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MOLYBDENUM AND CARBON ATOM AND CARBON CLUSTER SPUTTERING UNDER LOW-ENERGY NOBLE GAS PLASMA BOMBARDMENT

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering Sciences (Engineering Physics)

by

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2008
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Chair

Univiersity of California, San Diego

2008
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ABSTRACT OF THE DISSERTATION

MOLYBDENUM AND CARBON ATOM AND CARBON CLUSTER SPUTTERING UNDER LOW-ENERGY NOBLE GAS PLASMA BOMBARDMENT

by

Eider Oyarzabal

Doctor of Philosophy in Engineering Sciences (Engineering Physics)

University of California San Diego, 2008

Sergei Krasheninnikov, Chair

Exit-angle resolved Mo atom sputtering yield under Xe ion bombardment and carbon atom and cluster (C₂ and C₃) sputtering yields under Xe, Kr, Ar, Ne and He ion bombardment from a plasma are measured for low incident energies (75 -225 eV). An energy-resolved quadrupole mass spectrometer (QMS) is used to detect the fraction of un-scattered sputtered neutrals that become ionized in the plasma; the angular distribution is obtained by changing the angle between the target and the QMS aperture.

A one-dimensional Monte Carlo code is used to simulate the interaction of the plasma and the sputtered particles between the sample and the QMS. The elastic scattering cross-sections of C, C₂ and C₃ with the different bombarding gas neutrals is obtained by varying the distance between the sample and the QMS and by performing
a best fit of the simulation results to the experimental results. Because the results obtained with the QMS are relative, the Mo atom sputtering results are normalized to the existing data in the literature and the total sputtering yield for carbon (C+C₂+C₃) for each bombarding gas is obtained from weight loss measurements. The absolute sputtering yield for C, C₂ and C₃ is then calculated from the integration of the measured angular distribution, taking into account the scattering and ionization of the sputtered particles between the sample and the QMS.

The angular sputtering distribution for Mo has a maximum at θ=60°, and this maximum becomes less pronounced as the incident ion energy increases. The results of the Monte Carlo TRIDYN code simulation for the angular distribution of Mo atoms sputtered by Xe bombardment are in agreement with the experiments.

For carbon sputtering under-cosine angular distributions of the sputtered atoms and clusters for all the studied bombarding gases are also observed. The C, C₂ and C₃ sputtering yield data shows a clear decrease of the atom to cluster (C/C₂ and C/C₃) sputtering ratio as the incident ion mass increases, changing from a carbon atom preferential erosion for the lower incident ion masses (He, Ne and Ar) to a cluster preferential erosion for the higher incident ion masses (Kr and Xe).
Chapter 1

Introduction

This introductory chapter is intended to give the reader a clear idea of the motivation behind the work presented in this dissertation, as well as the key results obtained from it. Some basic concepts and a review of the previous work in the research topic of the dissertation are also provided.

1.1. Motivation:

Plasmas are used nowadays in a wide range of applications due to their unique properties, they are conductive and respond to electric and magnetic fields, which makes them useful in numerous applications where such control is beneficial. They can also be efficient sources of radiation, so they are usable when special sources of energy or radiation are required. Among other important applications are the etching of advanced semiconductor chips, their use in ion thrusters and the controlled thermonuclear fusion. Plasma–based surface processes are indispensable for manufacturing the integrated circuits used by the electronics industry, for the microfabrication of an integrated circuit, one-third of the ten to hundreds of fabrication steps are typically plasma based. In the case of electrostatic ion thrusters a noble gas plasma (usually Xe) is used to create the thrust by the acceleration of the ions through a grid. In controlled thermonuclear fusion, electromagnetic fields are used to generate
a plasma at very high temperatures and hold its particles together long enough for a substantial number of fusion reactions to take place.

In most of the applications where a plasma is used there is an interaction between the plasma and the wall material that is nearby. In some applications, this interaction can be the reason for the use of the plasma (like in the case of materials processing), in other applications, this interaction can be an unwanted, yet unavoidable source of problems (like in the case of ion thrusters and magnetic confinement thermonuclear fusion). In any case, the study of this plasma-material interaction is of great importance.

Whenever a plasma is in contact with a material surface, a number of different processes can take place depending on the plasma conditions (density, energy of the plasma particles, etc.). In this dissertation, we focus on the physical sputtering process. The physical sputtering of the surface is important for two reasons: first, it produces the erosion of the material, which can eventually lead to the failure of the component. For example, this is important for the grid of an ion thruster, the sputtering of the grid material will to some extend limit the lifetime of the grid and the thruster. Second, the particles that are sputtered from the material will enter the plasma or be redeposited on adjacent surfaces.

The introduction of eroded impurities into the plasma and the formation of redeposited layers of eroded material on adjacent surfaces can represent an important problem in some applications. To model the sputtering of a component and the possible redeposition of the sputtered material, the energy and angular distribution, as
well as the nature of the sputtered particles (ions, atoms or clusters), needs to be taken into account. Over the years, a lot of research has been done on physical sputtering of different materials under different bombarding particles, but most of this research has been done for high incident energies (>1000eV). For these high incident energies a fair theoretical description of the sputtering process exists, and the experimental data agrees well with the theoretically obtained energy and ejection angle distributions. This is not the case for lower incident energies, were less experimental data is available and the analytical theory used for high incident energies does not always apply. Nevertheless, in many cases, for the modeling of the physical sputtering at these low energies, the energy and angular sputtering distributions are assumed to be similar to those obtained in studies at high incident energies (there is more data available at these energies). However, this is not always true, especially for the case of the ejection angle distribution of the sputtered particles. Thus, we believe it is important to study the physical sputtering process at low energies, even though the experimental techniques that need to be used are more complicated for low incident energy; higher fluxes and detection capabilities are needed due to the lower sputtering yield and a measurement of the energy and angular distribution is necessary because they can not be assumed to be identical to the high energy theoretical distributions. Most of the previous studies also assume that for the case of physical sputtering the material is preferentially eroded as atoms, and this may not be true for all cases at these low energies. Previous results for the erosion of carbon during Xe ion bombardment at low incident energies [1] have shown a high sputtering yield of
carbon as dimers (approximately 10 times larger than the yield for individual carbon atoms).

In this dissertation, we present the ejection-angle resolved Mo atom sputtering yield under Xe ion bombardment and the carbon atom and cluster (C\textsubscript{2} and C\textsubscript{3}) sputtering yield under Xe, Kr, Ar, Ne and He ion bombardment, for low incident energies (75 -225 eV). In order to accomplish this goal, we developed a new experimental technique, which allows us to measure the energy and angle resolved sputtering yield for both atom and cluster emission.

Mo sputtering under Xe bombardment measurements were performed initially, in order to develop, understand and validate the experimental technique on the somewhat more straightforward system of metallic sputtering by non-reactive ions before performing the carbon sputtering measurements, which are more complicated (as will be discussed later). Mo sputtering under Xe bombardment at this low incident ion energy range is important for the case of sputtering due to low energy ions created by charge exchange reactions near the grid surfaces [2] or by potential hill structures located within existing ion thruster discharge chambers [3,4]. Information about the angular sputtering distribution for the thruster materials under these conditions is necessary in order to accurately simulate the net erosion of surfaces and subsequent contamination buildup on adjacent locations. Unlike carbon, Mo has been shown to sputter primarily as atoms [1], so only the Mo atom sputtering was studied in this case.

After gaining a good understanding of the new experimental technique from the Mo experiments and having shown the validity of the technique to obtain accurate
sputtering yields (good agreement between the results for the Mo sputtering yield from this work and previous data), the more challenging carbon experiments were initiated. In the case of carbon sputtering the presence of a small amount of oxygen impurity in the plasma that forms CO and CO\textsubscript{2} which produces an additional C signal resulting from the dissociation of the CO and CO\textsubscript{2} in the plasma, and the fact that the material is sputter as atoms and clusters (C\textsubscript{2} and C\textsubscript{3} clusters are observed in the present experiments) makes the analysis of the data more complicated than for the case of Mo. Sputtering of carbon is of great importance in order to correctly model and predict the net erosion of surfaces and subsequent contamination buildup on adjacent locations in many applications. Carbon erosion under Xe bombardment at low incident energies is of particular interest for its possible application as the grid material on long-life ion thrusters instead of Mo. Carbon erosion under low energy noble gas bombardment is also important to predict the contamination and deposition of the sputtered carbon for the case of noble gas puffing in detached divertors \cite{5} in controlled fusion devices. Fusion reactor operating scenarios with detached plasmas are being considered to reduce the peak heat flux onto the divertor. In the case of noble gas puffing detachment the cooling of the plasma edge is achieved by radiation. Some studies \cite{5} have shown that, at least for the case of Ne detached plasmas, the carbon erosion due to physical sputtering from Ne\textsuperscript{+} bombardment (Ne\textsuperscript{+} ions in the plasma can reach energies in the range from 175-350 eV) can be even higher than the carbon erosion for the case of attached plasma. The main interest of the present work was to perform a comprehensive study of the influence of the incident bombarding ion mass on the
physical sputtering of carbon at low incident energies (75 to 225 eV), particularly studying the angular sputtering distributions of the sputtered particles as well as the carbon atom to cluster sputtering ratio and their evolution with increasing incident energy.

1.2 Physical Sputtering concepts:

In this section some basic concepts of the physical sputtering process are addressed [6-8].

When energetic ions or atoms bombard a surface, different phenomena can take place due to their interaction with the condensed matter. The energy dissipation that occurs may lead to atomic relocation, roughly within the ion’s range, creating temporary or permanent defects, and eventually, may give rise to the emission of atoms and molecules from the surface [6].

For the case of physical sputtering, an incoming particle will collide with the atoms in the solid transferring energy to the nuclei. If the transferred energy is larger than the binding energy at the lattice site, a primary recoil atom is created. Once this happens, the primary recoil atoms will collide with other target atoms distributing the energy via a collision cascade. A surface atom becomes sputtered if the energy transferred to it has a component normal the surface larger than the surface binding energy, $U_b$, which is usually approximated by the heat of sublimation of the sputtered material [9].
Depending on the energy of the incident particles and the collision cross-section of the incident particles with the target atoms, different collision regimes can be identified for physical sputtering (Fig. 1.1):

- **The single knock-on regime:** This regime is observed for the case of light incident particles or low-energy heavier particles. In this case, the recoil atoms receive a sufficiently high energy from the incident particle target atom collisions to be sputtered, but not enough energy to generate a recoil cascade. This is the regime in which the present experiments are performed [6].

- **The linear cascade regime:** If the target is bombarded by medium or heavy particles with a few hundreds of eV incident energy, the recoil atoms receive enough energy from the collisions with the incident particles to generate a recoil cascade. In this case the density of recoil atoms is low, so the knock-on collisions with atoms of the solid at rest dominate and collision between moving atoms are infrequent [6]. Most of the experimental data available, as well as simulation and analytical studies of physical sputtering, have been performed in this regime.

- **The spike regime:** This regime applies for the incidence of heavy ions having a large collision cross-section and for the incidence of molecules or atom clusters. In this case the density of recoil atoms is so high that the majority of atoms in a certain volume is set in motion [6].
In this introduction we focus on the main differences between the linear cascade regime and the single knock-on regime to give an idea of the importance of performing more studies at low incident energies.

The total amount of sputtering is measured by the sputtering yield, $Y$, which is defined as the mean number of atoms removed from the surface of a solid per incident particle. In addition, the sputtered particles present a distribution in emission energy and emission angle. The most important analytical theory for sputtering in the linear collision cascade regime was proposed by Sigmund (7,10-12). This theory predicts a linear scaling of the sputtering yield with the energy deposited in elastic collisions at the surface, $F_D(E_0,\theta_0,x = 0)$

$$Y(E_0,\theta_0) = \Lambda F_D(E_0,\theta_0,0)$$  \hspace{0.5cm} (1.1)

where $\Lambda$ is a material specific constant and $E_0$ and $\theta_0$ are the incident energy and angle of incidence (normal to the surface) of the bombarding particles. $F_D(E_0,\theta_0,0)$ is the energy deposited by the bombarding particle in low-energy recoils in the depth
interval \((x, x + \Delta x)\) and it is proposed [10,11] to be proportional to the nuclear stopping cross-section, \(S_n\). \(\Lambda\) is evaluated from the surface potential barrier and the nuclear stopping cross-section. The simplest model for the binding of atoms at the surface is a planar energy surface barrier, \(U_b[7]\). Then, the probability of an atom to escape from the surface can be obtained from

\[
P(E_i, \theta_i) = \begin{cases} 
1 & E_i \cos^2 \theta_i \geq U_b \\
0 & E_i \cos^2 \theta_i \leq U_b 
\end{cases} 
\] (1.2)

where \(E_i\) and \(\theta_i\) are the energy and angle (normal to the surface) with which the atoms arrives at the surface from within the target. The planar surface potential produces a refraction of the path of the atom as it passes through the surface leading to a change in energy and emission angle given by

\[
E = E_i - U_b \\
E \cos^2 \theta = E_i \cos^2 \theta_i - U_b 
\] (1.3)

From Eq.1.3, the recoil density, and the stopping cross-section in the power law form, \(\Lambda\) is derived [7,10,11]

\[
\Lambda = \frac{\Gamma_m}{8(1-2m)NC_m U_1^{-2m}} \frac{1}{N} \int \frac{dE}{E} 
\] (1.4)

where \(N\) is the atomic density of the target, \(\Gamma_m\) and \(C_m\) depend on the specific cross-section used to model the energy transfer in the nuclear collisions [12] and \(m\) characterizes the power of the interatomic potential \(V(r) \propto r^{-1/m}\) employed to described the atomic collisions. From the same theory, Sigmund derives the differential yields with respect to the kinetic emission energy and the emission angle
of the sputtered atoms. The differential yield of atoms sputtered with an emission energy $E$, into the solid angle $\Omega$ around the polar emission angle $\theta$ is given by [7]

$$\frac{\partial^3 Y}{\partial E \partial^2 \Omega} = F_D(E_0, \theta_0, 0) \frac{\Gamma_m}{4\pi N C_m} \frac{1 - m}{(E + U_b)^{1-2m}} \cos \theta$$

(1.5)

Thompson derived an essentially identical result [13,14]. The energy distribution peaks at an energy that depends only on the binding energy of the sample, but not on the energy or mass of the incident particle

$$E_{peak} = \frac{U_b}{2(1-m)}$$

(1.6)

For high emission energies ($E \gg U_b$), the energy spectrum is predicted to fall-off as $1/E^{2-2m}$. In order to compare the results from the experiments with the theory, the following expression for the differential yield of atoms sputtered with energy $E$ is used

$$\frac{\partial Y}{\partial E} = \frac{E}{(E + U_b)^{\alpha + 1}}$$

(1.7)

with $U_b$ or $\alpha$, or both, as fitting parameters. The Sigmund theory also predicts a cosine law for the polar angular distribution of the sputtered flux from an amorphous solid, which is characteristic of an isotropic flux in the target.

For the case of light ion bombardment, or low incident bombarding energy (<1keV), the linear collision cascade may not be adequate to describe the energy distribution of the sputtered particles. Conversely, rather specific collision sequences may lead to atom ejection [15-17]. Figure 1.2 shows some of the possible collision sequences in the single knock-on regime. As the particle reflection increases with
decreasing energy, reflective scattering collisions near the surface contribute increasingly to sputtering.

![Diagram of collision sequences](image)

**Figure 1.2**: Possible collision sequences in the single knock-on regime [6].

Computer simulations have predicted these special collision sequences for different cases. Some computations [17] indicate that an optimum number of collisions in those sequences may exist which result in the highest emission energies. Eckstein et al. use the TRIM.SP code to identify near-threshold sputtering ejection mechanisms. They found that for light ion bombardment the only important process is due to a primary knock-on atom generated directly by the projectile in its way back out of the sample (Fig.1.2c). For heavier ions two mechanism are observed, the first one involves a primary knock-on with the ion moving into the target (Fig. 1.2a), while in the second a secondary knock-on atom created by the projectile is sputtered, possibly after further collisions with other target atoms (Fig.1.2d). The sputtering mechanisms can change drastically for oblique ion incidence, where processes like Fig. 1.2a and Fig. 1.2b can become relevant.
The bombarded material can not only be sputtered as atoms but also as clusters of atoms. Several theories for cluster formation and emission mechanisms have been proposed over the years. The most important of them are:

- **Direct emission mechanism**: This mechanism involves a single collision between a moving atom from the collision cascade and a molecule already existing at the surface. If the energy transferred to the center-of-mass of the molecule exceeds the surface binding energy of the molecule and the relative kinetic energy of the atoms remains lower than the bond strength, the molecule will be emitted as a whole.

- **Atomic combination mechanism**: In this case, the constituents of the cluster receive energy in relatively independent collisions, and eventually form the molecule at some stage during the ejection process.

- **Thermodynamic model**: The computer simulation results from Ref. 18 and Ref. 19 show that thermalization of the target surface may occur after bombardment with energetic ions. This effect leads to the vaporization of a part of the irradiated material, along with strong cluster abundance.

- **Shock wave model**: This model is proposed to describe the formation of large clusters \((n > 3)\) emitted when a high-energy heavy ion interacts with a solid surface [20]. The analysis of both the experimental and theoretical results [21,22] has shown that the clusters are formed with greatest probability under heavy ion bombardment. This leads to a
drastic increase of the sputtering yields due to the overlapping of elastic collision cascades. The overlap of the collision cascades and the formation of a high-density energy deposition region could be the source of a shock wave [20].

1.3 Previous work on physical sputtering

The spectral distribution in terms of the emission angle and the emission energy of the sputtered particles reflect, to some degree, the atomistic processes occurring during the dissipation of the incident particle’s energy in the solid and the sputtering event. Hence, from the energy and angular distribution of the sputtered species, information about the collisional cascade processes in the solid can be derived [6]. The energy and angular distributions of the sputtered particles is also important in order correctly model and predict the net erosion of surfaces and subsequent contamination buildup on adjacent locations in many applications. The mass of the sputtered particles (in some cases the bombarded material can be sputtered as clusters) is important as well in order to correctly model the deposition of the sputtered material and to understand the sputtering mechanisms. In this section we will describe the current state of the research in physical sputtering [6], focusing on the energy and angular distributions of the sputtered particles and on cluster emission for normal incidence.
1.3.1 Energy distribution of the sputtered particles:

In this section a review of the available data for the energy distribution of sputtered neutral atoms and clusters is presented [6]. The bombarded material can also be sputtered as ions, but the fraction of ion sputtering compared to neutral sputtering is usually very low [6].

A) Neutral atoms

For predominantly nuclear energy loss processes (for metal and semiconductors at keV energies) the measured energy spectra from the data accumulated in the past [8,23,24] usually exhibits a high-energy dependence close to the predicted $E^{-2}$ and a most probable emission energy in fair agreement with the predictions from the analytical model (Eq. 1.5), using the cohesive energy (difference between the energy per atom of a system of free atoms at rest far apart from each other, and the energy of the solid) as the value for $U_b$. However, it is very difficult to know if the observed variations in the high-energy slope and peak position are real or merely uncertainties from the measurements. In particular, the procedure often applied of fitting the spectra to Eq. 1.7 with $U_b$ or $\alpha$ or both as fitting parameters can introduce severe ambiguities.

Figure 1.3 shows the results of the energy spectra of Al [25], Ca [26] and Ag atoms [27] sputtered from the respective metals for the case of Ar$^+$ bombardment. The measure data was fitted to Eq. 1.7 with $\alpha = 2$ and the indicated $U_b$ values. For the case of Al atom sputtering the obtained $U_b$ value is distinctly different from the cohesive
energy ($E_{coh}=3.3\text{eV}$), while the values for the other atoms are moderately lower (about a 10-20%) than the respective cohesive energies.

![Energy spectra of Al, Ca, and Ag](image)

Figure 1.3: Energy spectra of Al [25], Ca [26] and Ag atoms [27] sputtered from the respective metals for the case of Ar bombardment and fitting to Eq. 1.7.

At very low bombarding energies the energy distribution does not agree anymore with Eq. 1.5, as the incident energy is reduced the prerequisite energy range $E >> U_t$ is never established. Energy spectra of sputtered atoms for low and near threshold energies show that the average energy of the sputtered particles decreases with decreasing incident energy [28,29]: the peak of the energy spectra tends to shift to lower energies and the width of the distribution becomes narrower.
Figure 1.4: Energy distribution of sputtered Cu atoms for the case of Ar bombardment at low energies from experiments and simulation [6,30].

Figure 1.4 shows the energy distribution of sputtered Cu atoms for the case of Ar$^+$ bombardment at low energies from experiments and simulation performed in [30]. The energy distribution presents a steeper falloff as the incident energy decreases, this falloff is nearly exponential over a wide emission energy range and the slopes over that energy range for the experimental and simulation results agree very well.

B) Clusters:

For the case of cluster emission under keV incident energy bombardment [25,27] the energy distribution typically presents a peak of the distribution similar to
the single atom emission energy distribution, while the exponent $\alpha$ of the high energy decay, $E^{-\alpha}$, is slightly higher for clusters than for atoms, but is largely independent of the cluster size. For example, 3.9keV Ar$^+$ bombardment of Cu produced $\alpha \approx 2.8$ for Cu atoms and $\alpha \approx 3.5$ for Cu$_n$ clusters, with $2 \leq n \leq 6$.

Figure 1.5: Energy distribution of Ag atoms and clusters for 5keV Ar$^+$ bombardment [6, 27].

Figure 1.5 shows the results for the energy distribution of Ag atoms and clusters for 5keV Ar$^+$ bombardment from Ref. 27. The values of $\alpha$ from the exponential fitting to the data are: $\alpha \approx 1.7$ for monomers, $\alpha \approx 2.9$ for dimmers and $\alpha \approx 4$ for all larger clusters.

Molecular dynamics (MD) simulations for Ag$_2$ dimer sputtering agree reasonably well with experimental results [31] and show that for keV range incident energy, the sputtered dimers originate mainly from nearest-neighbor sites and that a
true double collision mechanisms accounts for the majority of emitted dimmers. For larger clusters, simulations [32] show an emission mechanism in which, due to correlated motion in the collision cascade, a group of neighboring atoms at the surface receives, simultaneously, nearly parallel momentum producing the emission of a group of bonded atoms.

![Energy distribution for the case of Cu dimer sputtering for different Ar\(^+\) bombardment incident energies.][6, 30]

Figure 1.6: Energy distribution for the case of Cu dimer sputtering for different Ar\(^+\) bombardment incident energies. [6, 30]

For the case of low energy bombardment the energy distribution shows a steeper falloff in comparison with the energy distribution of sputtered atoms. Figure 1.6 shows the evolution of the energy distribution for the case of Cu dimer sputtering under low energy Ar\(^+\) bombardment with decreasing incident energy [30]. For this case, we also observe a steeper falloff of the energy distribution as in the case of Cu atoms sputtering, but for the dimers the high energy decay appears to reach a
limiting slope at a bombarding energy of about 300eV and the major part of the Cu\textsubscript{2} distribution changes little above that impact energy.

### 1.3.2 Angular distribution of the sputtered particles:

Even though the Sigmund analytical model for the linear cascade regime predicts a cosine law distribution, pure cosine distributions are rarely observed. For high energy bombardment the measured distributions [33,34] are often found to be overcosine and can be described empirically by \( \cos^y \theta \), where \( y \) is used as a fitting parameter. Typical values of \( y \) lay between 1 and 2, but also much higher values have been reported. The possible explanations for this overcosine distributions are based on a surface induced anisotropy of the recoil flux below the surface and/or anisotropic surface scattering of the flux passing through the surface [35].

Figure 1.7 shows the angular distribution of Ge atoms for the case of 80 keV Ar\textsuperscript{+} bombardment at normal incident. An over cosine distribution with a fitted \( y \) value of 1.57 was found for this incident energy. Figure 1.7 also shows the change in the value of the fitted \( y \) parameter with incident ion energy from the experiments [34] and from Monte Carlo computer simulations [36]. These calculations found a strongly backward directed recoil flux close to the surface that gives rise to the pronounced overcosine emission spectra. A non uniformity in the distribution of the deposited energy at the surface was identified as the most likely cause for the anisotropic recoil flux [36].
Figure 1.7: Angular distribution of Ge atoms for the case of 80keV Ar+ bombardment at normal incident (a) and fitted $y$ exponent vs. incident ion energy from the experiments [34] and simulations [36].

For the case of low energy bombardment, these cosine and over cosine distributions are no longer observed. As the incident bombarding energy is decreased below 1000eV, the emission distributions become increasingly “under-cosine”, less atoms are ejected normal to the surface and a larger fraction at oblique angles, for which fewer collisions are required to lead to an ejection event. Figure 1.8 shows the effect of the incident energy in the angular distribution for the case of neutral Ni and Mo sputtered from a Ni-based alloy bombarded with Ar+ [37]. A pronounced emission at an oblique angle of $\approx 30^\circ$ is found in all cases for the 100-200eV bombarding energies, for the higher energies the forward emission becomes more and more prominent.
Figure 1.8: Angular distribution of neutral Ni and Mo sputtered from a Ni-based allow bombarded with Ar+ for different incident energies [6,37].

For the case of sputtering by light ions the energy transfer is so small that the generation of successive recoils is improbable; therefore, the energy is deposited rather locally [38]. In these cases the direct interaction between the projectile and the recoil atoms dominates the ejection events. Both, experiments and simulations show that the main sputtering mechanism is emission of the surface atoms by backscattered projectiles. Then, at perpendicular incidence, the ejection should show a preferential component normal to the surface. This can be observed for the case of W sputtering under H ions with 4keV incident energy [39] in Fig. 1.9.

Figure 1.9: Angular sputtering distribution of W atoms under H ions with 4keV incident energy [39].
1.4 Experimental techniques:

A large amount of experiments studying the physical sputtering of various ion-target combinations have been performed since the 1950’s. Researchers have used a variety of techniques to measure sputtering yields, as well as energy and angular distributions of the sputtered particles. In this section we present a review of the most important techniques used [6].

1.4.1 Ion sources:

There are two main types of ion sources used to produce the sputtering of the target, plasma discharges and ion beams.

Plasma discharges were used more during the 1960’s and earlier. In this case, a plasma discharge surrounding the sample is created and the bombardment of the sample with the desired energy is achieved by applying the necessary negative voltage to the sample. The main advantage of this type of ion source is the high current densities that can be achieved. This is important for the case of low energy sputtering measurements where the fluxes of sputtered particles are quite low, it also helps to maintain a clean surface. Among the main disadvantages of this type of ion source are the difficulty to directly measure the current to the sample, due to secondary electron emission, and the concern that the sputtered atoms may be ionized in the plasma and subsequently bombard the target. Also, the plasma may be susceptible to impurities from the discharge chamber.
Ion beams can be produced with several types of devices, such as ion guns or Kaufman sources. The ion beams are focused using a series of electrostatic elements, where the voltages of the optics determine the diameter and current density of the beam spot, as well as the energy. The main advantage of these types of ion sources is the capability to produce a well-defined ion beam. The main disadvantage, particularly for the case of low energy sputtering, is that the achievable current densities are not as high as for the case of plasma discharges. Also, the fact that the line of flight of the ion beam to the sample must be clear introduces difficulties to measure the angular sputtering distributions.

1.4.2 Post ionization of sputtered neutrals:

Because several of the methods employed for determining energy and angular distributions can only be applied to charged particles, different techniques of post ionization have been developed. The post ionization can be achieved using energetic electrons (from a electron beam [40] or a low pressure plasma [41]) to ionize the sputtered neutrals or from the absorption of one or more photons from an intense laser field.

1.4.3 Methods for the determination of energy spectra:

The techniques favored nowadays for the measurement of the energy distribution of sputtered particles are the electrostatic energy analysis of charged species, fluorescence techniques and time of flight measurements [6].
A) Electrostatic energy analysis:

In this case an electrostatic energy analyzer is used to determine the mass-to-charge ratio of the ionized species. This method is usually employed together with post-ionization methods in order to analyze the energy distribution of the sputtered neutral flux, which gives more representative information than the sputtered ions (the fraction of sputtered ions is very small as well). Often this kind of set-up is combined with a mass analyzer, providing the possibility of studying the energy distribution of the different sputtered species. A set-up of this type is used in the present experiment to obtain the energy distribution of the sputtered particles (Mo atoms and C atoms and clusters) that get ionized in a plasma discharge.

B) Fluorescence techniques:

The photon emission from atoms excited in the sputtering process can give information about their velocity by measuring the light intensity as a function of distance from the target surface [42]. This technique is limited by the possible decay of higher excited states into the state under investigation.

A relevant technique which uses laser induced fluorescence (LIF) to excite the particles and the Doppler shift of the excitation wavelength to measure the velocity of the sputtered particles, is the so called Doppler shift laser fluorescence spectroscopy (DSFLS)[43]. For a particle that travels with velocity \( v \) directed at an angle \( \phi \) to the laser beam, the excitation frequency is shifted by an amount

\[
\Delta \omega = \frac{v}{c} \omega_0 \cos \phi
\]  

(1.8)
where $\omega_0$ is the non-shifted resonance frequency of the particle. By tuning the laser to the Doppler profile of the atoms and simultaneously recording the resulting fluorescence signal, the velocity distribution is obtained.

C) Time of flight measurements:

This approach uses a high spinning rotor for time resolved registration of particles sputtered by an electronically chopped ion beam. To detect the deposit, radioactive targets are employed and the radioactivity of the deposited material is determined after the sputtering. These TOF systems are not mass selective, so they will record the velocity distribution of the total sputtered flux. Once again, if a measurement of the velocity distribution of the different sputtered species is required the TOF system must be combined with a mass analyzer.

1.4.4 Methods for angular distribution measurements:

There are two possible set-ups to measure the angular sputtering distribution of the sputtered flux. The number of atoms emitted at every emission angle can be collected simultaneously or the number of atoms emitted at a certain angle can be detected and the angular distribution can be obtained by changing the angle between the detector and the sample normal.

A) Collector technique:

In this technique the emitted particles are collected at suitable collector foils (usually hemispherical or semicylindrical) placed near the target, perpendicular to the flux of sputtered particles. Then, from the thickness of the deposit formed, the angular
distribution of the total sputtered flux can be inferred. The determination of the thickness profile of the condensate on the collector usually necessitates a suitable technique for thin film analysis. From the many techniques that have been used for the analysis of the deposits the more favored ones are the electron beam induced X-Ray emission [44] and the light ion (Rutherford) backscattering spectroscopy [45]. The main disadvantages of this technique are the uncertainties related to the sticking coefficient of the atoms to the surface and the possible resputtering of the accumulated material (specially for experiments involving plasma discharges), and the impossibility to obtain the angular distribution for atoms and clusters separately.

B) Detection of the sputtered particles:

For the determination of the angular distribution of the different sputtered species, mass spectrometric techniques are required. In fact, most of the devices employed for the measurement of energy spectra contain a mass spectrometer. Due to the restricted angle of acceptance, these instruments exhibit some angular resolution which, however, is often limited to one specific angle.

An instrument for the detection of sputtered neutral species by combining a TOF mass spectrometer with laser photoionization has been devised in Ref. 46. A very interesting feature of this setup is the possibility to record the mass selected sputtered flux with respect to both emission angle and kinetic emission energy.

In the present work, we use a Hiden EQP mass and energy analyzer to detect the fraction of sputtered neutrals that becomes ionized in a plasma, which is used as well to procure the ion bombardment of the sample. The angular sputtering
distribution of the different species (Mo atoms and C atoms and clusters) is obtained by changing the angle between the QMS and the sample normal.

1.5. Key results from the present work:

The most important results obtained in the present work can be summarize as follows:

- A new experimental technique is developed to measure the exit-angle resolved Mo atom sputtering yield under Xe ion bombardment and the carbon atom and cluster (C$_2$ and C$_3$) sputtering yields under (Xe, Kr, Ar, Ne and He) ion bombardment from a plasma, for low incident energies (75-225 eV). A quadrupole mass spectrometer (QMS) is used to detect the fraction of sputtered neutrals that is ionized in the plasma and to obtain the angular distribution by changing the angle between the target and the QMS aperture. A Direct Simulation Monte Carlo code (DSMC) is developed to simulate the interaction of the sputtered particles with the background gas and to help analyze the energy spectra acquired with the QMS, so that the initial energy distribution of the sputtered particles can be inferred from it.

- A comparison of the total sputtering yield results of Mo with previous experiments shows good agreement. There is a large increase of about an order of magnitude in the sputtering yield from $E_{Xe} = 75$ to 125 eV, and a more moderate increase for higher energies. This result shows the validity
of the experimental procedure to correctly measure the sputtering behavior of the studied materials.

- The elastic-scattering cross-sections of C, C\textsubscript{2} and C\textsubscript{3} with the different bombarding gases are obtained by fitting the simulation data to the experimental results for different positions of the QMS.

- The measurements presented here show that the typically assumed cosine distribution of sputtered particles during low energy, high mass ion bombardment of surfaces is not valid. For both studied materials, Mo and carbon, and for all the studied incident ions, an “under-cosine” angular sputtering distribution with a maximum at around 60-75\textdegree is observed at these low incident ion energies (75-225eV). Similar under-cosine angular sputtering distributions have been reported previously during low energy bombardment for the case of high mass ratio between the incident ion and the target material [47-49]. At these low incident energies the kinetic energy of the heavy ions is too small to create collision cascades, resulting in a decrease of sputtered particles ejected normal to the surface [50] and an increase of sputtered particles ejected at oblique angles, for which fewer collisions are required to lead to an ejection event.
A nearly logarithmic decrease of the carbon to cluster sputtering yield ratio with increasing incident ion mass is observed. The sputtering evolves from carbon atom preferential erosion for the lower incident ion masses (He, Ne and Ar) to cluster preferential erosion for the higher incident ion masses (Kr and Xe). This effect has not been reported previously. It is an important effect and it should be taken into account when modeling carbon sputtering at low energies, instead of assuming carbon atom preferential sputtering for all incident masses.
Chapter 2

Experimental technique

In this chapter the experimental set-up and experimental instruments used to perform the experiments are presented in detail, as well as a description of the performed experiments and the data analysis process that leads from the QMS acquired raw energy scans of the sputtered ionized particles to the angular distribution and total sputtering yield results for Mo atoms and C atoms and clusters, shown in Chapter 3 and Chapter 4, respectively.

2.1. Experimental set-up

The schematic of the experimental set-up used to perform the present experiments is shown in Fig. 2.1. The experiments are carried out in a plasma-etcher chamber with an inductively coupled plasma source modified from the commercial plasma source M0RI [51,52]. The target and the target holder are mounted at the end of the target manipulator. This manipulator can move the target inside and outside the chamber (so the sample can be changed without venting the entire chamber), and allows the target (together with the target holder) to rotate to a set angle, $\theta$, between the target normal and the QMS aperture, as can be seen in Fig. 2.1.
Figure 2.1: Schematic of the experimental set-up.

Predominantly, neutral particles are sputtered from the target surface. Any ion component sputtered from the target will be returned to the surface due to the applied bias potential. The ionization efficiency of un-scattered sputtered neutrals, which have several eV of kinetic energy, in the QMS is insufficient for direct detection. However, sputtered neutral particles that are ionized by the background plasma can be measured by the instrument. The simultaneous charge/mass ratio and energy sensitivity of this instrument is then used to discriminate between ionized sputtered particles which have suffered a collision with a neutral gas atom or plasma ion, and those which have only been ionized by a collision with a plasma electron (since such electron collisions do not substantially alter the kinetic energy and momentum of the incident sputtered atom). In all the experiments the sample is bombarded by the plasma ions with an
incident energy equal to the difference between the plasma potential and the negative voltage applied to the sample through the power supply. The formation of the sheath in front of the surface of the target assures normal incident ion bombardment, independent of the angle between the target and the QMS aperture. A Langmuir probe [52], that can be moved horizontally and is placed at the same height as the sample, is used to measure the plasma density, temperature and the plasma potential profiles in the space between the sample and the QMS aperture (see Appendix).

The main components of the experimental set-up are presented in more detail in the following sections.

2.1.1. Plasma source:

The plasma source is an inductively coupled plasma source modified from the commercial plasma source M0RI [52]. This source contains magnetic field coils that allow it to operate as a helicon wave plasma source; however, in all of the work reported here these coils are not energized and the source operates in the unmagnetized inductively coupled mode. The source consists of a 100-mm diameter Pyrex bell jar surrounded by a double loop antenna that is driven at an RF frequency of 13.56 MHz. The two antenna loops are 110 mm in diameter and axially spaced 150 mm apart, and are designed such that the RF currents in the two loops are 180° out of phase. The bell jar is attached to a Pyrex bottom plate whose inner diameter is 114 mm and outer diameter of 166 mm. This bell jar and plate assembly sits on top of an anodized aluminum reaction chamber, with 350 mm diameter and 400 mm height. A gas injection ring is located on the ceiling of the process chamber at a radius of 93 mm
and injects gas into the plasma from four equidistant injection ports. The RF power is coupled to the antenna via a feedback controlled matching network capable of driving the antenna over a wide range of process gases and RF powers.

2.1.2. Langmuir probe:

A Langmuir probe is a small cylindrical wire that is inserted into the plasma and is used to measure the electron density and temperature. The probe is kept as small as possible to avoid disturbing the plasma equilibrium. When a bias voltage is applied to the probe tip, a sheath of positively or negatively charged particles forms surrounding the probe. The net charge in the sheath region is such that the electric field from the probe voltage does not extend past the sheath edge. In these experiments, the sheath is collisionless because the sheath thickness is less than the ion mean free path. The bias voltage will cause the probe to draw either positive or negative current from the plasma. The electron temperature and density can be determined by examining the current drawn by the probe versus the bias voltage applied to the probe tip. When a bias voltage is applied to the probe tip, which is then swept from negative to positive voltages, a characteristic \( I - V_B \) is obtained. A sample Langmuir probe \( I - V_B \) characteristic is shown in Fig. 2.2. The floating potential, \( \Phi_f \), is the potential at which an isolated probe that cannot draw a current will float. The plasma potential, \( \Phi_p \), is the potential of the plasma relative to the grounded chamber wall.
Figure 2.2: Typical $I-V_B$ characteristic for a Langmuir probe.

When the probe is biased to a sufficiently negative potential all the electrons approaching it will be repelled and only the ion saturation current is drawn [53]. At this voltage the collected current is equal to the ion saturation current

$$I_{sat} = \frac{1}{2} n_i q_i A c_s$$  \hspace{1cm} (2.1)

Where $n_i$ is the ion density, $q_i$ is the ion charge, $A$ is the probe collection area and $c_s = \sqrt{2T_e/m_i}$ is the ion sound speed (where $T_e$ is the electron temperature and $m_i$ is the ion mass). As the probe voltage is increased from negative values towards the plasma potential, electrons with high enough energy are collected by the probe. Assuming an isotropic velocity distribution of the plasma electrons, for a given probe bias, $V_B$, only electrons with velocities higher than a minimum, $v_{min}$, will be able to overcome the potential drop from the undisturbed plasma to the probe.
The electron mass [53].

For a planar probe (which our cylindrical probe approximates since its diameter is much larger than the Debye length and the sheath thickness) the current collected for each species assuming a Maxwellian velocity distribution is

\[
I_\alpha(V) = n_\alpha q_\alpha A \int_{v_{\text{min}}}^{\infty} v_x \left( \frac{m_\alpha}{2\pi kT_\alpha} \right)^{1/2} \exp \left( \frac{1}{2} \frac{m_\alpha v_x^2}{kT_\alpha} \right) dx
\]

When the probe is biased to potentials where all of the ions and some of the electrons are collected, the total current drawn by the probe is

\[
I(V) = I_{\text{sat}} - n_e e A \int_{v_{\text{min}}}^{\infty} v_x \left( \frac{m_e}{2\pi kT_e} \right)^{1/2} \exp \left( \frac{1}{2} \frac{m_e v_x^2}{kT_e} \right) dx
\]

where \( v_{\text{min}} = \sqrt{-2e(V_B - \Phi_p)/m_e} \) and only electrons with higher \( x \) component velocities will be collected, giving

\[
I(V) = I_{\text{sat}} - n_e e A \left( \frac{kT_e}{2\pi m_e} \right)^{1/2} \exp \left( \frac{e(V_B - \Phi_p)}{kT_e} \right)
\]

We obtain the plasma density, electron temperature and plasma potential from the fitting the \( I-V_B \) characteristic obtained from the Langmuir probe to Eq. 2.5.

In a RF plasma discharge, the plasma potential oscillates at the RF frequency with respect to ground [54,55]. These oscillations can distort the probe trace, which causes the electron temperature to be overestimated, and the floating potential to be
shifted to more negative voltages. To prevent this, RF chokes at the source frequency (13.56 MHz) are placed near the probe tip. These chokes provide a large impedance to the RF signals, but not to low frequency signals. Also, an auxiliary electrode is placed near the probe tip to sample the local plasma potential fluctuations. The area of this electrode is much larger than the probe area and is coupled to the probe tip by a large capacitor. A diagram of the Langmuir probe and the equivalent probe circuit is shown in Fig. 2.3, where $Z_{sh}$ is the sheath impedance and $Z_{ck}$ is the impedance of the RF chokes.

![Diagram of the Langmuir probe and equivalent probe circuit.](image)

Figure 2.3: Diagram of the Langmuir probe and equivalent probe circuit.

Disregarding the auxiliary electrode and the stray capacitance, $C_{sl}$, $Z_{sh}$ and $Z_{ck}$ form a voltage divider such that
\[ V_p = \frac{Z_{ck}}{Z_{sh} + Z_{ck}} V_s \]  \hspace{1cm} (2.6)

In order for the probe trace characteristics to be unaffected by the RF fluctuations, \( V_p - V_s \) must be held much less than \( kT_e/e \). This requires that

\[ \frac{Z_{ck}}{Z_{sh} + Z_{ck}} |V_{RF}| << kT_e/e \]  \hspace{1cm} (2.7)

This can be rewritten to give the requirement for \( Z_{ck} \)

\[ Z_{ck} >> Z_{sh} \left( \frac{e|V_{RF}|}{kT_e} - 1 \right) \]  \hspace{1cm} (2.8)

such that the electron temperature can be accurately measured in the presence of RF plasma potential oscillations. The stray capacitance, \( C_{st} \), is unavoidable, and the corresponding impedance, \( Z_{st} = 1/j\omega C_{st} \), must also satisfy Eq. 2.8. For large RF potential, the condition in Eq. 2.8 is typically impossible to satisfy. However, a large electrode can be added near the probe tip and coupled to the probe tip through a capacitor, \( C_{cp} \), which is large enough to be a short circuit for the RF signal but small enough to block the low frequency signal. The area of the electrode should be much larger that the area of the probe tip. This auxiliary electrode will cause the probe tip to follow the RF fluctuations through the impedance \( Z_x \), which is identical to \( Z_{sh} \) but smaller in magnitude, by the ratio \( A_x/A_p = Z_{sh}/Z_x \) where \( A_x \) is the area of the auxiliary electrode. In this case, the condition in Eq. 2.8 becomes

\[ Z_{ck}, Z_{st} >> Z_x \left( \frac{e|V_{RF}|}{kT_e} - 1 \right) \]  \hspace{1cm} (2.9)

Based on the probe dimensions and typical plasma parameters in our
experiment, the impedance of the choke, $Z_{ck}$, is smaller than the stray impedance, $Z_s$.

The choke impedance is determined by the value of the inductor and capacitor used, 82$\mu$H and 5.2$pF$ respectively, the resulting impedance at a frequency of 13.56$MHz$, the frequency of the RF power supply, is $Z_{ck} = 8.4k\Omega$. The sheath impedance is determined by the charge difference between the probe tip and the bulk plasma and is $Z_{sh} = 5.3k\Omega$. The auxiliary electrode is approximately 70 times larger than the probe area, giving $Z_s = 74k\Omega$. For an electron temperature of 3$eV$, Eq. 2.9 is satisfied provided $|V_{RF}| \leq 340V$. From the literature, the RF voltage on the antenna is typical approximately 200V; the potential oscillation in the plasma will certainly be no larger than this. Thus we expect that our probes can accurately measure the electron temperature in these discharges.

### 2.1.3 Hiden EQP mass and energy analyzer

The Hiden EQP (Electrostatic Quadrupole Probe) is a high transmission 45$^0$ sector field ion energy analyzer combined with a quadrupole mass spectrometer with which mass spectra, energy spectra and appearance potential profiles may be acquired, allowing detailed analysis of positive ions, negative ions, radicals and neutrals. The EQP used in the present experiments has a mass range of 300 a.m.u. and an energy range of $\pm 100$ eV, with constant transmission and constant resolution functions throughout the ion energy range. A diagram of the EQP is shown in Fig. 2.4. The EQP can operate in two different modes: RGA mode, which is used for neutral gas analysis and radical detection, and plasma/SIMS mode, which is used for positive and negative
ion analysis. For the present experiments, only the plasma/SIMS mode is used. The main difference between both modes of operation is the source of the ions. SIMS and plasma ions are generated outside the probe while RGA ions are generated in an internal ionization source.

![Diagram of the EQP mass and energy analyzer.](image)

**Figure 2.4:** Diagram of the EQP mass and energy analyzer.

Plasma ions enter through the extractor and are focused onto the internal ion source exit aperture by lens1. Neutrals enter by diffusion through the extractor and diffuse into the ion source. In the ion source, the neutrals may be ionized by electron bombardment from a filament and accelerated to a preset voltage. The trajectories of the ions from the ion source to the detector are the same for both modes. The ions are electrostatically energy filtered by passing through a 45° bend in the flight path. These energy-selected ions then enter the quadrupole mass filter, which allows transmission of ions with a desired mass/charge ratio. Finally, the ions arrive at the electron multiplier detector yielding an ion count rate.
In the following paragraphs a brief description of the main sections of the EQP is given.

**The extraction section**

The extraction section is composed of the orifice, which is mounted at the tip of the probe, and the transfer lens (lens1).

The orifice is set to a voltage given by the extractor variable, this voltage can be positive in RGA mode in order to prevent plasma ions from entering the QMS. For the case of ion detection it can be set to a positive or negative value (if we are looking for negative or positive ions, respectively) to facilitate the extraction of the ions from the plasma. The neutral particles can only be extracted from the plasma by diffusion from the (high-pressure) plasma chamber to the (low-pressure) ionization source of the EQP.

The transfer lens is only used in the plasma/SIMS mode to refocus the ion beam from the sampling orifice onto the exit aperture of the electron impact source.

**The ionization section**

Because the energy analyzer and the quadrupole mass spectrometer can only analyze charged particles, any neutrals must be ionized before they can be analyzed. The ionization of the neutrals particles is achieved with a dual-filament electron-impact ionization source, which forms the ions at a preset potential energy. This ionization source can also be used to perform appearance potential profiling.

For the case of plasma/SIMS operation mode the ion source in not necessary: it forms a field free drift space for the ions and is operated at the axis potential.
**Transfer ion optics (lens2)**

From the ion source, the ions are accelerated into the drift space, which they transit with an energy of the axis potential. Lens2 matches the ion source to the energy filter for efficient ion transfer.

**The energy filter**

The energy filter is a 45° sector field energy analyzer. Ions entering the sector field will be deflected according to their kinetic energy, so that only ions which have a transfer energy of 40 eV pass the bend. An energy resolution of ±0.25 eV is provided by the manufacturers.

If an ion enters the energy analyzer with an energy $\varepsilon$ in the $x$ direction, it will be deflected upon traversing the sector field a distance $s_y$ in the $y$ direction given by:

$$s_y = \frac{1}{4} l^2 E_y \sqrt{\frac{q}{\varepsilon}}$$

where $l$ is the length of the sector field section, $E_y$ denotes the sector field size and $q$ the ion charge. As it can be seen, the deflection of the incoming ion does not depend on the mass but only on the charge to energy ratio, $\frac{q}{\varepsilon}$. The fact that the ion deflection is inversely proportional to the $\sqrt{\varepsilon}$ forces the choice of a fixed input energy. Because the window of the sector field must have a finite size $\Delta s_y$, if a variable input energy was to be used (in which case one would perform energy separation by scanning $E_y$), the energy resolution would have some inverse relation to the ion energy itself, which would be inconvenient, and would furthermore lead to poor resolution at low energies.
To avoid this, the transfer ion lens is used to accelerate/decelerate ions of a particular energy to the pass energy of the sector field, ~40eV. Since this is merely a shift in the kinetic energies of the ions, a fixed and satisfactory energy resolution is achieved in this way [56].

The mass filter

The mass filter section consists of a standard quadrupole mass spectrometer, a schematic diagram of which is shown in Fig. 2.5.

![Schematic of a quadrupole mass spectrometer](image)

**Figure 2.5: Schematic of a quadrupole mass spectrometer [56].**

The quadrupole mass filter consists of four parallel metal rods. Each opposing rod pair is connected together electrically and a radio frequency voltage is applied between one pair of rods, and the other. A direct current voltage is then superimposed on the R.F. voltage, which produces a total potential of \( \Theta(t) = U + V \cos(\omega t) \) for two opposing rods and a potential of opposite sign, \( \Theta(t) \) for the other pair. Ions travel down the quadrupole in between the rods and their trajectories are affected by the time varying electric field that develops between the rods. Only ions of a certain mass-to-
charge ratio, $\frac{m}{q}$, travel all the way through the mass filter, while all other ions are thrown out of their path. The low-mass ions are removed by the RF field, while the high-mass ions are removed by the DC field. By varying the voltages, $U$ and $V$, and/or the frequency, $\omega$, of the oscillating component, a mass spectrum can be obtained. The transmission coefficient of the quadrupole mass filter presents a mass dependence of $M^{-1/2}$ as measured in Ref. 57, this needs to be taken into account when comparing results for particles of different mass.

**The detector**

The detector is an off axis mounted continuous dynode electron multiplier, which is operated in pulse mode. The three variables that control the detector are the first dynode voltage (this is the voltage on the front of the detector), the multiplier HT (this is the voltage across the detector) and a discriminator that is used to set a counting threshold on the pulse output from the multiplier.

The detection efficiency of this detector presents a $M^{-1/2}$ mass dependence [57]. Together with the quadrupole mass filter transmission dependence on the mass, the total transmission of the EQP system presents a $1/M$ dependence on the mass of the analyzed particles.

### 2.2 Experiments

For each studied material (Mo and C) and each bombarding gas a set of experiments is done in order to obtain the angular distribution of the sputtered particles for the different incident energies.
These experiments are performed in the following manner: the target is introduced into the chamber at a normal angle with respect to the QMS aperture ($\theta = 0^\circ$), and the plasma discharge is started. To make sure the discharge produces the desired plasma parameters the density and temperature of the plasma are measured with the Langmuir probe. When the plasma has stabilized, the target is biased to the desired voltage (to achieve the desired incident ion energy) and an energy scan for the sputtered ionized particles is acquired with the QMS (Mo ions for the case of Mo sputtering and C, C$_2$ and C$_3$ ions for the case of carbon sputtering). These ions enter the QMS through an aperture and are electrostatically energy filtered by passing through a $45^\circ$ bend in the flight path. These energy-selected ions then enter the quadrupole mass filter, which allows transmission of ions with a desired mass/charge ratio. The bombarding ions hit the target surface with an energy given roughly by the difference between the plasma potential (which is monitored with a Langmuir probe) and the bias voltage. The formation of the sheath in the surface of the target assures normal incident ion bombardment, independent of the angle between the target and the QMS aperture. While maintaining the same plasma parameters, the target is biased to the next voltage and a new scan is acquired. When the scans for the different incident energies are acquired, the plasma discharge is stopped and the angle between the target and the QMS aperture is changed. We repeat the process described above for all the angles studied. The acquired energy distributions are analyzed and integrated to obtain the angular sputtering distributions for the different incident ion energies and a
relative value of the total sputtering yield at each incident energy is obtained from the integration of the angular distributions.

We can not obtain an absolute value of the sputtering yield from the previous experiments due to the unknown transmission coefficient of the QMS. For the case of Mo sputtering, we use the absolute sputtering yield values from the literature to normalize our results. For the case of carbon sputtering, where we are interested in comparing the results for the different studied bombarding gases, the absolute value of the total sputtering yield for each bombarding gas is obtained by using a standard weight-loss technique.

The sample is weighted in a precision microbalance before and after being inserted in the etcher chamber and subjected to the bombardment of the plasma ions (at the highest incident energy studied, 225eV) for a prescribed period of time. The temperature and the density of the plasma (used to calculate the flux to the sample) are monitored during the experiments with the Langmuir probe. The total sputtering yield is then calculated from the total ion fluence and the measured weight loss, and it is used to normalize the rest of the C results in this work, as will be explained in the following sections. In order to take into account the mass of the implanted bombarding ions in the sample, before performing the weight loss experiments for each bombarding gas, the sample is subjected to the bombardment of the plasma ions for a small period of time (about 10 minutes) in which the saturation of the implanted ions in the sample is reached. The redeposition fraction for all the bombarding gases
(calculated with the DSMC code) is smaller than the error in the weight loss measurements, so it is neglected.

2.3 Analysis of the data

Figure 2.6 shows the QMS acquired energy spectra of Mo ions for the case of Mo sputtering under Xe bombardment and Fig. 2.7 shows the energy spectra of C, C\(_2\) and C\(_3\) ions for the case of carbon erosion under He bombardment. In both cases, the observed energy distributions can be interpreted using some basic plasma surface interaction behavior. Due to the formation of a sheath at the QMS wall, which is grounded, ions are accelerated before entering the QMS. The energy that the ions gain in going through this sheath region is equal to the plasma potential, \(\Phi_p\), in the region in front of the QMS entrance aperture. This potential energy must be subtracted from the energy scale of the raw data to obtain the actual ion energy distribution in the plasma.

![Plasma potential graph](image_url)

Figure 2.6. Mo ions acquired energy spectra for Mo erosion under Xe bombardment.
Figure 2.7 C, C$_2$ and C$_3$ ions acquired energy spectra for carbon erosion under He bombardment.
The acquired energy distributions present a low energy peak and a higher energy tail. Figures 2.6 and 2.7 show that even when the sample is not facing the QMS, i.e. when the sample normal is set at an angle of 135° with respect to the QMS flight path, we still detect a finite background ion signal, which corresponds to the low energy peak observed at angle 0. This background signal is due to elastic collisions of sputtered carbon containing particles with background heavy particles (i.e. plasma ions and neutral gas atoms), these particles then lose their directional energy and are driven toward thermal equilibrium with the plasma neutrals. The fraction of these near-thermal atoms and clusters that is ionized afterwards in the plasma accounts for the measured ion signal at angle \( \theta = 135° \); we call this ion population the “background population”. In the case of the C ion signal, we observe that this background signal is several orders of magnitude larger than the high-energy tail. This is mainly due to the C signal resulting from the dissociation of the CO and CO\(_2\) in the plasma (there is a small amount of oxygen impurity in the plasma that forms CO and CO\(_2\)). This is corroborated by the fact that we still observe this C ion signal when the bias of the sample is turned off, as can be seen in Fig. 2.7, while the C\(_2\) and C\(_3\) ions the signal disappears when no bias is applied to the sample. Due to the dissociation energy of CO and CO\(_2\) (around 10 eV) we observe a wide energy peak (about 15eV) for this C ion background signal, but as can be observed in Fig. 2.7 the background population of C ions have a maximum energy of around 35 eV, while the energy tail (which represents the un-scattered flux of sputtered particles) reaches energies of about 80 eV. For both the case of Mo (Fig. 2.6) and the case of C (Fig.2.7), we observe that the background
population energy distributions (angle 135) have a maximum energy lower than the high-energy tail of the ionized sputtered particles (angle 0). Therefore, the high energy tail from the acquired energy spectra can be used to infer the initial energy distribution of the sputtered particles directed towards the QMS.

In the case of Mo, we are only interested in the angular sputtering distribution of Mo atoms for different Xe ion incident energies and this can be easily done by integrating the acquired energy distribution (after the background signal subtraction) for every studied angle, as will be explained in more detail in Chapter 3. In the case of carbon sputtering, where we want to compare C, C$_2$ and C$_3$ sputtering for each bombarding gas, the differences in the ejection energy distributions, elastic scattering and ionization between the carbon atoms and clusters in the different studied background gases need to be taken into account. In order to do that, a deeper and a more complicated analysis of the data is required for the carbon experiments. In the following sections this analysis of the data is explained in detail.

### 2.3.1. Processes between the sample and the QMS

In order to extract meaningful data from the energy scans acquired with the QMS, a thorough understanding of the processes taking place between the sample and the QMS is necessary. A basic schematic of these processes can be observed in Fig. 2.8. When the studied sample is bombarded by the plasma ions, the sputtered particles (Mo atoms or C atoms and clusters) will be ejected in different directions depending on the angular sputtering distribution. The flux of sputtered particles that is ejected in the direction of the QMS will undergo collisions with the plasma particles. The elastic
collisions with the neutral gas atoms (collisions with ions are neglected because their density is two orders of magnitude smaller than the neutral density) will scatter some of the sputtered particles from the QMS line of sight, while the collisions with the plasma electrons will ionize some of the sputtered particles while leaving their momentum vector and kinetic energy essentially unchanged due to the large mass difference between the interacting particles. For the case of carbon sputtering, dissociation of $C_2$ and $C_3$ by electron impact can be neglected for these low electron temperatures [58], and the dissociative ionization cross-section is about 10 to 100 times smaller than the electron impact ionization cross-section for these temperatures [59], so it can be neglected as well. In addition, due to the formation of the plasma sheath and presheath near the target and the grounded QMS surfaces, the potential profile that develops between the sample and the QMS entrance will accelerate the ionized sputtered particles towards the sample, or the QMS, depending on their ionization location.

![Figure 2.8: Processes between the sample and the QMS.](image)
To observe how the energy distribution of the sputtered particles (as well as the energy distribution of the ionized sputtered particles) evolves with the distance from the sample, we use a one dimensional Direct Simulation Monte Carlo code [60] which models all of these processes.

2.3.2 Sheaths and presheaths

For the case of a confined plasma, like the ones we produce in the etcher chamber use for these experiments, the bulk region of the plasma is electrically neutral; the number of electrons and negatively charged ions is equal to the number of positively charged ions [61]. The electrons have a temperature of a few electron volts, while the ions are in equilibrium with the background neutral gas at a much lower temperature. Thus the electrons will move to the wall faster than the ions. Wherever there is a wall, the electrons will move to the wall faster than the ions. This will create a region with a net positive charge near the wall, called the sheath. This creates an electric potential difference between the bulk plasma region and the wall, called the sheath potential. The sheath accelerates the positive ions to the wall and retards the electron motion to the wall, allowing the flux of positive and negative particles to the wall to remain equal.

Following the derivation in Lieberman and Lichtenberg [61], in order to maintain flux continuity through the sheath, the ions must be accelerated to a higher velocity before reaching the sheath edge. This leads to the development of a presheath region that is essentially neutral, but has a small electric field for accelerating the ions. The necessary velocity can be determined by considering the ion and electron
densities through the sheath region. We assume that the electrons are in a Maxwellian distribution and that the ions are cold, $T_i = 0$. The plasma sheath boundary, defined as the boundary between the neutral and non-neutral regions, is defined to be located at $x = 0$. Also, the potential $\Phi$ is defined to be zero at this point. At $x = 0$, the ion and electron density are $n_i$ and $n_e$ respectively, and the ion velocity is $u_s$. From energy conservation for an ion traveling through the sheath

$$\frac{1}{2} M u_s^2(x) = \frac{1}{2} M u_s^2 - e \Phi(x)$$

(2.10)

From the continuity of ion flux in a collisionless sheath

$$n_i(x) u(x) = n_i u_s$$

(2.11)

Eliminating the velocity from the two equations yields

$$n_i(x) = n_i \left(1 - \frac{2e\Phi(x)}{M u_s^2}\right)^{-\frac{1}{2}}$$

(2.12)

The electron density is determined by the Boltzmann relation

$$n_e(x) = n_e \exp \left(\frac{\Phi(x)}{T_e}\right)$$

(2.13)

Since the ion and electron density are assumed constant at the sheath edge, the variable $n_s = n_i = n_e$ is introduced. The ion and electron density as a function of location in the sheath are used in Poisson’s equation to give

$$\frac{\partial^2 \Phi}{\partial x^2} = \frac{e}{\varepsilon_0} \left[ n_s \exp \left(\frac{\Phi}{T_e}\right) - n_s \left(1 - \frac{\Phi}{E_s}\right)^{\frac{1}{2}} \right]$$

(2.14)

Where the initial ion energy is given by
\[ eE_s = \frac{1}{2} Mu_s^2 \]  

(2.15)

Multiplying the above equation by \( \frac{\partial \Phi}{\partial \alpha} \) and integrating over \( x \) yields

\[
\int_0^\Phi \frac{d\Phi}{dx} \frac{d\Phi}{dx} \left( \frac{d\Phi}{dx} \right) dx = e_{\text{n}} \frac{\epsilon}{\epsilon_0} \int_0^\Phi \frac{d\Phi}{dx} \left[ \exp \left( \frac{\Phi}{T_e} \right) - \left( 1 - \frac{\Phi}{E_s} \right)^{\frac{3}{2}} \right] dx
\]

(2.16)

This integration yields

\[
\frac{1}{2} \left( \frac{d\Phi}{dx} \right)^2 = e_{\text{n}} \frac{\epsilon}{\epsilon_0} \left[ T_e \exp \left( \frac{\Phi}{T_e} \right) - T_e + 2E_s \left( 1 - \frac{\Phi}{E_s} \right)^{\frac{3}{2}} - 2E_s \right]
\]

(2.17)

In order for Eq. 2.17 to have a real solution, the right hand side must be positive

\[
T_e \exp \left( \frac{\Phi}{T_e} \right) - T_e + 2E_s \left( 1 - \frac{\Phi}{E_s} \right)^{\frac{3}{2}} - 2E_s \geq 0
\]

(2.18)

Expanding this in a Taylor series about \( \Phi = 0 \) yields

\[
T_e \frac{\varphi}{r_e} + \Phi \frac{\varphi}{r_e} + \frac{\Phi^2}{2T_e} \frac{\varphi}{r_e} - T_e + 2E_s \left( 1 - \frac{\Phi}{E_s} \right)^{\frac{3}{2}} \geq 0
\]

(2.19)

\[
-\Phi \left( 1 - \frac{\Phi}{E_s} \right)^{\frac{3}{2}} - \frac{\Phi^2}{4E_s} \left( 1 - \frac{\Phi}{E_s} \right)^{\frac{3}{2}} - 2E_s \geq 0
\]

(2.20)

Where \( \Phi' = 0 \). This simplifies to

\[
\frac{\Phi^2}{2T_e} - \frac{\Phi^2}{4E_s} \geq 0
\]

(2.21)

This gives a limit on the ion velocity as it enters the sheath. This velocity is called the Bohm velocity, \( u_B \)

\[
u_s \geq u_B = \left( \frac{eT_e}{M} \right)^{\frac{1}{2}}
\]

(2.22)
In order for the ion to have a velocity of \( u_B \) at the sheath edge, a small but finite electric field must exist in the region beyond the sheath. This region is called the presheath and is typically much wider than the sheath region. It also has no net charge, as the ion and electron densities are equal. Since the ions are accelerated to the Bohm velocity in the presheath region and the ion flux is conserved, the ion density must decrease in the presheath. The ion density and electric potential in the presheath and sheath region are shown in Fig. 2.9.

![Diagram showing ion density and electric potential in the presheath and sheath region.](image)

Figure 2.9: Ion density and electric potential in the presheath and sheath region [61].

The potential drop across a collisionless presheath, which accelerates the ions
to the Bohm velocity, is given by

\[ \frac{1}{2} M u_g^2 = e \Phi_p \] (2.23)

where \( \Phi_p \) is the plasma potential with respect to the potential at the sheath-presheath edge. Substituting for the Bohm velocity from Eq. 2.23, we find

\[ \Phi_p = \frac{T_e}{2} \] (2.24)

The spatial variation of the potential \( \Phi_p(x) \) in a collisional presheath has been estimated by Riemann (1991) to be determined from

\[ \frac{1}{2} - \frac{1}{2} \exp \left( \frac{2\Phi_p}{T_e} \right) - \frac{\Phi_p}{T_e} = \frac{x}{\lambda_i} \] (2.25)

where \( x \) is the distance from the Bohm point at the presheath-sheath edge and \( \lambda_i \) is the ion-neutral mean free path. The ratio of the density at the sheath edge to that in the plasma is then found from the Boltzmann relation

\[ n_s = n_b e^{-\frac{\Phi_p}{T_e}} \approx 0.61 n_b \] (2.26)

where \( n_b \) is the density where the presheath and the bulk plasma join.

In the present experiments, apart from the sheath that forms in the chamber walls, two additional sheaths will be formed, one at the QMS surface and one in the sample surface. The formation of these two sheaths and their respective presheaths gives rise to specific potential and density profiles between the sample and the QMS. These density and potential profiles for the different studied plasmas are shown in the Appendix.
2.3.3 One dimensional Direct Simulation Monte Carlo

In this section we present the basic concepts behind the DSMC code, the parameters and modifications used for the simulations performed in this work and the results obtained from the simulations for the case C sputtering in Xe and He plasmas, which present the extreme values in plasma density and temperature and ion mass from all the studied gases.

A) DSMC code overview

The DSMC method was first proposed by Bird [60] for the simulation of rarefied gas flows. This code simulates the movement and collisions of a small number of particles of each of the species present in the system (compare with the real values), and therefore each of the simulated particles represents a much larger number of real particles. The main basic assumption of DSMC is that the movement and interaction of the particles in the system can be decoupled. The system is integrated in time steps, $\Delta t$. At each time step every particle is first moved, according to its equation of motion, without interaction with other particles. External forces, such as the pre-sheath and sheath electric fields, are taken into account here. The movement of the particles can be calculated from an analytical solution of the equation of motion or from a standard numerical integration scheme. Next, the particle-particle interactions are simulated. The DSMC simulation does not calculate exact times and places for the collisions between the particles; instead it uses a stochastic algorithm. The particles are sorted into spatial cells of linear size $L$ and volume $V_c = L^D$, where $D$ is the
dimensionality of the system. Collisions occur only between particles in the same cell, which ensures that only particles which are close to each other may collide. In every cell with more than one particle, $M_c$ number of pairs of particles are chosen, with

$$M_c = \frac{N_A (N_A - 1) \sigma v_{\text{max}} \Delta t}{2 V_c}$$  \hspace{1cm} (2.27)

for collision among same species, and

$$M_c = \frac{N_A N_B \sigma v_{\text{max}} \Delta t}{V_c}$$  \hspace{1cm} (2.28)

for collisions among different species. Here, $N_A$ and $N_B$ are the number of particles of species A and B in the cell, $\sigma$ is the scattering cross-sections of the colliding particles and $v_{\text{max}}$ is an upper limit for the relative velocity between the particles. The value of $v_{\text{max}}$ is obtained from time to time from the velocity distribution of the particles. The correct number of collision is determined from an acceptance-rejection method. For a pair of particles $i$ and $j$ the collision is performed if

$$\frac{|v_i - v_j|}{v_{\text{max}}} < Z$$  \hspace{1cm} (2.29)

where $Z$ is an independent uniformly distributed random number in the interval $[0,1]$. This method leads to a collision probability proportional to the relative velocity of the particles. Since the collision takes place regardless of the particle positions in the cell, an impact parameter, $b$, needs to be chosen in order to calculate the post collision velocities. To do so, molecular chaos is assumed, and $b$ is drawn from a uniform distribution in the interval $[-R_c, R_c]$ in 2D or in a circle with radius $R_c$ in 3D, where
$R_c$ is the sum of the radiuses of the colliding particles. The post collision velocities $v'_i$ and $v'_j$ are then calculated as if the two particles collided with that impact parameter so that

$$v'_i = v_{cm} + \frac{m_j}{m_i + m_j} v_{rel} e$$  \hspace{1cm} (2.30)$$

$$v'_j = v_{cm} - \frac{m_i}{m_i + m_j} v_{rel} e$$  \hspace{1cm} (2.31)$$

where $e$ is the unit vector pointing in the direction of the relative velocities after the collision. For the hard sphere approximation $e$ is uniformly distributed over the unit sphere.

Like every simulation method, DSMC is based on certain approximations. The main one is that the interaction between the particles can be modeled by collisions. Furthermore, neither the location, nor the time of a collision, is calculated exactly. To keep the error small, three conditions must be fulfilled: (i) the system should be in the collisional regime, (ii) the mean free path should be larger than the cell size, (iii) the mean time between two collisions should be larger than the time step.

B) Simulation of the present experiments with the 1D DSMC:

We simulate the plasma and the sputtered particles between the sample and the QMS with a modified version of the 1D Direct Simulation Monte Carlo code used in Ref. 62. For the present simulation we use 10000 particles of each species (plasma
neutral atoms and ions and sputtered carbon neutrals) and we divide the distance between the sample and the QMS into 100 cells. The number of cells and the time step of the simulation are chosen as to fulfill the previously mentioned conditions. For the gas neutral atoms and plasma ions, the initial velocity and density distributions are set to the experimentally measured values, while the C neutral atoms are inserted with a Thompson velocity distribution at $x=0$ (defined to be the sample surface). At each time step all the particles move; the neutrals move with a constant velocity and the ions move with a velocity that changes due to the potential changes in space. After all the particles have moved, the collisions between the different species at each cell are simulated (using the elastic scattering cross-section from the hard sphere collision model), and the new velocities of the colliding particles are calculated. Ionization of the carbon neutral particles is simulated through collisions with the plasma ions (the density profiles of the plasma ions and electrons are the same) with a collision cross-section equal to the electron impact ionization cross-section, assuming a Maxwellian energy distribution for the electrons. Every time a carbon neutral is ionized in this manner, a new carbon ion is born with the velocity and the position of the collided neutral. The simulation is stopped after it reaches a steady-state and we are left with the velocity ($v_x, v_y, v_z$) and position ($x$) of each simulated particle for each time step.

C) 1D DSMC simulation results

We obtain the energy distribution of the flux of carbon neutrals at different distances from the sample from the velocity data of the simulated particles at those positions over time. Figure 2.10 shows the velocity distribution of the flux of sputtered
atoms at four different positions for the case of Xe and He plasma bombardment, respectively. We chose to show the data for Xe and He plasma bombardment, because these two plasmas present the extreme values in plasma density and temperature and ion mass from all the studied gases. The Xe plasma presents the highest plasma density and the lowest electron temperature, $2.2 \times 10^{18}$ m$^{-3}$ and 1.6 eV, respectively, while the He plasma presents the lowest plasma density and the highest electron temperature, $2.7 \times 10^{16}$ m$^{-3}$ and 8 eV, respectively. For both bombarding gases we observe that the energy distribution consists of a low energy peak (with the peak value around 0 eV) and a higher energy tail. The evolution of the energy distribution can be easily explained from the elastic collisions taking place between the carbon atoms and the gas neutrals. The low energy peak represents the population of carbon neutrals that undergo collisions with the gas neutrals losing some of their directional energy and equilibrating with the gas neutrals over time. In the Xe plasma this low energy peak is wider than in the He plasma, this difference is related to the difference in mass between Xe and He atoms (131 a.m.u and 4 a.m.u., respectively), the transmission of energy between the colliding particles is more effective for He-C collisions than for Xe-C collisions. On the other hand, the high-energy tail represents the population of sputtered neutrals that does not collide with the gas atoms, thus maintaining their initial directional energy. If we look at the energy distribution of the flux of particles that are deflected only between 0 and 5 degrees, we observe a Thompson velocity distribution (the initial distribution) that decreases with distance as

$$f(v, x) = f_0(v) \exp\left(-\sigma_{\text{elas}} n_n x\right)$$

(2.32)
where \( f(v,x) \) is the velocity distribution at a distance \( x \) from the sample, \( f_0(v) \) is the initial thompson velocity distribution, \( \sigma_{elas} \) is the elastic scattering cross-section used in the MC simulation and \( n_n \) is the neutral density.

Figure 2.10: Velocity distributions of the flux of sputtered carbon neutrals at different distances from the sample for Xe and He plasma.
In the same manner as with the carbon neutrals, we obtain the velocity distribution for the flux of ionized sputtered particles at different distances from the sample (Fig. 2.11). In this case, we observe a similar evolution of the velocity distribution with distance from the sample, but in the case of the ions the potential changes in space also affect the distribution. As explained before, the changes in the potential profile are due to the two presheaths that form in front of the sample surface and the QMS surface. Basically, there is an acceleration of the ions towards the sample in the region closer to the sample, or towards the QMS in the region closer to the QMS. This acceleration is responsible for the shift of the velocity distribution peak from negative values in the vicinity of the sample to increasing positive values as the distance from the sample increases. The shift of the velocity distribution peak is related to the potential drop in the presheath, which is related to the electron temperature of the plasma electrons, and explains why we observe a larger shift of the peak for the case of the He plasma than for the case of Xe plasma.

![Velocity distributions of the flux of ionized sputtered carbon atoms at different distances from the sample for Xe and He plasma.](image)

Figure 2.11: Velocity distributions of the flux of ionized sputtered carbon atoms at different distances from the sample for Xe and He plasma.
In order to compare these simulation results with the data from the energy scans acquired with the QMS, two more effects need to be taken into consideration. First, we need to simulate the sheath that develops in front of the QMS; this is done by increasing the energy of the ions by the same amount as the potential drop in the sheath. Second, we need to take into account that only the ions which are directed towards the QMS orifice within its acceptance angle will be analyzed. The acceptance angle of the QMS depends on the energy of the particles when they enter the orifice [63], but it reaches a constant value of about 50° for particles with energies over 15 eV, which is actually below the range we are interested. Then, to simulate the QMS acceptance angle, from the simulation results we only take into account C ions that are directed towards the QMS within a 50° range. Figure 2.12 shows the fit of the simulated energy distribution of the ionized sputtered particles flux to the energy scan acquired by the QMS (mass 12 ions) for the case of Xe and He bombardment at 225 eV incident energy. The fit is good for the high-energy part of the energy distribution. Figure 2.12 also shows the simulation results for the un-scattered flux of carbon atoms for the case of Xe and He bombardment. We observe that the high-energy tail of the measured energy distributions directly represents the energy distribution of the ionized un-scattered sputtered flux. This means that the initial energy distribution (ejection energy distribution) of the sputtered particles can be inferred from the fitting of the simulated un-scattered flux energy distribution to the high-energy tail of the measured distribution. The big difference observed in the magnitude of the low energy peak is mainly due to the carbon signal resulting from the dissociation of the CO and CO2 in
the plasma (there is a small amount of oxygen in the plasma that forms CO and CO$_2$), as has been shown before.

**Figure 2.12:** Simulated and experimental energy distributions of the flux of ionized sputtered carbon particles for the case of Xe and He bombardment at 225eV incident energy.
2.3.4 Simulation of the ionized sputtered particles motion

In order to obtain the total sputtering yield of C, C\textsubscript{2} and C\textsubscript{3} for every bombarding gas we need to know the values of the elastic scattering cross-sections of C, C\textsubscript{2} and C\textsubscript{3} for the different bombarding gases. Even though the DSMC simulation predicts the observed energy distributions adequately, the simulation time required to obtain this elastic scattering cross-sections from a fitting process is too long. For this reason, a simpler model for the ionized sputtered particle motion is developed. This model simulates the evolution of the ionized un-scattered flux of particles, it gives less information than DSMC code but its shorter simulation time allows us to infer the elastic cross-sections in a reasonable time scale. For this simulation, the distance between the sample and the QMS is divided into a certain number of cells. At each cell the velocity distribution of the un-scattered sputtered neutral flux, \( f_n(v, x\text{\textsubscript{cell}}) \), is given by

\[
f_n(v, x\text{\textsubscript{cell}}) = f_{n0}(v) \exp\left(-\sigma_{\text{elas}} n_n x\text{\textsubscript{cell}}\right)
\]  

(2.33)

where \( x\text{\textsubscript{cell}} \) is the distance from the sample to the cell, \( f_{n0}(v) \) is the initial velocity distribution (ejection velocity distribution) of the sputtered neutral particles, \( \sigma_{\text{elas}} \) is the elastic scattering cross-section between the sputtered neutral particles and the plasma neutrals and \( n_n \) is the plasma neutral density. At each cell, for \( t=0 \), the velocity distribution of the ionized un-scattered flux of sputtered particles, \( f_i(v, x\text{\textsubscript{cell}}) \), is obtained from the velocity distribution of the un-scattered sputtered neutral flux

\[
f_i(v, x\text{\textsubscript{cell}}) = f_n(v, x\text{\textsubscript{cell}})\left(1 - \exp\left(-\sigma_{\text{ion}} n_e x\text{\textsubscript{cell}}\right)\right)
\]  

(2.34)
where $\sigma_{\text{ion}}$ is the ionization cross-section (assuming a Maxwellian velocity distribution for the electrons) and $n_e$ in the electron density. This velocity distribution is divided into a certain number of velocity intervals (for each cell), and the evolution of the particles contained in each of these intervals is calculated over time. All the particles in a certain velocity interval are assumed to have the same position, $x$, and velocity, $v$. At each time step, the group of particles in each velocity interval will change their position due to their velocity as

$$x(t) = x(t-1) + v(t-1)\Delta t$$

(2.35)

where $t$ is the time step and $\Delta t$ is the time increment between time steps. The velocity of the group will change as

$$v(t) = v(t-1) + \Delta v(\Phi(x(t)) - \Phi(x(t-1)))$$

(2.36)

where $\Delta v(\Phi(x(t)) - \Phi(x(t-1)))$ is the velocity increment due to the potential change in space. And the density of particles in the interval, $n$, will decrease as the group of particles moves due to collisions with the background plasma neutrals as

$$n(t) = n(t-1) \exp\left(-\sigma_{\text{elas}} n_e |v(t) - x(t-1)|\right)$$

(2.37)

The simulation is stopped when all particles in all the velocity intervals have reached any of the limits of the simulation, the sample surface, $x=0$, or the QMS surface, $x = x_{\text{QMS}}$. In this simulation we are therefore following the movement of the ionized un-scattered particles from the moment they are born, at $t=0$, to the moment they hit the sample surface or the QMS surface. Then, the velocity distribution of the ionized un-scattered sputtered particle flux at a certain distance $x$ from the sample is obtained
from the density and velocity data of the groups of particles that go through the 
\([x - \Delta x, x + \Delta x]\) interval over time. Figure 2.13 shows a comparison between the 
velocity distributions obtained with the DSMC code (un-scattered flux) and this 
model. The results from the model are in excellent agreement with the DSMC code, so 
the initial energy distribution (ejection energy distribution) of the sputtered particles 
can be inferred from the fitting of the simulated ionized un-scattered sputtered flux 
energy distribution obtained with this model to the high-energy tail of the measured 
distribution.

![Velocity distribution comparison](image)

Figure 2.13: Comparison between the velocity distributions simulated with the DSMC 
code (un-scatter flux) and the model for the ionized sputtered particle motion for the 
case of He bombardment.

2.3.5 Elastic-scattering cross-sections measurements

We obtain the elastic-scattering cross-sections for C, C\(_2\) and C\(_3\) with every 
bombarding gas by fitting the simulation and the experimental data for the decay of
the energy distribution as the distance from the sample is increased. For each bombarding gas we perform a series of experiments in which the distance between the sample and the QMS (which can move horizontally in and out of the plasma) is changed. At each position of the QMS the carbon sample is bombarded with the highest incident energy studied and the energy scans for mass 12, 24 and 36 ions are acquired. The density, temperature and potential profiles are measured with the Langmuir probe and the neutral density profile is measured with the QMS. Then, we integrate the high-energy tail of the acquired energy distribution to obtain the decaying signal with increasing distance. In the simulation, we use the ionized sputtered particles motion model to simulate the same experiments with the density and potential profiles obtained from the Langmuir probe measurements (as explained in the Appendix), while varying the elastic scattering cross-sections. For each value of the elastic scattering cross-section, we integrate the simulated energy distributions for the four different distances and obtain a decaying signal with distance. Figure 2.14 shows the results of the simulation for three different elastic scattering cross-sections (6x10^{-20}, 7x10^{-20} and 8x10^{-20} m^2) and the result from the experimental data for carbon sputtering under He bombardment. For this case we obtain the best fit with an elastic scattering cross-section of 7x10^{-20} m^2. Figure 2.15 shows the comparison between the experimental energy distributions and the simulated distributions for the fitted elastic scattering cross-section value.
Figure 2.14: Integrated experimental and simulated carbon energy distribution vs. distance from the sample for He bombardment.

Figure 2.15: Experimental and simulated carbon energy distributions at different distances from the sample for the case of He bombardment.
2.3.6 Calculation of the total sputtering yield

For the case of carbon sputtering, the angular sputtering distribution of C, C\textsubscript{2} and C\textsubscript{3} for each bombarding gas at each incident energy is obtained by integrating the initial energy distribution (ejection energy distribution) obtained from the fitting of the simulated energy distributions to the high energy tail of the acquired energy scans at each angle. For the simulation, we use the electron impact ionization cross-section for C, C\textsubscript{2} and C\textsubscript{3} based on literature results [64] and the elastic scattering cross-sections previously measured.

Figure 2.16 shows the energy distributions for C, C\textsubscript{2} and C\textsubscript{3} ions acquired with the QMS for 225eV incident energy He ion bombardment, as well as the simulated energy distributions. For the case of C atom sputtering, the experimental distribution is fitted with a initial thompson distribution for a binding energy of 7eV (~sublimation energy for carbon), as expected. On the other hand, the sputtered cluster energy distributions exhibit a much steeper falloff at high emission energies. Similar energy distributions of cluster sputtering have been previously reported [27]. The energy distributions for the cluster sputtering are fitted with an initial distribution of the form

\[ f(E) = \frac{E}{(E + U_b)^{3.5}} \]  

(2.38)

which corresponds to Eq. 1.7 with \( \alpha = 2.5 \). The fitted values of \( U_b \) are 3eV for C\textsubscript{2} and 2eV for C\textsubscript{3}. The energy distributions for C, C\textsubscript{2} and C\textsubscript{3} appear to be fairly independent of the bombarding gas.
Figure 2.16: Experimental and simulated energy distributions for C, C$_2$ and C$_3$ ions for 225eV incident energy He ion bombardment.

The relative value of the total sputtering of C, C$_2$ and C$_3$ for each gas, at each incident energy, is obtained by integrating the angular sputtering distributions. An absolute value of the sputtering yield can not be obtained from the energy scans because the transmission coefficient of the QMS is unknown. However, we can obtain the C to C$_2$ and C to C$_3$ total sputtering ratio from the experimental results because the dependence of the transmission coefficient on the ion mass is known [57] (it is inversely proportional to the mass) and the differences in the ionization and elastic scattering between C, C$_2$ and C$_3$ ions in the plasma are already taken into consideration in the simulation.

Using these ratios and the total sputtering yield obtained from the weight loss measurements we get the total sputtering yield for C, C$_2$ and C$_3$ for each bombarding gas at the highest incident energy from
\[ Y_C = \frac{Y_{Total}}{1 + \frac{2}{R_{C/C_2}} + \frac{3}{R_{C/C_3}}} \]  

(2.39)

\[ Y_{C_2} = \frac{Y_C}{R_{C/C_2}} \]  

(2.40)

\[ Y_{C_3} = \frac{Y_C}{R_{C/C_3}} \]  

(2.41)

where \( Y_{Total} \) is the measured total sputtering yield, \( R_{C/C_2} \) and \( R_{C/C_3} \) are the C to C\(_2\) and C to C\(_3\) total sputtering ratios and \( Y_C \), \( Y_{C_2} \) and \( Y_{C_3} \) are the C, C\(_2\) and C\(_3\) total sputtering yields. Once we obtain the value of the total sputtering yield at the highest incident energy we normalize the rest of the results to this value.

2.4 Acknowledgments

Chapter 4 is an edited version of the material as it appears in “Carbon atom and cluster sputtering under low energy noble gas plasma bombardment” by E. Oyarzabal, R. P. Doerner, M. Shimada and G.R. Tynan submitted to the J. Appl. Phys. The dissertation author was the primary investigator and author of this paper.
Chapter 3
Molybdenum sputtering under low energy xenon ion bombardment

As has been explained previously, the Mo experiments were performed before the carbon experiments in order to acquire a good understanding of the technique used in the present work and to validate the same by comparing the total sputtering results obtained with this technique with the results from previous studies. In this Chapter the results for the Mo atom sputtering under Xe ion bombardment, with incident energies ranging from 75 eV to 225 eV are shown. The angular distribution of the sputtered Mo atoms for the different studied incident energies is presented, as well as the total sputtering yield vs. incident energy data and a comparison with previous data.

3.1 Introduction

Sputtering behavior of ion thruster materials is of great importance in order to model and predict their long-term performance. Although the sputtering of various materials has been previously studied in detail for higher incident ion energies [65-69],
there are only a few studies for energies under 200 eV [1,47,70]. This incident ion energy range is important for the case of sputtering due to low energy ions created by charge exchange reactions near the grid surfaces [2] or by potential hill structures located within ion thruster discharge chambers [3,4]. Information about the angular sputtering distribution for the thruster materials under these conditions is necessary in order to accurately simulate the net erosion of surfaces and subsequent contamination buildup on adjacent locations.

We present measured angular sputtering distributions of Mo atom (cluster emission can be considered negligible in this case [1]) for low energy, normal incidence Xe ion bombardment (with incident ion energy $E_{\text{Xe}}$ ranging from 75 to 225 eV). A Xe plasma generated in an inductively coupled plasma source is used to provide the singly ionized (due to the low electron temperature, $T_e$) Xe ion flux to the Mo target. The target is negatively biased relative to the plasma to produce the desired bombardment energies, and the sheath that forms in the target surface assures normal incident ion bombardment. Predominantly, neutral particles are sputtered from the target surface. Any ion component sputtered from the target will be returned to the surface due to the applied bias potential. The ionization efficiency of un-scattered sputtered neutrals, which have several eV of kinetic energy, in the QMS is insufficient for direct detection. However, sputtered neutral particles that are ionized by the background plasma can be measured by the instrument. The simultaneous charge/mass ratio and energy sensitivity of this instrument is then used to discriminate between ionized sputtered particles which have suffered a collision with a neutral gas
atom or plasma ion, and those which have only been ionized by a collision with a plasma electron (since such electron collisions do not substantially alter the kinetic energy and momentum of the incident sputtered atom). The angular sputtering distribution is obtained by changing the relative angle, \( \theta \), between the target normal and the QMS flight path, and these angular distribution measurements are repeated for various incident ion energies. An absolute calibration of the QMS is not possible due to the unknown transmission coefficient for fast Mo ions, thus, the results obtained in these experiments are relative. However, we normalize our data to the existent data from the literature.

A maximum of the angular sputtering distribution at approximately 60° away from the surface normal is observed, which is consistent with previous results that have been reported for low energy high mass bombardment [47-49]. Similar results are obtained from simulations performed using the Monte Carlo TRIDYN code [71]. The dependence of the sputtering yield on the incident ion energy is also shown, and a comparison with previous data is presented.

3.2 Experiments and data analysis

The experiments are performed as explained in Chapter 2. The plasma discharge is started with the desired parameters and once it stabilizes, the sample is bombarded by the plasma ions with an energy set by the bias voltage. The experimental parameters used for these experiments are shown in Table 3.1. For each studied incident energy (75, 100, 125, 150, 175, 200 and 225eV) and at each angle (0, 15, 30, 45, 60, 75 degrees) between the sample normal and the QMS line of sight a Mo
ion energy scan is obtained with the QMS. These energy scans must then be analyzed in order to obtain the angular distribution of the sputtered particles for the different incident energies.

Table 3.1. Plasma conditions and experimental parameters (Mo sample).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mTorr)</td>
<td>5</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>1000</td>
</tr>
<tr>
<td>$T_e$ (eV)</td>
<td>2</td>
</tr>
<tr>
<td>$n_e$ ($m^{-3}$)</td>
<td>$1 \times 10^{18}$</td>
</tr>
<tr>
<td>$\Phi_p$ (V)</td>
<td>10</td>
</tr>
<tr>
<td>Ion flux (ion sec$^{-1}$m$^{-2}$)</td>
<td>$7 \times 10^{20}$</td>
</tr>
<tr>
<td>$A_{QMS}$ (m$^2$)</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>$A_{Target}$ (m$^2$)</td>
<td>$1.17 \times 10^{-4}$</td>
</tr>
<tr>
<td>R (m)</td>
<td>0.09</td>
</tr>
</tbody>
</table>

As has been explained before, the Mo sputtering measurements were performed before the carbon sputtering measurements and the analysis of the data is slightly different. In the case of Mo, we are only interested in the angular sputtering distribution of Mo atoms for different Xe ion incident energies. As long as we are not comparing results for atoms and clusters we don’t need to measure the elastic scattering of the Mo atoms as in the case of carbon or to use a simulation to fit the data. The analysis in this case is less complicated.

As has been explained in Chapter 2, looking at the QMS acquired energy spectra of Mo ions for the case of Mo sputtering under Xe bombardment (Fig. 2.6), we observe a low energy peak (which is also observed when the sample normal is set at an angle of 135° with respect to the QMS flight path), which represents Mo sputtered
atoms that undergo elastic scattering, lose their directional energy, and are driven toward thermal equilibrium with the Xe neutrals, and a high energy tail, which represents the un-scattered sputtered particles. The energy distribution of the flux of particles with directional energy, i.e. un-scattered sputtered particles, will change with the distance from the sample due to the collisions with plasma neutrals. Since the sputtered Mo atom mass is close to that of the working gas (Xe) and plasma ion, a single elastic scattering event of a fast (few eV) Mo atom with a thermal (0.1 eV or less) Xe scattering center will result in a significant transfer of energy from the fast species to the slower species. Consider an initial sputtered particle flux energy distribution \( f_0(E) \) at a particular sputtering angle. Mo-Xe scattering changes this energy distribution with distance \( R \) from the sample as

\[
f(E,R) = f_0(E) \exp(-\sigma_{\text{Mo-Xe}} n_n R)
\]  

(3.1)

where \( \sigma_{\text{Mo-Xe}} \) is the Mo-Xe scattering cross section, and \( n_n \) is the neutral density. We neglect collisions with plasma ions here because the neutral density is at least two orders of magnitude higher than the plasma ion density for the conditions in our experiments. Essentially, the distribution function of the ions measured at a certain distance from the sample is a constant fraction of the original neutral sputtered particle distribution, because \( \sigma_{\text{Mo-Xe}} \) does not depend on the energy of the sputtered particles [72]. Thus, the measured ion energy spectra (with the background population subtracted) directly represents an attenuated sputtered neutral particle energy spectra.

In order to measure the angular distribution of the sputtered Mo, we subtract the background population of ions (which does not keep any directional information)
from the raw data, and obtain the count rate of the ion population with directional energy. The background population for each experimental condition is obtained by normalizing the peak value of the signal at $\theta =135^\circ$ to the peak value of the signal for that particular experimental condition. Fig. 3.1 shows the background population distribution normalized according to the procedure described above, and the resulting distribution of the particles with directional energy after the background subtraction in the case of $\theta=0^\circ$ and $E_{Xe}=175\text{eV}$. The energy difference between the peaks of these two populations corresponds to roughly half of the surface binding energy for Mo ($E_b\approx6.9\text{eV}$). This directed energy distribution of fast particles is then summed over the whole energy range to obtain a total ion signal $S_i$ for each experimental condition.

![Figure 3.1: Background population and population of the particles with directional energy vs. energy for Mo sputtering under Xe bombardment.](image)

Finally, the ion signal $S_i$ is normalized so that the total sputtering yield for 150 eV incident energy is the same as in previous low energy normal incidence Xe on Mo
bombardment literature data [73]. In this way, we obtain a differential sputtering yield for each observation angle at each incident energy.

3.3 Results

3.3.1. Angular distribution of the sputtered Mo particles:

Fig. 3.2 shows the polar plots of the obtained angular sputtering distributions of Mo under Xe bombardment for various incident ion energies. The data has been plotted as a mirror image around \( \theta=0^\circ \) to make the figures easier to visualize.

![Figure 3.2: Mo angular sputtering distribution for different incident ion energies. Data for 75eV and 125eV has been multiplied by 5 and 2 respectively. Data is mirrored around 0° for clarity.](image)

For all the incident energies studied in this work, the sputtering yield is “under-cosine”, with a maximum at an angle of 60°. This maximum is less pronounced as the incident energy increases. Similar under-cosine angular sputtering distributions have...
been reported previously during low energy bombardment for the case of high mass ratio between the incident ion and the target material [47-49].

Simulation of the angular distribution of Mo atoms sputtered by Xe bombardment using the Monte Carlo code TRIDYN [71] predicts similar results, as can be seen in the polar plot in Fig. 3.3. The code models the transport of incident energetic particles and generated recoils in an amorphous target as a sequence of independent binary collisions. The Krypton-C interaction potential [71] is used to describe the scattering processes within this collision cascade. When a Mo atom from the cascade leaves the surface with energy larger than the surface binding energy it is considered sputtered, and its exit angle relative to the surface normal is recorded. From the relative sputter yield of particles sputtered into a certain angle the angular distribution \( P(\theta) \) is calculated according to

\[
2P(\theta) = \frac{1}{Y_{E_x}} \frac{\gamma_{E_x}}{C_{\cos \theta}}
\]  

(3.2)

The results of the simulation show an “under-cosine” distribution with a maximum at around 45-60° for the lower energies (<500eV) and a cosine-like distribution for the higher energies (500 eV and 1000 eV). The results of the simulation are not in complete agreement with the experiments, which show a more pronounced maximum at 60° for both 100 and 200 eV incident energy. Nevertheless, both the simulation and the experimental results present a similar evolution of the angular distribution with the incident energy, showing an under-cosine angular sputtering distribution when the kinetic energy of the heavy ions is too small to create
collisional cascades, resulting in a decrease of sputtered particles ejected normal to the surface [50]. For much larger incident energies the simulated sputtering angular distribution evolves toward the well-known cosine distribution.

Figure 3.3: Simulated Mo angular sputtering distribution for different incident ion energies. Data is mirrored around $0^\circ$ for clarity.

3.3.2. Mo sputtering vs. incident energy:

The differential sputtering yield vs. incident energy for various observation angles is shown in Fig. 3.4.

Figure 3.4: Mo differential sputtering yield vs. incident ion energy for different sputtering angles.
The dependence of the sputtering on the incident energy is similar for the different sputtering angles. There is a large increase of an order of magnitude in the sputtering yield from \( E_{Xe} = 75 \) to 125 eV, and a more moderate increase for higher energies.

Figure 3.5: Comparison of the total sputtering yield vs. incident ion energy with previous experiments.

The dependence of the total sputtering yield on the incident ion energy is in good agreement with previous experiments, as can be seen in Fig. 3.5. This result gives us confidence in the validity of our experimental procedure to correctly measure the sputtering behavior of the studied material. The sputtering yield at higher energies in Ref. 1 appears to be somewhat smaller than that in the other studies. We believe the reason for this disagreement is likely due to the fact that the results of Ref. 1 were calculated by assuming a cosine distribution of the sputtered particles. We believe the present data can be used to estimate the magnitude of the correction necessary for the
data in Ref. 1, but such calculations will require both angular and sputtered particle
energy corrections and are outside the scope of this thesis.

3.4. Conclusions

The Mo angular sputtering distribution during low energy (75- 225 eV)
normal incidence Xe ion bombardment has been measured using a quadrupole mass
spectrometer (QMS) to detect the fraction of sputtered neutrals that is ionized in the
plasma. The results obtained in these experiments are relative and have been
normalized to the existing data in the literature.

An “under-cosine” angular sputtering distribution of Mo with a maximum at
around 60° for the studied Xe incident ion energy range (75-225eV) is observed. This
maximum becomes less pronounced as the incident energy increases. These kind of
under-cosine angular distributions, with maxima at approximately θ=60°, have been
reported previously during low energy sputtering experiments [47,49]. The same
angular distribution evolution with incident energy is observed in the simulations
performed using the Monte Carlo TRIDYN [71] code. For low incident ion energy
bombardment (<500 eV) the kinetic energy of the ions is too small to create collisional
cascades, resulting in a decrease of sputtered particles ejected normal to the surface
[50]. For larger incident energies the simulated sputtering angular distribution evolves
toward the well-known cosine distribution. The measurements presented here show
that the typically assumed cosine distribution of sputtered particles during low energy,
high mass ion bombardment of surfaces may not be valid. The angular distribution of
sputtered particles will to a large extent determine the locations where redeposited material may accumulate in ion thruster engines.

Comparison of the total sputtering yield results of Mo with previous experiments shows good agreement. There is a large increase of about an order of magnitude in the sputtering yield from \( E_{Xe} = 75 \) to 125 eV, and a more moderate increase for higher energies. This result gives us confidence in the validity of our experimental procedure to correctly measure the sputtering behavior of the studied material.

The present Mo sputtering experiments show the validity of the technique to obtain accurate sputtering yields (good agreement between the results for the Mo sputtering yield from this work and previous data) and give the necessary understanding as to apply it to the case of C sputtering, where a more complicated analysis is needed in order to extract the desired information from the measurements, as has been shown previously.

3.5. Acknowledgments

Chapter 4 is a edited version of the material as it appears in the paper “Molybdenum angular sputtering distribution under low energy xenon ion bombardment”, J. Appl. Phys. 100, Issue 6 (2006) 3301 by E. Oyarzabal, J. H. Yu, R. P. Doerner, G.R. Tynan, K. Schmid. The dissertation author was the primary investigator and author of this paper.
Chapter 4
Carbon atom and cluster sputtering under low-energy noble gas plasma bombardment

As has been stated before the main interest of the present work was to perform a comprehensive study of the influence of the incident bombarding ion mass on the physical sputtering of carbon at low incident energies (75 to 225 eV). In this chapter the results of this study are presented.

4.1 Introduction

Physical sputtering of carbon is of great importance in order to correctly model and predict the net erosion of surfaces and subsequent contamination buildup on adjacent locations in many applications. Although carbon erosion under noble gas bombardment has been previously studied for higher incident ion energies [65,74-80], there is little data for energies under 100 eV [1] and no information is available on the
angular distribution of sputtered carbon at these low energies. Also, most of the previous studies assume that carbon is mainly eroded as carbon atoms and this may not be true for all cases. Previous results for the erosion of carbon during Xe ion bombardment at low incident energies [1] have shown a high sputtering yield of carbon as dimers (approximately 10 times larger than the yield for individual carbon atoms). Carbon erosion under Xe bombardment at low incident energies is of particular interest for its possible application as the grid material on ion thrusters. This incident ion energy range is important for the case of sputtering due to low energy ions created by charge exchange reactions near the grid surfaces [2] or by potential hill structures located within ion thruster discharge chambers [3,4]. Carbon erosion under low energy noble gas bombardment is also important to predict the contamination and deposition of the sputtered carbon for the case of noble gas puffing in detached divertors [5] in controlled fusion devices.

We present measured angular sputtering distributions of carbon as C, C₂ and C₃ (higher order clusters are below the experimental limit of detection) for low energy normal incident ion bombardment (Xe, Kr, Ar, Ne and He), with the incident ion energy ranging from 75 to 225 eV. The bombarding gas plasma, generated in an inductively coupled plasma source, is used to provide the singly ionized (due to the low electron temperature, Te) bombarding ion flux to the carbon target. We use the well-characterized ATJ graphite (from Union Carbide) for the present experiments. This is a unidirectional molded graphite that is produced without re-impregnation; it has an average density of 1.74 g cm⁻³, a maximum grain size of about 150 μm, and a
between-grain pore size in the 3 to 4 $\mu$m range [81]. The graphite target is negatively biased relative to the plasma to produce the desired ion bombardment energies, and the sheath that forms near the target surface assures normal incident bombardment. Predominantly, neutral particles are sputtered from the target surface. Any ion component sputtered from the target will be returned to the surface due to the applied bias potential. The ionization efficiency of un-scattered sputtered neutrals, which have several eV of kinetic energy, in the QMS is insufficient for direct detection. However, sputtered neutral particles that are ionized by the background plasma can be measured by the instrument. The simultaneous charge/mass ratio and energy sensitivity of this instrument is then used to discriminate between ionized sputtered particles which have suffered a collision with a neutral gas atom or plasma ion, and those which have only been ionized by a collision with a plasma electron (since such electron collisions do not substantially alter the kinetic energy and momentum of the incident sputtered atom). The angular sputtering distribution is obtained by changing the relative angle, $\theta$, between the target surface normal and the QMS flight path. These angular distribution measurements are repeated for various incident ion energies and bombarding species. The direct simulation Monte Carlo (DSMC) code described before is used to simulate the interaction of the sputtered particles with the plasma and background gas between the sample and the QMS aperture. A simpler model, which simulates the motion of the ionized sputtered particles, is developed to obtain the elastic scattering cross-sections of C, C$_2$ and C$_3$ with the different bombarding gases by fitting the simulation data to the experimental results for different positions of the
QMS. The absolute C, C₂ and C₃ sputtering yields are obtained from the weight loss measurements.

A maximum of the angular sputtering distribution at approximately 60-75° away from the surface normal is observed for the ejected C, C₂ and C₃, which is consistent with previous results reported for low-energy, high-mass ion bombardment [47-49]. The dependence of the C, C₂ and C₃ sputtering yield on the incident ion energy is also shown, and a comparison with previous data is presented. A strong dependence of the carbon atom to cluster sputtering yield ratio on the incident ion mass is observed, evolving from carbon atom preferential erosion for the lower incident ion masses (He, Ne and Ar) to cluster preferential erosion for the higher incident ion masses (Kr and Xe). This effect has not been reported previously by any study. It is an important effect and should be taken into account when modeling carbon sputtering at low energies instead of assuming carbon atom preferential sputtering for all incident masses.

4.2 Experiments and data analysis

The experiments are performed as explained in Chapter 2. The plasma discharge is started with the desired parameters and when it is stabilized the sample is bombarded by the plasma ions with an energy set by the bias voltage. The experimental parameters used for the different bombarding gases are shown in Table 4.1. For each of the bombarding gases (Xe, Kr, Ar, Ne and He) and at each studied incident energy (75, 125, 175 and 225 eV) the C, C₂ and C₃ ion signal spectra is acquired with QMS at different angles (0, 15,30, 45, 60, 75 degrees) between the
sample normal and the QMS aperture. The angular sputtering distribution of C, C₂ and C₃ for each bombarding gas at each incident energy is obtained by integrating the initial energy distribution (ejection energy distribution) obtained from the fitting of the simulated energy distributions to the high energy tail of the acquired energy scans at each angle. For the simulation, we use the electron impact ionization cross-section for C, C₂ and C₃ based on literature results [64] and the elastic scattering cross-sections previously measured. The relative value of the total sputtering of C, C₂ and C₃ for each gas, at each incident energy, is obtained by integrating the angular sputtering distributions. For every bombarding gas, the absolute value of C, C₂ and C₃ at the highest incident energy is obtained from the C to C₂ and C to C₃ total sputtering ratios from the experimental results and the total sputtering yield obtained from the weight loss measurements. Once we obtain the value of the total sputtering yield at the highest incident energy we normalize the rest of the results to this value.

Table 4.1. Plasma conditions and experimental parameters (Carbon sample).

<table>
<thead>
<tr>
<th>Working gas</th>
<th>Xenon</th>
<th>Krypton</th>
<th>Argon</th>
<th>Neon</th>
<th>Helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mTorr)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<td>Tₑ (eV)</td>
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<td>2.1</td>
<td>2.75</td>
<td>6.6</td>
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<td>nₑ (m⁻³)</td>
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<td>9×10⁻¹⁷</td>
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<td>7.5×10⁻¹⁶</td>
<td>2.7×10⁻¹⁶</td>
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<td>Flux (ions.m⁻².s⁻¹)</td>
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<td>8.4×10²⁰</td>
<td>2.6×10²⁰</td>
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</tr>
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<td>A_QMS (m²)</td>
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<td>3×10⁻⁶</td>
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<tr>
<td>A_{target} (m²)</td>
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<td>1.17×10⁻⁴</td>
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</tr>
<tr>
<td>R (m)</td>
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4.3 Results

4.3.2. Elastic scattering cross-sections

As has been explained in Chapter 2, we obtain the elastic-scattering cross-sections for C, C\textsubscript{2} and C\textsubscript{3} with every bombarding gas by fitting the simulation and the experimental data for the decay of the energy distribution as the distance from the sample is increased. These experimentally obtained elastic scattering cross-sections are shown in Fig. 4.1.

![Elastic scattering cross-sections](image)

Figure 4.1: Elastic scattering cross-sections for C, C\textsubscript{2} and C\textsubscript{3} with the different bombarding gases.

As would be expected, the elastic scattering cross-section increases from C to C\textsubscript{2} to C\textsubscript{3} for every bombarding gas. We can compare the measured values with the theoretical values, assuming hard sphere collisions, for the case of carbon atoms, for which the effective atomic radius is well known. The good agreement between the
measured and the theoretical values of the elastic scattering cross-section for carbon atoms gives us confidence on the validity of the obtained elastic scattering cross-section for C₂ and C₃, for which there are not theoretical or experimental values available.

4.3.1. Angular sputtering distributions

Figures 4.2, 4.3, 4.4, 4.5 and 4.6 show the polar plots for C, C₂ and C₃ angular sputtering distributions of the ATJ graphite under He, Ne, Ar, Kr and Xe bombardment, respectively, for the different studied incident energies. The data has been plotted as a mirror image around θ=0° to make the figures easier to visualize. In the case of C sputtering in Xe and Kr discharges, and C₃ sputtering in Ar discharges, the QMS signals are too small to obtain an accurate angular distribution. For all the incident energies studied in this work, and for all the bombarding gases, the sputtering yield of carbon as C, C₂ and C₃ presents an “under-cosine” angular distribution, with a maximum at an angle of 60-75°. Similar under-cosine angular sputtering distributions have been reported previously for the case of atom sputtering during low energy bombardment for the case of high mass ratio between the incident ion and the target material [47-49]. There are no previous results of cluster angular sputtering distributions at these low energies.
Figure 4.2: C, C₂ and C₃ angular sputtering distributions of carbon under He bombardment.
Figure 4.3: C, C$_2$ and C$_3$ angular sputtering distributions of carbon under Ne bombardment.
Figure 4.4: C and C₂ angular sputtering distributions of carbon under Ar bombardment.
Figure 4.5: C₂ and C₃ angular sputtering distributions of carbon under Kr bombardment.
Figure 4.6: C$_2$ and C$_3$ angular sputtering distributions of carbon under Xe bombardment.
These observations suggest that at these low incident energies the kinetic energy of the heavy ions is too small to create collision cascades, resulting in a decrease of sputtered particles ejected normal to the surface [50] and an increase of sputtered particles ejected at oblique angles, for which fewer collisions are required to lead to an ejection event. In the case of light ions, where the energy transfer to the target atoms is so small that the generation of successive recoils is improbable, the ejection event is dominated by the direct interaction between the projectile and the target atoms. For such low mass ratio sputtering, previous experiments [50,82] predict an over-cosine distribution of the sputtered particles at incident energies as low as 1keV, but no lower energy data existed prior to our experiments. However, as can be seen in Fig.4.2 for the case of carbon atom sputtering under He bombardment obtained from the present experiments, as the incident energy is increased a larger number of atoms are ejected at normal angle, which could lead to the observed over-cosine distributions at higher energies. Except for the case of He bombardment, were we observe this tendency towards a more cosine-like distribution as the incident energy increases, we do not observe a clear evolution of the angular sputtering distribution with the incident energy for the rest of the bombarding gases.

Figure 4.7 shows the comparison of the angular sputtering distributions of C, C₂ and C₃ for the different studied bombarding gases at the highest incident energy, 225 eV. We observe that the maximum of the angular sputtering distribution for C, C₂ and C₃ is more pronounced for the case of high mass bombardment (Xe and Kr) and becomes less pronounced as the incident ion mass decreases.
Figure 4.7: C, C₂ and C₃ angular sputtering distributions of carbon under Xe, Kr, Ar, Ne and He bombardment.

4.3.2. Total Sputtering Yield vs. incident energy

Figures 4.8 show the total sputtering yield of carbon as C, C₂ and C₃ vs. the incident ion energy for all the studied bombarding gases. For the case of carbon cluster
sputtering, the increase with the incident energy seems to be more pronounced for the higher incident ion masses (Xe and Kr).

Figures 4.8: Total sputtering yield of carbon as C, C$_2$ and C$_3$ vs. incident ion energy for Xe, Kr, Ar, Ne and He bombardment.
Figure 4.9 shows the total sputtering yield vs. the incident energy obtained in the present experiments, as well as a comparison with previous data. There are not many data points from previous experiments at these low energies, but the results from the present work seem to be in good agreement with the existing data. The sputtering yield in Ref. 1 appears to be somewhat smaller than that in the present study. We believe the reason for this disagreement is likely due to the fact that the results of Ref. 1 were calculated by assuming a cosine distribution of the sputtered particles [51].

Figures 4.9: Total sputtering yield of carbon vs. incident ion energy for Xe, Kr, Ar, Ne and He bombardment from present work and previous experiments.

4.3.3. $C, C_2$ and $C_3$ total sputtering yield vs. incident ion mass

Figure 4.10 shows the total sputtering yield and the $C, C_2$ and $C_3$ sputtering yield dependence on the incident ion mass. Carbon erosion under Ne bombardment
presents the highest sputtering yield for C, C\textsubscript{2} and C\textsubscript{3}, as expected (Ne has the highest energy transmission coefficient with carbon). The sputtering yield of carbon atoms decreases considerably as the incident ion mass increases, there are two orders of magnitude of difference between Ne and Xe bombardment. For the case of sputtering as clusters, there is also a decrease as the incident ion mass increases, but it is not as pronounced (less than an order of magnitude between Ne and Xe).

Figures 4.10: C, C\textsubscript{2} and C\textsubscript{3} sputtering yield and total sputtering yield of carbon vs. incident ion mass.

We observe a strong dependence of the carbon atom to cluster sputtering yield ratio on the incident ion mass, as can be seen in Fig. 4.11. The sputtering changes from carbon atom preferential erosion for the lower incident masses (He, Ne and Ar) to cluster preferential erosion for the higher incident masses (Kr and Xe). The carbon atom to cluster sputtering yield ratio decreases nearly logarithmically with incident ion
mass and we observe a stronger decrease for the case of \( \text{C}_3 \) clusters as compared to that of \( \text{C}_2 \) clusters.

Figures 4.11: Carbon atom to cluster sputtering yield ratio vs. incident ion mass.

If we examine the evolution of the atom to cluster sputtering ratio variation with incident bombarding energy shown in Fig. 4.12 (we only have data for He and Ne), we observe that for both \( \text{C}_2 \) and \( \text{C}_3 \) clusters, this ratio increases with increasing incident energy. We believe the reason for this behavior is related to the change in the depth of origin of the ejected particles with incident energy. Figure 4.13 shows the depth of origin of ejected carbon atoms for the case Ne and He bombardment with different incident energies as simulated by the Monte Carlo code TRIDYN [71]. We see that most of the sputtered atoms at these low incident energies come from the first and second layers closer to the surface. As the incident energy increases the number of atoms ejected from deeper layers increases. Because the clusters are supposed to be ejected only from the surface layers [83], the increase in the number of ejected
particles coming from deeper layers with increasing incident energy would result in an increase of the carbon atom to cluster sputtering yield ratio with increasing incident energy, as observed.

Figures 4.12: Carbon atom to cluster sputtering yield ratio vs. incident energy for Ne and He bombardment.

Figures 4.13: TRIDYN simulation results for the depth of origin of ejected carbon atoms under Ne and He bombardment at different incident ion energies.
We also observe a change in the depth of origin of the ejected particles with incident ion mass. Figure 4.14 shows the depth of origin of the ejected carbon atoms for the different studied bombarding gases (225 eV incident energy) obtained from the Monte Carlo TRIDYN [71] code simulation.

Figures 4.14: TRIDYN simulation results for the depth of origin of ejected carbon atoms under Xe, Kr, Ar, Ne and He bombardment for 225eV incident energy.

For all the bombarding gases the majority of the ejected particles come from the first and second layers, but as the incident ion mass decreases the fraction coming from deeper layers increases. Even though this dependence of the origin of the ejected particles with the incident ion mass is in agreement with the observed change in carbon atom to cluster sputtering ratio, the effect is too small to explain the transition from a carbon atom preferential sputtering for the low incident ion masses to a cluster preferential sputtering for the higher incident ion masses. The strong dependence observed C/C$_2$ and C/C$_3$ Yield ratios may be related to the difference in the stresses
produced by the implanted bombarding ions (for the case of Xe bombardment a saturation value as high as 15% Xe atoms has been observed [1]). It is possible that the stresses produced by the implanted high mass bombarding ions are favorable to the formation of clusters in the surface. A study of the surface structure involved should be taken into account in trying to understand the reasons for the observed atom to cluster erosion ratio dependence on the incident ion mass, but this is beyond the scope of this thesis.

4.4. Conclusions

The angular sputtering distribution of carbon as C, C₂ and C₃ during low energy (75-225 eV) normal incidence noble ion bombardment (Xe, Kr, Ar, Ne and He) has been measured using a quadrupole mass spectrometer (QMS) to detect the fraction of sputtered neutrals that is ionized in the plasma. A DSMC code has been used to simulate the interaction of the sputtered particles with the background gas between the sample and the QMS aperture, and a model of the ionized sputtered particles motion has been developed to obtain the elastic scattering cross-sections of C, C₂ and C₃ with the different bombarding gases by fitting the simulation data to the experimental results for different positions of the QMS. Also, a weight loss measurement has been performed for each studied bombarding gas to obtain the absolute values of the C, C₂ and C₃ sputtering yields.

An “under-cosine” angular distribution of the sputtered carbon atoms and clusters with a maximum at around 60-75⁰ is observed for all the studied incident ions at these low incident ion energies (75-225eV). The maximum is more pronounced for
the case of high mass incident ion bombardment (Xe and Kr) and becomes less pronounced as the incident ion mass decreases. Similar under-cosine angular sputtering distributions have been reported previously during low energy bombardment for the case of high mass ratio between the incident ion and the target material [47-49]. At these low incident energies the kinetic energy of the heavy ions is too small to create collision cascades, resulting in a decrease of sputtered particles ejected normal to the surface [50] and an increase of sputtered particles ejected at oblique angles, for which fewer collisions are required to lead to an ejection event.

The obtained carbon total sputtering yields for the different bombarding gases are in good agreement with the previous existing data at these low incident energies. For the case of carbon cluster sputtering yield, the increase with the incident energy seems to be more pronounced for the higher incident ion masses (Xe and Kr). Carbon erosion under Ne bombardment presents the highest sputtering yield for C, C₂ and C₃, as expected (Ne has the highest energy transmission coefficient with carbon). We observe a nearly logarithmic decrease of the carbon to cluster sputtering yield ratio with increasing incident ion mass. The sputtering evolves from carbon atom preferential erosion for the lower incident ion masses (He, Ne and Ar) to cluster preferential erosion for the higher incident ion masses (Kr and Xe). This effect has not been reported previously by any study. It is an important effect and should be taken into account when modeling carbon sputtering at low energies instead of assuming carbon atom preferential sputtering for all incident masses.
The carbon atom to cluster sputtering yield ratio increases with increasing energy (for He and Ne, at least), this could be related to increase in the depth of origin of the ejected particles with increasing incident energy observed with the TRIDYN simulation. The depth of origin of the sputtered particles increases as well with decreasing incident ion mass, but this effect is not strong enough to explain the observed dependence of the carbon atom to cluster sputtering yield ratio on the incident ion mass. The strong dependence observed may be related to the difference in the stresses produced by the implanted bombarding ions. A study of the surface structure involved should be taken into account in trying to understand the reasons for the observed atom to cluster erosion ratio dependence on the incident ion mass.

4.5 Acknowledgments

Chapter 4 is an edited version of the material as it appears in “Carbon atom and cluster sputtering under low energy noble gas plasma bombardment” by E. Oyarzabal, R. P. Doerner, M. Shimada and G.R. Tynan submitted to the J. Appl. Phys. The dissertation author was the primary investigator and author of this paper.
Chapter 5

Summary and conclusions

In this dissertation the exit-angle resolved Mo atom sputtering yield under Xe ion bombardment and the carbon atom and cluster (C$_2$ and C$_3$) sputtering yield under (Xe, Kr, Ar, Ne and He) ion bombardment, are measured for low incident energies (75 - 225 eV). A new experimental technique has been developed in order to measure the ejection angle resolved sputtering yields of Mo atoms and carbon atoms and clusters. This technique uses the plasma ions produced in a plasma-etcher chamber as the bombarding incident ions by applying a bias voltage to the studied target. The formation of the sheath in front of the surface of the target assures normal incident ion bombardment under all conditions. The target is mounted in a manipulator which allows it to rotate to a set angle, $\theta$, between the target normal and the QMS aperture. A Langmuir probe, that can be moved horizontally and is placed at the same height as the sample, is used to measure the plasma density, temperature and the plasma potential profiles in the space between the sample and the QMS aperture. Predominantly, neutral particles are sputtered from the target surface. Any ion component sputtered from the target will be returned to the surface due to the applied bias potential. The ionization efficiency of un-scattered sputtered neutrals, which have several eV of kinetic energy, in the QMS is insufficient for direct detection. To obtain the sputtering yield of Mo atoms (for the Mo target) or C atoms and clusters (for the
carbon target) at each angle, the QMS is used to measure the sputtered neutral particles that are ionized by the background plasma. The simultaneous charge/mass ratio and energy sensitivity of this instrument is used to discriminate between ionized sputtered particles which have suffered a collision with a neutral gas atom or plasma ion, and those which have only been ionized by a collision with a plasma electron (since such electron collisions do not substantially alter the kinetic energy and momentum of the incident sputtered atom).

The DSMC code used to simulate the interaction of the sputtered particles with the background plasma between the sample and QMS aperture, shows that the high-energy tail of the energy scans acquired by the QMS directly represent the energy distribution of the ionized un-scattered sputtered flux of particles. For the case of Mo, the tail of the measured energy distribution is integrated for each angle between the sample normal and the QMS aperture in order to obtain the angular sputtering distribution at each incident energy, and a relative value of the total sputtering yield for each incident energy is obtained from the integration of the angular sputtering distributions. In the case of carbon sputtering, where we want to compare C, C₂ and C₃ sputtering for each bombarding gas, the differences in the ejection energy distributions, elastic scattering and ionization between the carbon atoms and clusters in the different studied background gases need to be taken into account. This is achieved by developing a model that simulates the ionized un-scattered sputtered particle flux evolution with the distance from the sample. For this simulation, we use the electron impact ionization cross-section for C, C₂ and C₃ based on literature results.
and the experimentally obtained elastic scattering cross-sections of C, C₂ and C₃ with the different bombarding gases by fitting the simulation data to the experimental results for different positions of the QMS. The angular sputtering distributions of C, C₂ and C₃ at each exposure condition are obtained by integrating the initial energy distribution inferred from the fitting of the simulated energy distributions at the QMS distance to the high energy tail of the acquired energy scans at each angle. The total sputtering yield (C+C₂+C₃) for each bombarding gas is obtained from weight loss measurements and the sputtering yield for C, C₂ and C₃ is then calculated from the integration of the measured angular distributions.

For both studied materials, Mo and carbon, and for all the studied incident ions, an “under-cosine” angular sputtering distribution with a maximum at around 60-75⁰ is observed at these low incident ion energies (75-225eV). In the case of Mo sputtering, this maximum becomes less pronounced as the incident ion energy increases; the same angular distribution evolution with incident energy is obtained from the simulations performed using the Monte Carlo TRIDYN code. For carbon sputtering, the maximum of the angular sputtering distribution is more pronounced for the case of high mass incident ion bombardment (Xe and Kr) and becomes less pronounced as the incident ion mass decreases. Similar under-cosine angular sputtering distributions have been reported previously during low-energy bombardment for the case of a high mass ratio between the incident ion and the target material. At these low incident energies the kinetic energy of the heavy ions is too small to create collision cascades, resulting in a decrease of sputtered particles ejected
normal to the surface and an increase of sputtered particles ejected at oblique angles, for which fewer collisions are required to lead to an ejection event.

Comparison of the total sputtering yield vs. incident energy results of Mo and carbon with previous experiments show good agreement. In the case of carbon, erosion under Ne bombardment presents the highest sputtering yield for C, C\(_2\) and C\(_3\), as expected (Ne has the highest energy transmission coefficient with carbon). This result gives us confidence in the validity of our experimental procedure to correctly measure the sputtering behavior of the studied material.

We observe a nearly logarithmic decrease of the carbon atom to cluster sputtering yield ratio with increasing incident ion mass. The sputtering evolves from carbon atom preferential erosion for the lower incident ion masses (He, Ne and Ar) to cluster preferential erosion for the higher incident ion masses (Kr and Xe). This effect has not been reported previously by any study. It is an important effect and should be taken into account when modeling carbon sputtering at low energies instead of assuming carbon atom preferential sputtering for all incident masses.

The carbon atom to cluster sputtering yield ratio increases with increasing energy (for He and Ne, at least), this could be related to an increase in the depth of origin of the ejected particles with increasing incident energy, as observed with the TRIDYN simulation. The depth of origin of the sputtered particles increases as well with decreasing incident ion mass, but this effect is not strong enough to explain the observed dependence of the carbon atom to cluster sputtering yield ratio on the incident ion mass. The strong dependence observed may be related to the differences
in the stresses produced in the lattice after the impinging ions have come to rest. A study of the surface structure involved should be taken into account in trying to understand the reasons for the observed atom to cluster erosion ratio dependence on the incident ion mass.

The measurements presented here show that the typically assumed cosine distribution of sputtered particles during low energy, high mass ion bombardment of surfaces may not be valid. Also, the typically assumed carbon atom preferential sputtering is shown not to be true for all incident masses, at least at these low incident energies.
Appendix

Temperature and density profiles

The density and potential profiles between the sample and the QMS are measured using a Langmuir probe, as has been explained in Chapter 2. The Langmuir probe can be move horizontally between the sample and the QMS, and the profiles are obtain by measuring the density and potential at different distances from the sample. Due to the inherent error involved in the Langmuir probe measurements and the consequent spread of the density and potential data, the measured profiles can not be directly used as input parameters in the DSMC code and the ionized sputtered particle motion model. For that reason, a combination of the Langmuir probe measurements and the theoretical profiles (using the sheath and presheath theory presented in Chapter 2) is used to obtain the input density and potential profiles for the simulations. Figures A.1, A.2, A.3, A.4 and A.5 show the density and potential data obtained from the Langmuir probe measurements and the density and potential profiles that have been used as input parameters in the simulations for the five studied plasmas, He, Ne, Ar, Kr and Xe plasma, respectively, for the four studied positions of the QMS (0.09, 0.115, 0.14 and 0.165 m from the sample).
Figure A.1: Density and potential profiles from Langmuir probe measurements (points) and density and potential profiles used as input parameters in the simulations (lines), for the He plasma.

Figure A.2: Density and potential profiles from Langmuir probe measurements (points) and density and potential profiles used as input parameters in the simulations (lines), for the Ne plasma.
Figure A.3: Density and potential profiles from Langmuir probe measurements (points) and density and potential profiles used as input parameters in the simulations (lines), for the Ar plasma.

Figure A.4: Density and potential profiles from Langmuir probe measurements (points) and density and potential profiles used as input parameters in the simulations (lines), for the Kr plasma.
Figure A.5: Density and potential profiles from Langmuir probe measurements (points) and density and potential profiles used as input parameters in the simulations (lines), for the Xe plasma.

The profiles used in the simulations are obtained in the following manner:

- The bulk density and potential values are obtained from the Langmuir probe measurements at the center of the distance between the sample and the QMS.

- The density at the sheath edge, \( n_s \), (sample surface or QMS surface) is obtained from the Boltzmann relation

  \[
  n_s = n_b e^{-\varphi_p/T_e} \approx 0.61 n_b
  \]

  where \( n_b \) is the bulk plasma density.

- The potential at the sheath edge is obtained by subtracting the potential drop across the presheath, given by

  \[
  \Phi_p = \frac{1}{2e} M u_y^2 = \frac{T_e}{2},
  \]

  to the bulk potential.
• The width and shape of the presheath profile is then obtained from the Langmuir probe acquired data.

We observe a pretty good agreement of the experimental profiles and this semi-theoretical profiles for the first two positions of the QMS, 0.09 and 0.115 m from the sample. For the last two positions of the QMS, 0.14 and 0.165 m from the sample, the density and potential values obtained from the Langmuir probe measurements are lower than the theoretical values in some cases. This could be related to higher errors for the Langmuir probe measurements closer to the plasma edge.

Anyway, the error that the observed differences could introduce in the elastic scattering values obtained from the fitting of the simulation to the data using this density and potential profiles has been taken into account and it is minimal. The reason for this, is that the decaying of the energy distribution of the un-scattered ionized sputter particle flux with the distance from the sample is mainly dominated by the elastic collisions of the particles (which depends primarily on the neutral density) and not by the ionization.
Bibliography


