Velocity distribution of titanium neutrals in the target region of high power impulse magnetron sputtering discharges

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Abstract

The velocity distribution function of titanium neutrals in the target region of a high power impulse magnetron sputtering discharge was investigated by optical emission spectroscopy. A high-resolution plane grating spectrograph combined with a fast, gated, intensified CCD camera was used to study the shape of selected optical emission lines. Doppler broadening and shift were analyzed to gain information about the velocity distribution of sputtered titanium neutrals. The velocity distribution function was found to depend on the discharge power for target power densities up to 0.6 kW cm⁻². Above that value, the velocity distribution was constant. The collision processes of sputtered neutrals close to the target were found to be describable using a modified version of the Krook collisional operator. Using this interpretation, evidence for strong scattering of the titanium neutrals in the target region was found. This scattering can be explained by resonant charge exchange with previously scattered titanium ions.

Keywords: HiPIMS, velocity distribution function, VDF, optical emission spectroscopy, magnetron sputtering, collisions, ionization region

1. Introduction

High power impulse magnetron sputtering (HiPIMS) is a relatively new method for the creation of ceramic or metallic coatings. HiPIMS discharges are traditional magnetron discharges driven with high voltage pulses instead of a continuous voltage. The high voltages and currents during each pulse lead to a very high ionization degree of up to 90% [1], which has been correlated with improved coating quality [2, 3].

Most of the discharge volume is well accessible by common plasma diagnostics like Langmuir probes and mass spectrometers. Mass spectrometry, in particular, can yield the velocity distribution of ions in a time-resolved manner. This velocity distribution of species arriving at the substrate is of great importance for the quality of the deposited coating. Ion velocity distribution functions (IVDF) have already been measured extensively for both direct current magnetron sputtering (DCMS) and HiPIMS discharges [4–9].

However, measurements involving probes or mass spectrometers are very invasive of the discharge target region. In this region, the electrons are magnetically confined and the plasma density is expected to be orders of magnitude higher than in the rest of the discharge volume. Moving a mass spectrometer into this sensitive region disturbs the discharge to the point that no meaningful information can be gained from this diagnostic [7].

Information about the velocity distribution function (VDF) of particles in the target region has been inferred by some researchers by extrapolating from measurements performed at the substrate position [10–12]. The difference between the VDF of neutrals and ions has also been exploited to probe the potential structure in HiPIMS [12, 13]. However, the VDF of neutrals is often only estimated.
An alternative approach to measuring the VDF is to use active or passive optical diagnostics, which do not disturb the discharge. Several groups have measured the VDF of sputtered species using laser-induced fluorescence (LIF) spectroscopy. By varying the laser wavelength, the Doppler shift of the excitation frequency was evaluated to determine the VDF. LIF has been performed in both DCMS [14–17] and HiPIMS, perpendicular [18] and parallel [19, 20] to the target surface. Palmucci et al found for HiPIMS that the line widths of the emission lines increase in the beginning of a discharge pulse before reaching a steady state. They identified this steady state plateau as a ‘rarefaction window’ during which almost all of the working gas (argon) is expelled out of the magnetic trap region [20]. However, their results were affected by a low signal-to-noise ratio, which made further interpretation of the line profile challenging.

Ball et al used a Fabry–Perot interferometer (FPI) to measure the optical emission lines of sputtered copper atoms in a DCMS discharge [21]. From the emission line broadening caused by the Doppler effect, the VDF of the atoms could be calculated. This method can easily be applied both parallel and perpendicular to the target surface. More recently, Britun et al have measured the VDF of several sputtered species using the same technique [22, 23].

However, FPI has so far not been applied to HiPIMS discharges, as synchronizing the FPI with the pulsed discharge adds additional challenges to the measurements [24].

In this work, the temporal evolution of the VDF of sputtered titanium neutrals in HiPIMS is investigated. The target region of the discharge is observed using a plane grating spectrograph instead of an FPI, thus trading spectral resolution for temporal resolution and quantum efficiency. The optical emission lines are fitted and their Doppler broadening is evaluated to determine the VDF of titanium neutrals.

2. Experimental setup

Figure 1 shows a schematic representation of the experimental setup. The discharge was ignited in front of a planar magnetron suitable for targets with a diameter of 2″. The magnetron was placed in a vacuum chamber with a base pressure of $1 \times 10^{-6}$ Pa. The discharge was operated in argon at a pressure of 0.5 Pa. A constant flow of Argon through the chamber was maintained via a gas shower at a rate of 45 sccm.

The power supply (TRUMPF Hüttinger TruPlasma Highpulse 4002) was combined with an external inductance which limits the current rise during the pulse. This allows for stable operation in the runaway regime. Current and voltage were measured in the cable connecting the magnetron to the power supply (Tektronix TCP A400, Tektronix P6015A). This electrical setup is described in more detail in [25].

The discharge was operated using titanium as the target material. All measurements were performed with a repetition frequency of 40 Hz and a pulse length of 100 μs. Figure 2 shows the discharge current of the three different discharge conditions investigated here. Only one voltage trace is shown, to keep the graph readable. The shown current and voltage were averaged over 128 discharge pulses. The current and voltage curves obtained with this setup have been discussed previously [25]. The voltages measured before breakdown occurred at 28 μV, 19 μV and 15 μV were 510 V, 590 V and 650 V. Maximum currents reached during the pulse were 25 A, 50 A and 75 A respectively, with maximum target current densities of 1.3 A cm$^{-2}$, 2.5 A cm$^{-2}$ and 3.8 A cm$^{-2}$. The shape of the discharge power curves (not shown) is very similar to the current curves in figure 2, since the discharge voltage is nearly constant after the discharge is ignited. The peak target power densities during the pulse were 0.6 kW cm$^{-2}$, 1.1 kW cm$^{-2}$ and 1.6 kW cm$^{-2}$ respectively.

Pulse-to-pulse variations of the breakdown time and the peak pulse current were found to be less than 1 μs and 1 A respectively. An additional slow drift of breakdown time and peak pulse current was observed over the course of the 20 min needed for the time-resolved measurement of a single discharge condition in one direction. This drift was found to be about 2 μs, leading to changes in the peak current of about 3 A.

The discharge could be observed from two directions, using the windows shown in figure 1. The light emission of the discharge was coupled into an optical fiber (diameter: 800 μm) using a biconvex lens. This lens limits the field of view to a small part of the discharge, as indicated in figure 3 by dotted lines. For the observation in the direction perpendicular to the target surface ($\perp$), a lens with a focal length of 120 mm was used, limiting the field of view to a 3 mm dot on the target’s racetrack at $r = 13.5$ mm (figure 3(a)). The light originates mostly from the bright region just in front of the target surface, indicated as the region of dominant emission in the figure. This region is so much brighter than the surrounding plasma that the
emission from the rest of the discharge volume in the field of view can be neglected. An explanation of how this region is defined will be given in section 5.1.

For the direction parallel to the target surface \((r, \parallel)\), a lens with a focal length of 150 mm was used (figure 3(b)). The field of view in front of the target was approximately 2 mm in diameter. The anode cover has a gap so that even emission very close to the target surface could be observed.

The position of the field of view could be varied by moving both the optical fibre and the lens, as indicated by the arrows in the figure.

The light was guided by the optical fiber to the spectrograph (Zeiss PGS2), which was equipped with an intensified CCD camera (Andor iStar DH320T−25U−A3). The spectrograph has a plane reflective grating with 1302 lines mm\(^{-1}\). All measurements were performed in the third diffraction order to obtain a sufficiently high spectral resolution. Thus, a spectral resolution of 1.5 pm (pixel to pixel) was achieved at the observed wavelength. Time resolution was achieved by synchronizing the camera’s gate to the power supply using a delay generator (Stanford Research Systems DG645) and then varying the gate delay. The gate width was set to values between 5 \(\mu\)s and 20 \(\mu\)s, and the emission was accumulated over 400 to 1000 consecutive discharge pulses.

The emission of a hollow cathode lamp (Cathodeon 3UNX Ti) was used for the measurement of the wavelength of the unshifted energy transition \(\lambda_0\). This was performed simultaneously with each measurement of the plasma emission by illuminating a separate part of the spectrograph entrance slit and integrating separately over the respective slit regions on the camera. The hollow cathode lamp was pulsed at 50 mA to provide sufficient light intensity even at the shorter gate widths. The hollow cathode lamp was also used to determine the instrumental profile, operated unpulsed at 10 mA to avoid broadening of the emission lines. More information on the determination of the instrumental profile is given in appendix A.

2.1. Emission lines

The selection of optical emission lines is very important. It is desirable to evaluate several emission lines simultaneously, thus increasing the data points available for the fit. The observed emission lines also need to be as bright as possible, to facilitate a high time resolution at an acceptable measurement duration. At the same time, ground state transitions should be avoided, as they are likely to be affected by self-absorption (thus changing the shape of the emission line). Additionally, Landé-g factors for the energy states involved should be available, to allow for the calculation of the Zeeman pattern of the line.

Taking all this into account, the titanium emission lines at 453.324 nm and 453.478 nm were identified as suitable candidates. As shown in table 1, the energies and electron configurations of the levels are very similar for both lines, which enables us to fit them with the same VDF parameters. This doubles the data points available for the fit, while only introducing the intensity of the second line as a single additional fit parameter. The emission lines considered here are shown in figure 4, together with the emission of the hollow cathode lamp (HCL), measured simultaneously. The titanium

![Figure 3.](image-url)
neutral emission lines are slightly affected by the wings of the titanium ion emission line at 453.396 nm. To take this into account, this line is also fitted but with a different set of VDF parameters. The VDF of ions in HiPIMS will be discussed in a subsequent paper.

In order to investigate whether the observed lines might be affected by self-absorption, two additional transitions were observed and the shape of the lines was compared. The lower level of the transition $3d^3(^4F)\rightarrow 3d^3(^4F)4s$ at 461.727 nm has a higher energy of 1.7 eV, and should thus be less affected by self-absorption. The line at 465.647 nm ($3d^3(^4F)4s\rightarrow 3d^2(^2D)4s^2$) transitions to the ground state, and should thus be more strongly affected by self-absorption. However, no difference between the line shapes could be observed. Since it is not plausible that all the lines should be equally affected by self-absorption, we conclude that the discharge can be treated as optically thin.

### 3. Line broadening mechanisms

In order to determine the VDF using the emission line broadening caused by the Doppler effect, other broadening mechanisms have to be separated from the Doppler broadening. To this end, the influence of the following broadening mechanisms has been considered:

- **The Doppler effect** itself has been shown to give rise to line broadening of between 2 pm and 10 pm in the HiPIMS target vicinity, during the on-time of the plasma [20].
- **The natural line width** is usually less than 0.1 pm, and can therefore be neglected [29].
- **van der Waals and resonance** broadening are only important at higher pressure, and can be neglected in this experiment [19].
- **Stark broadening** is caused by the interaction of emitters with ions and free electrons. At very high plasma densities, this effect is a convenient way to measure the electron density in a plasma. Using the measurements of Hermann et al [30] and the approximation formula of Griem [31], the line broadening caused by the Stark effect can be estimated. Assuming the electron density to be less than $10^{21} \text{m}^{-3}$ [32–34], the Stark broadening will be less than 1 pm, and can therefore be neglected.
- **The Zeeman effect** describes splitting of energy levels caused by strong magnetic fields. The effect can be calculated analytically, and was taken into account with a magnetic field strength of 0.1 T. The calculation was performed according to Condon and Shortley [35]. The outermost Zeeman components were shifted by around $±1.4$ pm.

The finite resolution of the spectrograph leads to an additional broadening. This instrumental profile can be determined using a suitably narrow emission line, e.g. of a hollow cathode lamp. The procedure that was used to determine the instrumental profile utilized in this work is described in appendix A.

In summary, we will assume that the Doppler effect, the Zeeman effect and the instrumental profile are the only factors which determine the shape and width of the optical emission line. All other effects can be neglected.

### 4. Physical model and fit process

Deconvolution of the measured signal is very challenging, because of the limited resolution of the spectrograph. Instead, a fit process is used. This, however, necessitates assumptions about the shape of the VDF.

The effect of collisions on the VDF can be approximated by the Krook collisional operator (sometimes also called BGK operator or tau approximation) [36–38]:

$$ \frac{df}{dt} = \frac{df}{dt} \bigg|_{\text{coll}} = -\frac{f - f_{eq}}{\tau}. $$

![Figure 4](image-url)
The formula describes how collisions cause a distribution function \( f \) to approach the equilibrium distribution \( f_{eq} \) in time \( t \) with the characteristic relaxation time \( \tau \). The equation can be solved to give [37, 38]

\[
f(t) = f_{eq} + (f(0) - f_{eq}) \exp(-t/\tau).
\] (2)

This solution can be used to describe the VDF of sputtered particles. They leave the target surface with the distribution \( f(0) \), enter the plasma and then experience collisions, driving the distribution function towards equilibrium. The initial distribution \( f(0) \) in our case is therefore the Thomson distribution \( f_T \), which describes the velocity of sputtered particles as they leave the surface [39]. The equilibrium distribution is the Maxwell–Boltzmann distribution \( f_M \) [38]:

\[
f(0) = f_T(E_b) \hspace{1cm} f_{eq} = f_M(T).
\] (3)

We can now reformulate equation (2) for our discharge:

\[
f = f_M + (f_T - f_M) \exp(-t/\tau)
\] (4)

\[
f = (1 - \exp(-t/\tau)) f_M + f_T \exp(-t/\tau)
\] (5)

\[
f(v, E_b, T) = \gamma \cdot f_M(v, T) + (1 - \gamma) \cdot f_T(v, E_b).
\] (6)

The factor \( \gamma = 1 - \exp(-t/\tau) \) describes the fraction of particles following the Maxwell distribution and will, therefore, be called the degree of relaxation. \( T \) and \( E_b \) are the parameters of the Maxwell and Thomson distributions, respectively.

The time \( t \) is an inconvenient parameter in this case, since newly sputtered titanium is continuously created during the on-time of the discharge. However, since the sputtered particles are moving away from the target, we can use the distance to the target surface, \( d \), as a measure for the lifetime of the observed particles:

\[
\gamma = 1 - \exp\left(-\frac{1}{\tau} \frac{d}{v_{tr}}\right)
\] (7)

with \( v_{tr} \) as the mean transport velocity with which the sputtered neutrals are moving away from the target surface: \( v_{tr} = \int_0^\infty v \cdot f_2(v) \cdot dv \).

\( E_b \), the parameter of the Thomson distribution, is often identified as the surface binding energy of the target and thus a material constant. In the case of titanium, \( E_b \) has been observed to be about 4.6 eV [40, 41]. In this work, however, we use \( E_b \) strictly as a fitting parameter, and compare to the material constant when appropriate.

In the direction perpendicular to the target surface, the following equations are used for the two VDF components [40]:

\[
f_T(v_{\perp}, E_b) = \frac{16}{\pi} \left(\frac{2E_b}{m}\right)^{3/2} \frac{v_{\perp}^2}{(v_{\perp}^2 + 2E_b/m)^3}
\] (8)

\[
f_M(v_{\perp}, T) = \left(\frac{m}{2\pi k_BT}\right)^{1/2} \exp\left(-\frac{m v_{\perp}^2}{2k_BT}\right)
\] (9)

with: \( v_{\perp} \) = perpendicular velocity

\( v_{\parallel} \) = parallel velocity

\( m \) = mass of particle

\( k_B \) = Boltzmann constant

\( T \) = temperature

\( E_b \) = Thomson parameter.

Equation (8) was derived from Thomson’s original formula, by not only changing to velocity coordinates but also transferring the distribution from a flux to a probability distribution. As such, the shorter residence time of faster particles is accounted for [42].

In the direction parallel to the target surface, the isotropic Maxwell distribution has the same formula. The Thomson distribution, however, becomes [43]

\[
f_T(v_{\parallel}, E_b) = \frac{E_b}{m} \left(\frac{v_{\parallel}^2}{v_{\parallel}^2 + 2E_b/m}\right)^{-3/2}.
\] (10)

It has to be noted that equation (8) assumes all particles to leave the surface in the normal direction. Correcting the formula to include the directional distribution requires exact knowledge of the geometry of the observed volume [44], which is not easily acquired in this experiment. Additionally, one would have to include the strongly non-uniform sputtering of the target surface, which would make the calculations very complex. As Bay et al discussed previously, this simplification should not drastically change the shape of the VDF, but might merely shift the Thomson distribution towards lower \( E_b \) values [44]. Within the limited resolution of our measurement, the VDF should, therefore, still be well parameterized, although the value of \( E_b \) might be lower than predicted in the literature.

The Doppler intensity profile \( D \) can be calculated from the VDF (equation (6)) using the relation \( v = c (1 - \lambda/\lambda_0) \). Apart from the Doppler profile, the total line shape is also influenced by the instrumental profile \( P \) and the calculated Zeeman pattern \( Z \). The convolution of these components yields the intensity profile of the emission line:

\[
I(\lambda, A, T, E_b, \gamma) = A \cdot D(\lambda, E_b, T) \ast P(\lambda) \ast Z(\lambda)
\]

\[
= A \cdot [\gamma \cdot D_M(\lambda, T) + (1 - \gamma) \cdot D_T(\lambda, E_b)] \ast P(\lambda) \ast Z(\lambda)
\] (11)

with: \( \lambda \) = wavelength

\( A \) = line intensity

\( D \) = complete Doppler profile

\( D_M \) = Doppler profile, Maxwell component

\( D_T \) = Doppler profile, Thompson component

\( P \) = instrumental profile

\( Z \) = Zeeman pattern

\( * \) = convolution operator.
This function can be fitted to the observed emission lines, optimizing the three free parameters of the VDF: the temperature \( T \), the Thompson parameter \( E_b \) and \( \gamma \) as the factor describing how far the VDF has progressed towards thermalization. In order to emphasize the difference between the parameters, \( T \) will be given in kelvins and \( E_b \) in electronvolts.

The VDF that we derive in this way is strictly speaking only the VDF of emitting titanium neutrals in the observed excited state. The VDF of titanium neutrals in other excited states or in the ground state could be different. However, the expected velocities of the sputtered neutrals are still too low to cause excitation under collision with other heavy particles. We will therefore assume excitation to occur via electron impact only. Furthermore, we assume that electron impact will cause only a very little change in the momentum of titanium due to the large mass difference between electrons and titanium. Under these two assumptions, the VDF of all excitation states of titanium neutrals is the same and this VDF can be observed by optical emission spectroscopy.

It is important to note that we do not expect the temperature \( T \) of the relaxed part of the titanium neutral VDF to correspond to the temperatures—or rather VFDs—of other species in the discharge. At the low pressure present in our experiment, a single gas temperature cannot be defined—as there are not enough collisions between neutral particles to cause a thermal equilibrium between the different species. As such, the temperature \( T \) describes the width of the Maxwell distribution, towards which the VDF is relaxing, but is not meant to imply that any form of thermal equilibrium is reached.

The magnetic field strength \( B \) and the wavelength of the natural transition \( \lambda_0 \) are not mentioned in equation (11) because they are not used as free parameters but instead set to a constant value to improve the fit. \( B \) was measured to be around 0.1 T in the first 5 mm distance to the target, where the dominant part of the emission originates, as will be shown later. This simplification should not introduce large errors, as the line broadening caused by the Zeeman effect is rather small. In similar situations, other authors have even decided to neglect this factor completely [16, 45].

\( \lambda_0 \) was measured using the emission of a hollow cathode lamp, and used as a constant. Thereby, the uncertainty of the fit of the measurement in the direction perpendicular to the target surface was reduced—the Thompson component of the Doppler profile being completely blue-shifted yet the Maxwell component isotropic.

The fit was performed using the ‘curve_fit’ function of the scipy.optimize package for the python programming language. The default ‘Trust Region Reflective’ algorithm was chosen for the fit. The algorithm allows the setting of bounds for the fitting parameter. This feature was used to constrain the fitting parameter to values above zero, since negative values and zero would cause an error in the calculation of the profile. The following values were used as the initial parameters: \( T = 80 \, 000 \, \text{K}, \ E_b = 5 \, \text{eV}, \ \gamma = 0.5 \).

5. Results and discussion

5.1. Origin of emission

In order to extract physical parameters from the observed spectral lines, it is essential to know where the observed light is originating from. The observed light is collected along the field of view, and a line-integrated profile observed. If the light originates from different regions—with, for example, very different neutral gas temperatures—then the line shape will be changed in a complex manner and fitting will be difficult. This could be the case in HiPIMS, where we expect the heavy particles to be very energetic close to the target, and thermalized with the cold background gas (\( \approx 1000 \, \text{K} \) [46, 47]) in the vicinity of the substrate.

In the direction perpendicular to the target surface, the field of view is limited to 3 mm in diameter (figure 3(a)). The emission is strongest directly in front of the target and becomes gradually fainter as the distance to the target surface increases. To measure this spatial dependence of the emission intensity along the \( z \)-axis, Abel inversion would need to be performed. However, that would necessitate a complete spatial scan of the emission, which is not feasible with the setup at hand. Using a camera for this measurement would make Abel inversion possible, but would require a filter with an optical width of less than 0.1 nm to distinguish the emission lines (compare figure 4).

Instead, the emission was observed in the direction parallel to the target surface and only the distance to the target was varied. This still yields an approximation of the profile along \( z \) that will be line integrated by the perpendicular measurement. The measurement was performed with a time resolution of 20 \( \mu \text{s} \) and the discharge was operated with a voltage of 590 V.

The normalized intensity (i.e. the line area) of the Ti I 453.324 nm emission line is plotted against the distance to the target (\( z \)) in figure 5 for the beginning (20 \( \mu \text{s} \) to 40 \( \mu \text{s} \)) and the end (80 \( \mu \text{s} \) to 100 \( \mu \text{s} \)) of the discharge pulse. The dark grey bars indicate the magnetron (left bar) and the anode cover (right bar). The light grey bars indicate additional vignetting due to the limited field of view (diameter: \( \approx 2 \), compare figure 3). The strongest part of the emission is located very close to the target surface. This is to be expected, since electrons are trapped there by the magnetic field and efficiently excite atoms. Later in the pulse, the emission is more concentrated close to the target, compared to the beginning of the pulse. As expected, these trends are the same as for the Ti I 453.478 nm emission line (not shown).

A simple approach is used to quantify this change. An exponential decay function is fitted to the data points not affected by vignetting, shown in the figure as dotted lines. Integrating this exponential decay function yields the collected light in the \( z \)-direction since each volume element along the \( z \)-axis is weighted equally under line integration [48]. We define the region of dominant emission as the volume from which 95% of the light originates. The region of dominant emission for the measurement perpendicular to the
target surface is thus a cylinder with a diameter of 3 mm as defined by the field of view and a length between 7 mm at the beginning and 5 mm towards the end of the pulse. A higher target power density leads to a shorter region of dominant emission, located closer to the target surface. The region of dominant emission in the perpendicular direction is shown in figure 3(a) with a length of 6 mm. Since the degree of relaxation $\gamma$ depends on the target distance (compare equation (7)), we will observe a line-integrated signal over regions with differing $\gamma$, and will thus only obtain an average value.

In the direction parallel to the target surface, the field of view is limited to a cylinder with a diameter of approximately 2 mm (figure 3(b)). The light originates from the region above the racetrack, which is a lot brighter than the surrounding plasma. The field of view is directed in such a way that it crosses the center of the target ($r = 0$). The field of view, therefore, crosses the ring shaped racetrack region twice. The spacial dependence of the intensity was measured in the same way as for the perpendicular observation before, this time scanning over the $r$-direction. It was found that the two regions of dominant emission become larger at the end of the pulse (not shown). Each of the two regions is about 14 mm long at the beginning and about 16 mm at the end of the discharge pulse. The two regions of dominant emission in the parallel direction are shown in figure 3(b) with a length of 15 mm.

Combining the intensity profiles in parallel and perpendicular direction can yield a 2D intensity map of the observed titanium neutral emission. For each point in time, the profiles in the $z$-direction and $r$-direction are multiplied together. The resulting emission intensity map is shown in figure 6 for three different times: $30 \mu s$, $50 \mu s$ and $90 \mu s$ after ignition. The color of each map is individually normalized to the maximum value of that map; however, the intensity scale on the right can be used for comparison. The map illustrates that the emission moves closer to the target surface with time but also gets wider, i.e. elongated in the $r$-direction. This change can most likely be explained by the higher electron density later in the pulse. The higher electron density will lead to a more rapid ionization of neutrals, which can thus penetrate less deep into the plasma bulk before being ionized. Additionally, the titanium neutral density over the racetrack will be depleted, because most of the sputtered material is ionized [49]. The normalized emission profile is thus elongated in the $r$-direction, emitting more strongly than before outside of the racetrack region.

5.2. Velocity component perpendicular to the target surface ($v_r/v_z$)

Figure 7 shows a representative measurement of the Ti I 453.324 nm emission line observed in the direction
perpendicular to the target surface. As mentioned before, the line is fitted together with the Ti I 453.478 nm line, which is not shown to keep the graph readable. The best fit is shown as a solid line, together with the Zeeman pattern as vertical lines and the other fit components as dashed lines.

The discharge was operated at a 590 V. The measurement was taken at 75 µs to 80 µs.

The emission line is blue-shifted with respect to λ0, marked by the vertical dashed line in the upper part of the figure. The peak of the emission line is shifted by about 5 pm, which corresponds to a velocity shift of about 2.5 km s⁻¹. The residue of measurement and fit is shown in the lower part of the figure. The residue is not randomly distributed, which indicates that the chosen fit function does not perfectly represent reality. This is to be expected, as the assumption about the shape of the fit function that was made here is a simplification. However, the residue is rather small (<5%) and the blue shift and overall shape of the line are well reproduced by the fit. This indicates that the Krook operator can indeed be used to adequately describe the VDF (compare equation (6)).

The fit yields a result for the three free parameters of the VDF: \( E_b = 4.2 \, \text{eV}, \gamma = 0.7 \) and \( T = 120 \, 000 \, \text{K} \) (11 eV). Each of these parameters will now be discussed in detail.

The calculated value of \( E_b = 4.2 \, \text{eV} \) is slightly lower than results from literature of 4.6 eV [40, 41]. There are three possible reasons for this difference:

(i) The influence of atoms moving in a direction other than normal to the target surface, which, as discussed above, is not included in equation (8).

(ii) Systematic errors arising from the determination of the instrumental profile, which has a strong effect on the absolute value of \( E_b \).

(iii) The limited validity of the Thompson distribution for sputtering by low energy/low mass ions [50–52].

The third possibility will be explored in more detail in section 5.4.

The high degree of relaxation, \( \gamma = 0.7 \), shows that most of the emitting titanium atoms in the target region do not follow the Thompson distribution, and have already collided at least once before being detected. For the estimation of the relevant momentum transfer cross sections, we will assume a total heavy particle density of \( 1 \times 10^{20} \, \text{m}^{-3} \), an ion density of \( 1 \times 10^{20} \, \text{m}^{-3} \) [33] and an average ion temperature of 50 000 K, which is about the mean of the high observed temperatures of titanium neutrals and those of argon neutrals (the latter being assumed to be around 1000 K) [46, 47].

The high degree of relaxation is surprising, since the mean free path of neutral particles in HIPIMS is believed to be several cm [9, 53, 54]. Calculating the mean free path assuming hard-sphere collisions of titanium with argon yields \( \lambda_{\text{MS}} \approx 50 \, \text{mm} \). Most of the sputtered particles should therefore pass through the region of dominant emission without any collisions, and \( \gamma \) should thus be much lower. A possible explanation for this discrepancy might be that polarization scattering on ions is the more important collision process [25]. Polarization scattering occurs when the electric field of a charged particle causes a neutral to be polarized and a Coulomb force thus acts on both particles [55]. Cross sections for this process could not be found; however, an approximation formula by Dalgarno et al can be used as an estimation [56, 57]. Using the tabulated polarizability of titanium [58], the mean free path for polarization scattering can be estimated to be of the order of 20 mm. This is still too large to explain the high degree of relaxation observed here.

To resolve this puzzle, we postulate a three step process:

(i) Sputtered neutrals are ionized by electron impact or by charge exchange with ions in the plasma. The cross section for resonant charge exchange is of the order of \( 10^{-14} \, \text{cm}^{-2} \) [55], implying a short free mean path of the order of 0 mm for the given ion density. This leads to the formation of energetic ions; (ii) The mean free path for large angle Coulomb collisions is only about 2 mm [55], implying a redistribution of the energy of the ion population and thus a high ion temperature; (iii) Resonant charge exchange from this hot ion population to neutral species causes the formation of a similar Maxwellian neutral population. This sequence of resonant charge exchange and Coloumb collisions might thus explain the observed high degree of relaxation. Under this assumption of relaxation caused by Coulomb interaction, the characteristic relaxation time for ions \( T_1 \) can be estimated using the work of Montgomery and Tidman [59] to be about \( T_1 \approx 1 \, \mu\text{s} \). For ions, the relaxation to a Maxwellian could thus occur after about 3 mm distance traveled.

These values should be treated with caution, since the cross section for Coulomb collisions \( (\sigma_C) \) depend strongly on the relative velocities \( (\nu_R) \) of the colliding particles \( (\sigma \propto 1/\nu_R^3) \). This also means that it takes a longer time to fill the high velocity tail of the Maxwell distribution [59]. The Maxwell distribution might thus only be a good approximation for the observed low energy part of the VDF and important differences might be present for higher velocities which are invisible to the employed diagnostic.

This proposed charge exchange coupling of titanium neutral and ion VDFs might also explain, why a previous study did not find significant differences between the VDFs of neutrals and ions [20], despite the strong electric fields present in the target vicinity of a HiPIMS discharge [60, 61].

This result can also be related to the generalized recycling model by Anders et al [62, 63]. In this model, a parameter \( \beta \) is used to denote the ratio of sputtered particles which return to the target. For titanium, this parameter is supposed to be around \( \beta = 0.9 \), which means that 90% of the sputtered titanium returns to the target surface [64]. This return effect is usually thought to be caused by the back attraction of ions by the electric fields. However, our results indicate that part of this return effect might be due to collisions.

The Maxwellian fraction of titanium neutrals has a high temperature of \( T = 120 \, 000 \, \text{K} \), which can be explained as follows. Because of the reduced argon density (rarefraction [65, 66]) and the small cross section for neutral–neutral collisions, the population of Maxwellian titanium neutrals mostly experience collisions with other titanium neutrals and ions. Because of its high average velocity, freshly sputtered material acts as a source of energy for this population. The
Temperature is therefore determined only by heating due to collisions with freshly sputtered material and cooling due to diffusion of high-energy particles out of the observed discharge volume. We therefore do not expect the titanium atoms to be thermalized with the working gas (argon), for which a much lower temperature (of the order of 1000 K) has been observed under similar discharge conditions [46, 47].

This explanation is supported by a comparison of the average energies of particles following the Thompson and Maxwell distribution with the observed parameters. For the Thompson distribution, the mean energy of particles leaving the surface can be calculated:

\[
\mathbb{E}_T = 2E_0 \ln \left( \frac{E_{\text{max}}}{E_0} \right) - 3E_0
\]

(12)

\(E_{\text{max}}\) being the maximal transferable energy of the impinging ions onto the target with an energy of \(E_0\):

\[
E_{\text{max}} = \frac{4m_i m_2}{(m_i + m_2)^2} E_0;
\]

(13)
equation (12) is derived in appendix B. If we assume the whole discharge voltage to drop over the cathode sheath, the energy of impinging ions should be around \(E_0 \approx 500 \text{ eV}\). The average energy of particles following the Thompson distribution then can be calculated: \(\mathbb{E}_T \approx 28 \text{ eV}\). The relation \(E_{\text{Max}} = \frac{1}{2}kT_\text{e}\) leads to the mean energy of the particles of the Maxwell part of the VDF: \(E_{\text{Max}} \approx 15 \text{ eV}\). The energy transferred from Thompson to Maxwell distribution is therefore about 55%. That is close to the value of \(2m_i m_2/(m_i + m_2)^2 \approx 0.5\) for the average transferred energy for a single hard-sphere collision [55].

Using the VDF parameters determined, various representations of the VDF can be calculated. This is useful for comparison with literature. Figure 8(a) depicts the VDF as a function of kinetic energy with components on a logarithmic scale. This representation is often chosen to present results of energy resolved mass spectroscopy.

Energy resolved mass spectroscopy in HiPIMS has so far only been performed on ions. Because the VDF of ions is additionally affected by electric fields and the measurement is usually performed at about 100 mm distance from the target, important differences can be found when comparing to the VDF of neutrals presented here. The main difference is that the VDFs of ions as measured using mass spectroscopy often show a high-intensity peak at low energies, which drops off much more quickly with energy than in the neutral VDF presented here. This feature is commonly explained by thermalization with the working gas, as mass spectrometers are usually positioned at several centimeters distance from the target [6, 8–10]. This feature is missing here because the emission originates from the region closest to the target, where the sputtered particles are not yet thermalized with the working gas. Another difference is that the interpretation of mass spectrometer data with our VDF assumptions (Maxwell + Thompson) has often been tried, but has usually not shown good agreement [9, 13]. This may originate from the fact that ions are additionally affected by electric fields. The strength and orientation of the fields traversed by the ions also depends on where the ionization occurred. Thus, the energy distribution of ions cannot be accurately described by the simple description employed here. Figure 8(b) shows the one-dimensional velocity distribution function according to equations (6) to (9), normalized to unity. Positive values denote particles moving in the \(z\)-direction, away from the target, and thus correspond to the blue-shifted part of the emission line. The VDF is shown on a linear scale, to facilitate comparability with literature and with the resulting emission as shown in figure 7. The shape of the VDF is similar to what can be observed in the emission line presented in figure 7, with a kind of kink noticeable between the peaks of the Maxwell and Thompson components. The peak of the velocity distribution function is \(v_{l, \text{mode}} = 2.5 \text{ km s}^{-1}\). The mean velocity of the distribution function can be calculated as follows:

\[
vmean = \frac{\int_{0}^{\infty} f(v_l) v_l \, dv_l}{\int_{0}^{\infty} f(v_l) \, dv_l} = 1.5 \text{ km s}^{-1}.
\]

The transport velocity away from the target is

\[
vT = \frac{\int_{0}^{\infty} f(v_l) v_l \, dv_l}{\int_{0}^{\infty} f(v_l) \, dv_l} = 4.3 \text{ km s}^{-1}.
\]

The FWHM of the distribution is 9.2 km s\(^{-1}\).

### 5.3. Velocity component parallel to the target surface (\(v_l/v_n\))

The top part of figure 9 shows a measurement of the Ti1453.324 nm emission line observed in the direction parallel to the target surface. Lens and fiber were positioned so that the field of view was very close to the target, located only 1 mm to 3 mm in front of the surface because the emission intensity is maximal there (compare figure 5).

The emission line observed parallel to the target surface is mostly symmetrical, as expected. A minor asymmetry is caused by the asymmetrical instrumental profile (compare appendix A). The symmetric nature of the VDF components, shown in the bottom part of the figure, makes it difficult to
separate them clearly. The small differences in the shape of the wings of the Maxwell and Thompson profiles are not significant enough to obtain the VDF parameters reliably. The calculated profile in figure 9 was thus not fitted, but was instead calculated using $E_b = 4.2$ eV and $T = 120\,000$ K, as obtained from the fit of the perpendicular measurement. $\gamma$ was then varied until good agreement between measurement and calculated profile was reached at $\gamma = 0.4$. The lower value for $\gamma$ is expected, since the field of view in this direction is very close to the target surface, whereas the line integration of the perpendicular observation includes regions further apart from the target, where a larger portion of the sputtered material has experienced collisions.

Although the data cannot be fitted, this comparison shows that the proposed VDF is consistent with the emission profile in parallel direction. The lower part of figure 9 shows the calculated VDF, and the contributions of the Thompson and Maxwell components. Since the VDF is symmetrical, the mean velocity is 0. The transport velocity is 3.4 km s$^{-1}$ and the FWHM of the distribution is 7.1 km s$^{-1}$.

5.4. Time and power dependence

The measurements perpendicular to the target surface were performed in a time-resolved manner, with a temporal resolution of 5 $\mu$s. The evolution of $E_b$, $T$ and $\gamma$ is shown in figure 10 together with the discharge current. The graphs show the average of five measurements, with $2\sigma$ as error bars.

At 20 $\mu$s, the discharge is ignited and the current begins to rise. At 100 $\mu$s, a value of 50 A is reached and the voltage is switched off. After that, the current drops within 20 $\mu$s to nearly zero. $E_b$ rises from 2.5 eV at 20 $\mu$s to approximately 4.2 eV at 45 $\mu$s and then stays relatively constant until 15 $\mu$s after the end of the pulse at 100 $\mu$s. From 115 $\mu$s to 130 $\mu$s, $E_b$ drops to about 2 eV. $T$ rises from 70 000 K at 20 $\mu$s to 120 000 K at 60 $\mu$s and then stays constant until the end of the pulse. After 115 $\mu$s, $T$ begins to drop sharply to about 50 000 K at 130 $\mu$s. $\gamma$ stays nearly constant during the pulse, showing only a small rise from 0.65 at the beginning of the pulse to a value of 0.7 at 100 $\mu$s.

The nearly constant degree of relaxation $\gamma$ in the perpendicular direction is at first surprising. The higher amount of sputtered material and the higher ion density later in the pulse should lead to a higher collision frequency and thus to an increase of $\gamma$ (compare equation (7)). At the same time, however, the region of dominant emission becomes smaller and moves closer to the target surface, where the freshly sputtered material is created (compare section 5.1). This corresponds to a lower $d_\perp$ in equation (7) leading to a
smaller $\gamma$ value. These two effects counteract each other. Additionally, $\gamma$ has a rather weak dependence on both the collision frequency and the length of the region of dominant emission, so that a change in either will cause only a minor variation of $\gamma$, which is what we observe here.

To understand the evolution of $E_b$ and $T$ during the pulse, it is important to determine whether the evolution is time-dependent or rather dependent on the discharge power at that point in time. For this purpose, the time-resolved measurements presented in figure 10 were performed for the three different discharge conditions described in section 2 (compare figure 2). For each of the discharge conditions, the measured current and voltage were used to calculate the time evolution of the target power density during the pulse. Figure 11 shows VDF parameters during the on-time of the discharge now plotted as a function of this (time-dependent) target power density instead of time.

Both $E_b$ and $T$ exhibit a steep rise until a target power density of approximately 0.6 kW cm$^{-2}$ is reached. After that, both parameters stay constant at about $E_b \approx 4.2$ eV and $T \approx 120$ 000 K. Within the accuracy of the measurement, these trends are the same for the three different conditions shown in figure 11. That leads to the conclusion that the VDF of sputtered titanium is only dependent on the discharge power for power densities below 0.6 kW cm$^{-2}$, and constant for power densities above that value.

This observation leads to the question of how the initial power dependence of $E_b$ and $T$, which disappears above a certain power threshold, can be explained. Palmucci et al observed the same behavior as an initial rise and then saturation of line width. They interpreted the changing line width as being caused by cooling due to interaction with the working gas and the saturation as a ‘rarefaction window’ in which interaction with the background gas ceases.

Another possible explanation is that the Thompson distribution works best for sputtering by heavy high-energy ions in the range of 1 keV and more. For sputtering by ions with low energy or mass, modifications to the distribution are commonly observed [50, 51]. For argon ions, these modifications were observed to appear at ion energies of around 500 eV [52], which is very close to the ion energies in the presented measurements (cathode sheath potential $\approx 500$ V). Those modified distributions exhibit a reduced probability for high energies, which could be interpreted as a Thompson distribution with a lower $E_b$ when observed with the limited spectral resolution of our experiment. The change in $E_b$ might thus indicate the transition from sputtering by lighter argon (40 u) to titanium (48 u) self-sputtering due to rarefaction. It seems reasonable to suppose that this transition is determined by the target power density.

Another possible explanation is the abovementioned coupling of neutral and ion VDFs via charge exchange collisions. The observed Thompson distribution might be partly populated
by ions affected by Coulomb drag or decelerated in electric fields and subsequently neutralized via charge exchange.

In both cases, the evolution of $T$ could then be understood as a dependence on $E_p$. If the temperature of the Maxwellian titanium population is mostly determined by heating from collisions with freshly sputtered material and by cooling by diffusion, the average energy of the Thompson and Maxwell part of the VDF should show a fixed ratio. This can be seen in figure 12. The upper part of the figure shows the average energy of the Thompson ($E_T$) and Maxwell ($E_M$) part of the VDF. The lower part shows the ratio: $E_M/E_T$. While the average energies of particles, following either of the two distributions, do rise with the discharge power density between 0 and 0.6 kW cm$^{-2}$, the factor stays constant at $E_M/E_T = 0.55 \pm 0.05$. This shows that the evolution of $T$ can indeed be explained by the change of $E_p$.

6. Conclusion

The velocity distribution of sputtered titanium in the target vicinity of a HiPIMS discharge was measured by evaluating the Doppler broadening of optical emission lines. The VDF of atoms close to the target can be adequately described by the Krook operator, as the sum of a Thompson distribution and a Maxwell distribution with a very high temperature of about 120 000 K (10 eV). In the region in front of the target surface, from which most (>95%) of the light originates, the distribution has already mostly relaxed to a Maxwellian. About 70% of particles follow a Maxwell-like distribution. The mean free path for momentum transfer of neutrals is too large to explain this high degree of relaxation. It is therefore assumed that this Maxwellian population might be created from ions, via resonant charge exchange.

The VDF changes with the applied power up to a power density of 0.6 kW cm$^{-2}$. Above that threshold, the VDF remains constant. The change of $E_p$ might be caused by charge exchange with titanium ions that were slowed down prior to neutralization or by the limited validity of the Thompson distribution for particles sputtered by low energy, low mass ions. In both cases, the change in $T$ is caused by the change in $E_p$, as collisions with freshly sputtered particles is the primary source of heating for the Maxwellian distribution.

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Appendix A. Instrumental profile

In order to determine the instrumental function of a spectrograph, it is customary to measure a narrow emission line. The measured profile equals the instrumental profile if this emission line is much more narrow than the instrumental profile of the spectrograph. In this work, a hollow cathode lamp was used as the source of narrow emission lines. A fit function was derived and fitted to three titanium neutral lines simultaneously, in order to improve the effective resolution of the fit. The fit function has no physical meaning, but is instead only derived to approximate the observed emission lines as closely as possible. An asymmetrical pseudo-Voigt profile was used, as the instrumental profile can be observed to be asymmetrical. An additional Gauss profile was added to this pseudo-Voigt profile, in order to approximate the right flank of the instrumental profile more closely:

$$P(\lambda) = \left( \frac{2\mu}{\pi} + 2(1 - \mu)\sqrt{\ln 2/\pi} \right)^{-1}$$

$$\cdot \left[ w_l^2 \frac{2\mu}{\pi} (4(\lambda - \lambda_0)^2 + w_R^2)^{-1} + 2(1 - \mu)\sqrt{\ln 2/\pi} \exp \left( -\frac{4\ln 2}{w_R^2}(\lambda - \lambda_0)^2 \right) \right]$$

$$+ \int G \sqrt{\frac{4\ln 2}{w_G^2}} \exp \left( -\frac{4\ln 2}{w_G^2}(\lambda - \Delta_G)^2 \right),$$

with $\mu = \mu_L, w = w_L$, for $\lambda \leq \lambda_0$

$\mu = \mu_R, w = w_R$, for $\lambda > \lambda_0$ (A.1)

The reason for the asymmetry of the profile is not clear. The asymmetry is not caused by the TiI 453.324 nm emission line, since it can always be observed when measuring narrow lines with our setup (e.g. from a helium neon laser or other hollow cathode lamps).

The measured emission lines might not be much more narrow than the instrumental profile in this case, because of the high spectral resolution. It is therefore important to include the actual emission line shape in the fit. Wagenaar and Galan found titanium emission lines in a hollow cathode lamp to be of Gaussian shape, and approximated the line with a Doppler profile with a temperature of 800 K to 950 K [67]. Thus, the instrumental function (equation (A.1)) is convolved with a Doppler profile with a temperature of 800K and the result fitted to the measured data. The fit and the resulting instrumental profile for a single line are shown in figure A1. Fit and instrumental function are nearly identical, meaning that the actual width of the line contributes only to the measured line shape—which is instead almost completely determined by the instrumental profile. This is fortunate, as it means that the uncertainty of the width of the actual line causes only a minor uncertainty in the determined instrumental profile. The parameters of the fit function (equation (A.1)) that were determined in this way were $w_L = 0.00653$ nm, $w_R = 0.00173$ nm, $\mu_L = 0.7795$, $\mu_R = 1.0$, $I_G = 1029.5$, $\Delta_G = 0.005$ nm and $w_G = 0.0115$ nm.
Appendix B. Mean energy of the Thompson distribution

The mean energy of an energy distribution \( f \) is defined as

\[
E = \frac{\int_0^\infty E f(E) dE}{\int_0^\infty f(E) dE}.
\]  

(B.1)

For the Thompson distribution,

\[
f_T(E) = \frac{2E_b E}{(E + E_b)^3},
\]  

(B.2)

integration is not performed to infinity, but instead to a value \( E_{\text{max}} \) which describes the maximal transferable energy of ions impinging onto the target with an energy \( E_0 \) [42]:

\[
E_{\text{max}} = \frac{4m_1 m_2}{(m_1 + m_2)^2} E_b.
\]  

(B.3)

We first perform the integration in the denominator of the fraction in equation (B.1):

\[
\int_0^{E_{\text{max}}} f_T(E) dE = -2E_b E_b + 2E_{\text{max}} \frac{E_{\text{max}}}{(E_b + E_{\text{max}})^2} \bigg|_0^{E_{\text{max}}}
\]

\[
= -E_b E_b + \frac{2E_{\text{max}}}{2(E_b + E_{\text{max}})^2} + 1 \approx 1.
\]  

(B.4)

The last step was performed assuming \( E_{\text{max}} \gg E_b \). In our case, \( E_{\text{max}} \) is about two orders of magnitude bigger than \( E_b \).

Integration of the numerator in equation (B.1) yields

\[
\int_0^{E_{\text{max}}} E f_T(E) dE = E_b \frac{3E_b}{(E_b + E_{\text{max}})^2} + 2E_b \ln(E_b + E_{\text{max}}) \bigg|_0^{E_{\text{max}}}
\]

\[
= E_b \frac{3E_b}{(E_b + E_{\text{max}})^2} + 2E_b \ln(E_b + E_{\text{max}}) - 3E_b \quad \text{for} \ E_{\text{max}} \gg E_b.
\]  

(B.5)

The second-to-last step is again only possible if \( E_{\text{max}} \gg E_b \). The mean energy of the Thompson distribution is thus

\[
f_T(E) = 2E_b \ln \left( \frac{E_{\text{max}}}{E_b} \right) - 3E_b.
\]  

(B.9)

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