MASTER

Time dependent collisional radiative model of an extreme ultraviolet driven plasma

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Time dependent collisional radiative model of an extreme ultraviolet driven plasma

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Abstract

The ever increasing demand for smaller and faster computer chips requires an ever decreasing size of semiconductor structures. ASML, one of the world’s leading providers of lithography systems for the manufacturing of chips, aims at using EUV (Extreme UltraViolet) radiation at 13.5 nm wavelength for its next generation of products.

Due to high attenuation at this wavelength, the whole optics system must be in vacuum and mirrors have to be used instead of lenses. The pulsed EUV source photoionizes the low pressure (1 Pa) background argon gas which causes a weakly ionized plasma. In the plasma sheath region at the mirror surface ions will be accelerated towards the surface and can cause undesired sputtering of the multilayer mirror surface.

In a previous Particle In Cell (PIC) model by Van der Velden et al.* predictions were made of the plasma parameters. In this research a time-dependent Collisional Radiative Model (CRM) is made based on the corona plasma regime. Using non-Maxwellian electron distribution functions (EEDF) provided by the PIC model the CRM model calculates the argon excited state densities and the spontaneous photon emission rate.

The results are compared to Optical Emission Spectroscopy measurements. The experiments show that the timescales on which the electrons in the EUV induced plasma lose their energy, are much shorter than predicted by the model. However, the general trends are predicted correctly. Furthermore, the 4p lines of ArI and ArII prove to be the best indicators of this process.

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*Kinetic simulation of an extreme ultraviolet radiation driven plasma near a multilayer mirror
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Chapter 1

Introduction

This work is aimed at the study of the plasma that is created when low pressure argon gas is exposed to pulsed extreme ultraviolet radiation.

Plasmas are gases that are partially ionized. The positive and negative charges can move somewhat independently, which gives a plasma unique properties unlike those of solids, fluids and gases. Plasma is therefore considered the fourth state of matter. Plasmas are in fact very common since over 99% of all visible matter in the universe is in the plasma state (e.g. stars and nebulae). Natural examples of plasmas on earth are lightning and the polar aurorae.

Artificially produced plasmas are nowadays also quite common, for example in fluorescent lamps and plasma displays. Plasmas are also often used as tools in the industry, for instance 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 ultraviolet (EUV) radiation. The ASML company in Veldhoven is currently developing such tools. For this reason a joint research project was started in 2001 by ASML and the research group Elementary Processes in Gas discharges (EPG) of the Eindhoven University of Technology (TU/e). This work is a part of that research project and focuses on the plasma that is generated in argon when it is exposed to EUV radiation.

This introductory chapter will give some background of the studied subject and a short road map of this thesis. The first two sections will give a general introduction into lithography, and EUV lithography in particular. In the following section one of the specific challenges that arise in EUV lithography, namely the interaction of the EUV driven plasma with the optical components of the lithography tool, will be described. After a summary of previous work on this matter, on which this research is based, follows a description of the subject of this work.
Chapter 1.

1.1 ASML

The company ASML, founded in 1984, is the world’s leading developer and supplier of lithography systems for the production of integrated circuits (IC’s). An IC consists of electronic components (transistors) which are linked together in certain patterns, so-called interconnects. The fabrication of IC’s is performed in several production steps, of which optical lithography is of fundamental importance. Fig. 1.1 shows the principles of a lithography tool as well as the lithography process.

Figure 1.1: (a) shows a schematic drawing of a lithography tool. The pattern (reticle) of a single layer for a single chip or die is projected onto the wafer. By moving the wafer, several chips can be made on one and the same wafer. (b) shows a simplified representation of the lithography process. After the wafer has been covered with a photoresist layer, a pattern is projected onto the wafer (I). The light chemically alters the photoresist layer (II), so that the illuminated parts can be etched away (III). By depositing certain materials in the created gaps (IV), the desired structures can be created.

A silicon wafer is first covered with a photosensitive layer (the photoresist). The desired pattern is then projected onto the wafer using a complex optical system. Where the photoresist is exposed, it is chemically altered. Depending on whether a negative or positive photoresist is applied the exposed or unexposed parts of the resist are then etched away. In the final step structures are created by deposition of various materials into the etched pattern. These steps are repeated many times to form complex IC’s consisting of several layers.

In order to meet market demands, the computer industry is constantly driven to increase the speed of computer chips and memory capacity, as well as to reduce the power consumption. Therefore the industry is continuously striving to reduce the feature-size of computer chips. In 1965 Gordon Moore presented his famous
Introduction

law, which states that the number of transistors on an IC is doubled every two years [1]. Figure 1.2 shows that after 40 years, Moore’s law is still valid.

![Figure 1.2: Growth of transistor density during the last 40 years [Source: Intel Corporation] and the prediction according to Moore’s law.](image)

Due to the fact that the size of the structures on an IC is mainly determined by the optical lithography system, it has been in the area of optical lithography where most of the advances have been realized. Two factors determine the minimum feature-size that can be etched into the photoresist layer: resolution and depth of focus, see figure 1.3. The resolution, which is the minimum width \( L_w \) of a line that can be projected onto the wafer from the reticle is limited by diffraction. The resolution is determined by:

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

(1.1)

where \( k_1 \) is a proportionality constant that depends on the optical system and photoresist, \( \lambda \) the wavelength of the used light, and \( NA \) the numerical aperture, defined as \( NA = \sin \theta \), with \( \theta \) the half-acceptance angle of the lens. The second parameter, depth of focus or \( DOF \), indicates up to which distance the projected
image is still acceptable, which means that the projected spot is within a certain percentage of the resolution. It is defined as:

\[ DOF = k_2 \frac{\lambda}{NA^2}, \]  

(1.2)

where \( k_2 \) is again a proportionality constant, which here depends on the precise definition of the \( DOF \).

As is evident from equation 1.1, there are three ways in which the resolution can be improved: decrease \( k_1 \), decrease \( \lambda \), and increase \( NA \). In the past decades all three possibilities have been pursued and implemented. Further improvements are, however, problematic. In top-of-the-line systems a value of \( k_1 = 0.3 \) has been reached, while the theoretical limit is found at \( k_1 = 0.25 \). The wavelength used in current systems is 193 nm, while for wavelengths below 150 nm there are no readily available materials for the lens optics. If the numerical aperture is further increased it will have an adverse effect on the depth of focus (1.2). Besides, the \( NA \) is already near its limit. A trick that has already been successfully commercially exploited is that of so-called immersion lithography, in which a liquid is introduced between the wafer and the surface of the last lens. The higher refractive index of the liquid (as compared to air) results in a higher effective numerical aperture. An added benefit is that the decrease of the depth of focus is only linearly proportional to the refractive index.

However, miniaturization of IC’s will have to continue beyond what is possible using immersion lithography. The next big step in the development of lithography is EUV lithography.

### 1.2 EUV lithography

EUV is an acronym that stands for Extreme UltraViolet. It is electromagnetic radiation with a wavelength in the range of 121 down to 10 nm. EUV lithography (EUVL) will use radiation in a 2% bandwidth around a central wavelength of 13.5 nm. It is a vast step in wavelength compared to the current lowest wavelength of 193 nm, and will enable the production of far smaller feature sizes then presently possible. The major drawback of using EUV radiation is that lens optics can not be used due to the very short attenuation length (100 nm in quartz). Also, the whole system must be kept in vacuum to prevent too much radiation from being absorbed by the background gas. The pressure of the background gas is determined by the so-called Dynamic Gas Lock (DGL). The DGL is a flow of argon gas which flushes hydrocarbons that are released by the photoresist during illumination. It is situated between the last optical element and the wafer. The DGL causes the background pressure to be between 0.1 and 1 Pa.

An artist’s impression of the EUV alpha demo tool is shown in Fig. 1.4. This tool was developed to gain insight into the development of EUVL and its commercialization. As stated, lenses can not be used in EUVL. Therefore reflective optics
Figure 1.4: Artist’s impression of the EUV alpha demo tool. The radiation from the EUV source is first focused by the collector mirror into the intermediate focus. A number of multilayer mirrors then shape the beam so that it is both parallel and uniform in intensity. The beam illuminates the reflective reticle, producing a pattern. This pattern is then demagnified four times, and imaged onto a wafer.

have to be used for the projection system. A distinction can be made between grazing incidence and (near) normal incidence mirrors. A grazing incidence mirror is used as the ellipsoidal collector mirror. The collector mirror captures a large solid angle of the EUV radiation into a second focus point, called the intermediate focus. Grazing incidence mirrors can reach high reflectivity if the right materials are used. With, for instance, ruthenium a reflectivity of more than 90% can be reached for angles smaller than 10° [2].

All other mirrors in the EUV tool are (near) normal incidence mirrors. At (near) normal incidence there are no materials that sufficiently reflect EUV radiation. However, if the mirror is built up out of many layers, and the reflections of the separate layers can be added up in phase, a sufficient total reflectivity can be reached. This is the principle of the multilayer mirror, Fig. 1.5. To reach optimum reflection the materials in the bi-layer must be chosen carefully. Not only must they have the right combination of refractive indices, it must also be possible to apply the materials in thin smooth layers and the layers must not intermix or react with each other. Two additional parameters that can be varied are the bi-layer thickness $d$, and the ratio of thicknesses $\Gamma$. A commonly used tandem of materials
Chapter 1.

![Diagram of multilayer mirror](image)

**Figure 1.5:** Principle of the multilayer mirror: when the thickness of a pair of layers (a bi-layer) $d$ is such that the path length from successive layers differs one wavelength, constructive interference will take place in accordance with Bragg’s law: $\lambda = 2d \sin \theta$.

is molybdenum and silicon. Fig. 1.6 shows the reflectivity of a Mo-Si multilayer mirror consisting of 50 bi-layers with $d = 6.9$ nm and $\Gamma = 0.4$.

![Graph of EUV reflectivity](image)

**Figure 1.6:** EUV reflectivity of a Mo-Si multilayer mirror. Data is computed by the X-Ray Interactions With Matter calculator at the Center for X-ray Optics website [3]. The reflectivity is computed for EUV radiation with a 90° angle of incidence onto a 50 bi-layer mirror consisting of molybdenum and silicon, with $d = 6.9$ nm and $\Gamma = 0.4$. As we can see, the reflectivity peaks at 74% for a wavelength of $\lambda = 13.5$ nm.

The data is taken from the Center for X-Ray Optics website [3]. The values shown are theoretical values. In reality, the maximum reflection is 69.5%, due to imperfections of the layer interfaces. To prevent oxidation of the silicon top layer, a capping layer is applied to the multilayer mirror.

The projection path in a commercial lithography system can require up to 10 mirrors, which results in a transmission of only 2.6% through the optical system. This means that a small decrease in reflectivity of each mirror will add up to a
significant transmission loss. It is therefore essential to prevent any effects that could decrease the reflectivity of the multilayer mirror.

1.3 EUV - mirror interaction

There are two ways in which the interaction of the EUV radiation with the mirror surface can influence the reflectivity:

1. carbon layer growing on top of the mirror surface;

2. sputtering by ions from the EUV driven plasma.

Each effect will be further explained.

1.3.1 Carbon growth

In a vacuum setup, any surface, and therefore also a mirror, will be covered by physisorbed hydrocarbon molecules. When the hydrocarbons are exposed to EUV radiation they will dissociate. A second cause of the dissociation are the electrons that are created by the photo-electric effect of the EUV radiation hitting the mirror surface. The cracked hydrocarbons will react with each other and the surface, forming an amorphous layer of partially hydrogenated carbon. The carbon layer that is formed will reduce the reflectivity by an estimated amount of $\sim 1.5\%$ per nanometer. However, the layer can be removed by exposing it to atomic hydrogen. Without affecting the capping layer, the carbon can be cleaned from the mirror. This enables the reflectivity to be fully restored. The downside of this method is that, during cleaning, the machine would have to be offline. This is commercially undesirable.

1.3.2 Sputtering

The photons, which the EUV radiation exists of, have enough energy (92 eV) to photoionize the background argon gas. This will create a relatively small amount of free electrons and positive argon ions, i.e. a plasma. The electrons are much more volatile than the ions, because they are much lighter. Near a wall (or mirror) the electrons will hit the wall and remain there, whereas the ions will hardly move (on very short timescales). The charge imbalance will result in a potential drop towards the wall, which in turn accelerates the positive ions in the direction of the wall. If the ions gain enough kinetic energy before they hit the wall it is possible that they can “knock” away atoms from the mirror surface, called sputtering. If enough atoms are sputtered the mirror will be damaged and reflectivity will drop.
1.4 Previous research

Both carbon growth and sputtering of the mirror surface were the subject of previous research by Van der Velden [4]. In that research a numerical model was used to simulate the creation of a plasma by EUV radiation, and the interaction of that plasma with a mirror surface. Also experiments at the EUV-lab of ASML were performed to measure the sputter rate using a pulsed EUV source. The main conclusions of that research are as follows:

- The simulations show that indeed a potential drop towards the mirror surface is created. This potential drop is the reason why argon ions are accelerated towards the surface and sputtering may occur. The potential drop is determined by the mean energy of the electrons in the plasma;

- When EUV irradiates the mirror, secondary photo-electrons are emitted from the mirror surface. These electrons have a low energy and lower the mean energy of the electrons. Because of this the potential drop is smaller, which results in a lower energy of the ions hitting the mirror, and thus a lower sputter rate;

- Sputtering is mainly caused by the \( \text{Ar}^{2+} \)-ions that are accelerated towards the wall and to a lesser extent by the \( \text{Ar}^{+} \)-ions. This is because the double charged ions gain twice the energy of single charged ions;

- When the pressure of the background gas is increased, the sputter rate also increases because more plasma is produced, which leads to more ions impacting on the mirror surface. However, because the inelastic collision frequency of the plasma electrons with the background gas also increases, the plasma electrons are cooled. The result of this is that the potential drop towards the mirror is reduced. The ions hitting the wall will have less energy and less sputtering will occur. Between these two opposing effects there is an optimum.

- The impact energy below which no sputtering occurs, called the sputter threshold, depends on the masses of the projectiles (plasma ions) and targets (atoms in the mirror). If the ions are light enough (such as \( \text{H}^{+} \) and \( \text{H}_2^{+} \)) they can not gain enough energy in the EUV driven plasma to reach the sputter threshold.

According to the model, the sputter rate decreases when hydrogen is added to the background argon gas. There are two reasons for this:

1. Because of the relatively high cross section for inelastic electron collisions of hydrogen, the plasma electrons lose their energy more rapidly. This reduces the potential drop towards the mirror.

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2. Because of their lower mass, the hydrogen ions are more mobile than the argon ions. They will therefore reach the mirror before the argon ions. The charge separation in the plasma is smaller and thus the potential drop towards the mirror is smaller, so the sputter rate is reduced.

- In the experimental setup, carbon growth was observed and the cleaning method with atomic hydrogen proved to be functional. The growth rate of the carbon layer is much faster than the expected sputter rate. The sputter experiments were therefore performed in cycles, and in between cycles the mirror surface was cleaned using atomic hydrogen.

The performed experiments did not show any sputtering when using an EUV filter. The EUV-filter blocks non-EUV radiation. Without this filter much more sputtering than expected was observed. Most likely, because the plasma was heated by electromagnetic interference from the source.

This does not, however, contradict the model, since the model predicted that the sputtering would be too low to be detected, given the parameters of the experiments. According to the model, sputtering would have been detectable if the measurements were performed for longer periods of time or using higher EUV intensity.

The research shows that sputtering is very low (≈ 1 nm per $10^9$ EUV pulses), though that could not be verified using the experimental setup.

The key to controlling the sputtering is the mean electron energy of the electrons in the EUV induced plasma. If the mean electron energy can be kept low enough the potential drop towards the wall can be controlled, so the ions in the plasma will not cause sputtering of the mirror surface. This can be accomplished by either increasing the background argon pressure or by adding hydrogen.

It is desirable to somehow monitor the effect these measures have on the EUV driven plasma, more specifically on the energy of the plasma electrons. The numerical model by Van der Velden was specifically designed to model the sputtering of a surface near an EUV induced plasma. The aim of this work is to experimentally validate that model, more specifically the part of the model that describes the creation and evolution in time of the plasma a certain distance from the wall.

The diagnostic technique that is used on the plasma is optical emission spectroscopy. In order to validate the model by Van der Velden with these measurements, we must first construct a collisional radiative model of the EUV driven plasma.

1.5 Outline

As described in the foregoing sections, sputtering can be a threatening process to the optics in future lithography systems. It is therefore necessary to understand the
mechanisms that cause this phenomenon. Chapter 2 will start with a description of the EUV-source and the radiation it produces. The plasma created by the EUV radiation will be treated in depth. This chapter will then give a short description of some diagnostic techniques, followed by a motivation for the chosen technique, optical emission spectroscopy. With spectroscopy the fluorescent light from the EUV driven plasma can be measured.

Chapter 3 contains the modeling efforts of this work. Since sputtering is mainly determined by the mean electron energy, this aspect of the model by Van der Velden is studied in more detail. Quasi analytical models are used to analyze the electron energy. A Collisional Radiative Model (CRM) is then introduced, which is used to simulate the radiation the EUV driven plasma produces.

The CRM is constructed to gain insight into the results of spectroscopic measurements. These experiments were performed in the EUV-lab at ASML Veldhoven, and are described in chapter 4. Both time-integrated and time-resolved measurements were performed.

In chapter 5 conclusions are drawn and recommendations for future work are given.
Chapter 2

EUV-induced plasma

This chapter will start with a description of the mechanisms of the EUV source that has been used for this research to get some understanding of the characteristics of the radiation that drives the plasma (section 2.1). In the following section (2.2) a number of plasma parameters will be estimated to get a general idea of the plasma under investigation. In the final section (2.3) a short description of common diagnostic techniques will be given. The chosen technique for this research is optical emission spectroscopy which will be treated in more detail.

2.1 EUV source

For EUV lithography radiation with a wavelength of 13.5 nm (photon energy of 92 eV) is required. This radiation can be produced in several ways. For commercial lithography, plasma sources are considered the only viable options. The desired plasma can be produced using either a high energy laser or a pulsed high voltage discharge. In the EUV-lab at ASML both methods are used, and were extensively studied by Kieft [5]. The sources available in the lab are specifically designed for experimental purposes.

The laser produced plasma (or LPP) is created by focusing a laser onto tin droplets. The tin absorbs the laser energy and a hot, dense plasma is formed that emits EUV radiation.

In this research EUV sources based on a discharge produced plasma (or DPP) were employed to generate EUV-induced plasmas. More specifically, two Hollow Cathode Triggered (HCT) xenon discharge plasma sources manufactured by Philips EUV were used. The principle of this particular setup is shown in Fig. 2.1. The geometry of the hollow cathode causes space charges and electric fields in such a way that external switching or triggering of the plasma is not required. While a voltage is gradually built up over the electrodes, a positive space charge is created between the electrodes, which grows in the direction of the hollow cathode. In the hollow cathode, electrons are created and accelerated. These electrons
Chapter 2.

Figure 2.1: Cross section view of a hollow cathode discharge (gas is fed in from the sides). The electrodes are connected to a battery of capacitors. This setup is free running and does not require a switch to operate.

partially escape through the hole in the anode, forming a pre-pinched electron beam. It is possible to use this electron beam for high speed triggering. The plasma between the electrodes enables a final breakdown of the discharge. The high current through the plasma causes a z-pinches, compressing the plasma, which will create adequate density and temperature for EUV radiation to be produced. To control the voltage at which the discharge takes place, the pressures of the gases between the electrodes can be manipulated.

The process described above, takes place in just a few hundred nanoseconds, which means that the source cannot radiate continuously. The EUV sources in the ASML lab are able to run at a repetition rate of up to 1 kHz, while a single EUV pulse lasts 100 ns.

The produced radiation consists of a wide spectrum of wavelengths. The EUV part of the spectrum is shown in Fig. 2.2(a). To avoid that non-EUV radiation enters the lithography tool, a zirconium filter is used. This filter consists of a zirconium foil of approximately 150 nm thick, supported by a nickel mesh. The transmittance curve of the filter along with the resulting spectrum is shown in Fig. 2.2(b) and 2.2(c). It is clear that radiation with a wavelength of 20 nm and up is removed from the spectrum.

The radiant energy per pulse at the intermediate focus is determined by placing an EUV-sensitive foil in the EUV beam path. When the foil is exposed to EUV radiation it changes color and by measuring the degree of coloring the radiant energy per pulse can be determined. For the calculations in this chapter the in-band radiant energy per square meter per pulse is taken to be $I_{\text{pulse}} = 0.6 \text{ J/m}^2$, which is a realistic value for the sources used at ASML. In-band means within a 2% bandwidth around the center bandwidth of 13.5 nm.

2.2 Plasma characteristics

As described briefly in the previous chapter the EUV radiation photo-ionizes the argon gas, thus creating a plasma. Photo-ionization takes place when the energy
of the photon exceeds the lowest electron binding energy of the argon atom. In this process a free, energetic ($E$) electron and an ion are created:

$$h\nu + Ar \rightarrow Ar^+ + e(E).$$

Figure 2.2: (a) Spectrum of the xenon HCT EUV source as measured by Kieft [5]. (b) Transmittance curve of a 150 nm zirconium foil. This data is calculated using the “Filter transmission” tool at the website of the Center for X-Ray Optics [3]. (c) The spectrum of (a) after filtering by (b). The grey line indicates the 13.5 nm (92 eV) wavelength.

For EUV radiation with a wavelength of 13.5 nm the photon energy equals $h\nu = 92$ eV. Fig. 2.3 depicts the electron configuration of argon and table 2.1 shows the electron binding energies for argon. In table 2.2 ionization energies are shown. Table 2.1 shows that EUV photons can only remove electrons from the outer shells, and from table 2.2 it is clear, that also double and triple photo-ionization
Table 2.1: Binding energies of electrons in their respective orbitals for argon [6].

<table>
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<tr>
<th>Electron orbital</th>
<th>Binding energy (eV)</th>
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<td>3p(_{3/2})</td>
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</tr>
<tr>
<td>3p(_{1/2})</td>
<td>15.7</td>
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</tbody>
</table>

Table 2.2: Threshold energies for multiple ionization of argon [6]. These are single step ionization processes.

<table>
<thead>
<tr>
<th>Ionization stage</th>
<th>Resulting 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>84.13</td>
</tr>
<tr>
<td>quadruple</td>
<td>Ar(^{4+})</td>
<td>143.94</td>
</tr>
</tbody>
</table>

are possible:

\( h\nu + Ar \rightarrow Ar^{2+} + 2e(E), \)
\( h\nu + Ar \rightarrow Ar^{3+} + 3e(E). \) (2.2)

Of course in a photo-ionization process energy must be conserved which means that the excess energy (92 − 15.7 = 76.3 eV for single ionization) is divided over the resulting electron and ion:

\[ h\nu - E_{ion} = T_e + T_i = \frac{|\vec{p}_e|^2}{2m_e} + \frac{|\vec{p}_i|^2}{2m_i}, \] (2.3)

with \( E_{ion} \) the ionization energy, \( \vec{p}_e \) and \( m_e \) the momentum and mass of the electron and \( \vec{p}_i \) and \( m_i \) the momentum and mass of the ion. Besides energy, also momentum must be conserved:

\[ h\vec{k} = \vec{p}_e + \vec{p}_i, \] (2.4)

with \( h\vec{k} \) the momentum of the photon, \( \vec{k} \) the wave vector of the photon with magnitude \( k = 2\pi\nu/c \) (\( c \) is the speed of light). The momentum of the photon is so small compared to the momenta of the electron and ion that it can be neglected. Because of the large difference in mass between the ion and electron (for argon:
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\( m_i/m_e \approx 7 \times 10^4 \) almost all of the energy will be transferred to the electron. This implies that the energy transferred to the ion can be neglected compared to the thermal energy at room temperature \( (\frac{3}{2} k_B T \approx 0.04 \text{ eV}) \).

It can be concluded that photo-ionization of the argon atoms by the EUV radiation creates fast electrons (initially \( \sim 77 \text{ eV} \)) and slow ions. The next step is to estimate the electron density.

### 2.2.1 Electron density

Since not every photon will collide with an atom, not every photon sent into the argon gas will lead to a photo-ionization process. Using the Beer-Lambert law, the decrease in irradiation (radiation energy per pulse per unit area) over a length \( dl \) is:

\[
\frac{dI}{I} = -n_a \sigma dl \quad \text{so that} \quad I(l) = I(l = 0) \exp[-n_a \sigma l]
\]

with \( I \) the irradiation, \( dI \) the change in irradiation, \( n_a \) the neutral argon density, and \( \sigma \) the photo-ionization cross section, which is a function of the energy of the photon, as plotted in figure 2.4. Over a length \( L \) the irradiation that is absorbed

\[
\Delta I = I_0(1 - \exp[-n_a \sigma L]).
\]  

(2.5)

Fig. 2.4 shows that for EUV radiation at 13.5 nm, the photo-ionization cross section is \( \sigma \approx 10^{-22} \text{ m}^2 \). For argon pressure of 10 Pa (or \( n_a \approx 2.4 \times 10^{21} \text{ m}^{-3} \)) (assuming room temperature \( T = 300 \text{ K} \)) it is evident that the absorption length \( (\lambda = (n_a \sigma)^{-1} \approx 4 \text{ m}) \) far exceeds the dimensions of the plasma, which is typically a few cm. Therefore it can be concluded that the plasma is optically thin for EUV radiation.
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Because $n_a \sigma L \ll 1$ the exponential function in (2.5) can be approximated 
\[ \exp[-n_a \sigma L] \approx 1 - n_a \sigma L, \]
so that the electron density created by this radiation is:
\[ n_e \approx \frac{I_0 n_a \sigma h \nu}{h \nu}, \tag{2.6} \]
with $h \nu$ the energy of a single photon.

As stated in section 2.1 the irradiation by the EUV beam is taken to be 
$0.6 \text{ J/m}^2$. Since the energy of a single photon is $1.47 \times 10^{-17} \text{ J}$, the electron density for a background pressure of $10 \text{ Pa}$ is $n_e \approx 10^{16} \text{ m}^{-3}$.

2.2.2 Plasma parameters

The electron density of the plasma is very low, as is the ionization degree $\alpha$ defined as:
\[ \alpha = \frac{n_e}{n_a + n_e} \approx 4 \times 10^{-6}. \tag{2.7} \]

There are three criteria for a plasma that can be checked to see whether we can actually speak of a plasma:

1. Charged particles must simultaneously interact with many other charged particles. This is the case when the number of particles in the Debye-sphere (a sphere with the radius of a Debye-length) is much larger than unity. The Debye length is the distance over which significant charge separation can occur. Its definition is:
\[ \lambda_D = \sqrt{\frac{\epsilon_0 k_b T_e}{n_e e^2}}, \tag{2.8} \]
with $\epsilon_0$ the permittivity of free space, $k_b$ the Boltzmann constant, $T_e$ the electron temperature, and $e$ the electron charge. In our case it is assumed that $\hat{T}_e = 10 \text{ eV}$, so $\lambda_D \approx 2.4 \times 10^{-4} \text{ m}$.

The number of particles in the Debye-sphere is
\[ N_D = \frac{4}{3} \pi n_e \lambda_D^3, \tag{2.9} \]
which is in our case $N_D \approx 5.5 \times 10^5$.

2. The Debye-length must be smaller than the size of the plasma. Since the EUV drive plasma is approximately cylindrical in shape and $2 \text{ cm}$ long and $2 \text{ mm}$ wide, this condition is met.

---

*Temperatures with a “hat” denote that the temperature is expressed in electronvolts (1 eV $\approx 11604.5 \text{ K}$).

†Usage of the electron temperature implies that the plasma electrons are in thermal equilibrium so that the electron energy distribution function is Maxwellian (in that case the electron energy distribution function can be described with a single parameter: the electron temperature). Due to the low electron density and transient nature of the EUV driven plasma this is certainly not the case. Here the term electron temperature is used to denote the mean energy of the plasma electrons.
3. The plasma frequency must be higher than the electron-neutral collision frequency. This means that the plasma electrons can adjust their position rapidly enough to shield external charges. The plasma frequency is:

\[ f_{pe} = \frac{1}{2\pi} \sqrt{\frac{n_e e^2}{m_e \epsilon_0}}, \tag{2.10} \]

with \( m_e \) the electron mass, so \( f_{pe} \approx 5.6 \) GHz. The electron-neutral frequency is defined as:

\[ \nu_{ea} = n_e \sigma_{ea} \sqrt{\frac{k_b T_e}{m_e}}, \tag{2.11} \]

with \( \sigma_{ea} \) the electron-argon collision cross section. A cross-section of \( 5 \times 10^{-20} \) m\(^2\) [8] gives \( \nu_{ea} \approx 0.2 \) GHz which is much lower than the plasma frequency.

The calculations show that we can indeed speak of a plasma. In the following section a few more parameters will be calculated to examine the dynamics of the plasma.

### 2.2.3 Plasma decay

Every EUV pulse will create a plasma. The pulses, with a duration of 100 ns, are \( 10^{-1} \) to \( 10^{-3} \) s apart. In between pulses the plasma will decay.

Electrons and ions can be removed from the plasma by three-particle recombination:

\[ e + Ar^+ + e \rightarrow Ar + e(E). \]

From [9], the three-particle recombination rate (in m\(^6\)/s) is taken:

\[ k_{\text{rec,3}} = 3.3 \times 10^{-21} (T_e)^{-9/2}, \tag{2.12} \]

which for the previously estimated electron density and temperature results in a recombination frequency of \( \nu_{\text{rec,3}} = k_{\text{rec}} n_e^2 \approx 2 \times 10^{-7} \) Hz. Compared to the EUV pulse frequency this is clearly negligible.

The electrons and ions will spread by diffusion. For electrons the diffusion coefficient is:

\[ D_e = \frac{k_b T_e}{m_e \nu_{ea}^{\text{mom}}}, \tag{2.13} \]

with \( k_b \) the Boltzmann constant, \( T_e \) the electron temperature, \( m_e \) the electron mass, and \( \nu_{ea}^{\text{mom}} \) the frequency for momentum transfer from electrons to atoms. Similarly, the diffusion coefficient for ions is:

\[ D_i = \frac{k_b T_i}{m_i \nu_{ia}^{\text{mom}}}, \tag{2.14} \]
with $T_i$ the ion temperature, $m_i$ the ion mass, and $\nu_{ia}^{mom}$ the frequency for momentum transfer from ions to atoms.

Because of their charges, electrons and ions in a plasma will not move independently. Whereas the ions will be at room temperature, the electrons will have a much higher energy. The electrons move much faster than the ions and this creates a charge imbalance. The resulting electric field drags the ions along with the electrons. The same diffusion rate can therefore be applied to both the electrons and ions. This is called ambipolar diffusion.

The ambipolar diffusion time is a good approximation for the lifetime of the plasma. The ambipolar diffusion coefficient is defined by

$$D_a = \frac{\mu_i D_e + \mu_e D_i}{\mu_i + \mu_e}, \quad (2.15)$$

with $\mu_i$ and $\mu_e$ the mobility of the ions and electrons respectively.

Taking into account that the mobility of the electrons is far greater than the mobility of the ions and using the Einstein relation ($\mu = D/k_BT$) this results in:

$$D_a \approx D_i \left(1 + \frac{T_e}{T_i}\right). \quad (2.16)$$

The momentum transfer frequency for the ions is the mean speed $\bar{v} = \sqrt{8k_BT_i/\pi m_i}$ divided by the mean free path

$$\lambda = 1/n_a\sigma_{ia}, \quad (2.17)$$

with $n_a$ the neutral particle density, and $\sigma_{ia}$ the ion-neutral collision cross section. The ambipolar diffusion coefficient is then:

$$D_a \approx \sqrt{\frac{8k_BT_i}{\pi m_i}} \cdot \frac{1}{n_a\sigma_{ia}} \cdot \left(1 + \frac{T_e}{T_i}\right). \quad (2.18)$$

$T_i$ is taken to be room temperature and from [11] we get $\sigma_{ia} \approx 10^{-18}$ m² so setting all remaining variables to the values that were previously stated we end up with $D_a \approx 25$ m²/s. Taking a realistic diffusion distance of $L = 10$ cm (e.g. distance to a wall were the ions can recombine) this results in a decay time of:

$$\tau_a = \frac{L^2}{D_a} = 4 \times 10^{-4} \text{ s.} \quad (2.19)$$

So, realizing that the repetition frequency of the pulsed EUV source is 1 kHz, the diffusion is fast enough to let the plasma decay in the period between two subsequent pulses.

It is, however, questionable whether we can actually speak of ambipolar diffusion. The mean free path of the ions is:

$$\lambda_{ia} = \frac{1}{n_a\sigma_{ia}} \approx 4 \times 10^{-4} \text{ m.} \quad (2.20)$$
Since the cylindrical plasma is approximately 2 mm in diameter, this means that the transport in this plasma is near the Knudsen regime.

Strictly speaking, the formulae using the electron temperature $T_e$ only apply to plasmas with a Maxwellian electron energy distribution function (EEDF) (see also footnote * on page 16). The EEDF will initially be a peak at 76 eV, at which energy the free electrons are introduced in the plasma by photoionization. Due to collisions between electrons, the EEDF will then relax towards a Maxwell distribution. The collision frequency for electrons with electrons is [12]:

$$\nu_{ee} = 4 \times 10^{-12} n_e \ln \Lambda \frac{\ln 3}{T_e^{3/2}},$$

(2.21)

with $\ln \Lambda = \ln(6\pi n_e \lambda_D^3)$ the coulomb logarithm. Using $\tilde{T}_e = 10$ eV again, we find for this frequency approximately 10 kHz and therefore the time between collisions about $10^{-4}$ seconds. This is of the same order as the diffusion time of the plasma, so before the energy of the electrons can be redistributed the plasma has already recombined at the wall.

### 2.2.4 Wall interaction

Both the plasma and the EUV radiation will interact with the wall. Near the wall, a so-called plasma sheath will be created, and when the EUV photons hit the wall, the wall will emit low energy electrons because of the photo-electric effect.

The plasma sheath is created because the electrons have much higher velocities ($\approx 5 \times 10^8$ m/s) than the ions ($\approx 350$ m/s). The electrons will reach the wall (and are removed from the plasma) before the ions do, which creates a charge imbalance: the plasma sheath. The space charge $\rho$ in the sheath creates an electric field that acts on the charged particles in the plasma. The electric field can be found using Gauss' law. When only singly charged ions are taken into account, this law reads:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} = \frac{e}{\varepsilon_0} (n_i - n_e).$$

(2.22)

The electric potential $V$ is defined by:

$$\nabla^2 V = \frac{e}{\varepsilon_0} (n_e - n_i).$$

(2.23)

A schematic depiction of the sheath is given in Fig. 2.5. The electric field in the sheath pulls back electrons into the bulk of the plasma, and pushes (positively charged) ions towards the wall. If the ions gain enough kinetic energy before they hit the wall, the impact can cause atoms to be ejected from the surface of the wall. This is called sputtering. It is an undesired effect, since damaging the surface of a mirror can negatively influence the reflectivity.

Because in a plasma charge separation can occur up to a distance of one Debye-length, the sheath is approximately this size. The potential difference over the
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Figure 2.5: Schematic depiction of the plasma sheath. The sheath region, in contrast to the bulk of the plasma, is not quasi-neutral. The resulting field accelerates positive ions towards the wall, in our case the multilayer mirror.

The potential in the sheath is determined by the mean energy of the electrons in the plasma. If the electron energy can be kept low, the potential difference is low, and thus the ions have less energy on impact with the wall. If this impact energy is low enough, no sputtering will occur.

When ions collide with neutrals before they reach the wall their energy can be substantially lowered. To see whether ions can freely accelerate to the wall the mean free path can be used:

\[ l_{\text{mfp}} = \frac{1}{n_a \sigma_{ia}} \]  

(2.24)

which is \( 4 \times 10^{-4} \) m. Comparing this to the size of sheath (in the order of the Debye length), shows that most ions in the sheath are not hindered in their motion towards the wall. If the mean free path is shortened by increasing the pressure, collisions with neutral background particles might slow down the ions before they reach the wall. This might decrease, or even prevent sputtering.

When metals are illuminated with a photon energy above the work function, they emit electrons. This so-called photo-electric effect is a three step process:

1. A photon is absorbed by the metal, creating an electron-hole pair. The electron is excited into a conduction band state and the excess energy is transferred to the electron.

2. On its way to the surface, the electron loses energy due to inelastic electron-electron scattering. This way many secondary photo-electrons are created.

3. If the electrons are energetic enough when they reach the surface they can escape from the metal.

An incident photon will result in a number of escaped secondary photo-electrons. This is called the secondary electron yield. For metals the energy distribution of
the liberated electrons peaks at 1 to 2 eV, and has a full width at half maximum that is usually below 10 eV. So exposure to EUV radiation releases low energy electrons into the plasma. This means that the mean energy of the electrons (near the wall) will drop. As we saw earlier, the potential difference over the sheath is determined by this mean energy, so this potential difference will also drop. The result is that the ions will gain less kinetic energy when they are accelerated towards the wall, so less sputtering will occur.

2.3 Diagnostics

In this section a short overview will be given of diagnostic techniques that can be applied to measure the properties of the EUV-induced plasma. For a more in-depth treatment the reader is referred to the work by Van der Velden [4].

Apart from the low electron density and low ionization degree there are other factors that make diagnostics on this plasma less straightforward. A major constraint is that the plasma is only present where there is EUV radiation. As previously stated the light from the EUV source is focused into a cylindrical volume of roughly 2 cm long with a diameter of about 2 mm. The volume of the plasma is very small so diagnostic techniques relying on line integrals through the plasma will yield relatively low signal levels.

Another aspect that makes measurements more difficult, is that the plasma is strongly time dependent: The plasma is created by an EUV pulse of only 100 ns and subsequently decays in a few microseconds. Performing time resolved measurements on the plasma require therefore high time resolution (10 to 100 ns).

Plasma parameters can in general not be measured directly but are deduced after measuring other physical quantities. One frequently used assumption in those deductions is that of a Maxwellian electron energy distribution in the plasma. As was previously shown this is not the case in the EUV driven plasma so in many cases adjustments have to be made to translate measurement results into meaningful plasma parameters.

Taking into account these factors the feasibility of various diagnostic methods can be investigated. Only the general principles of some commonly used techniques are described, along with a rough estimate of the expected measurement results. Most techniques are very complex and will probably not give usable results. Instead we opt for Optical Emission Spectroscopy (OES) which is a relatively straightforward, non-invasive technique. To understand the results of the OES measurements we will have to construct a collisional radiative mode of the EUV induced plasma.
2.3.1 Active techniques

Many different diagnostic techniques are available to measure several aspects of plasma. Here some active techniques will be described. Active means that the plasma is subjected to some form of interaction in the form of a laser or probe.

**Langmuir probe**

Langmuir probes are very common tools for plasma diagnostics. The technique is used to determine electron temperature and density, and electric potential. It works by inserting a probe (or more than one) into the plasma and measuring the electric current at different applied voltages, the so called I-V characteristic. An example is shown in Fig. 2.6. The measured current is caused by the charged particles from the plasma that recombine at the probe. Determining plasma parameters from the IV characteristic is however not straightforward, since it requires understanding of the perturbation of the plasma by the probe. The geometry of the probe is an important factor in this.

When the probe is inserted into the plasma a Debye sheath will form around it. Applying a strong negative voltage to the probe will cause all the electrons in the sheath to be repelled from the probe and only positive ions in the sheath will contribute to the measured current. This is called the ion saturation current.

When the potential is raised highly kinetic electrons can overcome the potential barrier to the probe and add to the flowing current. When the potential has dropped to the point where current caused by the ions is equal to the current from the electrons (i.e. no nett current) the so called floating potential has been reached.

![Figure 2.6: Example of an I-V characteristic.](image-url)
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Further raising the potential will lead to a point where the potential of the probe equals the potential of the plasma. At this point there will no longer be a sheath repelling the electrons and the electron saturation current is measured.

Langmuir probe measurements of the EUV driven plasma were attempted by Van der Velden [4]. It proved, however, not feasible to measure the electron temperature or ion density with this method. The main reason is that the photo-electric effect obscures the measurement of the I-V characteristic.

Microwave interferometry

Microwave interferometry relies on the fact that an electromagnetic wave that is transmitted through a plasma will undergo a phase shift. A microwave beam is split in two, with one beam going through the plasma. The phase shift can be determined by comparing the two beams.

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

\[ \Delta \phi = \frac{\lambda_0 e^2}{4 \pi c m_e \varepsilon_0} \int n_e dl, \]  

with \( \lambda_0 \) the wavelength of the microwaves. There are two restrictions to the frequency of the microwave:

1. A plasma is only transparent to microwaves with a frequency that is much higher than the plasma frequency;
2. The wavelength of the microwaves must be smaller than the distance over which the electron density changes significantly.

The plasma frequency is approximately 10 GHz. The EUV induced plasma is approximately 2 mm in diameter, so the wavelength is at most 1 mm. Using \( \lambda_0 = 1 \) mm for the microwave, the expected phase shift is \( \Delta \phi \approx 3 \times 10^{-5} \) rad.

Since the detection limit of the best interferometers is \( \Delta \phi \approx 10^{-3} \) rad, this method is not suitable to measure the electron density in the EUV driven plasma.

Thomson scattering

Thomson scattering relies on the principle that free charged particles in the plasma scatter electromagnetic radiation sent into the plasma. The mechanism is roughly as follows. The incident electromagnetic wave interacts with a charged particle in the plasma, and because of the electric and magnetic field of the wave the particle is accelerated. The charged particle emits electromagnetic radiation during this acceleration which is interpreted as the scattered wave. Since every charged particle interacts with the incident beam, the resulting radiation is a sum over all the charged particles. If the phases of all the contributions to the resulting
radiation are uncorrelated the summation is merely a sum of the individual powers. This is called incoherent Thomson scattering, and is present when

\[ \kappa \lambda_D \gg 1, \]  

(2.26)

with \( \kappa \) the wave vector of the incident wave and \( \lambda_D \) the Debye length.

Furthermore for electrons of relatively low energy \((\approx 10 \text{ eV})\) a non-relativistic dipole approximation can be used.

With these approximations the scattered wave resulting from the interaction of the incident wave with the plasma can be described with a cross section:

\[ \sigma_t = \frac{8\pi}{3} r_e^2, \]  

(2.27)

with \( r_e \) the classical electron radius, defined as

\[ r_e = \frac{e^2}{4\pi\epsilon_0 m_0 c^2}. \]  

(2.28)

In a plasma with electron density \( n_e \) the fraction of incident photons that will be scattered over a length \( L \) is \( \sigma_t n_e L \). With \( \sigma_t = 6.65 \times 10^{-29} \text{ m}^2 \) and again using \( n_e = 10^{16} \text{ m}^{-3} \) and \( L = 10^{-3} \text{ m} \) the scattered fraction is \( 6.65 \times 10^{-16} \). Adding to this that only a portion of this fraction can be picked up by the detector due to its limited solid angle of collection \((\approx 10^{-2})\) and quantum efficiency, it is evident that the scattered fraction of photons is extremely low. Even though this fraction can be increased by sending the beam back and forth through the plasma or using a stronger laser it is still unlikely that sufficient scattering can be picked up to perform practical measurements.

**Laser induced fluorescence**

Laser Induced Fluorescence (LIF) is a technique by which a laser beam at a very specific wavelength \( (\lambda_L = c/\nu_L) \) is sent through the plasma. The specific wavelength is close to some resonant line of an atom or ion in the plasma \((\nu_{\text{trans}})\). Particles with a velocity component \( v_\parallel \) parallel to the laser beam will absorb a photon when the Doppler shift condition is satisfied:

\[ \nu_L - \nu_{\text{trans}} = \frac{v_\parallel}{\lambda_L}. \]  

(2.29)

The excited particle will then decay sending out a photon which can be picked up by a detector (e.g. intensified CCD camera or photo multiplier tube). When the laser wavelength is scanned over the transition wavelength, an ion velocity distribution can be obtained. For absolute ion densities the results must be calibrated.

It is possible to use LIF with very low ion densities \((\approx 10^{14} \text{ m}^{-3})\). However, in the EUV driven plasma we are interested in the ion velocities near the mirror.
surface. The required spatial resolution is therefore below the Debye length (≈ $2 \times 10^{-4}$ m). Also, in this area the ions have much higher velocity than in the bulk plasma, so the ions density is likely much lower than in the bulk plasma. It is therefore unlikely that this method can be used to gain information on the impact energies of the ions.

2.3.2 Optical emission spectroscopy

In contrast to the techniques treated thus far optical emission spectroscopy (OES) is a passive diagnostic tool. In the plasma photons are created when excited atoms (and ions) decay to a lower state. This light, spontaneously radiated by the plasma, is recorded and can be further analyzed. In the EUV driven plasma the atoms will mostly be excited from the ground state by electron collisions. Decay to lower states will not be the result of collisions but radiative decay. This is the so called corona balance. For an atomic level the density will evolve according to:

$$\frac{\partial n(p)}{\partial t} = n_e n(1) K(1, p)(t) + \sum_{q>p} n(q) A(q, p) - \sum_{p>q} n(p) A(p, q),$$

(2.30)

with $n(p)$ and $n(q)$ the densities of (two separate) excited levels, $n(1)$ the ground level density, $K(1, p)$ the collisional excitation rate from the ground level, and $A(p, q)$ the Einstein coefficient for spontaneous emission from level $p$ to $q$. Note that levels are not only populated by electron collisions from the ground level, but also by radiative decay from higher levels.

To interpret the results of OES measurements knowledge of the collisional excitation rates is required. The rate is determined as follows:

$$K(p, q)(t) = \int_{E_{th}}^{\infty} \sigma_{p,q}^{exc}(E') f(E', t) v_e(E') dE',$$

(2.31)

with $f(E, t)$ the time dependent EEDF, $\sigma_{p,q}^{exc}(E)$ the electron collision excitation cross section from level $p$ to $q$, and $v_e(E)$ the electron speed. Note that the electrons need at least a threshold energy $E_{th} = E(q) - E(p)$ to excite the atom from level $p$ to $q$. Many cross sections are available from literature: experimental, theoretical, and semi-empirical. To this we will dedicate a separate section in chapter 3. A model has to be used to provide the EEDF’s.

Van der Velden [4] has modeled the EUV driven plasma using a Particle In Cell Monte Carlo (PIC-MC) method, which will be treated in section 3.5. Among other things this model calculates the electron densities and distribution functions during the evolution of the plasma. To gain insight into the creation of the EEDF’s we will investigate them separately (3.6).

Using these EEDF’s as input a Collisional Radiative Model (CRM) can be constructed to model the radiation from the plasma. The model, that will be introduced in the next chapter, will solve a set of equations in the form of (2.30).
When the (time dependent) densities and transition probabilities are known, the radiation from the plasma can be calculated and compared to experimental results. OES measurements are easily performed using readily available spectrometers. Because the EUV driven plasma is highly transient in nature it is desirable to perform time resolved measurements. An added difficulty is the low photon yield per pulse. The time resolved measurements, described in section 4.3, were performed using a fast photo multiplier tube attached to a monochromator.

Self-absorption

For spectroscopic measurements it is important to know to what extent the radiation from the plasma is absorbed before it reaches the detector. The absorption can be estimated as follows. The radiation transport in the plasma is described by:

\[
\frac{dI_\nu(\nu)}{dx} = -\kappa(\nu)I_\nu(\nu) + j_\nu(\nu),
\]

with \(\nu\) the frequency, \(I_\nu(\nu)\) the intensity (energy per of unit time, area, frequency range, and solid angle) in the \(x\)-direction, \(\kappa(\nu)\) the absorption coefficient, and \(j_\nu(\nu)\) the volume emissivity related to decay processes. The volume emissivity is:

\[
j_\nu(\nu) = n(u) \frac{h\nu}{4\pi} A(u,l) \phi_\nu(\nu),
\]

with \(n(u)\) the density of the upper level, \(h\) the Planck constant, \(A(u,l)\) the Einstein coefficient for spontaneous emission from level \(u\) to \(l\), and \(\phi_\nu(\nu)\) the line form function. This function is normalized so that:

\[
\int \phi_\nu(\nu)d\nu = 1,
\]

where the integration is performed over the whole transition. We will use a block form for this function, with a width of \(\delta\nu\), so \(\phi_\nu(\nu) = 1/\delta\nu\).

In equilibrium we will have:

\[
\frac{dI_\nu(\nu)}{dx} = 0 \quad \text{so} \quad \kappa(\nu)I_\nu(\nu) = j_\nu(\nu),
\]

and for the intensity (Planck):

\[
I_\nu(\nu) = \frac{2h\nu}{\lambda^2} \frac{1}{\exp(h\nu/k_bT) - 1}.
\]

Combining (2.33), (2.35), and (2.36), we get:

\[
\kappa(\nu) = \frac{j_\nu(\nu)}{I_\nu(\nu)} = \frac{1}{8\pi} n(u) \lambda^2 A(u,l) \phi_\nu(\nu) (\exp(h\nu/k_bT) - 1).
\]
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With:

\[
\frac{n(l)}{n(u)} = \frac{g(l)}{g(u)} \exp(h\nu/k_bT), \tag{2.38}
\]

with \(g(u)\) the degeneracy of level \(u\), we can write (2.37) as:

\[
\kappa(\nu) = \frac{1}{8\pi} \lambda^2 A(u, l) \phi_\nu(\nu) \left( n(l) \frac{g(u)}{g(l)} - n(u) \right) = \kappa_{\text{abs}}(\nu) + \kappa_{\text{ste}}(\nu). \tag{2.39}
\]

So the absorption coefficient is split into an effective absorption coefficient \(\kappa_{\text{abs}}\) and a stimulated emission coefficient \(\kappa_{\text{ste}}\). Stimulated emission adds to the radiation, so that coefficient is negative.

We are interested in the effective absorption, which we write as \(\kappa_{\text{abs}}(\nu) = n(l)\sigma(\nu)\), with:

\[
\sigma(\nu) = \frac{1}{8\pi} \lambda^2 A(u, l) \phi_\nu(\nu) \frac{g(u)}{g(l)}. \tag{2.40}
\]

So \(\sigma(\nu)\) is an absorption cross section.

For a calculation we will need the width of the line form block function, for which we will use the Doppler broadening:

\[
\delta\nu = \nu_0 \sqrt{\frac{k_bT}{mc^2}}. \tag{2.41}
\]

We are interested in radiation in the optical range and in argon the most intense lines will be those of the 4p-4s transitions. As an example we will use the line at 811.8 nm, with \(A = 3.3 \times 10^7\) s\(^{-1}\) and \(g(u)/g(l) = 7/5\). The Doppler broadening is \(\delta\nu \approx 3.1 \times 10^8\) s\(^{-1}\) so \(\phi_\nu(\nu) \approx 3.2 \times 10^{-9}\) s. The cross section will then be \(\sigma(\nu) \approx 4 \times 10^{-15}\) m\(^2\). For the absorption to be significant over a distance in the order of 1 cm, the density of the lower excited level would have to exceed the electron density. Since we can expect densities of the excited levels in the order of \(10^{14}\) m\(^{-2}\), the absorbed fraction over 1 cm is \(n l \sigma \approx 4 \times 10^{-3}\), so we can conclude that absorption is not an issue.
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Modeling

The calculations in the previous chapter show that the plasma created by the EUV pulse is very short-lived; after about a microsecond it has disappeared. In this chapter it will first be shown that it is necessary to apply modeling to describe the plasma (section 3.1), after which a motivation towards the balance equations used to build the model is given (section 3.2).

The model (described in section 3.3) that is constructed is a Collisional Radiative Model (CRM), already shortly introduced in the previous chapter. The model consists of a set of equations that describe the population of the excited levels of the argon atoms and ions in the plasma.

First, it is necessary to compile this set of equations, consisting of collisional and radiative processes (section 3.3). Second, we need parameters for these equations to achieve meaningful results. These parameters are transition probabilities for the radiative transitions, and cross sections for the collisional transitions (section 3.4).

Because the plasma is highly transient and the electron energy distribution function (EEDF) is far from equilibrium, we cannot use readily available EEDF’s. A Particle In Cell Monte-Carlo (PIC-MC) model by Van der Velden [4], that simulates the EUV driven plasma, is used to provide these EEDF’s. After a description of this model (section 3.5), analytical models are used to gain insight into the shape and evolution of the EEDF’s (section 3.6).

In the subsequent section (3.7) the implementation of the model is described, followed by the results (section 3.8).

3.1 Non-equilibrium

Any plasma has several equilibrium and non-equilibrium aspects. The degree of equilibrium departure is expressed by the ratio between the equilibrium and non-equilibrium parts. It can be described by dividing the plasma kinetics in forward and corresponding backward processes; so-called proper balances. Equilibrium is present on a detailed plasma aspect when the number of forward processes equals
that of the corresponding backward processes. Thus when the proper balances in question equilibrate. Since electrons are, in many situations, the main agents in performing (de)excitation kinetics we can expect that for increasing $n_e$ more proper balances will reach a state of equilibrium. The underlying aspects of the partial equilibrium features can easily be described with a few parameters using the well-known laws of statistical mechanics. In our case, however, due to the low electron density ($n_e \approx 10^{16}$ m$^3$) and strong transient nature with a decay time of typically $10^{-7}$ s, corresponding to $10^7$ Hz, the plasma is far from equilibrium. Let’s look at some (disturbed) equilibria in more detail:

- **Planck:**
  The underlying proper balance is in this case given by absorption and (stimulated) emission. As is shown in the previous chapter, the attenuation length for radiation generated by the plasma in the visible and UV-range exceeds the dimensions of the plasma by far. The plasma is therefore optically thin, which implies that the radiation generated by the plasma cannot be characterized by Planck’s radiation law.

- **Maxwell:**
  Here the proper balance is formed by the kinetic energy exchange between electrons in e-e collisions. The photon beam creating the plasma has a very distinct energy (2% bandwidth around 13.5 nm) so initially the EEDF will be sharply peaked at 76 eV. By e-e collisions the plasma might thermalize reaching a Maxwellian EEDF. However, the average time between collisions ($\tau_{ee}$) is in the order of the diffusion time, so the plasma will have recombined at the wall before Maxwellization can take place.

- **Boltzmann:**
  It is possible to describe the densities of the excited states using the Boltzmann distribution law, if at least two conditions are fulfilled. First, the relevant excitation and de-excitation processes are in equilibrium with each other. Second, the energy of the agents performing the excitation and de-excitation are distributed according to a Maxwell distribution. Since, in our case, there is no Maxwell distribution, Boltzmann cannot be used to describe the excited state populations.

- **Saha:**
  In order for the Saha distribution law to be applicable, the balance of ionization and the corresponding reverse process of two-electron recombination must be in equilibrium:

  $$\text{Ar} + e \leftrightarrow \text{Ar}^+ + e + e$$

  As stated in the previous chapter, the three-particle recombination rate is:

  $$k_{\text{rec},3} \approx 3.3 \times 10^{-21} T_e^{-9/2} = 1.7 \times 10^{-39} \hat{T}_e^{-9/2},$$

30
Figure 3.1: Schematic depiction of the corona balance (CB) and excitation saturation balance (ESB). In CB atomic levels are populated by means of electron excitation from the ground level, whereas depopulation is realized by means of spontaneous radiative decay to lower lying levels. In ESB the atoms are repetitively excited until the excited electron reaches the continuum and the atom is ionized. The critical principle quantum number which denotes the boundary between the two balance domains, is designated by $p_{cr}$.

which results in our case in a recombination frequency of

$$\nu_{rec,3} = k_{rec,3} n_e^2 \approx 10^{-7} \text{ Hz.}$$

This is much lower than the diffusion frequency, which was previously estimated at a value of $\nu_{diff} \approx 3 \times 10^3$ Hz. This means that the ions will have drifted away before an equilibrium can be established, so also Saha equilibrium is out of the question.

The foregoing considerations show that the well known equilibrium laws, as given by statistical mechanics, can not be used to describe our plasma. This means, that in order to find the light emission as a function of time, we have to describe the non-equilibrium reactions in detail. To that end we construct a collisional radiative model (CRM), consisting of appropriate balance equations.

### 3.2 Classification of excitation balance

To model the plasma it is necessary to construct a set of balance equations that describe the relevant mechanisms in the plasma. In our case the plasma is an ionizing plasma, meaning that the excited levels are populated by excitation from the ground level and not by the continuum. The electron density is relatively low, so it is to be expected that lower excited levels can be described with the corona balance (CB) and higher levels using the excitation saturation balance (ESB). The principles of both balances are shown in Fig. 3.1. In CB radiative decay is more
important than de-excitation by collisions with electrons, or

\[ n_e \sum_{q \neq p} K(p, q) \ll \sum_{q < p} A(p, q) \equiv A(p), \tag{3.1} \]

with \( K(pq) \) the electron collisional (de-)excitation rate from level \( p \) to \( q \), \( A(p, q) \) the Einstein coefficient for spontaneous emission from level \( p \) to level \( q \), from here on called transition probability, and \( A(p) \) the total transition probability. In ESB, on the other hand, collisions are dominant:

\[ n_e \sum_{q \neq p} K(p, q) \equiv n_e K(p) \gg \sum_{q < p} A(p, q) \equiv A(p). \tag{3.2} \]

From (3.1) and (3.2) it follows that there is a critical level \( p_{cr} \) for which

\[ n_e K(p_{cr}) = A(p_{cr}). \]

Levels with a lower principle quantum number \((p < p_{cr})\) are in the CB and states with a higher number \((p > p_{cr})\) in the ESB.

The boundary level \( p_{cr} \) is weakly dependent on the electron density and temperature and according to [13] determined by:

\[ p_{cr}^6 \approx 2 \times 10^{23} n_e^{-1} \frac{T_e^4}{\sqrt{T_e}} + 2, \]

Since in our plasma \( n_e \approx 10^{16} \text{ m}^{-3} \), we find that the boundary is at \( p_{eff} = 8 \), which is higher than any of the observable lines (spectroscopy measurements are treated in chapter 4). We can therefore conclude that the system is dominated by the CB.

In CB dominated systems the excited levels are populated by electron excitation of the ground level and depopulated by radiative decay. The balance equation describing the densities of the levels is therefore:

\[ \frac{\partial n(p)}{\partial t} = n_e n(1) K(1, p)(t) + \sum_{q > p} n(q) A(q, p) - n(p) \sum_{q < p} A(p, q), \tag{3.3} \]

with \( n(p) \) the density of level \( p \), \( n(1) \) being the ground level density. Note that only collisional excitation from the ground level is included. Because the densities of the excited levels are several orders of magnitude lower than the ground level density, the contribution from lower lying excited levels compared to the ground level will be negligible. Also note that every excited level can also be populated by radiative decay from higher levels, the so-called cascade contribution.

The electron collisional excitation rate is defined by:

\[ K(1, p)(t) = K_p(t) = \int_{E_{exc}}^{\infty} \sigma_{p}^{exc}(E') f(E', t) dE', \tag{3.4} \]
with $\sigma_{p}^{exc}(E)$ the electron excitation cross section from the ground level to level $p$, $f(E,t)$ the time dependent electron energy distribution function (EEDF), and $E_{exc}$ the excitation energy from the ground level to level $p$. Since only excitation from the ground level is included we will write the rate as $K_{p}(t)$. Note, that electrons with an energy below the threshold energy can not excite the atom to level $p$. Since only excitation from the ground level is included, the threshold energy is the energy of the excited level. If a plasma is in local thermal equilibrium (LTE) the EEDF is Maxwellian and can be described with one parameter, the temperature. In literature many rates are readily available measured and/or modeled using or assuming LTE. In our case, however, these cannot be used due to the strong non-Maxwellian nature of the EEDF. Rates have to be computed using cross sections and an EEDF.

The dominant lines observed in the spectroscopic measurements are those of the 4p-4s transitions. These transitions have a typical decay time of $\tau = 10^{-7}$ s, meaning that we cannot speak of a usual CB. The CB we deal with is highly transient.

### 3.3 Collisional Radiative Model

The model is implemented by explicitly solving the balance equations, representing the CB, given in (3.3). The calculations in chapter 2 showed that double ionized argon is likely to be present in the plasma. The PIC-MC model even showed that ArIII is the main source of sputtering. In the measurements, however, only lines of ArI and ArII could be identified, so only these species will be included in the model.

The model consists of a series of levels that are populated and depopulated by processes. The list is ordered according to energy level. The right-hand side of (3.3) can be split in a population ($P$) and a depopulation ($D$) term:

$$\frac{\partial n_{p}}{\partial t} = n_{e}n(1)K_{p}(t) + \sum_{q>p} n(q)A(q,p) - n(p)\sum_{q<p} A(p,q).$$  \hspace{1cm} (3.5)

When the densities of all levels are combined in a vector $\vec{n}$, equation (3.5) can be written in matrix form:

$$\frac{\partial \vec{n}}{\partial t} = \mathbf{M} \cdot \vec{n},$$

where matrix $\mathbf{M}$ contains both the population and depopulation terms.

The depopulation terms show up in the diagonal elements:

$$M_{p,p} = \begin{cases} -n_{e}(t)\sum_{q>1} K_{q}(t) & \text{if } p = 1 \\ -\sum_{q<p} A(p,q) & \text{if } p > 1 \end{cases},$$  \hspace{1cm} (3.7)
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Note that the depopulation term for the ground level consists only of collisional transitions to excited levels. Although the density of the ground level should remain constant, due to the abundance of the background gas, it is included in vector $\vec{n}$ as state $p = 1$. This means that the density of the ground level does not remain constant, but that there is “leakage” into the excited states. This, however, does not pose a problem, because the densities of the excited states are several orders lower than that of the ground level, so the drop in ground level density is negligible.

Population by collisional excitation appears in the first column of $M$:

$$M_{p,1} = n_e(t)K_p(t) \text{ if } p > 1,$$  \hspace{1cm} (3.8)

and population by the cascade contribution shows up in the upper off-diagonal part:

$$M_{q,p} = A(p,q) \text{ if } p > q.$$  \hspace{1cm} (3.9)

Equations (3.7), (3.8) and (3.9) result in the matrix:

$$M = \begin{pmatrix}
-n_e(t) \sum_{q>1} K_q(t) & A(2,1) & A(3,1) & \cdots & A(m,1) \\
n_e(t)K_2(t) & -\sum_{q<2} A(2,q) & A(3,2) & \cdots & A(m,2) \\
n_e(t)K_3(t) & 0 & -\sum_{q<3} A(3,q) & \cdots & A(m,3) \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
n_e(t)K_m(t) & 0 & 0 & \cdots & -\sum_{q<m} A(m,q)
\end{pmatrix}.$$  \hspace{1cm} (3.10)

Using the forward Euler method, equation (3.6) can be solved explicitly:

$$\frac{\vec{n}(t + \Delta t) - \vec{n}(t)}{\Delta t} = M(t) \cdot \vec{n}(t),$$

so

$$\vec{n}(t + \Delta t) = (1 + \Delta tM(t)) \cdot \vec{n}(t).$$  \hspace{1cm} (3.11)

This set of equations can be implemented in a model. However, matrix $M$ must first be constructed. To do this we need all relevant excitation rates as a function of time and transition probabilities.

### 3.4 Model parameters

Due to the highly transient nature of the plasma, the electron density and electron excitation rate are time dependent. As equation (3.4) shows, the excitation rate
Modeling

is time dependent through the electron energy distribution function (EEDF). The electron density and EEDF can be taken from a model, which will be treated in some more detail in the next section.

To further construct the matrix (3.10) information is needed about the relevant excitations and radiative transitions in the argon atom. The ArI and ArII system will be treated separately. First, we will make a selection of the radiative transitions that are taken into account. Second, we will need cross sections of all upper levels of these transitions.

For the radiative transitions we used the information of the National Institute of Standards and Technology [14]. The NIST website lists radiative transitions between excited states of the argon system, including the transition probability, or A-value (if known). From all these transitions we made a selection by the criterion that the transition probability should be sufficiently large. Since the plasma is highly transient, with timescales as short as $10^{-7}$ s, only transitions with a A-values of more than $2 \times 10^6$ s$^{-1}$ are included.

3.4.1 Notation

In this work both Passchen and Racah notation will be used. For the ArI system Racah notation will be used to denote groups of levels and will be written in bold. To denote separate levels in the ArI system we will use Passchen notation, written in italic. For instance, level group 4p consists of levels 2p$_1$ through 2p$_{10}$. Appendix A lists all levels used in this work in both notations. For the ArII system we will use Racah notation exclusively, so these states are written in normal font.

3.4.2 ArI

Radiative transition probabilities

The diagram in Fig. 3.2 shows the levels and radiative transitions that are included in the model for ArI. The levels shown are those that are involved in transitions with A-values of $2 \times 10^6$ s$^{-1}$ or higher. The vector $\vec{n}$ in (3.6) contains the densities of these levels, and all transitions constitute the radiative part of matrix (3.10).

For the collisional part of the matrix, the collisional population rate of the relevant excited level must be calculated, for which we confine ourselves to the levels that are radiative important ($A > 2 \times 10^6$ s$^{-1}$). This means that for every included level a cross section is needed.

Cross sections

The set of cross sections that are used in the model is compiled from several literature sources. Therefore experimental, theoretical, and semi-empirical cross sections are used.
Figure 3.2: The levels and transitions for the neutral argon atom included in the model. The number in parentheses is the number of levels of that group that are included. The italic numbers are the number of separate transitions between the level-groups.

Cross sections for the 4p levels are taken from Chilton et al. [15], and shown in Fig. 3.3. The wavelengths and A-values of the transitions are given in table 3.1. Cross sections of two 5s (2s5 and 2s3) and nine of twelve 3d levels are taken from another article by Chilton et al. [16]. The cross sections of the remaining 5s levels and an additional 3d level (3d5) are taken from Stewart et al. [17]. The cross sections to the 5s levels are shown in Fig. 3.4, and the levels to which they radiate are given in table 3.2.

The two remaining 3d levels are taken from an article by Boffard et al. [18]. The cross section for the 3s′-level, given by Boffard et al., is a so-called apparent cross section. This requires some explanation.

Apparent and optical cross sections

A simple level diagram is shown in Fig. 3.5. All levels are populated by electron excitation (only shown for the upper three levels) from the ground level, and decay
Figure 3.3: Cross sections for the excitation of 4p levels as function of electron energy as measured by Chilton et al. [15].

<table>
<thead>
<tr>
<th>Level</th>
<th>Wavelength [nm] (A [10^6 s^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p1</td>
<td>750.6 (44.5)</td>
</tr>
<tr>
<td>2p2</td>
<td>696.7 (6.4), 772.6 (11.7), 826.7 (15.3)</td>
</tr>
<tr>
<td>2p3</td>
<td>706.9 (3.8), 738.6 (8.5), 841.1 (22.3)</td>
</tr>
<tr>
<td>2p4</td>
<td>795.0 (18.6), 852.4 (13.9)</td>
</tr>
<tr>
<td>2p5</td>
<td>751.7 (40.2)</td>
</tr>
<tr>
<td>2p6</td>
<td>763.7 (24.5), 800.8 (4.9), 922.7 (5.0)</td>
</tr>
<tr>
<td>2p7</td>
<td>772.6 (5.2), 810.6 (25.0), 867.0 (2.4)</td>
</tr>
<tr>
<td>2p8</td>
<td>801.7 (9.3), 842.7 (21.5)</td>
</tr>
<tr>
<td>2p9</td>
<td>811.8 (33.1)</td>
</tr>
<tr>
<td>2p10</td>
<td>912.5 (18.9), 966.0 (5.4)</td>
</tr>
</tbody>
</table>

Table 3.1: The wavelengths at which the 4p levels radiate and in parentheses the transition probabilities of the radiative transitions in 10^6 s^{-1}.

to a lower level by radiation. Level L_{up,1} and L_{up,2} decay to level L_{cs}, which in turn decays to L_{low,1} and L_{low,2}. The A’s denote the different transition probabilities. The general procedure to measure cross sections is by exposing a gas to a mono-energetic electron beam. The strength of the fluorescence signal gives the
magnitude of the cross section. By doing this for many different electron energies the cross section as a function of electron energy can be determined. For instance the cross section for the excitation of level \( L_{cs} \) can be determined by measuring the fluorescence via the channels \( L_{cs} \rightarrow L_{low,1} \) and \( L_{cs} \rightarrow L_{low,2} \).

As Fig. 3.5 also shows, the population of level \( L_{cs} \) is not only determined by the direct population of that level by electron excitation from the ground level, but also by decay from the upper lying levels (the cascade contribution). When the radiation from the upper levels into level \( L_{cs} \) is simultaneously measured it is possible to correct for the cascade.

Level \( L_{cs} \) can radiate to more than one lower level. In Fig. 3.5 we give as an example two possible decay routes. In reality there are in general much more routes, although many of those can often be neglected due to the low transition probability. To accurately determine the cross section it is therefore necessary to measure the radiation of every possible decay route, otherwise the measured cross section will be too low. When the transition probabilities of all possible transitions from level \( L_{cs} \) are known it is enough to measure only one transition and correct the cross section by using a ratio of A-values. In our example, if only the transition

Table 3.2: The levels to which the \( 5s \) levels radiate (\( 0 \) denotes the ground level) and in parentheses the transition probabilities of the radiative transitions in \( 10^6 \text{ s}^{-1} \).
Figure 3.5: Schematic representation of the radiative processes concerning a certain level ($L_{cs}$) of which the cross section is to be determined. All levels are populated by electron excitation and radiate, though this is only shown for the top three levels ($L_{up,1}$, $L_{up,2}$, and $L_{cs}$). Upper levels $L_{up,1}$ and $L_{up,2}$ radiate to level $L_{cs}$, which radiates to lower levels $L_{low,1}$ and $L_{low,2}$.

$A_{low,1}$ is measured:

$$c_{S,\text{real}} = \frac{A_{low,1} + A_{low,2}}{A_{low,1}} c_{S,\text{measured}}.$$  \hspace{1cm} (3.12)

When the cross section is not corrected for cascade contribution from upper levels, it is called the apparent cross section. When the correction of the cross sections for the different routes is omitted as well, so the cross section only pertains to one particular radiative transition, it is called an optical cross section.

As stated, the cross section used for the $3s'$ level is an apparent cross section, and, since it does not include the cascade, it is expected to be too large. Madison et al. [19] calculated the cross sections for the $3d$ levels showing good agreement with the earlier mentioned experimental results. The calculated cross section of the $3s'$ state is higher than the experimental apparent cross section, so the cascade is assumed to be negligible, and the apparent cross section is used.

The cross sections of the $3d$ levels are shown in Fig. 3.6, and the transitions included in the model are given in table 3.3.

Chilton [16] also lists six apparent cross sections for the $4f$ levels, shown in Fig. 3.7 (end levels and A-values are given in table 3.4). These cross sections are the sum of two close lying levels that have not been resolved in the measurements. The two levels only differ in the spin orientation of the excited electron. Although the cross sections are apparent, and thus include the cascade, they are still used in the model. Since the NIST database does not list any transitions into any of
Chapter 3.

Figure 3.6: Cross sections for the excitation of the 3d levels as function of electron energy taken from [16], [17], and [18].

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Lower levels (A [10^6 s^-1])</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s':</td>
<td>0 (313), 2p_1 (5.2), 2p_2 (7.1), 2p_4 (4.5)</td>
</tr>
<tr>
<td>3s''':</td>
<td>2p_6 (6.2), 2p_6 (3.8)</td>
</tr>
<tr>
<td>3s'''':</td>
<td>2p_6 (15.0)</td>
</tr>
<tr>
<td>3s''''':</td>
<td>2p_6 (2.2), 2p_7 (13.0)</td>
</tr>
<tr>
<td>3d':</td>
<td>2p_8 (2.0), 2p_9 (3.1)</td>
</tr>
<tr>
<td>3d''':</td>
<td>2p_7 (7.3), 2p_8 (5.7)</td>
</tr>
<tr>
<td>3d_2:</td>
<td>0 (270), 2p_5 (4.3), 2p_7 (11.0)</td>
</tr>
<tr>
<td>3d_3:</td>
<td>2p_6 (2.5), 2p_10 (4.9)</td>
</tr>
<tr>
<td>3d_4:</td>
<td>2p_8 (11.0)</td>
</tr>
<tr>
<td>3d_5:</td>
<td>2p_10 (7.4)</td>
</tr>
<tr>
<td>3d_6:</td>
<td>2p_10 (8.1)</td>
</tr>
</tbody>
</table>

Table 3.3: The levels to which the 3d levels radiate (0 denotes the ground level) and in parentheses the transition probabilities of the transitions in 10^6 s^-1.

the 4f levels, it is assumed that the cascade is of negligible influence. The cross sections for the single 4f levels are determined by dividing the cross sections in two parts by using the ratio of the degeneracy of the two levels (they are comprised
of).

![Figure 3.7: Apparent cross sections for the excitation of 4f levels as a function of the electron energy taken from [16].](image)

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Lower levels (A [10^6 s^{-1}])</th>
<th>Upper level</th>
<th>Lower levels (A [10^6 s^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>4U: 3d'_4 (6.5)</td>
<td>4X: 3d_5 (4.6)</td>
<td>4V: 3d'_4 (5.4)</td>
<td>4Y: 3d_2 (5.9), 2d_3 (3.5)</td>
</tr>
<tr>
<td>4W: 3s'''' (9.0)</td>
<td>4Z: 3s'' (5.3), 3s'_1 (7.7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.4:** The levels to which the 4f levels radiate, and in parentheses the transition probabilities of the transitions in 10^6 s^{-1}. Note that every level shown here actually consists of two separate levels that lie very close to each other.

**Semi-empirical cross sections**

The rest of the needed cross sections are taken from a collisional radiative model by Vlček et al. [20], which uses three different semi-empirical formulae by Drawin [21]. They are shown in Fig. 3.8, and the transitions are given in table 3.5.

The article by Vlček et al. lists cross sections of all remaining levels and several additional ones, but most cross sections are for levels that are combined into groups. To get the cross sections for the separate levels the cross sections are divided according to the degeneracy of the individual levels (as done with the 4f levels).

The cross sections of the levels combined with the transition probabilities form too complex a system to make accurate predictions about the population of the levels without running the model (which still needs an EEDF). However, some trends can already be expected. Since the cross sections for the 4p levels are clearly larger than those for the higher lying levels, we can expect that 4p radiation will dominate the spectrum.
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Figure 3.8: Cross sections for the excitation of the 6s, 5p, 4d, 5d, and 6d levels that are included in the model as function of the electron energy taken from [20].

Table 3.5: The levels to which the included 6s, 5p, 4d, 5d, and 6d levels radiate, and in parentheses the transition probabilities of the transitions in 10^6 s⁻¹.

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Lower level (A 10^6 s⁻¹)</th>
<th>Upper level</th>
<th>Lower level (A 10^6 s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s₅:</td>
<td>2p₃ (6.5)</td>
<td>4d₆:</td>
<td>2p₁₀ (3.1)</td>
</tr>
<tr>
<td>3s₄:</td>
<td>2p₈ (5.4)</td>
<td>4d₅:</td>
<td>2p₁₀ (2.8)</td>
</tr>
<tr>
<td>3s₃:</td>
<td>2p₄ (9.0)</td>
<td>5d₅:</td>
<td>2p₁₀ (3.2)</td>
</tr>
<tr>
<td>3s₂:</td>
<td>2p₃ (4.6)</td>
<td>5d₄:</td>
<td>2p₁₀ (2.2)</td>
</tr>
<tr>
<td>3p₅:</td>
<td>1s₄ (5.9)</td>
<td>5d₄:</td>
<td>2p₃ (2.5)</td>
</tr>
<tr>
<td>3p₁:</td>
<td>1s₂ (5.3)</td>
<td>6d₆:</td>
<td>2p₁₀ (2.4)</td>
</tr>
</tbody>
</table>

Only the two 3d levels 3s₁' and 3d₂ have a large cross section, but these levels will mostly decay directly to the ground level, as table 3.3 shows. This means that although the cascade is likely to be of influence, collisional excitation will be the dominant mechanism for the population of the 4p levels. Furthermore, the two step cascade from the 4f levels seems to be of no substantial significance, due to the low cross sections.

Since the EUV-pulse creating the plasma will result in a large fraction of highly energetic electrons, the lines originating from levels with a larger cross section at
high energies are likely to be dominant. It is clear that the line at 750.6 nm will be the most intense.

3.4.3 ArII

The simple corona-balance model (i.e. excitation solely from the ground state) can be extended to the ion system of argon (ArII). For the excited ions, however, there are two possible population routes:

- excitation from the ion ground level, or

- simultaneous ionization and excitation from the neutral ground level.

Since the EUV-pulse creates electrons with an energy of up to 72 eV, the second process, requiring 32 to 38 eV, is certainly possible. Which of the two processes is most important can be determined by comparing the cross sections. According to Boffard et al. [22] the cross sections for populating the ArII $4p$ levels are 5-30 times larger out of the ion ground state than out of the atomic ground state. However, since the ion density is estimated to be at least four orders of magnitude lower than the atom ground state, simultaneous ionization and excitation is clearly the dominant mechanism and therefore cross sections out of the atom ground state are needed.

Direct cross sections could not be found in literature, though optical [3.4.2] cross sections for several ion lines are available from Boffard et al. [23]. Measurements of the EUV driven plasma, that will be presented in the next chapter, show that the dominant ion lines in the spectrum belong to $4p$-$4s$ transitions. Furthermore, investigation of the cascade for the ionic $4p$ levels shows that higher levels radiate very rapidly into the $4p$ levels. Transition probabilities are mostly in the order of $10^7$ s$^{-1}$ and many are over $10^8$ s$^{-1}$. Boffard also mentions that shapes of the ion cross sections show no significant pressure dependence. Because the cascade from higher levels is so fast it is assumed that the optical cross sections can be applied to this highly transient plasma. The optical cross sections are used in the model and no separate cascade for the ion lines is included.

The optical cross sections still have to be transformed into apparent cross sections, though. By taking all the transition probabilities of the desired levels from the NIST database, the branching ratios of the levels can be calculated. The apparent cross section is the optical cross section divided by the branching ratio. The calculated apparent cross sections are used in the model. Only the upper levels of the eight strongest lines in the measurements are included. These are shown in Fig. 3.9. The wavelengths at which those ArII levels radiate and the transition probabilities are given in table 3.6.
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![Figure 3.9](image)

**Figure 3.9:** Cross sections for the excitation of the ArII 4p levels that are included in the model as function of electron energy taken from Boffard et al. [23].

<table>
<thead>
<tr>
<th>Level</th>
<th>Wavelength [nm]</th>
<th>Transition Probability $\times 10^6$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4p^{'},^2P_{1/2}^o$</td>
<td>413.3 (85), 447.6 (29)</td>
<td></td>
</tr>
<tr>
<td>$4p^{'},^2P_{3/2}^o$</td>
<td>427.8 (80)</td>
<td></td>
</tr>
<tr>
<td>$4p,^2P_{3/2}^o$</td>
<td>454.6 (47), 476.6 (64)</td>
<td></td>
</tr>
<tr>
<td>$4p^{'},^2F_{7/2}^o$</td>
<td>461.1 (79)</td>
<td></td>
</tr>
<tr>
<td>$4p^4,^2P_{3/2}^o$</td>
<td>473.7 (58)</td>
<td></td>
</tr>
<tr>
<td>$4p,^2D_{5/2}^o$</td>
<td>488.1 (82)</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.6:** The wavelengths at which the ArII 4p levels radiate and in parentheses the transition probabilities of the radiative transitions in $10^6$ s$^{-1}$.

### 3.5 Particle In Cell Monte-Carlo model

The radiative part of the Collisional Radiative Model that is constructed to model the radiation from the EUV driven plasma is now complete. In addition all the cross sections of the relevant levels are determined. Since the electrons are responsible for the population of the excited levels we still require the electron density and EEDF, as equation (3.4) describes. Because the EEDF will be non-Maxwellian, we have to deduce it from a PIC-MC model for which we will use the model constructed by Van der Velden [4]. This will be treated briefly in this section. Also the modifications to the original model made for this specific application are discussed.

#### 3.5.1 PIC-MC

In this research a modified version of the PIC-MC model by Van der Velden is used. PIC-MC stands for Particle In Cell Monte-Carlo model. In this model the
plasma is simulated by following a number of particles in the plasma. The particles (electrons, argon atoms, and argon ions) interact with each other through collisions and through the field the charged particles create. Because it is impossible to simulate every single physical particle, test-particles are used that represent a number of physical particles (in the order of $10^9$).

To calculate the position of the test-particles at subsequent time steps it is necessary to know the electric (and magnetic) field at the position of every test-particle. One way of calculating the force exerted on a particle by all other particles is to simply calculate the forces between every possible pair of particles. A computationally more efficient way is to define a grid (particle mesh) of nodes, and assign a density to every node. This is shown in Fig. 3.10. The charge of every particle is distributed over the nodes according to an interpolation scheme. Solving the Poisson equation at the nodes gives the electric field at the nodes. The field at the position of a test-particle can be calculated by interpolation. In the Particle-In-Cell scheme the interpolation of the charges is determined with a first order scheme. Since the model by Van der Velden is one dimensional in coordinate space, this means that the charge of a particle is divided over the two closest nodes according to the distance to each node. The downside of the PIC scheme is that charge fluctuations at a scale smaller than the size of one grid cell are not resolved. This means that the grid cells must be smaller than the smallest length scale of the plasma, i.e. the Debye length. Furthermore, the time step must be smaller than the smallest time scale in the plasma, which is the inverse of the plasma frequency. An additional requirement is that the time step and size of a grid cell must be chosen such that a particle can not move more than one grid cell per time step.

The Monte-Carlo method is a generic term used for any method that uses stochastic techniques. In the PIC-MC model, these techniques are used for the collisions between particles. When a collision occurs, type (elastic, excitational or ionizing), and the outcome of the collision are determined by random numbers. The outcome of a photoionization process (by an EUV-photon) is also determined by a random number.

![Figure 3.10: Linear interpolation scheme as used in the PIC-MC model. Charge C is located between two nodes of the grid (n and n+1). The charge is linearly divided between those two (closest) nodes according to the distance to the node.](image-url)
3.5.2 PIC-MC model of EUV driven plasma

The purpose of the model by Van der Velden was to model the sputtering of a surface near an EUV driven plasma. The model is one-dimensional in coordinate space and three-dimensional in velocity space. The computational domain is divided into a grid, where initially no test-particles are present. Only ions and electrons are modeled, the argon background gas (denoted by neutrals) is assumed to be uniformly distributed at all times.

The simulation starts when the argon gas is exposed to an EUV-beam. The EUV photons can ionize (and double ionize) the argon gas, so electrons and ions (in the form of test-particles) are added to the plasma while the model is running. Electrons that have enough energy can cause excitation and ionization. The latter case adds another electron-ion pair (as test-particles) to the plasma. The test-particles created by photoionization processes are placed at a random position on the grid, with a velocity in a random direction.

The model works with discrete time steps. Every time step the program performs the following procedure (also shown in Fig. 3.11):

1. At every node the charge is calculated by linear weighing;
2. The Poisson equation is solved to determine the field at the nodes;
3. The field is calculated at the position of each test-particle using linear interpolation;
4. The new position and velocity of each test-particle is determined;
5. Test-particles that move beyond the boundaries of the grid are removed from the plasma (and the computation);

Figure 3.11: Particle In Cell scheme. The loop is executed every time step.
6. A Monte-Carlo routine determines whether a collision has occurred, and if so, determines the outcome of that collision (new velocity, possibly also of new particle).

Because it is assumed that the background density is about four orders of magnitude higher only collisions with argon atoms in the ground state (neutrals) are considered:

1. elastic electron–neutral:
   \[ e + Ar \rightarrow e + Ar \]

2. electron excitation\(^*\) of neutral:
   \[ e + Ar \rightarrow e + Ar^* \]

3. electron ionization of neutral:
   \[ e + Ar \rightarrow e + e + Ar^+ \]

4. elastic ion–neutral:
   \[ Ar^+ + Ar \rightarrow Ar^+ + Ar \]

5. ion–neutral charge exchange:
   \[ Ar^+ + Ar \rightarrow Ar + Ar^+ \]

During the EUV pulse (the first 100 ns) low energy electrons are also liberated from the wall material by secondary emission. Particles that reach the wall (end of the grid) are removed from the plasma (item 5 in the procedure list). Because electrons are much faster than the heavy particles, this will result in an area with lower electron density near the wall: the sheath. Because the plasma in this region is not quasi-neutral, the ions in this region will be accelerated towards the wall. When the ions hit the wall, they can cause sputtering.

Since in this model the position and velocity of all test-particles (each representing a number of “real” particles) is known the sputtering of the wall can be studied. Whenever an ion reaches the wall, this event is recorded. Combined with empirical sputter yield data, the sputter rate of the surface can be calculated.

### 3.5.3 Modifications

Just as it is possible to follow the ions in the plasma, it is possible to track the electrons. Not only the electron density as a function of time and position can be recorded, but also the electron energy distribution function (EEDF). The measurements of the EUV driven plasma in the current study are however not performed near a wall, but in the intermediate focus.

\(^*\)With \(Ar^*\) we refer to the excited states, that are in this model combined into a single level with an energy of 11.5 eV.
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Analysis of the results of the PIC-MC model show that the sheath is smaller than $1/5$ of the plasma dimensions. It is therefore assumed that the center third of the plasma is a good representation of the plasma if no wall would be present. The data for the electron density and EEDF are taken from this region.

To speed up the simulation somewhat, processes that are not relevant for the center of the plasma can be excluded from the model. These processes are secondary emission and the impact of ions on the wall.

The EEDF’s calculated by the PIC-MC model used in this research are presented in section 3.6.4.

3.6 Electron Energy Distribution Function

As stated before, the PIC-MC model described in the previous section can be used to calculate the electron energy distribution function. This EEDF is needed to model the population of excited argon levels by electron collisions. How the mechanisms in the model will result in an EEDF and how the EEDF will look is not evident. To understand the dynamics of the PIC-MC model a simplified analytical ladder-model for the EEDF is constructed.

The initial electrons in the plasma are the result of photoionization of the background argon gas by the EUV pulse. This will result in electrons of 76 eV, so the EEDF will be non-Maxwellian from the start. The electrons will then lose energy by collisions with the background gas (elastic, exciting and ionizing collisions). The electrons will lose their energy in steps, hence the name ladder-model.

The evolution of the EEDF caused by the collisions will be modeled analytically for every separate mechanism. For comparison, each of these mechanisms is also modeled separately using the PIC-MC model. Finally the EEDF’s of the PIC-MC model incorporating all the mechanisms will be presented. These EEDF’s (at different pressure) will be used for the collisional radiative model.

3.6.1 Elastic collisions

To justify that electrons will lose their energy in (more or less) discrete steps, we will first prove that the mechanism of gradual energy loss due to elastic processes can be neglected. We therefore solve a simplified form of the electron energy equation. This equation reads:

$$n_e \frac{3}{2} k_b \frac{\partial T_e}{\partial t} = -n_e n_a k_{\text{mom}} \cdot \frac{3 m_e}{M} [k_b (T_e - T_a)] ,$$

(3.13)

with $n_e$ the electron density, $n_a$ the background density, $k_b$ the Boltzmann constant, $T_e$ and $T_a$ the temperature of the electrons and background gas respectively, $m_e$.
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the electron mass, \(M\) the mass of the argon atom, and \(k_{\text{mom}}\) the rate coefficient for momentum transfer. Equation (3.13) can be written as:

\[
\frac{1}{T_e} \frac{\partial T_e}{\partial t} = -n_a k_{\text{mom}} \frac{2m_e}{M} = -\nu_{\text{elas}},
\]

where the approximation \(T_e - T_a \approx T_e\) has been used. This gives for the electron temperature as a function of time:

\[
T_e(t) = T_e(0) \cdot \exp(-\nu_{\text{elas}} t)
\]

The cross sections that are used in the PIC-MC model are shown in Fig. 3.12. At 76.2 eV we find:

\[
k_{\text{mom}} = \sigma_{\text{elas}} v \approx 2.5 \times 10^{-20} \cdot 6.3 \times 10^6 = 1.6 \times 10^{-13} \text{ m}^3/\text{s}.
\]

Taking \(n_a = 1.2 \times 10^{21}\), this gives for the frequency of elastic decay the value \(\nu_{\text{elas}} \approx 5 \times 10^3 \text{ s}^{-1}\). Compared to the time of an EUV-pulse (100 ns) it is clear that elastic processes will not be responsible for the cooling of electrons.

Note, that equation 3.13 is based on the assumption that a certain temperature can be assigned to the electrons. This is of course not the case in view of the deviation from a Maxwellian energy distribution function (see discussion in section 3.1). However, the result that the loss of energy during the EUV pulse due to elastic collisions can be neglected, will remain the same. Because it is not possible to assign a temperature to the electrons, the term “cooling of the electrons” is strictly speaking not correct. It is however used in this text to refer to the fact that the electrons lose energy.
3.6.2 Excitation

The second mechanism by which electrons can lose energy is the inelastic process of collisional excitation. It will be demonstrated that in contrast to elastic collisions, excitation is indeed an effective energy loss process. Moreover, it leads to a stepwise decrease in energy. To understand the impact of these excitation processes on the temporal behavior of the EEDF we construct a so called ladder-model. It is based on the same assumption as the PIC-MC model in the sense that all excited atomic argon levels are combined into one single level at 11.5 eV above the argon ground state. This means that after being created by a photon (of 92 eV) the electrons (initially all with an energy of $92 - 15.8 = 76.2$ eV) will decay in fixed steps of 11.5 eV, as shown in Fig. 3.13. The electrons are “cooled” in a chain-reaction until they reach the energy of 7.2 eV, where they are no longer able to excite any argon atoms. The result is that we have seven quasi discrete levels of electron energy. When the density of every quasi level is identified by a number as in Fig. 3.13, the seven steps can each be described by the following equation:

$$\frac{\partial n_i}{\partial t} = P_i - D_i n_i,$$

(3.14)

with $n_i$ the electron density of a certain level $i$, $P_i$ the population term for that level, and $D_i$ the depopulation frequency of level $i$ to level $i - 1$. The next level
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$(i - 1)$ is populated by the depopulation of the adjacent upper level $(i)$, so the population term of $i - 1$ equals the depopulation term of $i$: $P_{i-1} = n_i D_i$.

The depopulation frequency can be written as:

$$D_i = n_a v_i \sigma_i,$$

with $v_i$ the speed of those electrons, and $\sigma_i$ the excitation cross section of argon by those electrons (see Fig. 3.12).

In the first step the electrons are populated by photoionization, so:

$$P_7 \equiv P = \frac{\hat{I} n_a \sigma_{\text{ph}}}{h \nu},$$

with $\hat{I}$ the power per square meter of one EUV pulse, $n_a$ the density of the background gas, $\sigma_{\text{ph}}$ the photoionization cross section, and $h \nu$ the energy of an EUV photon. We assume that $\hat{I}$ is constant during an EUV pulse. $P$ is used for this term since it is the initial source of electrons. The energy of a single EUV pulse is $\hat{I} = 0.6$ J and the photoionization cross section is $\sigma_{\text{ph}} = 1.37 \times 10^{-22}$ m$^2$, so the population is $P = 6.7 \times 10^{22} \text{ m}^{-3}\text{s}^{-1}$ at 5 Pa and $P = 2.7 \times 10^{21} \text{ m}^{-3}\text{s}^{-1}$ at 0.2 Pa.

For the first step (level 7), equation (3.14) can now be written as:

$$\frac{\partial n_7(t)}{\partial t} = P - D_7 n_7(t) = \frac{\hat{I} n_a \sigma_{\text{ph}}}{h \nu} - n_a v_7 \sigma_7 n_7(t),$$

so, with $n_7(0) = 0$, the solution reads:

$$n_7(t) = \frac{P}{D_7} \left(1 - e^{-D_7 t}\right).$$

The occupations of the subsequent lower steps (levels) are ruled by the differential equations:

$$\frac{\partial n_i(t)}{\partial t} = D_{i+1} n_{i+1}(t) - D_i n_i(t),$$

for $i$ is 6 through 2, with initial condition $n_i(0) = 0$. As an example, the solution for the next highest level $(i = 6)$ is:

$$n_6(t) = \frac{P}{D_6} \left(1 + \frac{1}{D_7 - D_6} \left(D_6 e^{-D_7 t} - D_7 e^{-D_6 t}\right)\right).$$

The last level, at 7.2 eV, does not have enough energy to excite any atoms so it does not have a depopulation term:

$$\frac{\partial n_1(t)}{\partial t} = D_2 n_2(t),$$

with, again, $n_1(0) = 0$. 51
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<table>
<thead>
<tr>
<th>level ((i))</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>energy [eV]</td>
<td>76.2</td>
<td>64.7</td>
<td>53.2</td>
<td>41.7</td>
<td>30.2</td>
<td>18.7</td>
</tr>
<tr>
<td>(D_i \ [\times 10^6 \text{s}^{-1}] \ (5 \text{ Pa}))</td>
<td>76</td>
<td>74</td>
<td>72</td>
<td>70</td>
<td>64</td>
<td>25</td>
</tr>
<tr>
<td>(D_i \ [\times 10^6 \text{s}^{-1}] \ (0.2 \text{ Pa}))</td>
<td>3.0</td>
<td>2.9</td>
<td>2.9</td>
<td>2.8</td>
<td>2.6</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 3.7: Pressure dependent constants for all excitation steps in equation (3.15). Note that no constant is included for level 1, since electrons at that level are not energetic enough to excite atoms.

Figure 3.14: Analytically determined evolution for two pressures of the quasi levels as a function of time. The two top graphs are the same except for the scale of the y-axis, this makes the evolution of levels 7 through 3 more clear. Note that the scale of the x-axis is 10 times as long for the low pressure case.

The EUV pulse ends after \(10^{-7}\) seconds, so from that moment on there is no more initial population term \(P_7 \equiv P = 0\). The same equations need to be solved,
except that now the boundary conditions are the value at \( t = 10^{-7} \) s.

Table 3.7 shows the quasi levels and their depopulation frequencies \( D_i \).

Solving the equations for all seven levels, and employing the constants in table 3.7, leads to the results given in Fig. 3.14. Comparing the results obtained for 5 Pa to those of 0.2 Pa, it can clearly be seen that at high pressure the energetic levels are able to reach an equilibrium due to their high depopulation frequency. Electrons with high energy are swiftly channeled to the lowest level. Level 2 has the lowest frequency, so the density builds up much higher than the higher levels. Because the electrons can not go below level 1, all electrons are eventually accumulated in that level.

At low pressure the electrons lose their energy far more slowly (far less collisions), so the separate steps in the cooling of the high energy electrons are clearly visible. It takes much longer for all higher levels to be depleted and all electrons to end up in level 1.

In Fig. 3.15 the evolution of the same energy levels as Fig. 3.14 is shown, but here the values are obtained from the PIC-MC model in which only the excitational collisions are enabled. Instead of the rectangular shape of the population function in the analytical model, the PIC-MC uses a cut-off Gaussian profile.

When the electrons are created they all have the same energy (76.2 eV), but the EEDF from the PIC-MC model shows broadening. The EEDF at the end of the EUV pulse \( (t = 100 \text{ ns}) \) is shown in Fig. 3.16. The lines representing the levels in Fig. 3.15 are obtained by integrating the EEDF over a range of 11.5 eV around the center of each level. The broadening of the peaks is unexpected, since only exciting collisions are included that decrease the energy of the electron by exactly 11.5 eV. Further investigation into this issue showed that there are small fluctuations in the electric field caused by the moving charges. This leads to small fluctuations in electron energy and thus to broadening of the peaks.

At high pressure (5 Pa) the analytic model shows good agreement with the PIC-MC model, both in the densities that are reached as in the behavior in time. At lower pressure the densities that are reached with the PIC-MC model are lower and the levels evolve faster, though the shapes show good agreement. Because the peaks are broadened the electrons lose their energy faster. This increases the effective depopulation frequencies, which results in lower level densities, and a faster evolution.

### 3.6.3 Ionization

Another possibility for energetic electrons to lose their energy is by ionizing the background gas. This process is similar to the excitation mechanism with the important difference that there is not a well defined drop in energy. Moreover an essential feature of ionization is that a new free electron is created and the excess energy of the incident electron (electron energy minus the ionization energy) is divided over both electrons. This division is however not equal, but subject to
a certain distribution function. A semi-empirical function by Opal et al. [24]
is used in the PIC-MC model, and is illustrated in Fig. 3.17. Because of this
random distribution, the electrons will not lose their energy in well defined steps,
but the electrons will be a spread over a range of energies. Fig. 3.17 shows that
the excess energy after ionization is mostly divided unevenly. For an incident
electron energy of 76.2 eV (60.4 eV remaining), in around 50% of the cases less
than 10 eV is transferred to the new electron, and the incident electron keeps more
than 50 eV. This means that the step down in energy of an electron involved in an
ionization reaction is in most cases between 15.8 and about 35 eV. Most electrons
will therefore cool down to under 10 eV after just two ionizing collisions.

To circumvent the fact that in the PIC-MC model the remaining kinetic energy
after ionization is randomly divided over the two resulting electrons, it is assumed
Figure 3.16: The EEDF at $t = 100$ ns (the end of the EUV pulse) as calculated by the PIC-MC model using only excitational collisions at 5.0 Pa. The dashed lines represent the levels 1 through 7 that were used in the analytical model, as defined in Fig. 3.13. Note the broadening of the peaks.

Figure 3.17: Opal function [24] giving the distribution, according to a random number, of the energy of the ejected electron after ionization by a 76.2, and 50.8 eV electron (remaining kinetic energy 60.4 and 35 eV respectively), as used in the PIC-MC model. An incident electron of 76.2 eV ionizes an argon atom and loses 15.8 eV in the process. The remaining 60.4 eV is then divided between the incident electron and the electron that was liberated in the ionization process. The division is determined as follows: a random number between 0 and 1 is chosen and the Opal function (in this case the solid line) gives the amount of energy that is transferred to the new electron. Whatever energy is left will be the new energy of the incident electron (see also Fig. 3.18).

that the division of the remaining energy is fixed. For convenience we will assume that in all cases 9.6 eV will be transferred to the liberated electron. This will result in the scheme shown in Fig. 3.18. The equations describing the densities of the
### Figure 3.18

Schematic depiction of the levels used in the analytical model for the quasi electron levels relevant for the ionization process. All electrons start at level 4. When they ionize an argon atom they lose 15.8 eV (dashed arrow). Of the remaining 60.4 eV, 9.6 eV is transferred (solid arrow) to the liberated electron (level 1), leaving the incident electron with 50.8 eV (level 3). For electrons at level 3 and 2 the process repeats itself, populating level 1 and 2.

**Note** that the electrons liberated by the ionization step from level 2 will end up with no energy. There is no level with energy zero included in the model, so these electrons are not added to the density of level 1. This will not be of much influence.

The production term is identical to the excitation case (3.16). For the depopulation terms $D_i$ equation (3.15) is used, only now with the ionization cross section (shown in Fig. 3.12). The values of the depopulation frequencies are listed in Table 3.8. Note that these frequencies are roughly twice as high as those in Table 3.7, since the cross section for ionization is roughly twice as high as the excitation cross section.

The results of this analytical model are shown in Fig. 3.19. Just as in the previous subsection, where the excitational cooling mechanism was studied, the PIC-MC model was modified to include only the ionization process. The results
Table 3.8: Pressure dependent depopulation frequencies in equation (3.21). Note that no constant is included for level 1, since electrons at that level are not energetic enough to ionize atoms.

<table>
<thead>
<tr>
<th>level (i)</th>
<th>energy [eV]</th>
<th>$D_i \times 10^6$ s$^{-1}$ (5 Pa)</th>
<th>$D_i \times 10^6$ s$^{-1}$ (0.2 Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>76.2</td>
<td>173</td>
<td>6.9</td>
</tr>
<tr>
<td>3</td>
<td>50.8</td>
<td>131</td>
<td>5.3</td>
</tr>
<tr>
<td>2</td>
<td>25.4</td>
<td>48.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

3.6.4 Complete PIC-MC model

The EEDF’s that are computed by the PIC-MC model with all processes included, as listed in subsection 3.5.2, are shown in Fig. 3.22 for 5 Pa, and 3.23 for 0.2 Pa. The EEDF’s at three different time steps are shown in Fig. 3.24.

The EEDF’s show several striking features:

- At high pressure (5 Pa), the electrons lose their energy very rapidly. Almost instantly after the EUV pulse has ended (at 100 ns) there are no high energy electrons left;

- Fast decreasing density of high energy electrons means fast increasing density of low energy electrons. Already during the EUV pulse a high density of low energy electrons is reached in the 5 Pa case;

- At high pressure, there are four peaks visible:
Figure 3.19: Analytically determined evolution of the EEDF for two pressures of the quasi levels as shown in Fig. 3.18, as a function of time. The top pair and bottom pair graphs are the same except for the scale of the y-axis. Note also the difference in time scale (x-axis).

- At 76 eV: the peak of the electrons when they are initially introduced in the plasma by photoionization;
- At 65 and 53 eV: the energy the electrons have left after they have excited one argon atom and two argon atoms respectively (see also Fig. 3.13);
- At 40 eV: the energy the electrons have left after they have ionized an
Figure 3.20: Evolution of the EEDF of the quasi levels as a function of time, calculated with the PIC-MC model with only ionizing collisions enabled. Note the difference in scale of both axes.

- At low pressure the peak representing the initial electrons is still intact at the end of the EUV pulse. About 150 ns later the peak has collapsed, and a large fraction of the electrons still has a high energy;
- The density of low energy electrons increases slowly. Even 400 ns after the EUV pulse that density is still increasing.
Figure 3.21: The EEDF at $t = 50$ ns as calculated by the PIC-MC model using only ionizing collisions at 5.0 Pa. The dashed lines represent the locations of the levels as defined in Fig. 3.18.

Figure 3.22: Color map of the EEDF as computed by the PIC-MC model at 5 Pa. Blue represents zero density, and red maximum density of the peak at 76 eV.

- At low pressure only the peak at 76 eV can easily be recognized. Areas of higher densities can be seen at 65 and 40 eV.

The effect of both excitation and ionization processes can be seen in the EEDF’s. Especially at high pressure different steps are recognizable. At high pressure, the electrons lose their energy very rapidly. There will only be electrons with a high energy during the EUV pulse. At low pressure, even 200 ns after the EUV pulse has ended, there is still a considerable fraction of high energy electrons in the plasma. Low energy electrons appear very fast at high pressure, but only after the EUV pulse, at low pressure.

From these EEDF’s we can expect the following results for the Collisional Radiative Model:
Figure 3.23: Color map of the EEDF as computed by the PIC-MC model at 0.2 Pa. Blue represents zero density, and red maximum density of the peak at 76 eV.

Figure 3.24: EEDF’s as calculated by the PIC-MC model at 5 Pa and 0.2 Pa, at different moments in time.

- At high pressure, ArI lines will rise quickly and start their decay when the EUV pulse has ended;
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- At low pressure, ArI lines will rise more slowly, reaching their maximum well after the end of the EUV pulse;

- At high pressure, ArII lines will only be visible during the EUV pulse because they decay very rapidly ($A \approx 5 \times 10^7 \text{ s}^{-1}$);

- At low pressure, ArII lines will only appear at the end of the EUV pulse, and decay more slowly.

All the information for the Collisional Radiative Model is now complete. In the next section the implementation of the model will be treated.

### 3.7 CRM implementation

Equation (3.11) will be solved numerically. In order to do so, a program called CRMddt was written in C++. As is evident from equation (3.11) this program needs to be able to construct a vector of all excited levels taken into account, and a matrix containing all collisional and radiative transitions between the levels. The first step of the program is therefore to load configuration data describing all processes in the model.

#### 3.7.1 Input

In this model the electrons are considered an external agent that drives all the collisional reactions. To calculate the collisional rates in the matrix (3.10), the electron density and electron energy distribution function need to be known at every time step. The electron information is therefore the first source of input and is presented to the CRM in two separate files: a file containing the electron densities at subsequent time steps, and a file containing the corresponding electron energy distributions. Both these files can be obtained from the PIC-MC model described in section 3.5. Of course it is also possible to construct these files by hand so the effect of any form and evolution of the EEDF on the level densities can be studied.

The second form of input is a single file in XML (eXtensible Markup Language) format, describing all the levels taken into account and the interactions between those levels. An example of such a configuration file is shown in listing 3.1. The fact that the model exists of two parts (levels and the interactions between them) is reflected in the XML-file.

The first section of the XML-file is a description of all the levels (starting at line 3 with the `<levels>`-tag). Every level is described by a unique id (for easy addressing), a starting density, the energy of the level, and a few attributes describing the electron configuration.
The second part (starting at line 9) describes all the processes between the levels. For every level that has been defined, there is a list of transitions. Every transition is described by the type (collisional or radiative), and the id of the end level. Radiative transitions only need an extra attribute for the emission coefficient. Collisional transitions have an attribute denoting the function that is used to describe the cross section. Every function that is used must be included in the XML-file (here starting at line 22). The configuration in the example uses a fit function for the collisional excitation cross section (line 24). A fit function has several parameters, two of which are special: $e$ is the energy, and $e_0$ is the threshold energy. This particular fit function has one more parameter $p_1$, the value of which must be defined in the params-tag of the transition using this function (line 13).

It is also possible to define a look-up table for the cross section. In that case the <function>-tag has an attribute containing a list of values that form the look-up table, and in the definition of the transition scaling parameters can be provided.
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**Listing 3.1:** Example of an XML configuration file. The model consists of two levels: the ground state and an excited level. Both levels have a unique id, starting density, energy and configuration. There are two transitions included in the model: a collisional excitation from the ground level (id='0') to the excited level (id='1'), and a radiative transition from the excited level to the ground level.

The cross section functions that are used for the model in this research were described in section 3.4. The levels and transition probabilities were taken from the NIST website [14].

### 3.7.2 Program structure

As stated, the objective of the program is to solve equation (3.11). In order to do so the matrix in (3.10) needs to be constructed for every time-step. Since only the collisional part of the matrix is time-dependent (the first column) only this part needs to be recalculated.

The first step of the CRM model is to read the XML configuration file and store everything in a data structure. The use of the object-oriented programming language C++ enables us to store all the information in objects. The two main entities in the program, the levels and the transitions, each have their own type of object, or rather class, called `CLevel` and `CTransition`. This is illustrated in Fig. 3.25, where the different classes are shown for a simple two-level model similar to the listing in 3.1.

![Diagram](image_url)

**Figure 3.25:** A basic model with a ground level and a single excited level and the classes used to describe it.

The class `CLevel` (see listing 3.2) holds all the information for a level (a unique id, density and energy of the level, and the electron configuration) in member
variables.

```cpp
class CLevel
{
    string id;
    double energy;
    string config;
    string term;
    string j;
    vector<double> density;
    vector<CCollisional> collisional;
    vector<CRadiative> radiative;
}
```

**Listing 3.2:** The basic form of the CLevel class.

The density is stored as an array (in a vector<>-container) so that the density at every iteration can be saved. A level-object also has two arrays of transitions: one for the collisional transitions and one for the radiative transitions. Both these types of transitions are separate classes, though they are derived from a basic CTransition-class (see listing 3.3), which actually only holds the id of the resulting level of the transition.

```cpp
class CTransition
{
    string id_end;
    ...
};

class CCollisional:public CTransition
{
    CCrosssection cs;
    double rate(CDist& dist);
    ...
};

class CRadiative:public CTransition
{
    double A;
    double wavelength;
    ...
};
```

**Listing 3.3:** The three transition classes. First is the base class CTransition followed by the classes CCollisional and CRadiative which are both derived from the base class.

The collisional and radiative classes are derived from the general transition class since any class describing a transition will have some common features, most notably they will need to store the end level of the transition. Deriving the classes from a common base class means that they inherit the members of that base class.
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The radiative transition class has some extra members: the Einstein coefficient for spontaneous decay \((A)\), which determines the rate, and the wavelength at which the resulting photons are radiated (in case the spectrum needs to be calculated).

The collisional transition also has additional members. The collisional excitation rate is determined by \(\) the cross section and EEDF (3.4). The cross section for the transition is stored in an object of class \(\text{Crosssection}\). The rate is calculated by the member function \(\text{rate()}\) which takes an object of class \(\text{Dist}\) as input. The \(\text{Dist}\) class describes the EEDF at a certain time step.

### 3.7.3 Stability

The aim of this program is to solve equation (3.6) which will be done using the Forward Euler method. Under certain conditions this method can become unstable. The general form of the equation we are solving is:

\[
\frac{\partial n(t)}{\partial t} = k n(t),
\]

(3.22)

with \(n(t)\) the density at time \(t\), and \(k\) some rate coefficient. When we apply forward Euler, this becomes:

\[
n(t + \Delta t) = n(t) + k \Delta t n(t) = (1 + k \Delta t) n(t),
\]

(3.23)

with \(\Delta t\) the time step. If the rate is negative, the time step must be small enough or we will get negative densities: \(\Delta t < 1/k\).

In two cases the model has a negative rate:

- Excitation from the ground level: the rate is the collisional excitation rate;
- Radiative decay from any level: the rate is the sum of transition probabilities from that level.

For the ground level equation (3.23) looks like:

\[
n_1(t + \Delta t) = \left(1 - n_e \sum_{q>1} K_q \Delta t\right) \cdot n_1(t),
\]

(3.24)

where the cascade contribution has been left out. The excitation rate is determined by (3.4) and can be estimated to be lower than \(10^{-12} \text{ m}^3\text{s}^{-1}\) (using a cross section of \(10^{-19} \text{ m}^2\)). For an electron density of \(10^{16} \text{ m}^{-3}\) the time step must be smaller than \(10^{-4} \text{ s}\). Since the dynamics of the modeled system are on the sub-microsecond scale, this criterion will easily be fulfilled.

Concerning radiative decay, the largest transition probability determines the time step. The time step must be smaller than the reciprocal of the largest emission coefficient. When loading the configuration file this can easily be determined.
3.7.4 Computation

When all data is loaded the iterative procedure of calculating equation (3.11) can begin. To this end a simple vector and matrix class are defined, see listing 3.4.

```cpp
class CVector
{
    CVector operator*(double d_in);
    vector<double> data;
    ...
};

class CMatrix
{
    CVector operator*(CVector &v_in);
    CMatrix operator+(CMatrix &m_in);
    vector<vector<double> > data;
    ...
};
```

Listing 3.4: The basics of a simple vector and matrix class. In the vector class the data is stored as an array in a `vector<>`-container (line 4). Similarly, the matrix holds an array of arrays containing the matrix values (line 12). Also shown are the definitions of the multiplication operators. A vector can be multiplied by a scalar (a single `double` called `d_in`) resulting in a vector (line 3). A matrix can be multiplied by a vector (a `CVector` called `v_in`), which results in a vector (line 10). On line 11, a addition operator is also defined so matrices can also be added, resulting in a matrix.

For the actual computation, three matrices and two vectors are defined:

- a matrix containing the collisional excitation rates (first column of (3.10)), another containing the depopulation rates by spontaneous emission (diagonal of (3.10)), and one containing the population rates by cascade from higher levels (upper triangular part of (3.10)). The first matrix is time dependent because the excitation rates are dependent on the time dependent EEDF. The other two matrices are time independent and can be reused every time step.

- a vector containing the level densities of the previous time step and a vector for storing the densities of the next time step.

The main loop for the computation is shown in listing 3.5 and consists of the following steps:

- On line 1 and 2 the matrices and vectors are defined (an extra matrix `mat_tot` is defined for storing the sum of the first three matrices).

- On line 4 and 5 the matrices for the emission depopulation and cascade population rates are filled.
• On line 7 the loop starts. It will end when a predetermined end-time is reached.

• On line 9 the electron distribution function for the current time step is loaded.

• On line 11 the matrix for the collisional excitation rates (which depends on the EEDF) is filled.

• On line 13 the matrices are combined into a single matrix.

• On line 15 the level densities of the last step are loaded.

• On line 16 the new level densities are calculated (equation (3.11)).

• On line 19 the time for the next iteration step is determined.

```c
CMatrix mat_exc, mat_rad, mat_cas, mat_tot;
CVector dens_old, dens_new;

fill_matrix_rad(mat_rad, data);
fill_matrix_cas(mat_cas, data);

while (crm_time <= crm_time_max)
{
    CDist& edf = get_edf(crm_time);
    fill_matrix_col(mat_col, data, edf);
    mat_tot = mat_col + mat_rad + mat_cas;
    data.get_dens(dens_old);
    dens_new = mat_tot * dens_old * crm_time_step + dens_old;
    data.add_dens(dens_new, crm_time + crm_time_step);
    crm_time += crm_time_step;
}
```

Listing 3.5: The main loop of the program where equation (3.11) is calculated. The variable `data` contains all the level and transitions information.

The matrix containing all rates is calculated in three steps so that it is possible to determine the influence of the cascade on the population of the levels. For every level it is possible to study the contribution by collisional excitation and radiative decay.

### 3.8 CRM results

The results of the collisional radiative model will be presented in this section. For the ArI system the results of the eight strongest lines of the measured spectrum
(the experiments will be treated in chapter 4) are given. First, the population rates of the upper levels of those radiative transitions are shown. This will give insight into the influence of the cascade. Next, the evolution in time of the selected lines will be given, followed by integrated spectra that can be calculated from the results of the CRM.

3.8.1 Level population

The upper levels of the eight strongest lines in the experiments are given in table 3.9 for ArI and in table 3.10 for ArII.

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Wavelength [nm] ( (\text{A}^{-1} \text{ [ns]}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2p_1 )</td>
<td>750.6 (22)</td>
</tr>
<tr>
<td>( 2p_2 )</td>
<td>696.7 (156)</td>
</tr>
<tr>
<td>( 2p_3 )</td>
<td>706.9 (263), 738.6 (118)</td>
</tr>
<tr>
<td>( 2p_5 )</td>
<td>751.6 (25)</td>
</tr>
<tr>
<td>( 2p_6 )</td>
<td>763.7 (41)</td>
</tr>
<tr>
<td>( 2p_7 )</td>
<td>810.6 (40)</td>
</tr>
<tr>
<td>( 2p_9 )</td>
<td>811.8 (30)</td>
</tr>
</tbody>
</table>

**Table 3.9:** The selection of lines of the ArI system that will be shown in this section.

<table>
<thead>
<tr>
<th>Upper level ( 4p' )</th>
<th>Wavelength [nm] ( (\text{A}^{-1} \text{ [ns]}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2\text{P}_1/2 )</td>
<td>413.3 (12), 447.6 (34)</td>
</tr>
<tr>
<td>( ^2\text{P}_3/2 )</td>
<td>427.8 (13)</td>
</tr>
<tr>
<td>( ^4\text{P}_3/2 )</td>
<td>454.6 (21), 476.6 (16)</td>
</tr>
<tr>
<td>( ^2\text{F}_7/2 )</td>
<td>461.1 (13)</td>
</tr>
<tr>
<td>( ^4\text{P}_3/2 )</td>
<td>473.7 (17)</td>
</tr>
<tr>
<td>( ^2\text{D}_5/2 )</td>
<td>488.1 (12)</td>
</tr>
</tbody>
</table>

**Table 3.10:** The ArII levels that are included in the model.

The population rates by electron collision from the ground state and by radiative decay from upper levels (cascade) are shown in Fig. 3.26 and Fig. 3.27 for ArI and ArII lines at 5 Pa background argon pressure and in Fig. 3.28 and Fig. 3.29 at 0.2 Pa background argon pressure. There is no cascade contribution shown for the ArII levels, since the model does not include any levels that radiate into those levels.
Figure 3.26: Population rates of ArI levels at 5.0 Pa. In parentheses the included wavelengths in nm.
Figure 3.27: Population rates of ArII levels at 5.0 Pa. In parentheses the included wavelengths in nm.
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Figure 3.28: Population rates of ArI levels at 0.2 Pa. In parentheses the included wavelengths in nm.
Figure 3.29: Population rates of ArII levels at 0.2 Pa. In parentheses the included wavelengths in nm.
At high pressure, the collisional excitation rates closely follow the EUV pulse. The rates for the ionic levels almost exactly follow the shape of the EUV pulse with hardly any delay. The rates of the atomic levels show some delay. They reach their maximum around 20 ns after the maximum of the EUV pulse. At the end of the EUV pulse the atomic rates decrease rapidly and then more slowly. For up to 200 ns after the pulse atomic levels are still populated. Furthermore, population by radiative decay from higher levels (cascade) is of little influence for all ArI levels.

At low pressure, the shapes are quite different. The collisional rates of both atomic and ionic levels rise steadily during the EUV pulse, and reach their maximum at the end of the pulse. After the pulse, the rates of the ionic levels decrease about twice as fast as those of the atomic levels. The shapes of the rates are all similar, except for level $2p_9$. This can be understood when we examine its cross section as shown in Fig. 3.3. The cross section of this level is far more peaked than those of the other levels. The excitation rate will therefore reflect the evolution of the electron energy within a small energy range. In a small energy range, a small increase followed by a smooth transition into a decrease can be seen (see Fig. 3.23). In a wide energy range, only a steady decrease is visible. At low pressure the cascade is a much bigger factor, mostly so for level $2p_9$.

### 3.8.2 Time resolved spectral lines

The evolution in time of the spectral lines is shown in Fig. 3.30 and 3.31 for atomic and ionic lines respectively. At high pressure the atomic lines reach their maximum at the end of the EUV pulse, and decay rapidly because they are not populated anymore. At low pressure the lines rise more slowly. Most lines reach their maximum 50 ns after the EUV pulse has ended, and then decay slowly in about 500 ns. The most notable exception is the 811.8 nm line, that reaches its maximum 250 ns after the pulse because of the high population by the cascade.

The ionic lines at high pressure follow the EUV pulse closely. They reach their maximum around 20 ns after the EUV pulse is at maximum intensity. At the end of the EUV pulse they also decay very quickly. At low pressure the ionic lines behave similar to the atomic lines at high pressure. They increase until the end of the EUV pulse, after which they decay in 400 ns.

The behavior of the lines is as expected from the EEDF that were used (see 3.6). Also we see that the line at 750.6 nm is dominant as expected (3.4).

### 3.8.3 Time integrated spectrum

By integrating all the line profiles, as shown in Fig. 3.30 and 3.31, over time, we can calculate the spectrum. These spectra (at 5 and 0.2 Pa) can then be compared to the measured spectra (next chapter). The calculated spectra are shown in Fig. 3.32 and 3.33.
Figure 3.30: Line transitions for ArI. Note the difference in time scale.
Figure 3.31: Line transitions for ArII. Note the difference in time scale
Comparing the spectra at the two pressures, there is very little difference (apart from the scale). Only the line at 811.8 nm is stronger at high pressure. This is caused by the shape of the cross section, which is peaked near threshold. At high pressure the EEDF is less spread out than at low pressure. Therefore the cross section near threshold is of more influence than the average cross section over a longer range of energies. Near threshold the cross section of level $2p_9$ is the largest, so the 811.8 nm line will be the strongest.

The ionic lines scale linear with pressure (at 25 times the pressure the lines are 25 times as intense). The atomic lines scale superlinear with pressure (with an extra factor of two). The superlinear behavior is expected, because the electron
density scales with the background density and the density of excited levels scales with the product of electron density and background density, i.e. with the square of the background pressure. However, the highly transient nature of the plasma will make the scaling more complex. At a pressure of 5 Pa there are only ionic lines during the EUV pulse. This will not change for increasing pressure. However, below a certain pressure, excited ion levels will still be populated after the EUV pulse. So when the pressure is low enough we can expect the ionic lines to become relatively more intense.

The results of the Collisional Radiative Model show that we can expect to see changes in the spectroscopic measurements when the background pressure varies. These changes are the result of the way the EEDF reacts to altered background pressures. We can expect time-integrated measurements to show a change in ratio between atomic and ionic lines at different pressures. Time-resolved measurements should also reveal whether the models can accurately describe the difference in timescales, when the pressure is varied.
Chapter 4

Experiments

To verify the models treated in the previous chapter several experiments were performed. These will be described in this chapter. The aim is to measure the radiation generated by the plasma that is created when the EUV radiation interacts with the background gas. This fluorescent radiation is measured under different conditions both time-integrated and time-resolved.

This chapter is organized as follows: First, the general experimental setup will be treated (section 4.1), followed by a description and results of the time-integrated spectroscopic measurements (section 4.2). The time-integrated measurements are fairly straightforward and their main purpose is to get a grasp of the spectrum under investigation and the signal yield. Next, the time-resolved measurements will be described (section 4.3), which, due to the high constraints on time resolution and low signal strength, are more complex. Important factors are the triggering of, and the electromagnetic interference from the EUV source. The results of the time resolved measurements will further be compared to those of the model.

4.1 General setup

As stated in chapter 2 two types of EUV sources are used in the EUV laboratory at ASML for research purposes: laser produced plasma source (LPP) and discharge produced plasma source (DPP). In this research two of the available DPP EUV sources were used. These EUV sources are prototypes manufactured to study the processes which produce EUV radiation (as extensively studied by a.o. Kieft [5]), moreover they are employed as tools that produce EUV radiation for various experiments in the research of EUV lithography. An example is the fluorescence-experiment dealt with in this chapter. The two setups used are called the “in-situ” and “swan” setup. Figure 4.1 shows pictures of both setups.
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4.1.1 “In-situ” setup

The “in-situ” setup was previously used by Van der Velden [4] for sputtering experiments. Figure 4.2 shows a schematic drawing of this setup. The setup consists of roughly three parts: the source chamber, the collector chamber, and the measurement chamber. In the source chamber a small (∼1 mm) pulsed plasma (up to ∼1 kHz) is created, which needs a mixture of He, Ar, and Xe with a total filling pressure of 10−30 Pa. This plasma produces radiation in a wide wavelength range, among which the desired EUV radiation (see also Fig. 2.2(a)).

The source chamber is directly connected to the collector chamber. It contains an ellipsoidal mirror (the collector) with the function to collect the light originating from the source. The inside of the collector is coated with a gold layer to act as a grazing incidence mirror. To prevent debris originating from the plasma from entering the collector chamber and possibly damaging the optics, a foiltrap [25] is placed between the source and collector chamber. The collector mirror images the collected radiation at a focus point in the measurement chamber, the so-called intermediate focus. The focus is shown in Fig. 4.3.

As described in chapter 2, the collector is separated from the measurement chamber by a filter to prevent all but EUV radiation from entering the measurement chamber. The filter consists of a 150 nm thick Zr foil reinforced by a wire mesh so that it can withstand larger pressure differences between the chambers. The filter therefore enables control of the gas mixture and pressure in the measurement chamber independent of the situation in the source and collector chamber. While the pressure in the collector chamber is kept at a constant value of 0.1 Pa, the pressure in the measurement chamber can be varied from 10−4 up to 100 Pa.
Figure 4.2: Schematic drawing of the in-situ setup. The gas inlet valve and separate vacuum pumps allow for freely adjusting the composition and pressure of the gas in the measurement chamber.

The “in-situ” setup was designed to perform sputtering experiments and is equipped with a movable sample holder to place multilayer samples at various positions with respect to the intermediate focus. Furthermore, the measurement chamber is equipped with two photosensitive diodes (not shown in Fig. 4.2) to perform reflectivity measurements during sputtering experiments, hence the name “in-situ”. Using a configuration of mirrors the beam is split into two parts, each ending at one of the diodes while one of the beams is reflected by the sample in the holder before it hits the diode. In this way the relative reflectivity of the sample can be measured during a sputtering experiment. This takes several hours at minimum. Another diode is placed in the source chamber and picks up stray light from the source. This third diode is used to correct for variations in source intensity. It can also be used to determine the timing of the EUV pulse in the time-resolved OES measurements.

The position inside the EUV source where the actual discharge takes place, can differ somewhat between different sets of electrodes. This means that the location of the intermediate focus must be determined before an experiment with new electrodes can start. This is done by trial and error using EUV sensitive foil. When the transparent foil is exposed to EUV a blue color appears. The foil is placed where the intermediate focus is expected to be and exposed to ~ 20 EUV pulses. After the exposure the setup needs to opened again to check the foil. With this laborious procedure the location of the intermediate focus can be determined. As the degree of coloring of the foil depends on the intensity of the source, it is also used to measure the intensity.

The time-integrated measurements were performed on the “in-situ” setup. Be-
cause of technical difficulties it was not possible to continue with the time-resolved measurements using the “in-situ” setup. The EUV source proved to be too unreliable to perform measurements of more than one minute. A single time-resolved measurement, however, takes over an hour to complete. For this reason the setup connected to another EUV source, called the “swan” setup, was used for the time-resolved measurements.

### 4.1.2 “Swan” setup

The “swan” setup is in principle the same as the “in-situ” setup. The difference is that there is no separate measurement chamber. The desired measurements, however, require an environment in which the composition and pressure of the background gas can be freely controlled. To this end, a small separate measurement chamber was installed inside the collector chamber, see Fig. 4.4. The vacuum pump and gas inlet were connected with tubes running through the collector chamber. The downside of this configuration is that the measurement chamber had to be connected with a tube to the vacuum pump. Because the measurement chamber could not be properly sealed, and only tubes with a small diameter could be used, it was not possible to achieve a pressure in the measurement chamber that was lower than the pressure in the surrounding collector chamber (\( \sim 0.15 \) Pa). Because of the lack of sealing, it was also not possible to increase the pressure to above 5 Pa. Above this pressure the pressure in the collector chamber would become
too high and disrupt the EUV source. Furthermore, in the measurement chamber only argon could be used.

Due to the small size and shape of the measurement chamber the collimating lens could only be placed in an axial orientation with respect to the intermediate focus.

### 4.2 Time-integrated measurements

All the time-integrated measurements were performed on the “in-situ” setup. Three different spectrometers were used to register the radiation from the EUV generated argon plasma:

- two OceanOptics HR2000+ models, one with an operating range of roughly 200 to 600 nm, and the other with the range 400 to 850 nm,

- an Avantes AVS-S2000 spectrometer with an operating range of about 200 to 850 nm.

An OceanOptics 74-UV collimating lens with a diameter of 5 mm and a focal length of 10 mm was placed in the measurement chamber aimed at the intermediate focus. With an optic fiber the spectrometers are connected via a vacuum feedthrough to the lens. The optical resolution with the high wavelength range OceanOptics was 0.5 nm, and with the low wavelength range 1 nm. With the Avantes spectrometer the resolution was $\sim$2 nm.

Since the plasma is optically thin, the amount of light picked up by the lens can be maximized by measuring along a line with the longest path length through the EUV induced plasma.
This is the case when the lens is placed along the axis of the intermediate focus (and thus of the whole setup), as shown in Fig. 4.5(a). It is however possible that in that case not only fluorescent radiation from the EUV driven plasma is picked up but also from any other components in the setup in the lens’s field of view behind the EUV created plasma. Apart from the stray light originating from outside the setup (laboratory lighting) there are two additional sources that might influence the measured spectrum:

- The EUV source itself not only produces EUV radiation but also radiation in a wide range, including the visible range.
- The gas in the source chamber can also be excited and emit fluorescent radiation. Especially the argon in the source chamber can be of influence, since we are measuring lines of the argon plasma in the measurement chamber.

Both forms of background radiation are likely to be of no significance, since they will most probably not be able to penetrate the Zr filter.

Still, to investigate the influence of anything except the EUV induced plasma in the intermediate focus the spectrum was measured in the following ways:

1. With and without the EUV source turned on. To determine whether light is entering the measurement chamber from outside the setup.
2. With and without argon in the measurement chamber (without means a pressure below $\sim 10^{-4}$ Pa). When there is no argon in the measurement chamber, no plasma can be created by the EUV radiation, and no visible light should be registered by the spectrometers.
3. Placing the collimating lens in an axial and radial position with respect to the intermediate focus, as shown in Fig. 4.5(b). Changing the orientation of the lens with respect to the intermediate focus from radial to axial should give an increase in signal, due to the longer path length (see Fig. 4.5(a)). Radiation emanating from the source should also show up as non-argon lines in the axial measurement (in the form of He an Xe lines), but should be absent in the radial measurement.

### 4.2.1 Results

Measurements with the source turned off, and measurements without argon in the measurement chamber (with the source turned on) did not show measurable spectra. For these measurements the lens was placed in a radial position as well as axial. It can therefore be concluded that the measured spectra are resulting solely from the EUV driven plasma in the measurement chamber.

Figure 4.6 shows spectra measured using the two OceanOptics spectrometers. Tables 4.1 and 4.2 list the lines that have been identified from these spectra. Lines
Experiments

**Figure 4.5:** (a) Orientation of the line of sight with respect to the intermediate focus, here represented by a cylinder. 
(b) Detail of Fig. 4.2 showing possible positions of the lens with respect to the intermediate focus.

**Figure 4.6:** Spectra measured with the two OceanOptics spectrometers, after subtraction of dark spectra. Integration time 50 s, source running at 900 Hz, argon pressure 10 Pa.

from both ArI and ArII are seen but no ArIII lines could be identified. With the Avantes spectrometer not all of these lines could be resolved. The vertical lines in the table denote which wavelengths are combined into a single line in the spectra.
measured with the Avantes spectrometer.

<table>
<thead>
<tr>
<th>transition</th>
<th>wavelength [nm]</th>
<th>$g_kA_{ki}$ [10^6 s^{-1}]</th>
<th>relative intensity</th>
<th>$\frac{\text{rel.int.}}{g_kA_{ki}} \times 10^{-9}$</th>
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<td>0.165</td>
<td>1.5</td>
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</table>

**Table 4.1:** Identified ArI lines from the spectra in Fig. 4.6, together with the corresponding transitions. Also shown are the product $g_kA_{ki}$ (with $A_{ki}$ the transition probability and $g_k$ the statistical weight of the emitting level), the relative observed intensity, and the ratio of the relative intensity and $g_kA_{ki}$. The lines marked with * could not be identified separately with the OceanOptics spectrometer.

Tables 4.1 and 4.2 also list the $g_kA_{ki}$ values of the transitions. This is the product of $A_{ki}$, the Einstein coefficient for spontaneous emission for the transition from level $k$ to $i$, and $g_k$, the statistical weight of the upper level $k$, that is the emitting level. It is seductive to assume that the transitions with the strongest $g_kA_{ki}$ values will give the strongest lines. This is the case for plasmas for which a certain state of equilibrium is reached. However the plasma created by the EUV pulse is highly transient, and will not reach any form of equilibrium (as was treated
<table>
<thead>
<tr>
<th>transition</th>
<th>wavelength [nm]</th>
<th>$g_k A_{ki}$ $[10^7 \text{ s}^{-1}]$</th>
<th>relative intensity</th>
<th>$\text{rel. int.} \times 10^{-11}$</th>
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<td>0.021</td>
<td>17</td>
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</table>

*Table 4.2:* Same information as table 4.1 only for ArII lines.
in chapter 2 and 3). The EUV pulses are short (\(~100\) ns) and wide apart (\(~1\) ms). The transition probabilities are in the order of \(10^7\) s\(^{-1}\) or higher so the excited levels (populated by the plasma created by one EUV pulse) will be fully depleted once a new plasma is created by the next EUV pulse. The speed by which a level is depopulated is therefore not of influence to the intensity of a line. All radiation (reaching the lens) will be recorded, whether this takes a (relatively) long or short time does not matter as long as it is shorter than the time between subsequent pulses. For this reason, the time-integrated spectra will show no relation between the measured signal and transition probability. This is also evident from the last column in tables 4.1 and 4.2.

### 4.2.2 Radial versus axial

As was shortly described in the previous section, measurements were performed by placing the lens in a radial and axial orientation with respect to the intermediate focus. In Fig. 4.7 the spectra obtained with the Avantes spectrometer are shown. Both are normalized to their maximum value at 750 nm. The measured axial spectrum is at its maximum value 1.75 times higher than the radial spectrum. Whereas there is no discernible difference between the spectra in the bottom graph (all ArI lines), the top graph shows clearly a higher intensity of the ion lines for the the axial case. The atomic argon line at 420 nm and the lines around 550 nm
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Figure 4.8: Shape of the plasma with a longer path length through a higher density of high energy electrons in the axial direction than the radial direction.

also show hardly any increase for the axial measurement.

The relatively lower signal of the neutral argon lines is not due to absorption of that radiation by the plasma, because the attenuation lengths in the optical range are much larger than the size of the plasma (as shown in chapter 2). The difference can be explained by the shape of the plasma, if we assume a configuration as shown in Fig. 4.8. Excitation from the ion ground state is negligible compared to simultaneous ionization and excitation from the atom ground state (see section 3.4.3). A relatively higher density of high energy electrons will result in relatively more intense ion lines. In the axial direction the path length is relatively longer through a higher density of high energy electrons than in the radial direction. This will result in relatively stronger ion lines.

4.2.3 Pressure dependence

To study the influence of pressure the spectrum was measured at pressures ranging from 0.5 to 50 Pa. First the spectra were individually scaled to obtain a spectrum per pulse per pressure. Next, the eight neutral and ion lines with the most counts were taken of the spectra at the various pressures. Each graph (counts per pulse per pressure as a function of pressure) was then divided by its average value to be able to compare lines with different relative counts. The results are shown in Fig. 4.9 and 4.10. The first striking feature is the relative drop in counts for ArI lines contrary to the sudden rise below 1 Pa for ArII lines. The distinctly different behavior of the 420 nm ArI line is probably due to influence of nearby ArII lines that are also counted because of the low resolution of the spectrometer. Note, that the error increases rapidly when the pressure is lowered. The signal yield scales with the pressure, so at lower pressure the relative error increases. At the lowest pressure of 0.5 Pa the error is estimated at 20%.

The results of the atomic lines are similar to the CR model, in the sense that they show a more than linear increase in intensity for rising pressure. The fact that the lines relatively decrease somewhat in the range from 5 to 20 Pa is unexpected. Running the models for these pressures might give more insight in these results.

For a wide range of pressures the ionic lines scale linear with pressure. The sudden rise below 2.5 Pa is not predicted by the model. A possible explanation
Chapter 4.

![Pressure dependence of several lines of neutral argon.](image)

**Figure 4.9:** Pressure dependence of several lines of neutral argon.

![Pressure dependence of several lines of single ionized argon.](image)

**Figure 4.10:** Pressure dependence of several lines of single ionized argon.
is the lack of cascade in the model for ionic levels. At high pressure the plasma is so short lived that cascade can be considered unimportant. When the pressure low enough the plasma will have a longer lifetime (typically longer than the EUV pulse) and cascade can become a larger factor in the population of radiating levels. This would increase the relative intensity of the ionic lines below a certain pressure.

4.2.4 Comparison to model

A spectrum measured at 5 Pa background pressure and a spectrum calculated by the CRM for 5 Pa are shown in Fig. 4.11. The measured ionic lines are significantly lower than the modeled lines. This is probably due to the fact that the cross sections that were used in the model are apparent cross sections, so they include cascade from higher levels.

![Figure 4.11: The spectrum calculated by the CR model compared to the measured spectrum. The spectra are scaled so that the peaks at 750.6 nm are at equal height.](image)

Several atomic lines are also higher in the model. This might be due to inaccuracy of the cross sections. As was shown in the results of the model, not only the height but also the shape the cross section function can be of influence. Influence of the cascade is unlikely, since at 5 Pa the model showed that this is only a
small factor. The lines above 840 nm are probably attenuated by the measurement setup.

The time integrated show some similarities with the model, but also some differences. Time resolved measurements are performed to gain more insight into the way the spectral lines are formed.

### 4.3 Time resolved measurements

#### 4.3.1 Experimental setup

As already stated, the time resolved measurements were performed on the “swan” setup. Whereas the “in-situ” setup has a separate measurement chamber, the “swan” setup does not. As stated in section 4.1, an environment in which the pressure and composition of the background gas can be controlled independently of the rest of the setup is required. To this end a measurement chamber was placed in the collector chamber, shown schematically in Fig. 4.4. Because the measurement chamber could not be properly sealed, it was not possible to achieve a pressure in the measurement chamber that was lower than the pressure in the surrounding collector chamber (0.12 Pa). This means that we can not be certain that the radiation that was measured using this setup was exclusively caused by the argon plasma that is induced by the EUV radiation. Though unlikely, it is possible that radiation from outside the measurement chamber was recorded in this setup.

To record the evolution of the line intensities as a function of time the setup schematically depicted in Fig. 4.12 was used. The fluorescent light from the EUV created plasma picked up by by the collimating lens was led into a monochromator through an optical fiber. The monochromator (an Oriel 7240 with off-axis Ebert

![Figure 4.12: Schematic drawing of the setup for the time integrated measurements.](image)
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configuration) used a 1200 l/mm grating with a blaze wavelength of 500 nm. The width of the entrance and exit slit was 280 µm, which equals an approximate bandpass of 2 nm. With this configuration the usable wavelength region of the monochromator is 300 to 1000 nm. Narrower slits were available but were not used to maximize the signal yield. Because of the low resolution of the setup, in many cases some lines are measured simultaneously. Of the ArI system the lines at 750.6 and 751.6 nm are measure simultaneously, as are the lines at 810.6 and 811.8 nm. The measurements of all ionic lines will have some added radiation from neighboring lines.

The exit slit of the monochromator is connected to a photomultiplier tube (PMT). The PMT (Hamamatsu 6780-04) has a working range of 185 to 850 nm and a rise time of 0.78 ns. The signal of the PMT is then amplified by a 1 GHz preamplifier (Ortec 9306) before the signal is recorded by a digital oscilloscope (LeCroy WaveSurfer 454).

When the EUV source is running it also generates a high amount of EM-interference. The interference picked up by the preamplifier was several orders of magnitude larger than the signal from the PMT. It was therefore necessary to place all the electronics in a metal enclosure. The power supply for the PMT and the preamplifier were realized using batteries, which were also placed inside the enclosure. Although using this setup the interference was sufficiently reduced to receive a clear signal on the scope, some filtering still had to be applied.

The radiation of the plasma will be very weak. From the spectrometer we can make an estimate of the signal yield per pulse. At 5 Pa the OceanOptics spectrometer registers about 8000 counts from the 705.6 nm line when the spectrum is measured for 60 s and the source is running at 1 kHz. According to the manufacturer, the sensitivity is 41 photons per count. So, per pulse only 5 photons are registered.

Fig. 4.13 shows a typical single measurement. The two peaks are approximate 3 ns wide. By combining a large number of these measurements a meaningful graph can be constructed. First, a threshold function is applied to the measurements, so only the peaks remain. We then apply binning: the total time length of the measurement is divided into intervals, called bins. If a peak is located within the time interval of a certain bin, a value of one is added to that bin. The graphs of the time resolved measurements are comprised of at least 10,000 measurements per line.

Since many measurements need to be combined it is essential to accurately trigger the measurements. In Fig. 4.14 two possible trigger sources are shown. The photodiode signal originates from an EUV sensitive photodiode that is placed inside the collector chamber. The source monitor is a signal that is generated by the control electronics of the EUV source. It can be used to check whether the EUV source is running properly. It shows the buildup and discharge of the voltage over the electrodes inside the EUV source.
Figure 4.13: A single measurement of the EUV driven plasma, using the monochromator and PMT. Monochromator is set at 750 nm, background pressure is 1 Pa.

Figure 4.14: Signal of the EUV sensitive diode (located in the collector chamber), and the monitoring signal of the EUV source.

The signal of the photodiode reveals that the EUV pulse consists of two overlapping peaks, with a total width of 200 ns. This is unexpected since the source should produce 100 ns EUV pulses. During the course of the time resolved measurements this did not change.

There was too much variation in the signal of the EUV diode to reliably trigger the measurements. Therefore the monitor signal of the source was used. When the crossing of the signal with the x-axis was used as the trigger event, the jitter was no more than 10 ns. The fact that this trigger event takes place after the EUV pulse does not pose a problem. The digital oscilloscope can continuously record the signal from the PMT and when the trigger event occurs, the signal from 500 ns before till 1500 ns after the event can be stored. In this mode the oscilloscope can only perform 3 measurements per second, so it took an hour to reach 10,000 measurements.

In the “in-situ” setup it was relatively easy to check the alignment of the collector mirror, the foil trap, and the collimating lens with respect to the intermediate focus. In the improvised “swan” setup this was very difficult. The measurement chamber in the “swan” setup was in fact a sealed box. Alignment of the collector
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mirror, foil trap, and collimating lens was done by opening the EUV source and placing a small light bulb in the position where the EUV discharge would be. The alignment was not checked with EUV sensitive foil, because the risk of harming the fragile alignment was too great.

At the end of the measurements the source strength and alignment was checked using EUV sensitive foil. The result is shown in Fig. 4.15. When the setup

![Figure 4.15](image.png)

Figure 4.15: Intensity map of the EUV at the expected intermediate focus. The height and width of the image are approximately 1 cm. In the center the irradiation is 0.03 Jm$^{-2}$ per pulse.

is properly aligned only a dark spot of a few millimeter is visible. Apparently, the time resolved measurements were performed on an out of focus setup. The irradiation by the EUV pulse was approximately 20 times lower than expected.

4.3.2 Results

Both ArI and ArII lines were measured at different pressures. Several ArI and ArII lines were measured at 5, 1, and 0.2 Pa. The results are shown in Fig. 4.16 and 4.17.

Concerning the shape, there is very little difference between the atomic lines at 5 and 1 Pa. At both pressures the rising flanks have a delay of 50 ns with respect to the EUV pulse. The decay of at 1 Pa is only marginally slower than at 5 Pa. The ratios between the different lines are the same, with the 750.6 nm line being by far dominant. At 0.2 Pa there are more differences. The decay is clearly slower, but also the relative intensity of the 763.7 nm line is much higher.

The ionic lines follow the shape of the EUV pulse more closely. They reach their maximum during the EUV pulse. At 5 Pa the lines decay so fast, that they are only present during the EUV pulse. At lower pressure the decay is slower, and at 0.2 Pa the spectral lines are still visible 100 ns after the EUV pulse. At all pressures the line at 427.8 nm is the strongest, and the different lines hardly differ in relative intensity.

To further clarify the influence of pressure, the atomic line at 750.6 nm (combined with the 751.6 nm line) and 763.7 nm were measured at pressures ranging
Chapter 4.

Figure 4.16: The most intense ArI lines as function of time with different background pressures. From top to bottom: 5 Pa, 1 Pa, and 0.2 Pa. The outline of the EUV-pulse is also shown. The bin size is 10 ns for 5 and 1 Pa, and 20 ns for 0.2 Pa. The 0.2 Pa lines are smoothed by weighted average of three points.

from 5 down to 0.12 Pa. At the same pressures the ionic lines at 427.8 and 476.6 nm were measured. The results are shown in Fig. 4.18 and 4.19.
Figure 4.17: The most intense ArII lines as function of time with different background pressures. From top to bottom: 5 Pa, 1 Pa, and 0.2 Pa. The outline of the EUV-pulse is also shown. The bin size is 10 ns for 5 and 1 Pa, and 20 ns for 0.2 Pa. The 1 and 0.2 Pa lines are smoothed by weighted average of three points.

The atomic and ionic lines react oppositely to a change in pressure. Whereas the intensity of the atomic lines relatively increases with increasing pressure, the
ionic lines decrease. This was expected from the results of the time integrated measurements.

Lines of both systems decay slower at lower pressures. The line at 750.6 and 763.7 nm have a radiative decay time of 22 and 41 ns respectively, so it is clear that the upper levels are still begin populated after the EUV pulse. At lower pressure the maximum of the 763.7 nm line is also slightly shifted forward in time.

The 427.8 nm ArII line decays slower for decreasing pressure and the maximum is slightly shifted. For the 476.6 nm line there is no change in shape. It is possible that the different behavior of these lines with varying pressure is caused by a difference in cross section profile or a difference in cascade contribution. The cross sections taken from literature are very similar though. A more plausible explanation is that, because of the low resolution of the monochromator, radiation

Figure 4.18: Pressure dependence of two ArI lines. The top graph shows the 750.6 nm line, and the bottom graph the 763.7 nm line. The lines are scaled by dividing them by the background argon pressure. The outline of the EUV-pulse is also shown.
Figure 4.19: Pressure dependence of two ArII lines. The top graph shows the 427.8 nm line, and the bottom graph the 476.6 nm line. The lines are scaled by dividing them by the background argon pressure. The outline of the EUV-pulse is also shown.

from close lying ArI lines is also recorded, most notably the line at 426.1 nm.
4.3.3 Comparison to model

When we compare these experimental results with the results of the model we can make the following observations:

1. Atomic lines:

   (a) At high pressure (5 Pa), the overall behavior is similar, with respect to the rise and decay of the lines.

   (b) At low pressure, the experiments hardly show a longer delay in reaching the maximum, and the decay time is much shorter than in the model (∼400 ns).

   (c) In both the experiments and model the dominant line is at 750.6 nm. However, in the model the 811.8 nm line is the second strongest, and in the experiments this is the 763.7 nm line.

2. Ionic lines:

   (a) At high pressure, there is a similar delay in the rising slope, and the lines rapidly decay after the pulse.

   (b) At low pressure, the model shows a longer delay in reaching the maximum, than the experiment. Also the decay is more rapid in the experiments. Where the model shows a clear difference in delay at different pressures, this difference is far less pronounced in the measurements.

   (c) In the experiments the line at 427.8 nm is clearly dominant, though this might be caused by nearby atomic lines. The rest of the lines have a larger spread in intensity in the model than in the experiments. This suggests that the cross sections used in the model are not accurate.

   Overall, there are some similarities and some clear differences between the results of the model and the experiments. The most notable difference is the fact that the lines decay much quicker in the experiments than is predicted by the model, especially for the ionic lines. The model shows a very clear difference in decay time of the ionic lines between different pressures, but in the experiments the difference is small. This indicates that at low pressure the electrons loose their energy much more rapidly than expected. The fact that the EUV beam was out of focus might be of influence but it is not expected that this will have an effect on the temporal behavior.
Chapter 5

Conclusions

The goal of this research has been to validate the Particle In Cell Monte-Carlo model by Van der Velden [4]. Although the model is specifically designed to model sputtering, and thus the sheath region, the efforts in this work are aimed at the bulk of the plasma, far from the sheath. The mean electron energy in the plasma determines the potential drop towards the wall in the sheath. It is this plasma property in particular that is the subject of this research.

The fluorescent radiation from the EUV induced plasma was measured using optical emission spectroscopy. Because the interpretation of the results of these measurements is not straightforward the conclusions are discussed in two parts.

5.1 Modeling

The results of the PIC-MC model show that at 5 Pa background pressure the high energy electrons lose their energy very rapidly by excitation and mainly ionization. Almost immediately after the EUV pulse there are no high energy (> 20 eV) electrons left. This also means that low energy electrons are almost immediately present in the plasma.

At 0.2 Pa the electrons lose their energy more slowly. Long after the EUV pulse (200 ns) there is still a large fraction of electrons with an energy of 40 eV. Because of this slow decay, the density of low energy electrons rises slowly, reaching its maximum after the EUV pulse.

These results are reflected in the outcome of the CRM. At 5 Pa the lines rise and decay quickly, with the ions lines closely following the EUV pulse. The atomic lines show some delay (50 ns) in reaching their maximum and subsequently decay in 100–200 ns. At 0.2 Pa the ion lines evolve more slowly, reaching their maximum at the end of the EUV pulse, and decaying in 300 ns. The atomic lines also rise more slowly at 0.2 Pa. They reach their maximum after the EUV pulse and it takes more than 500 ns for them to decay.

At 5.0 Pa we can conclude that cascade is not of influence. At 0.2 Pa the
cascade is still of little importance for most lines. A notable exception is the line at 811.8 nm. Together with the distinct shape of its cross section, the cascade is the reason why this line peaks at 300 ns after the EUV pulse.

The results of the models show that one can expect time resolved spectroscopic measurements to give a clear and direct indication of the rate at which the plasma electrons lose their energy. In particular the ion lines are a good representation of this. Because the high transition probabilities, ion lines are only visible when electrons of $\sim 36$ eV are present (this goes for the modeled 4p-levels).

Atomic lines can be used to detect the presence of electrons of lower energy ($\sim 13$ eV). Though for some lines the cascade can become an important factor at low pressure, the 750.6 nm line has almost no cascade contribution. It is therefore usable as a measurement tool for low energy electrons.

Interpretation of the time integrated spectra is more complex. The processes in the plasma that occur on short timescales are only indirectly visible. It is however clear that the change in ratio between ionic and atomic lines gives an indication of the change in transient behavior of the plasma. To quantify this more modeling efforts are required.

## 5.2 Experiments

In the time integrated spectra no ArIII lines could be detected. It is possible to extend the CRM to verify whether this is expected. The measured spectra showed some large discrepancies with the model. The cross sections of the ion levels used in the model are clearly too large, which is most likely due to the fact that we used apparent cross sections. The intensities of the atomic lines at 811.8 and 810.6 nm are also lower than the model predicted. Furthermore these lines showed similar scaling behavior with respect to the background pressure as other lines. We therefore conclude that, contrary to the model, cascade is not important for these lines.

The pressure dependence of the time integrated spectra is similar to the model. Below 2.5 Pa the ion lines become suddenly relatively more intense. We assume that below this pressure the plasma decays more slowly, so that also after the EUV pulse high energy electrons are present in the plasma.

The time resolved measurements showed that in general the transient behavior is faster than expected. Though the behavior at 5 Pa is similar to the model, the decay at 0.2 Pa is much faster in particular for the ion lines. Some measurements show that, indeed, ion lines are still visible after the EUV pulse at 1 and 0.2 Pa, but measurements of the 427.8 and 476.6 nm line suggest that this is due to radiation from nearby ArI lines.

The particular behavior of the 811.8 nm line that, according to the model, peaks much later than the other lines was not observed.

Although the circumstances under which the measurements were performed
were far from ideal, this is not expected to be the cause of the observed temporal
differences between model and experiment.

In general we can conclude that the diagnostic technique is a viable method to
monitor the evolution of the energy of the electrons in the plasma. The PIC-MC
model is valid in the sense that the high energy electrons in the EUV plasma lose
their energy more quickly for higher pressure, but the model can not be validated
with respect to the timescales on which the electron processes in the plasma occur.
The experiments show that the timescales are much shorter, so the electrons lose
their energy much faster. This means that at a lower pressure than expected
sputtering will not occur.

5.3 Recommendations

It is evident that there is much room for improvement concerning the experimental
setup. A better controlled environment and correct focusing and alignment will
greatly improve the measurements. They will also enable the use of narrower slits
for the monochromator, thus improving the resolution and excluding radiation
from unwanted lines.

Because of the discrepancies between the models and experiments, further
study is needed of the processes that govern the decay of the electron energy
and of the plasma.

The research by Van der Velden showed that sputtering can not only be con-
trolled by increasing the background pressure but also by adding hydrogen to the
background argon gas. According to the PIC-MC model, the electrons lose their
energy more quickly when hydrogen is added, similar to increasing the pressure.
The CRM and diagnostic technique can be used to verify those results.
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Bibliography


## Appendix A

### Levels

<table>
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<tr>
<th>Orbital</th>
<th>Levels</th>
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<tr>
<td></td>
<td>(s_5 \quad s_4 \quad s_3 \quad s_2)</td>
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<td></td>
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<tr>
<td></td>
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<td>(U \quad V \quad W \quad X \quad Y \quad Z)</td>
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**Table A.1**: The orbitals (Racah notation) and the levels they consist of. The top line shows the Racah notation and the bottom line the corresponding Paschen notation (in italics). The prime in the Racah notation denotes the configuration of the core: \(P_{3/2}^o\) for unprimed, \(P_{1/2}^o\) for primed.
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Table A.2: The groups in Racah notation (top row) and the corresponding group in Passchen notation (bottom row). Note that the four primed d levels in Racah notation are denoted as s in Passchen notation.

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