, as is evidenced by mass spectrometry measurements which show no difference in the precursor consumption on application of RF bias.

The ion bombardment seems to have almost no influence on the refractive index (cf. Figure 5.8) and absorption coefficient (not shown). There might be a very small decrease in refractive index of about 3%. In analogy with our earlier reasoning on the relation between the refractive index and the substrate temperature the decrease in refractive index could be explained by an increased nitrogen incorporation with RF bias. Since nitrogen ions will be accelerated towards the substrate, it is expected that more nitrogen will be incorporated at higher bias voltage. However, this is not corroborated by the infrared spectra of the films, which do not show any significant changes with RF bias. We therefore believe that a possible bias-induced structural rearrangement should be excluded, unless “infrared invisible” processes, e.g. inclusion of N2 molecules [31], are involved. The very small change in refractive index may be attributed to a possibly different growth flux, arising from the increased dissociation in the vicinity of the substrate, or a change in film density.

The conclusion that the ion bombardment does not induce major structural changes in

![Figure 5.9: Hardness and Young’s modulus of a-C:H:N films deposited at different bias voltage $V_{\text{bias}}$.](image)
the a-C:H:N films is corroborated by nano-indentation measurements of these films. The results, shown in Figure 5.9, indicate that the bulk properties of the film remain the same under ion bombardment conditions. From this we conclude that despite the slight increase in growth rate and the small change in refractive index the application of RF bias does not lead to a major rearrangement of the bulk material and as such does not change the material quality in terms of hardness and elasticity. However, as was shown in section 4.3, the ion bombardment does on the other hand improve the “etching resistance” of the material, suggesting that a change in the film has really occurred; a change which is not linked with the infrared absorption or hardness of the film.

5.1.5 Conclusions
An expanding thermal plasma of an Ar/N₂ mixture into which C₂H₂ is injected, is used to deposit a-C:H:N films. Without external bias a maximum growth rate of 37 nm·s⁻¹ is obtained. The films contain chemically bonded C and N as is evidenced by infrared absorption spectroscopy. The infrared C≡N absorption at 2216 cm⁻¹ and NH absorption at 3200-3500 cm⁻¹ show an increase with increasing nitrogen concentration in the plasma, while at the same time the CHₓ absorption at 2700-3100 cm⁻¹ is decreasing and the broad absorption region 1475-1800 cm⁻¹ is becoming more pronounced. From this we conclude that incorporation of nitrogen causes dehydrogenation of the film leading to a polymeric structure in which hydrogen is preferentially bonded to nitrogen. There may even be evidence for the reported [5-10] increase in the number and/or size of graphite clusters on incorporation of nitrogen. The dehydrogenation effect of the nitrogen incorporation is corroborated by the ERDA and RBS results. Furthermore, comparison of XPS measurements reveals that films deposited from hydrogen-free precursors (cf. next section) have a much larger N/C ratio. Comparison with a-C:H films deposited with the same setup and under the same conditions, but without addition of nitrogen to the main flow, shows that another deposition mechanism should be considered: a mechanism in which N and H are in competition with each other during growth. The incorporation of nitrogen leads to a smaller refractive index. The smaller refractive index is yet another indication that addition of nitrogen is leading to more polymer-like films. The correlation reported for a-C:H films between the growth rate and the refractive index could not be confirmed, whereas the increase of the growth rate with increasing C₂H₂ flow was observed.

The hardness of the films shows a strong increase (from 1.95 to 9.41 GPa) with increasing acetylene flow, and the Young’s modulus shows the same upward trend (from 54.2 to 94.0 GPa). Both quantities seem to decrease on addition of N₂ (see Table 5.1), this decrease being again more distinct for the hardness than for the elastic modulus. The N/C ratio in the film on the other hand, increases to a maximum of 0.4 (see Figure 5.4) with increasing N₂/C₂H₂ ratio in the plasma, thus indicating that a higher N/C ratio in the film does not obviously imply that the material is harder. Moreover, the influence of the C₂H₂/N₂ ratio in the plasma on the hardness again reflects the effect nitrogen has on the polymerisation of the films. The observed correlation for a-C:H films between the hardness and the refractive index could not be confirmed for a-C:H:N films. Based on the results of this study concerning the influence of hydrogen on the polymerization, we conclude as others have done [3,5,26], that despite the high N/C ratios one may achieve, for deposition of harder
materials hydrogen-free precursors (like C\textsubscript{60} and graphite) must be investigated. The fact that much harder films have been obtained in the absence of hydrogen \cite{40,41} gives further support to this conclusion.

The material properties can be improved by changing the substrate temperature during deposition. The growth rate shows a strong decrease with increasing substrate temperature. At the same time the refractive index, hardness and elasticity (Young’s modulus) of the film increases and the surface roughness decreases. This is accompanied by a decrease of the infrared absorption of the C≡N bonds and an increase of the infrared C-H bond absorption, indicating that the material becomes more “a-C:H like”. These observations are explained by a model of the a-C:H:N material in which nitrogen is mainly embedded in the a-C:H matrix as voids which reduce the hardness of the material and lead to a more polymer-like film with lower refractive index. At elevated substrate temperatures less nitrogen is incorporated and the hardness and refractive index will approach the values of a-C:H films.

Application of RF bias during deposition does not seem to improve the hardness and elasticity of the films. However, the RF bias affects the growth rate, which becomes higher, and the refractive index of the films, which decreases slightly. The increased deposition rate can be explained either by an increased dissociation of the precursor gases close to the substrate due to the RF plasma or by an increased nitrogen- or hydrogen-induced etching which leads to more active sites to which radicals can stick.

The ion bombardment is not accompanied by a change in the bonding configuration of the material, as evidenced by infrared spectroscopy, and the hardness and/or elasticity of the film. However, the results presented in section 4.3 incontrovertibly show that the ‘etching resistance’ of the films improves with an additional ion bombardment, indicating that some kind of change in the material must have taken place. One possibility would be that under the influence of the RF bias a smoother surface or a denser material is formed.
5.2 Deposition of CN$_x$ films from a graphite nozzle

5.2.1 Introduction
From the study presented in the former section and work of others [3,5,26] it was concluded that for obtaining hard carbon nitride films incorporation of hydrogen should be avoided. With the Ar/N$_2$ plasma expanding through a graphite nozzle, which has been thoroughly discussed in section 3.5, it is possible to introduce hydrogen-free carbon precursors into the plasma. It has been shown in section 3.5 that the graphite etching is a chemical rather than physical process. As a possible etching mechanism the formation of CN radicals from nitrogen atoms in the plasma with carbon atoms in the solid was postulated. The high CN(X) ground state densities obtained from simulation of the emission spectrum close to the substrate could account for the observed growth rate, and hence make the CN radical a very plausible candidate as the dominant growth precursor in this type of plasma. From the results presented in section 3.5 the highest production of CN radicals is expected at high arc currents and nitrogen seeding and small nozzle diameter. In this section the deposition characteristics of the graphite nozzle plasmas will be investigated, and we will try to find more evidence for the statements made in section 3.5. Because of the completely different method of precursor ‘injection’ the growth rates obtained with the graphite nozzle are about ten times smaller than those obtained with acetylene injection. This means that the nitrogen-induced erosion of the film, which, as has been shown in section 4.4, is highly dependent on the substrate conditions, e.g. substrate temperature and bias voltage, may have a larger impact on the deposition process than for Ar/N$_2$/C$_2$H$_2$ deposition. Therefore in this section the effects of the substrate conditions on the deposition process and film properties will be explored too.

5.2.2 Experimental
For details on the experimental set-up we refer to section 3.5.2 and reference [14]. Argon and nitrogen are introduced in the arc with a total flow of 100 sccs. The amount of nitrogen is varied (0-30% of the total flow) as well as the current through the arc (30-89 A). The Ar/N$_2$ plasma expands through a graphite nozzle of which the diameter can be varied (3, 4 or 5 mm) as well as the exit diameter (2, 4 or 5 mm). In most experiments a 4 mm graphite nozzle is used without a fixed exit diameter. The films are usually deposited onto crystalline silicon substrates of 2.5 $\times$ 2.5 cm$^2$. In the cases that infrared reflection absorption measurements are performed either a metal or SIM substrate (see section 2.7) of 4.0 $\times$ 4.0 cm$^2$ are used. In the study on the influence of the substrate conditions the substrate temperature is varied from -25 °C to 380 °C and the RF bias voltage from floating potential (a few V) to –450 V. In all other cases the substrates are kept at floating potential and at a constant substrate temperature of 50 °C. The dependence of the bias voltage on RF power is shown in Figure 5.10 for one plasma setting. As has been discussed in section 5.1.2, the non-linear dependence between bias voltage and RF power indicates that part of the RF power is used for plasma creation near the substrate.
5.2.3 Influence of the plasma settings

In Figure 5.11 the growth rate is shown as function of nitrogen seeding in the arc and as function of the arc current. As can be seen, the growth rate increases with increasing nitrogen seeding and increasing arc current. From section 3.5 we know that both parameters determine the power input in the arc. On the other hand they also control the amount of nitrogen atoms produced: a higher nitrogen seeding simply means that more nitrogen is available and a higher arc current will result in a higher dissociation degree. When we assume that nitrogen atoms are required for the production of CN radicals and that these radicals are responsible for film growth, as

![Figure 5.10: The bias voltage $V_{bias}$ as function of applied RF power $P_{RF}$ for an Ar (70 sccs) / $N_2$ (30 sccs), $I_{arc} = 89 A$ plasma expanding through a 4 mm nozzle (■) and a normal copper nozzle (▲).](image)

**Figure 5.11:** Left picture shows the growth rate of CN$_x$ films as function of the nitrogen seeding in the arc for different graphite nozzle diameters at $I_{arc} = 89 A$ and $T = 50 \, ^{\circ}C$. Right picture shows the infrared reflection absorption of different vibrations within the film during deposition with an Ar (70 sccs) / $N_2$ (30 sccs) plasma as function of time for different arc currents (0 – 40 s: 80 A, 40 – 100 s: 50 A, 100 – 160 s: 30 A) at $T = 200 \, ^{\circ}C$. 

![Figure 5.11:](image)
Chapter 5

has been postulated in section 3.5, these results are therefore perfectly explainable.

Another interesting feature that is observed in Figure 5.11, is the dependence of the growth rate on the nozzle diameter. The increase in nozzle diameter corresponds, according to section 3.5, to a decrease in arc power. Therefore, the decrease of the deposition rate with increasing nozzle diameter is not surprising. The consequence of this effect is that during normal operation, in which the diameter of the graphite nozzle is slowly increasing due to the etching, the growth rate will decrease in time. The increase in nozzle diameter is furthermore accompanied by a decrease of the refractive index and absorption coefficient, as shown in Figure 5.12. The change of the growth rate, refractive index and absorption coefficient in time definitely introduces some uncertainty in the determination of their values. However, the change of these properties in time can be estimated – and corrected for – by extrapolation of the values found at different times for the same operating conditions assuming a linear time-dependence. The corrections found in this way are shown in Figure 5.13. It can be seen that as long as the deposition time is shorter than 500 s, the uncertainty in the

Figure 5.12: The refractive index (left) and absorption coefficient (right) at 632.8 nm as function of nitrogen seeding in the arc for different graphite nozzle diameters at \( I_{arc} = 89 \, A \) and \( T = 50^\circ C \).

Figure 5.13: The relative correction for the change of the growth rate \( R \), refractive index \( n \) and absorption coefficient \( k \) in time as function of the graphite nozzle diameter for an \( Ar (70 \, sccs) / N_2 (30 \, sccs) \) plasma at \( I_{arc} = 89 \, A \) and \( T = 50^\circ C \).
Deposition of a-C:H:N and CNx films

growth rate and absorption coefficient will be less than 5% and for the refractive index even less than 0.5%. The uncertainty will be smaller for larger nozzle diameters due to the decreased erosion rate.

Let us now consider the dependence of the material properties on the nitrogen seeding and nozzle diameter. As mentioned above and in section 3.5, an increase of the nitrogen concentration in the arc and a decrease of the nozzle diameter will lead to more atomic nitrogen. More nitrogen atoms will, if our postulated etching mechanism is true, i.e. \( \text{N(g)} + \text{C(s)} \rightarrow \text{CN(g)} \), result in a higher CN production. But at the same time a larger nitrogen flux will also cause etching of the deposited CNx film. Moreover, nitrogen atoms in the expansion vessel may lead to destruction of CN radicals via volume-reactions, as has been shown in section 3.5. The CN radicals themselves may also act as etching agents [32]. Therefore, the effective deposition rate and the film properties will depend on the balance between the flux of growth species and etching species at the substrate and the substrate conditions. The fact that at the same growth rate films with different optical properties may be found, as can be seen in Figure 5.14, is therefore not surprising.

In Figure 5.15 the FTIR transmission absorption spectrum of a CNx film is compared with the spectrum of an a-C:H:N film from an earlier study (section 5.1). It is evident that the bonding configuration of the films is different. The \( \text{C≡N} \) absorption at 2195 cm\(^{-1}\) is clearly observed in both the a-C:H:N and CNx (graphite nozzle) films. At the same time in the CNx spectrum the absorption from the CHx functional groups in the 2700 – 3000 cm\(^{-1}\) region is completely absent indicating that indeed no hydrogen is incorporated in the film. The absorptions observed in the CNx spectrum at 1370 cm\(^{-1}\) and 1543 cm\(^{-1}\) could be assigned to C-N and C≡N bonds respectively, although in literature many different assignments are given for these \( sp^2 \) and \( sp^3 \) bonds [17-25]. The CNx film also shows a distinct absorption at 1760 cm\(^{-1}\) that has been ascribed to a \( \text{N≡C-C≡N} \) structure [42]. The only other feature, which both films have in common, is the absorption at 1619 cm\(^{-1}\), which may be attributed to C=C bonds.

The XPS spectra reveal that the N/C ratio in the investigated CNx films is very high and may even exceed the stoichiometry of \( C_3N_4 \). This is remarkable, since reports of nitrogen concentrations exceeding 40 at.% in pure CN materials are very rare (see for reviews references [43,44,45]). Moreover, the N/C ratio in the CNx films is much

\[ \text{Figure 5.14: The refractive index (left) and absorption coefficient (right) at 632.8 nm as function of the growth rate for different graphite nozzle and exit diameters. In the nozzle series a total Ar/N_2 flow of 100 sccs with varying N_2 flow was used at I_{arc} = 89 A, T = 50^\circ C; in the exit series an Ar (70 sccs) / N_2 (30 sccs), I_{arc} = 48 A, T = 50^\circ C plasma was used with varying nozzle diameter.} \]
higher than in the a-C:H:N films, emphasizing the effect hydrogen has on the nitrogen incorporation. However, the hardness and elasticity of the films as measured by nano-indentation is extremely small (~1 GPa and ~20 GPa respectively) which suggests that the material is very graphite-like. Recently Vlcek et al. concluded that hard CN$_x$ films can only be obtained when substrate bias voltages between –500 and –700 V are used. This may explain why the hardness values of our films, which are deposited without additional bias, are so small [40]. Vlcek et al. used reactive magnetron sputtering of a graphite target in pure nitrogen to synthesize CN$_x$ films with a N/C ratio up to 0.35, hardness up to 40 GPa and elastic recovery up to 85 %. Moreover, they found evidence that the CN radicals and N atoms are the dominant growth precursors in their magnetron plasma. In our deposition plasma the CN radicals and N atoms are also expected to be dominant in the deposition process. In their case the hardness appears to increase with the nitrogen incorporation. However, in our films where the N/C ratio is considerably higher, according to the XPS results, the hardness is much smaller.

### 5.2.4 Influence of substrate conditions

In section 4.4 it has been shown that the etch rate of CN$_x$ films is strongly dependent on the substrate conditions. Due to the relatively small deposition rates their effect on the film growth using a graphite nozzle will be large, and under certain conditions the deposition may even go over in etching instead (cf. section 4.4). It is therefore interesting to investigate to what extent the surface chemistry, which is controlled by the applied substrate temperature and bias, is influencing the deposition process. In all experiments a nozzle with an (initial) diameter of 4 mm is used.

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**Figure 5.15:** Comparison between the infrared transmission absorption spectra of a CN$_x$ film deposited from a graphite nozzle (Ar (90 sccs) / N$_2$ (10 sccs), $I_{\text{arc}} = 50$ A, $T = 50^\circ$C) and an a-C:H:N film (Ar (90 sccs) / N$_2$ (10 sccs) / C$_2$H$_2$ (10 sccs), $I_{\text{arc}} = 75$ A, $T = 50^\circ$C).
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Substrate temperature

In Figure 5.16 the growth rate and refractive index are shown as function of the substrate temperature for two different settings. The different settings result in different growth rates, and this distinction reveals a remarkable feature: for the low deposition rate settings an increasing substrate temperature leads to a slight increase in growth rate, whereas the high deposition rate settings lead to a decrease in growth rate with increasing substrate temperature. (The fact that both plasma settings seem to converge to the same growth rate at high temperatures is probably purely coincidental). This observation indicates that at the surface a thermally activated process is taking place that depends on the particle flux towards the substrate.

One possible explanation could be that the incoming C≡N radicals are not only contributing to deposition, but also to etching, e.g. by formation of C2N2 molecules as suggested by Hellgren et al. [32]. A thermally induced diffusion of C≡N radicals at the surface, which is possibly needed for formation of volatile C2N2 species, may explain why at low growth rates, i.e. low C≡N radical density at the surface, the influence of the substrate temperature is much smaller. But of course there are much more thermally activated processes that could apply. In section 5.2.5, where a tentative growth model for the CNx deposition will be presented, we will give a few examples.

The refractive index clearly shows that the material structure is changing with substrate temperature. In the infrared transmission absorption spectra however no clear differences are observed. Therefore, we resort to in situ annealing measurements with infrared reflection absorption spectroscopy, shown in Figure 5.17, to get an idea of the effect of the temperature on the CNx film structure. As can be seen, at higher annealing temperature the absorption of C≡N bonds decreases while that of C=C or C=N bonds increases. This change of bond configuration is also observed after deposition [46] (cf. decrease of C≡N absorption in the first 300 s), although it is much slower at lower substrate temperatures. Both observations suggest that the CNx film structure is not relaxed and that a transformation to a more stable configuration from C≡N to C=C or C=N bonds is taking place in the film which is more pronounced at higher substrate temperatures. Note that this transformation is irreversible: when the temperature is lowered again, the bond configuration remains the same. If we

Figure 5.16: The growth rate (left) and refractive index at 632.8 nm (right) as function of the substrate temperature for two different plasma settings (Ar (70 sccs) / N2 (30 sccs), □ 75 A, ▲ 89 A).
extrapolate the annealing results to the deposition, the transformation from a polymer-like material with more $sp^1$ bonds at low substrate temperatures to a graphite-like material with more $sp^2$ bonds at high substrate temperatures may explain the increase in refractive index observed in Figure 5.16.

The surface roughness decreases with increasing substrate temperature, as can be seen in Figure 5.18. The decrease of surface roughness with increasing deposition temperature is attributed to an increased surface diffusion of species responsible for

**Figure 5.17:** The time-resolved infrared reflection absorption changes of the different bonds in the film upon annealing of a CN$_x$ film deposited with an Ar (70 sccs) / N$_2$ (30 sccs) plasma at $I_{arc} = 80$ A and $T = 150^\circ$C.

**Figure 5.18:** The root mean square (RMS) value of the surface roughness as measured by AFM over an area of 1 µm × 1 µm as function of the substrate temperature. Ar (70 sccs) / N$_2$ (30 sccs), $I_{arc} = 89$ A, $T = 50^\circ$C.
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growth and/or etching.
Despite the changes observed in the refractive index and surface roughness, the hardness and Young’s modulus of the CNx films does not change significantly with substrate temperature.

Substrate bias
The effect of the applied bias voltage on the etch rate of CNx films is very strong, as has been shown in section 4.4, and is therefore also expected to influence the growth rate considerably. The deposition rate as function of applied bias is shown in Figure 5.19. The growth rate is indeed decreasing with increasing ion bombardment as predicted for a constant growth flux and an increasing contribution from etching. However, the decrease in deposition rate of ~2 nm·s⁻¹ is much smaller than the increase in etching rate observed in Figure 4.13 for a pure Ar/N₂ plasma of ~18 nm·s⁻¹. This is first of all an indication that in the deposition plasma the ion density is lower. This can readily be deduced from the higher bias voltages achieved at the same RF power in comparison to an Ar/N₂ plasma (cf. Figure 5.10). Assuming that power is the product of voltage and current, a higher bias at the same RF power means a smaller ion current. It could also indicate that besides the etching the ion bombardment is actually promoting growth, either by creation of active sites or by generation of extra growth radicals in the “RF plasma” which may be present near the substrate. This assumption is corroborated by the observation that in Ar/N₂/C₂H₂ plasmas the deposition rate slightly increases with increasing bias voltage (cf. section 5.1).

The refractive index at 632.8 nm, shown in Figure 5.19, increases with increasing growth rate and tends to saturate at high growth rates, just like observed in the deposition without additional bias (cf. Figure 5.14). The refractive index deduced from simulation of the infrared spectra, however, shows the opposite behaviour, as can be seen in the same figure. At the same time the absorption coefficient (at 632.8 nm) increases with ion bombardment, indicating that the band gap is reduced. The decrease of the optical bandgap with ion bombardment has also been observed by others [47,48] and has been attributed to an increasing number and size of graphitic domains and/or introduction of defect states within the bandgap. The distinction between the refractive index in the visible and in the infrared reflects the different

![Figure 5.19: The growth rate (left) and the refractive index at 632.8 nm (right) as function of bias voltage for an Ar (70 sccs) / N₂ (30 sccs), Iarc = 89 A, T = 50 °C plasma.](image-url)
ways nitrogen is incorporated in the (graphitic) carbon matrix and the fact that one and the same bond may either contribute or hinder the conduction process depending on its environment [49].

When we think of the ion bombardment as merely an extra energy supply, which may force the film into a different bond configuration, the influence of (a low) bias voltage and of the substrate temperature on the material properties should be comparable. However, as can be seen by comparing Figure 5.16 and Figure 5.19, an increase of bias voltage leads to a decrease of the refractive index (at 632.8 nm), whereas an increase of the substrate temperature induces an increase in refractive index. This suggests that the ion bombardment does not only deliver extra energy to the substrate, but also changes the chemistry. Most probably this change is caused by the additional N⁺ and N₂⁺ chemistry, which changes the ratio of incoming CN radicals to etching species. As discussed above, an increase of this ratio will indeed lead to a lower refractive index (cf. Figure 5.14). Another explanation for the altered surface chemistry could be the influence of a “RF plasma” that may be generated close to the substrate.

In section 4.4 it was suggested that the influence of the ion bombardment on the etch rate, and hence film growth, may be divided into a low (< 100 eV) and a high voltage regime. Following literature [50,51,52], it was furthermore suggested that at low bias voltages mainly local reorganization of the film structure occurs, whereas at high bias voltages physical sputtering of the material prevails. All parameters displayed in Figure 5.19 and Figure 5.20 (growth rate, refractive indices at 632.8 nm and in the infrared, and the absorption coefficient at 632.8 nm) seem to exhibit two distinct regions above respectively below a bias voltage of ~100 V, in accordance with the findings in section 4.4. However, in the infrared spectra of the films no clear evidence for structural changes could be observed, which may indicate that the observed changes in optical properties are more connected with the density of the films.

**Figure 5.20:** The absorption coefficient at 632.8 nm as function of applied bias voltage for an Ar (70 sccs) / N₂ (30 sccs), I_{arc} = 89 A, T = 50°C plasma.
5.2.5 Tentative growth model

So far we have only been speculating about the CN radicals as being the main growth precursors in the CNx deposition. These speculations were based on the findings in Chapter 3. In the time-resolved infrared reflection absorption measurements, shown in Figure 5.22, we find additional evidence for our reasoning. The peak heights of the absorptions at different positions in the infrared spectrum are plotted relative to the baseline (measured at $t = 0$) as function of time. As can be seen, after the shutter is removed (at $t \sim 34$ s), the $C≡N$ absorption is present before the other absorptions (in this case of $C=N/C=C$ and $C-N/C-C$ bonds) appear. This strongly suggests that the $-C≡N$ radicals first have to stick to the surface before further film growth can occur. In the following we will introduce a tentative growth model which provides an explanation for this mechanism.

Let us assume that the flux arriving at the substrate consists of CN radicals only (step 1, Figure 5.21). The radicals have a certain sticking probability that may be temperature-dependent. After the radicals stick to the surface the energy of the newly created C-C bond ($\sim 3.5$ eV [53]) may be used to break the triple bond into a double bond to form a C≡N bond and a dangling bond (step 2). Finally, these C≡N bonds can recombine and form cross-links (step 3).}

**Figure 5.21:** Schematic representation of the three steps involved in the tentative growth model.

**Figure 5.22:** Absorption of different bonds ($C-N/C-C$ at 1360 cm$^{-1}$, $C=N/C=C$ at 1600 cm$^{-1}$ and $C≡N$ at 2250 cm$^{-1}$) during deposition on a metal substrate. Deposition conditions: 70 sccs Ar, 30 sccs N$_2$, $I_{arc} = 80$ A, $T = -25$ °C.
bond (step 2, Figure 5.21), for which less than 3 eV is required [53]. The probability that the triple bond is transformed is most likely increasing with increasing substrate temperature, as is hinted at by the annealing experiments that have been presented earlier (cf. Figure 5.17). In this way per incoming C≡N radical one C≡N bond is created and two dangling bonds. Due to the creation of dangling bonds where new CN radicals may stick the growth can continue. Finally, when the density of dangling bonds is sufficient, reconstruction of the dangling bonds may occur, either by bonding to a neighboring dangling bond or by replacing atoms (step 3, Figure 5.21). Such relaxation processes are usually also thermally activated [54].

So in this very simple picture each step involves a temperature-dependent process. In analogy with the tentative growth model presented by Gielen et al., we assume that the sticking probability of the CN radicals may be dependent on temperature. The probability for the second step, i.e. the transformation of the triple bond to a double bond and two dangling bonds, is expected to increase with temperature. The same holds for the third step, i.e. the recombination and cross-linking of the material.

To complete the picture also two etching reactions are proposed with CN and N radicals from the plasma. As has been shown in chapter 4, the etching will increase with substrate temperature. The fact that CN may contribute both to deposition and to etching may for instance account for the observed growth rate dependence with increasing substrate temperature, as mentioned above. When the flux of CN radicals towards the substrate is small (i.e. at a small deposition rate), the probability that two (physisorbed) CN radicals will desorb again from the surface as a C2N2 molecule will be smaller than at high radical fluxes. Therefore, at higher deposition rates a possible substrate temperature-induced desorption will have a larger impact on the growth rate. The effect of ion bombardment may be twofold: the creation of active sites by physical sputtering (predominantly at high bias voltages) and the promotion of N2⁺ and N⁺ ions towards the substrate.

The balance between all these thermally and ion-induced processes at the substrate will finally determine the growth rate and the film structure.

5.2.6 Conclusions

From Ar/N2 plasmas expanding through a graphite nozzle CNx films have been deposited. As suggested from the plasma characterization of this type of plasmas in section 3.5, the highest growth rates were achieved at high nitrogen seeding, high arc current and small nozzle diameters. These results confirm the idea that atomic nitrogen is needed to produce CN radicals, which are responsible for the film growth. More evidence for the requirement of CN radicals for deposition is found in the time-resolved infrared reflection absorption measurements which show that the C≡N absorption appears before any other absorption.

The refractive index and absorption coefficient of the deposited films depend on the plasma settings, but increase with increasing growth rate when the substrate conditions are kept fixed. The fact that at a constant deposition rate different optical properties may be found, shows that besides the flux of growth species also species capable of modifying the film structure should be present.

When the infrared transmission absorption spectrum of a CNx film is compared with that of an a-C:H:N film new features are observed. Although both type of films show a clear C≡N absorption, in the CNx film spectrum the CHx band absorption is totally absent, indicating that no hydrogen is incorporated in the film. The extremely small
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hardness and elasticity measured for these films suggest that the material is very graphite-like. The dependence of the growth rate on the substrate temperature depends on the rate itself: at high deposition rates the rate decreases with increasing temperature, whereas at a smaller deposition rate the rate slightly increases with increasing temperature. This shows that at least one thermally activated process is involved in the deposition. Despite the ambivalent behavior of the growth rate, the refractive index increases with increasing substrate temperature for both high and low deposition rate settings. The increase in refractive index is attributed to an increasing degree of graphitization, as suggested by in situ annealing experiments showing that at higher temperatures the C≡N absorption decreases while the C-N and C=O increases. Despite the changes observed in the refractive index and surface roughness, the hardness and Young’s modulus of the CN_x films did not change significantly with substrate temperature. When an additional ion bombardment is applied during deposition the deposition rate decreases considerably, as expected from the bias-induced etching experiments presented in section 4.4. However, the decrease in growth rate is much smaller than observed in a pure Ar/N_2 plasma, which, combined with the much higher value of the bias voltage, indicates that in the presence of the graphite nozzle the ion density is smaller. It may furthermore suggest that the ion bombardment is actually also promoting growth, e.g. by creation of active sites and/or radicals. The decrease in growth rate due to the ion bombardment is accompanied by a decrease in the refractive index at 632.8 nm and by an increase in the infrared refractive index. The absorption coefficient increases with bias voltage indicating that the band gap is lowered, probably due to an increasing number and size of graphitic clusters and/or defects. The dependence of the refractive index at 632.8 nm on the substrate temperature is the reverse of that found for the bias voltage. Therefore, it is suggested that the ion bombardment is not only an extra energy supply, but really changes the composition of the particle fluxes arriving at the substrate, most probably by promoting N^+ and N_2^+ ions. The growth rate and optical properties of the film show a clear distinction between the high voltage regime (starting at ~ 100 V) and the low voltage regime. These two different regimes are in agreement with the bias-induced etching experiments presented in section 4.4. Based on these experiments and on literature [50,51,52] we propose that at low bias voltages a restructuring of the bonds takes place due to a change in surface chemistry, and at high bias voltages mainly physical sputtering of the weaker bonds. In the infrared spectra of the films however no clear evidence for such structural changes could be observed, which may indicate that the observed changes in optical properties are more connected with the density of the films. A tentative growth model has been introduced which explains the film growth in three steps. First, CN radicals arrive at the surface where they may stick. Second, the triple bond is transformed into a double bond and two dangling bonds are created, guaranteeing further growth. And third, recombination and cross-linking of the dangling bonds occurs. During growth also etching may occur by CN radicals and/or N atoms. The influence of the substrate conditions on the growth rate and optical properties may be explained by the temperature-dependent probability associated with each step, and the balance between the number of active sites and the incoming flux of depositing and etching species which may be altered by the ion bombardment.
References

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[38] A. von Keudell, private communication.
Chapter 6

General Conclusions

In this thesis different aspects of the deposition of a-C:H:N and CNₓ films by means of an expanding thermal plasma have been discussed. Apart from the deposition plasmas, i.e. Ar/N₂/C₂H₂ in the case of a-C:H:N and Ar/N₂ expanding through a graphite nozzle in the case of CNₓ, also the Ar/CH₄, Ar/C₂H₂ and Ar/N₂ plasmas have been characterized. The other part of the work concerns the investigation of the etching by Ar/N₂ plasmas of a-C:H, a-C:H:N and CNₓ films and of the deposition of a-C:H:N and CNₓ films as function of the substrate conditions. Below the main conclusions resulting from these investigations are summarized:

- From simulation of the infrared gas phase absorption spectrum, which includes an analytical expression for the non-linear effect of the apparatus profile on the measured absorption, it is possible to obtain the rotational (gas) temperature of C₂H₂ in a plasma environment within ±100 K.

- The infrared reflection absorption signal can be enhanced by use of special substrates. A review of three types of such substrates, i.e. metal, optical cavity substrate and SiO₂ on top of a metal (SIM), reveals that the maximum enhancement is achieved with a SIM substrate. However, depending on the specific experimental conditions, the two other substrates may be preferable.

- When the components of a gas mixture are a priori known, the exact amount of each constituent can be extracted from the calibrated mass spectrometry data, even when the cracking patterns are overlapping.

- In an Ar/C₂H₂ plasma the argon ion-induced dissociation of acetylene may lead to full depletion, whereas in Ar/CH₄ plasmas 100 % consumption is not reached. This is attributed to the high polymerization rate of the low-sticking radicals formed in the methane dissociation. Furthermore, the methane depletion is not directly correlated with the deposition rate. This means that for the description of Ar/CH₄ plasmas other processes need to be included, besides the primary chemistry, i.e. dissociation of methane by charge exchange and subsequent dissociative recombination.

- A plug-down model can describe the plasma chemistry and deposition fairly good as long as the sticking probability of the radicals produced in the dissociation is larger than their reaction probability.

- In Ar/N₂ plasmas the main loss mechanism for ions and electrons is the charge exchange of atomic ions with nitrogen molecules in the background gas followed by dissociative recombination. This process is the main source for atomic nitrogen in the downstream plasma and leads to heating of the electrons.

- The consumption of acetylene in Ar/N₂ plasmas is larger than in pure argon plasmas. This is probably due to the involvement of both nitrogen ions and atomic
nitrogen in the dissociation of acetylene. The most abundant stable molecules formed in Ar/N2/C2H2 plasmas are HCN, H-C≡C≡N and C2N2.

- An Ar/N2 plasma expanding through a graphite nozzle induces chemical etching of the graphite and produces volatile species, most probably CN radicals, which may lead to deposition. The only stable molecule that is produced in small amounts is C2N2. The increase of the graphite nozzle diameter in time leads to a decrease in the arc power and thereby to a decrease in the growth rate.

- The etch rate of a-C:H, CNx and a-C:H:N films by Ar/N2 plasmas is dependent on the substrate temperature and bias, the arc power, the nitrogen seeding, the distance from the plasma source to the substrate, the exposure of the films to ambient pressure prior to etching and on the deposition conditions, i.e. the type of material. The etch rate is much higher for CNx films than for a-C:H and a-C:H:N films. The a-C:H:N and CNx films deposited with an additional ion bombardment show an improved resistance against etching by Ar/N2 plasmas.

- For both Ar/N2 and Ar/H2 plasmas the volatile products formed at the vessel walls during etching may be redeposited on the substrate. The deposition of etching products is not observed for Ar/O2 plasmas.

- Treatment of a-C:H films with an Ar/N2 plasma leads to a permanent change of the C-H bonds and introduction of C-N bonds in the uppermost 10 – 20 nm of the film. This ‘nitridization’ offers the possibility to combine the favorable bulk characteristics of carbon, e.g. high hardness, with the wear properties of carbon nitride.

- During etching of CNx films with both Ar/N2 and Ar/O2 plasmas the infrared absorption from \( sp^3 \) and \( sp^2 \) bonds (C-N and C≡N respectively) decreases, whereas that of the \( sp^1 \) bonds (C≡N) first increases and then decreases. The initial increase of the C≡N bonds is tentatively attributed to a transformation of part of the \( sp^3 \) and \( sp^2 \) bonds into \( sp^1 \) bonds.

- Incorporation of nitrogen in a-C:H:N films causes dehydrogenation of the film leading to a polymeric structure in which hydrogen is preferentially bonded to nitrogen, and which has a smaller hardness, Young’s modulus and refractive index. The correlation reported for a-C:H films between the growth rate and the refractive index on one hand and the hardness on the other hand could however not be confirmed.

- The growth rate of a-C:H:N films shows a strong decrease with increasing substrate temperature. At the same time the refractive index, hardness and elasticity (Young’s modulus) of the film increases and the surface roughness decreases. This is accompanied by a decrease of the infrared absorption of the C≡N bonds and an increase of the infrared C-H bond absorption, indicating that the material becomes more “a-C:H like”. Application of RF bias during deposition does not seem to improve the hardness and elasticity of the films, but affects the growth rate, which becomes higher, and the refractive index of the films, which decreases slightly.
For CN\textsubscript{x} films the highest growth rates are achieved at high nitrogen seeding, high arc current and small nozzle diameters, confirming the idea that atomic nitrogen is needed to produce CN radicals, which are responsible for the film growth. The infrared C≡N absorption, which appears before any other absorption, gives further support to this idea. The extremely small hardness and elasticity measured for these films suggest that the material is very graphite-like.

The deposition rate of CN\textsubscript{x} films decreases with increasing substrate temperature at high deposition rates, but slightly increases at smaller deposition rates, suggesting that at least two thermally activated processes are involved in the deposition. However, the refractive index increases with increasing substrate temperature for both high and low deposition rate settings, and is tentatively attributed to an increasing degree of graphitization. The hardness and Young’s modulus of the CN\textsubscript{x} films did not change significantly with substrate temperature. With additional ion bombardment the growth rate decreases dramatically, accompanied by a decrease in the refractive index at 632.8 nm and by an increase in the infrared refractive index. The growth rate and optical properties of the film show a clear distinction between the high voltage regime (starting at \textasciitilde 100 V) and the low voltage regime. We propose that at low bias voltages a restructuring of the bonds takes place due to a change in surface chemistry, whereas at high bias voltages mainly physical sputtering of the weaker bonds occurs. Since in the infrared spectra no clear evidence for such structural changes could be observed, the difference may also be connected with the density of the films.

A tentative growth model has been introduced which explains the CN\textsubscript{x} film growth in three steps. First, CN radicals arrive at the surface where they may stick. Second, the triple bond is transformed into a double bond and two dangling bonds are created, guaranteeing further growth. And third, recombination and cross-linking of the dangling bonds occurs.
Summary

Coating of a material, having the right bulk properties, with a thin film with complementary surface properties, offers the possibility to tailor the hardness, friction, and optical, thermal and electronic properties of a material to one’s needs. The compounds consisting of carbon, nitrogen and/or hydrogen (CNH materials) appear to have many favorable surface properties. Moreover, it has been predicted theoretically that a crystalline form of carbon nitride may even be harder than diamond. In this thesis we investigate the possibilities of depositing CNH materials with an expanding plasma deposition set-up with which in the past depositions at very high rates (up to 70 nm/s) have been performed. For this purpose both the deposition from an Ar/N2/C2H2 plasma and from a hydrogen-free plasma, existing of an Ar/N2 plasma expanding through a graphite nozzle, are scrutinized.

The properties of the deposited material are determined by the composition of the plasma and the substrate conditions. Therefore, in this thesis both the plasma and the material are characterized, and the influence of the substrate conditions is also investigated. For the characterization of the plasma two new diagnostic techniques are introduced: mass spectrometry (MS) and Fourier transform infrared absorption spectroscopy (FTIRAS). By deconvolution of the MS data it is possible to obtain the quantitative composition of a calibrated gas mixture within ±5%. The FTIRAS technique offers the possibility to obtain the composition of the gas mixture qualitatively without the need for a calibration or deconvolution. Moreover, a special method has been developed to extract the “gas” temperature of the plasma from the FTIRAS data within ±100 K uncertainty. To study the growth of the films in situ a new diagnostic technique has been implemented: Fourier transform infrared reflection absorption spectroscopy (FTIRRAS). A special substrate has been designed to be able to detect (sub-)monolayer films. The ex situ characterization of the films by means of various techniques yields information on the C/N/H concentration, the different type of bonds, the optical constants, the hardness, elasticity and surface roughness of the deposited films.

Characterization of Ar/C2H2 plasmas reveals that the dissociation of the precursor gas proceeds via charge exchange with argon ions followed by dissociative recombination of the molecular ion with electrons, and that under certain conditions full depletion can be achieved. The good agreement between the ion particle flow rates, following from quasi-one-dimensional modeling of the MS data, and as measured by Langmuir probe, suggests a one-to-one relation between the argon ions and acetylene molecules. It also supports the earlier idea that the highest quality hydrogenated amorphous carbon (a-C:H) films is deposited at high growth rates, i.e. when the ion particle flow rate is almost equal to the injected acetylene particle flow rate (so-called “critical loading” conditions). In Ar/CH4 plasmas full consumption of the precursor gas is not observed. This is attributed to the much smaller sticking probability of the radicals formed in the dissociation, which gives them more time to form higher polymers. The fact that in a methane plasma much more polymers (up to 20% of the injected CH4 gas flow) are formed than in an acetylene plasma (maximum 4%), supports this suggestion. To understand the behavior of the growth rate in the methane plasma two quasi-one-dimensional models are used.

In an Ar/N2 plasma the main loss mechanism for the ions and electrons is the charge exchange of atomic ions with N2 molecules in the background gas, followed by dissociative recombination of the molecular ions. This process leads to production of
nitrogen atoms, heating of the electrons and predominance of the molecular ion at the substrate. It appears that, similar to Ar/H₂ and Ar/O₂ plasmas, an Ar/N₂ plasma is capable of etching a-C:H, carbon nitride (CNₓ) and amorphous hydrogenated carbon nitride (a-C:N:H) films. The etch rate increases with increasing nitrogen atom flux, substrate temperature and ion bombardment. The etch rate depends furthermore on the refractive index and the type of material that is being etched: films deposited with additional ion bombardment have a smaller etch rate, and the etch rate for CNₓ films is about one order of magnitude larger than for a-C:H and a-C:H:N films. Etching of CNₓ films with both Ar/N₂ and Ar/O₂ plasmas shows a different response of the sp¹ (C≡N) bonds with respect to the sp² (C=N) and sp³ (C-N) bonds. Treatment of a-C:H films with Ar/N₂ plasmas leads to permanent changes of the bond structure in the uppermost 10-20 nm of the film, and offers the possibility to nitrate a-C:H films. The chemistry of Ar/N₂/C₂H₂ plasmas, which are used for the deposition of a-C:H:N films, is examined. It is clear that in the plasma nitrogen-containing radicals and stable monomers are formed, and that the acetylene consumption is larger than in a pure Ar/C₂H₂ plasma. The incorporation of nitrogen in the a-C:H:N film leads to a material with a smaller hardness, Young’s modulus and refractive index. The measurements show that with increasing nitrogen concentration a more polymer-like structure develops with less hydrogen, and in which the hydrogen is preferentially bonded to nitrogen. By increasing the substrate temperature during deposition the a-C:H:N films become more “a-C:H like”, as evidenced by an increase of the refractive index, hardness and elasticity, and the appearance of a-C:H infrared absorption features. Furthermore, a higher substrate temperature results in a decrease of the surface roughness. The influence of an additional ion bombardment on the material properties is almost negligible. The improved etching resistance of films deposited with additional ion bombardment should therefore be attributed to a densification of the material rather than to a change in the material structure.

From an Ar/N₂ plasma expanding through a graphite nozzle hydrogen-free carbon nitride (CNₓ) films may be deposited at a growth rate of several nm s⁻¹. The addition of nitrogen appears to be essential for the etching of the graphite nozzle, in which predominantly CN radicals are formed. The FTIRRAS measurements show that the C≡N absorption is dominant in the initial stage of film growth. This suggests that the CN radicals are also responsible for the deposition. At high growth rates the growth rate decreases with increasing substrate temperature, whereas at small growth rates a slight increase is observed. This points to at least two thermally activated processes in the deposition. Additional ion bombardment results in a dramatic decrease of the growth rate. However, the optical constants of the films suggest that at small bias voltages (below ~100 V) modification of the film structure is occurring, whereas at large bias voltages physical sputtering prevails. A preliminary model is presented which describes the growth via CN radicals, and with which the influence of the substrate conditions can be understood.
Samenvatting

Door een materiaal met de juiste bulkeigenschappen te voorzien van een dunne laag van een ander materiaal met toegevoegde oppervlakte-eigenschappen, is het mogelijk om de hardheid, wrijving, optische, thermische en elektronische eigenschappen van een materiaal aan te passen aan de wensen van de gebruiker. De stoffen die samengesteld zijn uit koolstof, stikstof en/of waterstof (CNH materialen) blijken veel geschikte oppervlakte-eigenschappen te bezitten. Bovendien is theoretisch voorspeld dat een kristallijne vorm van koolstofnitride harder zou kunnen zijn dan diamant. In dit proefschrift worden de mogelijkheden onderzocht om m.b.v. een expanderend plasma depositie opstelling, waarmee in het verleden zeer hoge groeisnelheden (tot 70 nm·s⁻¹) zijn gehaald, CNH materialen te deponeren. Voor dit doeleinde is zowel de depositie van een Ar/N₂/C₂H₂ plasma als de depositie van het waterstof-vrije plasma dat ontstaat als een Ar/N₂ plasma door een grafieten uitstroomstuk stroomt, nader onder de loep genomen. De eigenschappen van de gedeponeerde lagen worden bepaald door de samenstelling van het plasma en de substraatcondities. Daarom worden in dit proefschrift zowel de gebruikte plasma’s als de materiaaleigenschappen bestudeerd, en wordt bovendien de invloed van de substraatcondities onderzocht. Voor de karakterisatie van het plasma zijn twee nieuwe meetmethodes geïntroduceerd: massa-spectrometrie (MS) en Fourier transform infrarood absorptie spectroscopie (FTIRAS). Door deconvolutie van de MS data is het mogelijk de kwantitatieve samenstelling van een mengsel van gassen, die tevoren zijn gecalibreerd, binnen ±5% nauwkeurigheid te bepalen. De FTIRAS techniek biedt de mogelijkheid om zonder een calibratie of deconvolutie de samenstelling van het gas direct kwalitatief te vinden. Bovendien is een methode ontwikkeld om uit de FTIRAS data de “gas”temperatuur van het plasma binnen ±100 K nauwkeurigheid te bepalen. Om de groei van de films in situ te bestuderen is ook een nieuwe diagnostiek opgezet: Fourier transform infrarood reflectie absorptie spectroscopie (FTIRRAS). Hiervoor is een speciaal substraat ontworpen welke het mogelijk maakt (sub)monolaag gevoeligheid te halen. Ex situ karakterisatie van de films m.b.v. verschillende technieken geeft o.a. informatie over de C/N/H verhouding, de verschillende soorten bindingen, de optische constanten, de hardheid, elasticiteit en ruwheid van de gedeponeerde films. De karakterisatie van Ar/C₂H₂ plasma’s toont aan dat de dissociatie van het precursorgas verloopt via ladingsuitwisseling met de argon ionen gevolgd door dissociatieve recombinatie met de elektronen, en dat onder bepaalde omstandigheden volledige dissociatie plaatsvindt. De goede overeenkomst tussen de ionenstromen die uit de quasi-ééndimensionale modelering van de MS data volgen en die gemeten zijn m.b.v. een Langmuir sonde, suggereert een één-op-één reactie tussen de argon ionen en acetyleen moleculen. Het ondersteunt ook eerdere suggesties dat de beste kwaliteit amorf gehydrogeerde koolstof (a-C:H) films verkregen wordt bij hoge groeisnelheden, ofwel als de ionenstroom ongeveer gelijk is aan de geïnjecteerde acetyleengasstroom (ook wel “kritische inzaaiïng” genoemd). In Ar/CH₄ plasma’s wordt volledige dissociatie van het precursorgas niet gerealiseerd. Dit wordt toegeschreven aan de veel lagere plakkans van de radicalen die bij de dissociatie worden gevormd, waardoor zij meer tijd hebben om door te reageren naar hogere polymeren. Het feit dat in een methaan plasma veel meer polymeren (tot 20% van de geïnjecteerde CH₄ gasstroom) worden gevormd dan in een acetylene plasma (maximaal 4%), bevestigt dit idee. Om het gedrag van de depositionsnelheid in het
methaan plasma te begrijpen worden twee quasi-ééndimensionale modellen van de plasmachemie opgesteld.

In een Ar/N\textsubscript{2} plasma is het belangrijkste verliesproces voor ionen en elektronen de ladingsuitwisseling van atomaire ionen met N\textsubscript{2} moleculen in de achtergrond, gevolgd door dissociatieve recombinatie van de moleculaire ionen. Dit proces leidt tot produktie van stikstof atomen, verhitting van de elektronen en zorgt ervoor dat bij het substraat het moleculaire ion het dominante ion is. Het blijkt dat een Ar/N\textsubscript{2} plasma, net als Ar/H\textsubscript{2} en Ar/O\textsubscript{2} plasma’s, in staat is a-C:H, koolstof-nitride (CN\textsubscript{x}) en amorf gehydrogeneerd koolstof-nitride (a-C:H:N) films te etsen. De etssnelheid neemt toe met toenemende toever van stikstof atomen, substraattemperatuur en ionenbombardement. Verder hangt de etssnelheid af van de brekingsindex en het soort materiaal dat geëtst wordt: films die met additioneel ionenbombardement zijn gedeponerda vertonen een lagere etssnelheid, en de etssnelheid van CN\textsubscript{x} films is ongeveer een orde hoger dan voor a-C:H en a-C:H:N films. Het etsen van CN\textsubscript{x} films met zowel een Ar/N\textsubscript{2} als Ar/O\textsubscript{2} plasma leidt tot een verschillende respons van de sp\textsuperscript{1} (C≡N) bindingen t.o.v. de sp\textsuperscript{2} (C=N) en sp\textsuperscript{3} (C-N) bindingen. Behandeling van a-C:H films met een Ar/N\textsubscript{2} plasma zorgt voor veranderingen in de structuur van de eerste 10-20 nm van de film en biedt dus de mogelijkheid om a-C:H films te nitreren.

De chemie van het Ar/N\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} plasma, dat voor depositie van a-C:H:N films wordt gebruikt, is bestudeerd. Het blijkt dat in het plasma stikstof-bevattende radicalen en stabiele monomeren worden gevormd en dat de consumptie van acetylen hoger is dan in een puur Ar/C\textsubscript{2}H\textsubscript{2} plasma. De inbouw van stikstof in de a-C:H:N film leidt tot een materiaal met een lagere hardheid, Young’s modulus en brekingsindex. De metingen laten zien dat er met toenemende stikstofconcentratie een meer polymereachtige structuur ontstaat met minder waterstof, waarbij het waterstof bij voorkeur aan stikstof gebonden is. Door de substraattemperatuur tijdens de depositie te verhogen, gaan de a-C:H:N films steeds meer kenmerken van a-C:H films vertonen. Zo neemt de brekingsindex, hardheid en elasticiteit toe en verschijnt een vergelijkbaar infrarood karakteristiek. Tevens leidt een hogere substraattemperatuur tot een lagere oppervlakterugheid. Het gebruik van een additioneel ionenbombardement levert geen noemenswaardige veranderingen in de materiaaleigenschappen op. De verbeterde etswerkstand van films die met additioneel ionenbombardement zijn gedeponerda, moet daarom eerder toegeschreven worden aan een verdichting van het materiaal dan aan een verandering van de materiaalstructuur.

Met een Ar/N\textsubscript{2} plasma dat door een grafieten uitstroomstuk stroomt is het mogelijk waterstof-vrije koolstof-nitride films te deponeren met groeiselheid van enkele nm’s per seconde. Voor het etsen van het grafieten uitstroomstuk is de toevoeging van stikstof essentieel. De belangrijkste produkten die hierbij worden gevormd zijn CN radikalen. De FTIRRAS metingen laten zien dat de C≡N absorptie in de initiële fase van de groei dominant is, hetgeen suggereert dat deze radikalen ook verantwoordelijk zijn voor de groei. Voor hoge groeiselheden neemt de groeiselheid af met toenemende substrattemperatuur, terwijl voor lage groeiselheden een lichte stijging wordt waarneemden. Dit wijst ertop dat er bij de depositie tenminste twee thermisch geactiveerde oppervlakteprocessen van belang zijn. Additioneel ionenbombardement leidt tot een dramatische verlaging van de groeiselheid. De optische constanten van de films suggereren dat er bij lage bias-spanningen (beneden ~ 100 V) laagmodificatie plaatsvindt, terwijl bij hoge spanningen vooral fysisch sputteren optreedt. Er wordt een voorlopig model gepresenteerd waarmede de groei via CN radikalen beschreven kan worden en de invloed van substraatcondities op de groei van de film begrepen kan worden.
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Curriculum Vitae

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Stellingen

behorende bij het proefschrift

Deposition of CNH Materials: Plasma and Film Characterization

door Ariël de Graaf

1. Ten onrechte wordt vaak aangenomen dat tijdens plasmadepositie de radicalen waarvan de dichtheid vlakbij het substraat het grootst is, een dominante bijdrage leveren aan de depositie.


2. In een recombinerend, expanderend argon-stikstof plasma wordt een belangrijk deel van de energie die in de dissociatie van het stikstof is opgeslagen, gebruikt voor verhitting van het achtergrondgas.

3. De observatie van Gielen et al. dat de kwaliteit van a-C:H films bij “kritische inzaaiing” toeneemt met de boogstroom kan verklaard worden uit de toename van de relatieve acetyleen consumptie met toenemende boogstroom.


4. De grotere productie van polymeren in een expanderend argon-methaan plasma in vergelijking met een expanderend argon-acetyleen plasma duidt erop, dat bij de dissociatie van methaan, radicalen met een kleinere aanhechtingswaarschijnlijkheid worden geproduceerd dan bij de dissociatie van acetylen.

5. Het verschil in het honorarium van een getalenteerde voetballer en dat van een solomusicus is een indicatie voor het cultuurniveau van de maatschappij.

6. Het inwinnen van wetenschappelijk advies bij het nemen van politieke beslissingen leidt vaak tot een selectieve interpretatie van onderzoekresultaten.


7. De bevindingen van het Princeton Engineering Anomalies Research program tonen aan dat het menselijk bewustzijn de fysische werkelijkheid significant kan beïnvloeden.

8. Het succes van medicijnen in het onderdrukken van psychische klachten heeft ertoe geleid dat in de psychiatrie minder aandacht wordt besteed aan de emotionele oorzaak van het ontstaan van deze klachten. 


9. Hoewel mensen tegenwoordig langer leven, lijken zij steeds minder tijd te hebben.


11. ‘Technische Universiteit’ is een *contradictio in terminis*. 