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Interaction between Low-Energetic Plasmas and Hydrogenated Amorphous Carbon

A study of the fundamental erosion mechanisms

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Interaction between Low-Energetic Plasmas and Hydrogenated Amorphous Carbon
A study of the fundamental erosion mechanisms

The interaction between plasmas and surfaces play an important role in both low-temperature (industrial) plasma processing and experimental nuclear fusion reactors. Exerting control over the plasma-surface interaction leads to tunability of the growth rate of thin films and their material properties such as density or surface roughness. Furthermore, these interaction processes are of particular interest in high-temperature fusion plasmas since they are considered a significant obstacle in the development of nuclear fusion as a sustainable energy source for the future. A fundamental understanding of plasma-surface interactions is therefore indispensable in constructing the next generation experimental nuclear fusion reactors.

An important nuclear and industrial material with a variety of amorphous and crystalline structures is carbon. It is used as wall material in experimental nuclear fusion reactors and as a protective coating in daily applications such as razor blades and hard drives. To improve the material quality or lifetime of a reactor wall, the plasma deposition and erosion of carbon has been extensively investigated over the last 20 years. Hydrogenated amorphous carbon ($\alpha$-C:H) was used as a material model in this thesis to expand upon those plasma-surface interaction studies.

The goal of this thesis was the investigation of the fundamental erosion mechanisms of $\alpha$-C:H for ion kinetic energies between thermal energies (0.03 eV) and 10 eV. This energy range is expected to play a key role in ITER, the next generation fusion reactor. Moreover, the bond energy (3 – 5 eV) of the amorphous carbon network falls within this relatively unexplored energy range. Expanding thermal plasmas with an ion kinetic energy below 2 eV, without substrate biasing, were used to obtain that goal. Despite these very low ion energies, this thesis established a synergistic effect in the etch rate between hydrogen radicals and argon ions. Hydrogen ions with an ion energy up to 10 eV were likewise shown to play a role in the erosion of $\alpha$-C:H thin films, even though the fraction of hydrogen ions in the total flux was below 0.02%. These results indicate that ion-assisted chemical erosion is the dominant erosion mechanism.

Characterization of the $\alpha$-C:H thin films during plasma erosion — and also during plasma deposition — occurred via in situ spectroscopic ellipsometry (SE). Analysis of the SE data obtained was successfully carried out with B-splines; a first for thin carbon layers. B-splines are a purely mathematical approach and provide a fast and reliable method to determine thickness, roughness and opti-
cal constants of thin films. Their use not only simplifies the data analysis, but can also be applied to data sets with a limited wavelength range. This approach was furthermore instrumental in establishing a correlation between the SE surface roughness and the etch rate. For low etch rates, as in the case of pure argon and pure hydrogen plasmas, the surface roughness increases strongly from a few nanometers to tens of nanometers. For high etch rates, as in the case of mixed argon - hydrogen plasmas, the surface roughness fluctuates on the order of a few nanometers.

Carbon erosion inevitably releases etch products, such as methane and acetylene, into the plasma expansion. Fragmentation of these etch products occurs via charge transfer with the plasma ions, followed in rapid succession by dissociative recombination. It is known from previous deposition studies that polymerization of such hydrocarbon fragments occurs when the initial hydrocarbon density exceeds the ion density. Typical hydrocarbon densities during carbon erosion experiments, as carried out in this work, were, however, lower than the ion density. Nevertheless, the presence of H$_2$ — either from the plasma directly or as dissociation products from the hydrocarbons themselves — was shown in this thesis to have a negative impact on the ion density, thereby paving the way for the formation of higher hydrocarbons.

So far, the expanding thermal plasma has been used to gain insight into the carbon erosion mechanisms and the hydrocarbon plasma chemistry. The converse is possible as well: the carbon erosion process was used to investigate the gas flow dynamics of the plasma expansion. The distribution in electronically excited hydrocarbon species, produced via charge transfer and dissociative recombination reactions, is due to the convolution of the ion and hydrocarbon density throughout the reactor. Moreover, it was found that both the placement of a substrate and the movement of a shutter inside the plasma expansion affect the ion density and the rotational temperature of electronically excited CH radicals via a reorganization of the recirculation cells.

This thesis is a study of the fundamental erosion mechanisms of hydrogenated amorphous carbon by low-energetic plasmas and, therein, it has been concluded that the etch processes are dominated by ion-assisted chemical erosion.
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Chapter 1

Framework and overview of the research

Dear Reader,

With the title Interaction between Low-Energetic Plasmas and Hydrogenated Amorphous Carbon, you already started reading my thesis. The main focus of this work is to investigate the fundamental erosion mechanisms of hydrogenated amorphous carbon. In preparation thereof, the chemistry and flow dynamics of the plasma are studied as well. The main body of my thesis is the collection of four stand alone articles, either published or to be submitted. This introductory chapter will guide you through the various publications and will provide some background as well. Additional background information about the experimental setup and diagnostics is provided in the chapter hereafter. I wish you a pleasant reading and many new insights.

Terje Hansen
1.1 Plasmas are everywhere

A plasma, also called the fourth state of matter, can in its simplest form be described as a collection of neutral atoms and molecules, positive and negative ions (i.e. charged particles), electrons and photons as well [1]. They exist over a wide range of densities \( (10^3 \text{ to } 10^{30} \text{ m}^{-3}) \), temperatures (hundreds to millions of kelvin) and sizes (mm’s to lightyears). More than that, plasmas are the most common state of matter in the observable universe. Every star in the universe, our sun\(^2\) included, is a ball of plasma with several million kelvin in core temperature and a few thousand to tens of thousands kelvin in surface temperature [2]. Due to their intense gravity and core temperature, stars are able to convert lighter elements into heavier ones as an energy source. This process, called fusion, can be artificially recreated on Earth. Higher plasma temperatures are required to compensate for Earth’s lower gravity. Existing experimental fusion reactors routinely create plasmas with core temperatures in excess of 100 million kelvin. However, the energy input of these reactors still exceeds their energy output. Building and running a fusion reactor capable of a net energy output is one of the biggest scientific and engineering challenges for the coming two to three decades.

1.1.1 Divertor plasma

The next generation fusion reactor, currently under construction in the south of France, is called \textit{ITER} [3, 4]. Nuclear fusion reactors such as \textit{ITER} consist of millions of individual pieces spread out over thousands of components and thus rank amongst the most complicated devices ever built. Size-wise, several elephants could fit inside \textit{ITER}’s main reactor chamber. The goal of \textit{ITER} is to prove that the production of a net amount of energy is technologically feasible by fusing hydrogen isotopes into helium and neutrons. Under normal operation, the plasma temperature inside \textit{ITER}’s main reactor chamber would be on the order of 100 million kelvin as mentioned earlier. Only magnetic fields are capable of confining such a fusion plasma and minimizing contact with the main wall of the reactor. Even so, interaction with the outside world is necessary to produce the hydrogen isotope tritium\(^3\) and to remove helium (i.e. the ash of the fusion

\(^1\)For reference, the density of water is about \(10^{28}\) water molecules per cubic meter at room temperature.

\(^2\)The sun has a core temperature of about 15 million kelvin and a surface temperature of about 5800 K [2].

\(^3\)Tritium, one of the hydrogen isotopes involved in the fusion process, has a low natural abundance. \textit{ITER} as well as any future power plant will therefore have to provide in its own tritium. The nuclear interaction between the fast neutrons generated in the fusion process and lithium flowing
1.1. Plasmas are everywhere

process) from the plasma. By correctly shaping the magnetic field, however, the plasma can be diverted towards the bottom of the reactor that is specifically designed for interacting with the plasma. This part of a fusion reactor is called the divertor.

Carbon based materials, such as graphite and carbon fiber composites, are often used as divertor wall for their excellent thermo-mechanical properties and low mass [5]. Erosion studies of graphite in present-day nuclear fusion reactors as well as linear plasma generators have shown that the erosion yield decreases as the incident ion flux increases (Fig. 1.1). Despite this non-linear dependence of the yield on the ion flux and despite the much lower plasma temperature in the divertor (< 50000 K), the high energy density and flux of reactive species can still severely damage and erode the divertor wall [6, 7]. In ITER, a steady state energy flux of 5 to 10 MW m\(^{-2}\) is expected with a pulse duration of at least 500 s [8]. The lifetime of wall materials — carbon-based or otherwise — under such conditions remains an open question. Furthermore, areas of net erosion and net redeposition of — plasma-facing — carbon material as hydrogenated amorphous carbon (\(a\)-C:H) layers have been found throughout existing fusion reactors [9–12]. These \(a\)-C:H layers form a safety issue due to the incorporation and buildup of tritium\(^4\) via co-deposition with hydrocarbons [9,11]. In the 2007 design review of ITER, therefore, it was decided and reported upon by N. Holtkamp in 2009 that the plasma-facing components of the divertor will consist completely of tungsten in the deuterium\(^5\) – tritium operating phase [3,13].

Carbon will still be used during the hydrogen and deuterium startup and conditioning phase of ITER due to the higher radiation losses of tungsten. Radiation losses caused by the (partial) ionization of eroded wall material leads to a lowering of the plasma temperature. In turn, lower plasma temperatures (during the deuterium – tritium operating phase) can put an end to the fusion process itself. The production as well as the short and long term transport of plasma impurities such as carbon inside ITER’s main chamber and divertor remain an outstanding issue [21]. Besides to the tritium safety issue, the \(a\)-C:H layers also lack the thermo-mechanical properties required of a reactor wall. In 2006, J. Roth listed the re-erosion of \(a\)-C:H as one of the unresolved issues in the ITER project [14]. Moreover, part of the eroded carbon material will redeposit as \(a\)-C:H elsewhere in the reactor, including on plasma facing optical components that are used for monitoring and controlling the fusion plasma [22, 23]. Similar issues with car-

\(^4\)Tritium is a radioactive material with a half-life of about 12 years.

\(^5\)Deuterium or heavy hydrogen is a stable hydrogen isotope with a natural abundance of about 0.015%. It is routinely extracted from seawater and used in e.g. nuclear fission power plants.
Figure 1.1: Chemical erosion yield at $T_{\text{max}}$ as function of the incident ion flux as measured with ion beams, plasma beams (PSI1 and PISCES) and fusion reactors (TEXTOR, Tore Supra, JET, JT-60U). Based on the review paper of [14] with data from [5,15–20].

bon deposits on optical components can be found in e.g. particle accelerators and lithography devices [24,25]. Optical components affected in this way suffer from reduced performance.

1.1.2 Plasma processing

The semiconductor industry is one of the industries that relies strongly on the removal, deposition or modification of materials through plasma processing [26]. Low-temperature plasma etching can remove surface material completely or selectively create patterns and trenches through the use of lithography [27, 28]. Removal of photoresist during the lithography process, for instance, introduces carbon into the vacuum system which can then contaminate various (optical) subsystems. Replacing affected components, whether in a lithography device or a fusion reactor, might not always be possible due to overall performance reasons, safety concerns or simply practicality. In situ low-temperature plasma etching in combination with deposition mitigation is an alternative solution to maintain or restore optical performance [29]. With the ongoing construction of ITER and the push to EUV wavelength ranges in the semiconductor industry, the development of a comprehensive cleaning and deposition mitigation scheme has become
a current issue [23]. Despite all that, the presence of hydrogenated amorphous carbon is not always problematic. Thin films of $a$-C:H are often used as anti-reflection coatings as well as protective coatings in a variety of applications that range from hard disk drives, optical windows, steel wires and razor blades to solar cells [30–33]. The bio-compatibility and chemical inertness of $a$-C:H allows the material to be also used in food packaging and prosthetics [34,35]. One of the plasma deposition techniques used in both research and industry to deposit functional materials such as $a$-C:H is plasma enhanced - chemical vapour deposition (PE-CVD). This technique, which is also used in this thesis, can deposit $a$-C:H with high growth rates and uniformity-in-depth [36,37]. The precursors most often used in the PE-CVD process of $a$-C:H are methane\(^6\) (CH\(_4\)) and acetylene (C\(_2\)H\(_2\)).

1.1.3 Plasma-surface interaction

Both the carbon etch products from the divertor wall as the intentionally injected hydrocarbon precursors undergo the same plasma chemical reactions in the plasma phase [38–45]. A possible outcome of that interaction between the hydrocarbons and the charged plasma constituents is an exchange of energy or charge. In case of a molecule it can also be dissociated or, in other words, fragmented into smaller atoms, molecules or ions. These fragments in turn can polymerize or coalesce into different molecules, which were not necessarily originally present in the reactor. In case of carbon-based precursors, the resulting plasma chemistry can involve dozens, if not hundreds of possible reactions and molecules [45–49]. The plasma chemistry is thus, to say the least, a rich and complex system. Some of the more reactive molecules produced by the plasma will furthermore deposit on a surface (as $a$-C:H), hence the term plasma enhanced - chemical vapour deposition.

Not only the plasma chemistry, but also the plasma-surface interaction can result in growth of the deposition layer. Energetic ion bombardment\(^7\), for example, can prepare new surface sites onto which molecules can attach. Ion bombardment can furthermore densify the material (higher sp\(^3\) fraction), but can also physically damage and remove surface material [50, 51]. Even so, energetic ion bombardment is but one of many different mechanisms through which the plasma-surface interaction can take place. For instance, radicals\(^8\) produced by the plasma can

---

\(^6\)Natural gas, for example, consists for 80 to 90% of methane.

\(^7\)An additional voltage bias can optionally be applied to the deposition surface to increase the ion energy during ion bombardment.

\(^8\)Radicals are very reactive atoms or molecules. Atomic hydrogen (H) for example is very
likewise erode the surface. In case of $a$-C:H etching, atomic hydrogen (H) is one of the more effective radicals. Molecular hydrogen, as a source of atomic H, can be added to the plasma specifically for carbon etching. Moreover, the hydrocarbons themselves are another source of both atomic and molecular hydrogen. There is thus a continuous competition between deposition, modification and etching of the (carbon) surface during plasma treatment. The gas composition of the plasma, which can be heavily influenced by the experimentalist, will therefore determine the overall outcome of the plasma-surface interaction. Also the sticking coefficient of the gas molecules, the surface temperature and, in particular, the plasma properties play an important role [52,53].

### 1.1.4 Hydrogenated amorphous carbon

Hydrogenated amorphous carbon, the topical material of this thesis, is a dark appearing, chemically inert and semiconducting material with similar mechanical and optical properties as diamond [32]. For comparison, diamond is a transparent material with very high density, hardness and room temperature heat conductivity. It also has a wide band gap and is thus a good electrical insulator. Graphite on the other hand is black in color, slippery and a conductor. In contrast with $a$-C:H, both graphite and diamond are highly ordered or crystalline materials [54].

Carbon has four available valence electrons to bond with other atoms. The reason for the wide range of crystalline and disordered structures in which carbon exists, however, can be found in a reorganisation of the energy levels of these four electrons into so-called sp$^3$, sp$^2$ or sp$^1$ hybridization energy levels$^9$ [54]. Diamond and graphite consist for 100% of sp$^3$ and sp$^2$ energy levels, respectively. Amorphous carbon in turn is predominantly a mix of both sp$^2$ and sp$^3$ bondings, while hydrogenated amorphous carbon also contains a significant fraction of hydrogen$^{10}$. Furthermore, the many different types of $a$-C:H, whose properties are determined by the sp$^2$, sp$^3$ and hydrogen content, can be represented in a ternary phase diagram (Fig. 1.2) [32,37,43,55]. By controlling the plasma properties and surface temperature, among others, many of these $a$-C:H types can be deposited with PE-CVD.

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$^9$Briefly explained, the four valence electrons of carbon in an sp$^3$ configuration each form a single $\sigma$ bond with an adjacent atom. In an sp$^2$ configuration, however, only three of the four electrons are reorganised into a $\sigma$ bond. The fourth electron forms a weaker out-of-plane $\pi$ bond with an adjacent C atom. This $\pi$ bond will then form a double bond together with the $\sigma$ bond above which it is located. The third and last configuration, i.e. sp$^1$, has two $\sigma$ and two $\pi$ bonds. Both $\pi$ bonds together with one of the two $\sigma$ bonds form a triple bond between two C atoms [54].

$^{10}$Hydrogen forms a single $\sigma$ bond with an adjacent C atom.
1.1. Plasmas are everywhere

According to this diagram our Tauc gap is plotted as a function of sp

Figure 1.2: Ternary phase diagram. The dot indicates the type of a-C:H samples used in this thesis. After [32,37,43,55].
1.2 Research aim of this thesis

The thesis in front of you is a fundamental study on the plasma etching of hydrogenated amorphous carbon. This topic has direct applications in both high-temperature plasma fusion research and low-temperature plasma processing, as illustrated throughout the first part of this introduction. For instance, carbon cleaning of optical components without damaging the underlying structure has in recent years become an important issue in both disciplines. In addition, a better understanding of the underlying plasma and surface processes can lead to better (numerical) fusion reactor models as well as more control over the deposition or etching of different types of $a$-C:H [43,56]. Such information can lead to an improved lifetime of the reactor wall and the optical components. On the other hand, studies rooted in low-temperature plasma processing are generally more focused on the implications of carbon erosion for thin film growth and the quality of the deposited material.

As will be explained extensively at the end of this section, the main aim is to investigate the erosion mechanisms in the largely unexplored ion kinetic energy range between 0.03 and 10 eV. In preparation thereof, four additional supporting objectives will be identified and discussed. The first objective is to find a fast, easy-to-apply and optimal model for spectroscopic ellipsometry data analysis. Spectroscopic ellipsometry, which requires a multi-layered model of the target for data analysis, is one of the diagnostic techniques used to monitor the carbon target during erosion. A second objective is to investigate hydrocarbon recombination in hydrogen rich plasmas with low carbon content. Reconversion of the hydrocarbon etch products can facilitate their redeposition which in turn leads to a reduced effective etch rate. Furthermore, the ion density is an important factor in both the etch rate and the resulting plasma chemistry and vice versa. Objective three will therefore be to identify and evaluate the extent of external influences on the ion density and gas flow. The fourth objective is to obtain surface measurements of the incident ion flux in order to compare etch rates of different plasma systems.

Previous studies have shown that plasma exposure can modify the surface morphology as well as alter the $sp^2$ and $sp^3$ content of carbon material [57–61]. Since the hardness of this material is dependent on the $sp^x$ ($x = 1, 2, 3$) content, the etch rate can be influenced as well [58]. Etch rates have been determined with a variety of diagnostics, ranging from contact profilometry and colorimetry to single wavelength ellipsometry [62–66]. Ellipsometry, which will also be used in this thesis, is a non-invasive optical diagnostic widely used for thin film analysis. An implementation of this technique was recently developed for in situ
1.2. Research aim of this thesis

use in ITER [67]. Data analysis however requires a suitable model that describes the interaction of the incident light with the material. Such a model has to take into account the homogeneity and layer structure of the material under investigation. Current models for a-C:H are furthermore based on a completely physical description of the carbon layer properties, something which is not required for all applications [68–70]. Plasma cleaning of optical components, for example, requires only knowledge about the thickness of the carbon impurity layer and the dielectric function of the carbon impurity—optical component system. On top of that, the limited wavelength range of many ellipsometry devices often requires additional data to guarantee a successful fit of such a physical model to the measured data. The first objective of this thesis — in anticipation of a study on the erosion mechanisms later on — is to find a fast, easy-to-apply and optimal analysis model, independent of the measured wavelength range, to determine the surface morphology and thickness evolution during carbon etching.

Due to the limited access to the edge plasma near the divertor wall and in anticipation of new fusion reactors such as ITER, nuclear wall materials are often studied and tested in dedicated linear plasma reactors. Although linear reactors such as PSI-I/I1, NAGDIS-I/I1, PISCES-A/B and others have reached ion fluxes up to \(10^{23} \text{ m}^{-2} \text{s}^{-1}\), even higher fluxes up to \(10^{24} \text{ m}^{-2} \text{s}^{-1}\) are expected in ITER’s divertor [5, 7, 16, 18, 71–73]. New material-testing facilities, for instance IFMIF or the recently completed Magnum-PSI facility in The Netherlands, are therefore required to test wall material candidates under ITER-like plasma conditions [7, 74, 75]. IFMIF conducts irradiation studies with high-energy neutrons, whereas Magnum-PSI will study the erosion and redeposition process within a magnetized plasma beam [7, 76]. The angle between the magnetic field lines and the target, exposed to the plasma beam, can be varied.

The plasma sources used in Magnum-PSI and its predecessor Pilot-PSI are in their design based on a cascaded arc [77–79]. Compared to other plasma (processing) sources, the cascaded arc produces an expanding thermal plasma jet with a very low ion and electron energy (< 2 eV without additional substrate biasing) and relatively high radical and ion flux [77, 78, 80]. This type of arc, as developed in our group and explained in detail in section 2.1, is used in both industry and academic research for low-temperature plasma processing of functional materials, including a-C:H thin films [26, 36, 81, 82]. Earlier studies of the plasma chemistry in a hydrocarbon rich plasma showed that polymerization of the hydrocarbon deposition precursor plays an important role in a-C:H film growth [44, 45, 53]. Deposition precursors such as CH\(_4\) and C\(_2\)H\(_2\) are first fragmented

\[11\] The International Fusion Materials Irradiation Facility uses an accelerator-based neutron source, rather than a plasma-based ion and radical source.
via charge transfer and dissociative recombination reactions\textsuperscript{12} before any polymerization can take place \cite{40,43,45}. The number of ions available for charge transfer therefore determines to a large degree the amount of precursor consumption and polymerization \cite{39,45}. The carbon content of a divertor plasma due to wall erosion is however expected to be far lower, percentage wise, compared to a typical deposition plasma. Deposition and erosion are nevertheless two intertwined processes, as explained earlier in section 1.1.3. A second objective in this thesis is therefore to investigate how, if any, hydrocarbon reconversion occurs in a hydrogen rich plasma with low carbon content.

An important advantage of Magnum-PSI over many other plasma devices, fusion reactors included, is the ability to transport the target in vacuo to a battery of diagnostic and testing facilities for postmortem analysis \cite{7}. Material compositions and etch rates, for example, can be determined postmortem with Rutherford backscattering spectrometry and contact profilometry, respectively. Although such an analysis can provide estimates about the lifetime and hydrogen uptake of the material, amongst other things, it yields no dynamic information about the surface conditions or, for that matter, the erosion mechanisms. A range of passive and active optical diagnostics are therefore applied in plasma devices when feasible and are likewise envisaged (or under consideration) for Magnum-PSI to monitor the surface and plasma properties \cite{7,75,83}. The vibrational energy state and electronic band structure of the surface molecules, for instance, can be determined with sum frequency and second harmonic generation, respectively. Light emission from the plasma species and etch products, passively collected via optical emission spectroscopy, is another approach to study the plasma-surface interaction. Interpretation of these measured spectra depends strongly on the measurement position, the plasma conditions and origin of the excited species. The plasma chemistry, for instance, affects the gas composition and excitation levels, while the gas composition and (re-)-circulation in turn affect the plasma properties. A particular interest of this thesis is the redistribution of the hydrocarbon etch products, which is likewise affected by the gas flow dynamics of the reactor. A third objective in this thesis is therefore to determine the extent of external influences — from the target holder, for instance — on the ion density and gas flow. Related to this are ion flux measurements directly at the surface, which constitutes the fourth objective. Such ion flux measurements, combined with the etch rates of a material, result in an estimate of the etch yield for different plasma systems. This facilitates later on our understanding of the underlying erosion mechanisms.

In conclusion, erosion studies of either graphite or $a$-C:H have been carried

\textsuperscript{12}More information on these type of reactions can be found in chapters 2 and 3.
1.2. Research aim of this thesis

Figure 1.3: Experimental and numerical data of the erosion yield for (a) graphite exposed to D\(^+\) with an ion flux of 10\(^{20}\) fluxunits and (b) \(\alpha\)-C:H exposed to Ar and Ar/H\(_2\) plasmas. Based on the review paper of [84] with data from [5,14,18,85–91].
out in a variety of plasma devices and fusion reactors. This lead to the for-
mulation of several erosion mechanisms, each applicable under different plasma con-
ditions. Important parameters include the surface temperature, gas composition, ion
to radical flux ratio and the ion energy as explained in detail in chapter 6. The
results in chapter 6 will show that surface morphology plays an important role as
well. One of those mechanisms is chemical erosion in which $a$-C:H is exposed to
an atomic H beam [92–94]. This exposure leads to an increase in sp$^3$ content as
well as the removal of surface material [58]. Moreover, a synergistic effect in the
etch rate occurs when carbon is simultaneously irradiated by atomic hydrogen
and argon (or hydrogen) ions. This process is called chemical sputtering when
the ion energy exceeds the threshold for physical sputtering ($\sim 30 – 60$ eV) and
ion-assisted chemical erosion when the ions are less energetic. The ion energy
dependence of the etch yield, illustrated in Fig. 1.3.a for pure hydrogen plasmas
and in Fig. 1.3.b for Ar/H$_2$ plasmas, has been well established for H$^+$ ($\chi = 1 – 3$)
and Ar$^+$ ion energies between 10 eV and 5 keV [5, 14, 57, 64, 65, 85, 89, 95–99].
The binding energy of 3–5 eV of both C-H and C-C bonds falls in between ther-
mal energies and 10 eV [100,101]. Experimental data in this last energy range is
however relatively unavailable, as first noted by J. Roth [14], particularly in the
high flux regime expected in ITER. Investigating the erosion mechanisms within
this energy range, i.e. between thermal energies (0.03 eV) and 10 eV, is therefore
the primary aim of this thesis.

Finally, the research questions formulated in this thesis are complementary to
the research carried out on the Pilot- and Magnum-PSI setups at the FOM research
institute in Rijnhuizen, The Netherlands [7, 74, 75, 102]. Both research groups
try to understand the underlying fundamental physical and chemical processes
related to carbon erosion and deposition. In their approach, however, different
carbon allotropes are used. Fine grain graphite and hydrogenated amorphous car-
bon are primarily used in Rijnhuizen and Eindhoven, respectively. As mentioned
earlier in this section, the large majority of in situ and postmortem techniques
that are used — or planned — in Rijnhuizen to analyse the FGG targets pro-
vide only indirect information about the surface processes. The use of in situ
spectroscopic ellipsometry in this thesis for direct and dynamic measurements of
the $a$-C:H surface provides therefore already complementary information from a
diagnostic perspective. The reactor configurations are likewise complementary.
Magnetic fields, for instance, can confine the plasma as well as the hydrocarbon
etch products. This confinement increases the hydrocarbon redeposition rate near
their point of origin and, as such, can be studied in detail. The superconducting
coil on Magnum-PSI that generates the magnetic field however limits the number
of viewports as well as their size. Larger viewports on our setup — as well as
Pilot-PSI — provide access to a larger part of the plasma which facilitates studies of the gas flow dynamics and the recycling of eroded carbon material. This choice in materials, diagnostics and reactor configurations is moreover a reflection of the broader applications. The lifetime of a carbon wall and viability of other wall materials under ITER-like plasma conditions is the main application of the research in Rijnhuizen, whereas the main application for our research situates itself in tritium retention, cleaning of optical components and $a$-C:H thin film deposition for industry. Regardless of these differences in approach and application, both groups have and continue to contribute to a fundamental understanding of the underlying erosion and deposition processes.

1.3 Experimental approach

Over the last 15 to 20 years, the group Plasma & Materials Processing (formerly ETP) has extensively investigated the remote-plasma deposition of hydrogenated amorphous carbon thin films [38–45,77]. The plasma chemistry, material properties and deposition conditions have been — and still are — studied. The approach in this thesis is to leverage the knowledge gained in these deposition studies for the study of $a$-C:H plasma etching and reuse the deposition (or similar) setups and diagnostics.

The type of $a$-C:H used throughout this thesis is indicated in Fig. 1.2. Samples of this type are deposited in-house with a thickness of about 1 to 1.5 $\mu$m. For very thin films the carbon-substrate interface has to be taken into account, while stress in thicker films causes delamination. The surface area of these samples is 200 mm$^2$ to minimize the carbon content and redeposition in the reactor. Previous studies by Gielen et al. and Benedikt et al. have characterized similar films as graphitic carbon (i.e. a high sp$^2$ content) with less than 5% of sp$^1$ bonds [37,43]. These studies likewise determined an atomic density of around 1.7 g/cm$^3$ and a hydrogen and carbon content of about 30% and 70%, respectively. Characterisation by J.W. Weber of the films used throughout this thesis showed a sp$^2$ to sp$^3$ ratio of 0.52, in correspondence with an atomic sp$^3$ percentage of 56% [55]. The deposited films are furthermore homogeneous-in-depth and smooth as will be shown later in chapter 6. Although the difference in hardness or density between the various types of $a$-C:H (Fig. 1.2) can affect the growth or etch rate in absolute terms, the exact material characteristics are not of critical importance for the conclusions drawn in this thesis. Hydrogenated amorphous carbon in that sense functions in this thesis more as a generic material model for carbon.

Changes in the thickness and morphology of $a$-C:H during plasma processing
Figure 1.4: An argon plasma jet, admixed with H\textsubscript{2} and flowing from left to right, is deflected by the sample holder.

are investigated in this thesis with spectroscopic ellipsometry\textsuperscript{13}, rather than single wavelength ellipsometry [103–105]. Although single wavelength ellipsometry has a higher time resolution, the analysis does not provide a unique thickness solution without additional information about the initial sample thickness. The obtained SE results, moreover, are verified against atomic force microscopy (AFM) and cross-sectional scanning electron microscopy (SEM).

Fig. 1.4 shows the interaction between a plasma — generated by a cascaded arc inside a linear plasma reactor — and an α-C:H sample. These samples are exposed to pure argon and hydrogen plasmas as well as argon plasmas admixed with hydrogen. The primary component, relevant for carbon etching, in an argon and hydrogen plasma are Ar\textsuperscript{+} ions and H radicals, respectively. Both species are sufficiently present in the mixed Ar/H\textsubscript{2} plasma to investigate any synergistic effect between Ar\textsuperscript{+} and H with regard to the etch rate. The use of these three different plasma systems also allows for a clear distinction between the contribution of ions and radicals to carbon etching. Electrical probes measure the ion flux directly at the target and the ion density in the area around it, while the atomic H flux is estimated from previous work in our group [106–110]. Argon and hydrogen ion fluxes up to $10^{22}$ m\textsuperscript{-2}s\textsuperscript{-1} and $10^{19}$ m\textsuperscript{-2}s\textsuperscript{-1}, respectively, can be reached with the linear plasma reactors used in this thesis. Typical fluxes found in litera-

\textsuperscript{13}The basic working principle of spectroscopic ellipsometry and other diagnostics mentioned in this text can be found in chapter 2.3.
ture are on the order of $10^{18}$ m$^{-2}$s$^{-1}$ for both species [65,85,96,99]. Hydrogen ion fluxes in experimental fusion reactors and dedicated linear plasma reactors on the other hand routinely exceed $10^{20}$ m$^{-2}$s$^{-1}$ [6,111,112]. Although the ion flux in our reactors is lower than expected for ITER, the ion energy (without additional substrate biasing) stays below 10 eV. The atomic hydrogen flux ($\sim 10^{22}$ m$^{-2}$s$^{-1}$) is furthermore several orders of magnitude higher than the typical literature values of $10^{15} - 10^{20}$ m$^{-2}$s$^{-1}$ [5,57,65,92,96,99,109]. A cascaded arc, of the type employed in this thesis, is thus ideally suited to investigate the erosion mechanism of $a$-C:H for low ion energies and high atomic H fluxes. The inner workings of a cascaded arc as well as the known chemistry in the three plasma systems are explained in more detail in chapter 2.

As stated in the first part of this introduction, any plasma chemistry involving hydrocarbons is a rich and complex system. The plasma chemistry during $a$-C:H etching is for this reason emulated by adding low concentrations of different hydrogen and hydrocarbon precursor mixtures to an expanding thermal plasma. The resulting gas composition is analysed with residual gas analysis (RGA). This technique will prove sensitive enough to measure stable hydrocarbons etch products with a mass up to 60 amu under the plasma conditions found in this thesis.

The plasma chemistry is also investigated by means of (spatially and time resolved) optical emission spectroscopy [83,113]. For one of the excited species identified in the spectra during $a$-C:H etching, in casu CH*, the rotational and vibrational temperatures are determined with the spectrum simulation program LIFBASE [38,114,115]. These temperatures will provide information about the creation process of this radical. The hydrocarbon distribution and gas flow in the reactor are likewise investigated by mapping out the optical emission of the plasma in front of the substrate. Such measurements however take up a far greater amount of time than for the plasma to completely erode an $a$-C:H sample$^{14}$. A graphite target was therefore used in these particular experiments. Even though a different target type might affect the gas composition of the etch products, the plasma chemical processes will be very similar. The measured hydrocarbon distribution throughout the reactor is furthermore compared against numerical flow simulations. These calculations are performed with the DSMC$^{15}$ code developed by G.A. Bird [74,116–118]. An important part of this thesis consists of optical emission spectrometry measurements. The specific plasma conditions used in this thesis for carbon erosion are therefore selected to ensure an optimal signal on the optical emission spectrometer.

$^{14}$This applies specifically to our experiment and should not be taken as a blank statement.

$^{15}$Direct Simulation Monte Carlo
1.4 Outline and key results of this thesis

The topic and key results of the five remaining chapters are highlighted in this last part of the introduction. Chapter 2 explains the basic operation of the plasma reactor and diagnostics used throughout this thesis. It also summarizes the current understanding of the plasma chemistry and flow dynamics in the reactor. Chapter 3 deals with the hydrocarbon reconversion in a hydrogen rich plasma with low carbon content. The expectation for a plasma with low hydrocarbon to ion density ratio was complete dissociation of the hydrocarbons, rather than the conversion into heavier molecules. This result is attributed to a drastic reduction in the ion density caused by H₂. A synergistic effect in the production of CₓHᵧ (x = 3,4) is moreover observed when CH₄ and C₂H₂ are both mixed together. The last part of chapter 3 proposes a reaction path for the hydrocarbon polymerization in a low carbon environment for every gas mixture (i.e. CH₄, C₂H₂ and CH₄/C₂H₂). Hydrocarbon reconversion not only affects the gas composition but can also facilitate carbon redeposition, thereby reducing the effective etch rate.

Ion and radical densities are important factors in both the plasma and surface chemistry, as expressed earlier in section 1.2. The ion density as well as the gas flow and distribution of hydrocarbon etch products in an expanding thermal plasma are therefore investigated in chapter 4. The placement of a substrate inside the plasma expansion leads to a reorganization of the gas recirculation, thereby affecting the ion density. Convoluted of the ion and hydrocarbon density yields the distribution of electronically excited CH radicals. Production of these radicals, and the plasma chemistry in general, occurs via charge transfer and dissociative recombination. The internal energy of CH is furthermore related to the gas kinetic temperature via their parent molecules and therefore sensitive to changes in the gas flow as caused by e.g. the retraction and extension of a shutter\textsuperscript{16} in the plasma expansion. Chapter 4 ends with an appendix on the effect of H₂ on an argon plasma and the atomic H production for different Ar/H₂ gas mixtures.

Until now, the best models for the analysis of a-C:H thin films with spectroscopic ellipsometry were based on a Tauc-Lorentz oscillator [68–70]. A Tauc-Lorentz oscillator provides a physical description of the dielectric function of a-C:H, which is not required in all situations. Chapter 5 therefore introduces a new model based on B-splines for the analysis of a-C:H thin films [119]. B-splines provide a purely mathematical description of the dielectric function which requires no prior knowledge about the film. Moreover, this model is fast — in

\textsuperscript{16}Prior to a measurement, each graphite target and a-C:H sample is protected by a shutter against plasma exposure.
1.4. Outline and key results of this thesis

terms of both computational requirements and time requirements of the user — and easy to use for anyone familiar with spectroscopic ellipsometry. Although the B-spline model does not provide a physical description of the material, it can be a stepping stone to more physical models. Also note that the use of B-splines is not limited to a-C:H [119]. Chapter 5 will furthermore show that the deposited a-C:H films are smooth and homogeneous-in-depth.

As stated earlier, the research aim of this thesis is to study the erosion mechanisms of carbon in a low energetic plasma. Chapter 6 examines these mechanisms for the ion kinetic energy range between 0.03 and 10 eV, of which the significance was explained in section 1.2. A synergistic effect between Ar\(^+\) ions and atomic H is observed in the etch rate even though the incident ion kinetic energy is lower than the binding energy of either C-C and C-H bonds. Ion-assisted chemical sputtering is the primary etch mechanism in these low-energetic high flux plasmas, although a contribution of swift chemical etching at low substrate temperatures is not excluded. Lastly, thermal spikes at the surface caused by low energetic ions lead to graphitization and determine to a large extent the surface morphology during plasma etching.

To conclude, the publications and application note* related to these chapters are listed below.

**Chapter 3:** *H\(_2\): the critical juncture between polymerization and dissociation of hydrocarbons in a low-temperature plasma*
T.A.R. Hansen, M.C.M. van de Sanden and R. Engeln, To be submitted

**Chapter 4:** *Investigating the flow dynamics and chemistry of an expanding thermal plasma through CH(A-X) emission spectra*
T.A.R. Hansen, P.G.J. Colsters, M.C.M. van de Sanden and R. Engeln,
To be submitted

Detection of hydrocarbon radicals during plasma etching*

**Chapter 5:** *B-spline parameterization of the dielectric function applied to spectroscopic ellipsometry on amorphous carbon*
J.W. Weber, T.A.R. Hansen, M.C.M. van de Sanden and R. Engeln,

**Chapter 6:** *Synergistic etch rates during low-energetic plasma etching of hydrogenated amorphous carbon*
M.C.M. van de Sanden and R. Engeln, To be submitted
Chapter 2

Experimental setup and diagnostics

The experimental setups used throughout this thesis are in essence a low pressure vacuum chamber equipped with a temperature-controlled sample holder and a cascaded arc as plasma source. The inner workings of the cascaded arc and the flow characteristics of the generated expanding thermal plasma are explained in section 2.1. Different plasma systems are used throughout this thesis. The specific reactions, with their known rate coefficients, are given in the relevant chapters. Regardless thereof, the dominant mechanisms are summarized in section 2.2. Lastly, section 2.3 provides more details about the diagnostics previously mentioned in chapter 1.

2.1 Expanding thermal plasma

An expanding thermal plasma is generated inside a linear reactor with a cascaded arc. The arc used throughout this thesis consists of a stack of four water cooled copper plates [77, 78]. Each plate is electrically floating as well as electrically insulated from each other with PVC spacers (Fig. 2.1). The entire stack has a total length of 24 mm and a central bore of 4 mm in diameter. The purpose of these copper plates is to stabilize the plasma [120]. The head of the arc contains three tungsten cathodes and the gas injection port, while the anode plate on the other side of the stack is grounded. Both sides are connected to a high voltage power source. Running a high DC current (up to 75 A) from the cathode to the anode side ionizes the gas flowing through the channel, thus creating a plasma. Gas mixtures as well as pure gases such as argon (Ar) or molecular hydrogen (H₂)
can be ionized in the arc. Depending on the gas mixture, the input power ranges from about 2 to 9 kW. In addition to ionization, the atoms or molecules can also increase their internal energy without the loss (or gain) of one or more electrons. A molecular gas, due to its higher internal degrees of freedom\(^1\), is therefore more difficult to ionize than an atomic gas. Likewise, the recombination of an ion and an electron can produce a particle with high internal energy. One method for these excited particles to reduce their internal energy is through the emission of a photon, i.e. light emission. By itself the cascaded arc can thus be used as a high intensity light source [120].

In the majority of scientific and industrial applications, such as catalytic conversion or materials processing, the cascaded arc is connected to a low pressure vacuum chamber (hereafter reactor) and used as a source of ions, radicals or both [36,121]. Although still at sub-atmospheric pressure, the pressure in the arc (200 to 600 mbar) is a few hundred times larger than in the reactor itself (0.1 to 3 mbar). The large pressure difference creates a supersonic, expanding thermal plasma. When this supersonic plasma jet encounters the background gas, a barrel shock is created. The distance between the arc nozzle and the shock front can be estimated from:

\[
z_s = 18 \sqrt[4]{\frac{\Phi}{P_{bg}}} \sqrt{MT},
\]

with the gas flow \(\Phi\) in sccs \((1\text{ sccs} = 2.5 \times 10^{19} \text{ s}^{-1})\)\(^2\), the background pressure \(P_{bg}\) in Pa, the mass \(M\) in amu and the temperature of the plasma source \(T\) in eV [122]. After the shock, the plasma continues at subsonic speeds towards the sample holder. The expanding thermal plasma, or plasma jet, can be seen through the reactor windows in Fig. 2.1b. The plasma temperature of about 10,000 K inside the arc is very low compared to the core temperature in a nuclear fusion reactor. Since the external energy input from the power supply ends at the exit of the arc, the plasma temperature drops rapidly to 1500 K over the course of a few mm’s to cm’s [78]. After another 10 to 20 cm the plasma temperature is at most 1500 K. The generated plasma is furthermore radially symmetric and quasi-neutral, but not in local thermal equilibrium [77].

The gas residence time for the reactors and conditions used in this thesis falls typically in the range of 0.1 to 5 s. This can be calculated from the gas flow \(\Phi\) (in sccs), the pressure \(P\) (in Pa) and reactor volume \(V\) (in m\(^3\)) with \(\tau = \frac{10 \times PV}{\Phi}\). Within the expansion itself, however, the ions and electrons have a residence time

\(^1\)In contrast with an atom, a molecule can also store energy through vibration and rotation.

\(^2\)Standard cubic centimeter per second, abbreviated to sccs, is a unit for flow and defined as the number of particles in 1 cm\(^3\) at standard conditions (i.e. at room temperature and atmospheric pressure) that passes by each second.
Figure 2.1: (a) An argon plasma jet, admixed with H$_2$, as it exits the cascaded arc. (b) On the left a photo of a plasma reactor with an argon plasma jet visible through the view ports. On the right a schematic cross-section of a plasma reactor with cascaded arc and plasma jet.
on the order of 0.1 ms [123]. The much higher residence times of the background gas causes the background gas to recirculate and interact multiple times with the reactor wall. The resulting recirculation cells, wedged between the plasma jet and the reactor wall, are also responsible for a good mixture of the background gas. Background gas can moreover diffuse into the plasma over the entire length of the expansion and interact with the electrons and ions emanating from the arc [118]. In the supersonic part of the expansion, background species can enter through the barrel shock if their partial pressure inside the jet is lower than in the background [118]. This is particularly the case in the region right before the shock front, where the plasma is overexpanded [124]. The total pressure in this so-called zone of silence is lower than the overall background pressure. These recirculation cells, therefore, play an important role in the chemistry of the entire system [118,123–126]. The existence of such cells is relevant for chapters 3 and 4.

2.2 Plasma chemistry in an expanding thermal plasma

The high pressure difference between the cascaded arc and the reactor, as mentioned in the previous section, effectively uncouples the plasma chemistry in the arc from the chemistry in the reactor. The electron temperature within the reactor is much lower than the ionization energy of all the species encountered in this work. Electron ionization therefore does not occur within the confines of the reactor. Although the electron temperature within the arc is likewise below the ionization energy, the electron density is sufficiently high for stepwise electron excitation and ionization of an atom or molecule. The arc is thus the only place where ionization occurs through electron impact. This, however, does not exclude the formation of new ion species within the reactor. In case of a molecular plasma, such as the Ar/H\textsubscript{2} plasmas or pure H\textsubscript{2} plasmas used throughout this thesis, new ion species are formed via charge transfer (CT) between an ion (I\textsuperscript{+}) and a molecule (M):

\[ I^+ + M \rightarrow I + M^+. \]  (2.2)

With exception of surface losses, CT is followed by dissociative recombination (DR):

\[ M^+ + e^- \rightarrow \text{fragments}. \]  (2.3)

Rate coefficients for charge transfer are two or three orders of magnitude lower than for dissociative recombination. Charge transfer is thus the time-limiting
factor in the molecular dissociation process. Moreover, the molecular fragments themselves can undergo successive \text{CT} \text{ and } \text{DR} \text{ reactions.}

\text{CT}, \text{ followed by } \text{DR}, \text{ dominates both the arc and reactor chemistry and is responsible for the formation of hydrogen ions (e.g. } \mathrm{H}^+_2) \text{ and radicals in both } \mathrm{Ar}/\mathrm{H}_2 \text{ and pure } \mathrm{H}_2 \text{ plasmas [109, 127–131]. These hydrogen ions and radicals play an important role in carbon etching [14, 58, 64, 65, 85, 92, 94, 96, 97, 99, 111, 132]. An overview of the specific reactions involved in the formation of these hydrogen species will now be given. This overview will likewise show which species are dominantly present in the reactor. The overview starts, however, with a pure argon plasma, which is also used in this thesis for } a-\text{C:H etching.}

The dominant ion in a pure argon plasma is $\mathrm{Ar}^+$, as double charged ions are not observed in these low energetic plasma jets. Surface recombination is the main loss channel of $\mathrm{Ar}^+$ due to the low rate coefficient of three body recombination:

$$\mathrm{Ar}^+ + e^- + e^- \rightarrow \mathrm{Ar}^* + e^-.$$ \hspace{1cm} (2.4)

The rate for reaction (2.4) of $k \sim 1.7 \times (\hat{T}_e)^{-9/2} \times 10^{-39} \text{m}^6 \text{s}^{-1}$ with $\hat{T}_e$ in eV [133].

Molecular hydrogen ($\mathrm{H}_2$) can be admixed to the argon plasma via the reactor or directly via the arc. Charge transfer between $\mathrm{H}_2$ and $\mathrm{Ar}^+$ leads in both cases to the formation of H radicals, either directly via reactions (2.5a) and (2.5g) or via intermediate hydrogen ion species such as $\mathrm{H}_2^+$ (reactions (2.5b) and (2.5e)). Reaction (2.5b) is known to be of little importance below 0.5 eV, while reaction (2.5a) is ten times faster as well [127, 128]. Direct formation of H is thus the dominant process. Likewise, the high rates of reactions (2.5a) and (2.5g) make CT and DR the dominant loss mechanism of $\mathrm{Ar}^+$ ions when $\mathrm{H}_2$ is added to the plasma.

$$\mathrm{Ar}^+ + \mathrm{H}_2 \rightarrow \mathrm{Ar}^+ + \mathrm{H} \sim 1.2 \times 10^{-15} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5a)

$$\rightarrow \mathrm{Ar} + \mathrm{H}_2^+ \sim 1.7 \times 10^{-16} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5b)

$$\mathrm{H}^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_2^+ + \mathrm{H} \sim 2.5 \times 10^{-15} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5c)

$$\mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H} \sim 10^{-15} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5d)

$$\mathrm{H}_2^+ + e^- \rightarrow \mathrm{H}^+ + \mathrm{H} \sim 10^{-13} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5e)

$$\mathrm{H}_3^+ + e^- \rightarrow \mathrm{H}^+ + \mathrm{H} + \mathrm{H} \sim 10^{-13} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5f)

$$\mathrm{ArH}^+ + e^- \rightarrow \mathrm{Ar} + \mathrm{H}^+ \sim 10^{-13} \text{ m}^3 \text{s}^{-1}$$ \hspace{1cm} (2.5g)
Besides undergoing DR (reaction 2.5e), the H$_2^+$ ions can also instigate H$_3^+$ formation via reaction (2.5d). This occurs when the H$_2$ density exceeds the electron density by more than a factor of 100, as can be seen from the rate coefficients of reactions (2.5d) and (2.5e) [129, 130]. This is predominantly the situation within the reactor, but not necessarily within the arc itself when dealing with low H$_2$ gas flows. In a previous study, Meulenbroeks et al. reported that 3% of H$_2$ admixed via the arc is sufficient to cause a drastic change in the behaviour of the arc [134]. Similar percentages are found to change the ion density near the substrate when H$_2$ is injected via the reactor, as shown in appendix 4.A of chapter 4 in this thesis. Previously, Kessels et al. showed that H$_3^+$ is the most abundant ion species near the substrate when more than 3.5% of H$_2$ is admixed via the arc [135]. Thus, relatively small percentages of H$_2$ suffice to change the ionic composition of the plasma in favour of H$_3^+$. The H$_3^+$ ions themselves are converted into H radicals via reaction (2.5f) or lost to the surface.

The H$_2$ dissociation degree for small H$_2$ gas flows, furthermore, is nearly 100% within the arc [127]. This is likewise the situation in a pure hydrogen plasma [131]. However, much of the dissociated hydrogen will recombine on the surface of the arc’s nozzle into ro-vibrationally excited molecular hydrogen (H$_2^r$), effectively reducing the dissociation degree within the reactor to less than 20% [109, 131]. H$_2^r$ is likewise found inside the arc channel in a narrow region near the arc’s wall. Moreover, the creation of excited hydrogen radicals (H$^+$) through DR reactions facilitates hydrogen ionization via electron collisions\(^3\). The availability of both H$_2^r$ and H$^+$ enable reaction (2.5c) to take place [127]. Alternatively, the kinetic energy of H$^+$ can compensate for a lower or absent ro-vibrationally excitation energy of molecular hydrogen. Either way, the injection of H$_2$ through the arc leads to H$^+$ formation and thus — via reactions (2.5c) and (2.5d) — to a higher H$_3^+$ production.

Thus, depending on the argon to hydrogen ratio and the H$_2$ injection point, the cascaded arc is a source of atomic H; ro-vibrationally excited molecular hydrogen (H$_2^r$); H$^+$, H$_2^+$ and H$_3^+$ ions as well as Ar$^+$ ions. Whereby CT and DR play an important role in the production and destruction of these species.

Reactions (2.5d) to (2.5f) are also involved in a pure hydrogen plasma. The dominant ions in this type of plasma are H$^+$ and H$_3^+$. The same requirements for H$_3^+$ formation, which are H$_2^+$ ions and a low electron density, in an Ar/H$_2$ plasma apply here as well. This implies that H$_2^+$ formation has to precede H$_3^+$ formation, which can lead to a spatial division in the ion composition along the main axis of the plasma expansion. Such a spatial division occurs in both Ar/H$_2$ and pure

\(^3\)Molecular hydrogen can store the arc’s input power also as ro-vibrational energy. A hydrogen plasma requires therefore higher initial currents to start than an argon plasma.
2.3 Plasma and material diagnostics

Section 1.2 mentioned several diagnostics that are used in this thesis to investigate a-C:H plasma etching. The basic working principle of these diagnostics is explained in a nutshell in this section. More technical details can be found in the remaining chapters (Table 2.1). This section has been divided into three categories: surface and film diagnostics, plasma diagnostics and numerical simulations.

2.3.1 Surface and film diagnostics

Spectroscopic ellipsometry is a non-invasive optical diagnostic that can be used both ex situ and in situ to determine the thickness, roughness and dielectric function of thin films [103–105, 119]. When used in situ the growth or etch rate of the film can also be deduced in real time. The complex dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) describes how light of different wavelengths is reflected or absorbed by a material. It is connected to the refractive index \( n \) and extinction coefficient \( k \) via \( \sqrt{\varepsilon} = n + ik \) [104]. This diagnostic characterizes thin films by measuring the change in polarisation of (polychromatic) light reflected on a film. As can be seen in Fig. 2.2, (polychromatic) light is first linearly polarised and then reflected under an angle on the thin film. The reflected light, as a result of the interaction with the film, is now circularly polarised. This change in polarisation can be expressed in terms of the amplitude ratio \( \Psi \) and the phase shift \( \Delta \):

\[
\rho \equiv \tan \Psi e^{i\Delta},
\]

(2.6)
as indicated in the figure. With the exception of a few simplified cases, \( \Psi \) and \( \Delta \) can not be directly converted into the dielectric function \( \varepsilon \). Analysis of the obtained data therefore requires an appropriate (multi-layered) model that describes the interaction of the incident light with the film. In general, each layer of the
Table 2.1: The different diagnostics used in this work, divided into three categories: surface and film diagnostics (M), plasma diagnostics (P) and numerical simulations (N).

<table>
<thead>
<tr>
<th>Cat.</th>
<th>Ch.</th>
<th>Diagnostic</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>5, 6</td>
<td>Spectroscopic ellipsometry (SE)</td>
</tr>
<tr>
<td>M</td>
<td>5, 6</td>
<td>Atomic Force Microscopy (AFM)</td>
</tr>
<tr>
<td>M</td>
<td>5, 6</td>
<td>Scanning electron microscopy (SEM)</td>
</tr>
<tr>
<td>P</td>
<td>4</td>
<td>Optical emission spectroscopy (OES)</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>Residual gas analysis (RGA)</td>
</tr>
<tr>
<td>P</td>
<td>4, 6</td>
<td>Electrical probes</td>
</tr>
<tr>
<td>N</td>
<td>4</td>
<td>LIFBASE</td>
</tr>
<tr>
<td>N</td>
<td>4</td>
<td>DSMC</td>
</tr>
</tbody>
</table>

model has its own dielectric function, thickness, and — if applicable — other physical properties. The dielectric function itself can likewise be parameterized by a variety of functions, such as the Tauc-Lorentz oscillator [68, 70]. $\Psi$ and $\Delta$ are calculated from this model and compared against the measurement. Unknown parameters, for instance the film thickness, can then be determined by iteratively adjusting the model until the discrepancy between model and measurement have been minimized. Which analysis model is appropriate for a given film, depends on its layer structure and material composition.

Figure 2.2: Schematic representation of the basic principle behind spectroscopic ellipsometry. Linearly polarised light is reflected under an angle on a thin film. The change in polarisation after reflection is measured and analysed with an appropriate model.
Atomic force microscopy (AFM) and scanning electron microscopy (SEM) are two diagnostics that can only be used outside of the plasma reactor. In its simplest representation, AFM scans the surface of a thin film over a small area with a cantilever [136]. The (e.g. van der Waals) force between the tip of the cantilever and the surface deflects the cantilever as it moves across the film. By measuring this deflection, the surface morphology of the thin film can be quantified. Compared to AFM, SEM probes the surface morphology at a larger scale. It does this by targeting the film with an electron beam and measuring either backscattered electrons or secondary electrons emitted from the film. Also the layer structure and thickness of the thin film can be deduced from a cross-sectional SEM scan.

2.3.2 Plasma diagnostics

Electrical probes measure the electrical response of the plasma to an externally applied voltage [106,108,110]. Several plasma characteristics, including electron density and ion flux, can be determined from an amplitude or time modulated signal. The so-called ion flux probe was embedded in a sample holder and could thus measure the amount of ions that would impact the sample every second. In contrast with the fixed position of the ion flux probe, the double Langmuir probe was mounted on a movable arm and could map the electron density in the vicinity of the sample holder. Densities were however not obtained near the cascaded arc itself since the high electron density in that region damages the probe. A standard double Langmuir probe measurement, the so-called IV-characteristic, is shown in Fig. 2.3. The measured current on the y-axis is due to the electrical response of the plasma to the voltage shown on the x-axis. When the voltage is sufficiently negative, all ions in the vicinity of the probe are collected and the measured current is saturated. The intersection of the saturation region with the y-axis yields information about the density, while the slope at 0 V contains information about the electron temperature. Measured IV-characteristics are, in this thesis, analysed according to the theory by Peterson and Albot [107].

Optical emission spectroscopy is a technique whereby the light emission of the plasma is focused onto a spectrometer which spreads out the light over its different wavelengths [83,113]. The excited plasma species can then be identified through their characteristic peaks in the resulting spectrum. Spatially resolved measurements can determine the relative density, by proxy of the intensity, of these species throughout the plasma jet and e.g. identify the origin of certain species. Furthermore, temporal effects in the plasma, such as the depletion of hydrocarbons in the plasma, can be unraveled through time resolved spectroscopy. The number of species that can be monitored in space or time, depends on wave-
Figure 2.3: Typical IV-characteristic as measured by a double Langmuir probe. The intersection point with the y-axis (red dashed line) yields information about the density. The slope at 0 V (blue dashed line) is related to the electron temperature.

Residual gas analysis determines the gas composition of the entire reactor in less than a minute. Compared with optical emission spectroscopy, only stable and electrically neutral species that can be sampled from the reactor are measurable. Residual gas analysis, however, can identify and monitor a greater variety of species. Fig. 2.4 shows the basic principle behind this diagnostic. A small gas sample of the reactor is fed into the analyser. A filament near the gas inlet emits high energy electrons (70 eV) which ionize the sampled gas. To protect this filament, the residual gas analyser operates on a much lower pressure than the reactor itself. The working pressure inside the analyser is on the order of $10^{-6}$ mbar, or five to six orders lower than in the reactor. After ionization, the ions pass through a set of four rod electrodes. A high-frequency alternating voltage superimposed on a direct voltage is applied to each rod. Neighbouring rods, moreover, have opposite voltage signs. The resulting electric quadrupole field then selects for ions with a specific mass over charge (m/z) ratio. Different ions can be selected for by

\[4\text{Only two are shown in Fig. 2.4.}\]
2.3. Plasma and material diagnostics

changing the voltages applied to the four rods. Ions with the correct m/z ratio can pass through to the detector, while others are repelled by a separating field. The detector itself is a channeltron\textsuperscript{5}, which measures the total ion current. A mass spectrum, in the end, shows the relative ion current versus the mass over charge ratio. In addition to ionization, the high energy electrons can also fragment the sampled gas molecules. Multiple ionization is likewise a possibility. Each species will thus contribute to the mass spectrum in several different places. The converse is likewise true: the measured intensity of most m/z ratios can not be uniquely attributed to a single species. However, each species has its own unique cracking pattern of m/z ratio’s that can distinguish it from different species with the same mass. In each cracking pattern, moreover, the relative intensity is different for every m/z ratio. Even so, due to the large number of species and fragments, a completely resolved mass spectrum in terms of the contributing species can not be ensured in the case of a hydrocarbon gas mixture without the use of advanced mathematical models \cite{137,138}. These techniques were not applied in this work due to the low carbon content during $\alpha$-C:H etching. The residual gas analyser is in this work calibrated with a known quantity of argon, hydrogen, methane and acetylene. A comparison of the experimental data against the measured cracking pattern of these gasses yields a first order approximation of the gas composition. This procedure is explained in more detail in chapter 3.

2.3.3 Numerical simulations

Although strictly speaking not a diagnostic tool, numerical simulations do provide valuable insight into the plasma expansion. Monte Carlo simulations provide a good alternative to the Navier-Stokes equations, which can not adequately describe the strong gradients in the expansion \cite{116}. Monte Carlo simulations
rely on the repeated computation of a random solution for stepwise progressing of the problem at hand. Such programs are suited to study problems with a large number of coupled degrees of freedom, such as a plasma. The numerical simulation program DSMC 6 has been successfully applied in the past to model the plasma expansion and is used in this thesis as well [74,116–118]. Nevertheless, computational requirements are high and solutions can take days or weeks to calculate.

**LIFBASE** is a database and spectrum simulation program for the calculation of emission, absorption and laser induced fluorescence spectra. As a database program, it likewise calculates the Hönl-London factors, radiative lifetimes, Einstein coefficients and so on. Calculated intensities of a given line transition are furthermore convoluted with a lineshape (e.g. gaussian or lorentzian) to account, if necessary, for physical broadening (natural line broadening, doppler shift, pressure broadening, etc.) or instrumental broadening (i.e. the resolution of the spectrometer in our case).

LIFBASE is employed in this thesis to calculate the band emission spectrum of the CH molecule. Although LIFBASE can calculate multiple electronic transitions of CH, the focus in this thesis is on the transition from the first excited state A to the ground state X [114, 139]. CH is a diatomic molecule in which the individual atoms can vibrate and rotate with respect to its center of mass. The vibrational and rotational energy levels, therefore, have to be considered as well in the calculations. Every peak in the CH(A-X) spectrum can be coupled to a particular transition between these energy levels (Fig. 2.5).

In case of an emission spectrum, LIFBASE uses the Einstein coefficients 7 to calculate the probability and intensity of each possible transition [115,140]:

\[
I_{v',J'}^{v,J} \propto N_{v',J'} \sum_{v'',J''} A_{v'',J''}^{v',J'} \left( 1 - e^{-\frac{\tau}{T}} \right). \tag{2.7}
\]

\(N_{v',J'}\) represents the number of CH radicals in the upper energetic state, with vibrational state \(v'\) and rotational state \(J'\). \(A_{v'',J''}^{v',J'}\) is the Einstein coefficient of the transition from upper state \(v'J'\) to the lower state \(v''J''\). Furthermore, \(\tau\) is the effective lifetime of the upper energetic states:

\[
\tau = \frac{1}{\sum_{v',J'} A_{v',J'}^{v'',J''}} \tag{2.8}
\]

---
6Direct Simulation Monte Carlo
7The Einstein coefficients A give the probability per second for the spontaneous decay of an electron from a higher to a lower energy state.
Figure 2.5: Emission spectrum of CH as calculated with LIFBASE. The spectrum originates from the electronic transition from the first excited state A to the ground state X. Furthermore, the spectrum is ro-vibrationally resolved. Thus, each peak in the spectrum corresponds to a specific energy transition between two rotational levels. The difference in rotational quantum numbers ($\Delta J$) are +1,0,-1 for the R,Q,P-branch, respectively. Simulation parameters are 4900 K $T_{vib}$, 3300 K $T_{rot}$ and an instrumental resolution of 0.2 nm with a Gaussian line profile.
The Einstein coefficients themselves are likewise calculated by LIFBASE [115, 141]:

\[ \Lambda_{v'J'}^{v''J''} = \frac{g_e'}{g_e''} \frac{64\pi^4}{3h} \frac{S_{J''}}{2J' + 1} p_{v'J'}^{v''J''} \left( \nu_{v'J'}^{v''J''} \right)^3. \]  

(2.9)

The electronic degeneracy factor \( g_e \) represents the number of different states within one energy level. The Hönl-London factors \( S \) represent the strength of each transition, while \( \nu \) is the transition frequency and \( p \) the transition probability as calculated from [115]:

\[ p_{v'J'}^{v''J''} = \left( \int_{-\infty}^{\infty} \Psi_{v'J'}(r) R_e(r) \Psi_{v''J''}(r) dr \right)^2. \]  

(2.10)

In this last equation, \( R_e \) represents the electronic transition moment and \( \Psi \) the wave function of the energy state. As can be seen from eq. 2.7, the relative intensity of a transition depends on the internal energy distribution of the CH radicals. Such a distribution is a statistical measure for how many CH radicals, i.e. \( N_{v'J'} \), have an electron in one particular energy state \( v'J' \). The a priori assumption for both rotational and vibrational energy levels is a Boltzmann distribution. Separate rotational and vibrational temperatures for this distribution can be specified in LIFBASE. Furthermore, the most probable transitions are those with a maximum overlap in the wave functions \( \Psi \) of the involved energy states. The most dominant transitions have a constant vibrational quantum number \( v (\Delta v = v' - v'' = 0) \) and a difference in rotational quantum number \( J (\Delta J = J' - J'') \) of either 0 or \( \pm 1 \).

Based here upon, the line transitions are divided into different branches (Fig. 2.5). The R- and P-branches correspond with \( \Delta J = +1 \) and \( \Delta J = -1 \), respectively. The Q-branch corresponds with \( \Delta J = 0 \), of which the band heads are indicated with \( Q(v'',v') \). When the relative intensity for every possible rotational and vibrational state is calculated with these equations, the entire spectrum for CH(A-X) within the specified wavelength range can be constructed and compared against the measurement (see also App. 4.B in Ch. 4). Such a comparison can be used to determine the rotational and vibrational temperature of CH in the plasma [38].
Chapter 3

H₂: the critical juncture between polymerization and dissociation of hydrocarbons in a low-temperature plasma

abstract

The chemistry in an argon plasma jet, admixed with a small percentage of CH₄, C₂H₂, H₂ and mixtures thereof, is investigated by means of residual gas analysis. Polymerization of such hydrocarbon precursors is known to occur when their densities exceed the Ar⁺ ion density. This chapter shows that polymerization also occurs for precursor gas flows far below the initial Ar⁺ ion flow emanating from the plasma source. This is entirely due to the negative effect of H₂ on the Ar⁺ ion density. Adding 1 to 2% of H₂ to the total argon and hydrocarbon gas flow suffices to initiate polymerization. Although H₂ can be injected directly into the system, fragmentation of the hydrocarbon precursors themselves can likewise supply (part of) the required H₂. Polymerization is furthermore enhanced when both precursors are used together. The contribution of C₃H₇ species to the plasma chemistry will likewise be substantiated.
3.1 Introduction

Plasma-enhanced chemical vapor deposition (PE-CVD) is widely used for the deposition of hydrogenated amorphous carbon ($a$-C:H) thin films as e.g. protective coatings on steel wire, or anti-reflection coatings [30, 32, 33, 142]. One of the PE-CVD techniques is remote plasma deposition in which an acetylene precursor is admixed to an expanding thermal argon plasma, generated by a cascaded arc [45, 77, 78, 82, 143]. This method has been successfully used in our group for the deposition of $a$-C:H with very high nanohardness (> 16 GPA) at high growth rates (> 15 nm s$^{-1}$) [82]. The plasma chemistry in such a plasma with high carbon content has moreover been extensively studied in the past and is summarized in section 3.2.

A similar expanding thermal argon plasma, but admixed with $H_2$ instead of $C_2H_2$, can furthermore be used to investigate $a$-C:H etching (Ch. 6). Plasma etching of an $a$-C:H sample is, from the viewpoint of the plasma chemistry, comparable to the direct injection of a hydrocarbon precursor mixture. The carbon content of the plasma due to erosion is however much lower than during $a$-C:H deposition. Differences and similarities in the plasma chemistry between both plasma systems are investigated in this chapter. To that end, low gas flows of $CH_4$ and $C_2H_2$ precursors as well as mixtures thereof are injected into both a pure Ar and an Ar/$H_2$ plasma. The resulting gas composition of the reactor is determined with residual gas analysis. These measurements will show the formation of heavier hydrocarbons as well as the importance of $H_2$ in the plasma chemistry. This chapter ends with a discussion of the possible reaction pathways in the different plasma systems and the role of $C_3H_y$ species therein.

3.2 Plasma chemistry

The plasma chemistry during $a$-C:H deposition and in an expanding thermal plasma in general is well known from previous studies [45, 127, 128, 143]. The same plasma reactions apply during both deposition and erosion of $a$-C:H (see also Ch. 4) and are summarized in this section.

Argon injected under high pressure in the arc is ionized by a DC current. The resulting argon plasma expands into a low pressure reactor. The electron temperature near the arc nozzle is about 0.8 to 1.2 eV and drops to $\sim$ 0.1 eV at the level of the substrate [77, 78]. Due to this low electron temperature, the chemistry inside the reactor is dominated by charge transfer (CT) between argon ions ($Ar^+$) and molecular species (M). This step is followed by a fast dissociative
recombination (DR) reaction:

\[
\begin{align*}
\text{Ar}^+ + M & \rightarrow \text{Ar} + M^+. \quad (3.1) \\
M^+ + e^- & \rightarrow \text{fragments}. \quad (3.2)
\end{align*}
\]

Rate coefficients for charge transfer are overall lower than for dissociative recombination by 2 or 3 orders of magnitude. Moreover, the molecular fragments themselves can undergo successive CT and DR reactions. Molecular species such as C\(_2\)H\(_2\) or H\(_2\) are — in this chapter — either directly injected in the reactor or produced within the reactor via CT and DR. Recirculation cells in the background of the reactor are furthermore responsible for a complete mixture of these gasses (see Fig. 2.1b as well as Ch. 4).

The plasma chemistry for acetylene, methane and molecular hydrogen will now be discussed in more detail, starting with C\(_2\)H\(_2\) [39–45]. Rate coefficients for CT (3.3) and DR (3.4) are \(\sim 4 \times 10^{-16} \text{ m}^3\text{s}^{-1}\) and \(1 - 6 \times 10^{-13} \text{ m}^3\text{s}^{-1}\), respectively [144,145]. The branching ratio of C\(_2\)H\(_2\), as given in (3.4), was previously determined by means of threshold ionization mass spectrometry [45].

\[
\begin{align*}
\text{Ar}^+ + \text{C}_2\text{H}_2 & \rightarrow \text{Ar} + \text{C}_2\text{H}_2^+. \quad (3.3) \\
\text{C}_2\text{H}_2^+ + e^- & \rightarrow \text{C}_2\text{H} + \text{H} \quad 26\% \quad (3.4a) \\
& \rightarrow \text{C}_2 + 2\text{H} \quad 41\% \quad (3.4b) \\
& \rightarrow 2\text{CH} \quad 7\% \quad (3.4c) \\
& \rightarrow \text{CH}_2 + \text{C} \quad 26\% \quad (3.4d)
\end{align*}
\]

Furthermore, when the C\(_2\)H\(_2\) to Ar\(^+\) flow ratio

\[
F = \frac{\Phi(\text{C}_2\text{H}_2)}{\Phi(\text{Ar}^+)} \quad (3.5)
\]

is smaller than one, then all of the C\(_2\)H\(_2\) precursor is broken down into smaller hydrocarbon fragments [39,41,45]. When the flow ratio exceeds one, however, polymerization between excess C\(_2\)H\(_2\) and e.g. C\(_2\)H leads to the formation of C\(_4\)H\(_2\):

\[
\text{C}_2\text{H}_2 + \text{C}_2\text{H} \rightarrow \text{C}_4\text{H}_2 + \text{H}, \quad (3.6)
\]

with a rate coefficient of \(\sim 10^{-16} \text{ m}^3\text{s}^{-1}\) [45]. Note that in a plasma expansion with multiple molecular species, as will inevitably be the case with hydrocarbons
due to fragmentation, all molecular species should be taken into account in the numerator of $F$.

In the case of CH$_4$, charge transfer can lead to CH$_4^+$, CH$_3^+$ as well as CH$_2^+$ [38,146]:

$$\text{Ar}^+ + \text{CH}_4 \rightarrow \text{Ar} + \text{CH}_4^+ \quad \sim 10^{-16} \text{ m}^3\text{s}^{-1} \quad (3.7a)$$

$$\rightarrow \text{Ar} + \text{CH}_3^+ + \text{H} \quad \sim 10^{-15} \text{ m}^3\text{s}^{-1} \quad (3.7b)$$

$$\rightarrow \text{Ar} + \text{CH}_2^+ + \text{H}_2 \quad \sim 3 \times 10^{-16} \text{ m}^3\text{s}^{-1}. \quad (3.7c)$$

Based on these rate coefficients, 70% of the CH$_4$ is converted into CH$_3^+$ [146]. CH$_2$ and CH radicals are therefore expected to be the dominant methane fragments. The dissociative recombination step of CH$_3^+$ has a rate of $\sim 2 \times 10^{-13} \text{ m}^3\text{s}^{-1}$ [146].

Both methane and acetylene have been used for the deposition of $a$-C:H. The dissociation products of methane, i.e. CH$_x$ ($x = 3, 2, 1$) have a low sticking probability [146]. A large fraction of methane, up to 40% as shown by A. de Graaf, polymerizes therefore into higher hydrocarbons such as acetylene [146]. These hydrocarbons are then dissociated in a second set CT and DR reactions before contributing to the deposition process [146]. This intermediate step can thus be eliminated via the direct use of an acetylene precursor. Previous plasma chemistry studies moreover showed that C$_3$H$_y$ ($y = 0, 1$) radicals play an important role in the deposition of $a$-C:H [44,45,53]. Polymerization into higher hydrocarbons such as these C$_3$H$_y$ radicals requires that the precursor gas flow exceeds the Ar$^+$ ion flow emanating from the cascaded arc. If this is not the case, the injected precursor gas undergoes nearly complete dissociation via CT and DR as explained earlier in this section. Since the ionization degree of the arc is around 10% for Ar, a plasma with high carbon content is thus required for $a$-C:H deposition [40,147].

The third and last species which will be admixed to the reactor is molecular hydrogen. Charge transfer between Ar$^+$ and H$_2$ leads to the production of mainly atomic hydrogen (3.8a and 3.8c), but also of H$_2^+$ ions (3.8b). H production dominates because reaction (3.8a) is ten times faster than reaction (3.8b) and because reaction (3.8b) is of little importance when the kinetic energy of Ar$^+$ drops below 0.5 eV [127,128].

$$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \quad \sim 1.2 \times 10^{-15} \text{ m}^3\text{s}^{-1} \quad (3.8a)$$

$$\rightarrow \text{Ar} + \text{H}_2^+ \quad \sim 1.7 \times 10^{-16} \text{ m}^3\text{s}^{-1} \quad (3.8b)$$

$$\text{ArH}^+ + e^- \rightarrow \text{Ar} + \text{H}^* \quad \sim 10^{-13} \text{ m}^3\text{s}^{-1} \quad (3.8c)$$

The H$_2^+$ ions that are present in the reactor can either undergo DR (3.9a) or instigate H$_3^+$ formation in those regions of the plasma jet where the H$_2$ density exceeds
the electron density by more than a factor of 100 (3.9b) [129,130]. Previous work showed that — at a distance of about 30 cm from the nozzle — 2% H$_2$ in the gas flow falls within the transition from an Ar$^+$ to a H$_3^+$ dominated plasma (Ch. 4) [134,135].

\[
\begin{align*}
H^+_2 + e^- &\rightarrow H + H \quad \sim 10^{-13} \text{ m}^3\text{s}^{-1} \quad (3.9a) \\
H^+_2 + H_2 &\rightarrow H_3^+ + H \quad \sim 10^{-15} \text{ m}^3\text{s}^{-1} \quad (3.9b)
\end{align*}
\]

Similarly as for the other molecular ions, dissociative recombination of H$_3^+$ into atomic hydrogen has a rate coefficient of about $\sim 10^{-13} \text{ m}^3\text{s}^{-1}$ [129]. Hydrogen ions are thus an intermediate step in the production of H radicals in an Ar/H$_2$ plasma expansion. Both ions and radicals play an active role in the etching of carbon surfaces (Ch. 6 and references therein).

Only the ion-molecule chemistry in the plasma reactor has been discussed so far. The last part of this section briefly deals with the radical-molecule reactions. Even though the list of all possible reactions is too long to discuss here in detail [45–49], two groups of reactions will be addressed. The first group consists of reactions between carbon-based molecules, e.g. (3.6). Overall, reactions in this group have a rate coefficient on the order of $10^{-17} - 10^{-16} \text{ m}^3\text{s}^{-1}$. The second group involves hydrogen abstraction (e.g. (3.10b) and (3.11b)) and hydrogen attachment (e.g. (3.10a) and (3.11a)). Literature values for the rate coefficient $k_{3,11b}$ vary from $5 \times 10^{-18} \text{ m}^3\text{s}^{-1}$ to $7 \times 10^{-17} \text{ m}^3\text{s}^{-1}$. Both sets, i.e. (3.10) and (3.11), illustrate the wide range in rate coefficients which can go from $10^{-21} \text{ m}^3\text{s}^{-1}$ to $10^{-16} \text{ m}^3\text{s}^{-1}$.

\[
\begin{align*}
\text{C}_2\text{H} + \text{H}_2 &\rightarrow \text{C}_2\text{H}_2 + \text{H} \quad \sim 2 \times 10^{-17} \text{ m}^3\text{s}^{-1} \quad (3.10a) \\
\text{C}_2\text{H} + \text{H} &\rightarrow \text{C}_2 + \text{H}_2 \quad \sim 5 \times 10^{-20} \text{ m}^3\text{s}^{-1} \quad (3.10b) \\
\text{CH}_2 + \text{H}_2 &\rightarrow \text{CH}_3 + \text{H} \quad \sim 10^{-21} \text{ m}^3\text{s}^{-1} \quad (3.11a) \\
\text{CH}_2 + \text{H} &\rightarrow \text{CH} + \text{H}_2 \quad k_{3,11b} \quad (3.11b)
\end{align*}
\]

Overall, these reactions are as fast or slower than the charge transfer reactions. Variations in the densities of H, H$_2$, hydrocarbons, argon ions and hydrogen ions will thus determine which reaction dominates locally. In this chapter, however, residual gas analysis is used to determine the gas composition of the entire system and whether the net result is fragmentation of the hydrocarbons or polymerization as stated in the introduction.
3.3 Experimental setup

The experimental work was carried out on a linear plasma reactor with a cascaded arc as plasma source. The arc, which generates an expanding thermal plasma, consists of a stack of four water-cooled copper plates with a central bore of 4 mm in diameter and has a total length of 24 mm (Fig. 2.1b) [77,78]. The electrically floating plates are insulated from each other by PVC spacers [120]. The head of the arc contains three tungsten cathodes and the gas injection port. The injected gas, i.e. 100 sccs of argon (1 sccs ≈ 2.5 × 10^{19} s^{-1}), is ionized by a 75 A DC current that runs from these three cathodes through the bore towards an anode plate. The pressure in the arc is 540 mbar, while the background pressure in the reactor is around 97 Pa. Due to the pressure difference the argon plasma expands supersonically into the reactor. A shock front is formed at about 46 mm from the nozzle, after which the plasma jet continues subsonically towards the substrate. The substrate, located at 55 cm from the nozzle, is set to a constant 250 °C. The generated plasma is radially symmetric and quasi-neutral, but not in local thermal equilibrium [77]. Furthermore, H\(_2\), C\(_2\)H\(_2\), CH\(_4\) and mixtures thereof are injected directly into the reactor, either via an injection ring or via a reactor port. Both injection points are located at about 5 cm from the nozzle. The gas flow of each species varies between 0 and 3 sccs, for a total of maximum 5 sccs or less than 5% of the total gas flow.

The composition of the different gas mixtures, both with and without plasma, is analysed by means of residual gas analysis (RGA; Pfeiffer Vacuum QMS 200). A residual gas analyser detects only the stable and neutral species sampled from the reactor. However, species can be ionized and potentially fragmented within the residual gas analyser itself. Gas is sampled from the reactor via a side-port located near the substrate and transported via a ∼ 20 cm long gas line to the residual gas analyser. A pinhole of 80 µm in diameter, located within this gas line, separates the residual gas analyser from the reactor. Every RGA measurement shown in section 3.4 is averaged over 5 cycles. In each of these cycles the relative intensity of the mass over charge ratio (m/z) is measured between 0 and 100 m/z. The measuring time per 1 m/z is set to 0.2 s, with a completion time of 21.4 ± 0.1 s for the entire cycle. The residence time of the reactor is around 1 s. A minimum waiting period of 2 cycles (or about 43 s) between each RGA measurement, therefore, ensures a complete refresh of the gas content in the reactor. Also, the reactor is regularly cleaned both manually and with an Ar/O\(_2\) plasma to remove any wall deposits. At the beginning of each experimental campaign, an argon plasma is burned for several minutes to heat up the reactor and promote outgassing. Despite these precautions, the presence of impurities or wall deposits
3.3. Experimental setup

![Graph showing gas composition](image)

**Figure 3.1:** Gas composition of an Ar gas flow without plasma. H$_3^+$, Ar$^2+$, Ar$^3+$ and N are generated inside the residual gas analyser.

such as a-C:H can not be completely excluded.

Due to the injection of additional gas (e.g. H$_2$), the background pressure of the reactor varies between 97 and 100 Pa. The argon gas flow however remains constant throughout all the measurements. All measurements are therefore normalized to 40 m/z which corresponds to the highest intensity peak of argon. Several additional (background) peaks can be identified in Fig. 3.1, which shows the gas composition of a pure argon gas flow without plasma. The two most intense peaks at 20 and 40 m/z are due to double and single ionized argon, respectively. Likewise, Ar$^3+$ is known to have a contribution to the peak at 13 m/z in our RGA system. Moreover, argon isotopes yield peaks at 36 and 38 m/z (single ionization) as well as 18 and 19 m/z (double ionization; not indicated). When also sufficient quantities of H$_2$ are present in the gas mixture, then ArH$^+$ (41 m/z) as well as H$_3^+$ (3 m/z) are formed inside the residual gas analyser itself (e.g. Fig. 3.2).

In addition to argon, several impurities can be identified in the background mass spectrum. The most important one is water (16 to 18 m/z) located primarily within the residual gas analyser itself. Since no H$_2$ is injected in this instance, the peaks at 1, 2 and 3 m/z are built up by H$_2$O cracking and H$_2$ outgassing of the wall. Also N$_2$ (28 m/z), O$_2$ (32 m/z) and CO$_2$ (44 m/z) are present in the mass spectrum. Fragmentation of N$_2$ into N yields a peak at 14 m/z, whereas the
smaller peaks flanking $N_2$ are attributed to residual acetylene. Note that molecular oxygen (32 m/z) has a two orders of magnitude lower intensity than $N_2$ and can thus be neglected in our considerations of the plasma chemistry.

### 3.4 Experimental results

The experimental results presented here are all based on mass spectra of different gas mixtures taken during both the gas and plasma phase. Since no peaks above the background were detected between 60 and 100 m/z, the m/z range shown in the different graphs is limited to 0 – 60 m/z.

Fig. 3.2.a shows the gas composition of an $Ar/C_2H_2$ (100:1) mixture both with and without plasma, i.e. with and without an arc current. Similarly as in Fig. 3.1, several species in the gas phase are easily identified (not indicated): $H_2O$ (16 to 18 m/z), $Ar$ (20, 36, 38 and 40 m/z) and $CO_2$ (44 m/z). Also 13 and 28 m/z are again assigned to $Ar^{3+}$ and $N_2$, respectively. In this case, however, the acetylene precursor contributes as well to the measured intensity of both peaks. The contribution to 13 m/z in the form of CH is due to $C_2H_2$ fragmentation within the RGA. For 28 m/z, this is either a $C_2H_2$ isotope or $C_2H_4$ impurity in the gas supply. Fragmentation of $C_2H_2$ likewise yields contributions to $24 - 27$ m/z as well as to 12, 14 and 15 m/z. A necessarily result of fragmentation is that also $H_2$ (1 – 3 m/z) has a higher intensity compared to Fig. 3.1. This in turn leads to the formation of $H_3^+$ (3 m/z) and $ArH^+$ (41 m/z) within the residual gas analyser itself.

Based on the known $C_2H_2$ gas inflow (i.e. 1 sccs) and the observed fragmentation pattern and associated peak intensities for the gas phase, an estimate can be made of the remaining $C_2H_2$ content during the plasma phase. The gas phase measurements of the $Ar/CH_4$ and $Ar/H_2$ mixtures — shown in Fig. 3.2.b and Fig. 3.2.c, respectively — enable a similar calibration for $CH_4$ and $H_2$, respectively. The calibration shows that 96.0% of the measured intensity in the gas phase due to the $C_2H_2$ precursor falls in the $24 - 30$ m/z range. For methane, 99.8% of the measured intensity falls within the $12 - 16$ m/z range. In this calibration, the contribution of gas impurities such as $N_2$ is taken into account by subtracting the pure argon gas mass spectrum (i.e. Fig. 3.1). The change in $N_2$ content during the experiment due to e.g. leakage is considered negligible. In a first order approximation, the $12 - 16$ and $24 - 30$ m/z range are assigned exclusively to $CH_4$ and $C_2H_2$, respectively.

This approximation shows that the $Ar/H_2$ gas mixture contains less than 1/100 sccs of $CH_4$ and $C_2H_2$, as is to be expected. The $H_2$ content in the $Ar/CH_4$ and
Figure 3.2: Gas composition of three different systems, both with and without plasma: (a) Ar/C₂H₂ (b) Ar/CH₄ and (c) Ar/H₂. Both the C₂H₂ and CH₄ precursors are (nearly) completely consumed in the plasma phase. See also rows IA, IM and IH, respectively, in Table 3.1.
Ar/C$_2$H$_2$ gas mixtures is about 0.18 and 0.12 sccs, respectively. As mentioned earlier, this can be attributed to contributions from water and fragmentation of the carbon precursor.

Both the methane and acetylene precursors are completely consumed when a plasma is ignited as can be seen in both Fig. 3.2 and Table 3.1 with the estimated gas flows. The argon flow, however, remains constant regardless of arc current. The peak intensity for 13 m/z is thus expected to stay high during the plasma phase as can be seen in all of the figures. Furthermore, the change in 28 m/z (i.e. N$_2$) is less than 10% compared with the background peak in Fig. 3.1, whereas peaks exclusively associated with CH$_4$ or C$_2$H$_2$ (e.g. 24 m/z) drop 2 to 3 orders in intensity. This indicates that N$_2$, just like O$_2$, plays no role of importance in the chemistry.

The variation in H$_2$ content during the plasma phase, on the other hand, depends strongly on the precursor. In an Ar/H$_2$ plasma without any precursor, the hydrogen content decreases. Such a decrease is due to etching of carbon deposits on the wall by atomic hydrogen. Despite the low amount of etch products, Fig. 3.2.c clearly shows that CH$_4$ and C$_2$H$_2$ are the dominant etch products. Compared to the gas phase, the H$_2$ content of the plasma phase also decreases for Ar/C$_2$H$_2$ admixed with either 2 or 3 sccs of H$_2$ (Table 3.1). In all other plasma systems used in this chapter, however, the H$_2$ content increases while running a plasma (Fig. 3.3.b). More than that, there is ~1 sccs of additional H$_2$ for every injected sccs of methane (see e.g. rows 1H1M and 3H1M in Table 3.1). An increase in H$_2$ content for a plasma with a methane precursor was also previously observed by A. de Graaf [146].

An immediate effect of the increased H$_2$ content is a higher production level of ArH$^+$. Moreover, the methane precursor produces a small amount (about 0.02 sccs) of acetylene as well as C$_3$H$_y$ (36 – 44 m/z) and C$_4$H$_y$ (48 – 58 m/z). The peak distribution in the 48 – 58 range indicates that mainly hydrogen-poor species are present with diacetylene (C$_4$H$_2$; 50 m/z) the most abundant. In contrast, the Ar/C$_2$H$_2$ plasma produces neither any significant amount of methane nor any C$_x$H$_y$ (x = 3, 4) species (Fig. 3.2.a). However, adding only 1 sccs of H$_2$ to the Ar/C$_2$H$_2$ plasma suffices to start C$_x$H$_y$ (x = 3, 4) formation. The overall trend is that admixing an increasing amount of H$_2$ to either precursor results in correspondingly higher production levels of C$_x$H$_y$ (x = 3, 4) species. Even so, the increase in production of these C$_x$H$_y$ (x = 3, 4) species due to H$_2$ addition is higher for an acetylene precursor than for a methane precursor. Furthermore, these low H$_2$ gas flows simultaneously reduce the precursor consumption. Note that the 36 to 44 m/z range in our measurements is overshadowed by contributions from argon. Even so, the intensity of peaks 37, 42 and 43 m/z can be used
Table 3.1: The gas composition for different precursor mixtures, both with and without plasma and indicated in sccs. The values in
the last three columns are relative to row $1M$. The index column is an abbreviation of the gas flow as set by the operator: $H$ for $H_2$, $A$
for acetylene and $M$ for methane. The number in front of each letter indicates the set gas flow in sccs. The gas flows marked by a *
correspond to the setting of the gas flow controller and were used to calibrate the RGA.

<table>
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<tr>
<th>index</th>
<th>Without plasma</th>
<th>With plasma</th>
<th></th>
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<td>$CH_4$</td>
<td>$C_2H_2$</td>
<td>$H_2$</td>
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<td>$C_2H_2$</td>
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<td>$1^*$</td>
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<td>$1^*$</td>
<td>$0^*$</td>
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</tr>
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</table>
Figure 3.3: Gas composition during the plasma phase for (a) Ar/C$_2$H$_2$ and (b) Ar/CH$_4$, both admixed with 0 – 3 sccs of H$_2$. Heavier hydrocarbons, e.g. C$_4$H$_2$, have appeared in both systems. See also rows 1A, 1H1A, 2H1A, 3H1A and 1M, 1H1M, 3H1M, respectively, in Table 3.1.
as an indicator for the C$_3$H$_y$ species. Since no gases were available for an absolute calibration of the C$_x$H$_y$ ($x = 3, 4$) flow, their content in this chapter is determined relative to the Ar/CH$_4$ plasma.

C$_x$H$_y$ ($x = 3, 4$) species are also formed when both precursors are mixed together as can be seen in Fig. 3.4. Moreover, the additional amount of C$_x$H$_y$ ($x = 3, 4$) produced with the respect to the Ar/CH$_4$ base level is higher than the sum of the production levels of both precursors separately. This synergistic effect remains when 1 or 3 sccs of H$_2$ is added to the reactor (Fig. 3.4.b and Table 3.1). A pronounced example hereof is the C$_4$H$_y$ formation which more than doubles when 3 sccs of H$_2$ is added to the CH$_4$/C$_2$H$_2$ mixture. Two sets of measurements with similar C$_3$H$_y$ to C$_4$H$_y$ ratio’s in the plasma phase are furthermore identified. The precursor composition in the first set with a ratio of $0.75 \times$ I$_{C_3H_y}$/I$_{C_4H_y}$ is given by:

$$1C_2H_2 + 2H_2 \quad (3.12a)$$
$$1CH_4 + 1C_2H_2, \quad (3.12b)$$

with a gas flow in sccs. The second set, corresponding with the following precursor compositions:

$$1C_2H_2 + 3H_2 \quad (3.13a)$$
$$2CH_4 \quad (3.13b)$$
$$1CH_4 + 1C_2H_2 + 1H_2, \quad (3.13c)$$

has a ratio of about $0.65 \times$ I$_{C_3H_y}$/I$_{C_4H_y}$. Note that in both sets the stoichiometry fits for hydrogen over the different measurements, but differs in some cases with 1 carbon atom. A higher CH$_4$ gas flow of 2 sccs is used in one of the measurements of set 2 to get a matching stoichiometry. A similar picture about the stoichiometry of both sets can be sketched when considering the corresponding (measured) gas flows (without plasma) in table 3.1. To complement the picture, a measurement with 2 sccs of acetylene is likewise carried out. Although the precursor gas flow is equal in both cases, the resulting gas composition in the plasma phase is not. Similar as for the 1 sccs gas flow on which the RGA calibration is based (see earlier in this section), methane leads to higher production of H$_2$ as well as C$_x$H$_y$ ($x = 3, 4$) species than the acetylene precursor.

Finally, a comparison can also be made between the Ar/C$_2$H$_2$ (100:1) plasma on one hand and the Ar/C$_2$H$_2$/H$_2$ (100:1:1) and Ar/C$_2$H$_2$ (100:2) plasmas on the other hand. As a reminder, no significant C$_x$H$_y$ ($x = 3, 4$) production is observed in an argon plasma admixed with only 1 sccs of acetylene. When the precursor gas flow is doubled to 2 sccs, C$_x$H$_y$ ($x = 3, 4$) species start to appear while the
Figure 3.4: Gas composition of an Ar/CH₄/C₂H₂ mixture: (a) with and without plasma, (b) admixed with 0 – 3 sccs of H₂ during the plasma phase. See also row 1M1A and rows 1M1A, 1H1M1A, 3H1M1A, respectively, in Table 3.1.
acetylene consumption decreases. However, the additional H\textsubscript{2} gas flow leads to a higher production than the increased acetylene flow, even though in both cases the increase in gas flow is equal.

### 3.5 Discussion

Residual gas analysis was used to determine the gas composition of an argon flow, both with and without a plasma, admixed with different precursor combinations of methane, acetylene and molecular hydrogen. The starting point of the discussion in this section on the experimental results is the plasma chemistry as described by Benedikt et al. and elucidated in section 3.2 [42–45,142].

The gas flow of the carbon-based precursors was at most 2.5% of the argon gas flow, which is lower than the 10% Ar\textsuperscript{+} ions. When H\textsubscript{2} is included, the molecular gas flow goes up to 6%. In other words, the molecular to ion gas flow ratio \( F \) is smaller than 1 (Sec. 3.2). This implies that the majority of molecular species are broken down resulting in little to no polymerization. Higher hydrocarbons, as a result of polymerization, were not observed in the case of an Ar/C\textsubscript{2}H\textsubscript{2} plasma. For methane, however, polymerization up to C\textsubscript{4}H\textsubscript{y} did occur. The produced C\textsubscript{4}H\textsubscript{y} species were moreover poor in hydrogen content, thereby creating an excess of molecular hydrogen. This excess is also the reason why polymerization could occur in the first place. As can be seen from reactions (3.3) and (3.8a) in section 3.2, charge transfer between argon ions and hydrocarbons is 10 times slower than between argon ions and molecular hydrogen. The excess hydrogen will thus consume the argon ions more quickly. As a result of the lower ion density, the mean free path (mfp) for CT reactions between Ar\textsuperscript{+} ions and either CH\textsubscript{4} or C\textsubscript{2}H\textsubscript{2} will increase. A mfp for these hydrocarbons can be estimated from their thermal velocity, the rate coefficient for CT and the ion density. Measurements of the ion densities near the substrate yield \( \sim 10^{19} \text{ m}^{-3} \) and \( \sim 10^{18} \text{ m}^{-3} \) for an Ar and Ar/H\textsubscript{2} plasma, respectively (Ch. 4). Based on these densities, a thermal velocity of \( \sim 1 \text{ km s}^{-1} \) and a rate coefficient of \( 10^{-16} \) to \( 10^{-15} \text{ m}^{3} \text{s}^{-1} \) for C\textsubscript{1,2}H\textsubscript{y}, the mfp will increase by a factor of 5 to 10 [45,146]. In case of acetylene, for example, the mfp increases from 10 – 30 cm in a pure argon plasma to 50 – 150 cm in an Ar/H\textsubscript{2} plasma. Note that the mfp will depend on the local ion density which is higher near the arc and lower near the substrate. The lower ion density and higher mfp allow for a larger fraction of the heavier hydrocarbon molecules and fragments to avoid undergoing charge transfer and the subsequent dissociation for a longer time. These heavier hydrocarbons can then polymerize inside the recirculation cells where they have a longer residence time than in the plasma expansion itself. Fig. 3.5 shows the C\textsubscript{x}H\textsubscript{y} \( (x = 3,4) \) production as function of the molecular gas
The data points are categorized according to their precursor composition. The precursor composition is an important factor for the $C_xH_y$ ($x = 3, 4$) production as indicated by the scatter in data points. Even so, the overall trend shows an increase in CH production with increasing gas flow.

The difference in residence time between the recirculation cells and the expansion applies to molecular hydrogen as well. Atomic hydrogen, however, does not recirculate due to its large sticking and recombination coefficient on stainless steel (i.e. the reactor wall) [124]. This creates a H density gradient between the expansion, where the H is created, and the background. As a result, there is a net outward diffusion of atomic H towards the wall where it recombines into $H_2$. At the same time the $H_2$ that has accumulated inside the cells re-enters the plasma over the entire length of the expansion leading to consecutive dissociation processes (Ch. 4). A single hydrogen molecule can thus consume multiple $Ar^+$ ions, thereby bridging the gap between the $1 − 5\% \ H_2$ content and the 10% ionization degree at the nozzle. In chapter 4, it is shown 2% of $H_2$ at a distance of 30 cm from the nozzle is indeed sufficient to reduce the ion density by one order of magnitude. Admixing $H_2$ to the reactor in this work has furthermore a
similar effect on the chemistry as is evident from the increased hydrocarbon production. The experimental results showed moreover that adding H\textsubscript{2} to the reactor has a greater effect than increasing the acetylene flow by an equal amount. This corroborates that H\textsubscript{2}, through Ar\textsuperscript{+} ion consumption, has a large influence on the polymerization process in our plasma expansion.

A decrease in the H\textsubscript{2} content itself was furthermore measured for both the Ar/H\textsubscript{2} plasma without a carbon precursor and the Ar/C\textsubscript{2}H\textsubscript{2} plasma admixed with 2 – 3 sccs of H\textsubscript{2}. In all other cases, the H\textsubscript{2} content increased. The decrease for the Ar/H\textsubscript{2} plasma is attributed to etching of (pre-existing) carbon deposits on the wall. The ternary phase diagram of amorphous carbon bonding indicates that a-C:H deposits can contain at maximum 60\% hydrogen (Fig. 1.2 in Ch. 1) [32]. Materials deposited in our group typically contain 20 to 45\% of hydrogen [37,39].

The etch products, as was shown here, are mainly methane (25\% C,75\% H) and acetylene (50\% C,50\% H). Part of the injected H\textsubscript{2} will thus be incorporated into the etch products to balance out the discrepancy in H content. Furthermore, the precursor depletion in a pure Ar/C\textsubscript{2}H\textsubscript{2} plasma and the low or absent conversion to heavier hydrocarbons indicates that (part of) the injected carbon is deposited. The decrease in H\textsubscript{2} content for the Ar/C\textsubscript{2}H\textsubscript{2}/H\textsubscript{2} plasmas therefore shows that under those low gas flow conditions etching prevails over deposition.

However, the influence of H\textsubscript{2} on the plasma chemistry can not by itself explain all of the observed differences in the C\textsubscript{x}H\textsubscript{y} (x = 3,4) production between both carbon precursors. There is for instance a synergistic effect in the production of C\textsubscript{x}H\textsubscript{y} (x = 3,4) species when both precursors are mixed together. As was mentioned in section 3.2, there is a large number of possible chemical reactions with or between hydrocarbons. Determining the reaction path between two stable species without either a comprehensive kinetic model or knowledge about the intermediate radical species (e.g. CH\textsubscript{2}) under our experimental conditions can therefore only be speculative. Nevertheless, an overall route between the precursor and e.g. C\textsubscript{4}H\textsubscript{2} can be suggested. Fig. 3.6 visualizes the different possible reaction paths.

First of all, it is clear from section 3.2 that CT and DR leads to the dissociation of C\textsubscript{2}H\textsubscript{2} into CH\textsubscript{y} (y = 1, 2) and C\textsubscript{2}H\textsubscript{y} (y = 0, 1), whereas CH\textsubscript{4} can only be dissociated into CH\textsubscript{y} (y = 0 – 3). One to two additional steps are necessary to obtain C\textsubscript{4}H\textsubscript{y} after dissociation of the acetylene precursor. As an example, reaction (3.6) converts C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H into C\textsubscript{4}H\textsubscript{2} (route 1) while e.g. reactions (3.14a – 3.14b) yield C\textsubscript{4}H\textsubscript{4} via intermediate C\textsubscript{3}H\textsubscript{3} species (route 1’).

\[
\begin{align*}
C_2H_2 + CH_2 &\rightarrow C_3H_3 + H & (3.14a) \\
C_3H_3 + CH_2 &\rightarrow C_4H_4 + H & (3.14b)
\end{align*}
\]
Reactions (3.14a – 3.14b) have a rate coefficient of $3 \times 10^{-17}$ to $7 \times 10^{-17}$ m$^3$s$^{-1}$ and $3 \times 10^{-16}$, respectively [45,47,49]. The methane precursor requires however a minimum of two additional steps. Methane is converted in a first step into C$_2$H$_y$ (route 2) with e.g. reaction (3.15), which has a rate coefficient of $5.3 \times 10^{-17}$ m$^3$s$^{-1}$ [30]. After this step, the chemistry ties into routes 1 and 1'.

$$\text{CH}_2 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \quad (3.15)$$

When methane and acetylene are mixed together, the conversion of methane into C$_2$H$_y$ is no longer a prerequisite for polymerization. Or stated differently, CH$_y$ radicals from the methane precursor can now directly react with the C$_2$H$_y$ radicals from the acetylene precursor (route 3). This yields C$_3$H$_y$ and, in a subsequent reaction, C$_4$H$_y$. Fewer steps and no intermediate species are thus required to convert methane into heavier hydrocarbons. This can lead to a synergist effect between both precursors, as observed in the experimental results. C$_3$H$_y$ species are however described in the work by Benedikt et al. as end radical groups, which only participate in the deposition process and not in any of the polymerization reactions [45, 142]. Based on the observed synergistic effect and the proposed reaction scheme in Fig. 3.6, however, this chapter does contend that C$_3$H$_y$ can play a role in the formation of C$_4$H$_y$ species. A detailed study of these low gas flow conditions that includes the radical species in the reactor, which falls outside the scope of this chapter, should shed more light on this issue.

### 3.6 Summary

The chemistry in an argon plasma jet, admixed with hydrocarbon precursors, is dominated by a two step process of charge transfer between precursor and Ar$^+$ ions, followed by dissociative recombination. Subsequent reactions between the resulting dissociation products can lead to polymerization, provided that the initial precursor density exceeded the Ar$^+$ ion density. This requirement can be fulfilled by using precursor gas flows in excess of the Ar$^+$ ion flow emanating from the plasma source. This chapter, however, showed that polymerization can also occur for precursor gas flows below the initial Ar$^+$ ion flow (Fig. 3.5). Polymerization under such low gas flow conditions is possible due to the strong negative effect that H$_2$ has on the Ar$^+$ ion density. Even though the necessary H$_2$ can be supplied via fragmentation of the hydrocarbon precursors themselves, the effect can also be enhanced by injecting additional H$_2$ directly into the system. Moreover, adding 1 to 2% of H$_2$ to the total gas flow has proven sufficient to initiate polymerization. Lastly, the synergistic effect that takes place when both methane
and acetylene precursors are mixed together indicates that C\textsubscript{4}H\textsubscript{y} formation can also occur via intermediate C\textsubscript{3}H\textsubscript{y} molecules.
H₂: the juncture between polymerization and dissociation
Chapter 4

Investigating the flow dynamics and chemistry of an expanding thermal plasma through CH(A-X) emission spectra

Abstract

The gas flow in a linear plasma reactor and the plasma chemistry during hydrogenated amorphous carbon (a-C:H) and graphite etching are investigated via time and spatially resolved measurements of the ion density and CH emission. A convolution of the ion and hydrocarbon density shows the importance of charge transfer in the plasma chemistry which ultimately yields the CH emission. The spatially resolved measurements clearly visualize the plasma expansion in the reactor and its deflection on a substrate. A stagnation zone is furthermore formed in front of a substrate when placed inside an expanding thermal plasma. An increased ion density further upstream from the substrate is attributed to a reorganisation of the gas recirculation cells in the background of the reactor. The movement of a shutter in and out of the plasma expansion likewise affects these recirculation cells. This movement consequently redirects the energy flow to and from the background, as is deduced from the variation in rotational temperature of the CH radical.
4.1 Introduction

Linear plasma reactors are used in the development of new wall materials for nuclear fusion reactors as well as in low-temperature plasma processing [5, 16, 26, 35, 49, 71, 148]. An important advantage of such a reactor is the spatial separation between the plasma source and the substrate. This separation allows for high particle fluxes in addition to low plasma temperatures near the substrate. The resulting energy flux at the substrate surface can be further increased with additional substrate biasing [58, 80]. Several linear plasma reactors dedicated to the study of nuclear materials, such as PSI-I, PSI-II and PISCES, have reached ion fluxes above $10^{22} \text{m}^{-2}\text{s}^{-1}$ [5, 16, 71]. Even higher ion fluxes are expected in the next-generation nuclear fusion reactor ITER. Wall components inside ITER’s divertor will face an expected ion and energy flux of up to $10^{24} \text{m}^{-2}\text{s}^{-1}$ and 5 to 10 MW m$^{-2}$, respectively, for a duration of 500 s or longer [7]. The recently completed Magnum-PSI facility in The Netherlands is specifically developed to test new materials under the extreme plasma conditions expected in ITER [3, 4, 7, 74, 75]. Even though such extreme plasma conditions can be reached, linear plasma reactors in both research and industry are usually operated on lower ion and energy fluxes. Industrial applications for these type of reactors include the removal, deposition or modification of functional materials such as amorphous silicon nitride ($a$-SiN$_x$:H) and hydrogenated amorphous carbon ($a$-C:H) [32, 37, 43, 55, 81].

Plasma processing of such functional materials often requires the injection of deposition or etch precursors directly into the reactor. Depending on the injection point, these precursors will first mix with the background gas before diffusing into the plasma beam [118]. The resulting plasma chemistry leads to the formation of atomic and molecular species that were not originally present in the reactor. Additional chemical reactions with those newly formed species take place both in the background of the reactor and at the reactor wall or substrate surface. In case of an acetylene ($C_2H_2$) precursor, for example, $C_3H_y$ ($y = 0, 1$) production is considered to be an important factor in the deposition process of $a$-C:H [45]. The background gas, furthermore, recirculates when the residence time in the background is higher than in the plasma beam. This increases the number of interactions with the reactor wall. It likewise facilitates the complete mixture of the background gas, which is driven by diffusion. Similar as before, the background gas — including any reaction products — can diffuse back into the plasma beam. Gas recirculation cells inside the linear plasma reactor, there-

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1Plasma-Surface Interaction
2Plasma Interaction with Surface and Components Experimental Simulator
fore, play an important role in the chemistry of the entire system [118,123–126]. Molecular hydrogen, dissociated into atomic hydrogen by the plasma at the expense of the ions, can be used as an etch precursor for carbon erosion (Ch. 6). Ion bombardment can likewise erode the surface material or prepare new surface sites for deposition [149]. The ion density and flux towards the surface are thus equally important in plasma processing.

An understanding of the gas dynamics and plasma chemistry in a linear plasma reactor is important for the correct interpretation of experimental results obtained with this type of system. Characterization of such a reactor type, or any reactor for that matter, should therefore always be a first step before conducting surface-related experiments. This chapter will contribute to that characterization by investigating the effect of external influences — for example, an substrate — on the ion density, the gas flow and thus on the recirculation cells. The linear reactor used for that end is equipped with a cascaded arc as plasma source. This arc is similar in its basic design as the plasma source in Magnum-PSI and is used also for thin film deposition in e.g. the photovoltaic industry [77–79]. The expanding thermal plasma generated by such an arc has been extensively investigated in the past (see section 4.2). Typical for this type of plasma are the high fluxes (up to $10^{22} \text{ m}^{-2}\text{s}^{-1}$, depending on the plasma source and reactor configuration) and low electron and ion kinetic temperature ($\sim 1 \text{ eV}$) near the arc’s nozzle. These temperatures decrease to about 0.1 eV near the substrate. A bias voltage can furthermore be applied to the surface to increase the kinetic energy of the incident ions, thereby extending the range of plasma conditions relevant to ITER. Surface processes that occur during a-C:H erosion under these plasma conditions are largely unexplored and will be treated in a chapter 6. Furthermore, past studies showed that the chemistry inside the plasma expansion is dominated by charge transfer (CT) and dissociative recombination (DR) [38–41]. Ions emanating from the plasma source are thereby consumed in the charge transfer with molecular species. Dissociative recombination of the resulting molecular ions, which follows immediately after the charge transfer reaction, leads to electronically excited radicals. The flow dynamics of both the ions and molecular species plays a role in where and when these radicals are produced and can therefore affect the local plasma chemistry as well as the surface processes. Such excited radical species play a role in both fusion related research (i.e. plasma erosion) and plasma processing of functional materials (i.e. plasma deposition). The issues focused on in this work, i.e. perturbations of the flow dynamics and the local plasma chemistry, should therefore be considered in all linear plasma reactors.

An expanding thermal plasma is deflected by a substrate as can be clearly seen in the photographic images by van Helden et al. [121]. The presence of
a substrate in a plasma expansion may also lead to changes in the recirculation cells and thus affect where the diffusion of the background gas into the plasma occurs. The influence of a substrate is therefore investigated via spatially resolved measurements of the ion density in an Ar/H₂ plasma, both with and without a substrate. The contours of the expanding thermal plasma and its deflection on the substrate will be visualized with these measurements. The presence of a substrate, moreover, increases the ion density as will be shown. Next, the same plasma conditions are used for the erosion of both a-C:H and graphite targets. It will be shown that CT and DR between the hydrocarbon etch products of both targets and the Ar⁺ ions leads to the formation of ro-vibrationally excited CH radicals. The optical emission of these CH radicals consequently acts as a tracer for both the argon ions and the hydrocarbon etch products [83]. Spatially resolved measurements of the CH emission are used to determine the hydrocarbon redistribution near the vicinity of the target. Furthermore the rotational and vibrational temperatures of the CH radical are strongly affected by the reactor conditions which, in turn, are substantially influenced by the retraction or extension of a shutter in front of the a-C:H sample. The changes caused by both the substrate and shutter in either the ion density or the ro-vibrational CH temperature suggest a reorganisation of the recirculation pattern. Measurements related to the plasma chemistry are thus instrumental in investigating the gas flow and recirculation pattern in a linear plasma reactor.

### 4.2 Flow dynamics of an expanding thermal plasma

Both the flow dynamics of and the plasma chemistry in an expanding thermal plasma have been extensively investigated in the past and are briefly described in this section.

Gas injected under high pressure into a cascaded arc is ionized by a DC current. With a typical ionization degree of around 10%, the generated plasma consists of neutral species as well as ions and electrons. This plasma expands supersonically into the low pressure reactor until it encounters the background gas, at which point a barrel shock is created. After the shock, the plasma continues subsonically towards the substrate or reactor walls. The shock position \( z_s \) (in mm) on the plasma axis can be estimated from:

\[
z_s = 18 \sqrt{\frac{\Phi}{P_{bg}}} \sqrt{MT},
\]

with the gas flow \( \Phi \) in sccs (1 sccs = \( 2.5 \times 10^{19} \) s \(^{-1} \)), the background pressure
4.2. Flow dynamics of an expanding thermal plasma

Figure 4.1: Schematic cross-section of the reactor with movable plasma source and substrate. Recirculation cells are responsible for a complete mixture of the background gas.

$P_{bg}$ in Pa, the mass $M$ in amu and the temperature of the plasma source $T$ in eV [122]. The plasma expansion is furthermore radially symmetric and quasi-neutral ($n_e = n_{ion}$), but not in local thermal equilibrium [77].

Four regions have to be considered when discussing the thermal properties of the plasma. First: the electron, ion and neutral gas kinetic temperatures are in equilibrium within the arc itself, which is the only active region in the entire reactor. In other words, the arc produces a thermal plasma with an electron temperature of about 1 eV near the nozzle. Second: due to the low ionization degree, the supersonic part of the expansion behaves similar to that of a hot gas expansion [126]. The ions cool down adiabatically, thereby converting thermal energy into forward directed kinetic energy [77, 128, 133]. The electron kinetic temperature in the supersonic part furthermore decouples from the ion and neutral gas kinetic temperature since the energy exchange between heavy particles occurs more efficiently than between electrons and heavy particles [77]. Third: the temperature increases again across the shock due to the back conversion of forward directed kinetic energy into random thermal energy [124]. Fourth: particle transport in the subsonic part of the plasma expansion, i.e. the region of interest in this chapter, is controlled by diffusion [124]. This leads to heat loss at the wall and a subsequent temperature decrease. In this part of the plasma expansion, the electron, ion and neutral gas kinetic temperatures have thermalized and are on the order of 0.1 eV [133, 150].

The gas residence time in the reactor can be calculated from the gas flow $\Phi$ (in sccs), the pressure $P$ (in Pa) and reactor volume $V$ (in m$^3$) with $\tau = \frac{10 \times PV}{\Phi}$ and is on the order of a second during the experiments discussed in this chapter. Within the expansion itself, however, the ions and electrons have a residence time...
on the order of 0.1 ms [123]. The much higher residence time of the background gas causes the background gas to recirculate and interact multiple times with the reactor wall. The resulting recirculation cells, wedged between the plasma expansion and the reactor wall, are also responsible for a good mixture of the background gas (Fig. 4.1). This gas can moreover diffuse into the plasma over the entire length of the expansion and interact with the electrons and ions emanating from the arc [118]. In the supersonic part of the expansion, background species can enter through the barrel shock if their partial pressure inside the expansion is lower than in the background [118]. This is particularly the case in the region right before the shock front, where the plasma is overexpanded [124]. The total pressure in this so-called zone of silence is lower than the overall background pressure.

4.3 Experimental setup

The cascaded arc, as used in this chapter, consists of a stack of four water-cooled copper plates with a central bore of 4 mm in diameter and has a total length of 24 mm (Fig. 4.1) [77,78]. The arc is operated on a 60 A DC current, a gas flow of 50 sccs argon and a pressure of about 600 mbar. A constant background pressure of 100 Pa is maintained inside the reactor itself by regulating the opening of the pump valve, i.e. the effective pumping speed. Molecular hydrogen (H₂) with a gasflow of 1 sccs is moreover injected directly in the background of the reactor via a second gas inlet. The shock position under these conditions is located ∼32 mm from the nozzle, irrespective of the small H₂ inflow. An electrically floating substrate is furthermore positioned at ∼320 mm from the nozzle.

This arc configuration is used on two different reactors. Reactor one has an arc and substrate which can move independently with respect to a double Langmuir probe and each other. This double probe measures the ion density with a spatial resolution of 5 mm in both radial and axial direction. Length and diameter of the tungsten wires are 3.85 ± 0.05 mm and 0.85 ± 0.05 mm, respectively. Spacing between the wires is likewise 0.85 ± 0.05 mm. A Keithley 2400 source meter provides a voltage sweep from -5 V to 5 V in steps of 0.025 V and measures the current. The resulting I-V characteristic, averaged over 5 voltage sweeps, is analysed according to the theory by Peterson and Albot [107].

Reactor two has an arc and substrate with a fixed position (Fig 4.11). The substrate temperature is set to a starting value of 250 °C, which increases further due to plasma heating. Two types of carbon-based targets are exposed in this reactor to an Ar plasma, admixed with 1 sccs of H₂. Hydrogenated amorphous carbon samples (a-C:H) are the first type of target. These samples are pre-deposited in-
4.3. Experimental setup

Figure 4.2: Optical emission spectrum of an Ar/H$_2$ plasma during $\alpha$-C:H etching. CH, C$_2$ and two of the H Balmer ($H_\beta$, $H_\delta$) lines are clearly visible.

house by means of plasma-enhanced chemical vapour deposition [36,82]. During deposition, the arc current is 75 A with an argon gas flow of 100 sccs. The precursor gas flow is 15 sccs of acetylene (C$_2$H$_2$). The substrate temperature and background pressure during sample preparation are 250 °C and 31 Pa, respectively. The deposited samples are about 1 µm thick. After deposition, the samples are stored in a desiccator. For more details on the deposition process itself, see [151] and references therein. The second type of target is a commercially available fine-grain graphite block (FGG; R6650, SGL Carbon group) with a diameter of 30 mm. This is 45 mm smaller than the target holder itself, i.e. the substrate.

The erosion process of the carbon targets is monitored by residual gas analysis (RGA; Pfeiffer Vacuum QMS 200) and by optical emission spectroscopy (OES) [113]. Light from the plasma is collected during OES measurements by a lens (focal length = 5.7 ± 0.2 cm) and focused onto an optical fiber and transmitted to a commercially available spectrometer (AvaSpec-2048-4-DT, Avantes), resulting in a line-of-sight measurement. The wavelength resolution of the overview channel (150 – 1300 nm) is 1.3 nm and 0.3 nm for the high resolution channel (350 – 610 nm). The time resolution is 1 and 2.5 s during the plasma etching of $\alpha$-C:H and FGG, respectively. Of all the different carbon-based molecules present in our reactor, only the emission of CH and C$_2$ falls within the wavelength range
Figure 4.3: Measured and fitted spectrum of a typical CH(A-X) spectrum. Rotational and vibrational temperatures in this example are 3300 and 4900 K, respectively. The P ($\Delta J = 1$), Q ($\Delta J = 0$) and R ($\Delta J = -1$) branches as well as H$\gamma$ are indicated in the graph.

of our spectrometer as can be seen in Fig. 4.2. Moreover, the rotational ($T_{\text{rot}}$) and vibrational ($T_{\text{vib}}$) temperature of the electronic CH(A-X) transition can be determined by means of the spectrum simulation program LIFBASE [114, 115]. Fig. 4.3, as an illustration, shows a measured CH spectrum together with the corresponding fit. Rather than fitting all the spectra manually, the method as explained in appendix 4.B is used to determine the rotational and vibrational temperature of each spectrum.

4.4 Experimental results

The experimental results are divided into four sections. The first section discusses the ion composition and effective ion mass of the plasma. Section (4.4.2) deals with the influence of a substrate on the ion density in an Ar/H$_2$ plasma. The (re-)distribution and dissociation of hydrocarbon etch products is discussed in section 4.4.3. A connection between the ro-vibrational temperatures of the CH radical and the gas kinetic temperature will be show in the last section, i.e. 4.4.4.
4.4.1 Ion composition of the plasma

The ion composition and plasma chemistry in pure argon and Ar/H₂ expanding thermal plasmas have been studied in the past by our group and is therefore not extensively treated here [77, 78, 128–130, 134]. These studies showed that ionization or dissociation of neutral species via electron impact only occurs in the arc, where the electron temperature and density are high enough. Nevertheless, charge transfer and dissociative recombination within either the arc or the reactor likewise leads to the formation of new species. Rate coefficients for charge transfer are overall lower than for dissociative recombination by 2 or 3 orders of magnitude. Charge transfer is thus the time-limiting factor in this process. H₂ dissociation and ion formation via CT and DR in Ar/H₂ plasma is explained in appendix 4.A as well as in chapter 2.

The effective ion mass is a required input parameter in the analysis of the double Langmuir probe data when using the Peterson and Albot theory. This is 40 amu for Ar⁺ in a pure argon plasma. The ion composition in an Ar/H₂ plasma consists of Ar⁺, ArH⁺ and H₃⁺ and depends strongly on the gas mixture as discussed in appendix 4.A. The exact ion composition and thus the effective ion mass for the plasma conditions in this chapter remains however unclear. An ion mass of 40 amu is therefore used as well for the Ar/H₂ measurements in section 4.4.2, although this approach yields on overestimation of the ion density by up to a factor of four.

4.4.2 Influence of a substrate on the plasma expansion

Fig. 4.4 shows the spatial distribution of the ion density for three different plasma systems with a spatial resolution of 5 mm in both radial (r) and axial (z) direction. The shock position of the plasma falls outside the measured range. Figs. 4.4.a and 4.4.b show a pure argon plasma and an Ar/H₂ plasma, respectively, without a substrate. Notice that the scale in Fig. 4.4.b (and Fig. 4.4.c as well) is nearly one order of magnitude lower than in Fig. 4.4.a. This loss in Ar⁺ ions is due to an inflow of H₂ from the background which leads to atomic H production via CT and DR (App. 4.A). These spatially resolved measurements moreover show that the decrease in radical direction is stronger for larger z-positions. When ions are consumed at any given radial position, they are obviously no longer available further downstream for additional H₂ dissociation reactions. Downstream, H₂ will thus have to advance further towards the center before undergoing dissociation.

Fig. 4.4.c shows the influence of a substrate on the ion density in an Ar/H₂ plasma. Immediately noticeable is that the highest densities (> 3.8 × 10¹⁸ m⁻³)
**Figure 4.4:** Cross-section of the ion density for (a) a pure argon plasma, (b) an argon plasma admixed with 2% H\textsubscript{2} and the same Ar/H\textsubscript{2} plasma (c) with a substrate at floating potential. Note the difference in scale between frame a and frames b and c.
extend further into the reactor, towards the substrate. The density at 40 mm is about 50% higher when the substrate interacts with the plasma expansion. The last two to three data points in front of the substrate, on the other hand, show a relatively larger decline in density. Notice furthermore the appearance of indentations and protuberances on the plasma boundary and the deflection of the plasma on the substrate. The influence of a substrate on the ion density is further discussed in section 4.5.

4.4.3 Spatial and time resolved CH emission during carbon erosion

A similar Ar/H\textsubscript{2} plasma as shown in Fig. 4.4.b and Fig. 4.4.c is now used for the erosion of both graphite and a-C:H targets. Stable hydrocarbon species detected by RGA during plasma exposure of these two different targets are mainly CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{y} (y = 2, 4). Previous work in our group has shown that CT and DR with hydrocarbon deposition precursors leads to the formation of excited CH radicals [41]. Fig. 4.5 shows the relative intensity of the Q(0,0) band head of CH(A-X) transition at 431 nm with a spatial resolution of 5 mm. The scale on the axis is limited by the size of the viewport and, therefore, smaller than in Fig. 4.4. As can be seen in Fig. 4.5, CH radicals are likewise found throughout the reactor during carbon erosion (fine-grain graphite or FGG in this case). With a thermal velocity of \( \sim 1 \text{ km s}^{-1} \) and a lifetime of 500 to 700 ns for the first excited state, the CH radical can travel up to 0.77 mm before it decays [114]. This short travel distance excludes the carbon surface as the origin of these excited radicals. Electron ionization of existing CH radicals in the gas phase is likewise excluded due to the low electron temperature of the plasma. CH emission thus occurs in the immediate vicinity of its production, i.e. through CT and DR reactions between Ar\textsuperscript{+} and hydrocarbons such as CH\textsubscript{4} or C\textsubscript{2}H\textsubscript{2}.

A mean free path (mfp) for these hydrocarbon etch products is estimated from their thermal velocity, the rate coefficient for CT and the ion density. The thermal velocity is around 1 km s\textsuperscript{-1}, while the rate coefficient is on the order of \( 10^{-16} \) to \( 10^{-15} \text{ m}^3\text{s}^{-1} \) for C\textsubscript{1,2}H\textsubscript{y} [45, 146]. Acetylene, for instance, would have a mfp on the order of 10 – 30 cm in a pure argon plasma with an ion density of \( \sim 2 \times 10^{19} \text{ m}^{-3} \) (Fig. 4.4.a) [39, 45]. Fig. 4.4.c in turn yields a much lower ion density of \( 1 – 5 \times 10^{18} \text{ m}^{-3} \) for an Ar/H\textsubscript{2} plasma. This translates into a mfp for CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} on the order of 20 – 100 cm and 50 – 150 cm, respectively. Although uncertainties in ion density measured via electrical probes can be large, the ion density in our case is more likely overestimated (due to the uncertainty in the ion mass) than underestimated. This implies that the calculated mfp itself is underestimated. Regardless, the mean free path of the hydrocarbons — when
only considering the charge transfer reaction — is sufficiently large to fill up the entire reactor (500 mm in length, 400 mm in diameter) with etch products from the carbon surface. Likely candidates for the CH parent molecule therefore include these etch products, although hydrocarbon products of secondary chemical reactions in the background are not entirely excluded.

Six additional observations are made from Fig. 4.5:

1. The highest intensities are measured within the first 10 mm’s right in front of the fine-grain graphite (FGG) target from where the hydrocarbons originate.

2. The e-folding length of the measured intensity on the z-axis is $6.0 \pm 0.5$ mm, which is significantly smaller than the previously calculated mean free path of up to 100 cm for methane. Similar measurements conducted by Westerhout et al. in a pure hydrogen plasma showed a good correspondence between the e-folding length in the z-direction of the CH emission and the mean free path of methane, injected via the substrate [83]. The neutral density in our case is however one order of magnitude higher, which increases the number of neutral – neutral collisions. This reduces the effective travel

---

**Figure 4.5:** Spatially resolved line-of-sight measurements of the CH(A-X) band emission visualize the plasma expansion. The highest emission can be found right in front of the carbon target.
distance of the etch products prior to CT and DR and is thus expected to yield a smaller e-folding length.

3. Emission levels are lower at the edges of the FGG target, i.e. at a radial position of about ±20 mm, compared to the immediate surroundings. This indicates that the region around the sides of the 4 mm thick target is poor in either Ar\(^+\) ions or hydrocarbons.

4. The pump duct located at the bottom of the back flange, i.e. below the target, is responsible for the asymmetry in the measured intensity at larger radial positions (> 40 mm).

5. The CH emission accentuates the central axis of the plasma expansion for \(z > 10\) mm’s. It also shows the deflection of the plasma expansion by the substrate.

6. The spectrum at each location was measured several times during the measurement, which lasted over an hour. Nevertheless, the variation in intensity is less than 3%.

The (re-)distribution of hydrocarbons in the ground state, which can not be detected via optical emission spectroscopy, is furthermore determined via numerical simulations of the gas flow in the reactor. The DS2V code developed by G.A. Bird is a direct simulation Monte Carlo (DSMC) method and has been previously used to describe the plasma expansion [116–118]. Our simulation starts from a fully developed expansion of a pure argon gas. After a stable gas flow has been calculated, a secondary gas inlet of methane-like particles is added to the model at the position of the substrate to simulate the erosion of a carbon target. The injected flow ratio of argon to methane is a 100:1. The model contains neither charged particles, nor any gas phase chemistry. The results presented in Fig. 4.6 show the gas expansion and its deflection on the substrate. Cooling of the gas along the main axis can likewise be seen. In contrast with the CH emission, moreover, the injected methane-like particles are primarily found in front of the substrate and in the background of the reactor. The distribution in the CH emission, as measured in Fig. 4.5, is thus due to the convolution of the Ar\(^+\) ion density and the hydrocarbon density throughout the reactor.

A thick FGG target, as used so far, enables steady state measurements. The target type is now switched to \(a\)-C:H thin films for the study of time dependent effects in the gas flow. Optical emission from the plasma is measured a few mm’s in front of an \(a\)-C:H sample with a time resolution of 1 s. Note that the focus of the optical system in these measurements is located in between sample
Figure 4.6: Numerical simulation of the plasma expansion. Top image (a) shows the distribution in the reactor of a methane-like gas, injected at the substrate. Bottom image (b) shows the temperature in the reactor. The expansion and its deflection on the substrate are clearly visible.
and shutter (as can be seen in Fig. 4.9 later). This implies that little to no emission of any wavelength is recorded by the spectrometer when the plasma is blocked by the shutter. Fig. 4.7 shows the time evolution of the CH peak at 431 nm. When the shutter is retracted at 0 s, the measured intensity increases sharply. Afterwards the intensity increases steadily for about 220 s due to an increased etch rate caused by plasma heating (Ch. 6). Maximum intensity in the emission is reached a few seconds before the sample is completely eroded as indicated by spectroscopic ellipsometry (Ch. 5 and Ch. 6). Or in other words, CH emission starts to decrease as the hydrocarbon source (i.e. the a-C:H surface) is depleted. Between $\sim 250$ s and $\sim 470$ s, the measured intensity remains high due to a continuous redeposition and re-erosion and due to the etching of carbon impurities on the reactor walls. Closing the shutter at $\sim 470$ s blocks the plasma expansion again, which strongly reduces the overall light emission at the focal point of the optical measurement system. This verifies that CH emission is not measured when Ar$^+$ ions and electrons are unavailable for CT and DR at the focal point.

**Figure 4.7:** Evolution of the CH(A-X) emission a few mm’s in front of an a-C:H sample. The time resolution is 1 s. The gray bar indicates the uncertainty in when the sample is completely eroded according to spectroscopic ellipsometry. The elevated emission after 250 s is due to wall impurities.
4.4.4 Rotational and vibrational temperature of CH

The method described in section 4.B will now be used to determine the rotational and vibrational temperature of the CH radical for the previously discussed spatial and time resolved measurements.

Spatially resolved

Engeln et al. measured the density of CH in the ground state during deposition conditions, thereby assuming thermal equilibrium between CH and the background gas [41]. The rotational temperature in particular was assumed to be a measure of the gas kinetic temperature \( T_{\text{gas}} \) [41]. Ro-vibrational temperatures of the first electronically excited state CH(A-X), as shown in Fig. 4.8, are on the other hand higher than the gas kinetic temperature of 1000 – 2000 K. The highest temperatures are measured on the central axis of the plasma expansion and nearest to the cascaded arc. Both \( T_{\text{rot}} \) and \( T_{\text{vib}} \) decrease in axial direction towards the substrate as well as in radical direction. A similar trend for the gas temperature, seen in the bottom part of Fig. 4.6, indicates a connection between the electronically excited state and \( T_{\text{gas}} \) as well. The lifetime of the excited state (Sec. 4.4.3) however provides insufficient time to equilibrate with the background gas. A memory effect is therefore assumed between the ro-vibrational temperature of the electronically excited CH and the gas kinetic temperature by proxy of the CH parent molecule.

Time resolved

Fig. 4.9, which corresponds with Fig. 4.7, shows the time variation in the rotational and vibrational temperature. The intensity measured after 250 s is too low to accurately determine these two temperatures. A slow increase from \( \sim 4700 \) K to \( \sim 4800 \) K can be observed in Fig. 4.9.a. \( T_{\text{rot}} \), on the other hand, decreases exponentially from \( \sim 3200 \) K to \( \sim 2200 \) K. This decrease is explained in detail in section 4.5. Two spectra — averaged over 10 measurement points and normalized to the Q(0,0) band head — obtained near the beginning and end of the \( a\)-C:H erosion experiment are shown in Fig. 4.10. A variation in peak intensities relative to the Q(0,0) band head provides visual confirmation of a change in the ro-vibrational CH(A-X) temperature (see eq. 4.4a and 4.4b in App. 4.B). The larger variation in \( T_{\text{rot}} \) between beginning and end of the measurement suggests that the rotational energy levels are more sensitive to the gas temperature than the vibrational temperature. This can be expected in a low-temperature plasma.
since the rotational energy spacings (∼ 0.01 eV) are smaller than the vibrational energy spacings (∼ 0.2 eV) [1].

Figure 4.8: Spatially resolved (a) vibrational and (b) rotational temperature of CH(A-X) during plasma erosion of a FGG target. See also Fig. 4.5.
Figure 4.9: Vibrational and rotational temperature of CH(A-X) during plasma erosion of an α-C:H sample, corresponding to Fig. 4.7. The measured spectra at points a and b (red circles) are shown in Fig. 4.10.

Figure 4.10: Average of the measured spectra from (a) 5 to 14 s and (b) 210 to 219 s, corresponding to Fig. 4.9.
4.5 Discussion and conclusions

Placing a substrate inside the expanding thermal plasma has a clear effect on the ion density and the shape of the plasma expansion as shown in section 4.4.2. The lower ion density in front of the substrate is attributed to the formation of a stagnation zone with a thickness on the order of 10 mm in axial direction. An increased neutral particle (i.e. H$_2$) density in this stagnation zone increases the number of ion-neutral collisions via CT and thus also the ion losses. This effect can moreover be seen in the CH emission, whereby the excited CH radicals themselves are formed via CT and DR between Ar$^+$ and hydrocarbon etch products. As stated in section 4.4.3, the intensity of the CH emission is due to the convolution of the Ar$^+$ ion density and the hydrocarbon density throughout the reactor. An increased pressure in the stagnation zone augments the local hydrocarbon density, which is already high due to the vicinity of the carbon target. The combination of a substrate and a deflected plasma expansion furthermore leads to a restructuring of the recirculation cells in the background. Such a restructuring is moreover considered to be responsible for the reduced decline in ion density further upstream from the substrate (Fig. 4.4). CT reactions outside of the stagnation zone require a molecular gas inflow from the background (or alternatively from the arc, which is not the case here). Previous work in our group showed a bimodal component in the velocity distribution of argon for a pure argon plasma [118]. A hot, fast component originating from the cascaded arc and a slow, cool component from the inflowing background gas. Impeding this gas inflow via a restructured circulatory system in the background thus reduces the ion losses as was observed.

The vibrational and rotational temperature of CH in section 4.4.4 likewise provide information about the plasma expansion and indirectly about the recirculation cells. The steady-state measurements, first of all, visualizes the plasma cooling in both radial and axial direction, thereby relating the rotational and vibrational temperature of CH to the gas kinetic temperature in the expansion via the CH parent molecule. The plasma expansion is furthermore deflected by the shutter towards the walls, thereby displacing the recirculation cells (Fig. 4.11). The deflected plasma will subsequently heat up both the wall and the background gas. When the shutter is retracted to start the etch process, the walls and the background gas in the reformed recirculation cells no longer receive an energy influx from the plasma and start to gradually cool down. As the background cools down over time, the inflowing gas will likewise have a lower kinetic energy. This temporal variation in the gas kinetic temperature is reflected in the time-dependent rotational temperature of CH, as observed in section 4.4.4. Or in other words, the
Chemistry and flow dynamics of an expanding thermal plasma

Figure 4.11: Schematic cross-section of the reactor with fixed arc and substrate. The plasma is deflected by the shutter towards the wall, effectively dividing the reactor into two. The focus of the optical system falls in between the shutter and the substrate.

rotational temperature of the CH radical acts as a thermometer for changes in the background environment.

In conclusion, both the placement of a substrate and the movement of a shutter inside the plasma expansion affect the ion density and the CH temperature via a reorganisation of the recirculation cells. The ion density is likewise affected via the formation of a stagnation zone in front of the substrate. The distribution of electronically excited CH radicals, produced via charge transfer and dissociative recombination reactions, is due to the convolution of the Ar$^+$ ion density and the hydrocarbon density throughout the reactor. The rotational temperature of electronically excited CH is furthermore related to the gas kinetic temperature via their parent molecules.
4.A  Ion composition of an Ar/H₂ plasma

Analysis of an IV-characteristic measured by a double Langmuir probe by means of the Peterson and Albot theory requires the ion mass as input parameter [107]. The ion composition in an Ar/H₂ plasma is therefore discussed in this appendix.

Charge transfer between Ar⁺ ions and H₂ followed by the associated dissociative recombination reactions leads to the production of atomic H at the expense of the Ar⁺ ions. This however occurs via ArH⁺ and H₂⁺ as intermediate ions as can be seen in the reactions:

\[
\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}
\]  \hspace{1cm} (4.2a)

\[
\rightarrow \text{Ar} + \text{H}_2^+
\]  \hspace{1cm} (4.2b)

Reactions (4.2a) and (4.2b) have a rate coefficient of \(1.2 \times 10^{-15} \text{ m}^3\text{s}^{-1}\) and \(1.7 \times 10^{-16} \text{ m}^3\text{s}^{-1}\), respectively [128]. The first reaction is dominant as reaction (4.2b) is of little importance below 0.5 eV [127]. A third possible CT reaction with a rate of \(\sim 10^{-15} \text{ m}^3\text{s}^{-1}\) is given by [129,130]:

\[
\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}.
\]  \hspace{1cm} (4.3a)

The different DR reactions, not shown here, all have a rate coefficient around \(\sim 10^{-13} \text{ m}^3\text{s}^{-1}\). Reaction (4.3a) thus starts to play a role when the \(n_{\text{H}_2}\) over \(n_{\text{e}^-}\) ratio exceeds 100, as can be seen from the rate coefficients.

The ion composition of the plasma, which in turn determines the effective ion mass, is thus to a large degree dependent on the \(n_{\text{H}_2}\) over \(n_{\text{e}^-}\) ratio. Even so, the transition between a purely Ar⁺ and a purely H₃⁺ ion composition should be smooth. IV-characteristics are therefore measured as function of the H₂ gas flow admixed to an argon plasma and analysed for a range of ion masses: 3 and 38–41 amu (Fig. 4.12). Note that an ion mass of 40 amu is always used for 0% H₂, while a mass of 41 amu represents an ion composition of 100% ArH⁺. These measurements were taken in the center of the reactor at a distance of 31.5 cm from the plasma source, without the presence of a substrate. First of all, the difference in ion density is about 3 to 4% when analysed with a mass of 38 to 41 amu. Analysis of the data for a mass of 41 amu yields a density four times higher than for a mass of 3 amu. A factor of four difference would thus constitute the worst case scenario, not taking into account any other measurement errors. The graph furthermore shows the strongest decline in ion density between 0 and 2%, regardless of ion mass. Extrapolating this initial decline (for 40 amu) would yield a 100-fold decrease in ion density for a gas mixture with \(\sim 2.2\%\) H₂. The measured ion density for gas mixtures with more than 2% H₂ however remains
Figure 4.12: Ion density as function of the H₂ gas flow. IV-characteristics measured with a double Langmuir probe are analysed for different ion masses to obtain the ion density. An ion mass of 40 amu is used each time for a pure Ar plasma (0% H₂). The initial decline in ion density extrapolates to a > 100-fold decrease at a gas flow of ~ 2.2% when assuming a linear consumption of Ar⁺ ions. The higher than expected ion density above this gas flow of ~ 2.2% is attributed to H⁺₃ formation, which counteracts the loss of Ar⁺ in the total ion density.
higher than expected from a linear consumption of Ar$^+$ ions. This is attributed to H$_3^+$ formation, which counteracts the loss of Ar$^+$ in the total ion density. Previous work in our group also showed that more than 3% of H$_2$ in the gas flow leads to a drastic change in the ion composition or in the behaviour of the arc [134,135]. A gas mixture of $\sim$ 2% of H$_2$, as used in this work, falls within the transition from an Ar$^+$ dominated to an H$_3^+$ dominated plasma.

4.B Fitting CH(A-X) spectra

The spectrum simulation program Lifbase can determine the rotational and vibrational temperature of the electronic CH(A-X) transition. Manually fitting each spectrum is however not always feasible when large data sets are involved. Beulens et al. observed that $T_{\text{vib}}$, fortunately, depends heavily on the ratio of the Q$(0,0)$ and Q$(2,2)$ band heads, more so than $T_{\text{rot}}$ [38]. This allows for a separation between the rotational and vibrational temperatures based on the relative peak intensity. Therefore, the following empirical approach can be used. First, lifbase is used to simulate a set of CH(A-X) spectra for a wide range of rotational and vibrational temperatures. Two proportionality factors are then determined from this set:

$$P_{\text{vib}} = \frac{Q(2,2)}{Q(0,0)}$$  \hspace{1cm} (4.4a)

$$P_{\text{rot}} = \frac{\sum_{431\text{nm}}^{415\text{nm}} R(i,f)}{Q(0,0)}$$  \hspace{1cm} (4.4b)

with i and f the initial and final vibrational state, respectively. The Q$(0,0)$ band head is included in the sum of eq. (4.4b) as well. The difference in rotational quantum number ($\Delta J$) is 1 for the P-branch, 0 for the Q-branch and -1 for the R-branch. Second, two analytic expressions are obtained for these proportionality factors as function of the simulated temperature (Fig. 4.13):

$$P_{\text{vib}} = a + b \times \ln(T_{\text{vib}} + c)$$  \hspace{1cm} (4.5a)

$$P_{\text{rot}} = d \times T_{\text{rot}} + e,$$  \hspace{1cm} (4.5b)

with the inverse relations given by:

$$T_{\text{vib}} = a \times e^{P_{\text{vib}}/b} + e$$  \hspace{1cm} (4.6a)

$$T_{\text{rot}} = d \times P_{\text{rot}} + e.$$  \hspace{1cm} (4.6b)

Table 4.1 lists the fit parameters $a$ through $e$ for both sets of equations. The third and last step is to determine the ratios $P_{\text{vib}}$ and $P_{\text{rot}}$ for each measured spectrum. Both temperatures are then calculated from these measured ratios.
Table 4.1: Fit parameters for the equations (4.5a) to (4.6b).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(4.5a)</th>
<th>(4.6a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$-5.28 \pm 0.57$</td>
<td>$5729 \pm 640$</td>
</tr>
<tr>
<td>$b$</td>
<td>$0.600 \pm 0.06$</td>
<td>$0.537 \pm 0.045$</td>
</tr>
<tr>
<td>$c$</td>
<td>$4959 \pm 816$</td>
<td>$-4024 \pm 664$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(4.5b)</th>
<th>(4.6b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$</td>
<td>$(2.10 \pm 0.03) \times 10^{-4}$</td>
<td>$4737 \pm 63$</td>
</tr>
<tr>
<td>$e$</td>
<td>$2.04 \pm 0.02$</td>
<td>$-9638 \pm 181$</td>
</tr>
</tbody>
</table>

Figure 4.13: Proportionality factors for simulated rotational and vibrational temperatures of the CH(A-X) emission band. The fit functions are given by equations (4.5a) and (4.5b).
Chapter 5

B-spline parameterization of the dielectric function applied to spectroscopic ellipsometry on amorphous carbon*

Abstract

The remote plasma deposition of hydrogenated amorphous carbon (a-C:H) thin films is investigated by in situ spectroscopic ellipsometry. The dielectric function of the a-C:H film is in this chapter parameterized by means of B-splines. In contrast with the commonly used Tauc-Lorentz oscillator, B-splines are a purely mathematical description of the dielectric function. We will show that the B-spline parameterization, which requires no prior knowledge about the film or its interaction with light, is a fast and simple-to-apply method that accurately determines thickness, surface roughness and the dielectric constants of hydrogenated amorphous carbon thin films. Analysis of the deposition process provides us with information about the high deposition rate, the nucleation stage and the homogeneity in depth of the deposited film. Finally, we show that the B-spline parameterization can serve as a stepping stone to physics-based models, such as the Tauc-Lorentz oscillator.

5.1 Introduction

The chemical inertness, low to high nano hardness and thermal and conductive properties of hydrogenated amorphous carbon (a-C:H) thin films allows them to be used in a wide variety of applications, ranging from the microchip industry to protective (e.g. optical windows, magnetic storage disks) and biomedical coatings [32, 143]. Remote plasma deposition is used to deposit, among others, diamond-like carbon (DLC) films with a nano hardness in excess of 13 GPa at high deposition rates (> 10 nm/s), while maintaining good adhesion and chemical stability (see e.g. [42,82,143] and references therein).

In this chapter, remote plasma deposition of hydrogenated amorphous carbon thin films is investigated by in situ spectroscopic ellipsometry. Spectroscopic ellipsometry (SE) is a non-invasive optical diagnostic that can measure the change in polarisation of light reflected on a thin film [104,105,152]. This change in polarisation is determined by the ratio of the Fresnel reflection coefficients for both p- and s-polarised light, commonly expressed as \( \rho = r_p/r_s = \tan \Psi e^{i\Delta} \). Determining the dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) from the measured SE data requires a (multi-layered) model that describes the interaction of the incident light with the film. The dielectric spectrum of an a-C:H film (Fig. 5.1) is characterized by the \( \pi-\pi^* \) electronic transition around 4 eV and the \( \sigma-\sigma^* \) electronic transition around 13 eV\(^1\) [54,69,70]. In SE studies of these films, each transition is commonly modelled by a Tauc-Lorentz (TL) oscillator [68–70]. However, the majority of standard spectroscopic ellipsometers are not capable of reaching 13 eV or above, necessitating the use of complementary diagnostics, e.g. electron energy loss spectroscopy [153,154]. In situ measurements with such complementary diagnostics during film growth is in most cases, such as ours, practically not feasible. Also the (in)homogeneity in depth of the carbon film, which is not always known, needs to be taken into account in the optical model. For all these reasons, it is therefore not always possible to apply a model based on two Tauc-Lorentz oscillators to the measured SE data.

Even when two Tauc-Lorentz oscillators could be used, it is not necessary to apply such a physics based model if only the — evolution in — thickness and roughness (i.e. growth rate and nucleation) and an accurate parameterization of the dielectric function of the thin film are of interest to the experimentalist. The approach in this chapter, therefore, is to obtain a purely mathematical and Kramers-Kronig consistent parameterization of the dielectric function by means of B-splines [119]. Such a parameterization of the deposited carbon layer requires  

\(^1\)For comparison, the \( \pi-\pi^* \) transition in diamond is located at 7 eV and the \( \sigma-\sigma^* \) transition at 11.6 eV, whereas for graphite, this is 4.5 eV and 13-18 eV respectively [69].
5.1. Introduction

Figure 5.1: Wide range $\varepsilon_2$ spectrum for $\alpha$-C:H, as simulated by two TL oscillators. The parameters for the $\pi-\pi^*$ transition are $A_\pi = 19.5$ eV, $\Gamma_\pi = 6.35$ eV, $E_{0,\pi} = 4.55$ eV and $E_{g,\pi} = 0.82$ eV; and for the $\sigma-\sigma^*$ transition: $A_\sigma = 57.2$ eV, $\Gamma_\sigma = 10.1$ eV, $E_{0,\sigma} = 13.9$ eV and $E_{g,\sigma} = 3.37$ eV.
no prior knowledge about the film properties or assumptions about the interaction of light with the film. The optical model for our films consists of a substrate, the bulk of the film itself and a roughness layer, whereby each layer is defined by its own thickness and dielectric constants. While the dielectric function of the bulk layer is represented by B-splines, the roughness is modeled by a Bruggeman’s effective medium approximation (EMA) of 50% bulk material and 50% voids [155]. This layer structure, whereby the bulk carbon material is parameterized by means of B-splines, is hereafter referred to as the B-spline model. An ideal fit between model and data would give a value close to 1 for the unbiased maximum likelihood estimator $\chi^2$. Large deviations from 1 could indicate an incorrect or incomplete model. However, it can also point to the accumulation of very small experimental errors in the obtained data [105]. A model can quickly grow in complexity, while still reducing the overall $\chi^2$ due to an increase in the number of fitting parameters. Therefore, we verify the validity of the layer structure of the B-spline model for our carbon films by complementary experimental techniques, i.e. atomic force microscopy (AFM) and cross-sectional scanning electron microscopy (SEM) measurements. In addition to verifying the layer structure, we will also compare the B-spline parameterization - of an ex situ measurement - with a wavelength-by-wavelength fit.

*In situ* measurements, also analysed by the B-spline model, are used to calculate the deposition rate and to investigate the nucleation of the film. Although other methods - e.g. single wavelength ellipsometry [58] - are available to determine the film thickness during deposition, *in situ* SE and, in particular, the B-spline model have the advantage that the dielectric function can be accurately determined without the need for any assumptions about the film’s interaction with light. This will allow us to establish the (in)homogeneity in depth of the deposited layer. We will also show that the B-spline parameterization of the dielectric function can also serve as a stepping stone to a parameterization with a Tauc-Lorentz oscillator. Finally, the dielectric spectra of the $a$-C:H film in both vacuum and ambient air are tabulated in this chapter by means of B-splines.

## 5.2 Experimental setup

### 5.2.1 Reactor

Hydrogenated amorphous carbon thin films are deposited on a 1 mm thick silicon wafer with a 1.6 nm native oxide layer. The plasma source (Fig. 2.1b) used for deposition is a cascaded arc consisting of a stack of 4 water cooled copper plates with a 4 mm central arc channel [77,78]. A DC-current of 75 A runs from
three tungsten cathodes, through the arc channel, to the anode plate at the end. This current creates an Ar plasma (100 sccs) under high pressure (540 mbar) that expands supersonically into a low pressure reactor (30 Pa). After formation of a shock zone, the plasma continues subsonically towards the substrate holder, located at around 55 cm from the exit of the arc. The substrate temperature is kept at a constant 250°C throughout the 25 to 40 s deposition time, which is controlled by opening and (automatic) closing of the shutter. A He backflow of 1 sccs is used for improved thermal contact between substrate holder and sample [36].

The reactor is equipped with a load lock, a shutter to avoid direct exposure of the sample to the plasma jet and access ports for spectroscopic ellipsometry with a fixed angle of incidence of 68°. During ex situ spectroscopic ellipsometry measurements the angle of incidence is 70°. The precursor, 15 sccs of acetylene (C$_2$H$_2$), is injected through a ring, which is located 5 cm from the exit of the plasma source. The dissociation of the precursor occurs in the expanding plasma jet through charge transfer and dissociative recombination with the Ar$^+$ ions and electrons, respectively. This ion chemistry results in a high radical flux towards the surface, which causes a high deposition rate [42].

### 5.2.2 Spectroscopic ellipsometry

The in situ experiments are performed with a spectroscopic ellipsometer measuring in the visible and near infrared wavelength range (0.75-5.0 eV, J. A. Woollam Co., Inc. M2000U), whereas the deposited samples are characterized ex situ for the visible and ultra-violet wavelength range (1.2-6.5 eV, J. A. Woollam Co., Inc. M2000D). Both ellipsometers are rotating compensator ellipsometers. The data acquisition rate of the ellipsometer is set to 200 rev/measurement for the ex situ measurement, with the high accuracy mode enabled. This indicates that each measurement is the average of 200 revolutions of the compensator. To obtain the highest acquisition rate for the in situ measurements, 1 revolution per measurement without the high accuracy mode is used. The actual number of rev/measurement over which is averaged, depends on the processing power of the computer. Although this number is not included in the data file, it can be determined from the acquisition time between two datapoints [156]. The analysis software is WVASE32 3.668 and CompleteEASE 3.55 and 4.06, from J. A. Woollam Co., Inc.
Layer structure

Each optical model, used for the analysis of SE data, has a layer structure whereby each layer is defined by its own thickness and dielectric constants. A three-tiered layer structure is used for the a-C:H thin films investigated in this chapter. The first layer is a 1 mm thick silicon wafer with a 1.6 nm native oxide layer. The native oxide layer was measured prior to deposition and both thicknesses are fixed in the layer model. This is the substrate on which amorphous carbon, i.e. the second layer, is deposited. The third and last layer is the roughness, which is modeled by Bruggeman’s EMA of 50% bulk material and 50% voids [155]. The (in)homogeneity in depth of the carbon layer is discussed in section 5.3.3. This fairly simple and straightforward layer structure is used for the B-spline model, in which the dielectric function of the carbon layer is parameterized by means of B-splines.

B-splines

Basis-splines, commonly abbreviated to B-splines, are a recursive set of polynomial splines:

\[
B_i^0(x) = \begin{cases} 
1 & t_i \leq x \leq t_{i+1} \\
0 & \text{otherwise}
\end{cases} \quad (5.1a)
\]

\[
B_i^k(x) = \left(\frac{x-t_i}{t_{i+k}-t_i}\right)B_i^{k-1}(x) + \left(\frac{t_{i+k+1}-x}{t_{i+k+1}-t_{i+1}}\right)B_{i+1}^{k-1}(x), \quad (5.1b)
\]

where \(k\) is the degree of the B-spline and \(i\) is the index for the knots \(t_i\) that denote the position, on the x-axis, where the polynomial segments connect [119]. The total spline curve \(S(x)\), representing the dielectric function of the film layer, is then given by

\[
S(x) = \sum_{i=1}^{n} c_i B_i^k(x), \quad (5.2)
\]

with \(c_i\) the B-spline coefficients. \((t_{9+2}, c_i)\) denote the location of the control points of the B-spline curve. If there are \(n\) knots then there are \(n - k - 1\) control points, i.e. the last control point is located at \((t_{n-k+1}, c_{n-k-1})\). CompleteEASE uses cubic B-splines \((k = 3)\). With \(k = 3\), each control point influences only the two previous and the following two polynomial segments\(^2\). This is known as local support [119].

\(^2\)A change in one of the \(c_i\) coefficients affects the next four segments, as can be seen from the recursive formula.
The number of coefficients used to accurately describe the dielectric function should be kept as low as possible, while still adhering to the shape of the function. Although additional coefficients can provide a better description, too large a number leads to an unrealistic result in which only the noise is better described. It also increases the possibility of correlation between the coefficients.

B-splines can be ensured to have a physical meaning because of the following two properties. First, a Kramers-Kronig transform exists of a B-spline curve, i.e. \( \varepsilon_1 \) can be found from a Kramers-Kronig transformation of \( \varepsilon_2 \). This reduces the number of fitting parameters by two and therefore also reduces the probability of correlation between them. Kramers-Kronig consistency requires that \( \varepsilon_2 \) goes smoothly to zero. This is ensured by choosing knots at appropriate locations outside the measured range. These outer knots should, therefore, also be communicated. Second, B-splines have a property known as \textit{convex hull} [119]: if all coefficients \( c_i \) are positive then the total curve is also positive. Since \( \varepsilon_2 \) can never be negative, all \( c_i \)'s should be positive. By enforcing that the B-spline curve is Kramers-Kronig consistent and that all \( c_i \)'s are positive, a physical result for the parametrized dielectric function is ensured. Both conditions are enforced for all the B-spline parametrizations in this work.

The Cauchy model

Hydrogenated amorphous carbon thin films are semi-transparent, as is evident from the interference fringes in the long wavelength region in Fig. 5.2. The transparent part can be fitted by the empirical Cauchy dispersion relation (5.3a) for the refractive index [104, 157]. The Cauchy dispersion relation by itself is not Kramers-Kronig consistent, since \( \varepsilon_2 \) is assumed to be zero. However, absorptions can be accounted for by adding relation (5.3b) to the dispersion relation:

\[
\begin{align*}
n(E) &= A + BE^2 + CE^4 \quad (5.3a) \\
k(E) &= De^{F(E-E_{\text{edge}})} \quad (5.3b)
\end{align*}
\]

with \( A, B, C, D \) and \( F \) the fitting parameters and \( E_{\text{edge}} \) the band edge [104, 157]. Both relations together are hereafter referred to as the Cauchy model. Good estimates for thickness and roughness are found from this model. After determining thickness and roughness from the transparent part of the data, the optical constants for the entire spectrum, including the absorbing part, can be found by an exact direct numerical inversion. This inversion is carried out wavelength-by-wavelength. Due to noise in the experimental data, it is not guaranteed that the dielectric function, resulting from the numerical inversion, is indeed Kramers-Kronig consistent.
Figure 5.2: *Ex situ* measurement of Ψ and Δ as function of energy, which is a common representation of spectroscopic ellipsometry data. A film thickness and surface roughness of respectively 940 nm and 6 nm is derived for this α-C:H film by means of a Cauchy model.
5.2. Experimental setup

Tauc-Lorentz oscillator

Tauc-Lorentz oscillators describe the dielectric function of amorphous materials in terms of physical parameters such as the band structure. The particular parameterization of the dielectric function is derived from the Lorentz model and Tauc’s description of the interband mechanisms [68]. The Lorentz model itself views the material as a collection of non-interacting atoms and approximates the interaction of the applied electric field (from the incident light) with the electrons in the material as a damped mass-spring system between each electron and its nucleus [104]. Mathematically, a Kramers-Kronig consistent parameterization of $\varepsilon_2$ by the Tauc-Lorentz oscillator is given by:

$$
\varepsilon_2 = \begin{cases} 
\frac{AE_0\Gamma(E-E_g)^2}{E[(E^2-E_0^2)^2+\Gamma^2E^2]} & E \geq E_g \\
0 & E < E_g, 
\end{cases}
$$

(5.4)

where $E_g$ is the Tauc gap for amorphous materials and $A = \frac{e^2N_e}{\epsilon_0m_e}$ for the total number of electrons $N_e$ with mass $m_e$, $\epsilon_0$ the dielectric constant in vacuum and elementary charge $e$ [68,104]. The amplitude of the oscillator is $\frac{A}{\Gamma E_0}$, which has its maximum at $E_0$, and $\Gamma$ represents the full width, half maximum.

Pole

In the last part of the experimental results, ex situ data will be analysed by a Tauc-Lorentz oscillator in combination with a pole. This is a Lorentz oscillator without broadening:

$$
\varepsilon_{pole} = \frac{A}{E_{pole}^2 - E^2},
$$

(5.5)

with amplitude $A$ at an energy position $E_{pole}$. The pole, which affects only $\varepsilon_1$ of the dielectric function, takes absorptions outside the measured range (Sec. 5.3.4) into account [157]. Because $A$ and $E_{pole}$ are susceptible to correlation, the global fit option of CompleteEASE is used. A global fit divides the parameter space into a grid of starting values for the fitting procedure. The parameters we used for the global fit itself are 20 iterations for each set of starting values and a limitation of the measured data to 100 datapoints. The set of starting values with the lowest $\chi^2$ is subsequently used for an extensive fit. Compared to the B-spline method, a global fit of a pole is computationally much more demanding and thus takes a longer time to complete. Despite the higher computational requirements of a

\[ A \text{ Tauc-Lorentz oscillator only describes } \varepsilon_2, \varepsilon_1 \text{ is calculated from } \varepsilon_2 \text{ by means of the Kramers-Kronig relations.} \]
pole, it does give a physical representation of absorptions outside the measured range.

### 5.3 Experimental results

The experimental results are elucidated by means of two samples (Table 5.1). Sample A is used for the *ex situ* results in sections 5.3.1, 5.3.2 and 5.3.4. For the second sample, in section 5.3.3, the data is obtained during deposition.

#### 5.3.1 Cauchy model

Ψ and ∆, as shown in Fig. 5.2, are the results of a standard (*ex situ*) SE measurement of our a-C:H thin films. The transparent part of the film, characterized by interference fringes in Ψ and ∆, is dependent on the film thickness. This typically goes up to 2.4 eV for a thickness of around 1100 nm. An EMA layer of 50% bulk material and 50% voids is used for the roughness layer. The Cauchy model indicates that this particular sample has a film thickness and surface roughness of respectively 940 nm and 6 nm. The Cauchy dielectric function is used as a starting point for the B-spline parameterization in the section hereafter.

#### 5.3.2 The dielectric function in ambient air

Before ascertaining the (in)homogeneity in depth of the hydrogenated amorphous carbon thin film as deposited by remote plasma deposition, the dielectric function in ambient air of the carbon film will first be determined. This is entirely possible by means of the B-spline model, which makes no assumptions about the physical properties of the deposited film itself.

---

**Table 5.1:** Sample list.

<table>
<thead>
<tr>
<th>Section</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.1: Cauchy model</td>
<td>A</td>
</tr>
<tr>
<td>5.3.2: The dielectric function in ambient air</td>
<td>A</td>
</tr>
<tr>
<td>5.3.3: Growth rate and homogeneity</td>
<td>B</td>
</tr>
<tr>
<td>5.3.4: Tauc-Lorentz oscillator</td>
<td>A</td>
</tr>
</tbody>
</table>
Table 5.2: B-spline control points for constructing the $\varepsilon_2$ spectrum in ambient air (see also Fig. 5.3).

<table>
<thead>
<tr>
<th>knot position $t_i$ (eV)</th>
<th>B-spline coefficient $c_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.640</td>
<td>n/a</td>
</tr>
<tr>
<td>0.840</td>
<td>n/a</td>
</tr>
<tr>
<td>1.040</td>
<td>0.10434</td>
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<tr>
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<td>0.34326</td>
</tr>
<tr>
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<td>2.08341</td>
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<td>4.397</td>
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<td>5.449</td>
<td>1.90667</td>
</tr>
<tr>
<td>6.501</td>
<td>1.72861</td>
</tr>
<tr>
<td>10.001</td>
<td>2.37493</td>
</tr>
<tr>
<td>20.001</td>
<td>n/a</td>
</tr>
<tr>
<td>21.001</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Throughout the following steps, the roughness layer is included in every fit of the data. Although direct application of the B-spline model is possible, we first apply the Cauchy model to the transparent part of the measured data (Sec. 5.3.1). Optical constants obtained by the Cauchy model are parameterized by B-splines. These B-splines are fitted directly to the experimental data by expanding the data range in steps of $0.5 \text{ eV}$ from the band edge onwards to higher energies. If necessary, the number of nodes can be decreased to smooth out the dielectric function from the previous step. As a last step, Kramers-Kronig consistency of the B-spline parameterization is enforced (Sec. 5.2.2).

The dielectric function, expressed in $\varepsilon_1$ and $\varepsilon_2$, is shown in Fig. 5.3. Since the dielectric function is Kramers-Kronig consistent, only the spline curve for $\varepsilon_2$ is tabulated (Table 5.2). The spline curve of $\varepsilon_2$, for this particular sample, is defined by twelve knots and eight coefficients. Six nodes are equally spaced between 1.24 eV and 6.5 eV and six knots located outside this range at 0.64, 0.84, 1.04, 10, 20 and 21 eV. This means that eight B-spline coefficients are fitted: six for the knots in the measured range and two outside this range at 1.04 and 10 eV. The knots at 10, 20 and 21 eV are used to take into account the absorption outside the measured range. The fit quality ($\chi^2 = 3.2$) is very good as well. Since a B-spline parameterization is a purely mathematical description of the dielectric function,
increasing the number of nodes further will reduce $\chi^2$ even more. However, too many node points will only provide a better description of the noise and increase the — probability of — correlation between the coefficients. When using B-splines, a balance should be found between obtaining a low $\chi^2$ value and the number of nodes used to reach that value. The drop in $\chi^2$ should be significant, compared to the additional number of nodes. Therefore, it is better to provide the absolute minimum number of nodes required to obtain a good fit. In addition to the $\chi^2$ value, the correlation $r$ between the fitting parameters should be taken into account. The correlation between the different parameters for this particular sample is shown in Table 5.3. When the threshold for correlation vs no correlation between various parameter is set to $r = 0.92$, then there is no correlation between thickness, roughness and the b-spline coefficients. The B-spline coefficients that fall well within the measured data range show the lowest correlation values. The outer B-spline coefficients (i.e. outside of the measured range), however, do show higher values for the correlation with the B-spline coefficients at the edge of the data range. This is to be expected, since only a few B-spline coefficients contribute to the spline curve for any given wavelength value and the outer B-spline coefficients have no measured data to be compared against. The B-spline dielectric function in Fig. 5.3 is compared with the dielectric function obtained from the wavelength-by-wavelength fit of Sec. 5.3.1. There is significant overlap between the dielectric function obtained from the wavelength-by-wavelength fit and the B-spline parameterized dielectric function. This overlap between both parameterizations validates the use of the B-spline model for $a$-C:H films.

Together with the dielectric function, spectroscopic ellipsometry yields the film thickness and the roughness. With a roughness layer that is at most 1% of the total thickness, the deposited film can be considered smooth. The roughness obtained via SE is compared with an AFM roughness. An AFM (NT-MDT solver P47 with NSG 10 tips), operating in tapping mode to avoid damage to the sample, scans a $2 \times 2 \mu m^2$ area with a resolution of 512 by 512 points. If all the measured heights follow a normal distribution, then the AFM roughness is defined as the standard deviation $\sigma$ of the height distribution. The AFM and SE roughness are respectively 4.9 nm and 7.6 nm. The proportionality factor between the AFM and SE roughness is 1.55 for this $a$-C:H sample, whereas Kim et al. [61] found a proportionality factor of 2.1. The AFM roughness is in good agreement with the roughness as determined by SE. Cross-sectional SEM (model JEOL 7500FA) measurements (Fig. 5.4) of another sample indicates a thickness comparable with an SE thickness of around 1100 nm on average. With the exception of scattered debris near the edge, which was caused by the cutting process, the SEM image (Fig. 5.5) also shows a uniform, smooth film. The stack of layers visible in the
Figure 5.3: B-spline representation of the dielectric constants $\varepsilon_1$ and $\varepsilon_2$. Twelve knots points are used for $\varepsilon_2$: six equally spaced in the measured range of $1.24 - 6.50$ eV and six outside this range at 0.64, 0.84, 1.04, 10, 20 and 21 eV. This means that eight B-spline coefficients are fitted: six for the knots in the measured range and two outside this range at 1.04 and 10 eV. The dielectric spectrum obtained via a wavelength-by-wavelength fit is also plotted for comparison.
Table 5.3: Correlation values between the thickness, roughness and the eight B-spline coefficients, for a-C:H in ambient air (see also Fig. 5.3).

<table>
<thead>
<tr>
<th>Roughness</th>
<th>Thickness</th>
<th>1.04</th>
<th>0.894</th>
<th>16.0</th>
<th>0.219</th>
<th>0.415</th>
<th>0.194</th>
<th>-0.125</th>
<th>0.072</th>
<th>-0.073</th>
<th>0.473</th>
<th>0.437</th>
<th>10.001</th>
<th>100.0</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.325</td>
<td>60.0</td>
<td>0.142</td>
<td>0.104</td>
<td>0.075</td>
<td>0.263</td>
<td>0.101</td>
<td>10.0</td>
<td>0.056</td>
<td>0.449</td>
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<tr>
<td>0.925</td>
<td>0.219</td>
<td>0.273</td>
<td>0.37</td>
<td>0.132</td>
<td>0.085</td>
<td>0.341</td>
<td>0.167</td>
<td>0.085</td>
<td>0.014</td>
<td>0.072</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.515</td>
<td>0.415</td>
<td>0.194</td>
<td>0.105</td>
<td>0.38</td>
<td>0.334</td>
<td>0.334</td>
<td>0.273</td>
<td>0.472</td>
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<tr>
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<td>0.072</td>
<td>0.325</td>
<td>0.34</td>
<td>0.038</td>
<td>0.38</td>
<td>0.38</td>
<td>0.478</td>
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<tr>
<td>0.056</td>
<td>0.048</td>
<td>0.072</td>
<td>0.084</td>
<td>0.38</td>
<td>0.334</td>
<td>0.478</td>
<td>0.571</td>
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<tr>
<td>0.041</td>
<td>0.014</td>
<td>0.076</td>
<td>0.085</td>
<td>0.132</td>
<td>0.273</td>
<td>0.571</td>
<td>0.525</td>
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<tr>
<td>0.075</td>
<td>0.048</td>
<td>0.056</td>
<td>0.085</td>
<td>0.341</td>
<td>0.334</td>
<td>0.291</td>
<td>0.894</td>
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</tr>
<tr>
<td>0.072</td>
<td>0.048</td>
<td>0.056</td>
<td>0.085</td>
<td>0.38</td>
<td>0.334</td>
<td>0.291</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roughness</td>
<td>Thickness</td>
<td>1.04</td>
<td>1.24</td>
<td>6.55</td>
<td>3.345</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>0.437</td>
<td>0.437</td>
<td>1.24</td>
<td>6.55</td>
<td>3.345</td>
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</tr>
</tbody>
</table>

For a-C:H in ambient air (see also Fig. 5.3).
5.3. Experimental results

Figure 5.4: Cross-sectional SEM image of an $a$-C:H sample, with magnification 75000x. Crack lines, due to breaking the sample, are visible.

cross-section is a validation of the use of our multi-layered model.

5.3.3 Growth rate and homogeneity in depth of the $a$-C:H film

Assuming linear growth, only the deposition time and thickness after deposition are necessary to calculate a growth rate. From *in situ* SE measurements during deposition, however, also the linearity of the growth rate can be investigated. Also the homogeneity in depth of the deposited film is investigated by comparing the dielectric functions for every measured thickness. If the deposited carbon layer is homogeneous, then the dielectric constants should stay the same throughout the deposition process. *In situ* SE data are therefore gathered with the highest time resolution possible (4.8 Hz). By manually shutting down the plasma source after 32 seconds in this experiment, the shutter did not block the light path of the ellipsometer and the measurement could continue after the end of the deposition. The *in situ* data have a different wavelength range compared to the *ex situ* data. Therefore, a different set of knots is used (see Table 5.4 for the knot positions). At the moment, limitations in computing power, necessary to calculate the dielectric function for every datapoint, hinders us from performing real time *in situ* analysis. The *in situ* data is therefore analysed post-deposition. The analysis of this time dependent data occurs stepwise, whereby the dielectric function of
Figure 5.5: Cross-sectional SEM image of an a-C:H sample, with magnification 16000x. The film is uniform and smooth. The large features on the surface is debris from breaking the sample.

the previous datapoint acts as the starting point for the next datapoint. Since the film undergoes nucleation during the initial stages of growth; thickness, roughness and optical constants are correlated during this stage. Therefore, the data is analysed backwards in time. This allows for a good initial determination of the dielectric function.

Fig. 5.6 shows the total thickness evolution, i.e. \( d_{\text{total}} = d + \frac{1}{2} d_{\text{roughness}} \), as function of deposition time. The void fraction is kept constant at 50\%. The growth rate, here defined as the slope of a linear fit of the total thickness, is 35.7 ± 0.1 nm/s. Although the acquisition rate is set to one rev/measurement, the actual data are averaged over 4 rev/measurement [156]. With a growth rate of 35.7 nm/s, the film grows with about 7.5 nm during one acquisition interval.

Also the evolution of the \( \varepsilon_2 \)-spectra is plotted (Fig. 5.7). These spectra are averaged over the entire deposition interval. Since the B-spline coefficients in the first four seconds (i.e. nucleation) are correlated with the thickness and roughness, these coefficients are excluded from the average. The average of the B-spline coefficients for the \( \varepsilon_2 \)-spectra are tabulated in Table 5.4. The deviations in \( \varepsilon_2 \) at energies above 4 eV are attributed to relatively larger measurements errors in \( \Psi \) and \( \Delta \) for this energy range. With the exception of these deviations above 4 eV, \( \varepsilon_2 \) remains constant during deposition. The deposited film is therefore considered
Table 5.4: Average of the B-spline control points of the $\varepsilon_2$ spectrum during deposition (see also Fig. 5.7).

<table>
<thead>
<tr>
<th>knot position $t_i$ (eV)</th>
<th>B-spline coefficient $c_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.152</td>
<td>n/a</td>
</tr>
<tr>
<td>0.352</td>
<td>n/a</td>
</tr>
<tr>
<td>0.552</td>
<td>0.06600</td>
</tr>
<tr>
<td>0.752</td>
<td>0.00101</td>
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<tr>
<td>1.828</td>
<td>0.62602</td>
</tr>
<tr>
<td>2.903</td>
<td>1.87771</td>
</tr>
<tr>
<td>3.979</td>
<td>2.22973</td>
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<tr>
<td>5.054</td>
<td>1.85846</td>
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<td>10.054</td>
<td>1.01714</td>
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<tr>
<td>20.054</td>
<td>n/a</td>
</tr>
<tr>
<td>21.054</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 5.6: Evolution in total thickness (i.e. thickness plus half of the roughness) during deposition. After 32 s, the plasma is stopped.
homogeneous in depth.

Since the deposited $a$-C:H thin film is homogeneous in depth, the dielectric constants — as parameterized by the average B-spline coefficients — can be fixed for every measurement point. Re-fitting the data with fixed dielectric constants yields, for a second time, the evolution in thickness and roughness. The film thickness, averaged over the time interval from 33 to 48 s, is this time about 1.2% higher. The roughness evolution during deposition is shown in Fig. 5.8. In the first three seconds of deposition the roughness reaches a maximum of 4 nm, indicating the nucleation process at the start of the deposition. After nucleation, the roughness stays roughly constant at nearly 2 nm.

5.3.4 Tauc-Lorentz oscillator

The mathematically accurate description of the dielectric function, obtained via the B-spline model, is used as a starting point for the parameterization of the bulk layer by one or more Tauc-Lorentz oscillators. Such a parameterization provides a physical model for the homogeneous carbon bulk layer. Both the SEM and AFM measurements agree well with the layer structure as described for the B-spline model (Sec. 5.3.2). This layer structure is, therefore, reusable in a physics-based
5.3. Experimental results

Figure 5.8: Evolution in roughness during deposition. The inset shows the nucleation of the film. After 32 seconds, the plasma is stopped.

Carbon is a band gap material, with a wide gap between the $\sigma$ valence band and $\sigma^*$ conduction band and a smaller band gap between the valence and conduction bands of $\pi$ and $\pi^*$, respectively [32]. The $\pi-\pi^*$ and $\sigma-\sigma^*$ electronic transition dominate the dielectric function of $a$-C:H (Fig. 5.1). Each transition is commonly modelled by a TL oscillator. Although mixing of the $\pi$ and $\sigma$ bands occurs in the intermediate energy region between 5 eV and 8 eV, the resulting $\pi-\pi^*$ and $\sigma-\sigma^*$ electronic transitions can be neglected [158].

The same sample as in section 5.3.2 is reanalysed. The measurement range of the ex situ data is limited by the equipment to a maximum energy of 6.5 eV, which limits us to a single TL oscillator for the $\pi-\pi^*$ transition. However, absorptions outside the measured range, in particular due to the $\sigma-\sigma^*$ electronic transition, can be partially taken into account by adding a constant offset to $\varepsilon_2(\omega)$. It is obvious from the fit in Fig. 5.9, which has a $\chi^2$ of 12.7, that adding a constant offset to $\varepsilon_1$ is only sufficient up to 4 eV. This can be improved by replacing the offset with a pole, which reduces the $\chi^2$ to 5.8. In both variants of this model, the thickness (933 nm) and roughness (6.7 nm) of the layer were first determined by the B-spline model and subsequently fixed. The dielectric function of the carbon layer, as determined by the B-spline model, is then parameterized by a combina-
Figure 5.9: The bulk carbon layer is modelled by a TL oscillator in combination with an offset $\varepsilon_f$ or a pole to account for absorptions outside the measured range. The fit based on a TL oscillator with a pole starts to deviate around 4 eV.

The bulk carbon layer is modelled by a TL oscillator in combination with an offset $\varepsilon_f$ or a pole to account for absorptions outside the measured range. The fit based on a TL oscillator with a pole starts to deviate around 4 eV.

5.4 Discussion

We have shown that hydrogenated amorphous carbon thin films, as deposited by remote plasma deposition, can be represented by a fairly simple and straightforward set of layers. The first two layers are the substrate itself, consisting of a (semi-infinite) Si wafer of 1 mm thick and a native oxide layer of 1.6 nm. Layer three is the homogenous bulk carbon layer. The fourth and last layer is the rough-
5.4. Discussion

Table 5.5: The dielectric function of an a-C:H thin film is parameterized by a Tauc-Lorentz oscillator, with two variations. In the first variant, the $\sigma - \sigma^*$ transition is represented by an offset. In the second variant, the offset is replaced by a pole. The same sample was also analysed by the B-spline model, which gave a $\chi^2$ of 3.2.

<table>
<thead>
<tr>
<th>parameter</th>
<th>TL + $\varepsilon_\infty$</th>
<th>TL + Pole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2$</td>
<td>12.7</td>
<td>5.8</td>
</tr>
<tr>
<td>$A_\pi$</td>
<td>20.4 eV</td>
<td>21.0 eV</td>
</tr>
<tr>
<td>$\Gamma_\pi$</td>
<td>7.19 eV</td>
<td>6.64 eV</td>
</tr>
<tr>
<td>$E_{0\pi}$</td>
<td>5.08 eV</td>
<td>4.69 eV</td>
</tr>
<tr>
<td>$E_\sigma$</td>
<td>0.780 eV</td>
<td>0.818 eV</td>
</tr>
<tr>
<td>$\varepsilon_\infty$</td>
<td>2.73 eV</td>
<td>n/a</td>
</tr>
<tr>
<td>$A_{pole}$</td>
<td>n/a</td>
<td>195 eV</td>
</tr>
<tr>
<td>$E_{pole}$</td>
<td>n/a</td>
<td>11.0 eV</td>
</tr>
</tbody>
</table>

ness of the film, which is described by a Bruggeman’s effective medium approximation with a mix of 50% voids and 50% bulk material. We have verified this layer structure by cross-sectional SEM and AFM measurements.

The B-spline model, which was instrumental in determining the film thickness and roughness, also provides an excellent method to determine the dielectric function of the carbon film throughout the deposition, although only for post-deposition analysis. The average of the dielectric function shows a tail below 0.7 eV, outside of the measured wavelength range. Although the B-spline parameterization of $\varepsilon_2$ goes smoothly to zero within the measured wavelength range, it accomplishes this at the expense of the wavelengths outside of the measured range. This tail is, therefore, an artifact of the mathematical representation of $\varepsilon_2$. The B-spline parameterization can only accurately represent the available data. Extrapolation to wavelengths outside of the measured range is thus not possible, as illustrated by the tail below 0.7 eV. The evolution of the dielectric function was used to establish the homogeneity in depth of the a-C:H layer. Since the film is homogeneous, the average dielectric constants should be used when determining the thickness evolution during growth. However, the difference in thickness is about 1.2% when the dielectric constants are included in the fit. Fixing the dielectric constants to the average value is, therefore, not necessary to get a good determination of the thickness evolution. Previous studies on the growth of a-C:H under similar deposition conditions on the same setup used infrared in-
terferometry to determine the growth rate [37, 39]. The rate found by Gielen et al. is comparable to what we found by means of \textit{in situ} spectroscopic ellipsometry. Our analysis shows a deposition rate of about 36 nm/s. Even though the integrated thickness during one acquisition interval is 7.5 nm, the \textit{in situ} data acquisition was fast enough to observe the nucleation stage of the film, which lasted no more than 3 seconds. With a roughness layer thinner than than 1% of the total thickness, the film can be considered smooth.

The B-spline model served as a stepping stone for a physics-based model. In this model, the dielectric function is parameterized by means of a Tauc-Lorentz oscillator in combination with either an offset or a pole. Although the TL oscillator with a pole is based on a physical model, it is computationally slower than the mathematical approach via the B-spline model. Moreover, the B-spline model is less susceptible to correlation between the different fitting parameters. Therefore, if only the dielectric spectrum in the measured wavelength range and a fast and accurate thickness determination are of primary concern to the experimentalist, the B-spline model is recommended for hydrogenated amorphous carbon thin films. Application of the B-spline model is, however, not limited to hydrogenated amorphous carbon thin films [119]. The B-spline model is also suitable for \textit{in situ} monitoring the growth of e.g. \textmu c-silicon. The change from \textit{a}-silicon to \textmu c-silicon has a clear distinction in the dielectric function. It is envisaged that in due time, due to the ever increasing CPU computing speed, the B-spline method can be used to monitor real time the changes in the dielectric function of \textit{a-C:H} \textit{in situ}, during deposition or etching.

5.5 Summary

We have shown the versatility of the B-spline model as a tool in the analysis of \textit{a-C:H} thin films. We concluded that the deposited film is smooth and homogeneous in depth. The B-spline model can serve as a stepping stone to more physical models such as the Tauc-Lorentz oscillator. The expanding thermal plasma deposition technique has a high and constant deposition rate. In all, the B-spline model is an accurate and fast method to determine thickness, roughness and dielectric constants of - as has been shown - hydrogenated amorphous carbon thin films, both for \textit{ex situ} and \textit{in situ} measurements.
Chapter 6

Synergistic etch rates during low-energetic plasma etching of hydrogenated amorphous carbon

Abstract

The etch mechanisms of hydrogenated amorphous carbon (a-C:H) thin films in low-energetic (< 2 eV) high flux plasmas is investigated with spectroscopic ellipsometry. The results indicate a synergistic effect for the etch rate between argon ions and atomic hydrogen, even at these extremely low kinetic energies. Ion-assisted chemical sputtering is the primary etch mechanism in both Ar/H₂ and pure H₂ plasmas, although a contribution of swift chemical sputtering to the total etch rate is not excluded. Furthermore, ions determine to a large extent the surface morphology during plasma etching. A high influx of ions enhances the etch rate and limits the surface roughness, whereas a low ion flux promotes graphitization and leads to a large surface roughness (up to 60 nm).
6.1 Introduction

Carbon is widely used as wall material inside existing experimental nuclear fusion reactors. The next generation fusion reactor ITER will likewise use carbon in part of the divertor. Significant erosion of ITER’s divertor wall is expected due to the steady state particle and energy flux of up to $10^{24} \text{m}^{-2}\text{s}^{-1}$ and up to 10 MW m$^{-2}$, respectively [6–8]. This eroded carbon material is then redeposited throughout the reactor in the form of hydrogenated amorphous carbon ($a$-C:H). Such deposits have been found within the divertor, thus close to the carbon source, but also elsewhere inside existing fusion reactors [10,11]. However, the presence of these $a$-C:H layers is not without concern. The primary concern is co-deposition of tritium, a radioactive hydrogen isotope and part of the fuel mixture. This forms a safety issue as well as a fuel inventory problem [11]. ITER will therefore only use a carbon-based divertor wall during the hydrogen and deuterium startup and conditioning phase of the reactor [3,13]. A second issue is performance degradation of the plasma-facing optical components when coated with $a$-C:H [22,23]. In situ low-temperature plasma etching will be part of the maintenance procedure of these components since replacement will not always be immediately possible [22,23]. A third issue is that $a$-C:H lacks the good thermo-nuclear properties of the original carbon wall. How these layers and the wall in general behave under the plasma conditions expected in ITER remains an open question [7]. In particular, plasma etching of carbon with an ion energy in between thermal energy and 10 eV has not yet been fully investigated [14].

Previous studies of carbon etching — with ion energies between 10 eV and 5 keV — have established several etch mechanisms in literature [5,57,64,65,85,96,97,99]. Two of those mechanisms — i.e. chemical sputtering and ion-assisted chemical erosion — describe a synergistic effect in the etch rate when simultaneously exposing $a$-C:H to both radicals and ions (see also section 6.2) [65,97,149]. The ion energy is thereby higher than the binding energy ($\sim 3 – 5$ eV) for the carbon bonds, yet lower than the threshold for physical sputtering ($\sim 32 – 58$ eV). The difference between both mechanisms lies in the role of the the incident ions. These ions either facilitate the thermal desorption of etch products or participate in the etch process by breaking carbon bonds. This chapter investigates whether such a synergistic effect also exists for $a$-C:H thin films exposed to a low-temperature plasma with an ion energy below 2 eV. To that end, experiments have been carried out in a linear plasma reactor with pure argon and hydrogen plasmas as well as mixtures thereof. $a$-C:H thin films deposited with plasma-enhanced chemical vapour deposition are used as a model material [36,43,151]. The incident ion flux is thereby determined via electrical probe measurements,
while radical fluxes are estimated from previous work in our group. Variations in the particle flux between the different plasma systems can then be accounted for when comparing the etch rates of each system.

The etch rates themselves can be determined with a variety of methods such as colorimetry, contact profilometry and ellipsometry [62–66]. In contrast with contact profilometry on graphite, for instance, ellipsometry can be applied in situ on an a-C:H thin film. Single wavelength ellipsometry is widely used in literature to investigate plasma etching [63–65]. Although this method has a high time resolution, the data analysis does not provide a unique solution for the thickness evolution without additional information about the initial thickness. This issue can be circumvented through the use of spectroscopic ellipsometry [104]. Even so, both ellipsometry variants require a multi-layered optical model to describe the a-C:H thin film during etching. Each layer thereby has its own dielectric function and physical parameters such as thickness or roughness. Such a model includes, as a minimum, a substrate layer and the a-C:H as a bulk material layer. Previous studies, furthermore, showed that exposure to a plasma with high ion energy builds up a top layer of a few nanometers [58–60]. Atomic hydrogen can likewise penetrate the first 1 to 2 nm’s of the a-C:H film [159]. This top layer has slightly different material properties than the underlying bulk material. Even though surface material is removed during plasma etching at the expense of this top layer, the underlying bulk material is continuously converted. Or viewed differently, the top layer maintains a semi-constant thickness while the bulk thickness decreases. A last component in the layer model is surface roughness. As a consequence of the plasma exposure, the surface roughness of a-C:H can increase or decrease depending on the etch rate.

In situ spectroscopic ellipsometry is employed in this chapter to investigate the consequences of plasma etching for a-C:H thin films. The optical model used in the data analysis is based on the so-called B-spline model and is described in detail in section 6.3.2 [151]. An important difference with the previously described layer model is the absence of a top layer due to the low ion energy in an expanding thermal plasma. A second difference is that the dielectric function of a-C:H is parameterized by means of B-splines rather than the more commonly used Tauc-Lorentz oscillator [68, 104, 119, 151]. This purely mathematical approach with B-splines provides a fast and easy-to-apply method to determine the etch rate of a-C:H for the different plasma systems. The existence of a synergistic effect in a plasma with very low ion energy will then be ascertained from a comparison of these etch rates. Not only the etch rates, but also the evolution in surface roughness will be discussed for the different plasma systems. One of the more striking results is the extreme roughening of a-C:H in a pure hydro-
gen plasma. This phenomena will be explained via modification of the surface material by low kinetic energy ions.

6.2 Amorphous carbon etch mechanisms

The different etch mechanisms, as mentioned in the introduction, include chemical erosion, ion-assisted chemical erosion, chemical sputtering and swift chemical sputtering (Fig. 6.2). These four etch mechanisms will now be discussed in more detail. The reader is also referred to the review work by W. Jacob [84, 160].

Chemical erosion can occur when an a-C:H sample is exposed to an atomic hydrogen beam [92–94]. An important step in chemical erosion is the conversion of sp$^2$ into sp$^3$ groups through hydrogenation. This will lead in some situations to the formation of a dangling bond (DB). Passivation of such a DB by another incident hydrogen atom results in the formation of a sp$^3$ group (1A to 1C in Fig. 6.2). The DB can alternatively be passivated through the release of volatile CH$_3$ (or more general C$_x$H$_y$) radical groups, which results in a sp$^2$ group (1A to 1C’ in Fig. 6.2). A similar (back) conversion of sp$^3$ into sp$^2$ groups occurs though hydrogen abstraction, with a corresponding release mechanism of volatile hydrocarbon groups. The cross section for hydrogen abstraction is however one order of magnitude smaller than hydrogenation [93]. The result of chemical erosion is thus a net increase in sp$^3$ groups and removal of surface material. The etch rate for sp$^2$ rich films will also be lower than for sp$^2$ poor films, when the film is exposed to a constant flux of radicals [58]. Hydrogen abstraction furthermore is an Eley-Rideal process, in which the reaction proceeds directly without the surface first absorbing and thermalizing the incident H atom [93, 161, 162].

The erosion yield for chemical erosion with H — which is thermally activated — is negligible below 34 meV (400 K) and varies from 0.001 to 0.1 above 34 meV, with a maximum at 52 meV (600 K) [5, 92, 93, 99, 111]. These yields were reported for an atomic H flux of $10^{15}$ to $10^{20}$ m$^{-2}$s$^{-1}$. H$_2$ recombination above 600 K causes the reduction in the yield [6]. The activation energy ($E_a$) for the erosion of a methyl (CH$_3$) group from the carbon network of an a-C:H film falls in the range of 1.6 − 2.5 eV (Fig. 6.1) [58, 92, 93, 160, 163]. Similar values of 1.7 to 1.9 eV are found for graphite etching [6, 164, 165]. Even though this falls below the binding energy of 3.5 eV of a C$_{network}$−CH$_3$ bond, the energy gain from re-hybridization of the carbon network from sp$^3$ to sp$^2$ accounts for the low activation energy [93, 100, 160]. Weakly bonded hydrocarbons — either created after a chemical erosion reaction or (re-) deposited on the a-C:H surface — have an $E_a$ on the order of 0.6 eV for thermal desorption [166, 167]. Breaking the C$_{network}$ − CH$_3$ bond is thus the rate-limiting step in chemical erosion [92].
Figure 6.1: The release of a methyl group from the carbon network, i.e. α-C:H, is thermally activated. Moreover, energy gains from relaxation of the carbon network give rise to a low activation energy with respect to the binding energy. In ion-assisted chemical erosion, this activation energy can be provided for by an ion hitting the surface.
The erosion can moreover be enhanced by simultaneously irradiating the surface with ions \((10^{16} - 10^{24} \text{ m}^{-2}\text{s}^{-1})\) [5, 6, 14, 65, 85, 97, 99, 111, 148, 168]. The kinetic energy of the incident ions is thereby below the threshold for physical sputtering \((32 \text{ eV for H}^+; 58 \text{ eV for Ar}^+)\) [97]. When the ions transfer sufficient kinetic energy for the erosion of a CH\(_3\) (or higher C\(_x\)H\(_y\)) radical group, but do not break any bonds themselves, the process is called ion-assisted chemical erosion [97]. Chemical sputtering is a similar process, in which the incident ions do break carbon bonds within their surface penetration depth [65, 89, 95, 99, 149]. The incident hydrogen radicals immediately passivate the newly formed DB’s, thereby creating hydrocarbon groups that will eventually desorb. The energy required to break C-C and C-H bonds is about \(3 - 5 \text{ eV}\), with the energy of the incident ion at least a few eV’s above that [101]. The erosion yield \((10^{-3} \text{ to } 10^1)\) depends furthermore on the ion energy and incident ion flux and, all else being equal, is higher for a-C:H than for graphite [5, 6, 14, 85, 99, 111, 148, 166, 168].

The fourth and last mechanism explained here is swift chemical sputtering, which first came to light via numerical modelling of very high hydrogen fluxes (up to \(10^{29} \text{ m}^{-2}\text{s}^{-1}\)) incident on an a-C:H surface [87, 132, 169, 170]. An incident hydrogen radical enters the space occupied by a carbon-carbon bond. The nuclei are no longer shielded from each other and the bond will break, resulting in a dangling bond and a newly formed CH bond. This will remove material from the surface if the carbon bond was only the remaining connection to the carbon network of the a-C:H sample. Passivation of the DB occurs again either by another incident hydrogen atom, or through the release of a CH\(_3\) radical group, provided that the DB became part of the carbon network. As the name already suggests, swift chemical sputtering (SCS) is a very fast process that leaves no opportunity to the carbon network to thermalize before the bond is broken. SCS has no inherent temperature-dependent etch rate, although numerical simulations reveal a threshold of \(\sim 1 - 3 \text{ eV}\) [87, 170, 171]. The SCS yield for kinetic energies below 10 eV varies from 0.003 to 0.009 between 300 and 700 K [87, 132]. In this depiction, the incident hydrogen bonds to the eroded material. Salonen et al., however, notes that the hydrogen radical would also sometimes bond to the surface itself [87].

Two etch mechanisms which fall far outside of the experimental conditions of this chapter are radiation enhanced sublimation (> 1300 K substrate temperature) and hydrogen enhanced physical sputtering (150 eV argon ions). Another differentiator besides the ion energy is that the radical flux far exceeds the ion flux in both ion-assisted chemical erosion and chemical sputtering, whereas this situation is reversed in hydrogen enhanced physical sputtering. See e.g. [172, 173] for more details.
6.2. Amorphous carbon etch mechanisms

Figure 6.2: Schematic representation of: (1) chemical erosion, (2) chemical sputtering and (3) swift chemical sputtering.

(1A): a dangling bond (DB) is generated when a H radical breaks a C-C bond. The DB is either (1B) passivated by another H radical or (1B’) forms a new (double) bond with a neighbouring C atom. The end result is either (1C) the conversion of a single into a double bond or (1C’) the release of e.g. a C$_2$H$_3$ radical.

(2A): two DB’s are created when an incident Ar$^+$ ion breaks a C-C bond. (2B): one DB is passivated by an incident H radical, the other DB with a neighbouring C atom. (2C): the formation of a new C-C bond results in the release of e.g. a C$_2$H$_3$ radical. Alternatively, (2B’) both DB’s are passivated by incident H radicals. Thus, (2C’) converting a double into two single bonds.

(3A): a H$^+$ ion enters the space occupied by a C-C bond. (3B): by shielding the C nuclei from each other, the H$^+$ ion breaks the C-C bond and forms a C-H bond. (3C): this results in the release of e.g. a C$_2$H$_3$ radical.


6.3 Hydrogenated amorphous carbon

The properties of hydrogenated amorphous carbon are to a large extent determined by the sp² to sp³ ratio and hydrogen content of the material [32,69]. The variety in sp² to sp³ ratio and hydrogen content leads to several different types of a-C:H, many of which can be deposited by plasma-enhanced chemical vapour deposition (PE-CVD) [32,36,43,151]. PE-CVD is a well known technique in our group and is used in this work as well to prepare a-C:H samples for etching. The deposited carbon material should furthermore be seen as a generic material model for carbon rather than the study of a very specific type of a-C:H. Even so, the (initial) properties of these samples together with the deposition process are described in section 6.3.1. In situ spectroscopic ellipsometry (Sec. 6.3.2) monitors sample properties such as thickness and roughness during plasma etching.

6.3.1 Deposition and characteristics

a-C:H samples are pre-deposited by plasma enhanced chemical vapour deposition on a similar reactor as described in section 6.4 [36, 43, 151]. To deposit these samples, acetylene (15 sccs) is added via an injection ring to an Ar plasma (100 sccs, 75 A, 4.5 kW) at a background pressure of 30 Pa. The substrate temperature is 250 °C, with a backflow of helium (1 sccs) for improved thermal contact. Lastly, a deposition time of 30 seconds results in a film thickness of about 1 µm. The film carrier is a Si wafer with a 1.6 nm native oxide layer.

After deposition, these samples are stored in a desiccator to minimize exposure to the ambient air [174]. Of every deposited sample, a surface area of 200 mm² is exposed to the plasma during the etching experiments discussed in this chapter. Previous studies have characterized these a-C:H samples as graphitic carbon (i.e. a high sp² content) with less than 5% of sp¹ bonds [37,43]. The sp² to sp³ ratio is estimated to be around 0.52 [55]. With a density of $1.7 \times 10^6$ g/m³, an atomic content of 30% hydrogen and 70% carbon, the total number of atoms # in a 1 µm thick film is estimated to be $7 \times 10^{19}$. For a given etch rate $ER$ in nm/min (Sec. 6.3.2) and the total ion and radical flux $\Gamma$ in m⁻²s⁻¹, the yield $Y$ of eroded carbon atoms per incident particle can then be calculated with: $Y = 9.95 \times 10^{17} \times ER/\Gamma$.

6.3.2 In situ spectroscopic ellipsometry

In situ measurements are performed with a rotating compensator ellipsometer measuring in the visible and near infrared wavelength range (0.75 – 5.0 eV, J. A.
6.3. Hydrogenated amorphous carbon

Woollam Co., Inc. M2000U). The analysis software is CompleteEASE 3.55 and 4.06, from J. A. Woollam Co., Inc. The ellipsometer is mounted under an angle of $\sim 68^\circ$. The data acquisition rate of the ellipsometer is typically set to 25 revolutions of the compensator per measurement (r/m) for the plasma mixtures, and 100 r/m for the pure plasmas, with the high accuracy mode enabled. This indicates that each datapoint is averaged over 25 or 100 scans.

Analysis of spectroscopic ellipsometry data requires a (multi-layered) model that describes the interaction of the incident light with — as in our case — a diamond-like carbon thin film. The dielectric function of $a$-C:H is commonly described by one or more Tauc-Lorentz oscillators [68, 104]. However, as demonstrated in chapter 5 on the film growth of these $a$-C:H samples, the use of a purely mathematical description of the dielectric function by means of Basis-splines (B-splines) is also possible [119, 151]. This so-called B-spline model yields the thickness ($d_{\text{bulk}}$), roughness ($d_{\text{roughness}}$) and the dielectric function of the $a$-C:H sample [151]. The void fraction of the roughness layer, which is modeled by a Bruggeman’s effective medium approximation [155], can be included in the fit parameters as well. Even so, fitting both the void fraction of the roughness layer and the dielectric function of the bulk layer causes correlation in the fitting parameters. To avoid this, the void fraction is always fixed at 50% when the substrate temperature changes during plasma exposure.

The B-spline model does not include a thin top layer with its own dielectric function and thickness, even though both hydrogen ions and radicals — when present in the plasma — are known to modify the first few nanometers of the carbon layer in terms of the sp$^2$ to sp$^3$ ratio [58]. However, these changes were reported for very high ion energies (90 – 800 eV) [58–60], whereas the ion energy in an expanding thermal plasma at floating potential is less than a few eV’s (see also section 6.4.1). Moreover, the thickness of such a top layer would be either (much) smaller or comparable in size to the roughness layer of our samples. In addition, because our samples are homogeneous after deposition [151], the dielectric function of this top layer can not be determined beforehand since it has an effective thickness of zero at the onset of plasma treatment. The inclusion of a top layer in the model would, therefore, not yield the preferred results for our purposes. Although there is an apparent contradiction between this modification and excluding a top layer from the model ab initio, the etch rate under our plasma conditions can only be susceptible to the sp$^2$ to sp$^3$ ratio at the exposed surface.

Both growth rates and etch rates of a carbon sample are given by the first order derivative of the total thickness (i.e. $d_{\text{total}} = d_{\text{bulk}} + (1 - f_{\text{void}}) \times d_{\text{roughness}}$) as a function of time. The etch rates discussed in this chapter have also been smoothed by a first order Savitzky-Golay filter, with a window of 10 points wide.
Unless otherwise specified, *etch rate* in this text refers to the overall etch rate for the entire film. Furthermore, the etch rate is proportional to the reaction rate at the surface, provided that the incident particle flux at the surface remains constant. This is the case in these experiments as the plasma conditions are not changed during the entire erosion process of a particular a-C:H sample. The Arrhenius equation moreover applies to the reaction rate when the erosion is thermally activated:

$$k = Ae^{-\frac{E_a}{kT}},$$

(6.1)

with $E_a$ the activation energy, $k$ the Boltzmann constant and $T$ the temperature \([54,58,64,143]\). The pre-exponential factor or frequency factor $A$ includes terms such as the frequency and orientation of the collisions. The activation energy $E_a$ is determined in the standard way from a linear fit of the logarithmic etch rate as function of the inverse temperature.

### 6.4 Experimental setup

The experimental setup in which the hydrogenated amorphous carbon samples are exposed to a plasma is described in section 6.4.1. A capacitive probe, described in section 6.4.2, is used to measure the ion flux at the position of the sample.

#### 6.4.1 Expanding thermal plasma

The experimental setup is a linear plasma reactor with a cascaded arc as plasma source (Fig. 4.11). The arc is operated on a 60 A DC current and has an input power of 2.7 to 9 kW, depending on the gas mixture. It operates under high pressure and generates a thermal plasma which expands into a low pressure vacuum chamber with a background pressure set between 20 and 270 Pa. The substrate is located about 32 cm downstream from the arc. At the exit of the arc, the electron temperature $T_e$ is about 1 to 1.2 eV. This value drops to less than 0.3 eV (typically about 0.1 eV) at the position of the substrate \([78]\). When no external bias is applied on the substrate during plasma etching, the peak of the ion energy distribution (IED) at floating potential is situated around 1 to 2 eV as was previously measured by Kudlacek et al. under similar plasma conditions \([80]\). The arc is in this chapter operated on Ar, H$_2$, D$_2$ or a gas mixture thereof. In previous work in our group, it was determined the dominant ion near the substrate for each gas mixture (see also section 2.2 in the introduction). This is Ar$^+$ and H$_2^+$ (D$_2^+$) for a pure argon and pure hydrogen (deuterium) plasma, respectively \([129,130,133]\).
The dominant ion in case of an Ar/H$_2$ (Ar/D$_2$) plasma depends on the gas mixture. With less than 2 to 3% of H$_2$ (D$_2$), the ion composition consists of Ar$^+$, ArH$^+$ (ArD$^+$) and H$_3^+$ (D$_3^+$) [127, 128, 134]. In gas mixtures with a higher H$_2$ content, that role is again fulfilled by H$_3^+$ [135]. The cascaded arc and plasma expansion itself have been characterized in more detail elsewhere, e.g. [77,78].

Before any plasma is generated, the reactor is pumped down to a minimum base pressure of $5 \times 10^{-5}$ mbar. To minimize water content, the reactor wall is also kept at an elevated temperature of close to 310 K. The reactor is, furthermore, equipped with a shutter that protects a sample from direct exposure to the expanding thermal plasma. Prior to shutter retraction, a pure argon plasma is burned for 3 to 5 minutes to provide additional wall heating for outgassing and to replace, as much as possible, any gaseous impurities by argon. Despite these precautions, the presence of minute traces of hydrogen, oxygen or water in the system can not be excluded.

Furthermore, a backflow of helium (1 sccs) improves thermal contact between the substrate holder and the substrate (i.e. sample holder) itself. Despite active temperature control, an argon plasma will still heat up the substrate in this reactor. The temperature is, therefore, registered by a thermocouple, located a few mm’s to the side of the sample.

### 6.4.2 Capacitive probe

A direct measurement of the ion flux is obtained by operating a planar Langmuir probe as a so-called ion probe (i.e. a capacitive probe) [110, 175]. The design, operating procedure and characterization of an ion probe is described in detail by Petcu et al [110].

Our planar probe is embedded in a sample holder which provides a measurement directly at the position of the sample. The sample holder itself is electrically floating, whereas the collecting area (200 mm$^2$) is connected to a single external capacitor ($12.7 \pm 0.1$ nF).

A pulsed slope-shape waveform signal (Fig. 1 in ref. [110]) with a downward slope from -5 to -10 V (20 V peak to peak) is applied on this capacitor by means of a waveform generator (TTI TG4001). When the correct frequency is used, the bias voltage on the collecting area is constant (-14 V) during the downward slope. This also results in a constant ion energy, which can be controlled through varying the applied voltage. Thus, both the flux and energy of the ions remain constant by applying a sloped, rather than a squared waveform.

The voltage applied during the flux measurements is sufficiently large that only electrons and ions contribute to the charging and discharging, respectively,
of the capacitor (App. 6.A).

The current in the electric circuit \( I_c \) is determined from the time variation in the absolute voltage drop \( |V_{\text{drop}}| \) over the capacitor during the downward slope (eq. 6.2), which is equal to the ion current \( I_{\text{ion}} \) collected by the probe (eq. 6.3).

\[
I_c = C \frac{d|V_{\text{drop}}|}{dt} \tag{6.2}
\]

\[
I_{\text{ion}} = eA\Gamma_{\text{ion}}, \tag{6.3}
\]

with \( \Gamma_{\text{ion}} \) the ion flux, \( e \) the elementary charge and \( A \) the collecting area of the probe. Rewriting both equations yields a direct expression for the ion flux, which is independent of the ion mass:

\[
\Gamma_{\text{ion}} = \frac{C}{eA} \frac{d|V_{\text{drop}}|}{dt} \tag{6.4}
\]

6.5 Experimental results

This section on the experimental results is divided into three parts. The first part concerns the ion and radical flux incident on the \( a \)-C:H sample. The second part deals with the interaction between amorphous carbon and a pure hydrogen plasma, whereas Ar/H\(_2\) and Ar/D\(_2\) plasma mixtures are used in part three.

A newly deposited sample was used for every measurement. The deposition conditions and sample characteristics are mentioned in section 6.3.1. Starting values for the thickness, roughness and dielectric function for the samples discussed in this chapter are determined prior to plasma exposure.

6.5.1 Incident ion and radical flux

The etch rate of \( a \)-C:H depends on the incident particle flux. In this section the ion flux is measured directly at the surface by an ion probe, while estimates for the atomic hydrogen flux are given.

Fig. 6.3 shows the ion and H-flux in a pure hydrogen plasma (50 sccs H\(_2\)) as a function of background pressure. The width of the plasma expansion at low pressures is wider than the collecting area of the ion probe. An increase in background pressure focuses the plasma onto the ion probe, which leads to higher measured fluxes. The plasma chemistry however is dominated by charge transfer and dissociative recombination reactions, which increases in number together with the background pressure. This leads to a reduction in the ion flux. The competition between both effects results in a maximum for the ion flux at 33 Pa,
6.5. Experimental results

Figure 6.3: Ion and radical flux in a pure hydrogen plasma (50 sccs, 60 A). Ion flux measurements are taken with a capacitive probe, at the position of the sample. The highest ion flux can be found at 33 Pa. Radical fluxes are estimated from previous work [109].

as observed in Fig. 6.3. The measurement error with electrical probes is on the order of 10 to 20% [110].

The atomic hydrogen flux ($\Gamma_H$) in Fig. 6.3 is estimated from the density and thermal velocity of atomic H [1]:

$$\Gamma = \frac{n v_{\text{thermal}}}{4} = \frac{n \sqrt{kT/M}}{4},$$

(6.5)

with $T$ the thermal temperature (0.1 eV) and $M$ the hydrogen mass (1 amu). Atomic hydrogen densities have been previously measured in our group for similar plasma conditions [109]. The reported density at 20 Pa is $\sim 2 \times 10^{19}$ m$^{-3}$, which is 5 times lower than the density of $\sim 10^{20}$ m$^{-3}$ at 100 Pa [109]. The H density and thus flux at intermediate pressures are based on a linear extrapolation of these values. Higher background pressures lead to higher radical fluxes, whereas a maximum in the ion flux is observed in the — relatively speaking — low pressure range.

The ion flux has also been measured in pure and mixed argon plasmas for a background pressure of 100 Pa. The ion current in a pure argon plasma (50 sccs Ar) was too high to be measured directly with the ion probe. Ion saturation
Table 6.1: The ion and radical fluxes for different plasma systems. Arc current and background pressure are 60 A and 100 Pa, respectively, for all systems. BG indicates gas injection directly in the background of the reactor.

<table>
<thead>
<tr>
<th>Plasma conditions</th>
<th>Ion flux ( (m^{-2}s^{-1}) )</th>
<th>Radical flux ( (m^{-2}s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 sccs Ar</td>
<td>( 1.4 \times 10^{22} )</td>
<td>n/a</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs H(_2) (BG)</td>
<td>( 1.1 \times 10^{20} )</td>
<td>( 2.3 \times 10^{22} )</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs H(_2) (arc)</td>
<td>( 8.5 \times 10^{19} )</td>
<td>-</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs D(_2) (arc)</td>
<td>( 1.7 \times 10^{20} )</td>
<td>-</td>
</tr>
</tbody>
</table>

current measurements under the same plasma conditions, however, could be obtained with a double Langmuir probe in a similar reactor without substrate (see also Ch. 4). This yields an ion flux of \( 1.4 \times 10^{22} \, m^{-2}s^{-1} \) [176].

The gas flow for the mixed plasma systems consists of 50 sccs Ar and 1 sccs of either H\(_2\) or D\(_2\). H\(_2\) is injected via the arc or directly into the background (BG), whereas D\(_2\) is only injected via the arc. The ion flux in these three systems as measured with the ion probe can be found in Table 6.1. Immediately apparent is the drastic reduction (2 to 3 orders of magnitude) in ion flux when H\(_2\) or D\(_2\) is added to the reactor. Only the radical density in an Ar/H\(_2\):BG plasma was previously measured in our group under these plasma conditions. An atomic H density of \( 2.8 \times 10^{19} \, m^{-3} \) yields a flux of \( 2.2 \times 10^{22} \, m^{-2}s^{-1} \), assuming a thermal temperature of 0.1 eV. This is more than 2 orders of magnitude higher than the ion flux. H and D fluxes for the two remaining systems are expected to have the same order of magnitude. Etch rates for \( a\)-C:H under these plasma conditions are determined in section 6.5.3.

6.5.2 Changes in \( a\)-C:H properties

The results in this section will show the influence of a pure hydrogen plasma (50 sccs, 60 A) on the characteristics of an \( a\)-C:H sample as well as the influence of these evolving characteristics on the etch rate.

First, changes in the sample’s morphology are determined. The background pressure and substrate temperature are set to a constant 46 Pa and 241 ± 1 °C, respectively. The dielectric function is determined beforehand and fixed for every thickness (i.e. every datapoint). The unbiased maximum likelihood estimator \( \chi^2 \)
6.5. Experimental results

— which is a measure of the fit quality [105, 151] — for this particular sample reaches 68. If the void fraction is varied, on the other hand, \( \chi \) drops below 25 as can be seen in Fig. 6.4. Also shown are the time evolution in the thickness, the roughness, the etch rate and the void fraction of the EMA roughness layer during plasma exposure.

During plasma exposure, the roughness increases continuously from 7 to 62 nm. The initial roughness of 7 nm is thereby larger than the as-deposited roughness due to the pre-treatment with an argon plasma. A roughening is also seen in the cross-sectional scanning electron microscopy (SEM; model JEOL 7500FA) images (Fig. 6.5). The first image was taken from an as-deposited sample, whereas the sample in the second image was exposed to a hydrogen plasma. The large surface features is debris as a result from breaking the sample. Also notice the reduction in thickness between those two images. Although a roughness of 60 nm is too large for an AFM to probe [177], AFM measurements do show a change in topography from bump-like structures to more peaked structures (Fig. 6.6). The AFM (NT-MDT solver P47 with NSG 10 tips) is operated in tapping mode to avoid damage to the sample and scans a 2x2 \( \mu m^2 \) area with a resolution of 512x512 points. The RMS roughness of the AFM and SE roughnesses of the as-deposited sample are 4.8 and 7.6 ± 0.1 nm, respectively. These values are 11.8 and 25.0 ± 0.2 nm, respectively, for the etched sample in Fig. 6.6, which had an initial SE roughness of 6.0 ± 0.3 nm. Furthermore, an exponential fit of the autocorrelation function, i.e. the distance beyond which one peak no longer affects another peak, yields an e-folding length of 82.2 ± 1.8 and 69.2 ± 1.5 nm for the as-deposited and etched sample, respectively. This likewise indicates a roughening of the surface.

This change in morphology and the large increase in \( d_{\text{roughness}} \) indicates a preferential etching mechanism, whereby the surface valleys have a locally higher etch rate than the hills of the roughness layer. In contrast with the roughness, which increases as function of time, both the void fraction and the etch rate show a maximum as function of time. The void fraction determined with spectroscopic ellipsometry starts low (31%), but reaches a maximum (77%) rather quickly. Afterwards it decreases smoothly to 61%. The etch rate exhibits similar behaviour, although the maximum of 5.0 nm/min is reached at a later point in time. The etch rate drops more than 40% in the first 60 minutes after this maximum, while the reduction in the void fraction is less than 20% for the same length of time. Since the plasma conditions are not changed while etching, the incident ion and radical flux are assumed constant. If the surface area is furthermore assumed to be a linear function of both \( d_{\text{roughness}} \) and \( f_{\text{void}} \), then it can be stated that the etch rate decreases while the total surface area continues to increase.
Figure 6.4: An α-C:H sample is exposed to a pure hydrogen plasma (50 sccs, 60 A, 46 Pa) at a constant substrate temperature of 241 °C. (a) the fit quality of a B-spline model with variable void fraction, (b) void fraction of the roughness layer, (c) the roughness, (d) thickness and (e) etch rate of the sample.
6.5. Experimental results

Figure 6.5: Cross-sectional SEM images of an $a$-C:H sample (a) as-deposited and (b) after exposure to a pure hydrogen plasma (50 sccs, 60 A, 100 Pa). An increase in roughness and decrease in thickness can clearly be observed.

Figure 6.6: AFM image of an $a$-C:H sample (a) as-deposited and (b) after exposure to a pure hydrogen plasma (50 sccs, 60 A, 100 Pa). The plasma exposure has changed the morphology from bump-like features to more peaked features.
Second, Fig. 6.7 shows the temperature dependent etch rate for two different background pressures: 25 Pa and 100 Pa. This confirms that the erosion is thermally activated and that an activation energy can thus be determined from these measurements [54, 58, 64, 143]. The 100 Pa measurement can be described with an $E_a$ of $0.259 \pm 0.003$ eV over the inverse temperature range from $1.73 \times 10^{-3}$ to $2.54 \times 10^{-3}$ K$^{-1}$, as listed in the first part of Table 6.2. A single activation energy will clearly not suffice for the measurement at 25 Pa and is therefore divided into three intervals. The first interval, which goes from $1.81 \times 10^{-3}$ to $2.54 \times 10^{-3}$ K$^{-1}$, is comparable to the measured temperature range at 100 Pa and yields an $E_a$ of $0.284 \pm 0.005$ eV. The second interval with an $E_a$ of $0.094 \pm 0.005$ eV continues from $2.54 \times 10^{-3}$ K$^{-1}$ and extends up to $2.86 \times 10^{-3}$ K$^{-1}$. The large drop in etch rate, which is covered by a third interval, has an $E_a$ of $0.094 \pm 0.005$ eV. The activation energy will be further discussed in section 6.6.1.

Third, the etch rate at 100 Pa in Fig. 6.7 is 4 to 9 times higher than the etch rate at 25 Pa. Fig. 6.3 on the other hand shows that the ion flux at 100 Pa ($4.41 \times 10^{18}$ m$^{-2}$s$^{-1}$) is less than half of the ion flux at 25 Pa ($1.06 \times 10^{19}$ m$^{-2}$s$^{-1}$), while the atomic H flux increases with a factor of 4 from $\sim 2 \times 10^{22}$ at 25 Pa to $\sim 8 \times 10^{22}$ m$^{-2}$s$^{-1}$ at 100 Pa. This indicates that the incident atomic H flux plays...
Table 6.2: The activation energy for different plasma systems, as determined from Figs. 6.8 and 6.9. The arc current is 60 A for all systems. The background pressure is 100 Pa, unless otherwise specified. The last column shows the temperature range for which the activation energy was fitted. BG indicates gas injection directly in the background of the reactor.

<table>
<thead>
<tr>
<th>Plasma conditions</th>
<th>$E_a$ (eV)</th>
<th>$T^{-1}$ $(10^{-3} K^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 sccs H$_2$, 100 Pa</td>
<td>0.259 ± 0.003</td>
<td>1.73 – 2.54</td>
</tr>
<tr>
<td>50 sccs H$_2$, 25 Pa</td>
<td>0.284 ± 0.005</td>
<td>1.81 – 2.54</td>
</tr>
<tr>
<td>50 sccs H$_2$, 25 Pa</td>
<td>0.094 ± 0.005</td>
<td>2.54 – 2.86</td>
</tr>
<tr>
<td>50 sccs H$_2$, 25 Pa</td>
<td>1.1 ± 0.1</td>
<td>2.92 – 3.00</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs H$_2$ (BG)</td>
<td>0.227 ± 0.002</td>
<td>1.95 – 2.58</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs H$_2$ (arc)</td>
<td>0.265 ± 0.002</td>
<td>1.95 – 2.58</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs D$_2$ (arc)</td>
<td>0.221 ± 0.003</td>
<td>1.95 – 2.58</td>
</tr>
</tbody>
</table>

a dominant role in the erosion process of a-C:H. The yield per total hydrogen flux (i.e. radicals and ions combined) is on the order of $2 \times 10^{-4}$ at the high temperature range (515 K) and $2 \times 10^{-5}$ at the low temperature range (350 K), which are lower than the yields found in literature (Sec. 6.2).

The fourth and last point in this section concerns the ion energy itself. Fig. 6.8 shows the etch rate at 33 Pa, i.e. the highest ion flux according to Fig. 6.3. The substrate temperature during the measurement increases from about 364 to 371 K. This has a negligible effect on the etch rate as can be seen in Fig. 6.4. The ion energy is furthermore controlled by means of the capacitive probe (see also section 6.4.2), onto which an a-C:H sample can be clamped. Such a sample acts as an additional capacitor in the electrical circuit, which can distort the applied waveform signal and thus the bias voltage at the sample’s surface unless the film thickness $d$ is small relative to the Debye length $\lambda_d$:

$$d \ll \varepsilon_r \lambda_d,$$

(6.6)

with $\varepsilon_r$ the dielectric constant of the film [175]. A dielectric constant of 5.2 and a Debye length of 30 $\mu$m — for an electron density and temperature of $6.1 \times 10^{15}$ m$^{-3}$ and 0.1 eV, respectively — gives an upper limit of 156 $\mu$m for the film thickness [151]. The thickness in the measurement presented here decreases from $\sim 980$ to $\sim 870$ nm, thus well below this upper limit. This thickness evolution furthermore translates into a capacitance of $\sim 9$ to $\sim 11$ nF for the a-C:H film.
When the 1.6 nm thin native oxide layer of the Si substrate is considered as well, then the capacitance of the sample exceeds that of the external capacitor. This is a second, although less stringent, requirement for a proper functionality of the ion probe [110, 175]. Regardless, the bias voltage at the $a$-C:H surface can not be measured directly and distortions of the applied pulse shape can therefore not be completely excluded. The bias voltage as measured over the external capacitor is indicated in Fig. 6.8. The manually regulated frequency of the applied waveform signal is 1 to 12 kHz with a duty cycle of 90%.

The etch rate in Fig. 6.8 shows a nearly threefold increase when going from floating potential to a bias voltage of $-9.1$ V. This jump is repeated near the end of the measurement with a doubling of the etch rate. The etch rate in between both jumps steadily decreases together with the bias voltage. The effect of the surface roughness, which increased from about 5 to 26 nm, can however not be excluded as an alternative cause for this decreasing etch rate (Fig. 6.4). Nevertheless, both jumps in etch rate at the beginning and end of the measurement indicate that the ions in our hydrogen plasmas play a role in $a$-C:H etching even though they contribute less than 0.02% to the total incident flux.
6.5.3 Etch rates Ar/H\textsubscript{2} and Ar/D\textsubscript{2} plasmas

Fig. 6.9 shows the etch rate as function of the inverse substrate temperature for Ar/H\textsubscript{2} and Ar/D\textsubscript{2} plasmas. The etch rates are comparable for H\textsubscript{2} and D\textsubscript{2} when these gasses are injected via the arc, which is consistent with the small isotopic effect on the etch yields at low temperatures [5, 93]. Direct injection of H\textsubscript{2} into the reactor systematically lowers the etch rate as can be seen in the graph. This indicates a more efficient hydrogen radical production in the arc than within the reactor. The etch yields themselves are on the order of 10\textsuperscript{−2}.

Previous work in our group by Gielen et al. returned an etch rate of 18 to 60 nm/min for soft and hard a-C:H films [143]. Based on these etch rates and the experimental conditions (100 sccs Ar, 10 sccs H\textsubscript{2}, 48 A arc current) as used by Gielen et al., the Ar\textsuperscript{+} ion flux is expected to be lower than in our case (see also App. 4.A). Gielen et al. furthermore reported an activation energy of about 0.43 eV (1.7 − 1.9 × 10\textsuperscript{−3} K\textsuperscript{−1}) [143]. Activation energies for the three plasma systems in Fig. 6.9 are determined over the inverse temperature range from 1.73 × 10\textsuperscript{−3} up to 2.54 × 10\textsuperscript{−3} K\textsuperscript{−1}. The results — listed in the second part of Table 6.2 — vary from 0.221 ± 0.003 to 0.265 ± 0.002 eV and are much lower than Gielen’s value. A variation in the sample properties, such as the density or sp\textsuperscript{2} to sp\textsuperscript{3} ratio, between ours and Gielen’s work is a probable cause for this difference in activation energy.

The last result shown in this section concerns the roughness evolution during carbon erosion. In contrast with the pure H\textsubscript{2} plasma where a large increase is seen, the roughness in these three mixed systems fluctuates only about 1 nm around the initial value (Fig. 6.10). Larger variations are only observed near the end of the sample’s lifetime, during which the last remnants of the carbon layer are removed. Furthermore, the minima and maxima in the surface roughness coincide for the Ar/H\textsubscript{2} and Ar/D\textsubscript{2} plasmas, but runs out of phase after ∼ 2 minutes for the Ar/H\textsubscript{2}:BG plasma. This delay in the roughness evolution corresponds with the lower etch rate for the Ar/H\textsubscript{2}:BG plasma, relative to the Ar/H\textsubscript{2} and Ar/D\textsubscript{2} plasmas. The roughness evolution for both pure and mixed plasma systems will be further discussed in section 6.6.

6.6 Discussion

The discussion has been divided into two parts. Etch rates as well as ion and radical fluxes are compared for the pure hydrogen and mixed argon plasma systems in part one. A qualitative explanation for the etching mechanisms in these plasma systems are likewise formulated in this part, with the understanding that
Figure 6.9: The etch rate of $\alpha$-C:H in an argon plasma (50 sccs, 60 A, 100 Pa), admixed with 1 sccs of H$_2$ injected via the background (full line), H$_2$ injected via the arc (dashed line) or D$_2$ injected via the arc (dotted line).

the processes and variables involved in plasma-surface interactions are — even if only due to the wide range in properties of amorphous carbon — numerous and intrinsically interconnected [99, 178–180]. The roughness evolution during $\alpha$-C:H etching is discussed in part two of this section.

6.6.1 Etch mechanism

The etch rate of $\alpha$-C:H as well as the incident ion and radical flux in both Ar/H$_2$ and H$_2$ plasmas have been determined in the experimental results for a range of background pressures and substrate temperatures. These plasma systems are compared in Table 6.3 for a substrate temperature of 514 K and a 100 Pa background pressure. The etch rate in a pure argon plasma, which has not been discussed in section 6.5, is given as reference. Table 6.3 shows that the etch rate in an Ar/H$_2$ plasma exceeds the etch rate in both a pure H$_2$ and a pure Ar plasma by an order of magnitude. This also applies to the sum of the etch rates in these pure plasma systems. The ion flux is likewise 1 to 2 orders higher in an Ar/H$_2$ plasma compared to a pure H$_2$ plasma, whereas the atomic H flux decreases by a factor of 3 or more. Even so, the etch rate in an Ar plasma remains low despite the much higher Ar$^+$ ion flux and an absence of atomic H. These results indicate
Figure 6.10: The roughness of three different $a$-C:H samples exposed to an argon plasma (50 sccs, 60 A, 100 Pa), admixed with 1 sccs of: (full line) H$_2$ injected via the background, (dashed line) H$_2$ injected via the arc and (dotted line) D$_2$ injected via the arc. All three samples are completely eroded as indicated by the large variation in roughness that starts around 5 minutes.
Table 6.3: The etch rate and flux for different plasma systems at a substrate temperature of 514K. The arc current and background pressure are 60 A and 100 Pa, respectively, for all systems. BG indicates gas injection directly in the background of the reactor. *H₂ injection through the arc, rather than directly in the reactor, is furthermore expected to yield a higher H flux in an Ar/H₂ plasma.

<table>
<thead>
<tr>
<th>Plasma conditions</th>
<th>Etch rate (nm/min)</th>
<th>Ion flux (m⁻²s⁻¹)</th>
<th>Radical flux (m⁻²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 sccs Ar</td>
<td>~ 7</td>
<td>1.4 × 10²²</td>
<td>n/a</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs H₂ (BG)</td>
<td>~ 198</td>
<td>1.1 × 10²⁰</td>
<td>2.3 × 10²²</td>
</tr>
<tr>
<td>50 sccs Ar, 1 sccs H₂ (arc)*</td>
<td>~ 335</td>
<td>8.5 × 10¹⁹</td>
<td>-</td>
</tr>
<tr>
<td>50 sccs H₂</td>
<td>~ 21</td>
<td>4.4 × 10¹⁸</td>
<td>7.8 × 10²²</td>
</tr>
</tbody>
</table>

a synergistic effect between Ar⁺ ions and atomic H in a-C:H etching. Atomic H, as was previously discussed in section 6.5.2 for a H₂ plasma, plays a dominant role in these expanding thermal plasmas. Section 6.5.2 furthermore showed that hydrogen ions in a pure H₂ plasma do play a role in a-C:H etching, even though in our case they make up less than 0.02% of the total incident flux. To put this in perspective, the ion flux in an Ar/H₂ plasma is about 0.5% of the total flux. This allows for the possibility of a synergistic effect in a pure H₂ plasma as well.

Physical and chemical sputtering can immediately be ruled out as a possible etch mechanism due to the low ion energies involved in these plasmas. The ion energy distribution function at floating potential has a peak around 1 to 2 eV, whereas the C-C and C-H bonds have a binding energy of about 3 – 5 eV [80, 101]. An alternative synergistic etch mechanism is ion-assisted chemical erosion. The yield of 10⁻² determined in section 6.5.3 for an Ar/H₂ plasma is in line with the yields (10⁻³ to 1) found in literature for ion-assisted chemical erosion, thereby considering the variety in ion energies and fluxes [5, 6, 14, 65, 85, 148, 168]. Ion-assisted chemical erosion — but also chemical erosion — in a pure H₂ plasma has however much higher yield values in literature than the 2 × 10⁻⁴ found in this work [5, 6, 14, 85, 92, 93, 111, 148, 168]. Lower yields, thus lower etch rates, can be attributed to changes in surface roughness, composition (i.e. sp² to sp³ ratio) and surface coverage during etching. A decrease in etch rate, associated with an increasing surface roughness, has been established in section 6.5.2. This will be further expanded upon in section 6.6.2.

The activation energy of ~ 0.2 – 0.3 eV in both Ar/H₂ and H₂ plasmas is
likewise lower than previously reported values for both chemical erosion (1.6 – 2.5 eV) and ion-assisted chemical erosion (∼ 0.6 eV) of α-C:H or graphite [58, 92, 93, 160, 163, 166, 167]. As mentioned earlier in section 6.2, the energy gain due to relaxation of the carbon network during the erosion process leads to a reduced activation energy compared to the binding energy [160]. Differences in the initial configuration of the α-C:H-network, i.e. the sample characteristics in terms of the density or sp² to sp³ ratio, can therefore affect the activation energy and etch rate. Changes in the surface roughness or sp² to sp³ ratio during etching can likewise alter the binding network and therefore influence the activation energy [64, 181]. In ion-assisted chemical erosion, the activation energy can be provided — in whole or partially — by the kinetic or recombination energy of the incident ion. It is thus likewise conceivable that the activation energy is affected by the composition of the incident ion flux (Ar⁺ to H⁺ ratio) in addition to the recombination energy and chemical reactivity of each ion species.

It is furthermore entirely possible that a significantly lower activation energy, as determined in this chapter, indicates an alternative or secondary erosion mechanism. A large drop in etch rate can moreover be seen around 350 K in Fig. 6.7, which is expected to occur closer to 400 K if chemical erosion is the only etch mechanism involved. Swift chemical sputtering is a third etch mechanism known to occur for very low ion energies which could explain the observed erosion below 400 K [87, 170, 171]. SCS has however no inherent temperature dependent etch rate and has only been observed in numerical modelling for very high H fluxes (up to 10²⁹ m⁻²s⁻¹) [87]. Whether SCS partakes in these low energetic, high flux hydrogen plasmas is a dispute that requires further microscopic investigation and numerical modelling. Though, such an investigation falls outside the scope of this chapter. The influence, if any, of the ion flux composition on the activation energy can likewise be a point of interest for future experimental work.

### 6.6.2 Surface roughness

Intense ion bombardment of α-C:H in deposition studies have shown a decreasing surface roughness with increasing ion energy up to around 50 eV, after which the surface roughness remained smooth (< 2 nm) up to 10 keV [182–185]. Thermal spikes at the surface caused by low energetic ions promote the surface mobility of existing sp² groups and graphitization of the material [186–188]. Suppression of the sp³ bonding by these low energy Ar⁺ and C⁺ ions is associated with a rough surface [183, 184]. An increased substrate temperature (> 450 K) likewise promotes surface mobility and thus surface roughness [182, 183, 187, 189]. A higher sp² fraction and more interconnected carbon furthermore leads to lower
Synergistic effect during plasma etching

etch rates, even though atomic H preferentially attack sp² over sp³ sites [58,187]. The (initial) sp² content of the material is therefore an important factor in whether additional atomic H etching during (or after) deposition results in either an increase or decrease of the surface roughness. Regardless thereof, the reported surface roughness after deposition (or post-deposition treatment) is on the order of nanometers [94,185,187,190].

A surface roughness of a few nanometers is of the same order as the roughness found in this work during Ar/H₂ (or Ar/D₂) plasma etching. The roughness in a pure H₂ plasma on the other hand increased strongly as established in section 6.5.2. The etch rate moreover decreased once a larger surface roughness was developed. These are surprising results since higher surface exposure and H trapping within the roughness layer should increase the etch rate as well as the roughness roughness [27,177]. The following additional effects have to be taken into account to understand both the etch rate and the roughness.

First, H saturation of the a-C:H surface in a high flux regime decreases the carbon collision cross section [87,101,161,191]. H shielding therefore lowers the etch rate.

Second, graphite is known to have a high surface-recombination probability (up to 80%) for atomic H in the energy regime (0.05 − 0.9 eV) of our etch plasmas [192,193]. Since molecular hydrogen does not etch carbon [194], a similarly high recombination probability for a-C:H would likewise contribute to a decrease in the etch rate. A high surface roughness moreover implies that hydrogen conversion occurs preferentially within the trenches and valleys of the roughness layer. This should however lead to a flattening of the surface roughness or at the very least place a limit on the size of the surface roughness. This effect is a possible explanation for the observed roughness fluctuation of about 1 nm during Ar/H₂ etching, but not for the extreme surface roughness measured during pure H₂ etching.

Third, the etch rate is affected by changes in the material composition. As stated earlier, graphitic (i.e. sp² rich) has a lower etch rate than diamond-like (i.e. sp² poor) amorphous carbon [58]. Local variations in the sp² content as well as the formation of graphitic clusters lead to a roughness development [186,187]. These graphitic clusters act as a capping layer, similar to a-Si patches in c-Si etching (Fig. 6.11) [177]. The incident ions promote graphitization via thermal spikes, but likewise enhance the erosion rate as evident from the synergistic effect in the Ar/H₂ plasmas. The two extremes, as an illustration, are purely graphitization by the low amount of ions in a H₂ plasma and purely an enhanced etch rate by the high ion flux in Ar/H₂ plasmas. A low ion flux incident to the hills and upper parts of the sidewalls of the roughness layer will consequently roughen the
layer, as visualized in Fig. 6.11, whereas a large ion flux will smoothen it. The opening angle — through which ions or radicals can reach the surface — is larger on the hill tops than within the valleys, thereby creating an imbalance in the flux between hills and valleys (Fig. 6.11). H\(^+\) ions have furthermore a reflection coefficient below 0.2 around 1 eV, with a maximum of \(\sim 0.6\) around 5 eV [162]. The atomic H reflection is expected to be higher, up to 0.8 depending on the kinetic energy and angle of incidence [101,195,196]. More radicals than ions, percentage wise, will thus reach the valleys. This strengthens the view that ions primarily affect the hills and upper parts of the sidewalls of the roughness layer. The mechanism described in this last point explains the roughness evolution observed for both H\(_2\) and Ar/H\(_2\) plasmas.

### 6.7 Summary

Hydrogenated amorphous carbon thin films were successfully etched with both ions and neutrals far below the threshold of physical sputtering and even below the required energy to break C-C and C-H bonds (\(\sim 3 – 5\) eV). Moreover, the experimental results indicated a synergistic effect in the etch rate for Ar/H\(_2\) and Ar/D\(_2\) plasmas. Ion-assisted chemical sputtering is the primary etch mechanism
in these low-energetic high flux plasmas. Lower etch yields in pure H$_2$ plasmas are attributed to H shielding of the a-C:H surface. The etch rate at low substrate temperatures furthermore suggests a contribution of swift chemical sputtering. Further studies (on the microscopic level) are however required to resolve this issue. Lastly, thermal spikes at the surface caused by incident ions lead to graphitization and determine to a large extent the surface morphology during plasma etching.

6.A Ion probe

The contribution of the electron current to the total current during the downward slope of the pulse shaped waveform is neglected in the data analysis. This approach is only valid if the bias voltage is sufficiently negative. We will now derive a voltage limit for the validity of this approach.

We start by assuming that the electron and ion density, $n_e$ and $n_i$ respectively, are equal at the interface between the plasma sheath and pre-sheath. We also assume that the flux through the sheath is constant for both ions and electrons. This assumption is valid when the waveform generator applies a sloped pulsed signal, rather than a square pulsed signal.

The electron and ion flux are then given by:

$$\Gamma_e = \frac{1}{4} n_e \bar{v}_e e^{(V_{bias} - V_{plasma})/T_e},$$

(6.7)

and

$$\Gamma_i = n_i u_{bohm}$$

(6.8)

respectively, with $u_{bohm} = \sqrt{e \, \hat{T}_e / m_i}$ the bohm velocity and $\bar{v}_e = \sqrt{8 \, e \, \hat{T}_e / \pi \, m_e}$ the mean electron velocity [1]. $\hat{T}_e$ is the electron temperature in eV, $e$ the elementary charge, $m_i$ the ion mass, $m_e$ the electron mass, $V_{plasma}$ the plasma potential and, lastly, $V_{bias}$ the bias or wall potential.

A more detailed explanation of these steps so far, and Langmuir probe theory in general, is available in chapter 6 of reference [1].

The flux ratio $R$, with $n_e = n_i$, is given by:

$$R = \frac{\Gamma_e}{\Gamma_i} = \sqrt{\frac{m_i}{2\pi m_e}} e^{(V_{bias} - V_{plasma})/T_e}.$$  

(6.9)

Rewriting this expression in terms of the bias voltage yields:

$$V_{bias} = T_e \ln(A) + V_{plasma},$$

(6.10)
with:

\[ A = R \times \sqrt{2 \pi \frac{m_e}{m_i}}. \]  \hspace{1cm} (6.11)

The contribution of the electron current can then be neglected if it is less than 1\% of the ion flux (R = 0.01). With a conservative estimate of 0.5 eV for the electron temperature and 0.5 V for the plasma potential at the position of the substrate, the voltage limits are −3.49 V for H\textsubscript{3}\textsuperscript{+} and −4.15 V for Ar\textsuperscript{+}. The bias voltage, applied during the ion flux measurements in section 6.5.1, was sufficiently negative to neglect the electron current.
Synergistic effect during plasma etching
Conclusions, Implications and Applications

Conclusions

The motivation behind this thesis started with one main question: what are the fundamental erosion mechanisms of hydrogenated amorphous carbon in a low-energetic plasma (0.03 – 10 eV)? This question, first and foremost, led to ion-assisted chemical erosion as the dominant erosion mechanism in both mixed argon - hydrogen and pure hydrogen plasmas. That conclusion, drawn in chapter 6, was motivated by the existence of a synergistic effect between argon ions and hydrogen radicals for the etch rate. The fraction of hydrogen ions, incident to the carbon surface, in a pure H₂ plasma was less than 0.02% of the total flux. By varying the ion kinetic energy up to 10 eV, chapter 6 showed that hydrogen ions nevertheless play a role in the erosion of a-C:H thin films. This forms a second justification for ion-assisted chemical erosion as the dominant erosion mechanism in low-energetic plasmas. Even so, the experimental data at low substrate temperatures did not rule out a contribution of swift chemical sputtering to the overall etch rate. Chapter 6 furthermore showed a correlation between the surface roughness and etch rate. For low etch rates, as in the case of pure argon and pure hydrogen plasmas, the surface roughness increased strongly from a few nanometers to tens of nanometers. For high etch rates, as in the case of mixed argon - hydrogen plasmas, the surface roughness fluctuates on the order of a few nanometers. In both cases, ions incident to the surface play a key role by either enhancing the surface hardness via graphitization (low ion flux) or by enhancing the etch rate (high ion flux).

Determining the evolution in thickness and surface roughness of the hydrogenated amorphous carbon material during erosion were essential in answering the main question of this thesis. Such measurements of the thickness and surface roughness were obtained with in situ spectroscopic ellipsometry, which provided
the dielectric function of the material as well. As stated in the introduction of this thesis, spectroscopic ellipsometry requires a multi-layered model of the material for data analysis. This brings us to chapter 5 in which a model based on B-splines was developed for a-C:H thin films. Chapter 5 furthermore showed that the as-deposited carbon samples are smooth and homogenous-in-depth. This is important to know when interpreting etch rates, since the etch rate of an uniform material is expected to remain constant throughout the erosion process when all else remains equal.

The discussion in chapter 6 about the erosion mechanisms involved a comparison of the etch rates between different plasma systems. In addition to the etch rates, a convincing comparison requires that the ion and radical fluxes incident to the surface are known as well. This requirement was outlined in the secondary objectives in the introduction of this thesis. Values for the atomic hydrogen flux were based on previous work from our group, while the incident ion flux was measured by means of electrical probes (see e.g. Fig. 6.3). Unfortunately, only a limited number of data points for the atomic hydrogen flux was available for the plasma conditions as used in this thesis. Additional atomic hydrogen density measurements were therefore conducted by means of TALIF\(^1\), a laser based diagnostic, to further strengthen the conclusions of chapter 6. Preliminary analysis of the obtained data shows a similar increasing trend of the atomic hydrogen density in the pressure region relevant to this thesis. The final results will be incorporated into the forthcoming paper based on chapter 6.

Although ion flux measurements directly at the surface are in themselves sufficient to discuss the erosion mechanisms, the number of incident ions is mainly determined by the gas flow and plasma conditions within the reactor itself. The ion density in a pure Ar and an Ar/H\(_2\) plasma, both with and without a substrate, was therefore mapped out in chapter 4 in accordance with the secondary objectives of this thesis. These ion density maps (Fig. 4.4) clearly showed the diffusion of H\(_2\) into the plasma expansion as well as the deflection of the plasma by the substrate. Additionally, it turned out that the retraction of the shutter has a lingering effect on the gas flow dynamics which was reflected in the ro-vibrational temperature of the CH molecule. The CH molecules themselves are the result of a charge transfer reaction between argon ions and etched carbon material, followed by dissociative recombination with an electron. Charge transfer and dissociative recombination are the dominant reaction mechanisms in a plasma with low ion and electron kinetic energy. Moreover, the distribution of electronically excited CH radicals throughout the reactor is due to the convolution of the ion density and the hydrocarbon density as substantiated in chapter 4.

\(^1\)Two-photon Absorption Laser Induced Fluorescence
H$_2$ diffusing into the plasma expansion likewise undergoes charge transfer and dissociative recombination. This produces the atomic hydrogen that is — partly — responsible for the carbon erosion. Given the a-C:H sample sizes used in thesis, the resulting carbon content of the plasma is very small compared to the argon and hydrogen density. This situation can be compared to an experimental nuclear fusion reactor which contains traces of carbon impurities due to wall etching. Although argon itself would never be present in a fusion reactor, the use of an argon plasma in this thesis did allow an investigation of the effect of H$_2$ on the chemistry in a plasma with low carbon content. This investigation was embedded in a larger study on the hydrocarbon reconversion in hydrogen rich plasmas with low carbon content; one of the secondary objectives outlined in the introduction.

Previous studies showed that hydrocarbon polymerization occurs when the initial hydrocarbon density exceeds the ion density. When this is not the case, the hydrocarbons are fully dissociated via charge transfer and dissociative recombination reactions. However, the results in chapter 3 indicated that the presence of H$_2$ enhances or even enables hydrocarbon polymerization by reducing the ion density of the expanding thermal plasma. Such a reduction in ion density prevents complete fragmentation — via charge transfer and dissociative recombination — of the hydrocarbon species. H$_2$ can either be added directly to the plasma or be present in the plasma as dissociation products from the hydrocarbons themselves. Furthermore, a synergistic effect between methane (CH$_4$) and acetylene (C$_2$H$_2$) leads to an increased production of the higher hydrocarbons.

**Implications and Applications**

**Extending the lifetime of the reactor wall**

One of the outstanding issues in the development of a nuclear fusion reactor is the design and lifetime of the reactor wall. In **ITER**, the next generation experimental nuclear fusion reactor, steady state ion and energy flux densities of up to $10^{24}$ m$^{-2}$s$^{-1}$ and 5 to 10 MW m$^{-2}$, respectively, are expected at the divertor wall for a plasma pulse duration of 500 s or longer [7,8]. Transient events such as edge localized modes or ELMs can however lead to significantly higher power loads on the wall [197, 198]. These plasma instabilities, which lead to sudden outbursts of energy and particles towards the wall, are due to the semi-periodic buildup of a large pressure gradient [199]. Without mitigation of these ELMs by at least a factor of 30, **ITER**’s reactor wall is not expected to meet the lifetime requirements [198–200]. Part of the mitigation strategy is to induce more frequent but less
severe ELMs. Gas injection near the wall can likewise reduce the power load by increasing radiative losses in the plasma [198]. Additional techniques to extend the lifetime of the divertor wall include optimized wall geometries and wall material choices [201–203]. As mentioned earlier, a correlation between etch rate and surface roughness was shown in this thesis. Applying a rough microstructure to the top layer of a carbon wall could thus in principal extend the lifetime of the wall. The highest surface roughness mentioned in this work goes up to about 60 nm (0.06 µm). However, depending on intensity and duration, the amount of eroded material during a single ELM can be on the order of a ~ 1 µm [197]. In practice, therefore, the effect of micro structuring the carbon surface will most likely be negligible.

**Cleaning of optical components**

The objective for chapter 5, as formulated in the introduction of this thesis, was to find a fast, easy-to-apply and optimal analysis model (for spectroscopic ellipsometry data), independent of the measured wavelength range, to determine the surface morphology and thickness evolution during carbon etching. This was accomplished by means of B-splines which provide a purely mathematical description for the dielectric function of the thin film. Compared to standard physical models, this approach often yields a faster and better result. Particularly so when characteristic peaks in the dielectric function, or significant parts thereof, fall outside of the measured wavelength range. Important to know is that a B-spline model yields no information about the underlying physical properties of the material itself. Nevertheless, this approach remains well suited for applications that require only knowledge about the thickness, surface roughness and dielectric function of the material. One such application is the cleaning of optical components in e.g. lithography devices and experimental nuclear fusion reactors such as ITER [22–25]. Ensuring a high uptime of the apparatuses and, at the same time, an optimal performance of these optical components requires in situ maintenance. Plasma cleaning is one option to remove any impurities from the optical components, yet requires safeguards to prevent damage. In view of this, a control system could connect the plasma source with a real time monitoring system based on spectroscopic ellipsometry and a B-spline analysis algorithm.

**Enhancing the hydrophobicity of a-C:H**

Hydrogenated amorphous carbon is hydrophobic in nature [32, 204]. Surface roughness can moreover enhance the hydrophobicity of the material [61]. Post-deposition plasma treatment with an expanding thermal hydrogen plasma, which
leads to high surface roughness, should in principal further enhance the hydrophobicity of $\alpha$-C:H thin films as well. Whether this will indeed be the case requires further investigation, but this falls outside the scope of this thesis.

**Measuring the H flux via carbon etching**

Direct measurements of the H flux (or density) often involve laser based diagnostics such as TALIF. These type of measurements not only require expensive equipment but can also be quite time consuming to set up. An alternative approach consists of exposing an carbon sample with known material characteristics to the plasma or atomic H source. Based on the etch rate, the H flux can then be estimated. This method has been applied in the past as a calibration tool for an atomic H source [205]. Long term exposure however leads to significant modification of the sample, thereby affecting the etch rate and thus the H flux estimates. In particular, a H$_2$ plasma with relatively low ion density causes a large increase in surface roughness and reduction in etch rate, as was discussed earlier. Caution is therefore required when estimating the flux with this method.

**The effect of plasma perturbations on the CH emission**

Fusion reactors use strong magnetic fields to confine the hot fusion plasma and to keep it away from the main reactor chamber walls. This plasma flows primarily along the magnetic field lines until it eventually reaches the divertor area of the reactor. Once inside the divertor, the plasma cools down and partially recombines into neutral gas. This cold, partially ionized plasma continues along the magnetic field lines towards the divertor wall, thus leading to wall erosion. The divertor is specifically designed to deal with this interaction and to keep the (neutral) gas from flowing back into the main reactor chamber. This gas, which contains unspent and spent fuel as well as eroded wall material, is removed from the reactor via pump ducts located within the divertor area. A plasma confined by a strong magnetic field, as found inside a fusion reactor, can flow freely alongside the magnetic field lines but has only restricted movement in lateral direction. When also the plasma density is high enough, the neutral gas gets dragged along with the plasma. The Magnum-PSI facility — i.e. a linear plasma reactor tasked to investigate the lifetime of wall materials under ITER like plasma conditions — at the FOM-Rijnhuizen institute is therefore equipped with a superconducting coil for magnetizing the plasma and thus to better mimic the conditions found inside a fusion reactor. Furthermore, plasma turbulence and instabilities such as edge localized modes (ELMs) alter the gas flow dynamics in the edge region of the reactor.
This results in larger lateral movement of the plasma with respect to the magnetic field lines. This thesis moreover showed that both substrate and shutter affect the gas flow dynamics inside a linear plasma reactor which, in turn, affected the local plasma chemistry and ro-vibrational CH temperatures. While not comparable in scope or outcome, both the influence of the shutter movement on the CH temperature and recovery from an ELM crash, in terms of plasma stability and confinement, occur on a longer timescale than the event itself [208]. A continuation of this thesis therefore would be an investigation of the gas flow dynamics in a magnetized plasma. Possible research questions include a) if, how and to which extent external disturbances influence the gas flow in a magnetized plasma and b) what are the consequences thereof for the (local) plasma chemistry and ro-vibrational CH temperatures. Such an investigation should also be conducted on the Magnum-PSI facility to better characterize the reactor in terms of the gas flow dynamics and the influence thereof on the erosion studies.
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Oh, and one more thing. This thesis was made on a Mac.
Curriculum Vitae

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