Radiation Generated Plasmas
a challenge in modern lithography

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op woensdag 14 mei 2008 om 16.00 uur

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This research was financially supported by ASML.

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NUR 928
Trefwoorden : plasmafysica / plasma-wand interacties / plasmasimulatie / lithografie / sputteren / foto-ionisatie
Subject headings : plasma physics / plasma-wall interactions / plasma simulation / EUV lithography / sputtering / photoionisation / plasma sheaths

Cover: A collimated beam of EUV radiation is made visible by fluorescence radiation, emitted by excited low-pressure nitrogen gas.
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1

Introduction

1.1 Introduction

This work is aimed at the study of the interaction between a plasma and the optical components of a future generation lithography device for the semiconductor industry.

Plasmas are gases which, for a considerable fraction, consist of charged particles (electrons and ions). As a result, plasmas conduct electricity, and can be manipulated with electromagnetic fields. Of all the visible matter in the universe over 99% is in the plasma state, predominantly in the form of stars and nebulae. On earth, plasma are encountered in natural phenomena such as lightning and fire, but perhaps more importantly, many man-made plasmas nowadays exist. For example, plasmas are used for lighting in the form of discharge lamps and plasma display panels. In the industry, plasma torches are used for cutting and welding. Reactive plasmas play an important role in the computer industry, where they are used for etching and deposition of materials.

Plasmas will also play an important role in future generation lithography tools, which will use extreme ultra-violet (EUV) radiation. Such lithography tools are currently being developed by the ASML company in Veldhoven. For this reason, a joint research project between ASML and the group Elementary Processes in Gas discharges of the Eindhoven University of Technology was started in 2001. This thesis describes part of theoretical and experimental work done within the joint research project to study the effect of a plasma that is generated by EUV radiation inside the lithography tool on the optical components of the apparatus.

This chapter will first provide a general introduction into the field of next generation lithography, and focuses on the challenges in EUV lithography. At the end of the chapter the scope and outline of the remainder of the thesis will be given.

1.2 Moore’s law

Moore’s Law [1] is the empirical observation made in 1965 by Gordon E. Moore that the number of transistors on an integrated circuit for minimum component cost doubles every
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24 months. This observation has held for more than 40 years already. Shrinking the feature size of a transistor has important advantages: smaller transistors can switch faster, use less energy to switch and cost less money per transistor.

Currently, the achievable feature sizes of components of silicon-based integrated circuits are for a large part determined by the resolution of the optical lithography process. In this process, shown in Fig. 1.1, a mask (or reticle) with the desired pattern is illuminated with UV radiation and the pattern is projected and demagnified by an optical system onto a silicon wafer, that has been coated with a photo-sensitive resist layer. In a later process step, the exposed parts of the photoresist can be etched away.

Figure 1.1: Principle of optical lithography.

The resolution of the imaging process is limited by the diffraction of the radiation used for illumination. The smallest line width \( L_w \) that can be achieved with lithography system is written as

\[
L_w = k_1 \frac{\lambda}{NA},
\]

where \( \lambda \) is the wavelength, \( NA \) the numerical aperture (the sine of the maximum allowed opening angle of the projection lens system) seen at the wafer, and \( k_1 \) a constant determined by both the optical system and by the properties of the photoresist material.

Historically, to improve the attainable resolution, optical lithography has seen a shift towards shorter illumination wavelengths. Earlier lithography tools first used the 436 nm and later the 365 nm emission line of a mercury arc lamp. With the development of powerful excimer lasers, the radiation wavelength decreased to the 248 nm krypton fluoride (KrF) laser wavelength. Nowadays, the 193 nm of a argon fluoride (ArF) laser is state-of-the-art. Below this wavelength, radiation is absorbed by the quartz lenses of the optical system and optical lithography with these lenses becomes impossible.

Alternatively, calcium fluoride (CaF2) lenses can be used, which are sufficiently transparent to the 157 nm radiation of a fluorine (F2) laser. However, these lenses are very expensive. Attempts to introduce 157 nm lithography tools have not been commercially successful, as these expensive systems were introduced during an economic downturn. Additionally, it was discovered that the CaF2 lenses show intrinsic birefringence [2]. Smart
optical designs were developed to counter the effect of birefringence at the expense of even more costly optical lens elements.

In recent years, immersion lithography has been introduced to extend the possibilities of current 193 nm systems. In immersion lithography, the usual air gap between the projection lens and the wafer is replaced with a liquid medium that has a refractive index larger than unity. Water, for instance, has a refractive index of 1.44 at the 193 nm wavelength. The refraction when the light exits the lens is reduced because of the higher refractive index of the liquid, as can be seen in Fig. 1.2.

Figure 1.2: Principle of immersion lithography with water between the lens and the wafer instead of air.

With water between the lens and wafer the attainable feature sizes shrink with 30 – 40% [3]. Next generation immersion fluids, with refractive indexes approaching ∼ 1.7, will yield even smaller feature sizes.

The main challenges in immersion lithography are the removal of air bubbles from the fluid, the control of pressure and temperature variations of the fluid, and the elimination of defects created by the interaction between the fluid and the photoresist. The latter include residual water left on the wafer after exposure, and the leaching of resist components into the liquid.

While the 193 nm optical lithography technology is reaching its boundaries, new technologies are being developed to sustain Moore’s Law for the next decades. These include EUV lithography, which uses a wavelength of 13.5 nm, maskless lithography, and nanoimprint lithography. The latter two were added to the International Technology Roadmap for Semiconductors [4] (ITRS) in 2003.

1.2.1 Maskless lithography

In Maskless Lithography (ML), the desired pattern is written onto a resist layer on the wafer with a focussed beam of either electrons or ions (charged particle maskless lithography) or photons (optical maskless lithography). This removes the need for expensive masks. This is especially important for wafers that are not produced in large numbers, such as prototypes, where the mask costs per wafer are relatively high.

The sequential exposure of pixels in maskless lithography implies that ML is a slow process compared to optical lithography, where the entire pattern is illuminated at once. The throughput of maskless lithography is limited to 10 wafers per hour, whereas with optical lithography a throughput of more than 100 wafers per hour can be attained.
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To expose an entire 200 mm wafer with ML, takes typically 10 hours, whereas the throughput of optical lithography is several tens of wafers per hour.

Various ways are being investigated to combine the high throughput of optical lithography with the flexibility and reduction on mask costs of ML systems. For instance, the system developed by IMS Nanofabrication and Vistec Electron Beam, uses a programmable mask in form of a aperture plate system [5] that is illuminated by a parallel electron beam. The silicon aperture plate contains many apertures that divide the electron beam into an array of beamlets. The array of beamlets is scanned over the wafer and the apertures are electronically switched on and off in accordance with the pattern of the desired IC. Similar parallel electron beam systems are being developed by the Dutch MAPPER Lithography company [6], and ADVANTEST Technology in Japan.

1.2.2 Nano-imprint lithography

Nano-Imprint Lithography (NIL) was originally developed by Chou [7] and coworkers at Princeton. Since then, many different forms and systems have been under investigation.

The NIL principle is shown in Fig 1.3. Nano-imprint lithography involves the deposition of a low viscosity monomer on the substrate, and subsequently, lowering a template into the fluid which then flows into the patterns of the template. Following this fill step, the monomer is exposed to UV light to cross-link it and converted into a solid, whereafter the template is removed, leaving the solid pattern on the substrate [8].

The main challenge in NIL is to minimize defects. In contrast to optical lithography, where the desired pattern is demagnified onto the wafer, NIL does not provide such demagnification step. As a result the technique is much more susceptible to defects.

With NIL, structures with feature sizes below 10 nm lower can be obtained. Since multi-level or curved features can be built into the templates, the technology has the capability for three-dimensional printing. The simplicity and the cost effectiveness make NIL a suitable candidate for lithography in the second half of the next decade when feature sizes are expected [4] to reach 10 nm. However, for the near future EUV lithography is expected to be the technology of choice and is expected to be introduced to the lithography market in 2009.

1.3 Extreme ultra-violet lithography

On the continued path towards shorter wavelengths, and therefore smaller feature sizes, efforts are underway to extend optical lithography into the Extreme Ultra-Violet (EUV) region of the spectrum. EUV lithography uses radiation of 13.5 nm in wavelength, a dramatic jump in wavelength from the current 193 nm ArF laser systems.

Traditional lenses are not sufficiently transparent to EUV radiation. Instead, reflective optical elements are employed in the form of multilayer coated mirrors, which will be further discussed in Chapter 2. Because the reflectivity of a multilayer mirror is only 68%, the number of these mirrors in the optical path of a lithography tool cannot be too large. The
mirrors need to be very smooth to control the scattering of radiation [9]. Furthermore, to correct for aberrations the mirrors need to have an aspheric shape, which makes it difficult to meet the stringent demands on surface roughness.

Figure 1.4 shows the optical path of a EUV lithography tool. The EUV radiation is produced by a plasma source, to be further discussed in Chapter 2. The plasma source is situated in the focus point of an ellipsoidal collector mirror. With the collector mirror, a large solid angle of the EUV radiation is captured and collimated into a second focus point.
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(Intermediate Focus). From thereon, the radiation is reflected by a number of multilayer mirrors to produce a beam that is both parallel and uniform in intensity. This beam is used for the illumination of a reflective reticle (mask) containing the desired pattern. Next, the pattern is demagnified four times and imaged onto the wafer by a number of multilayer mirrors that make up the projection lens system. In Fig. 1.5, typical examples of projection lenses are shown for a refractive and reflective system. Clearly, the number of optical elements in a reflective system is much smaller than for a refractive system.

The whole optical path of the EUV tool needs to be enclosed in a vacuum vessel in order to minimize radiation losses due to absorption by the background gas.

The background pressure is determined by the Dynamic Gas Lock (DGL). The DGL consist of an argon shower, positioned just above the wafer. Its purpose is to prevent hydrocarbons, that are released from the photo-resist during illumination of a wafer, from contaminating the optics. As a result the system will have a background argon pressure between $10^{-3}$ and $10^{-2}$ mbar.

The argon background gas will be partially ionized by the EUV radiation. After each EUV pulse, a plasma is formed that recombines on the walls of the EUV tool. The lifetime of the plasma is much shorter than the time between EUV pulses. Still, this radiation driven plasma is potentially dangerous to the multi-layer mirrors. Because the mobility of electrons is much higher than that of the heavy ions, the electrons will reach the mirror surface first and establish a plasma sheath in front of the mirror surface. The potential of the plasma will be positive with respect to the walls. As a result positively charged ions will be accelerated towards the mirror surface. If the ion kinetic energy upon impact is high enough, the mirror will be damaged by sputtering.

1.3.1 EUV masks

The reticle for EUV lithography, see Fig. 1.6 consists of a low-expansion substrate on which a multilayer stack has been coated to provide reflectivity. On top of this stack is a capping layer for environmental protection. A buffer layer and absorber layer are added that define the required pattern. Finally, a resist layer is coated onto the absorber, after which the desired pattern is written with either electron beam lithography or laser exposure. Subsequently, the absorber is etched away until the buffer layer is reached. Finally, after
absorber repair, the buffer layer is etched away. The backside of the reticle is coated with a conductive material so that the reticle can be electrostatically clamped and handled.

![Schematic cross-section of an EUV reticle.](image)

Figure 1.6: Schematic cross-section of an EUV reticle.

One of the critical issues in EUV lithography is the required low defect level. As the feature sizes shrink, smaller mask defects also become more critical. In optical lithography a small, highly transparent membrane is placed over the reticle to provide protection against small (dust) particles that would otherwise fall on the reticle and cause defects. The membrane, called a pellicle, is placed some distance from the reticle, out of the plane of focus. In EUV lithography, such a pellicle can not be used, because it would absorb too much radiation. Instead, removable covers have been developed to protect the reticle during transport and handling. Still, the production of defect free reticles, and the possibility to inspect and repair the mask (if required) at a reasonable cost is considered an important issue in the development of EUV lithography.

1.3.2 Photo-resist

Another challenge in EUV lithography, is the development of an effective EUV photoresist. At the 4th International EUVL Symposium [10], EUV resist was voted the most critical issue for EUV lithography. For high throughput, it is important that the exposure time per wafer is short. For this purpose, the number of photons per unit of surface area required to 'switch' the resist should be low.

Current photo-resists use the principle of chemical amplification [11]. The exposure energy is not directly used to cause a solubility switch. Instead, the exposure energy is used to generate a catalyst (acid), which initiates a chain reaction or promotes a cascade of solubility switching reactions around the exposed spot. In this way, the sensitivity of the resist is chemically amplified.

The size of the switched area is determined by the acid diffusion length. A large acid diffusion length gives high amplification, but at the expense of resolution, i.e. if the acid diffusion length is too large the image will become blurred.

Simultaneously, the sensitivity of the resist has an impact on the line-edge roughness (LER). Increasing the amplification means that the number of photons incident near the edge of a line will decrease. According to Poisson statistics, this will increase the uncer-
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tainty in the number of photons. For EUV photoresists, where the energy per photon is high, the LER is directly influenced by shot noise.

Table 1.1: Requirements for EUV photoresist [4]

<table>
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<th>Parameter</th>
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<tr>
<td>Sensitivity</td>
<td>5 mJ cm$^{-2}$</td>
</tr>
<tr>
<td>Line Edge Roughness [3σ]</td>
<td>1.6 nm</td>
</tr>
<tr>
<td>Resolution</td>
<td>32 nm</td>
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Table 1.1 list the requirements for the EUV photoresist. The main difficulty is to simultaneously satisfy all requirements.

1.4 Scope

The required lifetime of the optical components in future generation EUV lithography tools is specified at 30,000 illumination hours. Because it is not feasible to perform lifetime test of such long duration, fundamental understanding is required of the processes that limit the lifetime.

One of the potential threats to the lifetime of the optical components is the presence of the EUV radiation generated plasma, which is formed by photo-ionization of the background gas in the tool. Ion bombardment can cause damage to the mirrors in the tool through physical sputtering.

The scope of this thesis is to investigate the effect of EUV generated plasmas on the lifetime of the multilayer mirrors both through numerical modeling and experimental methods. The focus of the study will be on the mechanism of sputtering. If possible, solutions will be investigated that reduce the threat of sputtering.

Characterization of the properties of the EUV generated plasma by standard plasma diagnostic methods is difficult as a result of the low density of the charged particles in the plasma in combination with the transient nature of the EUV pulses. This also complicates the numerical modeling, because the plasma will be far from equilibrium. As a result, traditional plasma modeling methods, such as the fluid approach, cannot be used. Instead, a particle model is required, which is computationally demanding.

Each model has a number of parameters which must come from either literature or experimental investigations. In the present work, sputter yield measurements had to be performed at near-threshold energies to provide input for the numerical model. The purpose of the numerical modeling is to give insight into the mechanism of sputtering and to provide predictions, which can be experimentally tested. Therefore, the experimental work focusses on the measurement of the sputter rate of the EUV generated plasma.
1.5 Outline

Chapter 2 is devoted to an introduction into the field of optical components such as grazing incidence mirrors and multilayer coated mirrors, that are encountered in the imaging process at extreme ultra-violet wavelengths. Chapter 3 focusses on the properties of the EUV radiation generated plasma with a theoretical analysis of the generation and decay of the plasma. In Chapter 4, an overview is given of the diagnostics that can be employed to measure the plasma properties such as the density and temperature of the plasma constituents.

In Chapters 5-8, results are presented of numerical simulations, that aim to calculate the rate at which multilayer mirrors are sputtered by the ions of the EUV generated plasma. Chapter 5 starts with an overview of plasma modeling with an emphasis on Particle-In-Cell modeling. The remainder of the chapter provides detailed descriptions of the Particle-In-Cell Monte Carlo model that has been developed to calculate the sputter rate of multilayer mirrors. In Chapter 6, the effect is studied of photo-electron emission from the multilayer mirror on the sputter rate. Besides photo-electrons, the role of doubly charged argon ions is investigated as well. Furthermore, Chapter 7 contains a parameter study of the sputter rate as a function of the background argon pressure and the intensity of the EUV radiation at which the multilayer mirror is illuminated. Finally, in Chapter 8 the effect of the composition of the background gas on the sputter rate is studied. For this purpose, the numerical model has been extended to investigate mixtures of argon and hydrogen gas.

Chapters 9 and 10 are devoted to experimental work. Chapter 9 gives the result of measurements at Argonne National Laboratory, Illinois, that aim to measure the amount of atoms that are removed from the top of the multilayer mirror per incoming argon ion as a function of the kinetic energy of the ion. For this purposed, measurements have been performed with a low-energy ion gun in combination with a sensitive quartz crystal microbalance. Chapter 10 describes experiments performed at the EUV laboratory at ASML. The aim of these experiments is to measure the sputter rate under conditions that are typical for multilayer mirrors in an EUV lithography device. For this purpose, diagnostic methods such as in-situ EUV reflectivity and secondary photo-electron emission measurements, and ex-situ X-ray photo-electron spectroscopy have been employed.

Special precautions have to be taken to reduce the growth rate of thin films of carbon contamination on top of the multilayer mirrors under exposure to EUV radiation.

Finally, in Chapter 11, general conclusions are drawn and recommendations for future work are given, based on the findings in the preceding chapters.

References


Chapter 1: Introduction


Abstract. The strong absorption of EUV radiation by all materials prevents the use of refractive optical components in EUV lithography. Instead, reflective optical elements, such as grazing incidence mirrors and multilayer coated mirrors, must be used for the imaging process.

In this chapter, we will first describe the properties of these mirrors. We will see, that the lifetime of the mirrors is important, as these mirrors are expensive. We conclude with a description of two important mechanisms that potentially threaten the mirror lifetime: sputtering by argon ions from the EUV-induced plasma and carbon contamination.
2.1 Optical elements for EUVL

2.1.1 Transmission and reflectivity at EUV wavelengths

In lithography, optical elements are used to image the desired pattern onto a silicon wafer. An optical lithography tool, hereto contains a large number of lenses. However, for EUV lithography, lenses cannot be used because the transmission of lens materials, or any other solid material for that matter, at EUV wavelengths is very poor. For example, the attenuation length of 13.5 nm radiation through quartz is only 100 nm. The attenuation length $\ell$ is the exponential decay length of the transmission $T$

$$T(x) = \exp \left[ -\frac{x}{\ell} \right].$$

(2.1)

The reason for the poor transmission at EUV wavelengths is that the photon energy exceeds the energy at which outer shell electrons are bound to their atoms. The photon energy couples to the atomic energy levels in processes called photo-excitation and photo-ionization, in which the photon is lost due to absorption.

To understand the reflective and refractive properties of materials at EUV wavelengths we must consider the refractive index, which is sketched in Fig. 2.1 as a function of photon energy. When we go from the visible to the ultra-violet range of the spectrum we scan across the outer shell electronic resonances and the refractive index changes from larger than unity to a value less than unity. If we go further up in photon energy we come across the inner shell electronic resonances. Beyond this, we move into the x-ray region.

![Figure 2.1: A sketch of the real part of the refractive index across the spectrum.](image)

In the EUV wavelength region the refractive index is slightly smaller than unity. Mathematically, the absorption losses of radiation can be taken into account by introducing a complex refractive index

$$\tilde{n} = 1 - \delta - i\beta,$$

(2.2)

where $\delta \ll 1$ represents the strength of atomic scattering and $\beta \ll 1$ is a measure for the strength of photoabsorption processes, which is related to the attenuation length $\ell$
according to

\[ \ell = \frac{\lambda}{4\pi\beta}, \quad (2.3) \]

with \( \lambda \) the radiation wavelength.

In the EUV region lenses cannot be used and mirrors are used instead. The normal incidence reflectivity \( R \) of a perfectly smooth surface, given by the Fresnel equation, may at EUV wavelengths be approximated \([1]\) as

\[ R = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right|^2 \simeq \frac{1}{4}(\delta^2 + \beta^2). \quad (2.4) \]

Table 2.1 lists the value of normal incidence reflectivity at the EUV lithography wavelength for a number of materials. Clearly, the reflectivity is too low for single layer mirrors to be used at normal incidence angles in practical applications.

<table>
<thead>
<tr>
<th>material</th>
<th>( \delta )</th>
<th>( \beta )</th>
<th>reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>0.022</td>
<td>0.011</td>
<td>( 1.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>0.11</td>
<td>0.17</td>
<td>( 3.7 \times 10^{-3} )</td>
</tr>
<tr>
<td>Rhenium</td>
<td>0.078</td>
<td>0.16</td>
<td>( 8.4 \times 10^{-3} )</td>
</tr>
<tr>
<td>Palladium</td>
<td>0.12</td>
<td>0.046</td>
<td>( 5.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>Gold</td>
<td>0.10</td>
<td>0.052</td>
<td>( 3.6 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Historically, two methods have been employed for mirrors as optical elements at EUV wavelengths:

- Grazing incidence mirrors
- Multilayer coated mirrors

### 2.1.2 Grazing incidence mirrors

The reflectivity improves when the angle, as measured from the normal to the plane of incidence, increases. This can be deduced from the Fresnel equations, which for respectively, s and p-polarization read

\[ R_s = \frac{\left| \sin \theta - \sqrt{1 - \tilde{n}^2 \cos^2 \theta} \right|^2}{\sin \theta + \sqrt{1 - \tilde{n}^2 \cos^2 \theta}}, \quad (2.5) \]

\[ R_p = \frac{\tilde{n} \sin \theta - \sqrt{1 - \tilde{n}^2 \cos^2 \theta}}{\tilde{n} \sin \theta + \sqrt{1 - \tilde{n}^2 \cos^2 \theta}}^2, \]
where the grazing angle $\theta$ is measured from the plane of the mirror surface. Because at EUV and X-ray wavelengths, the refractive index is smaller than unity, total external reflection can occur. Whenever the angle of incidence is smaller than the critical angle $\theta_c$, reflectivity goes to unity. To find the critical angle, the square root term in the Fresnel equations must equal zero $\sqrt{1 - \tilde{n}^2 \cos^2 \theta} = 0$. For small angles, the cosine can be approximated by $\cos \theta \approx 1 - \theta^2/2$ and for the refractive index we take $\tilde{n} = 1 - \delta$, ignoring absorption $\beta = 0$, we find

$$\theta_c = \sqrt{2\delta}. \quad (2.6)$$

In practical applications, the reflectivity will not be unity even at angles below the critical angle: Absorption losses, oxidation of the surface material, and surface roughness diminish the reflectivity. Figure 2.2 shows measurement results [2] of the reflectivity at 13.5 nm as a function of the grazing angle for a number of materials that are often used for grazing incidence mirrors in EUV lithography.

![Figure 2.2: Reflectivity at 13.5 nm for ruthenium (triangles), palladium (circles) and gold (squares), as measured by Bergman et. al. [2].](image)

Building a lithography device using only grazing incidence mirrors would be very impractical. Because of the small angles, the numerical aperture of such a tool be too small for practical use, and also the aberrations would be enormous. Instead, specially coated mirrors are used which provide enough reflectivity at normal incidence.

### 2.1.3 Multilayer coated mirrors

The normal incidence reflectivity at EUV wavelengths is only $10^{-4} - 10^{-3}$, where the reflectivity is defined as

$$R = \left| \frac{\hat{E}_{\text{out}}}{\hat{E}_{\text{in}}} \right|^2, \quad (2.7)$$
with $E_{in}$ and $E_{out}$ the electric field amplitudes of, respectively, the incoming and outgoing radiation. This means that the amplitude reflection $\sqrt{R}$ of a single layer is between $1/30$ and $1/100$. Hence, if the reflection of $30 - 100$ layers can be made to add up in phase, a mirror with a reflectivity in the order of unity can be obtained. This is the principle of the multilayer mirror, which has a special coating that consists of a stack of materials having alternately high and low refractive indices. The thickness $d$ of a layer pair, or bi-layer, is chosen in such a way that the path length difference between reflection from successive bi-layers is equal to the radiation wavelength $\lambda$, in accordance with Bragg’s law

$$\lambda = 2d \sin \theta,$$

with $\theta$ the angle of incidence, as shown in Fig. 2.3.

![Figure 2.3: Principle of a multilayer mirror, which consists of a stack of material with alternately high and low refractive index. The total reflectivity is highest when the contributions from each interface add up in phase. For this purpose, the bi-layer thickness $d$, the angle of incidence $\theta$ and the radiation wavelength $\lambda$ must satisfy Bragg’s equation.](image)

In order to optimize the total reflectivity of the stack, the $\Gamma$ parameter, which is the ratio of the thickness of the materials with high refractive index to the thickness of the bi-layer, must be chosen in such a way that absorption losses are at a minimum. In principle, any combination of materials can be used, but for the best result materials must have the right combination of refractive indexes (high contrast, low absorption). Furthermore, it must be possible to apply the materials in thin smooth layers (low roughness). Also, the materials must not intermix (low thermal diffusion) or react with each other (low reactivity).

Two successful material combinations in the EUV region are molybdenum-beryllium, with a peak reflectivity of $\approx 70\%$ at $\lambda = 11.4$ nm, and molybdenum-silicon with a reflectivity of $68\%$ at $13.5$ nm. The development of Mo-Si multilayer mirrors [3] is the most important enabling technology for EUV lithography [4]. Figure 2.4 shows the spectral reflectivity of a Mo-Si multilayer mirror consisting of 50 bi-layers with a period of $d = 6.9$ nm, and a $\Gamma = 0.4$ as calculated with the X-ray interaction with Matter Calculator from the Center for X-Ray Optics [5]. The calculator uses the Fresnel equation to calculate the reflectivity based on atomic scattering factors [6]. Practically, the peak reflectivity of $74\%$
shown in Fig. 2.4 cannot be achieved, because in real life the interfaces between the layers are not perfectly sharp. The highest multilayer reflectivity that can be achieved, mainly limited due to the non-zero interface widths [7], peaks at 69.5%.

Clearly, multilayer mirrors only provide reflectivity in a narrow bandwidth around the central wavelength of 13.5 nm. The transmission of EUV lithography tools, averaged over this narrow bandwidth $\delta\lambda$, is proportional to

$$\frac{\int_{\delta\lambda} \prod_{i=1}^{n} R(\lambda) d\lambda}{\int_{\delta\lambda} d\lambda},$$

with $n$ the number of multilayer mirrors in the optical train of the device. For commercial EUV lithography tools, $n$ can be as high as 10, which means that a small decrease in mirror reflectivity will lead to a substantial transmission loss.

Multilayer coatings are produced with either DC-magnetron sputtering [8, 9] or with electron beam evaporation in combination with low energy ion beam polishing [10]. To achieve the smooth thin layers the silicon substrate on which the Mo-Si layers are applied must be extremely polished to a RMS-roughness of $\sigma \leq 0.1$ nm.

To further improve reflectivity, layers of boron carbide or carbon [9] with a thickness between 0.25 – 0.4 nm are applied between the Mo-Si layers to act as diffusion barriers. This prevents the formation of silicide, which is responsible for the diffuse interfaces in normal Mo-Si stacks [8].

Besides interface barriers, another special layer, called the capping layer, is added on top of the multilayer stack to prevent reflectivity loss due to oxidation of silicon top layer when exposed to air. A large number of candidate materials have been investigated as capping layers both numerically [11] and experimentally [12, 13]. Besides limiting the diffusion of oxygen into the underlying silicon layer, the material must also have high EUV reflectivity, high resistance to oxidation and must not react with the underlying layers. Of these
candidates ruthenium seems to be the one that has received the most attention [14, 15]. From hereon, in our investigation of the effect of EUV-induced plasma on mirror life time we restrict ourselves to ruthenium capping layers. The structure of a multilayer mirror is shown in Fig. 2.5. The thickness of the Ru capping layer is typically only 1.5 nm.

![Cross-section of multilayer coated mirror.](image)

**Figure 2.5:** Cross-section of multilayer coated mirror.

### 2.2 Lifetime of optics

An economically viable lithographic tool must have a lifetime of about 7 years. As the repetition rate of future EUV sources is expected to be around 10 kHz, this means that the tool has to withstand $10^{11}$ EUV pulses. During that time the reflection loss of a multilayer mirror should be smaller than 1%.

Two important mechanisms that contribute to reflection loss are: sputtering by the EUV-induced plasma, and carbon growth.

#### 2.2.1 Carbon growth

It has long been observed that the reflectivity of gratings and mirrors in the monochromators of synchrotrons and vacuum ultra-violet spectrometers decreases over time as a result of the build-up of carbon layers. In 1983 the first systematical investigation into the mechanism of carbon build-up was performed by Boller et al. [16]. Similar carbon layer growth has been observed at EUV wavelengths [17, 18].

Just like any surface in a vacuum setup, the surface of a multilayer mirror will be covered by a monolayer of physisorbed hydrocarbon molecules. In most vacuum setups the physisorbed layer can be partially removed when the walls of the vessel are heated. However, the vacuum system of a EUV lithography tool cannot be baked.

Upon exposure to EUV radiation the hydrocarbons will be partially dissociated, either by the EUV photons (photodissociation), or by the electrons (electron stimulated dissociation) that are emitted from the multilayer mirrors as a result of the photo-electric effect,
Chapter 2: Optics for EUV lithography

as will be discussed in Chapter 10. The radicals thus formed will react with the substrate, providing a fast mechanism for carbon growth.

The carbon layer will decrease the reflectivity of the mirrors. It is estimated [13] that a carbon layer thickness of $\sim 1$ nm corresponds to a relative reflectivity loss of $1.5\%$. Fortunately, the effect is reversible. If the carbon layer is removed, the reflectivity goes back to normal. In Chapter 10 carbon growth and the removal of carbon layers are investigated.

2.2.2 Sputtering

In the previous chapter it was explained that the background gas in the EUV tool contains mainly argon (as a result of the dynamic gas lock, see section 1.3). In the EUV lithography tool, a small amount of the EUV radiation is absorbed by the argon background gas. In this way, unintentionally, a plasma is formed that mainly consists of neutral argon atoms, and a small amount of electrons and positively charged argon ions. The charged particles are removed from the plasma when they hit the optical components and other plasma boundaries. Because electrons travel much faster than ions, they will reach the walls first, which creates a charge imbalance in the near vicinity of the walls. In this way an electric field is generated, that accelerates ions towards the walls. If accelerated to high enough velocities, the argon ions from the radiation driven plasma will damage the mirrors by sputtering.

In this thesis we aim to investigate, both experimentally and numerically, the rate at which the EUV-induced plasma sputters the multilayer mirrors.

In Chapter 3 the properties of the EUV-induced plasma are investigated analytically, and in Chapter 4 a summary is given of diagnostic methods to measure these properties.

Because of the low density and the transient nature of the EUV-induced plasma, analytical investigation of the plasma can only carry so far. Therefore, Chapters 5-8 are devoted to the numerical investigation of the sputtering mechanism with a Particle-In Cell Monte Carlo model.

For this model, information is required on the sputter yield, which is the amount of material removed from the mirror per incoming argon ion as a function of the ion impact energy. For this purpose, measurements with a low-energy argon gun have been performed at the Argonne National Laboratory, which is operated by the University of Chicago. Results will be given in Chapter 9.

Finally, Chapter 10 is devoted to the measurement of the sputter rate which a experimental setup at the ASML EUV laboratory.

Bibliography

2.2 Bibliography


Chapter 2: Optics for EUV lithography


Abstract. The extreme ultra-violet radiation used for EUV lithography is generated by a plasma source, but as the EUV radiation travels through the optical column of the lithography tool it creates a secondary plasma through photo-ionization of the background gas. This radiation-generated plasma interacts with the optical components of the EUV lithography tool.

In this chapter, the properties of the EUV-induced plasma are investigated by means of analytical methods. Given the EUV irradiation and the background pressure, the electron density can be calculated from the photo-ionization cross-section. From an estimate of the electron temperature, characteristic time and length scales of the EUV-induced plasma can be derived. Finally, the sputtering mechanism is explained.
Chapter 3: EUV-induced Plasmas

3.1 Introduction: Formation of the EUV-induced plasma

The EUV radiation used for EUV lithography is generated by a pulsed plasma source, which produces a hot, high-density plasma that emits EUV radiation in all directions. A large fraction of the EUV radiation is reflected off the collector optic, and is subsequently transmitted through the imaging system of the tool. As the EUV radiation travels through the optical column of the lithography tool, a fraction of the radiation is absorbed by the low-pressure background gas in the tool. In this way, unintentionally, a secondary plasma is created through photo-ionization of the background gas. This radiation-generated plasma interacts with the optical components of the EUV lithography tool.

In this chapter, the properties of the EUV-induced plasma are investigated by means of analytical methods. After a short introduction on EUV sources, the photo-ionization process will be considered. Given the EUV irradiation and the background pressure, the electron density can be calculated from the photo-ionization cross-section. From an estimate of the electron temperature, characteristic time and length scales of the EUV-induced plasma can be derived. Finally, the sputtering mechanism is explained.

3.2 EUV generation

Although EUV radiation can be generated in the laboratory in several ways [1], only plasma sources are considered economically viable candidates to meet the required specifications [2] for EUV lithography, which are listed in Table 3.1. The main challenge is to build sources that can deliver sufficient output power in a 2% bandwidth around the central wavelength of 13.5 nm, so-called in-band EUV. This bandwidth is determined by the full-width half-maximum of the reflectivity curve of the Mo/Si multilayer coated mirrors, see Fig. 2.4.

Plasma sources [3] can be divided into two groups: laser produced plasmas (LPP’s) and gas discharge produced plasmas (DPP’s).

LPP’s are generated by focussing a high-intensity laser onto a target material. The laser energy is absorbed and a hot, dense plasma is created that emits EUV radiation.

DPP’s usually consist of two electrodes, which are connected to a high-voltage battery of capacitors. After ignition, the magnetic field generated by the high current (few kA) leads to a contraction of the plasma, the so-called pinch effect, as a result of which the density of the plasma increases sufficiently to cause emission of EUV radiation.

The conversion efficiency of electrical power into in-band EUV radiation in a \(2\pi\) solid angle of a current DPP source is in the order of \(2-3\%\). In order to attain 115 Watt in-band EUV radiation at the intermediate focus, approximately 50 kWatt of electrical input power is required, which is mainly transferred into heat and is deposited onto the solid materials around the plasma. It is a major challenge to design sources with enough cooling capacity to remove all this heat.

Initially, xenon fueled DPP’s have been the main focus of research, since the Xe XI ion stage emits at 13.5 nm, and because Xe is inert and therefore does not produce chemically active debris, which might contaminate the lithography tool. Because of strong absorption
Table 3.1: Source requirements for EUVL high-volume manufacturing tools as expressed by features at the IF (Intermediate Focus).

<table>
<thead>
<tr>
<th>Source Characteristic</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>13.5 nm</td>
</tr>
<tr>
<td>In-band EUV power at IF</td>
<td>&gt; 115 Watt</td>
</tr>
<tr>
<td>Source cleanliness at IF</td>
<td>≤ 30,000 hours</td>
</tr>
<tr>
<td>Repetition frequency</td>
<td>≥ 6000 Hz</td>
</tr>
<tr>
<td>Etendue</td>
<td>≤ 3.3 mm²sr</td>
</tr>
<tr>
<td>Energy stability</td>
<td>±0.3%, 3σ over 50 pulses</td>
</tr>
</tbody>
</table>

of neutral and low ion stages at 13.5 nm the conversion efficiency of Xe is limited [4].

The last three years has shown the attention shift towards tin-fueled discharge sources, because the conversion efficiency for tin is 2 – 3 times higher than for xenon. In Sn, the transitions occur in a range of adjacent ion stages that overlap to produce an unresolved transition array centered at 13.5 nm radiation. The downside of using tin based sources is that, besides EUV radiation, a lot of debris is produced in the form of small tin droplets, and highly energetic ions and atoms. For a DPP, it is estimated that ~ 1 kg of tin debris is produced per billion EUV pulses [5]. For comparison, 1 nm of tin deposited on top of a multilayer mirror accounts for ≈ 6% relative EUV reflectivity loss [6]. Additional measures need to be taken to prevent the debris from reaching the optical surfaces of the lithography tool.

At the moment, LPP sources are considered the most viable option for EUV lithography. The main advantage of LPP’s, beside the fact that there are no electrodes that wear out with time, is that the efficiency at which laser power is converted into EUV emitting plasma is relatively high, so that the heat load to the target region can be relatively low. In principle, the required output power of the source is easily achievable by simply adding more lasers modules, but the main challenge will be to do this in a cost-effective way. Furthermore, the extra conversion step required to generate the laser power makes the power consumption of LPP plasmas much higher compared to DPP’s.

In the ASML EUV laboratory, two types of DPP sources are available; a Xe-fueled, hollow cathode triggered discharge source and a laser-triggered discharge in tin vapor. In the past, extensive investigations of the EUV plasma produced by both these sources have been undertaken by Kieft [7]. For the experimental investigations described in this thesis, the Xe fueled source was used. This source produces EUV pulses with a duration of typically 100 ns at a repetition frequency between 1 Hz and 1 kHz.
3.3 Photo-ionization

Most laboratory plasmas use an electric field to supply the input power to the plasma. Electrons are accelerated in the electric field and generate a plasma by electron-impact ionization, i.e. the electrons gain enough kinetic energy in the electric field to knock more electrons free when colliding with neutral atoms, creating ions in the process. In turn, these electrons and ions are accelerated by the electric field and through collisions with other particles create more charged particles.

In our case, rather than by an electric field, the input power to the plasma is supplied by radiation. Radiation with a photon energy higher than the ionization threshold of the background gas, in our case argon, will be partially absorbed due to a process called photo-ionization, in which the photon is absorbed by the atom and an electron is ejected from the atom, leaving behind a positively charged ion

\[
hν + Ar \rightarrow e^- + Ar^+.
\] (3.1)

The energy of EUV radiation with a wavelength of 13.5 nm corresponds to a photon energy equal to \(hν \approx 92\text{ eV}\), which well exceeds the ionization potential of argon \(E_{\text{ion}} \approx 15.8\text{ eV}\). Of course, in the photo-ionization process, energy must be conserved. An energy amount \(E_{\text{ion}}\) is used to free the electron from the atom. The excess energy \(hν - E_{\text{ion}}\) is transferred into kinetic energy of the electron \(Γ_e\) and ion \(Γ_i\)

\[
hν - E_{\text{ion}} = Γ_e + Γ_i = |p_e|^2/2m_e + |p_i|^2/2m_i,
\] (3.2)

with \(p_e\) and \(p_i\) the momenta and \(m_e\) and \(m_i\) the masses of, respectively, the electron and ion. Because momentum also needs to be conserved, the extra momenta gained by the electron \(p_e\) and ion \(p_i\) in the photo-ionization process must add up to the momentum of the photon \(ℏk\), with \(k\) the wave vector of the photon \(|k| = 2πν/c\), where \(c\) is the speed of light. Thus the following equality must hold

\[
p_e + p_i = ℏk \approx 0.
\] (3.3)

In fact, the momentum of the photon is so small compared to the momenta of the other particles that it may well be neglected.

Because the electron mass \(m_e\) is much lower (\(≈ 7.3 \times 10^4\) times) than the Ar ion mass \(m_i\), the excess energy will not be equally divided between the particles. As it turns out almost all the excess energy of the photo-ionization process (a fraction \(m_i(m_e + m_e)^{-1}\) is transferred to the electron. The remaining energy \(m_e(m_e + m_i)^{-1}(hν - E_{\text{ion}})\) is transferred to the ion. This amount is so small that it is negligible compared to the thermal energy \(k_B T \approx 0.03\text{ eV}\) of an argon atom at room temperature. Therefore, we can conclude that the EUV-induced plasma upon creation through the photo-ionization process, consists of fast electrons, which have received an energy of \(hν - E_{\text{ion}} \approx 76\text{ eV}\), and a much slower argon ions, which moves with the thermal energy of the initial argon atoms.
3.3 Photo-ionization

3.3.1 Multiple photo-ionization

Until now, we have considered the single photo-ionization process. In this process, only one electron is stripped from the argon atom, which has a $1s^22s^22p^63s^23p^6$ electron configuration. From the electron binding energies [8] for the argon atom, listed in Table 3.2, it can be deduced that the EUV radiation is not energetic enough to remove electrons from the inner $K$ or $L$-shells of the argon atom.

![Table 3.2: Binding energies for the argon electron shells](image)

Table 3.2: Binding energies for the argon electron shells

<table>
<thead>
<tr>
<th>Shell</th>
<th>electron</th>
<th>Binding energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>$1s$</td>
<td>3205.9</td>
</tr>
<tr>
<td>$L_I$</td>
<td>$2s$</td>
<td>326.3</td>
</tr>
<tr>
<td>$L_{II}$</td>
<td>$2p_{1/2}$</td>
<td>250.6</td>
</tr>
<tr>
<td>$L_{III}$</td>
<td>$2p_{3/2}$</td>
<td>248.4</td>
</tr>
<tr>
<td>$M_I$</td>
<td>$3s$</td>
<td>29.3</td>
</tr>
<tr>
<td>$M_{II}$</td>
<td>$3p_{1/2}$</td>
<td>15.9</td>
</tr>
<tr>
<td>$M_{III}$</td>
<td>$3p_{3/2}$</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Table 3.3: Threshold energies for multiple photo-ionization of argon

<table>
<thead>
<tr>
<th>Ionization stage</th>
<th>ion</th>
<th>threshold energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>single</td>
<td>$Ar^+$</td>
<td>15.76</td>
</tr>
<tr>
<td>double</td>
<td>$Ar^{2+}$</td>
<td>43.39</td>
</tr>
<tr>
<td>triple</td>
<td>$Ar^{3+}$</td>
<td>84.30</td>
</tr>
<tr>
<td>quadruple</td>
<td>$Ar^{4+}$</td>
<td>144.11</td>
</tr>
</tbody>
</table>

However, the photon energy of 92 eV is high enough to remove two or three outer electrons from the atom. In fact, besides single photo-ionization, also double and triple photo-ionization of argon will occur,

$$h\nu + Ar \rightarrow 2e^- + Ar^{2+},$$

$$h\nu + Ar \rightarrow 3e^- + Ar^{3+},$$

as can be derived from the threshold energies [9] for multiple photo-ionization of argon, which are listed in Table 3.3.
In Fig. 3.1, cross-sections for the three photo-ionization processes are given. The threshold energy for the double photo-ionization process is $43.4 \text{ eV}$ [11], whereas the triple photo-ionization process has a threshold energy of $84.3 \text{ eV}$ [12]. At the relevant EUV photon energy the cross-section for double photo-ionization is 5 times lower and the triple photo-ionization cross-section is about 500 times lower than the single photo-ionization cross-section. This means that initially the plasma mainly consist of $\text{Ar}^+$ ions, with a fraction ($\approx 20\%$) of $\text{Ar}^{2+}$ ions and a negligible amount of $\text{Ar}^{3+}$ ions.

### 3.4 Spectrum EUV source

EUV lithography devices are aimed at operating in a 2% bandwidth around the central wavelength of 13.5nm. This narrow bandwidth is dictated by the reflective properties of the Mo/Si multilayer coated mirrors, as has been discussed in section 2.1. However, only a fraction of the radiative power that is produced by the sources used for EUV lithography will be in this narrow bandwidth. Figure 3.2(a) shows the spectrum of the xenon fueled hollow cathode triggered discharge that is used in the ASML EUV-laboratory, as measured with a EUV spectrometer by Kieft [13]. Clearly, the source not only radiates in the narrow EUV lithography band, but over the complete vacuum ultra-violet region of the spectrum.

This has important consequences for the properties of the EUV-induced plasma close to the source, because radiation in the entire region of the spectrum will be partially absorbed by the argon background gas.

The transmission $T(E)$ of a gas as a function of photon energy $E$ is given by

$$T(E) = \exp[-Ln \sigma(E)], \quad (3.5)$$
where \( L \) is the length of the beam path, \( n_a \) the neutral number density of the background gas, and \( \sigma(E) \) the total cross-section for photo-absorption. In Fig. 3.2(c), \( \sigma(E) \) is plotted for argon [14] [6]. Figure 3.2(b) shows the fraction of absorbed energy as a function of photon energy at \( L = 10 \) cm distance from the source. We assume that \( n_a = 10^{19} \) m\(^{-3} \), which is a realistic value for the argon density directly behind the source.

Two conclusions can be drawn from Fig. 3.2(b). Firstly, the fraction of absorbed energy is very low (\( \approx 10^{-7} \) \(- 10^{-4} \)) over the complete range of the spectrum. Therefore, the EUV-induced plasma will be optically thin at all relevant wavelengths.

Secondly, the EUV-induced plasma directly behind the source, e.g. near the collector mirror (Fig. 1.4), will be generated mostly by radiation with a photon energy between 16 – 30 eV. As a result, the electrons that are generated in the photo-ionization process by relatively soft photons will also be much less energetic than those generated further down the optical path, where there are mainly 92 eV photons due to the spectral properties of the multilayer coated mirrors. As will be shown in Chapter 5, the energy at which ions impact on the mirror is determined by the average energy of the electrons and the damage to the mirror per ion is significantly reduced at lower impact energy. Although the ion density will be higher near the collector mirror, the damage as a result of the EUV-induced plasma can be expected to be much less for collector mirrors than for multilayer mirrors.

### 3.5 Plasma properties

At the EUV radiation wavelength of 13.5 nm the plasma is optically thin, because the absorption length \( \ell = (n_a\sigma)^{-1} \) is in the range of 40 – 400 m (for a background argon pressure between 0.1 and 1 Pa), which is much larger than the size of the plasma. Therefore, the initial plasma electron density \( n_e \) can be estimated given the EUV irradiation \( I_{\text{pulse}} \) (radiation energy per pulse per unit of area)

\[
n_e = \frac{I_{\text{pulse}}[1 - \exp(-Ln_a\sigma)]}{h\nu L} \approx \frac{I_{\text{pulse}}n_a\sigma}{h\nu},
\]

with the approximation \( [1 - \exp(-Ln_a\sigma)] \approx Ln_a\sigma \), because the plasma is optically thin \( (Ln_a\sigma \ll 1) \). Substitution of a realistic value for the ASML EUV source as used in experiment of \( I_{\text{pulse}} = 0.6 \) Joule m\(^{-2} \) gives \( n_e = 7 \times 10^{14} \) m\(^{-3} \).

The peak plasma electron density can be up to three times higher, because after photo-ionization, the liberated electron can have up to 76 eV of kinetic energy, which is enough to cause additional ionization by electron-impact ionization

\[
e^- + Ar \rightarrow 2e^- + Ar^+.
\]

The density is much lower than the density of most laboratory plasmas, and also the ionization degree \( \alpha \), defined as

\[
\alpha = \frac{n_e}{n_a + n_e} \approx 10^{-5},
\]

where \( n_e \) is the number density of electrons, \( n_a \) is the number density of neutral atoms, and \( \alpha \) is the ionization degree. The plasma is optically thin at all relevant wavelengths, and the initial plasma electron density can be estimated given the EUV irradiation \( I_{\text{pulse}} \). Substitution of a realistic value for the ASML EUV source as used in experiment of \( I_{\text{pulse}} = 0.6 \) Joule m\(^{-2} \) gives \( n_e = 7 \times 10^{14} \) m\(^{-3} \).
Figure 3.2: (a) Spectrum for the Philips EUV hollow cathode triggered discharge as obtained by Kieft [13]. (b) Spectrum of the energy absorbed by $L = 0.1$ m of argon for a density $n = 10^{19}$ m$^{-3}$. For this calculation, (c) the CXRO-data for the photo-absorption cross-section of argon, is used.
3.5 Plasma properties

is very low. To determine whether we can still speak of a plasma, can be checked by the following criteria:

1. Charged particles must interact with many other charged particles simultaneously, or mathematically formulated: the number \(N_D\) of electrons contained in a Debye sphere, (a sphere with the radius of a Debye length) must be larger than unity. That is

\[
N_D = \frac{4\pi n_e \lambda_D^3}{3} \gg 1.
\]

The Debye screening length \(\lambda_D\) is the characteristic length scale over which charge-imbalance can occur in a plasma

\[
\lambda_D = \sqrt{\frac{\epsilon_0 k_B T_e}{n_e e^2}},
\]

with \(k_B\) the Boltzmann constant, \(T_e\) the electron temperature \(^1\), \(\epsilon_0\) the permittivity of free space, and \(e\) the electron charge. For \(n_e = 10^{15} \text{ m}^{-3}\) and \(T_e = 10\text{ eV}\), we find \(\lambda_D \approx 7 \times 10^{-4}\text{ m}\) and \(N_D \approx 2 \times 10^6\).

2. The plasma must have a well defined bulk region where the plasma is quasi-neutral, i.e. the electron density is equal to the average ion density \((n_e \approx n_i)\). In other words, the size of the plasma boundary region, estimated by the Debye length, must be smaller than the size \(L\) of the plasma

\[
\lambda_D \ll L.
\]

In our laboratory, the plasma density of \(10^{15} \text{ m}^{-3}\) can only be obtained by focussing an EUV beam into a small, cylindrically shaped region \((L = 20\text{ mm in the axial direction and } L = 2\text{ mm in the radial direction})\).

3. The plasma electrons must adjust their positions rapidly enough to shield charges. Therefore, the time scale \(\tau_p\) associated with oscillations of the electrons in the electric field of the ions, equal to the inverse of the plasma frequency \(f_p\), must be shorter than the time scale \(\tau_{ea}\) of electron-neutral collisions, which is the inverse of the electron-neutral collision frequency \(\nu_{ea}\)

\[
f_p \gg \nu_{ea},
\]

with

\[
\tau_p^{-1} = f_p = \frac{1}{2\pi} \sqrt{\frac{n_e e^2}{m_e \epsilon_0}}, \quad \text{and} \quad \tau_{ea}^{-1} = \nu_{ea} = n_e \sigma_{ea} \sqrt{\frac{k_B T_e}{m_e}}.
\]

Table 3.4 lists the relevant time and length scales for the EUV-induced plasma, where it is estimated that \(n_e = 10^{15} \text{ m}^{-3}\) and \(T_e = 10\text{ eV}\). Clearly, all three criteria are satisfied, and it can be concluded that the EUV-induced plasma is truly a plasma.

\(^1\)Strictly speaking, the concept of a electron temperature can only be applied when the plasma electrons are in thermal equilibrium. Because of the low electron density and the transient nature of the EUV radiation generated plasma, no such equilibrium exists. In this chapter, we loosely apply the term electron temperature (multiplied by \(k_B\)) to denote the average electron energy in the plasma.
Table 3.4: Length and times scales of the EUV-induced plasma for $n_e = 10^{15} \text{ m}^{-3}$ and $T_e = 10$ eV. For the calculation of the electron-neutral collision frequency, a value of $\sigma_{ea} = 6 \times 10^{-20} \text{ m}^2$ for the cross-section for electron-neutral collisions for Ar is used, which is valid for an electron energy between $1 - 50$ eV [15].

<table>
<thead>
<tr>
<th>Scale</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>Plasma Size</td>
<td>$10^{-3} - 10^{-2}$ m</td>
</tr>
<tr>
<td>$\lambda_D$</td>
<td>Debye length</td>
<td>$7 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>$\ell$</td>
<td>EUV attenuation length</td>
<td>200 m</td>
</tr>
<tr>
<td>$\tau_{EUV}$</td>
<td>EUV pulse duration</td>
<td>$10^{-7}$ s</td>
</tr>
<tr>
<td>$f_{rep}^{-1}$</td>
<td>Time between pulses</td>
<td>$10^{-3} - 10^{-1}$ s</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>Inverse plasma frequency</td>
<td>$4 \times 10^{-9}$ s</td>
</tr>
<tr>
<td>$\tau_{ea}$</td>
<td>Electron-neutral collision time</td>
<td>$7 \times 10^{-8}$ s</td>
</tr>
</tbody>
</table>

3.6 Decay of the plasma

After the EUV pulse the plasma diffuses to the walls where it recombines. The lifetime of the plasma is much shorter than the time between the pulses, which is in the order of $10^{-3} - 10^{-1}$ s. Three-body recombination can be neglected as the density is too low. The time scale for three-body recombination $\tau_{tbr}$ can be estimated from

$$\tau_{tbr} = (k_{rec} n_e^2)^{-1} \approx 10^8 \text{s},$$

(3.14)

with $k_{rec} \approx 10^{-38}$ m$^6$s$^{-1}$ the recombination rate. The weakly ionized low density plasma will be far from equilibrium. Initially the 'temperature' of the electrons $T_e$ will be very high, whereas the ions will remain at room temperature $T_i$. The ambipolar diffusion time $\tau_{amb} = L^2 / D_a$ can be calculated from the ambipolar diffusion coefficient $D_a$ given by [16]

$$D_a = \frac{2}{3 n_a \sigma_{ia}} \sqrt{\frac{k_B T_i}{\pi m_i} \left(1 + \frac{T_e}{T_i}\right)},$$

(3.15)

with $\sigma_{ia}$ the ion-neutral momentum transfer cross-section. For $T_e = 10$ eV, $T_i = 0.03$ eV, $L = 0.05$ m, and $n_a = 10^{20}$ m$^{-3}$ we get $\sigma_{ia} \approx 10^{-18}$ m$^2$ s$^{-1}$ [17], $D_a \approx 4 \times 10^2$ m$^2$s$^{-1}$ and an ambipolar diffusion time $\tau_{amb} = 7 \times 10^{-6}$ s. This is clearly much smaller than the time between pulses. Actually, it is questionable whether we can actually speak of ambipolar diffusion, because the ion mean free path $\lambda_{ia} = (n_a \sigma_{ia})^{-1} \approx 0.01$ m is of the same order of magnitude as the dimensions of the plasma. The transport in the plasma is somewhere in the transition between being diffusion dominated and the Knudsen regime.

Strictly speaking, these formulae only apply to plasmas with a Maxwellian electron energy distribution function (EEDF), which is certainly not applicable during the EUV-pulse. The EEDF will relax towards a Maxwell distribution as a result of collisions between
3.7 Plasma sheath

electrons. The electron collision time $\tau_{ee}$ can be estimated by [18]

$$\tau_{ee} = \frac{6\sqrt{2} \pi^{\frac{3}{2}} e_0^2 \sqrt{m_e (k_B T_e)^{\frac{3}{2}}}}{e^4 n_e \ln \Lambda},$$

(3.16)

with $m_e$ the electron mass, $n_e$ the electron density, $\epsilon_0$ the permittivity of free space, $k_B$ the Boltzmann constant and $\Lambda$ the Coulomb parameter given by

$$\Lambda = \frac{12\pi \epsilon_0 (k_B T_e)^{\frac{3}{2}}}{\sqrt{n_e e^3}}.$$  

(3.17)

Inserting $T_e = 10$ eV and $n_e = 10^{15}$ m$^{-3}$ yields $\tau_{ee} \approx 8 \times 10^{-3}$ s, which is much longer than the diffusion time. Before the electron gas gets a chance to thermalize, the plasma has already recombined at the walls.

Resuming, we may state that the plasma will decay in $\approx 10^{-5}$ s; a time that is much smaller than the period between the EUV pulses. This decay is due to recombination at the walls. Due to the low $n_e$ value the electrons do not have time to thermalize.

3.7 Plasma sheath

When the plasma is created the plasma is quasi-neutral, i.e. the electron density $n_e$ is equal to the average ion density $n_i$. Upon creation, the electrons will have much higher velocities $\approx 5 \times 10^6$ m s$^{-1}$ than the ions in the plasma, which will move at the thermal velocity of the neutral argon $\approx 350$ m s$^{-1}$. Therefore, the electrons will reach the walls (and will be removed from the plasma) before the ions can. This creates a charge-imbalance in the plasma near the walls, the so-called plasma sheath region. The charge-imbalance, or space charge $\rho$, in the plasma generates an electric field that acts on the charged particles in the plasma. The electric field $\mathbf{E}$ can be found from Gauss’ law

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} = \frac{e}{\epsilon_0} (\Sigma_i Z_i n_i - n_e),$$

(3.18)

with $Z_i$ the charge state of the ions of type $i$. Since the curl of the electric field is zero, it is defined by a scalar electric potential field $V$ according to

$$\mathbf{E} = -\nabla V.$$ 

(3.19)

Eliminating $\mathbf{E}$ by substitution, a form of Poisson’s equation is obtained

$$\nabla^2 V = \frac{e}{\epsilon_0} (n_e - n_i),$$

(3.20)

where we have made the assumption that there are only singly charged ions ($Z_i = 1$). The width of the sheath region can be estimated by the Debye length $\lambda_D$, which is the characteristic length scale in a plasma over which charge-imbalance can occur.
In the sheath region, the plasma is not quasi-neutral. Negative charges are accelerated by the resulting electric field towards the bulk region and positive charges towards the wall.

The electric field in the sheath region is directed in such a way that electrons are pulled back towards the bulk of the plasma, whereas the positively charged ions in the plasma sheath region are pushed out towards the walls of the vessel in which the plasma is contained, as shown in Fig. 3.3.

Upon impact the ions can erode the walls through a process called physical sputtering. In Chapters 5 and 6, the sputtering mechanism will be discussed in detail, where we will see that the formation of the plasma sheath is also influenced by the emission of photo-electrons from the wall.

### 3.8 Secondary electron emission

Metals emit electrons when illuminated by electromagnetic radiation with a photon energy $h\nu$ above the work function $W$ of the metal. This effect, the so-called photo-electric effect, was first discovered by Hertz in 1887 [19].

The emission of photo-electrons was first described by Berglund and Spicer [20] as a 3-step process.

1. **Excitation:** the photon is absorbed and a electron-hole pair is created in the metal. The electron is excited into a conduction band state. The excess energy is transferred to the kinetic energy of the (primary) electron.

2. **Transport:** the primary electron that moves towards the surface will lose energy by electron-phonon scattering and by inelastic electron-electron scattering. One primary photo-electron can produce many secondary photo-electrons.

3. **Escape:** once a (secondary) electron reaches the surface, the electron can only escape
from the metal if it has sufficient energy to overcome the surface barrier energy of the material.

**Figure 3.4:** Inelastic Mean-Free-Path as a function of electron energy according to the TPP-2M formula for ruthenium (dots) and carbon (squares) [21]. The TPP-2M formula is a modified version of the Bethe equation for inelastic electron scattering in matter, which contains four fit parameters that are empirically related to material constants.

The inelastic mean-free-path (IMFP) for electrons in a metal is given by the TPP-2M formula [21]

\[ \lambda = \frac{E}{E_p^2} \left[ \beta \ln(\gamma E) - \frac{C}{E} + \frac{D}{E^2} \right], \tag{3.21} \]

where \( \lambda \) is the IMFP (in Å), \( E \) the electron energy (in eV), \( E_p = 28.8\sqrt{(N_v\rho/M)} \) the free-electron plasmon energy (in eV), \( \rho \) the density (in g cm\(^{-3}\)), \( N_v \) the number of valence electrons per atom (for elements) or molecule (for compounds) and \( M \) the atomic or molecular weight. The terms \( \beta, \gamma, C \) and \( D \) are parameters given by

\[
\beta = -0.0216 + 0.944/(E_p^2 + E_g^2)^{1/2} + 7.39 \times 10^{-4} \rho, \tag{3.22}
\]

\[
\gamma = 0.191\rho^{-0.50}, \tag{3.23}
\]

\[
C = 1.97 - 0.91U,
\]

\[
D = 53.4 - 20.8U,
\]

\[
U = N_v\rho/M = E_p^2/829.4,
\]

and \( E_g \) is the band gap energy (in eV) for nonconductors. Figure 3.4 shows the IMFP as a function of energy in ruthenium and carbon.

At EUV wavelengths the mean-free-path of electrons in a solid is typically below one nanometer, i.e. much smaller than the photon attenuation length, which for 92 eV photons in metals is in the range 10 – 100 nm [6]. Therefore, photo-electrons are likely to escape into the gas phase only when the absorption process occurs close to the surface. For this reason, the secondary electron emission is very sensitive to the chemical state of the surface.
Chapter 3: EUV-induced Plasmas

3.8.1 Secondary photo-electron yield and energy distribution

The number of secondary photo-electrons liberated per incoming photon is called the secondary electron yield. For clean Ru capped multilayer mirrors, a yield of $\sim 0.020$ was measured at the Brookhaven National Synchrotron Light Source [22] for a photon energy of 92 eV. This is in good agreement with the value of $\sim 0.021$ reported by Hollenshead and Klebanoff [23].

For metals, the energy distribution of the escaping electrons peaks at about 1 to 2 eV, and has a full width at half-maximum that is usually below 10 eV. For photon energies above 100 eV, the distribution is independent of photon energy. According to Henke et al. [24] the secondary electron energy distribution $S(E)$ for metals is proportional to

$$S(E) \sim \frac{W^2 E}{(E + W)^2},$$

with $W$ the work function of the material. Recently, measurements of the secondary electron energy distribution for Ru capped multilayer mirrors were reported by Yakshinskiy et al. [22]. Figure 3.5 shows a reasonable agreement between the measured energy distribution and the distribution of equation 3.24.

![Figure 3.5: Secondary Electron Energy distribution from Ruthenium capped multilayer mirror according to equation 3.24 (solid line), and measurements at NIST [22] (dotted line).](image)

The emitted photo-electrons affect the electric field in the plasma sheath region. The effect of the photo-electrons on sputtering by the EUV-induced plasma is further investigated in Chapter 6. In the next chapter, an overview is given of experimental methods to measure the properties of the plasma.
Bibliography


Chapter 3: EUV-induced Plasmas


Abstract. This chapter contains a feasibility study of several plasma diagnostic techniques that can be applied to measure the properties of the EUV-induced plasma. Information is required on properties such as the electron temperature, the ion and electron densities, the electron energy distribution function and the velocities of ions in the plasma sheath region. Measurement of these properties is not easy, because of the low plasma density, the small size of the plasma, the transient nature of the EUV sources, and the fact that the plasma is far from equilibrium. Results of Langmuir probe measurements are presented together with a feasibility study of Thomson scattering, microwave interferometry, laser-induced fluorescence, and optical emission spectroscopy.
4.1 Introduction

In principle, several diagnostic tools are available to investigate characteristic parameters of the EUV-induced plasma like the electron temperature, the ion and electron densities, and the electron energy distribution function (EEDF).

In this chapter, the following diagnostic tools and their applicability to investigate the EUV-induced plasma will be discussed:

- Langmuir probes
- Thomson scattering
- Microwave interferometry
- Laser-induced fluorescence
- Optical emission spectroscopy

The applicability of these methods is partially determined by the experimental setup that is used to study the EUV-induced plasma. Figure 4.1 shows a schematic layout of the experimental setup, which will be more extensively described in Chapter 10.

![Figure 4.1: Schematic of experimental setup.](image)

The EUV source is contained in a vacuum vessel. When the source is in operation the pressure in the source chamber is about 0.1 Pa. The vacuum vessel is separated into two chambers by a bandpass filter, which consists of a 150 nm thick Zr foil with a wire mesh support structure. The filters have a transmission of ≈ 50% for the EUV and less than 1% for VUV and other long-wavelength radiation. The plasma in the measurement chamber will therefore be mainly generated by the EUV radiation. The purpose of the filter is twofold: besides acting as bandpass filter, it also operates as a flow resistance. As a
result the pressure in the measurement chamber can be varied independently from the fixed pressure of 0.1 Pa in the source chamber. Directly behind the source a foil trap is placed to stop atomic and ionic debris coming from the source. The collector mirror captures a large solid angle of radiation emitted by the source and images it at a focus point in the measurement chamber. The inside of the ellipsoidal collector mirror is coated with a gold layer to act as a grazing incidence mirror. Figure 4.2 shows a picture of the EUV-induced plasma in the focus region of the collector mirror.

![Figure 4.2: Picture of the EUV-induced plasma in the focus point of the collector. Instead of argon, the vessel was filled with nitrogen at increased pressure, which emits more visible radiation when excited by EUV photons.](image)

Accurate measurements of the plasma parameters is hampered by the following properties of the plasma

1. Low density: The electron density \( n_e \approx 10^{15} \text{ m}^{-3} \) is considerably lower than in most laboratory plasmas. As a result, the measured signal will be low as well.

2. Limited size: In the laboratory, the plasma density of \( 10^{15} \text{ m}^{-3} \) can only be realized by focussing an EUV beam into a small, cylindrically shaped region (20 mm in the axial direction and 2 mm in diameter).

3. Strongly time-dependent: The transient nature of the EUV sources (100 ns pulse duration) puts hard demands on the temporal resolution of the diagnostics if one aims to make time-resolved measurements.

4. Far from equilibrium: The short lifetime of the plasma in combination with the low electron density implies that the plasma is far from equilibrium. Therefore, some assumptions commonly used to interpret measurement results are not valid. For instance, the electron-electron collision rate is not high enough to expect the EEDF to be Maxwellian and the concept of a electron temperature is not applicable.
4.2 Langmuir probes

Conceptually, the most straightforward way to measure the plasma characteristics is to use a Langmuir probe [1–3]. A wire is inserted into the plasma and the current $I$ is measured at various applied voltages $V$. The difficulty is to design the Langmuir probe in such a way that it does not disturb the plasma. Furthermore, interpretation of the measured I-V curves is not straightforward [4]. Figure 4.3 shows a typical example of an I-V curve.

![Figure 4.3: Example of an I-V characteristic.](image)

When the probe is inserted, a plasma sheath establishes in front of the probe. The thickness of the plasma sheath is of the order of the Debye length, as this is the characteristic distance over which charges are shielded in a plasma.

For a probe potential above the plasma potential $V_{pl}$, equal to the potential difference between the plasma volume and the vessel walls, positively charged ions are repelled from the probe and electrons are collected. For a probe potential below the plasma potential just the opposite occurs.

In principle, the electron velocity distribution and the ion density can be obtained from the I-V curve. The interpretation of the I-V curve, however, depends on the shape of the probe (planar, cylindrical, spherical) and how the dimensions of the probe $R$ compare to important plasma length scales such as the ion mean-free-path $\lambda_{ia}$ and the Debye length $\lambda_D$.

The simplest case arises for a planar probe and a thin, collisionless plasma sheath ($\lambda_D \ll R \ll \lambda_{ia}$). Under the assumption of single ionized ions and a Maxwellian electron velocity distribution $f(v_x)$, the current of electrons $I_e$ to the probe as a function of the
probe potential $V_p$ can be obtained from

$$I_e = -e n_e A \int_{v_m}^{\infty} v_x f(v_x) dv_x,$$

$$= -e n_e A \sqrt{\frac{kT_e}{2\pi m_e}} \exp \left[ \frac{e(V_{pr} - V_{pl})}{kT_e} \right],$$

(4.1)

where $A$ is the probe surface area and $v_m = \sqrt{2e(V_{pr} - V_{pl})/m_e}$ the minimum required velocity of electrons to overcome the potential barrier. In this simple case, the electron temperature can be obtained from an exponential fit of a part of the I-V curve (designated by the encircled region in Fig. 4.3).

For high positive potentials, the electron current shows saturation for $V_{pr} > V_{pl}$, as all electrons that enter the plasma sheath are collected. In order to repel all the electrons and observe the ion saturation current $I_{sat}$, the probe potential must be negative and have a magnitude near $\sim k_B T_e/e$. To satisfy the quasi-neutrality condition at the sheath edge, ions arriving at the periphery of the probe sheath are accelerated toward the probe with an energy $k_B T_i$, which is much larger than their thermal energy $k_B T_e$. The ion saturation current is then approximately given as

$$I_{sat} = n_i e A \sqrt{\frac{kT_e}{m_i}},$$

(4.2)

with $m_i$ the ion mass. Even though the ion flux-density at the tip of the probe is larger than the incident flux-density at the periphery of the collecting sheath, the total particle flux is still conserved because the area of the probe tip is smaller than the outer collecting area at the sheath boundary. The ion density $n_i$ can in principle be obtained from the ion saturation current once the electron temperature $T_e$ is known from the other part of the I-V curve.

The situation gets more complex for a thick plasma sheath, where the size of the probe $R$ is smaller than the width of plasma sheath ($R \leq \lambda_D$). In this case, the planar probe result is no longer applicable. Fortunately, exact solutions still exist for cylindrical and spherical probes. A number of extensive theories have been proposed that account for the motion of ions through a thick sheath: the original Orbital Motion Limited by Langmuir [3], Laframboise theory [5] and Allen-Boyd-Reynolds theory [6].

4.2.1 Probe design

Attempts have been made to measure the I-V curves of the EUV-induced plasma as a function of time. For the experiment, a cylindrical probe is used, with a probe tip of 2 mm in length and a radius of $R = 0.25$ mm. The tip is connected to the central wire of a coaxial cable, which is surrounded by insulation material. A 80 mm long hollow, cylindrical tube, connected to the outer wire of the coaxial cable, acts as a reference electrode.

Figure 4.5 shows two different schemes that have been used to measure the probe current. The probe is connected to the measurement circuit using a coaxial cable and an
vacuum feed-through. The reference electrode is connected to the ground of the power supply. In both cases, the current is obtained by measuring the voltage drop over a $50 \, \Omega$ resistor.

In Fig. 4.5(a), the potential difference is measured by a Techtronix differential amplifier, which has a time-resolution of $1 \, \mu s$. The output is connected to a 300 MHz Techtronix oscilloscope. In the other scheme, see Fig 4.5(b), the signal before and after the $50 \, \Omega$ resistor is connected to two different channels of the oscilloscope. Subtraction is done on the oscilloscope. The scope is set to AC coupling. The purpose of the two $7 \, \text{nF}$ capacitors in combination with the $2 \, \text{M} \Omega$ internal resistor of the scope is to act as a high-pass filter with a cut-off frequency of $\sim 70 \, \text{Hz}$. The function of the $2 \, \mu \text{F}$ capacitor is to reduce the voltage drop over the internal resistance of the power supply.

![Figure 4.4: Schematic of the cylindrical Langmuir probe.](image)

![Figure 4.5: Schematic of the measurement circuit. The current is obtained by measuring the voltage drop over a $50 \, \Omega$ resistor.](image)
4.2.2 Time scales

The probe is inserted into the plasma at the intermediate focus of the EUV beam. The current to the probe is measured as a function of time for various probe potentials. A typical measurement result is shown in Fig. 4.6.

![Figure 4.6: Current as a function of time for various probe potentials at an argon pressure of $p = 1.0 \times 10^{-3}$ mbar.](image)

Negative currents correspond to the collection of ions or the emission of electrons as a result of the photo-electric effect, whereas positive currents indicate the collection of electrons. The short peaks at the first 100 ns correspond to the time when the EUV radiation is generated. The measurement is repeated at different argon pressures to verify whether this peak is caused by the plasma or by the photo-electric effect. In Fig. 4.7, the result for a high negative probe voltage is plotted for three different background pressures. The difference between the currents for $p = 1 \times 10^{-5}$ mbar and $p = 1 \times 10^{-3}$ mbar is very small and therefore it is assumed that these currents are mainly the result of photo-electrons leaving the probe. If the pressure is raised by another order of magnitude then the amplitude of the current increases slightly as a result of the combined effect of photo-electrons emitted and plasma ions collected. A closer look reveals that the increase in current with pressure is negligible during the EUV pulse compared to the increase after the pulse. Therefore, the large peak during the EUV pulse most likely is the result of the photo-electric effect alone. Possibly, after the EUV pulse, ions also contribute to the measured current. It is not clear whether the current after the pulse is caused by ions alone.

A similar measurement is performed for a high positive probe potential as shown in Fig. 4.8. The sign of the current changes, because the probe is collecting electrons from the plasma. Note that the magnitude of the current after the EUV pulse is much larger now than in the previous case.

The measured current during the EUV pulse also has a positive sign. This appears to
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Figure 4.7: Current as a function of time for a probe potential of $V_{pr} = -100$ Volt at various argon pressures.

contradict the assumption that the current during the EUV pulse is primarily related to the photo-electric effect. Most likely, the contribution is the result of collecting photo-electrons that are emitted from the reference electrode of the probe.

Figure 4.8: Current as a function of time for a probe potential of $V_{pr} = +100$ Volt at two different argon pressures.

For the highest pressure, two time scales are visible: a short ($\approx 100$ ns) time scale during the EUV pulse, where the plasma is generated and the photo-effect is present, followed by a longer time scale ($\approx 10$ µs) as a result of the decay of the plasma. In all cases, the plasma lifetime is much shorter than the time between EUV pulses.
4.2 Langmuir probes

4.2.3 I-V curves

I-V curves have been measured using the differential amplifier scheme. Data points have been averaged on the oscilloscope over 500 EUV pulses to cancel out the pulse-to-pulse variation of the source.

Figure 4.9 shows a semi-log plot of the measurement results for $p = 3.0 \times 10^{-5}$ mbar at various points in time. The plasma potential is indicated by the position of the bend in the I-V curve at $\approx 19 \pm 1$ V. Only for the curve measured at 1 $\mu$s the position of the bend is not so clear. The electron temperature can be determined from the slope of the I-V curve left of the bend. A steep slope corresponds to a low electron temperature, whereas a shallow slope indicates a high temperature. The slope of the characteristic at $t = 1 \mu$s is much steeper (indicating a lower electron temperature) than the other I-V curves. This is unexpected, because no more power is supplied to the plasma after the EUV pulse. For this reason, a decrease in electron temperature of the plasma is expected after 1 $\mu$s.

![Figure 4.9: I-V curves at various times for a pressure of $p = 3.0 \times 10^{-3}$ mbar.](image)

For a further investigation the I-V curves are fitted with a function $f(V) = I_{\text{ion}} - c_1 \exp(V/T_{\text{el}})$, with $I_{\text{ion}}$ the fit parameter for the ion current, and $T_{\text{el}}$ the fit parameter for the electron temperature. Both experimental data and fits are shown in Fig. 4.10. The fits describe the data points fairly well for $t = 2 \mu s$ and $t = 3 \mu s$. However, this is not the case for $t = 1 \mu s$.

A considerable jump in current occurs between $V_{pr} = -20$ and $V_{pr} = -15$ Volt, which coincides with a change of power supply. For the measurements between $V_{pr} = -15$ and $V_{pr} = +15$ Volt a Delta-type power supply was used, whereas a Tektronix power supply was used for the other experiments. Somehow, the power supply influences the measurements. Further investigation revealed that both power supplies pick up a disturbance from the
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Figure 4.10: I-V curves at various times for a pressure of \( p = 3.0 \times 10^{-3} \) mbar. The data points are fitted with a function \( f(V) = I_{ion} - c_1 \exp(V/T_{el}) \), with \( I_{ion} \) the fit parameter for the ion current and \( T_{el} \) the fit parameter for the electron temperature in eV's.

EUV discharge. Therefore, the disturbance is strongest during the pulse, which is included in the I-V curve at \( t = 1 \mu \) due to the 1 \( \mu \)s time resolution of the differential amplifier.

From the fits, the electron temperatures and ion density can be calculated. The results are shown in Figs. 4.11 and 4.12. According to Fig. 4.12, the plasma density hardly depends on the argon background pressure. Furthermore, the ion density seems two orders of magnitude higher than estimated on the basis of the EUV photo-ionization cross-section. Most likely, the current for negative potentials is not caused by the collection of ions alone, but mainly related to the photo-electric effect.

The fit function does not take the photo-electric effect into account. This leads to an overestimation of the electron temperature at \( t = 1 \mu \)s. Furthermore, the assumption that the ion current is independent of the probe potential is not valid. The ion current increases as the probe potential becomes more negative as a result of the expansion of the plasma sheath in front of the probe. The simple Langmuir theory does not apply for such low plasma densities as the Debye length is of the same order of magnitude as the probe tip size. The effect of the sheath-expansion can be taken into account by using a more sophisticated probe theory.

4.2.4 Probe out of the EUV beam

In principle, the problem with the photo-electric effect can be reduced by moving the probe out of the EUV beam. Therefore, the same measurement procedures have been repeated with the probe just outside the intermediate focus. In the ion collection part of the I-V characteristic, the magnitude of the measured current is now two orders of magnitude lower.
4.2 Langmuir probes

Figure 4.11: Electron temperature as a function of time for three different values of the argon background pressure. The 100 ns long EUV pulse starts at $t=0$.

Figure 4.12: Ion density as a function of the argon background pressure at 1 $\mu$s after the start of the EUV pulse.

and amplification of the signal with the differential amplifier is required. Unfortunately, the signal-to-noise ratio is too low to generate useful results. To reduce the noise (picked up from the EUV discharge by the power supply), a power supply of batteries in a shielded box has been used. Figure 4.13 shows the result for the current as a function of time for different distances of the probe from the intermediate focus. The probe potential is set at $V_{pr} = 18$ Volt using two 9 V batteries in series. The measurements have been performed with the high-pass filter scheme. The results indicate that even with batteries, noise is being picked up from the EUV discharge, although the amount of noise is significantly reduced.
4.2.5 Conclusion

The Langmuir probe measurements provide information on the time scales of plasma generation and decay. The plasma is created in the EUV beam and after the pulse it recombines at the walls. With Langmuir probes, it is not feasible to measure electron temperature and ion density for two reasons:

First, the data analysis method is invalid. The expected ion density is too low for the thin sheath approximation to be valid. Thick sheath theory has to be applied to account for the movement of the ions through the sheath and the expansion of the sheath with higher (negative) probe potential.

More importantly, the photo-electric effect obscures the measurement of the I-V curve. In the ion collection part of the I-V curve, the measured current is mainly the result of the emission of photo-electrons from the probe tip. Possibly, the top part of the reference electrode is also in the EUV beam. A longer probe tip should be used to avoid this. In an attempt to eliminate the photo-electric effect, measurements outside the EUV-beam have
been performed. In the current situation, the signal-to-noise ratio is too poor to measure the ion current outside the EUV beam. The main problem comes from noise picked up from the EUV discharge by the power supply, although this can be considerably reduced when a battery power supply is used.

Another, non-intrusive diagnostic is needed to characterize the plasma. For this purpose, we investigate the feasibility of Thomson scattering as a plasma diagnostic at this low electron density.

4.3 Thomson scattering

If the free electrons in the plasma are irradiated by a laser, they will oscillate in the electric field of the laser beam. The acceleration of electrons will cause emission of electromagnetic radiation, which can be considered as scattering of the incident radiation. Elastic scattering of radiation by free electrons in the plasma is called Thomson scattering. The power of scattered radiation $P_s$ of a scattering volume with length $L_{det}$ along the incident beam is

$$P_s = P_i \cdot n_e L_{det} \frac{d\sigma_T}{d\Omega} \Delta\Omega,$$

(4.3)

where $P_i$ is the incident power, $\Delta\Omega$ the solid angle of detection and $d\sigma_T/d\Omega$ the differential Thomson scattering cross section

$$\frac{d\sigma_T}{d\Omega} = r_e^2 (1 - \sin^2 \theta \cos^2 \varphi),$$

(4.4)

with $\theta$ the scattering angle, $\varphi$ the angle between the plane of scattering and the polarization of the laser and $r_e$ the classical electron radius

$$r_e = \frac{e^2}{4\pi\epsilon_0 m_e c^2} = 2.818 \times 10^{-15} \text{ m.}$$

(4.5)

Because of the velocity $v$ of the electrons the observed frequency $\omega_s$ of the scattered light will be Doppler shifted with respect to the frequency $\omega_i$ of the incident radiation. The total Doppler shift $\Delta\omega$ is given by

$$\Delta\omega = \omega_s - \omega_i = \mathbf{k} \cdot \mathbf{v} \quad \text{and} \quad \frac{\Delta\omega}{\omega_i} \approx 2 \sin (\theta/2) \cdot \frac{v_k}{c},$$

(4.6)

with the scattering vector $\mathbf{k} = \mathbf{k}_s - \mathbf{k}_i$ given by the difference between the wave vectors of the scattered and incident radiation, $v_k$ the velocity component along $\mathbf{k}$, and $\lambda_i$ the wavelength of the incident radiation. The probability $S_\lambda(\Delta\lambda)$ that the wavelength of a scattered photon lies within a range $d\lambda_s$ is related to the probability $F_k(v_k)$ that the scattering-electron has a velocity component along $\mathbf{k}$ around the velocity $v_k = \Delta\omega/k$

$$S_\lambda(\Delta\lambda)d\lambda_s = \frac{c}{2\lambda_i \sin (\theta/2)} F_k(v_k) dv_k,$$

$$= \frac{c}{2\lambda_i \sin (\theta/2)} \cdot F_k \left( \frac{c}{2 \sin (\theta/2)} \cdot \frac{\Delta\lambda}{\lambda_i} \right) d\lambda_s.$$

(4.7)
For a Maxwellian velocity distribution, this transformation gives a Gaussian shaped scattering spectrum

\[ S_\lambda(\Delta \lambda) d\lambda_s = \frac{1}{\Delta \lambda_{1/e} \sqrt{\pi}} \exp \left[ -\left( \frac{\Delta \lambda}{\Delta \lambda_{1/e}} \right)^2 \right] d\lambda_s, \]  

(4.8)

with \( \Delta \lambda_{1/e} \) the half 1/e width of the scattering spectrum

\[ \Delta \lambda_{1/e} = \lambda_i \cdot 2 \sin (\theta/2) \cdot \frac{\hat{v}}{c}, \]  

(4.9)

where \( \hat{v} \) is the most probable velocity of the electrons \( \hat{v} = \sqrt{\frac{2k_B T_e}{m_e}} \). For our experimental conditions \((T_e = 10 \text{ eV})\), we expect \( \Delta \lambda_{1/e} = 9 \text{ nm} \). For a Maxwellian EEDF\(^1\) the electron temperature can be obtained from a measurement of \( \Delta \lambda_{1/e} \). The electron density can be obtained by integration of the total Thomson spectrum. As this involves an absolute measurement, the Thomson setup needs to be calibrated. This is usually done by measuring the Rayleigh scattering signal. Rayleigh scattering is elastic scattering from bound electron clouds surrounding atoms and ions. The differential cross-section for Rayleigh scattering by an atomic gas is determined by the polarizability \( \alpha \) of the atoms [7]

\[ \frac{d\sigma_R}{d\Omega} = \frac{\pi^2 \alpha^2}{e^2 \lambda_i^4} \cdot (1 - \sin^2 \theta \cos^2 \varphi). \]  

(4.10)

For our purposes \((\text{argon gas, } \lambda_i = 532 \text{ nm and } \theta = 90^0)\), the differential cross-section is equal to \( \frac{d\sigma_R}{d\Omega} = 5.40 \times 10^{-32} \text{ m}^2 \text{ sr}^{-1} \). For the ionization degree of the EUV-induced plasma, the measured Rayleigh spectrum is expected to be \( \approx 400 \) times stronger than the Thomson signal, but much narrower due to the much lower thermal velocities of the background argon atoms.

For typical parameters in our experiment, listed in table 4.1, the fraction of scattered photons entering the detection branch, given by

\[ L_{det} n_e \frac{d\sigma_T}{d\Omega} \Delta \Omega = 6.4 \times 10^{-19}, \]  

(4.11)

will be very low. This means that, for a quantum efficiency of 10\%, less then one of every \( 10^{19} \) photons will be detected. The critical question here is whether or not such a low signal will still be detectable.

4.3.1 Detection limiting factors

The detection limit for Thomson scattering is defined as the minimum electron density at which the Thomson signal can be distinguished from other contributions to the signal

\(^1\)As shown in the previous chapter, the electron-electron collision time is larger than the lifetime of the EUV-induced plasma. Therefore, the electrons of the EUV-induced plasma are not in thermal equilibrium, and as result the EEDF will deviate from a Maxwellian energy distribution. Still, for the feasibility study in this chapter the EEDF is approximated by a Maxwellian distribution.
Table 4.1: Experimental parameters

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{det}$</td>
<td>2 mm</td>
</tr>
<tr>
<td>$n_e$</td>
<td>$2 \times 10^{15}$ m$^{-3}$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>90°</td>
</tr>
<tr>
<td>$\Delta\Omega$</td>
<td>0.02 sr</td>
</tr>
</tbody>
</table>

with a certain amount of accuracy. Besides the Thomson and Rayleigh spectrum, the recorded spectrum contains a continuous background caused by continuum radiation from the plasma and dark current in the detector. These contributions can be subtracted from the recorded spectrum but their noise remains. Therefore, in many cases the detection limit is determined by noise.

Additionally, stray light from the surroundings of the plasma will show up in the spectrum as a narrow peak at the laser wavelength. With a triple grating spectrograph [8], the central part of the spectrum can be blocked to eliminate the stray light. The downside of this method is that also the central part of the Thomson signal is blocked, but because of the high electron temperature the Thomson signal will be very broad so that blocking the central wavelength region will not be problematic. Stray light can cause real problems when measuring with the laser beam close to electrodes or other surfaces. In our application, the nearest surface is 125 mm away from the plasma. Normally, stray light is suppressed by baffles and diaphragms, but some amount of radiation will always reach the detector after multiple reflections.

In many cases, the detection limit is determined by the background emission of the plasma. At the moment it is not clear what the emission of the plasma is. With the naked eye, no radiation is visible at optical wavelengths. Before attempting Thomson scattering it is advisable to measure the emission of the plasma with an intensified CCD camera.

Interaction between the laser and the plasma can lead to heating of the plasma. This effect is the detection limiting factor of Thomson scattering diagnostics applied on the high density EUV plasma source [9]. Plasma heating effects are the result of either inverse bremsstrahlung or absorption by radiative transitions close to 532 nm followed by collisional de-excitation.

For our application, plasma heating is not expected to pose a problem. Because of the low argon density inverse Bremsstrahlung can be neglected ($\Delta T_e/T_e \approx 10^{-9}$). Also, for argon there are no transitions close to $\lambda = 532$ nm and because of the low density both line broadening and the collision frequency will be low as well.
4.3.2 Statistical noise

The statistical noise on the detected Thomson signal is the result of the following processes. First, the laser pulse-to-pulse variation is estimated to be 10%. For \( n \) laser pulses, the relative standard deviation will be \( 0.1/\sqrt{n} \).

After Thomson scattering the photon will pass through the optics of the triple-grating spectrograph (with transmission \( \eta \)) and generate a photo-electron (with quantum efficiency \( \xi_1 \)) in the photo-cathode of the intensified CCD camera. The generated photo-electrons \( N_T \) will have a binomial distribution, which, because of the low scattering probability, can be approximated by a Poisson distribution. The relative noise on the number of photo-electrons will be \( 1/\sqrt{N_T} \).

In the Multi-Channel Plate (MCP) the photo-electrons will be amplified with a gain factor \( g \), but the standard deviation is mainly determined by the first amplification step, which has an average gain of \( g_1 = 1.35 \). This leads to a relative standard deviation of \( 1/\sqrt{g_1 N_T} \) for photo-electrons entering the MCP.

Next, the photo-electrons are accelerated towards a fluorescent screen where they are converted into photons. A fibre-optic taper guides the photons to the smaller CCD chip where they are collected as electron-hole pairs with a quantum efficiency \( \xi_2 \). The average amplification factor of the intensified CCD camera has been measured by Van de Sande [8] to be \( g_2 = 3.5 \times 10^3 \). Therefore, the relative standard deviation of the number of electrons produced in the CCD chip as a result of Thomson scattering will be \( \sqrt{(1-\xi_2)/(N_T g_2 \xi_2)} \).

Overall, the total relative standard deviation \( \zeta_T \) of the number of electrons on the CCD chip \( S_T = N_T g_2 \xi_2 \) can be approximated by quadratically adding the relative standard deviations of the processes mentioned above

\[
\left( \frac{\zeta_T}{S_T} \right)^2 \approx \frac{0.01}{n} + \frac{1}{N_T} + \frac{0.74}{N_T} + \frac{1-\xi_2}{N_T g_2 \xi_2} \quad (4.12)
\]

The first term can be neglected, because the number of detected Thomson photo-electrons per laser shot is small at the detection limit \( N_T \ll n \). Furthermore, the noise generated in the CCD chip can be neglected due to the high gain factor of the intensified CCD camera \( g_2 \xi_2 \gg 1 \), which leads to the following result

\[
\frac{\zeta_T}{S_T} \approx \frac{1.3}{\sqrt{N_T}}. \quad (4.13)
\]

The statistical noise on the Thomson scattering intensity is only 30% higher than predicted by the Poisson statistics on the number of Thomson photo-electrons \( N_T \).

Besides stray light and plasma radiation there are other sources contributing to the background noise. Dark current and Equivalent Background Illumination (EBI) are the result of thermal generation of electron-hole pairs in the CCD chip and photo-electrons in the photo-cathode. Dark current can be strongly reduced by cooling the CCD chip to \(-40^\circ C\) and EBI and plasma radiation are suppressed by 6 orders of magnitude by gating the camera, i.e. using the intensifier on the camera as an ultra-fast shutter.
Increasing the measurement-time leads to better photon statistics and is the easiest way to improve the signal-to-noise ratio. Of course the stability of the plasma will put some practical limits to this. At a certain point the benefit of improved photon statistics will be outweighed by the increased background noise due to erosion of the electrodes, reflectivity loss of the collector optics and degradation of the filter.

At the highest resolution setting the CCD array used by Van de Sande [8] provides $385 \times 385$ pixels. In the horizontal direction, information on the energy distribution or spectrum of the plasma is recorded, whilst in the vertical direction spatial information on the plasma parameters is provided. By changing the setting of the CCD camera, pixels can be grouped together into super-pixels. In this way, more electrons-hole pairs per (super-) pixel are collected with better signal to noise ratio. To increase the detection limit, it would be advisable to group all 385 pixels in the vertical direction together into 1 super-pixel, i.e. averaging the spatial information. In this way, the detection limit is improved at the expense of spatial information on the plasma parameters.

To increase the Thomson signal, a number of things can be done:

- Increasing the density of the plasma;
- Increasing the detection length;
- Increasing the solid angle of detection;
- Increasing laser power.

### 4.3.3 Increasing plasma density

The electron density at the intermediate focus linearly depends on the intensity of the EUV source, the background argon pressure in the measurement chamber, and the collection efficiency of the collector mirror. The intensity supplied by EUV source is fixed, but with the current turbo-pumps the argon pressure can be increased by a factor of 2 without difficulty. Additionally, the collection efficiency of the collector mirror can be altered. With a larger sized collector, the EUV intensity at the intermediate focus can be further increased. A collector with an ellipsoidal shaped inner surface with long half-axis $a$ and short half-axis $b$ will have a focal length $f$ given by $f = \sqrt{a^2 - b^2}$, see Fig. 4.14. Increasing the size of the collector will also lead to a shift in the position of the intermediate focus. This additional effect can be exploited to move the intermediate focus to a position in the experimental set-up where there is much better optical access.

To improve the collection efficiency, the collector-design shown in Fig. 4.14 is being investigated. In this design, $x_s$ denotes the position of the source, $x_f$ specifies the position of the intermediate focus and $L$ is the length of the collector. Compared to the old design with $b = 50$ mm, the collection efficiency of the new collector should increase by a factor $2 - 3$. For this calculation, it is assumed that the angular reflectivity $R(\theta)$ of the gold coated mirror is equal to $R(\theta) = 1 - \xi \theta$, with $\xi = 0.033$ degrees$^{-1}$ a materials constant [10].
4.3.4 Increasing detection length

The detection length is determined by the diameter of the EUV cone at the intermediate focus. For the current collector, this diameter is approximately 2 mm. With a multi-pass cell of the Herriott type [11], the detection length can be increased.

![Herriott multi-pass cell](image)

The Herriott cell consists of a cavity formed by two spherical mirrors separated by almost their radius of curvature, as shown in Fig. 4.15. The laser beam enters the cell through an off-axis hole in one of the mirrors in an off-axis direction. The laser beam circulates a number of times into the cell before exciting through the same hole. The number of passes $N$ can be adjusted by varying the angle of incidence. After each reflection the laser beam is refocussed at the intermediate focus located at the center of the cell.

The maximum allowed number of passes is determined by the number of laser spots with diameter $d$ that can be accommodated on a ring with radius $r$ on the surface of the mirror without overlap of the laser spots

$$N = \frac{2\pi r}{d}. \quad (4.14)$$

To prevent damage to the mirrors, the diameter of the laser spot should be such that the peak laser pulse intensity is below the damage threshold of the mirrors, which is $40 \text{ J cm}^{-2}$. 

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With the current collector, the maximum radius of the mirror \( \approx 35 \text{ mm} \) is limited by the available space in the vacuum setup. For a Gaussian laser beam with a laser spot diameter \( d = 2.2 \text{ mm} \), this gives \( N = 100 \). With the new collector-design, larger mirrors can be accommodated so that mirror damage is no longer limiting the number of passes.

The mirrors should be mounted in the vacuum to minimize laser intensity losses at the windows of the vacuum setup. With mirrors in the vacuum, alignment of the cavity will be difficult. Therefore, mirrors should be mounted on a frame so that they can be aligned outside the vacuum, preferably with a continuous laser that emits at a wavelength that is visible to the human eye. After alignment, the frame with the mirrors should be mounted as a whole inside the vacuum setup.

A disadvantage of using the Herriott cell is that the amount of stray light will be significantly increased (as will the Rayleigh signal). If the triple grating spectrograph is used, then the effect of the straylight increase can be reduced.

4.3.5 Increasing solid angle of detection

With the current collector-design, optical access to the intermediate focus is poor as photons have to pass through the small windows of both vacuum chambers. The solid angle of detection \( \Delta \Omega = 0.011 \text{ sr} \) is limited by the size of the window in the source chamber.

With the new collector-design, the intermediate focus will shift to a position in the setup with good optical access. As a result the solid angle of detection is restricted by how close the first lens of the spectrometer can be positioned to the windows of the vacuum setup. It is possible to achieve a value of \( \Delta \Omega = 0.10 \text{ sr} \).

The only way to get an appreciable solid angle of detection with the current collector is to mount a tube containing an optical telescope between the source chamber and the measurement chamber. Although this will further complicate the alignment of the spectrograph, it would increase the solid angle of detection to \( \Delta \Omega = 0.13 \text{ sr} \).

4.3.6 Increasing laser power

The currently used laser has a pulse energy of \( E_p = 0.4 \text{ Joule} \) at a repetition rate of \( f_{\text{rep}} = 10 \text{ Hz} \). With a state-of-the-art Q-switched YAG laser, this can be increased to \( E_p = 0.6 \text{ Joule at } f_{\text{rep}} = 30 \text{ Hz} \). However, increasing the laser power is expensive (Quantel YG series 65,000 euro). Increasing the repetition rate of the laser does not directly lead to more signal, but enables shorter measurement-times and thus improves the signal to noise ratio.

4.3.7 Discussion

In order to quantify the suggested improvements to the system, the expected number of detected Thomson photons per hour is calculated. Results are summarized in table 4.2 for the current setup, for the new collector, for the multi-pass cavity, for both these improvements, and for both these improvement including a state-of-the-art laser system.
Table 4.2: Experimental parameters, expected number of detected Thomson photons \( dN_T/dt \) per hour.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Current setup</th>
<th>New collector</th>
<th>Multi-pass cavity</th>
<th>New collector and cavity</th>
<th>New laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_{det} ) [mm]</td>
<td>2</td>
<td>2</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>( n_e ) [m(^{-3})]</td>
<td>( 2 \times 10^{15} )</td>
<td>( 4 \times 10^{15} )</td>
<td>( 2 \times 10^{15} )</td>
<td>( 4 \times 10^{15} )</td>
<td>( 4 \times 10^{15} )</td>
</tr>
<tr>
<td>( \Delta \Omega ) [sr]</td>
<td>0.011</td>
<td>0.10</td>
<td>0.011</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>( E_p ) [Joule]</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>( f_{rep} ) [Hz]</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>( dN_T/dt ) [hr(^{-1})]</td>
<td>( 1.6 \times 10^3 )</td>
<td>( 2.9 \times 10^4 )</td>
<td>( 6.5 \times 10^4 )</td>
<td>( 1.2 \times 10^6 )</td>
<td>( 5.3 \times 10^6 )</td>
</tr>
</tbody>
</table>

In the calculation of detected Thomson photons per hour, the following assumptions have been made:

- scattering angle of \( 90^\circ \); 
- transmission of triple grating spectrograph \( \eta = 0.12 \); 
- quantum efficiency of detector \( \xi = 0.10 \); 
- \( 4 \times 385 \) pixel binning on CCD camera.

The detected Thomson photons should be compared to the noise on the expected background after one hour of measurement. The detected background will most likely be dominated by either stray light or plasma emission. However, it is not possible to give an estimate of the expected stray light level, especially not with the multi-pass cell. Plasma emission can be measured with a single grating spectrograph and intensified CCD camera.

For Thomson scattering measurements on a RF helium plasma in a quartz tube [8] a background intensity of \( I = 1.6 \times 10^{-4} \) photo-electrons per pixel (mainly due to stray light) was measured. For the current triple grating spectrograph, laser system and intensified CCD-camera a detection limit of \( n_e = 1.8 \times 10^{15} \) m\(^{-3}\) (limited by photon statistics) is claimed [8] for a measurement of 1 hour with a laser with a pulse energy of 0.4 J and a repetition rate of 10 Hz, a detection length of 11 mm, and an electron temperature of \( T_e = 1 \) eV.

If, for the sake of argument, we would assume to have the same number in our experiment with multi-pass cell and new collector than for a five minute measurement the detection limit would be \( n_e = 1.0 \times 10^{15} \) m\(^{-3}\) (limited by the background emission). For a longer measurement-time of 1 hour, a density of \( n_e = 2.7 \times 10^{14} \) m\(^{-3}\) would still be detectable (limited by background). Details of this calculation are listed in table 4.3.
4.4 Microwave interferometry

Generally speaking, if detection is limited by photon statistics, then the detection limit will be proportional to the inverse of the measurement-time \( n_e \sim t^{-1} \). In case the background emission is limiting detection, i.e. for long measurement-times, then the detection limit is proportional to the inverse of the square root of the measurement-time \( n_e \sim t^{-1/2} \).

<table>
<thead>
<tr>
<th>Source</th>
<th>5 minutes</th>
<th></th>
<th>1 hour</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>Noise</td>
<td>Intensity</td>
<td>Noise</td>
</tr>
<tr>
<td>Thomson scattering</td>
<td>9.1 \times 10^4</td>
<td>2.3 \times 10^4</td>
<td>2.8 \times 10^5</td>
<td>4.1 \times 10^4</td>
</tr>
<tr>
<td>background light</td>
<td>2.6 \times 10^5</td>
<td>3.9 \times 10^4</td>
<td>3.1 \times 10^6</td>
<td>1.4 \times 10^5</td>
</tr>
<tr>
<td>EBI</td>
<td>2.3 \times 10^1</td>
<td>3.7 \times 10^3</td>
<td>2.7 \times 10^2</td>
<td>1.3 \times 10^3</td>
</tr>
<tr>
<td>dark current</td>
<td>2.0 \times 10^5</td>
<td>4.5 \times 10^2</td>
<td>2.4 \times 10^6</td>
<td>1.5 \times 10^3</td>
</tr>
<tr>
<td>readout noise</td>
<td>2.3 \times 10^1</td>
<td></td>
<td>1.4 \times 10^3</td>
<td></td>
</tr>
<tr>
<td>total noise</td>
<td>4.5 \times 10^4</td>
<td></td>
<td>1.4 \times 10^5</td>
<td></td>
</tr>
<tr>
<td>detection limit</td>
<td>1.0 \times 10^{15}</td>
<td>m^{-3}</td>
<td>2.7 \times 10^{14}</td>
<td>m^{-3}</td>
</tr>
</tbody>
</table>

4.3.8 Conclusion

The question whether it is feasible to measure a plasma density of \( n_e = 2 \times 10^{15} \text{ m}^{-3} \) with Thomson scattering is difficult to answer. Detection will probably be limited by stray light and plasma emission. Plasma emission should be measured before starting with the Thomson scattering measurements. The stray light level cannot be determined beforehand. If the stray light level is comparable to that of an helium RF plasma in a quartz tube (which has a much higher plasma density of \( n_e = 1 \times 10^{19} \text{ m}^{-3} \)) then it should still be possible to measure the plasma density provided the multi-pass cell (to extend the detection length) and the new collector optics (to increase the solid angle of detection) are used.

4.4 Microwave interferometry

Microwave interferometry is a well established technique to measure the electron density of a plasma (along a line-of-sight). For this purpose, the phase shift \( \Delta \Phi \) of microwaves transmitted through the plasma is measured, compared to a reference path [12]. The refractive index \( \bar{n} \) for an electromagnetic wave with frequency \( f \) traveling through a plasma.
Chapter 4: Plasma diagnostics

is given by

$$\tilde{n}(f) = \sqrt{1 - \frac{f_p^2}{f^2}},$$ (4.15)

with $f_p$ the plasma frequency. Strictly speaking, equation 4.15 only applies to collisionless plasmas for which the plasma frequency is high compared to the electron collision frequency ($f_p \gg \nu_{ea}$), see Table 4.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_e$</td>
<td>Electron density</td>
</tr>
<tr>
<td>$L$</td>
<td>Plasma Size</td>
</tr>
<tr>
<td>$f_p$</td>
<td>Plasma frequency</td>
</tr>
<tr>
<td>$\nu_e$</td>
<td>Electron collision frequency</td>
</tr>
</tbody>
</table>

Table 4.4: Characteristic parameters of the EUV-induced plasma

The measured phase shift is proportional to the line-integrated electron density

$$\Delta \Phi = \frac{\lambda_0 e^2}{4\pi cm_e \epsilon_0} \int n_e dx,$$ (4.16)

with $\lambda_0$ the wavelength of the microwaves. To increase the sensitivity of microwave interferometry, it is better to use long wavelengths. However, for the plasma to be transparent to the microwaves, the frequency of the microwaves must be well above the plasma frequency ($f \gg f_p$).

Furthermore, the wavelength of the microwaves must be smaller than the distance over which the electron density changes significantly ($2\lambda_0 < L$). Because the interaction length $L$ with the plasma is short ($L = 2$ mm the wavelength of the microwaves must also be very short.

If $\lambda_0 = 1$ mm microwaves ($f = 300$ GHz) would be used to measure the electron density of the EUV-induced plasma, the expected phase shift would be $\Delta \Psi = 6 \times 10^{-6}$ rad, see Table 4.5. This is well below the detection limit of even the best microwave interferometers, which are capable of detecting phase shifts as small as $\Delta \Psi = 10^{-3} - 10^{-2}$ rad [13–15].

Therefore, it can be concluded that the low plasma density in combination with the short interaction length between the microwaves and the plasma makes microwave interferometry unsuited for measuring the electron density of the EUV-induced plasma.

4.5 Laser-induced fluorescence

Laser-Induced Fluorescence (LIF) measurements [16–18] are widely used to measure the velocity distribution of plasma ions. Laser light with frequency $\nu_L$ and wavelength $\lambda = c/\nu_L$
Table 4.5: For microwave interferometry with 300 GHz microwaves (\(\lambda_0 = 1 \text{ mm}\)): expected values for the electron density and phase-shift for the parameters of the EUV-induced plasma are given. The last column gives the detection limit for microwave interferometry and the corresponding electron density.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expected value</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_e)</td>
<td>(2 \times 10^{15} \text{ m}^{-3})</td>
<td>(2 \times 10^{17} \text{ m}^{-3})</td>
</tr>
<tr>
<td>(\Delta \Psi)</td>
<td>(1 \times 10^{-5} \text{ rad})</td>
<td>(1 \times 10^{-3} \text{ rad})</td>
</tr>
</tbody>
</table>

is fired into the plasma. The laser frequency is tuned close to the transition frequency \(\nu_0\) between a ion metastable state and a higher excited level. Ions moving with velocity component \(v_{\parallel}\) parallel to the laser beam will absorb a photon when the Doppler shift condition is satisfied

\[
\nu_L - \nu_0 = v_{\parallel} / \lambda.
\] (4.17)

After excitation the ion emits a fluorescence photon, which can be detected by a photomultiplier tube or intensified CCD camera. By scanning the laser frequency over the transition frequency a ion velocity distribution can be obtained. For argon, many transition schemes can be used with either tunable dye lasers or diode lasers. The integrated ion distribution function is proportional to the ion density. To obtain absolute ion densities, the result should be calibrated. Often, Langmuir probe measurements are used for the calibration, but as was shown earlier, the method of using Langmuir probes to measure the ion density of the EUV-induced plasma is questionable.

Goecker et al. [19] have used LIF to measure the ion density distribution in the plasma sheath region of a low density \((n_i \approx 10^{14} \text{ m}^{-3})\) multi-dipole plasma. For this purpose, a laser beam was reflected at normal incidence from one of the electrodes. As a result their fluorescence signal displayed two peaks, one from the incoming and one from the outgoing beam. In this way, a absolute measure for the ion velocity was obtained.

It would be interesting to see whether this method could be applied to measure the ion velocities in the plasma sheath of the EUV-induced plasma.

First, the spatial resolution of the LIF measurement must be small enough to resolve the plasma sheath-thickness, which can be estimated by the Debye length \((\lambda_D = 7 \times 10^{-4} \text{ m}\)).

Ultimately, only the energies at which ions collide with the surface are truly of interest. This requires the measurement of the ion velocities in the part of the plasma sheath closest to the surface, which puts even stricter demands on the spatial resolution of the LIF measurements. Such a measurement would require the laser beam to be very close to the surface, which is otherwise impractical.

Furthermore, the ion density close to the surface will be significantly lower than \(10^{15} \text{ m}^{-3}\). In a steady state plasma sheath, the ion flux \(n_i v_{\parallel}\) is conserved. As we move closer to
the wall, the velocity of the ions increases as they are accelerated in the electric field and consequently the ion density must decrease. Although the EUV-induced plasma is not a steady state plasma, this effect will certainly play a role.

Therefore, it can be concluded that, although LIF can be employed to measure the ion energies in a plasma (pre)-sheath, it is not likely that it can give information on the impact energies of the ions.

4.6 Optical emission spectroscopy

So far, different kinds of methods have been discussed to measure the properties of the EUV-induced plasma. These methods have in common that they are active methods, where the plasma is subjected to an interaction with a laser or probe.

It is also possible to explore passive diagnostics: observation of the plasma via the emitted radiation. Although inherently non-intrusive, this method is difficult because the signal is so low that the naked eye does not see any plasma glow.

In plasmas, atoms are excited as a result of collisions and radiative capture of photons from the radiation field. In Optical Emission Spectroscopy (OES), line emission from the plasma is measured to obtain information on the population densities of the excited states. With a collisional-radiative model (CRM), the population densities can be related to plasma properties such as the electron energy distribution function and the electron density.

For the EUV-induced plasma, the corona balance is applicable: excited states are populated by collisional excitation (electron-neutral collisions), and are de-populated by radiative decay to lower lying states, as shown in Fig. 4.16.

\[ \frac{\partial n_p}{\partial t} = n_e n_p \kappa_p(t) - \sum_{q < p} n_p A(p, q) + \sum_{q > p} n_q A(q, p), \]  
\[(4.18)\]

**Figure 4.16:** Corona balance: atoms are excited by collisions with electrons. Excited states are de-populated by radiative decay.

For each excited state \( p \), the time evolution of its population density \( n_p \) is given by the following differential equation
4.6 Optical emission spectroscopy

with $\kappa_p(t)$ the collisional excitation rate from the ground state to $p$ at time $t$, $A(p, q)$ the Einstein coefficient [20] for spontaneous emission to a lower lying state $q$, and $A(q, p)$ the transition probability from a higher excited state with population density $n_q$ to state $p$. In principle, the population densities can be found by solving this set of coupled first order differential equations.

To obtain the collisional excitation rate, the energy dependent electron excitation cross-section $\sigma_{ex}^p(E)$ [21, 22] must be convoluted with the electron energy distribution function $f(E, t)$ at time $t$

$$\kappa_p(t) = \int \sigma_{ex}^p(E') f(E', t) dE.$$ \hspace{1cm} (4.19)

The EEDF and the electron density can be obtained from the plasma simulation model that will be described in Chapters 5-8.

Figure 4.17 shows the result of such a calculation giving the time evolution of the population densities for a number of excited states of the argon atom.

![Figure 4.17: Time evolution of population densities of some atomic levels of the EUV-induced argon plasma.](image)

Besides population densities, the collision-radiative model can predict the time-evolution of the emitted spectrum of the plasma. With time-resolved OES measurements, the predicted spectrum can be directly verified.

In this way, the combination of time-resolved OES measurements with the collisional-radiative model provides an interesting way to probe the electron density and electron energy distribution function of the EUV-induced plasma, and to validate the plasma simulation model.
Bibliography


Abstract. A Particle-In-Cell Monte Carlo code has been developed to study the behavior of the charged particles in the plasma sheath region of an extreme ultra-violet radiation generated plasma.

This chapter starts with an introduction into the field of computational plasma physics with a focus on kinetic modelling, in particular on Particle-in-Cell models in combination with the method of Monte Carlo collisions. In the remainder of the chapter, a description is given of such a plasma model, and its application to simulate the sputter mechanism in EUV radiation generated plasmas. From the simulations, the flux and energy distribution of ions that collide with the plasma boundaries are obtained. Given the sputter yield, the rate of sputtering is estimated.
5.1 Introduction

In computational plasma physics, the theoretical framework is often based on the classical description of a collection of particles. An important tool in this description is the one-particle distribution function $f_\alpha(x, p, t)$ in 6-dimensional phase-space. It is defined as the number of particles of species $\alpha$ which, at time $t$, have positions lying within a volume element $d^3r$ about $r$ and momenta lying within a momentum-space element $d^3p$ about $p$. For sufficiently low pressures, the time evolution of the plasma species $\alpha$ is given by the Boltzmann equation

$$\frac{\partial f_\alpha}{\partial t} + \frac{p}{m_\alpha} \cdot \frac{\partial f_\alpha}{\partial x} + \frac{\partial f_\alpha}{\partial p} \cdot F_\alpha = \left. \frac{\partial f_\alpha}{\partial t} \right|_{coll}, \tag{5.1}$$

with $F_\alpha(x, p, t)$ the external force field acting on the particles of type $\alpha$, and $m_\alpha$ the particle mass. The term on the right-hand side describes the collisions between particles. To obtain the external force field, the Boltzmann equation for the electrons can be coupled to the Maxwell equations.

There are two main approaches to solving the Boltzmann equations: the fluid approach and the kinetic approach.

In the fluid approach, the plasma is considered as a multi-fluid that can be described by macroscopic quantities such as density, mean velocity and average energy (velocity moments of the distribution function) of its constituent species. The time evolution of the velocity moments can be obtained by integration of the Boltzmann equation multiplied by the various velocity moments over the momentum coordinates. This is done for all relevant species and requires the assumption of a velocity distribution function of these species. Furthermore, transport coefficients such as mobility and diffusion coefficients need to be determined, which are also averages over the a priori unknown velocity distribution.

In the kinetic approach, no assumptions for the velocity distributions need to be made. In some special cases, the Boltzmann equation can be solved directly, for instance, when the plasma can be considered collisionless (in which case the right-hand side term of the Boltzmann equation equates to zero and the Boltzmann equation reduces to the so-called Vlasov equation). Even then, solving the Vlasov-Maxwell equations is restricted to two or three phase-space components because of computer memory limitations.

Another approach to kinetic modeling is to represent the distribution function by a number of test particles. In the model, the trajectories of these test particles are followed in the self-consistent electromagnetic field. The number of test particles $N$ needs to be sufficiently high to accurately represent the distribution function.

Early kinetic models [1] were dealing with only one particle type (in most cases the electron) and the test particles were modeled as point-particles. The force acting on a particle was obtained by summation over the $N - 1$ interactions with the other test particles. In such a particle-particle (PP) model, $N(N - 1)/2$ interactions have to be taken into account per time step, which severely limits the number of test particles that can be employed.

This problem was solved with the introduction of the Particle-In-Cell (PIC) method in the mid sixties by Buneman and Hockney [2] for application to plasmas, after the
method had originally been invented around 1955 by Harlow et al. [3, 4] for applications in compressible fluids. In the PIC method, a spatial grid (mesh) is defined on which the charge and current densities are accumulated through an interpolation scheme. The Maxwell equations can then be solved on this grid, and the electric and magnetic fields can be interpolated back to the positions of the test particles. With this particle-mesh (PM) technique, the number of computational operations per time step is proportional to \( N \), which allows for much more particles to be followed.

In such plasma models, the error that is made in the calculation of the Coulomb interaction depends on the type of the interpolation scheme that is used in the calculation of the charge density. The simplest (zeroth order) interpolation scheme is the nearest grid point (NGP) scheme in which the charge of the test particle is simply assigned to the nearest grid point. The Cloud-In-Cell (CIC) scheme is a first order interpolation scheme in which a charge is distributed between the two nearest grid points (for a one-dimensional mesh). The fraction of the charge assigned to one of these grid points is proportional to the distance between the position of the charge and the other neighboring grid point. The concept of the CIC interpolation can also be applied to a two-dimensional grid. Here, the charge is divided between the four nearest grid points, where each point receives a fraction of the charge proportional to the area of the rectangle spanned by the particle and the diagonally opposed grid point.

The accuracy of these interpolation schemes can be seen in Fig. 5.1, which shows a comparison of the NGP and CIC forces to the actual Coulomb force between two oppositely charged particles as a function of their inter-particle separation. For this calculation, a one-dimensional grid is used with a total size \( L \) of 10 grid spacings \( L = 10\Delta x \) and we assume periodic boundary conditions.

![Figure 5.1:](image)

**Figure 5.1:** Electric force between a negative and a positive charge as a function of their inter-particle separation for the nearest grid point (NGP) scheme (dotted line) and the Cloud-In-Cell (CIC) scheme (dashed line) compared to the Coulomb force (solid line) on a one-dimensional grid with a total size of 10 grid spacings \( (L = 10\Delta x) \) and with periodic boundary conditions.
Clearly, the CIC force is more accurate than the stepwise force of the NGP interpolation scheme. However, at inter-particle distances smaller than one grid spacing, both schemes fail to accurately represent the Coulomb interaction.

Models [5, 6] have also been developed that combine PP interactions at small inter-particle distances with PM interactions at larger length scales. These models are often referred to as PP-PM or \( \text{P}^3\text{M} \) methods.

### 5.1.1 Particle-In-Cell

In this thesis, we apply a Particle-In-Cell (PIC) model (PM method with CIC interpolation scheme) to investigate the EUV-induced plasma, because we are primarily interested in the collective behavior of the plasma, which is largely determined by the long-range Coulomb interactions. The introduction of the spatial grid smoothens the short-range Coulomb interactions and charge fluctuations at distances smaller than the grid size spacing \( \Delta x \) are not resolved. Therefore, in PIC plasma simulations the grid spacing must be smaller than smallest length scale of the plasma [7], given by the Debye length. A similar restriction applies to the time-domain, i.e. the time step \( \Delta t \) in a PIC model must be smaller than the fastest relevant time-scale of the plasma [8], which is the period of the plasma frequency. In addition, the grid size \( \Delta x \) and time step \( \Delta t \) must be chosen in such a way that a particle cannot move more than one mesh spacing in one time step. This is needed to preserve the self-consistency of the simulation [2].

The introduction of the spatial grid can also cause numerical heating as a result of aliasing [2, 7]. The finite size of the grid implies that the fields that are defined on the grid points are discrete samples of continuous fields. According to the Nyquist-Shannon theorem [9] the smallest spatial structure that can accurately be represented on the mesh has a size \( 2\Delta x \), or alternatively formulated in the language of Fourier transforms, the shortest wavelength \( \lambda_s \) that can be represented is \( \lambda_s = 2\Delta x \). This implies that any smaller spatial structure will be falsely interpreted by the grid and show up as long wavelength oscillations in the simulation. In this way, aliasing is feeding energy from the short wavelength modes into modes supported by the grid: numerical heating.

In PIC plasma simulations, the position \( \mathbf{x} \) and velocity \( \mathbf{v} \) of each particle of mass \( m \) and charge \( q \) is updated after each time step based on the Newton-Lorentz equations of motion

\[
\frac{d\mathbf{x}}{dt} = \mathbf{v}, \\
\frac{d\mathbf{v}}{dt} = \frac{q}{m} (\mathbf{E} + \mathbf{v} \times \mathbf{B}),
\]

with electric field \( \mathbf{E} \) and magnetic field \( \mathbf{B} \). For application to the EUV-induced plasma, the \( \mathbf{v} \times \mathbf{B} \) contribution to the Lorentz force can be neglected. For reasons of computational resources, our PIC model is limited to one spatial dimension.
5.1 Introduction

In order to discretize the equations of motions, we apply the so-called leap-frog scheme, which is second order accurate in time for constant integration time step $\Delta t$

$$x^{n+1} = x^n + v^{n+1/2} \Delta t,$$

$$v^{n+1/2} = v^{n-1/2} + qE^n \Delta t/m,$$  \hspace{1cm} (5.3)

with $n \in \mathbb{N}$. Positions are defined at integral time steps, whereas velocities are calculated at half-integral time steps. In our one-dimensional model, the electric field only has a non-zero component $E$ in the direction of $x$, which is calculated from the electric potential $V$ by solving the Poisson equation on the grid, which is written in second order accurate terms as

$$\frac{V_{i+1} - 2V_i - V_{i-1}}{\Delta x^2} = -\frac{\rho_i}{\varepsilon_0},$$  \hspace{1cm} (5.4)

with $\rho_i$ the space charge density at the $i$-th grid point. The electric field $E_i$ at a grid point can then be obtained from the electric potential of its neighboring grid points

$$E_i = \frac{V_{i+1} - V_{i-1}}{2\Delta x}.$$  \hspace{1cm} (5.5)

The electric field at the position of the particle $E(x)$ can be found by applying the same CIC interpolation scheme

$$E(x) = \frac{(x_{i+1} - x) \cdot E_i + (x - x_i) \cdot E_{i+1}}{\Delta x}.$$  \hspace{1cm} (5.6)

After each time step it is checked whether particles have moved beyond the boundaries of the simulation in which case they are removed from the plasma. Thereafter, it is checked whether the particle has collided with another particle. For this purpose, the PIC method is combined with the method of Monte Carlo collisions.

5.1.2 Monte Carlo collisions

When the ionization degree of a plasma is sufficiently low, the density $n$ of the neutral ground state particle species in the plasma can be considered constant across the volume of the plasma with a value that can be derived from the equation of state $p = nk_BT$. Other species in the plasma, like electrons, ions and excited state neutrals are represented in the model by super-particles, where each super-particle represents $10^7 - 10^9$ real particles. Each super-particle has the same charge to mass ratio as each of the many real particles it represents, and therefore, the super-particle will react in the same way to electromagnetic forces as real particles would. In many cases, the density of these species is sufficiently low that it is not necessary to consider collisions amongst these particles themselves at the time scales of interest. Only collisions with ground state neutrals, which have a much higher density, have to be taken into account through the method of Monte Carlo collisions [10, 11].

In this method, random numbers are used to sample a number of probabilistic distribution functions that describe, when a collision occurs, what the type of collision is, and
what the outcome of the collision is. In the next section, this will be explained in more detail, and a more elaborate description can be found in [12].

Besides Monte Carlo collisions, other methods can be applied to treat collisions in a plasma. The direct simulation Monte Carlo (DSMC) technique, originally developed for the simulation of dilute gas flows [13], can be combined with the Particle-In-Cell method (PIC-DSMC) by introducing a second, courser mesh on which the collisions are evaluated [14].

Collisions do not only occur in the plasma volume, but also when a particle strikes the plasma boundaries. Monte Carlo (MC) or molecular dynamics (MD) simulations can be applied to describe the sputtering of the target [15, 16].

In this thesis, a PIC model is combined with the Monte Carlo method to describe the collisions in the plasma volume. For the description of the sputtering of multilayer mirrors by the EUV-induced plasma, MD simulations are not used. Instead, a more simple approach is taken. Every time an ion hits the mirror in the PIC-MC model, the damage to the mirror is assessed using a semi-empirical fit formula [17, 18] for the sputter yield (the number of atoms removed per incoming ion as a function of the impact energy of the ion). The damage is then multiplied by the particle weight of the ion, which is equal to the number of real ions the simulation particle represents. Measurements have been conducted to verify the applicability of the sputter yield function for the combination of argon ion projectiles on a ruthenium target. These will be presented in Chapter 9.

In this chapter, we will describe the PIC-MC model and calculate the rate at which the mirror is sputtered by the $\text{Ar}^{+}$ ions. In Chapter 6, we investigate the effect of the photo-electron emission from the mirror on the sputter rate, and extend the PIC-MC model to also incorporate sputtering by $\text{Ar}^{2+}$ ions. In Chapter 7, the dependence of the sputter rate on parameters such as the pressure and EUV irradiation is studied. Thereafter, in Chapter 8 the effect of adding hydrogen to the gas mixture is investigated. The remainder of this chapter is a integral representation of an earlier publication [19].

5.2 Particle-In-Cell Monte Carlo simulations of an extreme ultra-violet radiation driven plasma

To meet the semi-conductor industries continuous demand for printing ever-smaller structures on silicon wafers, future lithographic tools are designed to operate using Extreme Ultra-Violet (EUV) radiation in a 2% bandwidth around the central wavelength of 13.5 nm. Since no material is sufficiently transparent to EUV radiation, refractive optics cannot be used and instead multi-layer coated mirrors are required [20].

Additionally, as the mean free path of EUV radiation at atmospheric pressures is very short, the whole optical path is contained in a vacuum system. The residual argon background gas at a pressure of $0.1 - 1$ Pa, is (partially) photo-ionized by the EUV radiation, creating a weakly-ionized plasma. The EUV radiation is generated by a hollow cathode discharge [21, 22], which generates EUV-pulses of approximately 100 ns duration at a repetition rate of typically 1 kHz. Consequently, the plasma will show strong time-dependence.
As a result of the low plasma density ($n_e \approx 10^{15} \text{ m}^{-3}$) recombination will occur predominantly on the walls of the tool. Like in any bounded plasma, a plasma sheath will develop in which the ions will be accelerated towards the vessel walls. The plasma is potentially dangerous to the optical elements in case the ions will gain enough energy to damage the multi-layer mirrors through physical sputtering. A plasma model is applied to calculate the flux and energy of the ions impacting on the mirror.

The low plasma density and the strong time dependence imply that the plasma is far from equilibrium. Furthermore, at such a low pressure the plasma is in the non-local regime and a kinetic model is needed for an accurate description. Particle-In-Cell (PIC) kinetic models provide a way to self-consistently calculate the fields and the energy and velocity distributions, without the need for equilibrium assumptions [2, 10]. Collisions can be represented statistically by combining PIC methods with Monte Carlo collisions (MC) [11].

### 5.3 Description of the model

The plasma is simulated using a Particle-In-Cell Monte Carlo code, which is one-dimensional in configuration and three-dimensional in velocity space. Electrons and argon ions are computationally represented by ‘super-particles’. Each super-particle corresponds to typically $10^9$ real particles. The computational grid divides the plasma into a number of cells. Each cell must contain at least 100 particles to ensure proper statistics.

The PIC scheme will be described only briefly as this is well documented elsewhere [2, 10]. The general scheme of the explicit PIC model is shown in Fig. 5.2. For each time step $\Delta t$:

1. Charges are assigned to the nodes of the computational grid by a linear weighing, the so-called Cloud-In-Cell scheme [23];

2. The Poisson equation is solved to obtain the electric field at the nodes;

3. To determine the force on each particle, a linear weighing is applied to find the electric field at each particle position;

4. The Newton equations of motions are applied to advance the position and velocity of the particles. Positions and fields are defined at integral time levels whereas velocities are defined at half-integral time levels;

5. Particles that have moved beyond the boundaries of the computational grid are removed;

6. The Monte Carlo routine checks if a particle has collided and adjusts the velocity accordingly.
5.4 Monte Carlo collisions

In the model, charged particles collide with neutrals only. Because of the low plasma density, collisions between charged particles can be neglected. A collision is treated here as an instantaneous process that only changes the particle’s velocity. Assume that the particle species have \( N \) types of collisions with the background gas. The total collision cross-section \( \sigma_T(E) \) is the sum

\[
\sigma_T(E) = \sum_{i=1}^{N} \sigma_i(E),
\]

(5.7)

where \( E \) is the kinetic energy of the incident particle and \( \sigma_i(E) \) the cross-section for the \( i \)th type of collision. The flight time between collisions depends on the background density \( n(x) \) and the energy and is equal to the inverse of the collision frequency \( \nu \)

\[
\nu(x, E) = n(x)\sigma_T(E)\sqrt{\frac{2E}{m}},
\]

(5.8)

with \( m \) the incident particle mass. The probability \( P(t)dt \) that a particle will experience a collision within an infinitesimal time interval \( dt \) after having travelled through the background gas for a time \( t \) is

\[
P(t)dt = \nu \exp(-\nu t)dt.
\]

(5.9)

To determine when a collision takes place, we have to integrate equation (5.9) along the particle trajectory. Numerically this is very time consuming because the background density and the kinetic energy of the particle change along its path and we have to calculate \( \nu \) after each time-step \( \Delta t \) of the PIC loop. Therefore, we use a numerical trick called ‘null collision method’ [11] to speed-up the calculations. For this purpose, an extra collision type is introduced, which has a cross-section such that, when added to equation (5.7), results in a total collision frequency with a constant value \( \nu_m \)

\[
\nu_m = \max_{x,E} \left\{ n(x)\sigma_T(E)\sqrt{\frac{2E}{m}} \right\}.
\]

(5.10)
In our case, the plasma is only weakly ionized with a homogeneous background density and we only have to obtain the maximum over $E$. The extra collision type is called ‘null-collision’ as no real interaction occurs. To obtain the time $t_m$ to the next collision, we integrate the right-hand side of equation (5.9) from zero to $t_m$ replacing $\nu$ by $\nu_m$ and equate the left-hand side to $R \in [0, 1)$, a random number between zero and one. All random number mentioned hereafter, are drawn from this interval. Solving for $t_m$ gives

$$t_m = -\frac{\ln (1 - R)}{\nu_m}. \quad (5.11)$$

Upon creation at time $t_0$, each individual particle is assigned a collision time $t_c = t_0 + t_m$. After each time step of the PIC loop it is evaluated whether the particle needs to collide, i.e. it is checked if $t \geq t_c$. If so, the collision frequency $\nu_i(E)$ of each process at $t_c$ is calculated to determine the collision type from

$$0 < R \leq \frac{\nu_1(E)}{\nu_m} \quad \text{type 1}$$
$$\frac{\nu_1(E)}{\nu_m} < R \leq \frac{\Sigma_i \nu_i(E)}{\nu_m} \quad \text{type 2}$$
$$\ldots$$
$$\frac{\Sigma_i \nu_i(E)}{\nu_m} < R < \frac{\Sigma_i \nu_i(E)}{\nu_m} \quad \text{null collision}$$

with $R$ a random number. Once the collision type is determined the velocity of the particle is adjusted accordingly. After the collision the time to the next collision $t_m$, using equation (5.11), is added to the particle’s collision time.

### 5.4.1 Collision types

The following binary collision types are taken into account

1. Elastic electron-neutral collisions:
   $$e^- + \text{Ar} \rightarrow e^- + \text{Ar};$$

2. Inelastic electron-neutral collisions:
   $$e^- + \text{Ar} \rightarrow e^- + \text{Ar}^*;$$

3. Electron-impact ionization collisions:
   $$e^- + \text{Ar} \rightarrow 2e^- + \text{Ar}^+;$$

4. Elastic ion neutral collisions:
   $$\text{Ar}^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{Ar};$$

5. Charge-exchange collisions:
   $$\text{Ar}^+ + \text{Ar} \rightarrow \text{Ar} + \text{Ar}^+.$$}

Cross-sections for these processes are the same as the ones used by Phelps [24] for their description of cold-cathode discharges over a wide range of electric field to gas density ratios ($E/n = 15 \text{ Td}$ to $100 \text{ kTd}$). The collision frequencies for electron-argon scattering associated with these cross-sections are plotted in Fig. 5.3.
5.4.2 Electron-neutral collisions

Elastic collisions

In the low energy limit, electron-neutral scattering is isotropic, but at higher energies the scatter angle $\theta$ will increasingly be in the forward direction. In the first Born-approximation [25] the quantum mechanical differential cross-section $\sigma(\varepsilon, \theta)$ for screened-Coulomb electron-neutral scattering is given by [26]

$$\frac{\sigma(\varepsilon, \theta)}{\sigma(\varepsilon)} = \frac{1}{4\pi} \frac{1 + 8\varepsilon}{(1 + 4\varepsilon - 4\varepsilon \cos \theta)^2},$$  \hspace{1cm} (5.12)

with $\varepsilon = E/E_0$ a dimensionless energy parameter and $E_0 = 27.21$ eV the atomic unit of energy, which can be expressed in fundamental constants. For atomic collisions, scattering is isotropic in the azimuthal direction and therefore the differential cross-section does not depend of the $\varphi$-coordinate. The scattering angle $\varphi$ in the azimuthal direction is found from $\varphi = 2\pi R$ with $R$ a random number. To find the scattering angle $\theta$ of an electron in the polar direction, we sample the angle from the differential cross-section. For this purpose, we first calculate the cumulative probability by integration of equation (5.12) over all solid angles with $\theta' \in [0, \theta]$ and equate the result to a random number

$$R = 2\pi \int_0^\theta \frac{\sigma(\varepsilon, \theta')}{\sigma(\varepsilon)} \sin(\theta')d\theta'. \hspace{1cm} (5.13)$$

Solving for $\theta$ yields

$$\theta = \arccos \left(1 - \frac{2R}{1 + 8\varepsilon(1 - R)}\right). \hspace{1cm} (5.14)$$
This expression gives the scattering angle for an electron with dimensionless energy $\varepsilon$ in the center-of-mass frame. Because the electron-neutral mass ratio is a very small number, energy transfer from the electron to the neutral will be small and the scattering angle in the laboratory frame will be approximately the same.

**Excitation**

In inelastic collisions, energy is transferred to the internal states of the argon atom. In the model, all internal states are merged into one single excitation level with an energy of $E_{\text{exc}} = 11.5$ eV above the argon ground state [24]. First, the excitation energy is subtracted from the electron kinetic energy after which the scattering angle is determined from equation (5.14).

**Ionization**

If the kinetic energy $E_{\text{in}}$ of the incoming electron is above the argon ionization energy $E_{\text{ion}}$, an ionizing electron-argon collision can occur, in which an electron-ion pair is created. The excess energy $E_{\text{in}} - E_{\text{ion}}$ is carried away by the two electrons, whereas the kinetic energy of the ion will be equal to the initial (thermal) energy of the neutral. In the model, the velocity of the target neutral is sampled from a Maxwellian velocity distribution that corresponds to a temperature of $T = 300$ K.

It is not possible to predict how the excess energy will distributed between the incoming and ejected electron. Therefore, we apply an empirical formula for the distribution function based on the work of Opal [27] as mentioned in Surendra and Graves [28]

$$S(E_{\text{in}}, E_{\text{ej}}) = \frac{A}{E_{\text{ej}}^2 + B^2(E_{\text{in}})},$$

with $A$ a normalization constant that can be obtained from integration over $E_{\text{ej}}$ from 0 to the maximum energy $E_{\text{max}} = (E_{\text{in}} - E_{\text{ion}})/2$, which is half the excess energy due to the indistinguishability of the two electrons involved

$$A = \left\{ \int_0^{E_{\text{max}}} S(E_{\text{in}}, E_{\text{ej}}) dE_{\text{ej}} \right\}^{-1}$$

$$= \frac{B(E_{\text{in}})}{\arctan \left[ (E_{\text{in}} - E_{\text{ion}})/2B(E_{\text{in}}) \right]}.$$  

For argon $B(E_{\text{in}}) \approx 10$ eV in the energy range $1 - 70$ eV [27].

Upon collision, we first obtain the energy of the ejected electron by drawing a random number $R$ to sample the distribution of equation (5.15) according to

$$E_{\text{ej}} = B(E_{\text{in}}) \tan \left[ R \arctan \left( E_{\text{max}}/B(E_{\text{in}}) \right) \right].$$

The ejected electron is created at the position of the incoming electron and the scattering angle is determined by equation (5.14). Next, the energy of the incoming electron is reduced by the sum of the ionization energy and the energy of the ejected electron after which the scattering angle is again determined from equation (5.14).
5.4.3 Ion-neutral collisions

Because the masses of ions and neutrals are almost the same, the collisional energy exchange between them is considerable and has to be properly taken into account. Therefore, collisions between ions and argon atoms are treated in the center-of-mass frame. The velocities of the target neutrals are sampled from a Maxwellian velocity distribution at room temperature ($T = 300$ K). For ion collisions, we assume scattering to be isotropic with a scattering angle in the center-of-mass frame equal to

$$\theta = \arccos (1 - 2R),$$

with $R$ a random number. After the collision the velocity of the argon ion is transferred back to the laboratory frame.

5.5 Generation of particles

Figure 5.4 shows a schematic of the geometry used in the simulations. The radiation driven plasma is bounded by a multi-layer mirror on the left side and a metal wall on the right side. The top layer of the mirror is assumed to be ruthenium, because in EUV lithography this material is often applied as a capping layer (thickness of $\approx 1.5$ nm) to provide a barrier against oxidation of the underlying Mo/Si multi-layers [29]. Both multi-layer mirror and wall are assumed to be grounded. At the multi-layer mirror the EUV radiation is partially reflected, with a reflection coefficient of typically $R_{ml} = 68\%$ [30]. The remaining 32% of the radiation is absorbed by the mirror material and is transformed mainly into heat.

![Figure 5.4: Schematic of the geometry used in simulations. The EUV radiation is partially reflected by the mirror. It is assumed that the EUV radiation between the mirror on the left and a plain wall on the right to be monochromatic and homogeneous in intensity.](image)

The spatial distribution of the EUV radiation is assumed to be homogeneous, whereas the temporal distribution $G(t)$ is modelled with a cut-off Gaussian with a total duration
of $2\tau = 100$ ns

$$G(t) = \frac{\alpha I_p}{\tau} \exp \left[ -\frac{(t-\tau)^2}{2\tau^2} \right], \text{ for } 0 < t < 2\tau, \quad (5.19)$$

with $\alpha$ a numerical constant to normalize $G(t)$ to the pulse-averaged EUV intensity $I_p$.

Electron-ion pairs are generated as a result of photo-ionization of the argon background gas. The EUV photon energy of $h\nu = 92$ eV is well above the argon ionization energy $E_{ion} = 15.8$ eV. Consequently, in the volume argon can be photo-ionized by EUV radiation, creating a fast electron with kinetic energy $T_e = h\nu - E_{ion}$ and a slow Ar$^+$ ion, with kinetic energy equal to the thermal energy of argon at room temperature.

The total number $N_{pi}$ of photo-ionization events per EUV-pulse per $m^3$ is equal to

$$N_{pi} = \frac{I_p}{h\nu L} \left[ 1 - \exp(-n_{Ar}\sigma_{ph}L_{opt}) \right], \quad (5.20)$$

with $I_p$ the pulse averaged EUV intensity, $n_{Ar}$ the argon density, $\sigma_{ph}$ the photo-ionization cross-section [31] and $L_{opt} = L(1 + R_{ml})$ the effective optical path length that takes into account the partial reflection of the EUV beam from the mirror as indicated in Fig. 5.4.

### 5.6 Results/Discussion

The simulation parameters are listed in table 5.1. The chosen EUV intensity is typical for our laboratory setup. In our simulations, we set the argon background pressure at 0.5 Pa. At this low pressure the plasma will be in the non-local regime and the plasma sheath will be almost, but not quite, collisionless, as we estimate the average number of ion-neutral collisions for an ion crossing the sheath with an energy between $20 - 100$ eV to be $\approx 0.2$.

**Table 5.1: Simulation parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Background density</td>
<td>$n_{Ar}$</td>
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<tr>
<td>EUV intensity</td>
<td>$I_p$</td>
</tr>
<tr>
<td>Time step</td>
<td>$\Delta t$</td>
</tr>
<tr>
<td>Particle weight</td>
<td>$PW$</td>
</tr>
<tr>
<td>Number of cells</td>
<td>$N_c$</td>
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<tr>
<td>Length</td>
<td>$L$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$n_{Ar}$</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$I_p$</td>
<td>$6 \times 10^{-4} W m^{-2}$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$1 \times 10^{-12}$ s</td>
</tr>
<tr>
<td>$PW$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>$N_c$</td>
<td>300</td>
</tr>
<tr>
<td>$L$</td>
<td>$5 \times 10^{-2}$ m</td>
</tr>
</tbody>
</table>

We divide the length of the computational domain into $N_c = 300$ cells, so that the cell size is smaller than the Debye screening length, which is $\lambda_D \approx 5 \times 10^{-4}$ m for our application. Each species is represented by $10^5$ super-particles to ensure proper statistics. The time step of the PIC-loop must be small compared to the time it takes a fast electron
Chapter 5: Numerical Simulations

to travel across a cell, which for a 100 eV electron and for our cell size corresponds to \( \approx 30 \) ps. This is two orders of magnitude smaller than the fastest time-scale of the plasma, which is given by the inverse of the plasma electron frequency.

Figure 5.5 shows the cell-averaged energy of the plasma electrons as a function of position at various times. Initially, the plasma is very hot and the energy of the electrons is close to \( h\nu - E_{ion} \approx 76 \) eV. The plasma cools mainly due to inelastic and ionizing collisions of electrons with the neutral background. After the 100 ns long EUV-pulse the photo-ionization process ceases and the average electron energy decreases rapidly as no more fast electrons are generated. As can be seen in Fig. 5.5, the spatial fluctuations of the average electron energy decrease with time as more super-particles are added to the simulation, thereby improving the statistical representation.

\[ \text{Figure 5.5: Cell-averaged electron energy profile at five different times.} \]

The development of the plasma sheath can be seen in Fig. 5.6, which shows the plasma density profile near the mirror region at three different times. Near the mirror, the ion density exceeds the electron density and a positive space charge region forms as the highly mobile electrons have escaped to the wall, leaving the more inert ions behind. At the end of the EUV-pulse, most electrons still have sufficient kinetic energy to cause further ionization processes. That is why the maximum plasma density \( n_e = 4 \times 10^{15} \text{ m}^{-3} \) is reached long after the EUV-pulse at \( t = 500 \) ns. After that, the plasma density starts to decay on a timescale that is short compared to the time between EUV-pulses.

The formation of the plasma sheath can also be studied by considering the potential, shown in Fig. 5.7. The maximum plasma potential of \( \approx 80 \) Volts is reached during the EUV-pulse. The plasma is at a positive potential with respect to the walls as a result of the positive space charge in the sheath, thus creating an electric field in the sheath that directs electrons into the plasma and accelerates ions towards the walls. After the EUV-pulse \( (t > 100 \text{ ns}) \) the plasma potential gradually decreases, because the charge separation in the plasma sheath is reduced as a result of the decrease in average electron energy.
In Fig. 5.8, the kinetic energy of ions impacting on the mirror is shown as a function of time. For clarity’s sake, the moving average over 50 consecutive ion impacts is taken. The dotted line shows the temporal shape of the EUV-pulse. Due to their inertia the ions reach the mirror after the EUV-pulse. The ion impact energy reaches a maximum of \( \approx 40 \) eV at \( t = 270 \) ns.

Whether this ion bombardment translates into mirror damage goes beyond this model. It needs to be determined experimentally. However, as a first order estimation we can apply the Bohdansky [17] model for light ion sputtering. This semi-empirical model gives the sputter yield \( Y(E) \), i.e. the number of atoms removed from the solid per incoming ion with energy \( E \). Only ions with an energy above the sputter threshold contribute. The sputter threshold can be calculated from

\[
E_{th} = \begin{cases} 
\frac{U_s}{8U_s \left( \frac{m_1}{m_2} \right)^2} & \text{for } \left( \frac{m_1}{m_2} \right) < 0.3 \\
\frac{38}{5} U_s \left( \frac{m_1}{m_2} \right)^2 & \text{for } \left( \frac{m_1}{m_2} \right) > 0.3 
\end{cases}
\]  

(5.21)

with \( U_s \) the surface binding energy of the solid which can be approximated by the sublimation heat and with \( \lambda \) the fraction of energy that is transferred from the projectile (with mass \( m_1 \)) to the target atom (with mass \( m_2 \)) in case of a head-on collision

\[
\lambda = \frac{4m_1m_2}{(m_1 + m_2)^2}.
\]

(5.22)

For Ar\(^+\) on Ru \( \lambda = 0.812 \), \( U_s = 6.74 \) eV and \( E_{th} = 37.2 \) eV.

In Fig. 5.8, the sputter threshold is indicated by the bold dashed line. Only a fraction of the ions has an impact energy above the sputter threshold. Therefore, we expect the damage to the mirror as a results of physical sputtering to be modest.
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**Figure 5.7:** Potential profile at five different times: at $t = 10$ ns (thick solid line), $t = 50$ ns (dashed line), $t = 100$ ns (dotted line), $t = 200$ ns (dash-dotted line) and $t = 1000$ ns (thin solid line).

**Figure 5.8:** Solid line: the energy in eV’s of ions that have impacted on the mirror. For clarity, the depicted energy is the moving average over fifty consecutive ion impacts. Dotted line: the temporal profile of the EUV intensity in arbitrary units. Dashed line: the Boldansky sputter threshold.
A word of caution is in place. Because the ion energies are close to the sputter threshold the calculated sputter rate is very sensitive to the value for the sputter threshold. For instance, the Yamamura [18] model for ion sputtering predicts a sputter threshold that is 10 eV lower. Figure 5.9 shows the sputter yield according to the Bohdansky and Yamamura model together with the, to our knowledge, only available experimental data set [32] for this specific target-projectile combination.

![Figure 5.9: Sputter yield for Ar$^+$ on Ru as a function of ion energy according to the Bohdansky model (solid line), the Yamamura model (dashed line) and the experimental data of Laegreid and Wehner (circles).](image)

If we convolute the sputter yield with the ion flux we obtain the total number of atoms removed per EUV-pulse. For the Bohdansky and Yamamura model, this amounts to respectively 6.2 and 205 nm per $10^{12}$ EUV-pulses. Clearly, the Yamamura model predicts higher sputter rates than the Bohdansky model mainly due to the lower sputter threshold. The predicted sputter rates are too low to be experimentally verified. In the calculation of the sputter rate, we have only considered the impact of ions. However, charge-exchange collisions in the sheath region will result in a flux of fast neutrals to the mirror surface, that will also contribute to the sputter rate. In our low-pressure application, the neutral flux is very low, because the mean free path for charge-exchange collisions for energetic ions ($E = 30 - 100$ eV) is $\approx 10$ times higher than the thickness of the plasma sheath. Hence, sputtering by neutrals can be neglected.

### 5.7 Conclusions

In conclusion, we have demonstrated that with PIC-MC simulations it is possible to describe transient plasmas in the non-local regime without the need for equilibrium assumptions for the fields or the velocity distributions of the charged particles.
Furthermore, the EUV radiation driven plasma is found to be weakly-ionized (ionization degree \(< 0.1\%\)) with a low plasma density \(n_e = 4 \times 10^{15} \text{ m}^{-3}\).

The simulations show that the potential drop across the plasma sheath is dictated by the electron energy. Ions are accelerated across the sheath, but due to their inertia, most ions reach the mirror after the EUV-pulse has ended.

Based on two models for the sputter yield, we conclude that only a small fraction of the ions impacting on the optics will have sufficient energy to sputter. However, the calculated sputter rate strongly depends on which model is applied, mainly because the two models employ a different value for the sputter threshold. Further experimental investigation is required to determine the value of the sputter threshold. The predicted sputter rate is very low \(< 1 \text{ nm per } 10^9 \text{ EUV-pulses}\) and cannot be measured directly. Future investigations should aim to verify the other predictions of the simulations regarding the ion impact energy distribution, plasma density and electron energy distribution.

Bibliography


Abstract. With Particle-In-Cell Monte Carlo simulations the plasma parameters of the extreme ultra-violet radiation driven plasma can be predicted, as was shown in the previous chapter. The simulations aim to calculate the flux and energy distribution of ions that are accelerated in the plasma sheath towards the plasma boundaries, such as multilayer mirrors.

In this chapter, the PIC-MC model is extended to study the influence of photo-electron emission from the mirror on the sheath dynamics and on the ion impact energy distribution. Furthermore, the model predicts that the sputter rate is dominated by the presence of doubly ionized argon ions.
Chapter 6: Effect of photoelectron emission

6.1 Introduction

Over the last two decades lithography equipment, used in the chip-making industry, has seen a continuous shift towards shorter operating wavelengths in order to achieve shrinking device sizes and faster chip performance. Next generation lithography tools will use extreme ultra-violet (EUV) radiation with wavelength of 13.5 nm [1, 2]. As EUV radiation is strongly absorbed in virtually all materials, refractive optical elements, such as lenses cannot be used and instead multilayer coated mirrors [3] are required for imaging.

Furthermore, to decrease absorption losses, the optical path is enclosed in a vacuum system. However, the residual argon background gas at a pressure of $1 \times 10^{-1}$ Pa will be partially photoionized by the EUV radiation, which will generate a weakly-ionized plasma in the tool.

Like in any bound plasma, a plasma sheath will develop, in which the ions will be accelerated towards the plasma boundaries such as multilayer mirrors. Provided the potential drop across the plasma sheath is large enough, the ions will gain sufficient kinetic energy to cause damage to the multilayer mirrors through physical sputtering. Our aim is to model the plasma sheath region to calculate the flux and energy of the ions impacting on the mirrors.

The plasma description is made more arduous by the transient nature of the EUV sources. A hollow cathode discharge [4] is employed to generate EUV pulses with a duration of approximately 100 ns at a repetition frequency of typically 1 kHz.

Because of the low plasma density ($n_e \approx 10^{15}$ m$^{-3}$) and the strong time dependence the plasma will be far from equilibrium. The low pressure implies that the plasma is in the nonlocal regime and a kinetic model is required for an accurate description. For this reason, we apply a Particle-In-Cell (PIC) model [5]. The main advantage of such a model is that it enables the self-consistent calculation of the fields and the energy and velocity distributions, without the need for equilibrium assumptions [6]. PIC models have the disadvantage that they are computationally demanding [7]. Collisions between charged species and background neutrals can be represented statistically by combining PIC methods with Monte Carlo collisions (MC) [8, 9].

In our earlier work [10] a PIC-MC model was presented that had been applied to describe the development of the plasma sheath and to calculate the energy at which the ions impact on the mirror. It was found that the impact energies of the ions are in the near-threshold sputter regime [11], where the sputter yield (i.e., the number of atoms removed per incoming ion) strongly depends on the ion impact energy.

In this paper, we aim to study the effect of photo-electron emission from the mirror surface on the energies of the ions impacting on the mirror. The electrons, that are emitted due to the photo-electric effect when the EUV radiation strikes the mirror, will influence the sheath dynamics.

Furthermore, we have added the double photoionization process to the model. Doubly ionized atoms will gain twice the amount of energy in the plasma sheath compared to singly ionized atoms, and will therefore substantially contribute to the sputter rate.

Details of the PIC-MC model can be found in Ref. [10] and we will only give a short
6.2 Model description

The PIC-MC code is one dimensional in configuration and three dimensional in velocity space. Charged species are computationally represented by ‘superparticles’. Each superparticle corresponds to typically $10^9$ real particles. A computational grid divides the plasma into a number of cells. Each cell must contain a sufficient number of particles (> 100) to ensure proper statistics.

The general scheme of the explicit PIC model is shown in Fig. 6.1. For each time step $\Delta t$:

1. The particle charges are assigned to the nodes of the computational grid by a linear weighing [12].

2. The Poisson equation is solved on the nodes to obtain the electric field.

3. A linear weighing is applied to find the electric field at the position of each superparticle.

4. The Newtonian equations of motions are applied to advance the positions and velocities of the super particles using a second order leapfrog scheme.

5. The particles that have moved beyond the boundaries of the computational grid are removed from the simulation.

6. The MC routine checks if a particle has collided with the background gas and adjusts the velocity accordingly. New superparticles are created in the case of an ionizing collision.

In the model, only collisions between charged particles and neutrals are taken into account. Collisions between charged particles can be neglected due to the low plasma density.

**Figure 6.1:** Particle-In-Cell scheme.
A collision is treated here as an instantaneous process that changes the particle’s velocity in both magnitude and direction. We use the ‘null collision’ technique [13] to determine the free-flight time of each particle between collisions. Because of the low ionization degree of the plasma, we can assume a homogeneous neutral density.

When a collision takes place, it is stochastically determined which type of collision occurs based on the relative collision frequencies of the relevant processes. The collision frequency of each process is proportional to the collisional cross section for that collision type and to the velocity of the particle. The following binary collision types are taken into account:

1. Elastic electron-neutral collisions:
   \[ e^- + \text{Ar} \rightarrow e^- + \text{Ar}; \]

2. Inelastic electron-neutral collisions:
   \[ e^- + \text{Ar} \rightarrow e^- + \text{Ar}^*; \]

3. Electron-impact ionization collisions:
   \[ e^- + \text{Ar} \rightarrow 2e^- + \text{Ar}^+; \]

4. Elastic ion-neutral collisions:
   \[ \text{Ar}^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{Ar}; \]

5. Charge-exchange collisions:
   \[ \text{Ar}^+ + \text{Ar} \rightarrow \text{Ar} + \text{Ar}^+. \]

Cross sections for these processes are the same as the ones used by Phelps [14].

First upon collision, the velocities of both particles are transformed to the center-of-mass frame. Then, the scattering angle is determined stochastically, based on the angular cross section at that energy. Next, the velocities of the particles are adjusted accordingly, and finally, the particle velocities are transformed back to the laboratory frame.

### 6.2.1 Plasma generation

In our simulations, the geometry shown in Fig. 6.2 is used. The EUV driven plasma is bounded by a multilayer mirror on one side and a metal wall on the other side. The mirror is assumed to have a ruthenium surface, because in EUV lithography this metal is often applied as a capping layer (thickness \( \approx 1.5 \) nm) to provide a barrier against oxidation of the underlying Mo/Si stacks [15]. The EUV radiation is partially reflected by the mirror with a reflection coefficient of \( R_{ml} = 68\% \), which is typical for Mo/Si multilayer mirrors [1, 16]. The remaining 32\% of the radiation is absorbed and is converted primarily to heat. In the model, the interaction between the EUV radiation and the wall is not taken into account. Both mirror and wall are assumed to be grounded.

Because the bandwidth of the radiation used in EUV lithography is very narrow (2\%), we can make the approximation that the EUV radiation is monochromatic. The EUV
6.2 Model description

Figure 6.2: Schematic of the geometry used in calculations. The EUV radiation is partially reflected by the mirror. The EUV radiation between the mirror on the left and a plain wall on the right is assumed to be monochromatic and homogeneous in intensity. Photo-electrons are only emitted from the surface of the mirror.

radiation is assumed to have a uniform intensity with a temporal distribution $G(t)$ that is modeled with a cutoff Gaussian with a total duration of $2\tau = 100$ ns

$$
G(t) = \frac{\alpha I_p}{\tau} \exp \left[ -\frac{(t - \tau)^2}{2\tau^2} \right], \text{ for } 0 < t < 2\tau,
$$

(6.1)

with $\alpha \approx 0.584$ a numerical constant to normalize $G(t)$ to the pulse-averaged EUV irradiance $I_p$.

Charged particles are generated in two ways:

1. Electron-ion pairs as a result of photoionization of the argon background gas.

2. Emission of electrons from the mirror surface as a result of the photo-electric effect.

Photoionization

The EUV photon energy of $h\nu = 92$ eV exceeds the argon photoionization threshold of $E_s = 15.8$ eV. In case of a photoionization event, an electron-ion pair is generated in the volume. As the momentum carried by the photon is negligible, the sum of the momenta of the created electron and ion must be approximately zero. This implies that most of the excess energy $T_e = h\nu - E_s$ will be transferred to the electron, because the $Ar^+$ ion is much heavier than the electron. In the model, it is assumed that the ion kinetic energy is equal to the thermal energy of the neutral prior to ionization. The ion, created in the photoionization process, receives an amount of kinetic energy sampled from a Maxwellian energy distribution at room temperature ($T = 300$ K).

The threshold for double photoionization of argon is $E_d = 43.4$ eV. This means, that besides singly ionized, also doubly ionized argon ions will be formed. For every double photoionization event, one $Ar^{2+}$ ion and two electrons are created. It is assumed that the $Ar^{2+}$ ion receives the kinetic energy of room temperature neutral argon, whereas the excess energy $T_e = h\nu - E_d$ is randomly distributed over the two electrons, i.e. the first electron receives an amount of energy $E_1 = R(h\nu - E_d)$ and the second electron $E_2 = (1 - R)(h\nu - E_d)$, with $R \in [0, 1)$ a random number.
Chapter 6: Effect of photoelectron emission

The total number $N_{pi}$ of single photoionization events per EUV pulse per $m^3$ is equal to

$$N_{ph} = \frac{2\tau I_p}{h\nu L} [1 - \exp(-n_{Ar}\sigma_s L)][1 + R_{ml} \exp(-n_{Ar}\sigma_s L)], \quad (6.2)$$

where the factor $2\tau$ arises from the integration of $I_p$ over the pulse duration, with $L$ the distance between the multilayer mirror and the wall, $n_{Ar}$ the argon density and $\sigma_s = 1.4 \times 10^{-22} m^2$ the single photoionization cross section at 92 eV [17]. Equation 6.2 takes into account the partial reflection of the EUV beam from the mirror with reflectivity coefficient $R_{ml}$. Because $n_{Ar}\sigma_s L \ll 1$, the plasma is optically thin for EUV radiation, and we can make the following approximation

$$N_{ph} \approx \frac{2\tau I_p}{h\nu} (1 + R_{ml}) n_{Ar}\sigma_s. \quad (6.3)$$

The same formula can be applied to calculate the total number of double photoionization events by replacing $\sigma_s$ with the double photoionization cross section $\sigma_d = 2.1 \times 10^{-23} m^2$ [18].

Photo-electric effect

The EUV radiation is partially absorbed in the multilayer mirror leading to the emission of photo-electrons from the surface (photo-electric effect). In case photon absorption takes place close to the surface, the generated primary electrons can directly escape the solid with a kinetic energy equal to the photon energy reduced by the work function or surface binding energy of the solid. However, as the absorption length for EUV radiation is much larger than the mean free path for electron-electron collisions in the solid, in most cases the primary electrons will undergo many scattering events before reaching the surface. This leads to the emission of low-energy secondary electrons from the solid. For photon energies above 100 eV, the shape of the energy distribution of secondary electrons emitted from the surface is essentially independent [19] of the photon energy and is given by

$$S(E_e, W) = \frac{6W^2E_e}{(E_e + W)^4}, \quad (6.4)$$

where $W$ is the work function or surface binding energy. We can sample the electron energy from this distribution according to

$$E_e = W \left[ \sqrt{\frac{4}{1 - R}} \cos \left( \frac{\pi - \arccos \sqrt{(1 - R)}}{3} \right) - 1 \right], \quad (6.5)$$

with $R \in [0, 1)$ a random number. The emitted electrons are assumed to have a $\cos(\theta)$ distribution around the surface normal, which is a good approximation as long as the electrons that are generated inside the solid by the photoionization process are distributed isotropically.
6.3 Results/Discussion

The simulation parameters are listed in table 6.1. The chosen background pressure and pulse-averaged EUV irradiance are typical for our laboratory EUV setup. The length of the computational domain is divide into $N = 300$ cells, so that the cell size is smaller than the Debye screening length $\lambda_D$, which is the characteristic length scale for charge separation in a plasma. For our application $\lambda_D \approx 5 \times 10^{-4}$ m. Each species is simulated with $10^5$ superparticles to ensure proper statistics. The time step of the PIC-loop must be small compared to the time it takes a fast electron to travel across a cell, which for a 100 eV electron and for our cell size corresponds to $\approx 30$ ps. This is two orders of magnitude smaller than the fastest time scale of the plasma, which is given by the inverse of the plasma electron frequency.

Table 6.1: Simulation parameters

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</tr>
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<td>$N = 300$</td>
</tr>
<tr>
<td>Length</td>
<td>$L = 5 \times 10^{-2}$ m</td>
</tr>
</tbody>
</table>

We investigate the following three cases to study the effect of the photo-electrons on
Chapter 6: Effect of photoelectron emission

the ion sputtering:

a No photo-effect.

b Primary photo-electrons only. The photo-electrons each have kinetic energy $h\nu - W$.

c Secondary photo-electrons only. A photo-electrons has a kinetic energy sampled from the energy distribution of Eq. (6.4), which is shown in Fig. 6.3.

In reality, about 50%–90% of the emitted photo-electrons can be expected to be low-energy secondary photo-electrons [19].

6.3.1 Plasma sheath

The formation of the plasma sheath near the mirror can be seen in Fig. 6.4, where the plasma density profile is shown at the start of the EUV pulse ($t=10\,\text{ns}$), at the maximum EUV intensity ($t=50\,\text{ns}$) and after the EUV pulse ($t=500\,\text{ns}$).

Figure 6.4(a) shows the case of no photo-effect. The depicted effective ion density $n^*_i = \rho^+ / e$ is equal to the charge density of all positive ions (both singly and doubly charged) scaled by the elementary charge. Near the mirror the ion density exceeds the electron density as the highly mobile electrons are lost at the wall leaving the more inert ions behind. At the end of the EUV pulse, most electrons still have sufficient kinetic energy to cause electron-impact ionization processes. Therefore, the plasma density reaches a maximum when the EUV pulse has already ended. It was found that the maximum of $n_e = 3 \times 10^{15} \, \text{m}^{-3}$ is attained 500 ns after the start of the 100 ns long EUV pulse. After that the plasma density starts to decay on a timescale that is long compared to the pulse duration, but short compared to the time between EUV pulses.

The photo-emission from the mirror changes the dynamics of the sheath buildup (Fig. 6.4(b) and Fig. 6.4(c)). At the start of the plasma formation ($t = 10\,\text{ns}$) the electron density exceeds the ion density near the mirror due to the emission of photo-electrons. In the case of secondary photo-electrons, the negative space charge is much more concentrated near the mirror, than in the case of the more energetic primary photo-electrons, which penetrate further into the plasma in the same amount of time. Somewhat later ($t = 50\,\text{ns}$) the volume effect becomes dominant as the electrons from the gas phase have had time to escape to the mirror surface.

Figure 6.5 shows the cell-averaged energy of the plasma electrons as a function of position. Initially, the electron energy of the electrons is close to $h\nu - E_{\text{ion}} \approx 76 \, \text{eV}$. After that, the average electron energy decreases due to inelastic collisions of electrons with the neutral background. The primary photo-electrons slightly increase the electron energy (Fig. 6.5(b)), because their initial energy $h\nu - W$ exceeds the 76 eV at which the gas phase electrons are generated. Likewise, in Fig. 6.5(c), we see a strong decrease of the average electron energy, as the secondary photo-electrons have much lower energies.

The formation of the plasma sheath can also be studied by considering the potential. Without photo-electric effect, we obtain symmetric potential profiles, as represented in
6.3 Results/Discussion

(a) No photo-electrons.  
(b) Primary photo-electrons.  
(c) Secondary photo-electrons.

Figure 6.4: Plasma density profile near the mirror at $t = 10$ ns, $t = 50$ and $t = 500$ ns. The thick lines show the electron density, whereas thin lines indicate the effective ion density $n_i^* = \rho^+ / e$. Three cases are shown: (a) No photo-effect. (b) Primary photo-electrons. (c) Secondary photo-electrons.
Chapter 6: Effect of photoelectron emission

(a) No photo-electrons. (b) Primary photo-electrons. (c) Secondary photo-electrons.

**Figure 6.5:** Cell-averaged electron energy at different times for three cases: (a) No photo-effect. (b) Primary photo-electrons. (c) Secondary photo-electrons.
6.3 Results/Discussion

(a) No photo-electrons.  
(b) Primary photo-electrons.  
(c) Secondary photo-electrons.

**Figure 6.6:** Potential profile at different times for three cases: (a) No photo-effect. (b) Primary photo-electrons. (c) Secondary photo-electrons.
Fig. 6.6(a). The maximum plasma potential of $\approx 75$ Volts is reached during the EUV pulse. The plasma is at a positive potential with respect to the walls as a result of the positive space charge in the sheath. After the EUV pulse ($t > 100$ ns) the plasma potential gradually decreases because the average electron energy decreases. If we compare the case of no photo-effect to our earlier results [10], we find that including the double photoionization process to the model does not significantly alter the electron density, the mean electron energy or the potential.

Figure 6.6(b) and 6.6(c) show the potential profiles in case of, respectively, primary and secondary photo-electrons. The negative space charge near the mirror in the early stages of the plasma is reflected by the negative potential near the mirror at $t = 10$ ns. Now, the maximum in the plasma potential occurs after the EUV pulse, because it takes more time to overcome the negative space charge and buildup the positive space charge near the mirror. The maximum in the plasma potential is lower because the average electron energy is lower after the EUV pulse.

![Graph](image1)

(a) Ar$^+$ ions.  
(b) Ar$^{2+}$ ions.

Figure 6.7: The solid lines show the energies of (a) singly and (b) doubly charged argon ions, that have impacted on the mirror as a function of time. For clarity, the depicted energy is the moving average over fifty consecutive ion impacts. The horizontal line indicates the Yamamura sputter threshold. The dashed line in (a) shows the temporal behavior of the EUV intensity in arbitrary units.

In the sheath regions, ions will be accelerated over the positive potential drop between the plasma and the walls. In Fig. 6.7, the energy of Ar$^+$ and Ar$^{2+}$ ions impacting on the mirror is shown as a function of time. For clarity’s sake, the moving average over 50 consecutive ion impacts is taken. The dashed line represents the temporal shape of the EUV pulse. Due to their inertia the ions reach the mirror after the EUV pulse. The impact energy of Ar$^{2+}$ ions is approximately two times higher compared to Ar$^+$ because, when accelerated across the same potential drop, the doubly charged ions gain twice the energy. The observation from Fig. 6.7, that the impact energy of Ar$^{2+}$ is more than two times higher, can be attributed to the fact that the Ar$^{2+}$ ions reach the mirror at an earlier moment in time, when the potential drop across the sheath is still higher.

In the case of primary photo-electrons, the impact energy is the highest, whereas for
6.4 Conclusion

secondary photo-electrons it is the lowest. This is a direct consequence of the fact that the potential drop across the plasma sheath is determined by the average electron energy (Fig. 6.5 and 6.6).

6.3.2 Mirror damage

Now that the flux and energy of the ions impacting on the mirror are known, we can estimate the damage to the mirror as a result of physical sputtering. To calculate the amount of target material that is removed per EUV pulse, we convolute the ion impact energy distribution with the sputter yield \( Y(E) \), i.e. the number of atoms removed from the solid per incoming ion with energy \( E \). For the sputter yield, the Yamamura [20] model for light ion sputtering is used (Fig. 6.8(a)). In this semi-empirical model, only ions with an energy above the sputter threshold contribute. The sputter threshold can be calculated from

\[
\frac{E_{\text{thr}}}{U_s} = \begin{cases} 
\frac{6.7}{1+5.7(m_1/m_2)} & \text{for } m_1 > m_2, \\
\lambda & \text{for } m_1 \leq m_2,
\end{cases}
\]

with \( U_s \) the surface binding energy of the solid which can be approximated by the heat of sublimation [21] and with

\[
\lambda = \frac{4m_1m_2}{(m_1 + m_2)^2},
\]

the fraction of kinetic energy that is transferred from the projectile (with mass \( m_1 \)) to the target atom (with mass \( m_2 \)) in case of a head-on collision. For Ar on Ru \( \lambda = 0.812 \), \( U_s = 6.74 \) eV and \( E_{\text{thr}} = 27.0 \) eV. In Fig. 6.7, the sputter threshold is indicated by the horizontal line.

Figure 6.8(b) shows the sputter rate in units of nm of mirror material removed per billion EUV pulses. For the case of primary photo-electrons, the sputter rate is \( \approx 2 \) times higher compared to the case of no photo-effect and \( \approx 7 \) times higher than for secondary photo-electrons. The case of no secondary photo-electrons is closest to reality, because 50% - 90% of the emitted electrons will be low-energy secondary photo-electrons [19].

The sputter rate is for the most part caused by the doubly charged ions despite the fact that density of Ar\(^{2+} \) ions is more than an order of magnitude lower than the Ar\(^+ \) density. Sputtering by Ar\(^{2+} \) ions is most dominant for the case of secondary photo-electrons, because here, the impact energy of only a small fraction of the Ar\(^+ \) ions is above the sputter threshold. Since the ion energies are close to the sputter threshold, the calculated sputter rate is very sensitive to the value for the sputter threshold. For instance, the Bohdansky [22] model for ion sputtering predicts a sputter threshold that is 10 eV higher.

6.4 Conclusion

With the Particle-In-Cell Monte Carlo method, the description of the plasma sheath region can be achieved without the need for steady-state assumptions, even for a plasma in the
nonlocal regime. Additionally, plasma-wall interaction processes, like the photo-electric effect, can be incorporated.

The simulations show that only a small fraction of the ions impacting on the optical components will have sufficient energy to sputter. Therefore, the predicted sputter rate is very low (\( \approx 1 \text{ nm per} \ 10^9 \text{ EUV pulses} \)) and cannot be measured directly.

Photo-electrons emitted from the mirror alter the potential drop over the plasma sheath and therefore will influence the ion impact energy. The simulations predict that highly energetic, primary photo-electrons will increase the sputter rate, whereas slow, secondary photo-electrons will have the opposite effect. In reality, most of the emitted photo-electrons will be low energetic and as a result the photo-electric effect will reduce the sputter rate.

The sputter rate is dominated by doubly charged ions as these ions gain twice the kinetic energy of Ar\(^+\) ions when accelerated over the same sheath potential drop.

### Bibliography


Abstract. In extreme ultra-violet (EUV) lithography, a weakly-ionized plasma is in direct contact with the multilayer mirrors in the optical column. The plasma is formed when radiation from a pulsed EUV source photo-ionizes the argon background gas in the lithography tool. Plasma ions are accelerated in the plasma sheath region towards the mirror surface. With a Particle-In-Cell Monte Carlo model, the flux and energy of ions that impinge on the mirror are calculated.

The ion bombardment can cause damage to the mirror through physical sputtering. The sputter rate depends on both the background pressure, and on the irradiation (radiative energy per unit of area per pulse) at which each mirror is exposed. With our numerical model, the sputter rate is investigated as a function of these parameters. The parameter study shows that the sputter rate increases monotonically with the irradiation, whereas the pressure dependence shows a more complex behavior. With increasing pressure, the ion flux to the mirror increases, but the energy at which ions impact on the mirror decreases as a result of the lower mean electron energy in the plasma.

Submitted to Journal of Applied Physics
Chapter 7: Pressure and irradiation scaling

7.1 Introduction

Future generation lithography devices will use extreme ultra-violet (EUV) radiation from a pulsed source to print patterns as small as 22 nm half-pitch by 2011 [1]. This spectral region in a 2% bandwidth around a wavelength of 13.5 nm is dictated by the reflective properties of Mo/Si multilayer mirrors that are used in the imaging process [2, 3].

With each radiation pulse, a weakly-ionized plasma is formed through photo-ionization: a fraction of the 92 eV photons is absorbed by the argon background gas in the lithography device. Because the plasma electrons are more mobile than the plasma ions, a plasma sheath is established in front of the multilayer mirrors. Ions are accelerated in the voltage drop over the plasma sheath towards the ruthenium capped mirrors [4, 5]. If accelerated to high enough velocities, the ions could cause damage to the multilayer mirrors by physical sputtering.

In previous studies [6, 7], the sputter rate of multilayer mirrors in a EUV lithography device has been investigated with a Particle-In-Cell Monte Carlo (PIC-MC) model. It was shown that Ar$^{2+}$ ions are the main contributors to the sputter rate, and that photo-electron emission from the mirror surface plays an important role by cooling the plasma.

These simulations were performed for conditions that are typical for the experimental setup, which is used to measure the sputter rate. In general, the sputter rate depends on both the background pressure in the tool, and on the EUV irradiation, i.e. the amount of EUV radiation energy received per unit of area per pulse. In our previous work, calculations were performed for a background argon pressure of 0.5 Pa, and an irradiation of 0.6 J m$^{-2}$ per EUV pulse.

In the EUV lithography tool, however, not every multilayer mirror will receive the same level of irradiation. In general, the irradiation will be high when the mirror is small in size and located at the beginning of the optical train of the device. The reason behind the decrease of radiation on its way through the optical column is that the reflection of each multilayer mirror is $\sim$68%. Furthermore, the background pressure will vary slightly from mirror to mirror depending on the way the tool is pumped. Therefore, it is important to investigate how the sputter rate varies with both irradiation and pressure.

Another reason to study the effect of these parameters is to obtain scaling laws. Once the scaling laws are known, it becomes possible to perform accelerated lifetime tests. To obtain accurate measurement data, experiments should be conducted at conditions where the sputter rate is high. With the scaling laws, the results could then be translated back to a situation that is more in accordance with the actual conditions in the lithography apparatus. In this way, the lifetime of the multilayer mirrors could be experimentally determined within a reasonable time frame.

This work is devoted to the effect of both pressure and irradiation on the sputter rate. First, a number of extensions that have been made to the numerical model will be discussed. These extensions are needed to decouple the photo-ionization processes in the bulk of the plasma from the photo-electron emission from the mirror surface, and to investigate the role of fast-neutral sputtering. Next, the results of the parameter study will be given. Finally, the results are compared to a similar type of parameter study done by Wieggers.
et al. [8] for the sputter rate of the collector mirrors in the lithography device.

7.2 Extensions to the PIC-MC model

7.2.1 Statistical weight factors

In previous studies [6, 7] it was shown, that two sources of charged particles have an effect on the sputter rate: photo-ionization of the background gas in front of the mirror and secondary photo-electron emission from the EUV mirror. Together, these two effects determine the energy at which ions hit the mirror. Of these two, only the first effect is dependent on the background pressure. As the pressure is varied over a wide range both groups of particles should still be accurately represented in the numerical model. To ensure the statistical representation, each group is given its own statistical weight factor, which is the number of real particles represented by one computer particle. Electrons and ions that are generated in the photo-ionization process are given a statistical weight factor $\xi_1$. Photo-electrons emitted from the mirror get a statistical weight factor $\xi_2$. When these particles collide with the background gas and more particles can be created, for instance through electron-impact ionization. In that case, the newly created electron and ion inherit the statistical weight factor of the parent particle. In this way, the particle groups are only coupled through the electric field created by the charge separation. When the background pressure of the simulation is varied, only $\xi_1$ is adjusted accordingly. As a result, the total amount of computer particles generated by either photo-ionization or photo-electric effect is kept at a constant number of about $\sim 4 \times 10^6$.

7.2.2 Fast neutral sputtering

In the simulation model, neutral particles are not explicitly followed. It is assumed that the background gas is at room temperature and that the neutral density is uniformly distributed.

However, fast neutrals are produced in the sheath region by charge-exchange collisions between ions and neutrals: $Ar_f^+ + Ar_s \rightarrow Ar_f + Ar_s^+$. As these fast neutral atoms also attribute to the sputter rate they should be taken into account.

As a quick solution to the calculation of the sputter rate of fast neutrals, the following method is implemented. When a charge-exchange collision occurs, the position and velocity of the fast neutral immediately after the collision, is taken equal to the position and velocity of the ion just before the collision. Given the velocity and position of the fast neutral, it is then calculated at what moment in time the fast neutral will strike the wall towards which it is moving. The impact energy $E$ is set equal to the kinetic energy of the neutral just after the charge-exchange collision. The sputter yield of fast neutrals $Y(E, \theta)$ is taken equal to the sputter yield for ions $Y(E)$ [9, 10], but with a correction for the impact angle

$$\frac{Y(E, \theta)}{Y(E)} = \cos^{-f}(\theta) \exp \left[ -f \cos(\alpha_0) \left( \frac{1}{\cos(\theta)} - 1 \right) \right],$$

(7.1)
where the semi-empirical fit parameters $f$ and $\alpha_0$ are specific for the target-projectile combination \cite{11} under investigation.

It is implicitly assumed that the fast neutral does not collide any further on its way towards the wall. At low pressure this approach is valid, because the chance that the neutral will collide is small. However, at elevated pressures the fast neutral will experience many collisions before it reaches the wall, in which a significant amount of its kinetic energy is lost. Because we do not take into account these collisions, we will systematically overestimate the sputter rate of fast neutrals.

On the other hand, in this pressure regime ions will also collide many times in the sheath region. As a result, the ion receives only a fraction of the sheath potential energy between collisions. Although these less energetic ions will create fast neutrals by charge-exchange collisions, the kinetic energy of each individual fast neutral will be too low to cause sputtering.

### 7.3 Results

The geometry of the computational domain is the same as in previous studies \cite{6, 7}. The mirror on the left side and the wall on the right side are separated by a 5 cm gap. Both mirror and wall are assumed to be grounded. Photo-electrons are emitted from the mirror only.

Wieggers et al. \cite{8} have recently published a similar type of parameter study for the sputter rate of collector mirrors. The collector mirror is the first mirror in the lithography apparatus, which is located closest to the EUV source. For this reason, \cite{8} use a spherical geometry in their simulations to account for the $1/r^2$-decrease of irradiation with distance to the EUV source. Because we are mainly concerned with multilayer mirrors, which are located further away from the source, we use a planar geometry. This makes the results somewhat hard to compare. Aside from the geometry, their model uses similar input data (photoionization cross-sections, secondary electron yield, collision cross-sections etc.).

Besides the desired 13.5 nm radiation with 2% bandwidth, EUV sources also emit significant amounts of out-of band radiation, mostly at longer wavelengths \cite{12}. As a result of the reflective properties of the multilayer mirrors, the out-of-band radiation is prevented from being transmitted further down the optical column of the lithography tool. Therefore, in our numerical model, the assumption is justified that the EUV radiation is monochromatic with a wavelength of 13.5 nm, which corresponds to a photon energy of $\sim 92$ eV. Wieggers et al. use the same assumption for their calculation of the sputter rate of collector mirrors despite the fact that collector mirrors do receive the out-of-band emission from the EUV source. Out-of-band radiation with a photon energy in the range between 15.7 and 40 eV has a much higher cross-section for photo-ionization of argon than the cross-section at 92 eV, as can be seen in Fig. 7.1. As a consequence, the EUV generated plasma in front of a collector mirror will have a significantly lower mean electron energy, because the photons from which it is created, will, on average, have lower energy. This has important consequences for the sputter rate, because the voltage drop across the plasma
sheath, and thereby the maximum energy towards which ions are accelerated, is determined by the mean electron energy. Hence, the omission of out-of-band radiation will lead to an overestimation of the sputter rate for collector mirrors.

Figure 7.1: Photo-absorption cross-section for argon [13].

7.3.1 Pressure dependence

In the first simulation, a background pressure of $p = 0.5$ Pa, and an EUV irradiation of $I_p = 0.6$ J m$^{-2}$ per pulse are taken. These values are exactly the same as in previous studies [6, 7]. The only difference is the value of the secondary electron yield, i.e. the number of secondary photo-electrons liberated per incoming photon. For clean Ru capped multilayer mirrors, a yield of 0.020 was recently measured at the Brookhaven National Synchrotron Light Source [14]. This is in good agreement with the value of 0.021 reported by Hollenshead and Klebanoff [15]. This number is $\sim 14$ times higher than the value that was used in previous studies.

Figure 7.2 shows the potential in the plasma at various time intervals after the beginning of the 100 ns long EUV pulse. Immediately after the start of the EUV pulse the potential on the left side is negative as a result of photo-electron emission from the mirror. This potential barrier prevents further photo-electron emission into the bulk of the plasma. Thus, the photo-electron emission is space-charge limited. On the other hand, electrons that are generated in the bulk of the plasma by photo-ionization have sufficient energy to overcome the space charge barrier and reach the walls. In this way, a plasma sheath is established, in which positively charged ions are accelerated towards the walls. The potential drop over the plasma sheath reaches a maximum $\sim 60$ ns after the EUV pulse has ended (thus at $t \approx 160$ ns). Thereafter, the potential drop starts to decrease again, because the average kinetic energy of the electrons decreases as a result of inelastic collisions with
the background gas, and because only high-energy electrons can reach the walls, whereas low-energy electrons remain trapped inside the plasma.

![Figure 7.2: Time evolution of the potential profile of the plasma. Profiles are plotted for six moments in time after the beginning of the 100 ns long EUV pulse for a background pressure of \( p = 0.5 \) Pa and an EUV irradiation of \( I = 0.6 \) Joule m\(^{-2}\) per pulse.](image)

From Fig. 7.2, we conclude that the acceleration of the plasma ions takes place after the EUV pulse has ended. The time it takes an argon ion with mass \( m \) and charge \( q \) to be accelerated by a potential \( V \) across the width \( \Delta x \) of the plasma sheath region can be estimated by

\[
\Delta t = \sqrt{\frac{2m\Delta x}{qV}} \approx 0.4 \mu s, \tag{7.2}
\]

for \( \Delta x = 1 \) mm, \( V = 50 \) Volt. This implies that the fast ions that cause sputtering originate from the plasma sheath region, not from the bulk of the plasma.

Figure 7.3 shows the energy at which ions impact on the mirror as function of time for various pressures. The EUV irradiation is kept at a constant value of \( I = 0.6 \) Joule m\(^{-2}\) per pulse. The moving average over 50 consecutive computer ion impacts has been taken to improve readability of the plots. The sputter threshold energy for argon projectiles on a ruthenium surface is indicated by the horizontal line. The impact energy of the doubly charged ions (Fig. 7.3(b)) is higher than for singly charged ions (Fig. 7.3(a)), because for Ar\(^{2+}\) ions the Coulomb force is twice as strong as for Ar\(^+\) ions.

During the 100 ns duration of the EUV pulse the ions have not yet arrived at the mirror. When the pressure is increased, more photo-ionization events will occur, which leads to a higher plasma density. As a result, the plasma sheath will become smaller in width, as the Debye length decreases. As a consequence, ions will arrive at the mirror at a earlier moment in time, because the distance that ions have to cover to traverse the plasma sheath is smaller.
More important, however, is the fact that, when the pressure is increased, the impact energies of the ions is reduced. The reason for this effect is that the impact energy of the ions is determined by the kinetic energy of the plasma electrons. When the pressure is increased more collisions between electrons and the background gas occur. In this way, electrons lose some of their kinetic energy to excitation and ionization of the background gas. As a result, this energy can not be used to build up the plasma sheath potential in which ions are accelerated.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure7.3a}
\hspace{1cm}
\includegraphics[width=0.4\textwidth]{figure7.3b}
\caption{(a) $\text{Ar}^+$ ions \hspace{2cm} (b) $\text{Ar}^{2+}$ ions}
\end{figure}

\textbf{Figure 7.3:} Average ion impact energy as a function of time for five different argon background pressures for an EUV irradiation of $I = 0.6$ Joule m$^{-2}$ per pulse. The horizontal line indicates the sputter threshold energy for argon projectiles on a ruthenium target, which according to the Yamamura formula \cite{Yamamura} equals 27.0 eV.

In order to calculate the sputter rate, the ion impact energy distribution needs to be convoluted with the sputter yield $Y(E)$, which is shown in Fig. 7.4. In the model, the sputter rate is calculated by the summation over all ion impact events, where for each impact the sputter yield that corresponds to the energy at which the ion hits the mirror is multiplied by the statistical weight of the computer particle. If the impact energy is below the sputter threshold (27.0 eV for Ar on Ru), the sputter yield equals zero, in which case the impact event does not contribute to the sputter rate. The expression for the sputter yield, and sputter threshold can be found in Appendix A.

Figure 7.5 shows the sputter rate as a function of pressure. The total sputter rate has three contributions: from $\text{Ar}^+$ ions, $\text{Ar}^{2+}$ ions, and fast neutrals. At all simulated pressures the sputter rate as a result of fast-neutrals turned out to be negligible (less than 1% of the sputter rate). The total sputter rate is the highest for a background pressure of 0.1 Pa.

With respect to the pressure-scaling of the sputter rate, two effects are important: the number of ions that hit the mirror, and the energy at which the ions impact on the mirror. The former increases with pressure, whereas the latter decreases. Because the sputter yield falls of rapidly when the energy gets closer to the sputter threshold \cite{Yamamura, SputterYield}, the effect of the lower impact energy of the ions will eventually become dominant at higher pressures.
Figure 7.4: Sputter yield for Ar on a Ru according to the Yamamura formula [9]. The sputter yield equals zero below the sputter threshold at 27.0 eV.

Figure 7.5: Sputter rate as a function of pressure for Ar$^+$ ions (crosses), Ar$^{2+}$ ions (triangles) and their sum (open squares), for an irradiation of $I_p = 0.6$ J m$^{-2}$. For comparison, the results of Wieggers et al. [8] are given (closed squares) for an irradiation of $I_p = 1.8$ J m$^{-2}$. 
The results of Wieggers et al. show a similar pressure dependence of the sputter rate, although their calculation of the sputter rate has higher values. Moreover, the maximum in the sputter yield is found at a higher pressure. The difference between the calculations is probably due to the fact that the irradiation in their calculation was 3 times higher than in our parameter study. Hence, we will now discuss the irradiation scaling of the sputter rate.

### 7.3.2 Irradiation dependence

A similar investigation has been conducted for the irradiation scaling, the results of which are shown in Fig. 7.6 and 7.7 for a background pressure of $p = 0.5 \text{ Pa}$.

![Average ion impact energy as a function of time for five different values of the EUV irradiation](image)

Figure 7.6: Average ion impact energy as a function of time for five different values of the EUV irradiation. The background pressure is kept at a constant value of $p = 0.5 \text{ Pa}$.

When the irradiation is increased more plasma is generated. The higher plasma density $n_e$ leads to a smaller Debye length $\lambda_D \sim \sqrt{\frac{T_e}{n_e}}$, which translates into a reduced width of the plasma sheath. This means that at higher irradiation the distance that ions have to cover to cross the plasma sheath is smaller. Therefore, the ions will reach the mirror at an earlier moment in time, when the potential drop over the plasma sheath is still relatively high, as can be concluded from the time evolution of the potential profiles shown in Fig. 7.2. As a result, ions are accelerated to higher velocities in the plasma sheath. The impact energy of the ions will increase with the irradiation, because the potential drop across the plasma sheath, averaged over the time it takes the ions to cross the sheath, is higher.

Besides the higher average impact energy of the ions also the ion flux increases with the irradiation. Both effects will lead to an increase of the sputter rate.

The results for the irradiation scaling of the sputter rate show a similar trend as those found in Wieggers et al. [8]. However, calculations in [8] show a lower value of the sputter rate for a background pressure that is 3 times higher than in our simulations. This is
Chapter 7: Pressure and irradiation scaling

Figure 7.7: Sputter rate as a function of irradiation per EUV pulse (open squares) for an argon pressure of 0.5 Pa. For comparison, the results of Wieggers et al. [8] are shown (closed squares) for a pressure of 1.5 Pa.

in accordance with our previous calculation of pressure dependence of the sputter rate, because we are on the right side of the sputter rate maximum (Fig. 7.5). At that side of the curve, the sputter rate goes down with increasing pressure. The reason is that the electrons loose more energy, because the rate of inelastic electron-neutral collisions increases.

For a further comparison, we have also conducted a simulation at exactly the same parameters. For a background pressure of 1.5 Pa and an irradiation of 1.8 J m\(^{-2}\) per EUV pulse, we calculate a sputter rate of 0.37 nm per \(10^9\) EUV pulses, whereas Wieggers et al. find 0.56 nm per \(10^9\) EUV pulses. The small difference between these calculations is possibly the result of the difference in geometry.

7.4 Conclusions

To study the scaling behavior of the sputter rate of multilayer mirrors in an EUV lithography apparatus, the effect of both background pressure and irradiation level have been investigated.

We have shown that fast neutral sputtering as a result of charge exchange collisions in the plasma sheath region do not significantly contribute to the sputter rate. Ar\(^{2+}\) ions are the main contributor to the sputter rate.

The sputter rates increases monotonically with the irradiation.

The pressure dependence shows a more complex behavior as there are two competing effects. Increasing the pressure leads to a denser plasma. Consequently, the ion flux to the multilayer mirror increases. However, in the denser plasma more electron neutral collisions occur, which lead to a lower mean electron energy. Because the voltage drop over the
plasma sheath is determined by the kinetic energy of the electrons, the pressure increase will result in a lower impact energy per ion. As a consequence, the pressure dependence of the sputter rate shows a maximum.

This has important implications for accelerated lifetime tests. The only way to speed up the lifetime acceleration tests is to increase the irradiation. Increasing the pressure, which experimentally would be much easier, does not lead to the required enhancement of the sputter rate.

Bibliography

Chapter 7: Pressure and irradiation scaling


Effect of hydrogen on the sputter rate

Abstract. In extreme ultra-violet (EUV) lithography, a plasma is in close contact with the multilayer mirrors in the optical column of the device. This weakly-ionized plasma is formed when EUV radiation from the pulsed source photo-ionizes the low-pressure argon background gas. The plasma is potentially dangerous to the mirrors in case ion bombardment leads to physical sputtering of the mirror. With a Particle-In-Cell Monte Carlo model, the effect of adding hydrogen to the background gas on the sputter rate is investigated. For the ion energies under investigation, hydrogen ions do not contribute to the sputtering as a result of poor energy transfer between the light ions and the much heavier atoms of the mirror material. However, hydrogen does have an influence on the argon ions.

It is found that the sputter rate is significantly reduced for two reasons. Firstly, electron-hydrogen collisions effectively cool the plasma electrons, thereby reducing the sheath potential over which argon ions are accelerated. Secondly, the lower charge over mass ratio of hydrogen ions makes the hydrogen ions reach the mirror before the heavier argon ions can, which also lowers the sheath potential that the argon ions encounter.
8.1 Introduction

In future generation lithography devices [1], extreme ultra-violet (EUV) radiation will be used to print small patterns onto slabs of semiconductor material. The EUV radiation will have a photon energy in a 2% bandwidth around 92 eV. The bandwidth is determined by the reflective properties of Mo/Si multilayer coated mirrors [2] that are used as optical elements in the imaging process.

The EUV radiation from a pulsed plasma source photo-ionizes the low-pressure background gas in the tool. The electrons in the plasma are more mobile than the ions, which leads to a charge-imbalance at the plasma boundaries. As a consequence, a plasma sheath develops in front of the mirrors. Ions are accelerated towards the mirrors by the electric field in the plasma sheath region. The formation of the weakly-ionized plasma in the optical column is potentially dangerous to the optical elements, because ion bombardment of the mirrors can cause damage through physical sputtering.

Previously [3, 4], we have discussed the results of numerical Particle-In-Cell Monte Carlo (PIC-MC) simulations that aim to calculate the sputter rate of the multilayer mirrors that are in direct contact with the radiation-induced plasma. In these studies, argon was taken as a background gas with a pressure of typically 0.5 Pa. It was found that the main contribution to the sputter rate arises from Ar$^{2+}$ ion bombardment, supplemented by a smaller contribution from Ar$^+$ ions. Besides argon, other gases, or mixtures of gases can be used as a background gas in the lithography tool. It is the aim of this study to investigate whether other gases will result in a lower rate of sputtering.

Sputtering occurs because, for a short period of time, the impact energy of the plasma ions exceeds the sputter threshold energy, which can be estimated by the Yamamura expression [5] for the sputter threshold energy

$$E_{thr} = \begin{cases} \frac{6.7}{1+5.7(m_1/m_2)} & \text{for } m_1 > m_2, \\ \frac{1+5.7(m_1/m_2)}{\lambda} & \text{for } m_1 \leq m_2, \end{cases}$$

(8.1)

with $U_s$ the surface binding energy of the solid, and with

$$\lambda = \frac{4m_1m_2}{(m_1 + m_2)^2},$$

(8.2)

the fraction of kinetic energy that is transferred from the projectile (with mass $m_1$) to the target atom (with mass $m_2$) in case of an elastic head-on collision. In Fig. 8.1, the sputter threshold energy is plotted as a function of atomic mass number of the projectile atom for a ruthenium target. We choose Ru, because in EUV lithography this material is often applied as a capping layer (thickness of $\approx 1.5$ nm) to provide a barrier against oxidation of the underlying Mo/Si multi-layers [6]. The threshold energy will be high in case of either light projectiles ($m_1 \ll m_2$), or heavy projectiles ($m_1 \gg m_2$), because in both cases the energy transfer between projectile and target atoms is very poor. Because Ru is relatively heavy (atomic mass 101.07 u), the sputter threshold energy is particularly high for light projectiles.
In Table 8.1, threshold energies are summarized for (molecular) hydrogen, helium, argon and ruthenium projectiles. Only for hydrogen the threshold energy of 97.9 eV is higher than the typical energies at which argon ions impact on the multilayer mirror, as calculated in previous studies [3, 4, 7, 8].

**Table 8.1: Sputter threshold energy for various ions on a ruthenium surface**

<table>
<thead>
<tr>
<th>ion</th>
<th>Mass number</th>
<th>$E_{thr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>2</td>
<td>97.9 eV</td>
</tr>
<tr>
<td>helium</td>
<td>4</td>
<td>56.4 eV</td>
</tr>
<tr>
<td>argon</td>
<td>40</td>
<td>27.0 eV</td>
</tr>
<tr>
<td>ruthenium</td>
<td>101</td>
<td>45.1 eV</td>
</tr>
</tbody>
</table>

**Figure 8.1:** Sputter threshold energy as a function of projectile atomic mass number on a ruthenium target according to the Yamamura formula (Eq. 8.1). The threshold energies for (molecular) hydrogen, helium, argon and ruthenium projectiles are also listed in Table 8.1.

What would happen if, instead of argon, hydrogen would be used as a background gas? Would sputtering still occur? To answer this question, the sputter threshold energy has to be compared to the maximum energy that ions can gain in the potential drop over the plasma sheath region, which is determined by the energy of the electrons $E_e = h\nu - E_{ion}$ that are created in the photo-ionization process. For molecular hydrogen, with an ionization energy of $E_{ion} = 15.4$ eV, and for $h\nu = 92$ eV photons, the energy of the electrons is $E_e = 76.6$ eV, which is still considerably lower than the sputter threshold energy. This implies that if, instead of argon, hydrogen is used as a background gas, then damage to the mirror as a result of sputtering would be eliminated.
For mixtures of Ar/H\textsubscript{2}, it can still be expected that the Ar\textsuperscript{+} and Ar\textsuperscript{2+} bombardment will result in sputtering, but as will be shown, the presence of hydrogen will have an effect on the rate of sputtering. Sputtering in Ar/H\textsubscript{2} plasmas has been investigated by other authors for both glow discharges \cite{9-11} and RF discharges \cite{12-14}.

In this chapter, the effect of adding hydrogen to the argon background gas on the sputtering rate is investigated. For this purpose, the PIC-MC model needs to be extended to incorporate hydrogen as a background gas. These extensions to the model will be discussed in the next section. Thereafter, results and conclusions will be given.

### 8.2 Adding H\textsubscript{2} to the PIC-MC model

When hydrogen is added to the gas mixture, a small fraction will get photo-ionized by the EUV radiation. In fact, in photo-ionization of H\textsubscript{2} at $h\nu = 92$ eV, three types of reactions can occur \cite{15-17}

- **a** Single photo-ionization: $h\nu + H_2 \rightarrow e^- + H_2^+$ (80%);
- **b** Dissociative photo-ionization: $h\nu + H_2 \rightarrow e^- + H + H^+$ (15%);
- **c** Double photo-ionization: $h\nu + H_2 \rightarrow 2e^- + 2H^+$ (5%).

For each reaction type, the listed percentage between parentheses resembles the branching fraction. Thus, both atomic and molecular hydrogen ions are produced with branching fractions of, respectively, 20% and 80%.

The chemistry in an argon-hydrogen plasma is quite extensive \cite{18}. Besides electrons and argon ions, species that are formed include H\textsuperscript{+}, H\textsubscript{2}\textsuperscript{+}, H\textsubscript{3}\textsuperscript{+} and ArH\textsuperscript{+} ions as well as atomic hydrogen atoms. In their description of a Ar/H\textsubscript{2} glow discharge, Bogaerts and Gijbels \cite{19} have identified 63 relevant reaction types in which these species participate.

In order to keep the chemistry of the model simple, it is assumed that only the first photo-ionization reaction (single photo-ionization) occurs with a total cross-section $\sigma = 6.1 \times 10^{-23}$ m\textsuperscript{2} at 92 eV that is equal to the sum of the three possible photo-ionization processes. Hence, in the model only H\textsubscript{2}\textsuperscript{+} particles (thus, not protons and H-atoms) are followed. It should be noted that the photo-ionization reaction of hydrogen is approximately 20 times smaller than that for photo-ionization of argon. This suggests that only high concentrations of hydrogen in the mixture will have a significant effect on the sputter rate.

In order to treat mixtures of gases, the Monte Carlo part of the model has been extended. Now, each species can have multiple process lists: one for reactions with argon and one for reactions with hydrogen. Reactions between electrons and argon are the same as in our earlier study \cite{3}: elastic electron scattering, electron excitation, and electron-impact ionization. For the reaction of electrons with hydrogen, four inelastic processes and one elastic process have been added to the model, see Table 8.2. For the inelastic processes, the minimum required electron energy $E_m$ as well as the average energy lost in the process $\Delta E$ according to Janev et al. \cite{20} are listed.

The ion reactions that are added to the model can be seen in Table 8.3.
8.2 Adding H\textsubscript{2} to the PIC-MC model

**Table 8.2: Electron processes added to the PIC-MC model**

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>(E_m)</th>
<th>(\Delta E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Electron impact ionization</td>
<td>(e^- + \text{H}_2 \rightarrow 2e^- + \text{H}_2^+)</td>
<td>15.4 eV</td>
<td>15.4 eV</td>
</tr>
<tr>
<td>(2) Vibrational excitation of (\text{H}_2)</td>
<td>(e^- + \text{H}_2 \rightarrow e^- + \text{H}_2^\star)</td>
<td>0.7 eV</td>
<td>0.7 eV</td>
</tr>
<tr>
<td>(3) Excitation of the (\text{H}_2) singlet</td>
<td>(e^- + \text{H}_2 \rightarrow e^- + \text{H}_2^{**})</td>
<td>11.1 eV</td>
<td>12.1 eV</td>
</tr>
<tr>
<td>(4) Excitation of the (\text{H}_2) triplet</td>
<td>(e^- + \text{H}_2 \rightarrow e^- + \text{H}_2^{***})</td>
<td>8.1 eV</td>
<td>10.0 eV</td>
</tr>
<tr>
<td>(5) Elastic scattering</td>
<td>(e^- + \text{H}_2 \rightarrow e^- + \text{H}_2)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 8.3: Ion processes added to the PIC-MC model**

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar\textsuperscript{+} ions</td>
<td>(6) Charge transfer with (\text{H}_2)</td>
</tr>
<tr>
<td>(7)a H-atom transfer</td>
<td>(\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}_2)</td>
</tr>
<tr>
<td>(\text{H}_2\textsuperscript{+} ) ions</td>
<td>(8)b Proton transfer with (\text{H}_2)</td>
</tr>
<tr>
<td>(9) Charge transfer with (\text{H}_2)</td>
<td>(\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2^+)</td>
</tr>
<tr>
<td>(10) Proton transfer with (\text{Ar})</td>
<td>(\text{H}_2^+ + \text{Ar} \rightarrow \text{H} + \text{ArH}^+)</td>
</tr>
<tr>
<td>(11)a Charge transfer with (\text{Ar})</td>
<td>(\text{H}_2^+ + \text{Ar} \rightarrow \text{H}_2 + \text{Ar}^+)</td>
</tr>
</tbody>
</table>

\(\text{a}\) with \(\text{Ar}^+\) instead of \(\text{ArH}^+\)

\(\text{b}\) with \(\text{H}_2^+\) instead of \(\text{H}_3^+\)

In reaction 7 and 10, ArH\textsuperscript{+} ions are created, but these ions are not followed as such in the model. Instead, ArH\textsuperscript{+} ions are treated as Ar\textsuperscript{+} ions. The error made by assigning the wrong mass is small. However, from glow discharge studies it is well known that adding small fractions of hydrogen to argon can increase the sputtering, because ArH\textsuperscript{+} particles that are formed lose their kinetic energy in collisions with neutrals much less inefficient than Ar\textsuperscript{+} ions. On the other hand, in our plasma the pressure is low, which results in a lower collision frequency of these ions in the plasma sheath region [4]. Therefore, it can be expected that the error made by replacing the ArH\textsuperscript{+} ions is small. A similar substitution is applied to reaction 8. After creation, the H\textsubscript{2}\textsuperscript{+} ion is treated as a H\textsubscript{3}\textsuperscript{+} ion.

Cross-sections for the processes 1-11 have been taken from Bogaerts and Gijbels [11]. For a discussion of the accuracy of these cross-sections, the reader is referred to their article and references listed therein.
8.2.1 Monte Carlo collisions

For sufficiently low pressures, collisions between charged particles can be neglected, and only collisions with neutrals have to be taken into account. In the model, a collision is treated as an instantaneous process that only effects the velocity of the charged particle involved. The free-flight time between collisions is given by the inverse of the total collision frequency

\[ \nu(E) = \sum_{i=1}^{M} \sum_{j=1}^{N} \sigma_{ij}(E)n_j \sqrt{\frac{2E}{m}}, \]  

(8.3)

with \( E \) the kinetic energy, \( m \) the mass of the incident particle, \( \sigma_{ij}(E) \) the cross-section for the \( i \)-th type of collision with background particles of type \( j \), and homogeneous density \( n_j \). The low ionization degree of the EUV plasma implies that the background density can be considered uniform across the volume of the plasma.

To speed up the simulation, the ‘null collision method’ [21] is applied. For this purpose, an extra ‘dummy’ collision type is defined, which has an energy dependent cross-section such that when added to equation (8.3), it results in a total collision frequency with a constant value \( \nu_m \)

\[ \nu_m = \max_E \{ \nu(E) \}. \]  

(8.4)

After having traveled through the background gas for some time \( t \), the particle may or may not collide. The probability \( P(t)dt \) that a particle will experience a collision within an infinitesimal time interval \( dt \) is given by

\[ P(t)dt = \nu \exp(-\nu_m t)dt. \]  

(8.5)

To obtain the time \( t_m \) to the next collision, the right-hand side of equation (8.5) is integrated from zero to \( t_m \) and the left-hand side is equated to a random number \( R \in [0,1) \) between zero and one. Solving for \( t_m \) gives

\[ t_m = -\frac{\ln(1-R)}{\nu_m}. \]  

(8.6)

Upon creation at time \( t_0 \), each individual computer particle is assigned its own collision time \( t_c = t_0 + t_m \). After each time step of the PIC loop it is evaluated whether the particle needs to collide, i.e. it is checked for which computer particle \( t \geq t_c \). If so, another random number between zero and one is drawn to select the collision type. The probability that a certain type of collision is selected is equal to the ratio of the collision frequency \( \nu_{ij}(E) \) of that particular collision type to the total collision frequency. Once the collision type is determined, the velocity of the particle is adjusted accordingly and subsequently the time to the next collision is evaluated.

8.3 Results

For the calculation of the sputter yield, the same configuration is taken as the one used in previous studies. The PIC-MC model is one-dimensional in configuration and three-
dimensional in velocity space. Two grounded electrodes are separated by a 5 cm wide gap. The radiation field in the gap has an irradiation of 0.6 J/m² per EUV pulse. One of the electrodes is a multilayer mirror from which photo-electrons are emitted.

The number of secondary photo-electrons liberated per incoming photon, is called the secondary electron yield. For clean Ru capped multilayer mirrors, a yield of 0.020 was measured at the Brookhaven National Synchrotron Light Source [22]. This is in good agreement with the value of 0.021 reported by Hollenshead and Klebanoff [23].

In order to investigate the effect of hydrogen addition, the motion of electrons and ions in the gap between the electrodes, during and after the 100 ns long EUV pulse, is simulated. Simulations are performed for a number of Ar/H₂ mixtures with a hydrogen fraction between 0 – 80%, where the hydrogen fraction is defined as the ratio of the partial hydrogen pressure to the total pressure. For all simulations, the partial pressure of the argon background gas is taken equal to \( p_{\text{Ar}} = 0.5 \) Pa, so that the total pressure ranges between 0.5 and 2.5 Pa.

The PIC-MC model calculates the ion flux to the mirror, and the energy at which ions impact on the mirror. To obtain the sputter rate, the ion impact energy distribution is then convoluted with the sputter yield \( Y(E) \) [5], the number of target atoms removed per incoming projectile with kinetic energy \( E \), which is shown in Fig. 8.2 for Ar on Ru.

![Figure 8.2: Sputter yield for Ar on a Ru according to the Yamamura formula [5]. The sputter yield equals zero below the sputter threshold of 27.0 eV.](image)

The sputter rate is calculated by the summation over all ion impact events, where for each impact the sputter yield that corresponds to the energy at which the ion hits the mirror is multiplied by the statistical weight of the computer particle. If the impact energy is below the sputter threshold (27.0 eV for Ar on Ru), the sputter yield equals zero, in which case the impact event does not contribute to the sputter rate.

Figure 8.3 shows the calculated sputter rate as a function of the hydrogen fraction of the Ar/H₂ mixture. It can be seen that the sputter rate decreases when the hydrogen
fraction is increased. When the partial pressure of hydrogen is increased from 0 to 80% the sputter rate decreases by more than two orders of magnitude.

![Figure 8.3: Sputter rate as a function of H\textsubscript{2} fraction. In these series of simulations, the partial pressure of argon is kept at a constant value of 0.5 Pa. As a result, the total pressure increases with the hydrogen fraction.](image)

To determine the cause of this drastic effect, the contribution to the sputter rate of the various ion species is considered. Figure 8.4 shows the energies at which Ar\textsuperscript{+}, Ar\textsuperscript{2+} and H\textsubscript{2}\textsuperscript{+} ions impact on the multilayer mirror as a function of time for different Ar/H\textsubscript{2} mixtures.

The impact energies of the H\textsubscript{2}\textsuperscript{+} ions (Fig. 8.4(c)) stays well below the sputter threshold energy of 97.9 eV for these type of projectiles. For the Ar\textsuperscript{+} ions, the impact energies are just above the sputter threshold (which is indicated in Fig. 8.4(a) by the dashed line) when the hydrogen fraction is small, but only for a short period of time. When the hydrogen fraction is increased above 20% the impact energies drop below the sputter threshold and the Ar\textsuperscript{+} ions no longer contribute to the sputter rate. The main contribution to the sputter rate, must therefore be the result of the impact of Ar\textsuperscript{2+} ions (Fig. 8.4(b)).

When hydrogen is added to the mixture, H\textsubscript{2}\textsuperscript{+} ions are created, but as we have seen, these do not contribute to the sputtering of the multilayer mirror. On the other hand, the addition of hydrogen to the background gas does increase the total pressure, thereby increasing the collision frequency of the plasma constituents. Plasma electrons will thus undergo more inelastic collisions with the background gas in which they rapidly loose their kinetic energy. In previous studies [3, 4], it was shown that the impact energy of the ions, determined by the potential drop over the plasma sheath, is determined by the kinetic energy of the electrons. In this way, adding hydrogen to the mixture cools the electrons of the EUV generated plasma, so that the velocities that ions can reach in the plasma sheath are reduced.

Besides this cooling effect, another effect plays a role. The acceleration of the various ion species in the plasma sheath is determined by their charge over mass ratio. For instance,
8.3 Results

(a) Ar$^+$ ions  
(b) Ar$^{2+}$ ions  
(c) H$_2^+$ ions

**Figure 8.4:** Average ion impact energy as a function of time for argon hydrogen mixtures. The dashed line in (a) and (b) indicates the value of the sputter threshold for Ar on Ru.

When the impact energies of Ar$^+$ and Ar$^{2+}$ ions are compared, it can be observed that the impact energies are higher for the doubly charged ions because these ions experience an electric force that is two times higher than for singly charged ions. In fact, the impact energies are *more* than a factor of two higher, because doubly charged ions cross the plasma sheath faster than singly charged ions, at the moment when the potential drop across the plasma sheath is still higher. The Ar$^{2+}$ ions experience a higher potential drop, averaged over the time that they require to cross the plasma sheath region.

This charge over mass effect is even more pronounced when the Ar$^+$ ions are compared to the H$_2^+$ ions. In Fig. 8.4, it can be seen that light hydrogen ions reach the multilayer mirror well ahead of the heavy argon ions. In this way, the charge-imbalance between ions and electrons is reduced by the more mobile H$_2^+$ ions before the argon ions can arrive at the mirror. As a result, the argon ions will experience a smaller potential drop in the plasma sheath reach than in the case that no hydrogen ions are present.
Chapter 8: Ar-H₂ mixtures

Thus, the addition of hydrogen to the background gas reduces the sputter rate for two reasons: a higher collision frequency of electrons, and higher charge over mass ratio than for pure argon. To determine which of these two causes is more important, another simulation is performed in which the mass of the H₂⁺ ions is set equal to the mass of the argon atoms. In this artificial experiment, the mass of all the ions is the same, and any reduction of the sputter rate can be solely ascribed to the higher electron collision frequency.

Results for this simulation with 'heavy' hydrogen are shown in Table 8.4, and Fig. 8.5. The addition of 0.5 Pa of 'normal' hydrogen to the argon background gas reduces the sputter rate to 16%. If instead the same amount of 'heavy' hydrogen is added then the sputter rate is reduced to only 31%. Therefore, it can be concluded that the reduction of the sputter rate is mainly caused by the higher electron collision frequency and to a lesser extend by the effect of the lower charge over mass ratio. In Fig. 8.5(c), it can be seen that the 'heavy' hydrogen ions impact on the mirror at a later moment in time than normal hydrogen do, when the potential drop across the plasma sheath is already lower. As a result, heavy hydrogen ions have a lower impact energy. The lower impact energy of the argon ions, see Fig. 8.5(a) and 8.5(b), is the result of the higher inelastic electron collision frequency.

8.4 Conclusions

The sputter rate of multilayer mirrors in EUV lithography depends on the composition of the background gas in the device. The maximum voltage drop across the plasma sheath region is determined by the photon energy of the EUV radiation minus the ionization potential of the background gas. The factual voltage drop is lower due to cooling mechanisms of the plasma electrons. By adding molecular gases this cooling can be enhanced considerably.

For each ion mass, a sputter threshold energy exists, below which ions do not contribute to sputtering. For argon gas, the sputter rate is low, because the impact energy of the argon ions is in the near-threshold regime. Light gases, such as hydrogen and helium have relatively high sputter threshold energies, and will therefore have even lower sputter rates. For pure hydrogen, the sputter rate equals zero because the sputter threshold energy exceeds the maximum energy that ions can gain in the sheath.

With the addition of hydrogen to the background gas mixture, a significant reduction of the sputter rate can be achieved. Two properties of hydrogen are responsible for the reduction of the sputter rate. Most importantly, high cross-sections for inelastic electron-neutral collisions have a cooling effect on the plasma. The mean electron energy in the plasma is effectively reduced, which leads to a reduction of the sputter rate, because the voltage drop over the sheath region is determined by the kinetic energy of the electrons.

Next, the higher charge to mass ratio of H₂⁺ ions accounts for the fact that hydrogen ions hit the mirror before the argon ions do. In this way, the charge-imbalance between electrons and ions is reduced at the moment when the argon ions cross the plasma sheath, so that the argon ions experience a lower voltage drop over the sheath than in the case no
8.4 Conclusions

Table 8.4: The effect of hydrogen addition to the background gas on the sputter rate.

<table>
<thead>
<tr>
<th>Background gas</th>
<th>partial pressure [Pa]</th>
<th>Sputter rate (nm per 10⁹ EUV pulses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure argon</td>
<td>0.5</td>
<td>0.21</td>
</tr>
<tr>
<td>50% hydrogen</td>
<td>0.5</td>
<td>0.032</td>
</tr>
<tr>
<td>50% 'heavy' hydrogen</td>
<td>0.5</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Figure 8.5: Average ion impact energy as a function of time for the parameters listed in Table 8.4.
hydrogen ions had been present.

When the hydrogen fraction is increased from 0 to 80% the sputter rate is reduced by more than two orders of magnitude. Absorption losses as a result of the hydrogen addition are modest, because at EUV wavelengths the photo-ionization cross-section of H$_2$ is $\sim$20 times lower than that for Ar. Despite the low photo-ionization cross-section of H$_2$, the addition of only a small amount of hydrogen has a large effect on the sputter rate, because the cooling of electrons depends, not on the H$_2^+$ ion density, but on the density of H$_2$ neutrals. Therefore, hydrogen addition is a simple but effective solution to reduce the sputter rate of multilayer mirrors in a EUV lithography tool.

Bibliography

8.4 Bibliography


Experimental investigation of the sputter yield for $\text{Ar}^+$ on Ru in the near-threshold regime

Abstract. The absolute value for the sputter yield of $\text{Ar}^+$ on ruthenium at normal incidence has been measured in the near-threshold regime, between 40 and 100 eV. Argon ion projectiles from the low-energy ion gun of the IMPACT facility at Argonne National Laboratory are directed towards a thin ruthenium film. The sputtered atoms are collected on a sensitive Quartz Crystal Microbalance (QCM) facing the target. Under the assumption of a cosine dependence of the angular distribution of sputtered particles, absolute sputter yields can be calculated from the measured mass increase on the QCM detector.

The energy dependence of the measured sputter yield is compared to semi-empirical fit formulas. The results are in good agreement with the Yamamura formula, which predicts a sputter threshold energy of 27 eV for $\text{Ar}^+$ on Ru. Deviations are found at the lowest measured energy of 40 eV, which are possibly the result of a break-down of the assumption of a cosine-distribution of sputtered particles.

Experiments performed at Argonne National Laboratory’s IMPACT facility.
Chapter 9: Sputter yield measurements

9.1 Motivation

Future extreme ultra-violet lithography (EUVL) will use radiation in a narrow band around a wavelength of 13.5 nm. The bandwidth is determined by the reflective properties of Mo/Si multilayer coated mirrors that are used as optical elements in the device [1, 2]. Often, these mirrors are capped by a thin Ru layer to prevent oxidation of the underlying multilayer stacks [3, 4].

The radiation generates a weakly-ionized plasma in the tool by photo-ionization of the argon background gas. Ions are accelerated in the plasma sheath towards the optical components [5–7], potentially causing damage through physical sputtering. Information is required on the sputter yield (atoms removed per incident ion) for argon on ruthenium in the appropriate energy range. The impact energy of the ions was estimated through Particle-In-Cell Monte Carlo simulations to be limited to 50 eV. The only available experimental data [8, 9] for the sputter yield for the Ar on Ru system is at higher energies (60 − 600 eV).

Past research on low energy sputtering has mainly been restricted to energies relevant for etch processes and sputter deposition (between 0.5 and 10 keV) [10]. Theoretical descriptions [11] of the sputtering process in this regime are well established, but they break down in the near-threshold regime (below 100 eV), because there are only a small number of atoms involved in the collision cascade, and the assumption that the recoil energy flux of the atoms in the collision cascade is distributed isotropically no longer holds. At decreasing bombardment energies, the recoil atoms are increasingly distributed in a forward direction [12]. Furthermore, the description of the sputtering process in terms of binary collisions no longer applies as projectiles interact with multiple atoms simultaneously [13, 14].

Several attempts [15, 16] have been made to develop semi-empirical formulas for the sputter yield at low energies based on scaling laws. In these formulas, see Appendix A, the sputter yield drops to zero at the sputter threshold, which is a function of the surface binding energy and the masses of the projectile and target particles. For the $\text{Ar}^+$ on Ru system, these formulas predict the sputter threshold energy to be between $27 − 37$ eV. The large uncertainty in this number is the motivation to experimentally determine the sputter yield. For this purpose, measurements have been performed at the IMPACT facility at Argonne National Laboratory.

9.2 Method

We aim to measure the sputter yield by directing a well-defined mono-energetic beam of $\text{Ar}^+$ ions at a Ru target and measure the mass of sputtered material deposited on the surface of a Quartz Crystal Microbalance (QCM) facing the target [17], as shown in Fig. 9.1.

The total mass $\Delta m_d$ of sputtered material deposited on the QCM is equal to

$$\Delta m_d = m_{\text{Ru}} D Y C_f S,$$  

(9.1)
where $m_{Ru}$ is the mass of a single sputtered particle, $D$ is the ion dose (number of ions), $Y$ is the sputter yield in units of atoms per ion, $C_{fr}$ the fraction of the normalized distribution of sputtered particles subtended by the QCM crystal and $S$ is the dimensionless sticking coefficient, which is defined as $S = 1 - R_{QCM}$, with $R_{QCM}$ the reflection coefficient for sputtered species off the QCM crystal calculated by either molecular dynamics or TRIM-SP simulation [18]. For Ru, the sticking coefficient is taken equal to unity.

The mass deposited onto the crystal changes the resonance frequency of the shear thickness vibration of the crystal. The measured variation in the crystal frequency $\Delta f$ is proportional to the mass deposited on the crystal according to

$$\frac{\Delta m_d}{m_{cr}} = -\frac{\Delta f}{f},$$

(9.2)

with $m_{cr}$ the mass of the QCM crystal. Therefore, the yield corresponds to

$$Y = -\frac{1}{DC_{fr}S m_{Ru}} \frac{\Delta f}{f}.$$

(9.3)

Only a fraction of the sputter particles emitted from the sample is deposited onto the surface of the QCM. The collected fraction $C_{fr}$ can be calculated by integration of the normalized angular sputter distribution $Y(\theta)$ over the solid angle $\Omega_{QCM}$ subtended by the QCM

$$C_{fr} = \frac{1}{2\pi} \int_{\Omega_{QCM}} Y(\theta) d\Omega.$$  

(9.4)

More information on the geometry involved in the calculation of the collected fraction can be found in [19] and in Appendix B.
Chapter 9: Sputter yield measurements

In the linear cascade regime, the projectile ions isotropically transfer momentum to the atoms of the target material. The probability that these particles will escape to the surface is proportional to the momentum component in the direction normal to the surface. Hence, the angular sputter distribution will show a cosine dependence \( Y_{lc}(\theta) = \cos \theta \). In the single-knock-on regime, momentum transfer is no longer isotropic, but more directed in the forward scattering direction. Therefore, the fraction of sputtered particles is greater at lateral angles than at normal angles to the target. As a result, the angular sputter distribution will tend to be under-cosine [20–22], as can be seen in Fig. 9.2.

Figure 9.2: Angular sputter distributions in the linear cascade regime (solid line) and in the single-knock-on regime (dashed line).

9.2.1 Temperature influence on QCM measurement

The Quartz Crystal Microbalance (QCM) uses the piezo-electric effect to measure the resonance frequency \( f_0 \) of the shear thickness vibration of the crystal. In 1959, Sauerbrey [23] discovered that variations in frequency \( \Delta f \) are proportional to the mass change of the crystal \( \Delta m_{cr} \)

\[
\Delta f = \frac{-2f_0^2 \Delta m_{cr}}{A\sqrt{\rho_q\mu_q}},
\]

with \( A \) the piezo-electrically active area, \( \rho_q \) the density of quartz, \( \rho_q = 2648 \text{ kg m}^{-3} \) and \( \mu_q \) the shear modulus of quartz, \( \mu_q = 2.947 \times 10^{10} \text{ kg m}^{-1} \text{ s}^{-2} \).

The crystal temperature has a strong effect on the stability of the frequency of the crystal as both the density \( \rho_q \) and shear modulus of quartz \( \mu_q \) vary with temperature. Typically, the relation between the frequency of the crystal and temperature can be approximated by a cubic function, as shown in Fig. 9.3. The frequency stability of the crystal is best near the inflection points. In absence of thermal gradients, the position of the inflection points is mainly determined by the angle of cut of the crystal relative to the crystallographic axes of quartz.

Thermal gradients in the crystal can cause the \( f - T \) relation to change. When the temperature is cycled, from one temperature to another and back, the crystal shows thermal hysteresis, even if the rate of temperature change is slow. The amplitude of the hysteresis
increases with the rate of temperature change. Rapid temperature variations cause heat flow between the crystal and the mounting holder, which induces stresses that alter the $f - T$ relation.

Besides temperature fluctuations, the frequency of the crystal is also influenced by absorption and desorption of background molecules such as water. To eliminate these contributions, we use a dual QCM unit, with two identical crystals in thermal contact. One exposed sensor acts as the deposition crystal, whereas the other covered sensor is used as a reference. For the yield calculation, the change in the difference between the frequencies of the crystals is measured, before and after the ion irradiation.

9.3 Experimental setup

The relative positions of the target holder, the ion gun and the dual QCM unit are shown in the schematic in Fig. 9.4. The UHV chamber is pumped by turbo molecular pumps to attain base pressures of $10^{-9} - 10^{-7}$ mbar. The partial pressures of the background gases in the system during the experiments are monitored with a residual gas analyzer and typical values are listed in Table 9.1. The ion beam source for our experiment is a 1402A electron impact ionization gun from Nonsequitur Technologies, designed for inert gasses at low energy in the energy range between 10 and 1000 eV. It is capable of delivering up to $1\mu$A of current to the target with current densities of $3 - 30\mu$A/cm$^2$ for projectile energies in the range of 30 – 100 eV. Beam intensities are controlled by selecting the energy, filament emission current, and extractor and lens voltages.

The system is further equipped with an electron gun, ion gun and PHOIBOS MCD 100 hemispherical energy analyzer to provide in-situ surface analysis diagnostics such as Ion Scattering Spectroscopy (ISS) and Auger Electron Spectroscopy (AES) to monitor the
elemental and chemical state of the eroded target surface.

When the target holder is retracted the total current of the ion beam can be measured with a Faraday cup. To monitor the beam current during the experiment, the sample holder is connected to the ground through a Keithley picoamp-meter.

### 9.3.1 Ion beam characterization

To verify the positioning of the ion beam with respect to the target, a metal plate with a 1 mm hole is placed above the target. With the octopole deflection lenses at the aperture of the ion gun column, the ion beam is directed through the hole.

At energies above 300 eV a large fraction of the beam (>90%) is transmitted through the hole, but at threshold energies only a small fraction of the beam is transmitted, indicating that the beam size increases considerably as the energy is reduced. It is further observed that, besides the beam size, also the beam direction changes with energy. At lower energies the spot of the ion beam moves towards the edge of the sample.

To optimize the definition of the ion beam, we position a metal plate containing a 3 mm hole over the target and at each ion energy maximize the current to the sample holder by
adjusting the optics settings of the ion gun. The beam profiles, obtained after optimization, can be seen in Fig. 9.5. To measure the ion beam profile a metal plate, positioned over the target, is moved in a direction parallel to the target and the beam current on the sample holder is measured as a function of the position of the plate. After smoothing, the derivative of the current with respect to the position is taken to obtain the beam profile. The same settings are used in the remaining sputter experiments.

9.4 Results

9.4.1 Sample preparation

The $1 \times 1$ cm target contains a 20 nm thick Ru film on top of a gold layer on a silicon substrate. Before the experiment we measured the RMS surface roughness of the samples with an Atomic Force Microscope to be $\sigma = (1.1 \pm 0.2)$ nm over a $2.5 \times 2.5$ µm area.

After sample cleaning with methanol, the sample was placed into position through the load lock. Before the experiment the sample was bombarded with 500 eV Ar$^+$ for two minutes to remove any remaining impurities on the surface. Both AES and ISS measurements confirm that any remaining impurities on the sample were removed after the Ar$^+$ bombardment.

Before the low energy sputter experiments the surface of the QCM deposition crystal is coated with a few monolayers of ruthenium to ensure that the sticking coefficient is $\sim 100\%$. 

![Figure 9.5: Beam profiles for different projectile energies after optimization of the ion optics of the 1402A ion gun.](image-url)
9.4.2 First results

In the first series of experiments, we irradiate the sample with projectile energies between 30 and 100 eV. Figure 9.6 shows the frequency of both crystals as a function of time. The scales on the right show, respectively, the temperature of the QCM holder and the ion current to the sample as a function of time. The frequency oscillations on the reference crystal are correlated with the temperature fluctuations. The frequency of the deposition crystal shows similar fluctuations, but with a negative slope superimposed on them during the irradiations. The short current spike before each irradiation is the electron current from the AES scan.

![Diagram](image)

**Figure 9.6:** Frequency of the QCM crystals (top graph), frequency difference (middle graph), sample current and temperature of the QCM holder (bottom graph) as a function of time for a series of irradiations with projectile energies between 30 and 100 eV.

In Fig. 9.7, the frequency difference between the QCM crystal is plotted as a function of time for the 50 eV irradiation. The scale on the right shows the current that is measured on the sample. During the exposure, the frequency difference has a negative slope corresponding to a mass increase, whereas the slope before and after the reference crystal is close to zero.

The yield is calculated from the slope $\dot{\Delta}f_{ir}$ of a linear fit to the frequency difference between the crystals during the irradiation. To account for background changes, the time weighed slope of the difference before $\Delta f_{bf}$ and after $\Delta f_{af}$ the irradiation is subtracted according to
9.4 Results

Figure 9.7: Frequency difference between the QCM crystals (left scale) and sample current (right scale) as a function of time for a 50 eV Ar$^+$ irradiation.

\[
\dot{\Delta}f = \dot{\Delta}f_{ir} - \frac{\dot{\Delta}f_{bf} \Delta t_{bf} + \dot{\Delta}f_{af} \Delta t_{af}}{\Delta t_{bf} + \Delta t_{af}}.
\] (9.6)

When the irradiation of the ruthenium sample is stopped, the slope of the QCM signal does not go to zero immediately. There is a further mass increase of the deposition crystal, that is believed to be associated with the oxidation of the ruthenium on the surface of the QCM crystal. The sputtered particles are energetic enough to break up bonds of water molecules on the crystal surface. The oxygen thus released, reacts with ruthenium to form an oxide layer. To confirm this idea, the experiment is repeated with an Au target. As expected, the slope of the QCM signal goes to zero immediately after the exposure, because gold is much more oxidation-resistant than ruthenium.

9.4.3 Sputter yield

Before the next series of experiments, the crystals of the QCM are replaced. The $f - t$ relation of the new RC type crystals is shown in Fig. 9.8. For some reason, the $f - t$ curve does not show the cubic relation that was obtained before. Instead, the crystal frequencies respond linearly with temperature. As a result the crystal frequencies are very sensitive to temperature fluctuations. We choose to operate the crystals at a temperature of 90 °C. In further experiments, the temperature on the QCM is actively controlled by a PID-controller. With this feedback loop, the temperature fluctuations are reduced to less than 0.2 °C. The influence of the temperature fluctuations averages out when the duration of the irradiations is increased.

Figure 9.9 shows the measured yield for Ar on Ru as a function of energy. The lines indicate literature values for the sputter yield of Ar$^+$ on Ru according to the semi-empirical
formulas of Bohdansky and Yamamura. These formulas are extrapolations of yield measurements at higher ion energies. The thick vertical lines show the position of the associated sputter threshold energies.

The results are in good agreement with the predictions of the Yamamura formula for projectile energies of 50 eV and higher. Only for the lowest energy of 40 eV the sputter yield is considerably higher, even larger than the sputter yield at 50 eV. A possible explanation for this is that the ion beam is not well aligned with the target at the lowest energy. Since the beam spot becomes larger with decreasing energy, the beam alignment with respect to the target is more critical at low projectile energies. Another explanation is that in the calculation of the sputter yield using equation 9.3, it is implicitly assumed that the collected fraction and the sticking coefficient do not depend on the projectile energy. While the latter assumption seems reasonable, the collected fraction will certainly change with energy, because with decreasing projectile energy the angular distribution of the sputtered particles will increasingly deviate from the cosine distribution that was assumed for the yield calculation. At lower energies the angular distribution tends to be under-cosine, resulting in an overestimation of the sputter yield at low energies if this effect is not properly taken into account.

9.5 Conclusions and recommendations

Accurate sputter yield measurements at near-threshold energies are only possible with a well-defined ion beam. The ion optics of the ion gun should be optimized at each energy setting to ensure a sufficiently small beam spot.

The accuracy of the sputter yield experiments is limited by the fluctuations of the crystal temperature. Future measurements should be performed at the temperature where
the crystal has an inflection point to reduce the noise of the temperature fluctuations. The sputter yield measurements for Ar$^+$ on Ru show good agreement with predictions based on the Yamamura formula for energies of 50 eV and higher. Deviations occur for lower energies, which are possibly the result of the break-down at low energies of the assumption that the angular distribution of sputtered particle has a cosine distribution. Additional information is required on how the angular distribution of sputtered particles changes with projectile energy. This could be done by placing witness plates at various angels with respect to the sample during the sputter experiment. Afterwards, the angular sputter distribution can be deduced from the the measured thickness of the deposited Ru layer on the witness plates.

If all these three conditions are satisfied, then measurements of absolute sputter yields that are an order of magnitude lower, should be achievable.

9.6 Acknowledgements

The author wishes to acknowledge support from J.P Allain and his team at Argonne National Laboratory: V. Titov, C. Chrobak, E. Hinson, M. Hendricks, P. Plotkin and M. Nieto. Furthermore, Brian Rice from Intel Corporation is acknowledged for his support.

This work has been created in part by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable world-wide license in said work to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.
Chapter 9: Sputter yield measurements

Bibliography


Experimental investigation of the sputter rate

Abstract. The lifetime of multilayer mirrors in an EUV lithography tool is adversely affected by carbon deposition and ion sputtering. Both mechanisms have been experimentally investigated at the EUV laboratory at ASML in Veldhoven with in-situ EUV reflectometry combined with secondary photo-electron emission measurements, and ex-situ XPS analysis. The measured carbon growth rate is much higher than the expected sputter rate, which obstructs accurate sputter rate measurements under normal conditions.

With atomic hydrogen cleaning, the carbon contamination can be removed from the mirror. This technique is applied to reduce the influence of the carbon deposition on the ability to measure the sputter rate. Evidence is presented of sputtering of multilayer mirrors as a result of the impact of ions from the EUV radiation generated plasma.

Experiments performed at ASML’s EUV laboratory.
Chapter 10: Sputter rate measurements

10.1 Introduction

The lifetime of multilayer coated mirrors in an EUV lithography tool is specified at 30,000 illumination hours [1]. The lifetime of multilayer mirrors is adversely affected by several mechanisms such as oxidation, carbon deposition and ion sputtering. Of these three mechanisms, ion sputtering is the main topic of research in this thesis.

At the EUV laboratory at ASML, efforts have been undertaken to experimentally determine the sputter rate of Ru capped multilayer mirrors by argon ions from the EUV radiation generated plasma. For this purpose, EUV radiation from a pulsed EUV source is collected by an elliptically shaped grazing incidence mirror and focussed onto a multilayer mirror.

However, besides sputtering, carbon deposition is observed when mirrors are exposed to EUV radiation. The carbon contamination prevents accurate measurement of the sputter rate. Therefore, this chapter is divided into two parts.

In the first part of this chapter, the mechanism of the carbon growth is investigated with a simple model. The carbon growth rate is further studied with in-situ EUV reflectometry and secondary photo-electron emission measurements. It will be shown that the carbon contamination can be removed from the mirror with atomic hydrogen cleaning.

In the second part, the atomic hydrogen cleaning technique is applied to counteract the carbon growth so that the sputter rate can be measured. Two experimental setups have been used for the sputter rate measurements.

10.2 Carbon growth

10.2.1 Introduction

In EUV lithography, the growth of thin, carbonaceous films on the surfaces of irradiated optical elements, such as Mo/Si multilayer mirrors, is generally observed [2–6]. This effect is undesired, because a fraction of the EUV radiation is absorbed by the carbon containing layers, which reduces the reflectivity of the multilayer mirrors. Similar forms of carbon contamination are commonly encountered on exposed mirror surfaces in synchrotrons [7], and in electron microscopy [8].

It is believed [9–11] that the carbon contamination is the result of EUV radiation-induced dissociation of adsorbed hydrocarbon molecules. The carbon layers grow in a three-step process. In the first step, hydrocarbon molecules from the gas phase are adsorbed on the surface (physisorption). In the second step, these weakly-bound hydrocarbon molecules are dissociated, either directly by photo-dissociation or indirectly by photo-electron-induced dissociation, into smaller fragments that are more chemically active. In the third step, the cracked fragments thus formed, chemically react with the surface and with each other, to form an amorphous, graphitic, but partially hydrogenated, layer. The layer will continue to grow as long as hydrocarbon molecules and EUV radiation are supplied.
10.2 Carbon growth

10.2.2 Theory

The growth rate of the carbon layer thickness $D$ under EUV irradiation is equal to

$$\frac{dD}{dt} = \sigma_d I_0 N \left[ \frac{M}{\rho} \right],$$

(10.1)

with $\sigma_d$ the effective cross-section for dissociation of hydrocarbons, $I_0$ the photon flux density in units of $\text{m}^{-2}\text{s}^{-1}$, $N$ the hydrocarbon surface concentration (the number of adsorbed hydrocarbons per unit of area), and the term in brackets the volume of a hydrocarbon molecule (molecule mass $M$ divided by mass density $\rho$). The effective cross-section for dissociation of hydrocarbons is the sum of two contributions

$$\sigma_d = \sigma_{ph} + \sigma_{SE} \gamma(D),$$

(10.2)

with $\sigma_{ph}$ the cross-section for EUV radiation-induced dissociation of adsorbed hydrocarbons, $\sigma_{SE}$ the cross-section for electron-induced dissociation, and $\gamma(D)$ the secondary photo-electron yield (the number of electrons emitted per incoming EUV photon). The value of $\gamma$ is different for either Ru or C. Hence, $\gamma$ depends on the thickness $D$ of the carbon layer on top of the ruthenium capping layer according to

$$\gamma(D) = \gamma_{Ru} e^{-D/\lambda_{Ru}} + \gamma_C (1 - e^{-D/\lambda_C}),$$

(10.3)

with $\lambda_{Ru}$ and $\lambda_C$ the inelastic mean free paths for, respectively, Ru and C which can be calculated with TPP-2M formula (Eqn. 3.21). For the secondary photo-electron yields of Ru an C at 92 eV, we use the same values as in [10].

It is assumed that the surface concentration of physisorbed hydrocarbons is the result of a balance between three processes:

a. Adsorption of gas phase molecules;

b. Thermal desorption into gas phase;

c. EUV radiation-induced dissociation.

Mathematically, this can be formulated in the following differential equation for the surface concentration

$$\frac{dN}{dt} = s \Gamma \left( 1 - \frac{N}{N_m} \right) - \frac{N}{\tau} - N \sigma_d(D) I_0,$$

(10.4)

where the first term accounts for the adsorption rate with $s \approx 1$ the effective sticking coefficient, $\Gamma = \frac{1}{2} \sqrt{8k_B T / \pi M}$ the molecular flux to the surface and $N_m = (M/\rho)^{\frac{3}{2}}$ the maximum surface concentration. In this way, the surface concentration of physisorbed hydrocarbons is limited to one Langmuir. The thermal desorption rate term contains the residence time $\tau = \nu_0^{-1} \exp(E_M/RT)$, with $\nu_0$ the escape frequency, $R$ the universal gas constant, and $E_M$ the molar desorption energy of the molecules.
The cross-section for the photon-induced dissociation of hydrocarbons is the same as used by Hollenshead and Klebanoff [10], i.e. from the CXRO website [12] the total adsorption cross-sections for carbon and hydrogen atoms are obtained. Subsequently, for a hydrocarbon molecule, the single atom contributions of the constituent atoms are added up. For the hydrocarbon dissociation cross-section due to secondary electrons, we estimate \( \sigma_{SE} \approx 10^{-21} \text{m}^2 \). The density of the carbon film is estimated to be \( \rho = 1125 \text{ kg m}^{-3} \), which is less than the density of graphitic carbon \( \rho = 2200 \text{ kg m}^{-3} \).

The desorption process is characterized by the residence time \( \tau = \nu_0^{-1} \exp \left( \frac{E_M}{RT} \right) \). The residence times for alkanes on a Ru(001) surface have been obtained from thermal desorption measurements by Brand et al. [13] and for alkanes on graphite by Paserba and Gellman [14]. For alkanes \( C_n H_{2n+2} \), the molar desorption energy was found to scale linearly with the chain length \( n \) of the molecules [15]

\[
E_M = \Delta E + n \Delta E_{CH}.
\]

Table 10.1 shows the thermal desorption parameters for linear alkanes on ruthenium and graphite. Calculated residence times are shown in Fig. 10.1.

<table>
<thead>
<tr>
<th>surface</th>
<th>( \Delta E ) [kJ/mol]</th>
<th>( \Delta E_{CH} ) [kJ/mol/CH]</th>
<th>( \nu_0 ) [s(^{-1})]</th>
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<td>Ruthenium</td>
<td>28</td>
<td>5.8</td>
<td>( 10^{15.3} )</td>
</tr>
<tr>
<td>Graphite</td>
<td>27.2</td>
<td>7.5</td>
<td>( 10^{19.6} )</td>
</tr>
</tbody>
</table>

**Figure 10.1:** Residence time of linear alkanes for ruthenium and graphite surface.
Table 10.2: Simulation parameters for alkanes $C_nH_{2n+2}$

<table>
<thead>
<tr>
<th>$n$</th>
<th>desorption energy [kJ/mol]</th>
<th>residence time [s]</th>
<th>dissociation cross-section [m$^2$]</th>
<th>Maximum surface coverage [atoms m$^{-2}$]</th>
</tr>
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<td>45.4</td>
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<td>$1.92 \times 10^{-22}$</td>
<td>$6.19 \times 10^{+18}$</td>
</tr>
<tr>
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<td>$2.54 \times 10^{-22}$</td>
<td>$5.15 \times 10^{+18}$</td>
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<tr>
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<td>$6.1 \times 10^{+09}$</td>
<td>$1.25 \times 10^{-21}$</td>
<td>$1.79 \times 10^{+18}$</td>
</tr>
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</table>

10.2 Carbon growth
To estimate the rate of hydrocarbon growth in our laboratory setup, the differential equations are numerically solved. For each alkane, the background pressure and total radiation dose must be specified as initial conditions.

Figure 10.2 shows the calculated carbon thickness in units of monolayers as a function of the background pressure of alkanes in the vessel after an exposure to $4 \times 10^{22}$ photons per m$^{-2}$, which corresponds to $10^6$ EUV pulses at an irradiation typical for our laboratory setup of 0.6 J m$^{-2}$ per pulse.

At low pressures, the carbon thickness is proportional to the pressure, because the growth rate is limited by the influx of hydrocarbons from the gas phase. Saturation occurs at elevated pressures, where the growth rate becomes limited by the influx of EUV photons.

The carbon thickness is different for each alkane as a result of thermal desorption. The desorption rate of light alkanes is so fast that the surface coverage of these molecules is low, and consequently the growth rate is low. The growth rate increases for heavier alkanes, but saturates when the desorption time becomes the slowest time scale in the system.

From Fig. 10.2, it can be concluded that the carbon contamination of multilayer mirror in an EUV lithography tool is not caused by light hydrocarbons, for which the growth rate is limited due to the fast desorption rate. For heavy hydrocarbons, the growth rate is limited by the adsorption rate on the multilayer mirror. Most heavy hydrocarbons will remain stuck to the walls of the vessel, and consequently the background pressure of heavy hydrocarbons in the vessel will be low. Therefore, hydrocarbons with mass in the intermediate regime ($n \sim 10$) will be the source of carbon contamination of multilayer mirrors in an EUV lithography device.

Figure 10.2: Computed carbon thickness in units of monolayers after $10^6$ EUV pulses at a irradiation of 0.6 J m$^{-2}$ per pulse as a function of the hydrocarbon pressure for alkanes $C_nH_{2n+2}$, with $n$ the number of carbon atoms per molecule.
10.2 Carbon growth

10.2.3 Experimental setup

Figure 10.3 shows the experimental setup at the EUV laboratory at ASML, which is used to study the effect of the EUV radiation on the lifetime of multilayer mirrors. The setup consists of three linked vacuum chambers. The EUV source is located in the first chamber. The second chamber is pumped by a 3000 l/s turbo pump and contains the collector mirror and the EUV reflectometer. The third chamber contains a cleaning station and mirror assembly and is pumped by a 1000 l/s turbo pump.

![Schematic of the experimental setup at the ASML laboratory.](image)

The EUV radiation is generated by a Xe fueled hollow cathode discharge [16], which produces EUV pulses with a duration of typically 100 ns at a repetition rate up to 1 kHz. The pinch plasma, with a spatial dimension of less than 1 mm, is positioned at one of the focus points of the collector mirror. This elliptically shaped, grazing incidence mirror collects a solid angle of $\Omega = 0.076$ sr and focuses the radiation onto a second focus point in the third vacuum chamber. The collector mirror images a cone of light with opening angles between 8 and 12 degrees, onto a circular spot with a diameter of 1 mm.

A foil trap [17] is placed between the plasma and the collector mirror to prevent damage to the mirror as a result of fast ions and small particulates that are produced by the source. The foil trap consists of a ring with 30 metal plates that are placed parallel to the radiation. Debris particles are scattered by the buffer gas between the foils and are subsequently deposited on the foils.

The second and third vacuum chamber are separated by an EUV filter, which consists of a thin Zr foil (thickness of 150 nm) supported by a nickel wire mesh. The EUV filter serves two purposes. Firstly, the filter blocks vacuum ultra-violet (VUV) radiation generated by the source with over 99% efficiency, but is about 50% transparent to EUV radiation with a wavelength between 10 and 17 nm [18]. Secondly, the filter acts as a flow restriction, so...
Chapter 10: Sputter rate measurements

that we can set the pressure in the third chamber roughly between $10^{-8}$ and $10^{-1}$ mbar, while maintaining a pressure in the second chamber of $10^{-3}$ mbar.

Two multilayer coated test mirrors with a 1-inch diameter can be mounted on the mirror holder assembly. The mirror holder is attached to a manipulator on a linear-rotary feedthrough, as shown in Fig. 10.3. With the manipulator, the mirrors can be placed exactly at the focus point of the collector mirror. The manipulator is mounted off-axis, so that rotation of the manipulator results in an arc-shaped line-scan of the EUV spot over the mirror surface.

Reflectometer

To determine the EUV reflectivity after an experiment, multilayer mirrors are usually sent to synchrotron facilities. Although reflectivity measurements at synchrotrons are very accurate ($\sigma \pm 0.05\%$ reflectivity), the method also has an important disadvantage: mirror samples have to be removed from the vacuum system and are exposed to air for several days before reflectivity measurements can take place. With in-situ measurements, the EUV reflectivity can be monitored during an experiment without the need to contaminate the mirror by exposing it to air.

The in-situ reflectometer consists of two EUV-sensitive photodiodes, three multilayer coated mirrors and two diaphragms all mounted on a CF-120 flange, as shown in Fig. 10.4. Two multilayer mirrors are put back-to-back at an angle of 45 degrees with respect to the incoming radiation cone. The periodicity of these multilayer stacks is such that the EUV reflectivity is optimized for an angle of 45 degrees at a wavelength of 13.5 nm.

![Figure 10.4: Picture of the in-situ reflectometer mounted on a CF-120 flange. The arrows indicate the path of the EUV radiation from the collector towards the photodiodes.](image)

The multilayer mirrors are positioned such that the top half of the radiation cone is not clipped by the first 45 degree mirror. After reflection from the mirror under test, the radiation is reflected by the second 45 degree mirror towards the first photodiode (measurement photodiode). The bottom half of the radiation cone is deflected by the first
45 degree mirror towards the normal incidence mirror, which directs the radiation towards the second photodiode (reference photodiode). Because of the extra normal incidence mirror, both branches of the reflectometer have the same number of reflections. This is necessary to ensure that both branches have similar spectral properties, because the multilayer mirrors are optimized for a wavelength of 13.5 nm, and will therefore spectrally filter the incoming 10 – 17 nm radiation from the source. Figure 10.5 shows the spectral reflectivity of a typical multilayer mirror.

![Figure 10.5: Spectral reflectivity of a Mo/Si multilayer mirror.](image)

The ring-shaped aperture at the entrance to the reflectometer and the circular aperture at the exit from the reflectometer both prevent stray light outside the opening cone of the collector from reaching the test mirror. Additional EUV filters have been placed in front of the photodiodes to ensure that only EUV radiation is detected.

The signals of the photodiodes are integrated over the duration of the EUV pulse and are sent to a computer. Here, the signals are averaged over a large number of EUV pulses (5000 – 10000) to reduce the influence of the pulse-to-pulse variation of the EUV source. Hence, the EUV reflectivity of a mirror is defined as the ratio of the signal of the measurement photodiode to the reference photodiode. Rotation of the manipulator results in a line-scan across the mirror surface.

The irradiation (in J m$^{-2}$) of the EUV pulse at the focus point of the reflectometer can be measured with photosensitive foil. The coloration of the foil after EUV exposure has been calibrated against a EUV sensitive photodiode. The diameter of the EUV spot at the focus point of the collector has a full width at half maximum of 0.5 mm.

Extensive calibration procedures are required to measure the absolute value of the EUV reflectivity. Because we are more interested in changes in reflectivity during an experiment, such calibrations can be avoided. Instead, the EUV reflectivity of the mirror under test (test mirror) is measured relative to the reflectivity of an unexposed mirror (reference mirror) which can be placed at the same position.
Chapter 10: Sputter rate measurements

Each measurement consists of two line-scans: one of the test mirror and one of the reference mirror. The relative EUV reflectivity is defined as the reflectivity of the test mirror at that particular position, divided by the reflectivity averaged over the line-scan across the reference mirror.

Figure 10.6(a) shows the reflectivity of the mirrors measured three times to test the reproducibility of the in-situ EUV reflectivity measurement. The statistical error of the measurement is estimated as $\sigma = 0.4\%$.

Simultaneously with the EUV reflectivity, the secondary photo-electron current (SE-emission) that is emitted from the mirror holder is measured and integrated over the duration of the pulse. To compensate for the pulse-to-pulse variation of the source, the signal is divided by the signal of a photodiode, which is located in the collector chamber. This photodiode detects stray light EUV radiation emitted by the EUV source. To block out longer wavelength radiation, a Zr bandpass filter is positioned in front of the photodiode.

The signal thus obtained is measured for both the test and reference mirror. In the same way as for the reflectivity, the relative SE-emission is defined as the signal of the test mirror at a particular position divided by the signal averaged over a line-scan across the reference mirror. Figure 10.6(b) shows the relative SE-emission, with a statistical error of $\sigma = 2\%$.

**Atomic hydrogen cleaning station**

When the manipulator is fully retracted, the test mirror assembly is positioned at the cleaning station, which consists of a tungsten filament in front of a hydrogen inlet. The tungsten wire is electrically heated to a temperature between $2100 - 2500 \ K$, which is sufficient to dissociate a small fraction ($\approx 1\%$) of the hydrogen [19, 20]. The filament temperature is monitored with an infrared pyrometer. The mirror assembly is positioned
such that the bottom mirror (reference mirror) is shielded behind a stainless steel plate. Only the top mirror (test mirror) is exposed to the atomic hydrogen flow. The distance between the mirror and the filament is 40 mm.

For calibration purposes, the atomic hydrogen cleaning setup was tested on glass plates with a thin carbon layer deposited on top. The thickness of the carbon contamination before and after atomic hydrogen cleaning was deduced from optical transmission measurements of the glass plates, performed at TNO Eindhoven. Figure 10.7 shows the cleaning rate as a function of the filament temperature.

![Figure 10.7: The cleaning rate of deposited carbon on a glass plate as a function of the filament temperature.](image)

### 10.2.4 Results

In the first experiment, a test mirror is positioned at the intermediate focus of the collector for a total of 30 million EUV pulses (abbreviated as 30 Mshot). During the exposure, the pressure in the measurement chamber is $10^{-6}$ mbar as a result of leakage through the EUV filter of Ar and Xe from the source chamber. When the source is turned off, the pressure in the unbaked measurement chamber is typically $10^{-8} - 10^{-7}$ mbar. At the start of the experiment, the EUV irradiation at the intermediate focus is 0.6 J m$^{-2}$ per pulse. At intervals of 5 Mshot, line-scans of the mirror (and reference mirror) are taken to measure both the EUV reflectivity and SE-emission. After each measurement, the mirror is put back into its original position for another exposure.

Results are shown in Fig. 10.8. At the exposed spot, both the EUV reflectivity and SE-emission of the mirror decrease, whereas in the unexposed spot they remain the same as in the first scan (which is taken as a base-line). X-ray photo-electron spectroscopy (XPS) measurements performed at TNO Delft after the experiment, confirm that a layer of carbon has grown in the exposed spot. It is estimated that every nm of carbon corresponds to 1.5% relative EUV reflectivity loss.
Based on the reflectivity loss a carbon layer with a thickness of $\sim 2 - 3$ nm has grown at the exposed spot. The small difference in EUV reflectivity loss between measurements after 20, 25 and 30 Mshot suggests that the carbon growth stops after 20 Mshot. Possibly, the system is getting cleaner. However, similar experiments with more EUV pulses, showed that the carbon contamination keeps growing with the number of pulses.

The SE-emission signal shows a large decrease at the exposed spot after 5 Mshot. Thereafter, increasing the number of EUV pulses does not lead to further SE-emission loss. The observed difference in SE-emission corresponds to the difference in the secondary photo-electron yield between C and Ru. According to synchrotron measurements [10], the secondary photo-electron yield of carbon ($\gamma_C = 0.13$) is $\sim 40\%$ lower different than the yield of ruthenium ($\gamma_{Ru} = 0.21$). The saturation of the SE-emission signal after 5 Mshot occurs, because the inelastic mean free path of the photo-electrons in the solid is only $\sim 0.35$ nm. Therefore, the SE-emission signal is only sensitive to changes of material in the top layer with a thickness of $\sim 1$ nm.

The source of the carbon is not known. No hydrocarbons were intentionally introduced to the system. The baseline pressure in the unbaked measurement chamber is typically in the range $10^{-8} - 10^{-7}$ mbar. In a similar setup at the ASML laboratory, the carbon growth could only be stopped when the entire vessel was cleaned in a plasma cleaner. Possibly, the hydrocarbons originate from the oil that is used in the machining of the stainless steel walls of the vessel.

The deposition rate of carbon is approximately 60 times faster than the predicted sputter rate [21] of the EUV-induced argon plasma ($\sim 1$ nm per $10^9$ EUV pulses). In fact, the carbon growth obstructs the ability to measure the sputter rate. Fortunately, the carbon contamination on the mirror can be removed by atomic hydrogen cleaning.

![Figure 10.8](image)

(a) Reflectivity

(b) SE-emission

**Figure 10.8:** Line-scan of the relative EUV reflectivity(a) and relative SE-emission(b) of a test mirror after several exposures of 5 million EUV pulses each. The arrow indicated the position of the EUV spot on the mirror during exposure.

In the second experiment, a mirror is first exposed for 30 Mshot under the same con-
conditions as in the previous experiment. Next, the exposed mirror is cleaned with atomic hydrogen in four steps of 10 minutes each. For this purpose, the mirror is positioned at the cleaning station. During cleaning, the tungsten filament is heated to 2200 K in 2 Pa of hydrogen gas. Results are shown in Fig. 10.9, where the relative EUV reflectivity and SE-emission before the 30 Mshot exposure are taken as a baseline. The observed drift of the EUV reflectivity signal is possibly the result of the wearing of the electrodes of the EUV source, which increases the size and changes the position of the EUV pinch.

![Figure 10.9: Line-scan of the relative EUV reflectivity(a) and relative SE-emission(b) of a test mirror after a 30 Mshot exposure, followed by four cleaning steps with atomic hydrogen, each 10 minutes in duration.](image)

After 40 minutes of hydrogen cleaning, the carbon contaminated spot is completely removed. Atomic hydrogen radicals that are formed at the tungsten filament react with the carbon layer. Small and volatile molecules such as methane $CH_4$ are formed that desorb from the surface.

### 10.2.5 Conclusions/Discussion

Carbon growth in a EUV lithography tool is the result of cracking of physisorbed hydrocarbons under bombardment with EUV photons and secondary photo-electrons. Light hydrocarbons do not contribute much to the carbon growth rate because of their high rate of desorption. Also, the carbon growth rate as a result of heavy hydrocarbons will be limited, because the background pressure of these heavy molecules can be expected to be very low.

With the in-situ EUV reflectometry and secondary photo-electron emission measurements, it is possible to monitor the surface of a multilayer mirror during experiments relative to an unexposed reference mirror. The reproducibility of the EUV reflectivity measurements is $\sigma = 0.4\%$. For the SE-emission measurements, the reproducibility is $\sigma = 2\%$. The SE-emission signal is very sensitive to changes within the first nm of material as a result of the short inelastic mean free path of the photo-electrons.
When a test mirror is exposed to EUV radiation, a film of carbon contamination grows at the exposed spot. The source of the hydrocarbons is unknown, although it is suspected that the carbon originates from the stainless steel walls of the vessel. With atomic hydrogen cleaning, it is possible to remove the carbon contamination from the mirror.

10.3 Sputter rate measurements

Because the carbon deposition rate is much faster than the sputter rate of the EUV radiation generated plasma, it was not possible to measure the sputter rate under normal conditions in a long term experiment. Two solutions are possible: measurements in a cleaned system where the carbon growth rate is much lower, or balancing the carbon contamination with atomic hydrogen cleaning. In the remainder of this chapter, these two methods are investigated.

10.3.1 Carbon growth suppression with atomic hydrogen cleaning

Method

For sputter rate measurements of multilayer mirrors, it is required that the Ru capping layer of the mirror is not covered by carbon contamination. The carbon growth rate can be balanced by atomic hydrogen cleaning to ensure that the Ru layer is at the surface. With the reflectometer setup at ASML, it is not possible to clean a sample with atomic hydrogen while exposing it with EUV radiation at the same time, mainly because the EUV source cannot be operated at the high hydrogen pressure required for cleaning. However, it is possible to expose the mirror for a duration short enough to ensure that, at the exposed spot, the mirror is only partially covered by carbon contamination (less than a monolayer). After the exposure, the mirror can be cleaned with atomic hydrogen to remove the carbon contamination.

In principle, the cycle of exposures and cleaning can be repeated indefinitely. Practically, the duration of the experiment is limited by the lifetime of the electrodes of the EUV source, which is typically limited to 50-100 Mshot for the hollow cathode Xe source at ASML.

Results

In the first experiment, a mirror sample is exposed for a total of 45 Mshot. During the exposure, the argon background pressure in the measurement chamber is 10 Pa at an irradiation of 0.6 J m$^{-2}$ per EUV pulse. The source is operated at 500 Hz, so that the total duration of the experiment is $\sim$ 30 hours.

After each 3 Mshot exposure, the mirror is transferred to the cleaning station where the mirror is treated with atomic hydrogen for 10 minutes to remove the carbon contamination.

After the last exposure, the test mirror is removed from the setup and sent to TNO Delft where the sample is analyzed with X-ray photo-electron spectroscopy (XPS). Similar
to previous experiments, a layer of carbon has grown on the mirror sample at the exposed spot. No imprint of argon sputtering is observed. Apparently, the carbon growth rate still exceeds the sputter rate.

The carbon layer is removed with atomic hydrogen. XPS analysis reveals that the underlying Ru capping layer is undamaged: no difference is measurable between the thickness of the Ru layer in and outside the exposed spot. The accuracy of the XPS-measurement is $\sim 0.1$ nm.

The experiment is repeated with slightly different parameters. Instead of after 3 Mshot, the mirror is cleaned after each 1 Mshot exposure for a total of 68 Mshot. Between exposures, the sample is treated with atomic hydrogen for 2 minutes. Again, XPS-analysis shows carbon contamination and no measurable signs of damage to the Ru capping layer as a result of argon sputtering.

**Discussion/Conclusion**

The method of alternating EUV exposures with atomic hydrogen cleaning steps to keep the Ru capping layer at the surface during the sputter experiments has not resulted in a measurement of the sputter rate for a number of reasons.

According to the predictions of the PIC-MC model (1 nm of Ru removed per $10^9$ EUV pulses at 0.5 Pa of argon pressure), the total number of pulses of the experiment is too short to detect a significant amount of sputtering. For an experiment of 50 Mshot, this would result in a decrease of Ru capping layers of 0.05 nm, which is already below the detection limit of the XPS-analysis method. To increase the sputter rate, the argon pressure in the experiment was elevated to 10 Pa. However, the simulations in Chapter 7 show that the increase of pressure leads to a decrease of the sputter rate as a result of cooling of the plasma electrons in inelastic collisions with neutrals. Instead, to increase the sputter rate the irradiation should be increased, but unfortunately this is not feasible with the current hollow cathode Xe source.

Furthermore, the fact that the Ru layer is partially covered during the EUV exposure with carbon contaminations also significantly reduces the sputter rate of the Ru layer by the EUV generated plasma.

### 10.3.2 Measurements in a cleaned setup

**Experimental conditions**

The sputter rate of the EUV-induced plasma has also been investigated with another, similar experimental setup at the ASML EUV laboratory. To reduce the carbon growth rate, this setup has been taken apart and cleaned in a plasma cleaning facility. Like the reflectometer setup, this cleaned setup consists of a source chamber with a Xe fueled hollow cathode EUV source that is separated by a foil trap from a chamber which contains the collector mirror. Through a load lock, mirror samples can be introduced to the measurement chamber, which is separated by an EUV filter from the collector chamber. In the
load lock, mirror samples can be cleaned with atomic hydrogen.

In this setup, five samples are exposed, each for a total of $5 \times 10^7$ EUV pulses (50 Mshot). After each 10 Mshot exposure, the sample is transferred to the load lock and cleaned with atomic hydrogen for 10 minutes. The experimental conditions for each mirror sample are summarized in Table 10.3. After the exposure, the samples are sent to TNO Delft for XPS analysis.

Table 10.3: Experimental parameters for mirror sample exposures in the cleaned setup.

<table>
<thead>
<tr>
<th>Sample</th>
<th>gas</th>
<th>pressure</th>
<th>condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2 Pa</td>
<td>Ar</td>
<td>no EUV filter</td>
</tr>
<tr>
<td>2</td>
<td>0.01 Pa</td>
<td>Ar+Xe</td>
<td>no EUV filter</td>
</tr>
<tr>
<td>3</td>
<td>0.2 Pa</td>
<td>He</td>
<td>no EUV filter</td>
</tr>
<tr>
<td>4</td>
<td>0.2 Pa</td>
<td>Ar</td>
<td>support mesh only</td>
</tr>
<tr>
<td>5</td>
<td>0.2 Pa</td>
<td>Ar</td>
<td>with filter and -200 V on sample</td>
</tr>
</tbody>
</table>

Results

To enhance the sputter rate, the first mirror sample is exposed without EUV filter between the collector and measurement chamber. As a result the mirror will not only receive EUV radiation, but the entire spectrum emitted by the EUV source. The measurement chamber is filled with argon gas at a pressure of 0.2 Pa.

After the experiment, dramatic evidence of sputtering can be observed as a large number of alternating lighter and darker concentric rings is visible on the mirror surface. The rings correspond to the Mo/Si layers of the multilayer stacks under the Ru capping layer. Towards the center of the exposed spot, the spacing between the rings is smaller. Apparently, at the position of the exposed spot a crater has been sputtered in the multilayer mirror. The depth of the crater can be determined with XPS analysis.

Figure 10.10(a) shows the result of a high resolution XPS line-scan across the mirror sample. Atomic concentrations for molybdenum, silicon, oxygen and ruthenium are plotted. The Ru capping layer is almost completely removed. Only at the unexposed edge of the mirror Ru is visible. Oscillations in the Mo and Si signal correspond to the position of the rings. The number of oscillations from the edge of the mirror to the exposed spot indicates the number of bilayers that have been sputtered. The thickness of a bilayer is 6.7 nm. In total, 13 bilayers have been sputtered which corresponds to a depth of $\sim 90$ nm. The observed sputter rate is about thousand times higher than predicted by the PIC-MC simulations.

To investigate whether the anomalously high sputter rate of the first experiment is caused by fast ions emitted by the EUV source, the second sample is exposed under the
10.3 Sputter rate measurements

Figure 10.10: Line-scan of the exposed mirror samples with XPS analysis. The atomic concentrations are shown for Mo 3d, Si 2p, O 1s, Ru 3d and Ru 3p. (a) For 0.2 Pa of Ar, the Ru capping layer and 13 bilayers of Mo and Si are sputtered away. (b) For 0.01 Pa of Ar and Xe, only the capping layer and the first Mo layer are sputtered. (c) For 0.2 Pa of He, the Ru capping layer is partially sputtered.

same conditions, but without argon gas supply. The pressure during the exposure is 0.01 Pa of xenon and argon gas that leaks from the EUV source into the measurement chamber. After the experiment, a small spot is visible at the position of the exposed spot. From the result of the XPS analysis of the sample, shown in Fig. 10.10(b), it can be concluded that at the exposed spot the Ru capping layer and the first Mo layer have been sputtered away. The sputter rate is much slower than in the first experiment, where the Ar pressure was 20 times higher. Therefore, the sputtering is not caused by fast ions from the EUV source, but by the ions of the radiation-induced plasma. The observed sputter rate is about hundred times faster than the rate predicted by the PIC-MC simulations.
Chapter 10: Sputter rate measurements

For the third exposure, the experimental conditions are again the same as in the first experiment, but with helium gas instead of argon. No damage to the mirror was visible after the exposure with the naked eye. From the XPS line-scan in Fig. 10.10(c) it can be concluded that the Ru capping layer is partially sputtered. The underlying Mo and Si layer are slightly oxidized, also close to the edges of the mirror. Compared to Ar, the sputter rate of He is much lower. Again, the results confirm the idea that the sputtering is the result of ions from the radiation-induced plasma. Because helium ions are much lighter than argon ions, their sputter yield is much lower as a result of poor energy transfer between the ions and the Ru atoms.

For the fourth mirror sample, the conditions of the first experiment are repeated, but with the EUV filter replaced by a nickel wire mesh with an optical transmission of 83%. After the 50 Mshot exposure, two concentric rings are visible on the mirror sample.

From the line-scan in Fig. 10.11(a) it can be seen that the maximum depth occurs at the second Si layer. The sputter rate is much less ($\approx 6$ times) than in the first experiment, although the irradiation is approximately the same.

Possibly, plasma electrons are heated by the electromagnetic radiation from the EUV source in the microwave or radio frequency ranges. The increased electron temperature increases the voltage drop across the plasma sheath region so that plasma ions impact on the mirror at energies higher than calculated by the PIC-MC simulations in previous chapters. The mesh partially shields the electromagnetic radiation, so that the sputter rate is reduced.

To confirm the idea of shielding, the fifth mirror sample is exposed with an EUV filter between the collector and measurement chamber. To enhance sputtering, a negative voltage of 200 V is applied to the sample holder to attract the positively charged argon ions. After the experiment, the surface of the mirror looks undamaged. Figure 10.11(b) shows the result of the XPS line-scan of the mirror sample. The Ru capping layer shows no indication of sputtering. Apparently, the EUV filter successfully shields the electromagnetic interference from the source.

Furthermore, even without carbon contamination and with -200 V applied to the mirror it is still not possible to measure sputtering by the EUV generated argon plasma.

10.3.3 Conclusions

The observed sputtering of multilayer mirrors in the cleaned setup is the result of ions from the EUV-induced plasma. The sputter rate of argon ions is much higher than for helium ions, which can be expected because the sputter threshold energy for He on Ru is 56.4 eV, which is much higher than the 27.0 eV threshold energy for Ar on Ru.

The anomalous sputter rate in the first experiment, without EUV filter, is possibly the result of electromagnetic interference from the EUV source in the radio or microwave ranges, which heats the plasma electrons. Consequently, the higher electron temperature would result in a higher voltage drop over the plasma sheath in front of the mirror. As a result ions impact on the mirror at higher energies, which increases the sputter rate.
10.3 Sputter rate measurements

Figure 10.11: Line-scan of the exposed mirror samples with XPS analysis. (a) For 0.2 Pa of Ar and a wire mesh between the chambers, the Ru capping layer and almost 2 bilayers of Mo and Si are sputtered away. (b) For 0.2 Pa of Ar and a EUV filter between the chambers, no indication of sputtering is visible.

The electromagnetic interference can be partially shielded by a metal wire mesh, which significantly reduces the sputter rate. With an EUV filter between the collector and measurement chamber, no sputtering of the mirror is observed. Possibly, the EUV filter shields the EM-interference from the EUV source.

Because the carbon growth rate in the cleaned setup is much lower, it should in principle be possible to measure the sputter rate of the EUV-induced argon plasma. However, at the moment, the lifetime of the electrodes of the EUV source is the limiting factor.

Efforts to enhance the sputter rate by applying a negative potential of 200 V on the mirror sample to increase the impact energy of the positively charged argon ions did not result in a detectable sputter rate. Although the sputter rate was too low to be detected, this result does not contradict the predictions for the sputter rate of the PIC-MC model.
10.3.4 Acknowledgements

The author wishes to acknowledge Luc Stevens and John de Kuster from the EUV laboratory at ASML for their technical support. Yuuri Sidelnikov from ISAN, Troitsk is acknowledged for developing the in-situ EUV reflectometer. Furthermore, from TNO Delft E. van Kimmenade and N. Faradhev are acknowledged for their expertise in the field of XPS analysis, and E. te Sligte for the calibration of the atomic hydrogen cleaning method.

Bibliography


[18] Transmission of the Zr filters can be found online at [http://www.luxel.com](http://www.luxel.com).


General conclusions and discussion

The main goals of the research described in this thesis have been to study the effect of a plasma generated by EUV radiation on the lifetime of the multilayer mirrors in a EUV lithography device, to investigate the mechanism of sputtering, and to find ways to avoid or reduce the rate of sputtering.

This chapter will first give a summary of the main conclusions of previous chapters. Thereafter, recommendations will be presented.

- Photo-ionization of the background gas in the EUV lithography tool generates a weakly-ionized, low-density plasma in the optical column. The excess energy after photo-ionization is mainly transferred to the plasma electrons. Initially, after photo-ionization the plasma consists of cold ions and hot electrons. The plasma is optically thin, and short-lived. Plasma recombination occurs at the plasma boundaries such as multilayer mirrors. This happens before the plasma electrons can thermalize.

- Because of the low plasma density ($\approx 10^{15}$ m$^{-3}$) and short lifetime (few microseconds) it is difficult to investigate the plasma with diagnostic techniques such as microwave interferometry, Thomson scattering, or laser induced fluorescence. Attempts to measure the plasma density and electron temperature with a Langmuir probe have been inconclusive as a result of photo-electron emission from the tip of the probe.

- Numerical simulations with a Particle-In-Cell Monte Carlo model reveal that the mechanism of sputtering is the formation of a plasma sheath in front of the mirror. In the electric field thus formed, positively charged ions are accelerated towards the mirror. The model calculates the energy and the number of ions that collide with the mirror.

  The advantages of the PIC-MC model are that the electric field is calculated self-consistently and that no assumptions have to be made for the energy and velocity distributions of the charged particles.

- To determine the sputter rate additional information is required on the sputter yield (the number of atoms sputtered per incoming ion as a function of the impact energy).
Sputter yield measurements with a low-energy ion gun in combination with a sensitive quartz crystal microbalance have been performed in the near-threshold regime. The measurements for Ar on Ru are in good agreement with the semi-empirical formula of Yamamura, which predicts a sputter threshold energy at 27 eV.

- Secondary photo-electrons emitted from the multilayer mirror effectively decrease the average energy of the plasma electrons during the EUV pulse. After the EUV pulse, the potential drop across the plasma sheath region rapidly rises, and ions are accelerated towards the mirror.

- The sputtering as a result of the EUV radiation generated argon plasma is mainly the result of doubly charged argon ions with a smaller contribution from singly charged ions, because the doubly charge ions gain twice the energy in the potential drop over the plasma sheath region.

- According to PIC-MC simulations, the sputter rate increases monotonically with the EUV radiation (energy of the EUV radiation per unit of area per pulse).

- The pressure scaling of the sputter rate shows a maximum. On the one hand, the increase of the pressure in the tool leads to the production of more plasma through photo-ionization which results in more ion impact events. On the other hand, the increased pressure also increases the inelastic collision frequency of the plasma electrons. Thus, the plasma electrons are cooled, which reduces the potential drop over the plasma sheath region. As a result the energy at which ions impact on the mirror is reduced, which reduces the sputter rate per ion.

- The sputter threshold (the ion impact energy below which no sputtering occurs) depends on the masses of the projectiles and target atoms. Light ions such as H$^+$ and H$_2^+$ have a sputter threshold that exceeds the energy available to the ions of the EUV-induced plasma. Hence, these light ions do not contribute to sputtering.

The PIC-MC model predicts that the addition of hydrogen to the argon background gas decreases the sputter rate of argon ions for two reasons.

Firstly, the hydrogen gas increases the inelastic collision frequency of the plasma electrons, which cools the plasma electrons and decreases the potential drop over the plasma sheath region.

Secondly, the light hydrogen ions are much more mobile than the argon ions. Therefore, the hydrogen ions reach the multilayer mirror before the argon ions do. In this way, the hydrogen ions reduce the charge separation (and therefore the potential drop) over the plasma sheath region before the argon ions can arrive. As a result, the argon ions experience a lower potential drop over the plasma sheath, which reduces the sputter rate.
When exposed to EUV radiation, a thin film of carbon contamination grows on top of the multilayer mirrors. The carbon contamination is the result of EUV-induced dissociation of physisorbed hydrocarbons, either directly by EUV photons, or indirectly by photo-electron impact.

The carbon growth rate has been measured with in-situ EUV reflectometry and secondary photo-electron emission measurements, and ex-situ with XPS analysis. Experimental investigation of the sputter rate is hampered by carbon contamination, because the observed growth rate of hydrocarbons is much faster than the expected sputter rate. The carbon contamination can be removed with atomic hydrogen cleaning. The sputter rate has been measured in two ways.

The first method uses cycles of EUV irradiation followed by atomic hydrogen cleaning to ensure that the mirror surface is only partially covered by hydrocarbons during sputtering. This method did not lead to accurate sputter rate measurements, possibly because the argon pressure during the experiment was chosen to high.

The second method used a cleaned setup in which the carbon growth rate is much slower. Evidence is found of sputtering by the EUV radiation generated plasma. The sputter rate was much higher for argon than for helium gas.

In general, it can be concluded that the sputter rate as a result of the EUV radiation generated argon plasma is predicted to be very low ($\approx 1 \text{ nm per } 10^9 \text{ EUV pulses}$), although this value is to low to be verified with our experimental setup.

The rate at which material is removed from the multilayer mirror as a result of sputtering, is much lower than the rate at which carbon contamination is deposited onto the mirror. For practical applications, it would be desirable if a balance could be found between these mechanisms. Ideally, a thin layer of carbon contamination protects the mirror from sputtering, while simultaneously an increase of the thickness of the carbon contamination layer is prevented by sputtering.

The work in this thesis suggests several ways to reduce the sputter rate. The most obvious method is to replace the argon background gas in the EUV lithography tool by light gases such as hydrogen, which has a much higher threshold energy for sputtering. However, the reason that the argon gas is present in the tool is the result of the dynamic gas lock. A jet of argon is blown over the wafer to prevent outgassed photo-resist molecules from diffusing towards the multilayer mirrors, which would otherwise result in mirror contamination. In principle, such a dynamic gas lock can also be operated with hydrogen, but this would require a much higher flow rate than in the case of argon. As a result the background pressure in the tool would be much higher and the design of the vacuum system would have to be altered.

A less invasive method would be to keep the argon gas and introduce additional hydrogen gas to the system. According to the simulations in Chapter 8, this would significantly reduce the sputter rate, because the average electron energy of the EUV radiation generated plasma would be reduced as a result of inelastic collisions between electrons and hydrogen molecules.
Appendix A: Sputter yield formula

When fast moving particles such as atoms, ions or molecules impact on a solid target, they can cause damage to the target. The removal of target atoms as a result of particle bombardment is called sputtering. The sputter yield, the number of removed target atoms per incoming projectile, strongly depends on the energy of the projectile. Detailed quantum mechanical calculations are required to obtain the sputter yield.

Here, we shall use a more basic physical description of the sputter process: if a surface atom receives an energy transfer, such that the kinetic energy component directed normally outward to the surface exceeds the surface binding energy of the target material, it will be ejected from the surface. This kinetic energy transfer ejection process is termed physical sputtering.

Historically, attempts have been made to come to a general expression for the energy dependence of the sputter yield. These semi-empirical expressions require a limited number of fit parameters that are specific for each projectile-target combination. A more elaborate overview can be found in [1, 2]. The semi-empirical expressions of Bohdansky [3] and Yamamura [4] for the energy dependence of the sputter yield $Y(E)$ are modifications of the sputter formula as derived by Sigmund [5]

\[
Y(E) = 0.042 \frac{U_b}{\alpha S_n(E)},
\]

(12.1)

with $U_b$ the surface binding energy of the target material in units of eV, $\alpha$ a dimensionless fit parameter that is a function of the target mass $M_2$ to projectile mass $M_1$ ratio, and $S_n(E)$ the nuclear stopping cross-section (in units of eV per Å²) for an ion with kinetic energy $E$ in units of eV, for which an analytical expression has been developed by Lindhard [5]

\[
S_n(E) = \frac{84.78Z_1Z_2}{\sqrt{\left(Z_1^{2/3} + Z_2^{2/3}\right)}} \frac{M_1}{M_1 + M_2} s_n(\epsilon),
\]

(12.2)

with $Z_1$ and $Z_2$ the atomic numbers of, respectively, the projectile and target atoms.
Chapter 12: Appendix A

The nuclear stopping cross section can be rewritten in terms of the reduced elastic cross section, which is a function of the reduced energy. The reduced energy, \( \epsilon \) is given by \[5\]
\[
\epsilon = 0.03255 \frac{Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3})^{1/2}}{M_1 + M_2} E. \tag{12.3}
\]

The reduced elastic cross section can be calculated with the analytical expression \[6\]
\[
s_n(\epsilon) = \frac{3.441 \sqrt{\epsilon} \ln(\epsilon + 2.718)}{1 + 6.355 \sqrt{\epsilon} + \epsilon (-1.708 + 6.882 \sqrt{\epsilon})}. \tag{12.4}
\]

The Sigmund sputter formula does not take into account the threshold behavior of the sputter yield at low energies (below 100-200 eV). At these low energies, the collision cascades, which are modeled by the Sigmund formula, do not fully develop. Instead, sputtering is the result of knock-on processes. Two modified versions of the Sigmund formula are often used to predict sputtering yield at lower energies: the Bohdansky formula, and the Yamamura formula (sometimes also referred to as the Third Matsunami formula). These formulas apply a correction factor to Sigmund’s formula for better correlation with published experimental results for sputtering yields.

**Bohdansky Formula**

The Bohdansky formula for the sputter yield is
\[
Y(E) = \frac{0.042 \alpha S_n(E)}{U_b} \frac{R_p}{R} \left[1 - \left(\frac{E_{th}}{E}\right)^{2/3}\right] \left[1 - \left(\frac{E_{th}}{E}\right)\right]^2, \tag{12.5}
\]
with the ratio of the projected range \( R_p \) of the projectile to the average path length \( R \) given by
\[
\frac{R_p}{R} = \frac{1}{0.4 \left(\frac{M_2}{M_1}\right) + 1}, \tag{12.6}
\]
and
\[
\alpha = 0.3 \left(\frac{M_2}{M_1}\right)^{2/3}. \tag{12.7}
\]

The threshold energy, \( E_{th} \) is calculated as
\[
E_{th} = \begin{cases} 
\frac{U_b}{\lambda (1-\lambda)} & \text{for } \left(\frac{M_1}{M_2}\right) \leq 0.3 \\
8U_b \left(\frac{M_1}{M_2}\right)^{2/5} & \text{for } \left(\frac{M_1}{M_2}\right) > 0.3 \end{cases}, \tag{12.8}
\]
with \( \lambda \) the fraction of energy that is transferred from the projectile to the target particle in a head-on collision
\[
\lambda = \frac{4M_1 M_2}{(M_1 + M_2)^2}. \tag{12.9}
\]
Yamamura Model

In the 1980’s, researchers at the Institute of Plasma Physics at Nagoya University have extensively analyzed sputter yield data for a wide variety of target and projectile combinations. Their research led to the development of the Yamamura or Third Matsunami formula for the sputter yield. The latest version, published in 1996, is

\[
Y(E) = 0.042 \frac{Q \alpha^* \left( \frac{M_2}{M_1} \right)}{U_s} \frac{S_n(E)}{1 + \Gamma k_e \epsilon^{0.3}} \left[ 1 - \sqrt{\frac{E_{th}}{E}} \right]^s,
\]

(12.10)

where

\[
\Gamma = \frac{W}{1 + (M_1/T)^3},
\]

(12.11)

\[
k_e = 0.079 \frac{(M_1 + M_2)^{3/2}}{M_1^{3/2} M_2^{1/2}} \frac{Z_1^{2/3} Z_2^{1/2}}{(Z_1^{2/3} + Z_2^{2/3})^{3/4}},
\]

(12.12)

and

\[
\alpha^* = \begin{cases} 
0.249(M_2/M_1)^{0.56} + 0.0035(M_2/M_1)^{1.5} & \text{for } M_1 \leq M_2 \\
0.0875(M_2/M_1)^{-0.15} + 0.165(M_2/M_1) & \text{for } M_1 > M_2
\end{cases}
\]

(12.13)

The threshold energy is calculated as

\[
\frac{E_{th}}{U_s} = \begin{cases} 
\frac{6.7}{1 + 5.7(M_1/M_2)} & \text{for } M_1 \leq M_2, \\
\frac{4.7}{1 + 5.7(M_1/M_2)} & \text{for } M_1 > M_2
\end{cases}
\]

(12.14)

The fit parameters, \(Q\), \(W\), and \(s\) are functions of \(Z_2\) and are tabulated in Ref. [4]. For a Ru target, \(Q\) is 1.31, \(W\) is 2.36, and \(s\) is 2.5.

In Fig. 12.1 the Bohdansky and Yamamura expressions for the sputter yield for Ar on Ru are plotted.
Chapter 12: Appendix A

Figure 12.1: Sputter yield for Ar$^+$ on Ru as a function of ion energy according to the Bohdansky model (solid line), and the Yamamura model (dashed line).

Bibliography


Appendix B: Collected fraction of sputtered atoms

To measure the sputter yield of a projectile-target combination, the target is bombarded with a mono-energetic beam of ions. A fraction of the sputtered target material atoms is accumulated on a QCM crystal, see Chapter 9. The sputter yield can be deduced from the mass added to the QCM detector, which is detected as a frequency shift of the QCM crystal. For this purpose, it is necessary to calculate the collected fraction, which is equal to the part of the normalized angular sputter distribution integrated over the solid angle subtended by the QCM detector. For the calculation of the collected fraction, we use a spherical coordinate system with the origin at the point where the ions hit the target. The geometry of the system is depicted in Fig. 13.1. The rectangle represents a cross-section of the QCM. Four parameters are required to describe the geometry:

- The distance $a_0$ between the source and the center of the QCM;
- The radius $b_0$ of the circular surface of the QCM;
- The tilt-angle $\alpha$ of the QCM plane with respect to the line-of-sight of the source;
- The polar angle $\beta$ of the normal to the source plane with respect to the line-of-sight of the source.

The polar angle $\theta$ is bounded between $\beta - \beta_1$ and $\beta + \beta_2$. From Fig. 13.1(a) we deduce

\[
\tan \beta_1 = \frac{b_0 \sin \alpha}{a_0 + b_0 \cos \alpha}, \quad \tan \beta_2 = \frac{b_0 \sin \alpha}{a_0 - b_0 \cos \alpha}.
\] (13.1)

However, the values of $\beta_1$ and $\beta_2$ change with the azimuthal angle $\varphi$, since the QCM surface is planar (does not follow the curvature of field of the $r = a_0$ surface), and because the QCM surface is circular (not rectangular). These two effects can be taken into account by rewriting Eqn. 13.1 in the following way

\[
\tan \beta_1 = \frac{b(\varphi) \sin \alpha}{a(\varphi) + b(\varphi) \cos \alpha}, \quad \tan \beta_2 = \frac{b(\varphi) \sin \alpha}{a(\varphi) - b(\varphi) \cos \alpha}
\] (13.2)
where \( a(\varphi) \) is the distance between the source point and the surface of the QCM at polar angle \( \theta \) as a function of the azimuthal angle \( \varphi \) (Fig. 13.1(b)), and \( b(\varphi) \) is half the height of the detector viewed at a angle \( \varphi \) (Fig. 13.1(c)).

\[
\Delta a = \sqrt{\Delta x^2 + \Delta y^2} = \Delta x \sqrt{1 + \tan^2 \varphi} \quad \text{with} \quad \Delta x = a_0(1 - \cos \varphi). \quad (13.3)
\]
Hence, the total distance is given by

\[ a(\varphi) = a_0 + \Delta a = a_0 \left[ 1 + (1 - \cos \varphi) \sqrt{1 + \tan^2 \varphi} \right]. \quad (13.4) \]

The front view in Fig. 13.1(c) shows that the half-height of the detector changes with \( \varphi \) according to

\[ b(\varphi) = \sqrt{b_0^2 - a_0^2 \sin^2 \varphi}. \quad (13.5) \]

With the use of Eqns. 13.2, 13.4, and 13.5 the collected fraction \( C_{fr} \) of particles emitted with a normalized angular sputter distribution \( Y(\theta) \) can be calculated

\[ C_{fr} = \frac{1}{2\pi} \int_{-\varphi_{max}}^{\varphi_{max}} d\varphi \int_{\beta-\beta_1(\varphi)}^{\beta+\beta_2(\varphi)} Y(\theta) \sin \theta d\theta. \quad (13.6) \]

with \( \varphi_{max} = -\varphi_{min} = \arcsin(b_0/a_0) \). Given the parameters \( \alpha, \beta, a_0 \) and \( b_0 \), the integral can be calculated with standard numerical techniques.
Summary

Radiation Generated Plasmas
a challenge in modern lithography

This thesis deals with the study of the properties of plasmas generated by extreme ultra-violet (EUV) radiation and the interaction of these plasmas with multilayer mirrors. The presence of the radiation generated plasma in front of the multilayer mirrors forms a potential threat to the lifetime of the optical components of lithography tools. In the plasma boundary layer in front of the mirror, ions are accelerated by the self-generated electric field towards the mirror. In case these ions gain sufficient velocity, they can damage the mirror surface in a process called physical sputtering.

The properties of the plasma are investigated in two ways: by experimental observations and by theoretical considerations. The plasma is far from equilibrium due to the low densities of the plasma constituents and the transient nature of the EUV sources. This puts severe limitations on the plasma diagnostic techniques that can be used to measure the plasma properties.

A computer code has been written to obtain better fundamental insight into the dynamics of the ion acceleration in the plasma boundary layer. The code combines a one-dimensional Particle-In-Cell model with the method of Monte Carlo collisions. In this kinetic plasma model, the motion of the charged particles is followed under the influence of their self-generated electric field. The PIC-MC simulations calculate the flux and energy distribution of the ions that hit the multilayer mirror. It is found that the energy at which ions hit the mirror is limited by the average electron energy in the plasma.

To obtain the damage to the multilayer mirror, the distributions must be convoluted with the sputter yield, which is the number of target atoms removed per incoming ion as a function of the kinetic energy of the ion projectile. The sputter yield shows a threshold behavior. Ions with an impact energy below the sputter threshold energy do not contribute to sputtering.

It is found that the damage to the mirror is mainly the result of doubly charged argon ions, whereas singly charged argon ions contribute only for a small amount. The predicted sputter rate is extremely low, typically 1 nm per billion EUV pulses.

Furthermore, the impact energy of the ions is influenced by the energy of electrons that are emitted from the mirror as a result of the photo-electric effect. Most of the emitted
photo-electrons are much less energetic than the electrons that are created in the bulk of the plasma by photoionization. The photo-electrons decrease the average electron energy in the plasma, which in turn leads to a smaller electric field in the plasma boundary layer, and as a result, a lower impact energy of the ions on the multilayer mirror.

With the PIC-MC model, a parameter study has been carried out to determine the effect of both the pressure and the EUV intensity on the sputter rate. Simulations show that the sputter rate increases monotonically with the intensity. The pressure dependence shows a more complex behavior.

Besides argon, also mixtures of argon with hydrogen gas have been simulated with the PIC-MC model. When hydrogen gas is added to the background gas the sputter rate decreases, mainly because the hydrogen acts as an energy sink for the electrons in the plasma as a result of inelastic electron-neutral collisions.

To study the plasma-wall interaction, experiments have been performed. To verify the energy dependence of the sputter yield, measurements have been carried out at Argonne National Laboratory, Illinois. Results show good agreement with the semi-empirical formula of Yamamura that is used in the PIC-MC model.

In a test facility at ASML, Veldhoven, experiments have been conducted to experimentally determine the sputter rate of multilayer mirrors. For this purpose, a collimated beam of EUV radiation is focussed on a mirror sample. With EUV reflectometry and secondary photo-electron emission measurements, the condition of the top layer of the mirror can be monitored in-situ. In combination with ex-situ X-ray Photo-electron Spectroscopy (XPS) changes to the thickness of the top layer can be measured.

The sputter rate measurements are hampered by the EUV radiation induced growth of a thin layer of carbon on top of the mirror. It is shown that with atomic hydrogen cleaning the carbon contamination can be removed from the mirror. During the sputter rate measurements EUV exposures are alternated with atomic hydrogen cleaning cycles.

Furthermore, sputter rate measurements have been carried out on a separate experimental setup, which has been cleaned to reduce the carbon growth rate. On this setup the sputter rate is too low to be detected. However, if the EUV bandpass filter at the entrance to the measurement chamber is removed strong sputtering as a result of the radiation generated plasma is observed.

In conclusion, the investigations in this thesis provide better understanding of the mechanism of sputtering in EUV radiation generated plasmas. The measurement results are in agreement with the predictions of the PIC-MC simulations that the sputter rate of multilayer mirrors is extremely low. Moreover, with the addition of hydrogen to the background gas the sputter rate can be even further reduced. The PIC-MC model provides a sound basis for future research on transient phenomena in low-density plasmas.
Samenvatting

Stralingsgegeneerde Plasma’s
een uitdaging in de moderne lithography

Dit proefschrift gaat over de studie van de eigenschappen van plasma’s die ontstaan door extreem ultraviolette (EUV) straling en de interactie van zulke plasma’s met multilaagspiegels. De aanwezigheid van een door straling gegenereerd plasma in de onmiddellijke nabijheid van multilaagspiegels vormt een mogelijke bedreiging voor de levensduur van deze optische onderdelen van lithografiemachines. In de grenslaag van het plasma worden ionen versneld richting de spiegel door het zelfgegenereerd elektrische veld. Als deze ionen voldoende snelheid ontwikkelen kunnen zij schade aanrichten wanneer zij botsen met het spiegeloppervlak. Dit proces heet fysisch sputteren.

De eigenschappen van het plasma zijn op twee manieren onderzocht: door experimenten te verrichten en door theoretische beschouwingen. Het plasma is ver uit evenwicht vanwege de lage deeltjesdichtheid in het plasma en vanwege de gepulste aard van de EUV bronnen. Dit stelt hoge eisen aan de diagnostische methoden die gebruikt kunnen worden om de eigenschappen van het plasma te meten.

Om fundamenteel inzicht te krijgen in de dynamica van het versnellen van ionen in de grenslaag van het plasma is een computerprogramma ontwikkeld. Dit programma combineert een 1-dimensionaal Particle-In-Cell model met de methode van Monte Carlo botsingen. Dit kinetische plasmamodel simuleert de beweging van geladen deeltjes onder invloed van hun zelfgegenereerd elektrisch veld. Met de PIC-MC simulaties kunnen de flux- en energieverdeling van de ionen die botsen met de spiegel worden berekend. Hieruit is gebleken dat de energie waarmee de ionen de spiegel raken wordt begrensd door de gemiddelde energie van de elektronen in het plasma.

Om de schade die aan de multilaagspiegels wordt toegebracht te kunnen uitrekenen, moeten de flux- en energieverdeling worden gewogen met de sputteropbrengst: het aantal atomen dat van de spiegel wordt afgeslagen per inkomend ion als functie van de kinetische energie van het ion. De sputteropbrengst vertoont drempelgedrag. Ionen met een energie onder de drempelenergie dragen niet bij aan het sputterproces.

Uit de simulaties is verder gebleken dat de schade aan de spiegels vooral ontstaat door dubbelgeladen argon ionen, terwijl enkelgeladen argon ionen in veel minder mate bijdragen. De voorspelde sputtersnelheid is extreem laag: 1 nanometer per miljard EUV pulsen.
Verder is gebleken dat de energie waarmee de ionen de spiegel raken wordt beïnvloed door elektronen die worden uitgezonden door de spiegel, het zogenaamde foto-elektrisch effect. Het grootste deel van de uitgezonden foto-elektronen heeft een veel lagere energie dan de elektronen die in het volume van het plasma gegenereerd worden door foto-ionisatie. Op deze manier wordt de gemiddelde energie van de elektronen gereduceerd, hetgeen leidt tot een lager elektrisch veld in de grenslaag van het plasma, hetgeen op zijn beurt weer leidt tot een lagere botsingsenergie van de ionen.

Met het PIC-MC model is een parameterstudie verricht om te achterhalen wat het effect is van de druk en de EUV intensiteit op de sputtersnelheid. Hieruit blijkt dat de sputtersnelheid monotoon stijgt met de intensiteit, maar dat de drukafhankelijkheid meer complex gedrag vertoont.

Behalve argon gas, zijn ook mengsels van argon met waterstof onderzocht met het PIC-MC model. De toevoeging van waterstof blijkt de sputtersnelheid te verlagen, vooral vanwege het feit dat elektronen een deel van hun energie verliezen door inelastische botsingen met waterstofmoleculen.

Om de plasma-wand interactie te bestuderen zijn er experimenten verricht. Ter verificatie van de energieafhankelijkheid van de sputteropbrengst zijn er metingen gedaan bij Argonne National Laboratory in Illinois. De resultaten hiervan zijn in goede overeenkomst met de semi-empirische formule van Yamamura die wordt gebruikt in het PIC-MC model.

In het EUV laboratorium van ASML in Veldhoven zijn metingen gedaan om de sputtersnelheid van de spiegels te bepalen. Bij deze metingen wordt een bundel EUV straling gefocussed op een multilaagspiegel. Door het meten van de EUV-reflectie en de secundaire foto-elektronenstroom kan de toestand van de spiegel tijdens de belichting worden gevolgd. Na afloop worden de spiegels geanalyseerd door middel van XPS-analyse, waarmee de afname in dikte van de toplaag van de spiegel kan worden gemeten.

Het meten van de sputtersnelheid wordt bemoeilijkt doordat zich een dun koolstoflaagje vormt op de spiegel onder invloed van de EUV straling. Uit experimenten blijkt dat dit laagje vervolgens weer kan worden verwijderd door de spiegel bloot te stellen aan atomair waterstof. Bij de meting van de sputtersnelheid worden daarom periodes van belichting met EUV straling afgewisseld met periodes van behandeling met atomair waterstof.

Verder zijn er metingen van de sputtersnelheid uitgevoerd met een andere experimentele opstelling, die van tevoren speciaal schoongemaakt was om de aangroesnelheid van de koolstoflaagjes te verlagen. Bij deze opstelling was de sputtersnelheid te laag om te kunnen meten. Echter, een zeer hoge sputtersnelheid wordt gemeten wanneer het filter, dat alleen EUV straling doorlaat, bij de toegang tot de meetkamer wordt verwijderd.

Er kan worden geconcludeerd dat het onderzoek, zoals beschreven in dit proefschrift, heeft geleid tot een beter begrip van het mechanisme van sputteren in EUV stralingsgegeneerde plasma’s. Metingen zijn in overeenstemming met de voorspelling van PIC-MC simulaties: de sputtersnelheid van multilaagspiegels is extreem laag. Bovendien kan de sputtersnelheid nog verder worden gereduceerd door het toevoegen van waterstof aan het achtergrondgas. De PIC-MC simulaties bieden een gezonde basis voor toekomstig onderzoek naar snelle verschijnselen in ijle plasma’s.
Dankwoord

De term dankwoord impliceert een bondigheid die onrecht doet aan de inspanningen die een aantal mensen zich getroost hebben bij de totstandkoming van dit manuscript. Daarnaast impliceert deze term dat ik een aantal mensen enorm dankbaar ben en dat is zeker zo belangrijk om te vermelden.

Allereerst wil ik mijn eerste promotor Joost van der Mullen bedanken voor zijn begeleiding en advies, voor het delen van zijn kennis van de plasmafysica, en zijn motiverende woorden. En daarbij ging dit alles gepaard met een lichtvoetige humor die zeldzaam is onder gewijkte fysici zoals hijzelf.

De afgelopen jaren hebben mij doen beseffen dat wetenschap uitdagend werk is voor nieuwsgierige mensen, soms frustraties kan opleveren, maar ook heel bevredigend kan zijn. Een promotieonderzoek is een beetje een ritje te vergelijken met een ritje in een achtbaan in het donker: avontuurlijk, vol onverwachte wendingen en ontwikkelingen, met hoogte- en dieptepunten. Je bent altijd nieuwsgierig naar wat komen gaat, maar de meeste tijd sta je in de rij voor het station te wachten tot je apparatuur gerepareerd is of totdat de computer-simulatie is uitgedraaid. Tenslotte eindig je op dezelfde plek waar je begon, maar ben je een schat aan ervaring rijker.

De achtbaan waarin ik de afgelopen jaren heb mogen rondrijden betrof een shuttledienst tussen de groep Elementaire Processen in Gasontladingen van de TU Eindhoven en het EUV laboratorium van ASML in Veldhoven.


Een groot gedeelte van mijn tijd heb ik me bezig gehouden met plasmasimulaties. Het gebruikte model borduurt voort op de practicum-code ontwikkeld door Wouter Brok. Wouter, bedankt voor de discussies over Monte-Carlo botsingen en je geduldige uitleg van de numerieke architectuur. Ook ben ik Vladimir Ivanov van ISAN en Rob Wieggers van het Plasma Instituut FOM Rijnhuizen erkentelijk voor hun bijdrage aan de discussie.
Het experimentele gedeelte van mijn onderzoek heb ik verricht in het EUV lab bij ASML in Veldhoven, onder supervisie van Roel Moors (tevens mijn copromotor) en Vadim Banine (tevens eigenaar van een zwembad). Roel en Vadim, bedankt voor het creatief meedenken, het aandragen van vele ideeën voor experimenten en voor jullie positieve instelling.

Deze experimenten zouden niet mogelijk zijn geweest zonder de kundige hulp van twee bijzondere mensen: Luc Stevens en John de Kuster. Eenieder die met EUV bronnen heeft gewerkt weet hoe belangrijk het is om goede support te hebben. Voor niet-ingewijden een korte definitie van een EUV bron in een experimenteel ontwikkelingsstadim: in theorie een doosje waar onzichtbaar licht uitkomt als je op de knop drukt. In de praktijk blijkt wat eruit komt inderdaad vaak vrij onzichtbaar, ongeacht of je wel of niet op de knop drukt. Luc en John, bedankt voor jullie inzet!

Verder dank ik mijn collega-promovendi bij ASML, Erik Kieft en Kurt Gielissen, voor de goede samenwerking. Daarnaast wil ik Wouter Graef bedanken voor zijn hulp met de metingen bij ASML en het voetbaltoernooi van de faculteit (als doelman schier onpasseerbaar) en hem succes wensen met zijn afstudeeronderzoek naar tijdsopgeloste emissiespectroscopie.

De in-situ reflectometer is het geesteskindje van Yurri Sidelnikov van ISAN. Yurri, thank you for your efforts and advice. Verder ben ik een aantal mensen van TNO erkentelijk voor de plezierige samenwerking: Bas Wolschrijn, Rik Jansen, Greg Alcott, Nadir Faradzhev, Emiel van Kimmenade en Edwin te Sligte en anderen.

During my stay at Argonne National Laboratories, I have truly enjoyed working with the people in the group of Jean Paul Allain: Vladimir Titov, Martin Nieto, Perry Plotkin, Matt Hendricks, Chris Chrobak, Ed Hinson and others. Thanks for the opportunity J.P. and I wish you lots of success at your new job at Purdue University.

Verder wil ik de commissieleden bedanken voor hun inspanningen en suggesties: Wim Goedheer, Marie-Paule Delplancke en Marnix van der Wiel.

Naast collega’s hebben natuurlijk ook vrienden en familie indirect een belangrijke rol gespeeld bij het tot stand komen van dit boekwerk. In het bijzonder wil mijn teamgenoten van heren 1 van de volleybalclub uit Bladel vermelden. Dankzij jullie stond ik de afgelopen jaren, in ieder geval in de weekenden, niet met twee benen op de grond.

Natuurlijk wil ik mijn ouders, mijn broer Eric en zijn vriendin Patricia bedanken voor hun liefdevolle ondersteuning en begrip. En tenslotte een speciaal dankjewel voor de liefstallige Chantal.

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