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Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

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Abstract. Reactive high power impulse magnetron sputtering (HiPIMS) of metals is of paramount importance for the deposition of various oxides, nitrides and carbides. The addition of a reactive gas such as nitrogen to an argon HiPIMS plasma with a metal target allows the formation of the corresponding metal nitride on the substrate. The addition of a reactive gas introduces a new dynamic to the plasma process, such as hysteresis, target poisoning and rarefaction of two different plasma gases. This dynamic is investigated for the deposition of chromium nitride by a reactive HiPIMS plasma using energy- and time-resolved ion mass spectrometry, fast camera measurements and temporal and spatial resolved optical emission spectroscopy. It is shown that the addition of nitrogen to the argon plasma gas strongly changes the appearance of the localized ionization zones, so called spokes, in HiPIMS plasmas. In addition, a very strong modulation of the metal ion flux within each HiPIMS pulse is observed, with the metal ion flux being strongly suppressed and the nitrogen molecular ion flux being strongly enhanced in the high current phase of the pulse. This behavior is explained by a stronger return effect of the sputtered metal ions in the dense plasma above the racetrack. This is best observed in a pure nitrogen plasma, because the ionization zones are most confined implying a very high local plasma density and thereby also an efficient scattering process.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

1. Introduction

High power impulse magnetron sputtering (HiPIMS) plasmas are characterized by a high degree of ionization and a very energetic metal growth flux leading to superior material properties [1, 2]. Power densities at the target of several kW cm\(^{-2}\) are realized by using short pulses of 10 to 200 µs and duty cycles of a few percent only.

Many studies focus on unraveling the dynamic of a HiPIMS plasma. The intense sputter wind in a HiPIMS pulse causes gas rarefaction after a time span of 10...30 µs after the onset of the plasma pulse [3]. At target power densities above 1 kW cm\(^{-2}\), localized ionization zones, so-called spokes, are observed which rotate along the plasma torus with a typical velocity of 10 km s\(^{-1}\) [4, 5, 6, 7]. It is assumed that the localized ionization zones correspond to regions of high electrical potential, and are, therefore, the source of an energetic group of ions of typically few tens of eV in the growth flux on the substrate [8, 9, 10]. The spoke pattern depends on target material, plasma gas, power density and pressure [11]. By adding a reactive gas such as oxygen or nitrogen to a HiPIMS plasma specific oxides and nitrides can be deposited on the substrate. The dynamic of such reactive HiPIMS process might be similar to that of a non-reactive HiPIMS plasma, but there are significant differences. In the case of a reactive admixture to the argon plasma gas, the dynamic of a HiPIMS plasma is strongly influenced by three factors: (i) target poisoning occurs, when the reactive component not only reacts at the substrate, but also at the target side of the process to form a compound. This may lead to hysteresis, because target current and voltage depend on the secondary electron emission coefficient at the target which in turn depends on the compound formation on the target. A starting point to model reactive magnetron sputtering is often the Berg model [12]. Later the implantation of unbounded reactive ions into the target was considered in the Reactive Sputter Deposition (RSD) model [13] which is capable to explain abrupt poisoning of the target. Nevertheless, reactive magnetron sputtering even in DC is still not fully understood. Observations like double S-shaped hysteresis process curves [14] or the lack of hysteresis under certain operating conditions cannot be fully explained by the described models. (ii) the power dissipation in the plasma is strongly affected, because molecular gas possess many more degrees of freedom such as rotational and vibrational states, which can dissipate the energy of the electrons, without leading to ionization [15]. Therefore, the plasma density is lower and the impedance of a plasma containing molecular species is usually much higher. (iii) charge exchange reactions can become much more efficient, when the electronic states of the collision partners are comparable. Usually resonant charge exchange reactions are very efficient, when the collision partners are identical, because identical electronic states overlap, which allows efficient charge transfer according to Fermis golden rule. This holds for the charge transfer between the same species being charged and neutral. The threshold where charge exchange reactions dominate above momentum transfer for N\(^{+}\) ions in N\(_2\) is around 40 eV [16]. Consequently, especially the high energy tail of the Thompson distribution of sputtered and ionized nitrogen contributes to the production of slow
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

$N_2^+$ ions. In the case of a collision between metal atoms and plasma gas atoms such as argon or nitrogen, a similar behavior is expected. Since a noble gas atom possesses much less electronic excited states compared to molecular species, the charge transfer between metal ions and argon is much less efficient compared to the very same process with molecular ions. These charge exchange reactions are strongly affecting the growth flux in HiPIMS, because any collisions will thermalize an energetic growth flux, which deteriorates the desired energy input during film growth.

The impact of the addition of a reactive gas to a HiPIMS plasma on film deposition and on the energy distribution of ions are studied by several authors. It was demonstrated that any hysteresis can be mitigated during reactive HiPIMS of $\text{ZrO}_x$ [17] due to a higher compound erosion rate at the target. This led to better film qualities and even an improved deposition rate compared to dcMS. Furthermore, it was observed that the hysteresis can be suppressed by selecting an optimum pulsing frequency of the HiPIMS plasma for titanium sputtering in Ar/$\text{O}_2$ mixtures [18]. HiPIMS of titanium oxide showed, that moderate peak power densities resulted in improved film qualities compared dcMS with only a small loss in deposition rate [19]. Finally, reactive HiPIMS deposition of $\text{CrN}$ films was found to increase surface smoothness and density slightly while drastically decreasing the deposition rate [20].

Greczynski et al. applied time- and energy-resolved mass spectrometry to HiPIMS of chromium in Ar/$N_2$ mixtures to measure the ion energy distribution functions (IEDF)[21]. The temporal resolution of their mass spectrometer setup was 10 $\mu$s and the energy resolution 1 eV. Nitrogen admixtures were varied from 0% up to 83%. The IEDF of $\text{Cr}^+$, $\text{Cr}^{2+}$, and $N^+$ show similar characteristic. The same holds for the IEDF of $\text{Ar}^+$ and $N_2^+$. Time-resolved IEDFs showed that the composition of the ion flux varies throughout the pulse. At the beginning, the ion flux is dominated by the plasma gas, followed by an increase in the metal ion flux. The final part of the discharge is dominated again by thermalized working gas ions, because the target current is significantly reduced due to the peculiar characteristics of the power supply in use.

This illustrates that the dynamic of reactive HiPIMS processes is much more complex compared to non-reactive HiPIMS. The plasma impedance is changing again in a complicated manner with the gas mixture and target poisoning and hysteresis effects heavily influence the performance of the process [22]. In this paper, we want to address the question how the growth flux in a HiPIMS plasma is affected when going from a non-reactive process using argon as plasma gas only to a very reactive process using nitrogen gas only. Since the energetic growth flux is influenced by the state of localization of the ionization zones, we combine three diagnostics, namely energy and time-resolved mass spectrometry to analyze the growth flux itself, simultaneous ICCD camera measurements to characterize the formation and shape of the ionization zones and time resolved optical emission spectroscopy. By a correlation of the results of these diagnostic methods, the temporal evolution of the identity and the energy of species arriving at the substrate is unraveled as well as the physical mechanisms leading to specific energies for the different species.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

2. Experiment

Voltages are measured directly at the target and currents are measured at the output of the Huettinger power supply. The employed VI-probes consist of a calibrated Pearson probe and a high voltage probe. All signals are monitored with an oscilloscope (sample interval $dt = 40$ ns). The voltage pulses are very rectangular and only the current varies strongly during the pulse, as shown in Fig. 1a. One may identify three prominent phases in the temporal evolution of the current: (i) the ignition lag - the current does not rise immediately when applying the voltage at the beginning of the pulse. This delay is typical for HiPIMS plasmas and differs with target material, magnetic field strength, depth of the racetrack in the target, working gas composition and duty cycle; (ii) ignition and current rise - after ignition, the plasma builds up and the current rise usually saturates after typically 40 $\mu$s due to gas rarefaction, reaching a high current at the end of the pulse; (iii) voltage and current drop - at the end of the pulse, the voltage and current drop. This variation does not occur instantaneously due to the inductance in the low pass filter connected to the target, as discussed below.

Fig. 1b shows the current and voltage wave forms for a discharge in pure nitrogen. It is typical for discharges to ignite later in reactive gases compared to noble gases. In the reactive case, the ignition occurs at around 40 $\mu$s while in the non-reactive at around 10 $\mu$s. The discharge current does not reach a plateau regime before the end of the pulse and the current is continuously rising. A change of the chemical composition of the target, which leads to a change in secondary electron emission coefficient and sputter yield, changes the dynamics of the discharge and leads to a slower increase of the discharge current.

A careful inspection of the current and voltage curves at the end of the plasma pulse comparing argon and nitrogen show a significant difference. Whereas the current for nitrogen drops similar to the current for argon, the voltage in the nitrogen case remains high for 20 $\mu$s after the end of the pulse. This behavior is not observed for the case of pure argon in Fig. 1a. Here a negative peak is observed in the rising flank of the discharge voltage. This voltage peak occurs where the time constant of the falling current $i(t)$ at around 167 $\mu$s is changing and is caused by the inductance of the low-pass filter $u_L(t) = L\frac{d}{dt}i(t)$. A similar effect is seen for argon/nitrogen mixtures (not shown here).

The difference between the argon and nitrogen case may be explained by the different time constants $\tau = L/R$ for the discharging of the target electrode, approximated as a plate capacitor, after switching off the power source: a voltage at the inductor in the low pass filter builds up after switching off the current due to self-induction. The remaining plasma acts as a charge reservoir and closes the circuit to ground. Hence $L$ is given, the 2.2 k$\Omega$ resistor in the low pass filter and the changing conductivity of decaying plasma determine the time constants. Naturally, also the conductivity of the target surface will have an influence and might change especially in the nitrogen case due to nitride formation.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

Apparently, this effect is more efficient in the case of nitrogen as plasma gas, because the voltage seems to remain constant despite switching off the current. A simple electronic equivalent circuit model is supporting this reasoning qualitatively. Any quantitative interpretation is, however, ambiguous, because this electronic equivalent circuit model cannot describe a decaying plasma very well. This interpretation of the differences in the IV curves when comparing pure argon HiPIMS and pure nitrogen HiPIMS plasmas is consistent with the general analysis of a pure nitrogen plasma in this paper. As will be demonstrated below, a nitrogen HiPIMS plasma exhibits a very high local plasma density in front of the target. This high local density can very efficiently maintain the charge state at the target by recombination at the target surface after switching off the current.

Time-resolved ion energy distribution functions (IEDF) of \( \text{Cr}^+ \) and \( \text{Cr}^{2+} \) are measured using a HIDEN EQP 300 HE mass spectrometer (MS). The extraction potential of the MS is -122 V. Such a high extraction voltage may induce secondary ions due to secondary electrons accelerated inside the mass spectrometer, if the background pressure in the vacuum housing of the EQP is poor. This is not the case here, and we used different extraction voltages in different setups without seeing any influence on the IEDFs. The target and the MS are facing each other with a distance of 13 cm, with the MS pointing at the racetrack on the target using a 50 \( \mu \)m orifice. The adjustment onto the racetrack required a tilt of 3\(^\circ\). Measurements of the ions were performed with the main and less abundant isotopes. The main isotopes have a higher count rate and thus show more details in the IEDF but have the disadvantage of causing saturation of the SEM detector when intensities are too high. Less abundant isotopes show weaker signal but prevent saturation. The IEDF shown later consists either of measurements of the main isotope or of a composition of two isotope measurements. For energies ranging from 0 eV to 100 eV in 0.2 eV steps the ions arriving at the SEM detector are counted for 170 pulses. The detector output is connected to a transient recorder (Multichannel Analyzer, FAST ComTec GmbH), which gives a time resolution of 100 ns. The data were averaged over 20 points, resulting in a time resolution of 2 \( \mu \)s. Each measurement for a specific energy consists of 30000 data points, which corresponds to a total time of 3 ms. The time-of-flight (TOF) inside the MS was subtracted from the measured data for all species. Time-of-flights from target to MS were not subtracted, as they depend on the energy of an ion which varies over a great range. Also not every ion is created in front of the target, thus the travel distance varies. This leads to a shift in time between measured current and IEDF.

The spokes are recorded using a fast intensified CCD camera (PIMAX 1024, Princeton Instruments), mounted facing the target surface. The total plasma emission is recorded with a time resolution of 100 ns, and a spatial resolution of 0.03 mm\(^2\) pixel\(^{-1}\). The gate width of 100 ns was chosen to be shorter than the characteristic spoke motion time of 10 km/s. Images of several pulses often show different patterns as the formation of spokes is a highly dynamical process. This makes it hard to identify a typical spokes pattern for given discharge parameters. Thus for each set of parameters 200 images were
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium.

taken. The intensity profile of every image was then compared to the other 199 images and the correlation coefficient was calculated for every azimuthal shift between the two intensities. The maximum correlation coefficient then was used for each combination of two images. The image with the highest average correlation coefficient to all other images then shows the most probable spoke pattern for these discharge parameters.

A dual channel spectrometer from Avantes was used to measure the temporal and spatial resolved intensity profile of chromium neutrals. The two channels of the spectrometer are able to measure different ranges of the optical emission spectrum, with channel one ranging from 200 nm to 750 nm and channel two ranging from 650 nm to 1100 nm. The optical resolution of the spectrometer was 2.4 nm. The optical fiber of the spectrometer was positioned outside the chamber in a way to measure the emission parallel to the target surface. It was moved away from the surface in 1 mm steps for two cm. After the first two cm the step width was increased to 5 mm. After the next three cm the step width was increased to 10 mm. A length of 80 mm was covered by this method. The spectrometer allowed for time resolved measurements with a temporal resolution of 10 µs. The emission line at a wavelength of 359.2 nm was used to measure the chromium neutral emission.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium.

Figure 1. Voltage and current for a 150 µs HiPIMS pulse in 0.5 Pa argon (a) and nitrogen (b). Schematic of the experimental setup consisting of power supply, low pass filter, target and EQP mass spectrometer.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

3. Results and Discussion

Hysteresis effects in reactive magnetron sputtering need to be controlled to establish reproducible plasma properties. Therefore, we assessed the hysteresis in our experiment for the intended parameter range of different precursor gas mixtures of nitrogen and argon and different total target currents. The voltage at the target is then adjusted by the power supply to assure any preset average power level. The value of the target voltage reflects the degree of poisoning of the target surface and a hysteresis may be obtained when decreasing or increasing the reactive gas admixture. Such a hysteresis is observed for a current of 30 A, where different target voltages are obtained depending whether the nitrogen admixture to the argon plasma gas is increased or decreased. A decrease in discharge voltage was observed at 50% nitrogen admixture when increasing the nitrogen flow. The discharge voltage increased when the flow ratio of nitrogen was lowered to 0% again. In the case of the experiments performed at 80 A, no hysteresis is observed, although it should be mentioned that the discharge voltage still decreased with increasing nitrogen flow. This is consistent with findings in the literature. A more detailed analysis of the hysteresis effects will be presented elsewhere.

The left and right column in Fig. 2 shows ICCD images of the racetrack of the target for different nitrogen admixtures to the argon plasma gas as indicated in the figure. The colorbars show the light intensity. Any discussion of the absolute values is omitted here, since the windows through which the images were taken became coated by sputtered metals. Therefore, they had to be changed frequently, resulting in different absolute transmissions for each measurement. The images show the appearance of spokes clearly. Their shape is changing with target current, but also with the percentage of nitrogen admixture. For the case of a pure argon discharge, these spokes may also disappear at high currents, as can be seen on the topmost ICCD image on the right column in Fig. 2. If nitrogen is added to the HiPIMS plasma at 80 A, spokes appear despite the high current and the plasma emission pattern evolves into a very narrow ring above the racetrack. This is similar to the ICCD images taken for the lower current of 30 A shown in the left column in Fig. 2.

From other authors it is known that a significant fraction of discharge current is flowing through spokes [23]. It is therefore important to study the change in current density for the different operating conditions. Since the actual conducting surface of a spoke cannot be assessed without target probes the full width at half maximum of the plasma torus for every ICCD image was extracted. A measure for the peak current density was then calculated by dividing the discharge current by the half width. Fig. 3a shows the curves of the peak current density at 30 A and 80 A, for different nitrogen ratios. For 30 A the peak current density shows a sudden increase at 50% nitrogen admixture. This fits to the hysteresis behavior of the discharge voltage, which is described above. Thus 50% nitrogen admixture is the point at which the discharge operates in the poisoned mode for 30 A. The 80 A case did not show a hysteresis behavior in the voltage measurement, but a small decrease of voltage with increasing nitrogen admixture.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium.

Flow ratio. The current density increases with increasing nitrogen ratio with its highest value at 100% nitrogen admixture. As the peak discharge current stays constant for the measurements, this increase in peak current density results from a decrease in the discharge area.

Another important aspect is the extension of the plasma in axial direction from the target towards the substrate. Fig. 3b shows the intensity profiles of a single chromium neutral emission line measured with the Avantes spectrometer. Shown in blue is the pure argon case and green shows the pure nitrogen case. A deposited film on the window of the chamber reduces the intensity of light arriving at the spectrometer. Thus, the profiles are normalized to unity, as their intensities can not be compared. The x-axis shows the distance from the target with the target being at 0 cm. Although measurements were done up to 8 cm only the first four cm are shown here, as the profile does not show any relevant information at distances higher than 4 cm. Both measurements share a similar
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

profile with a peak in intensity close to the target surface and a decline in intensity towards higher distances. The main differences are the position of the peak and the width of the profiles. For the pure argon case the maximum is at around 0.7 cm while the maximum in the nitrogen case is at around 0.5 cm. The profile of the pure nitrogen case is half as thin as the profile of the argon case. This shows that additionally to the increase in current density due to a localization in radial direction, as it can be seen in Fig. 2, the chromium rich region of the discharge shows also a higher localization and a shift towards the target with a high nitrogen content.

Figure 3. a) Estimated peak current density for discharge currents of 30 A (blue) and 80 A (green), depending on nitrogen flow ratio. b) Intensity profile of chromium neutral emission lines for pure argon (blue) and pure nitrogen (green) case. The discharge current of this measurement was 80 A.

Fig. 4 shows the IEDFs for chromium ions as contour plots (left column) for a HiPIMS plasma at 80 A target current but different gas mixtures, ranging from: (a) pure argon, (b) nitrogen/argon ratio of 1:1, (c) pure nitrogen. Individual IEDFs at characteristic times are shown in the right column of Fig. 4. The temporal location of these specific IEDFs can be located on the contour plots by the very same color of the vertical lines. The beginning and end of the pulse are marked by vertical red dashed lines in Fig. 4. The exact temporal positions of the begin and end of the pulse are extracted directly from the data. The begin of the voltage pulse is at \( t = 0 \mu s \), however the MS records the ions only when they arrive at the orifice of the MS causing a temporal shift of the IEDFs due to the time-of-flight between target and MS (the transit time of the ions inside the MS is taken into account). This shift is typically in the order of 25 \( \mu s \).

The time- and energy-resolved IEDF of chromium in a pure argon discharge, shown in Fig. 4a, is very typical [9, 10]. In the beginning a small maximum in ion current is observed (marked as black line). The maximum in ion energy is at 10 eV (black curve in the right column of Fig. 4a). After that the current reaches the high current phase due to gas rarefaction. The maximum energy of \( \text{Cr}^+ \) increases slightly to 15 eV (blue curve in the right column of Fig. 4a). After switching off the plasma, the ions cool down and
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

thermalize and a high peak in ion current in the afterglow is observed, when the ions are released from the magnetic trap above the racetrack [9].

The behavior of the IEDFs in pure nitrogen is completely different to the pure argon case, as illustrated in Fig. 4c. Already the contour plot illustrates that a maximum in the Cr\(^+\) flux occurs only at the begin of the pulse (marked as black line) and after the end of the pulse (marked at as red line). In the high current phase of the pulse, the Cr\(^+\) flux seems to be strongly suppressed. A fully poisoned target may also cause this, because the sputter yield is reduced leading to a low metal ion flux at the mass spectrometer. However, the observed temporal variation of the ion flux during a single pulse is much stronger despite the fact that only a percent of a monolayer is quantitatively exchanged at the target surface during each 200 \(\mu s\) pulse. In addition, we observe that the discharge does not transit into the fully poisoned mode for high currents. Consequently, we assume that the modulation of the ion flux is a plasma effect rather than a surface effect. A simple interpretation would be a strong gas rarefaction effect, which could explain the decrease in ion flux after the onset of the pulse. After the end of the pulse, energetic Cr\(^+\) ions are again observed, because the current is decreasing, but the target voltage remains still high for 20 \(\mu s\) in the setup, as discussed above.

The variation of the IEDFs is also illustrated at specific times within the pulse, as shown in the right column of Fig. 4c. This will be discussed below. Fig. 4b shows the IEDF of a HIPIMS plasma of chromium for a nitrogen and argon mixture. These IEDF appear intermediate between the case of a pure argon plasma and a pure nitrogen plasma. The reduction of the chromium ion fluxes during the plasma may be identified. The specific IEDFs shown in the right column of Fig. 4b during the pulse and after the end of the pulse appear to be rather similar, consisting of a low energy peak and a high energy tail.

The peculiar decrease of the chromium ion flux in the high current phase of the pulse can be better analyzed by regarding the characteristic IEDFs at specific times, as shown in Fig. 5 (same data as in Fig. 4c). In addition, Thompson sputtering distributions for chromium with a surface binding energy of 7.4 eV are plotted with a factor three different scaling (dotted and dashed line in Fig. 5). The Thompson distribution is shifted by 10 eV to account for the acceleration of the ionized neutrals in the substrate sheath.

A comparison of the IEDFs for the pure nitrogen case in Fig. 5 with the prediction from Thompson distributions reveals two prominent deviations at low energies indicated by LE and at high energies indicated by HE. The narrow low energy peaks and the broad high energy peaks are denoted as LE1 and HE1 for the IEDF at 92 \(\mu s\), as LE2 and HE2 for the IEDF at 120 \(\mu s\), and as LE3 and HE3 for the IEDF at 178 \(\mu s\). The low energy peaks can be explained by the scattering of ions on their path between target and substrate. This causes a thermalization and the ions accumulate in a narrow energy window constituting the LE peaks. The LE1 peak at the beginning of the pulse is at 12 eV. The LE2 peak exhibits a slightly higher energy of 15 eV indicating a higher plasma temperature in the later phase of the pulse. In addition, the LE2 peak is a factor 2 higher than the LE1 peak. These thermalized ions are born outside the spokes
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

Figure 4. Time and energy resolved IEDFs shown as contour plots for Cr\(^+\) ions for pure argon as precursor gas (a), for a 50:50 mixture of argon and nitrogen (b) and for a pure nitrogen discharge (c). The start and end of the 150 µs HiPIMS pulse is indicated by red vertical dashed lines. The right column IEDFs at particular times within the HiPIMS pulse. The colors of the lines are identical to colors of the vertical lines in the contour plot indicating the moment in time.

where the plasma potential is low. The main source for the shift is therefore mainly the potential drop in the substrate sheath. Therefore, the energy position of the LE peaks is a measure for the sheath voltage at the substrate side and to a lesser extent the plasma potential where the ion was created.

After switching off the pulse, the peak LE3 is much smaller, although the energy is still a bit higher at 17 eV. This small spike in energy after the end of the pulse is explained
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium elsewhere [9]. The high energy peaks HE1, HE2, and HE3 originate from ionization inside a spoke and the acceleration of species in its electrical potential structure [8, 10]. The HE1 peak is at 40 eV, increases during the pulse to 70 eV for HE2, and reduces to 50 eV for HE3 directly after switching off the pulse. The HE peaks are not very pronounced compared to the HE peaks in the IEDFs for pure argon discharges or HiPIMS of other elements such as titanium [10].

The dynamic of the IEDFs shown in Fig. 5 may be interpreted as follows: in the beginning of the pulse the IEDF at 92 µs corresponds to a typical Thompson-like distribution. Apparently, the sputtered species undergo very little collisions and almost all ions reach the substrate with an energy originating from the sputtering process itself, plus the acceleration in the substrate sheath. As the HiPIMS pulse proceeds, the IEDF at 120 µs shows a very different shape: a re-distribution in energy space is observed since the contribution of high energy species decreases, whereas the contribution of low energy species increases. This redistribution in energy space cannot be explained by simple gas rarefaction, because it would imply a reduction of the ion fluxes for all energies which is not observed. After switching off the pulse, the low energy peak LE3 disappears, but a HE3 peak for the energetic ions re-appears. This energetic peak is a consequence of the high target voltage even after switching off the current by the power supply induced by the low-pass filter, as discussed above. Summarizing, one can conclude that the dynamic of the high energy part of the IEDF can be best explained by a dominant scattering process which is only present during the high current phase of the plasma pulse leading to a re-distribution of the sputtered metal ions in energy space from the high energy tail to the narrow low energy peak.

The analysis of the IEDFs in Fig. 5 leads to the hypothesis of a dominant scattering process during the high current phase of the HiPIMS pulse in pure nitrogen. The scattering of sputtered metal atoms in the gas phase is influenced by three factors: (i) the density of the scattering partner, (ii) the identity of the scattering partner, (iii) and the cross section for the scattering process. Since the process needs to be dominant only during the high current phase of the pulse the scattering partners need to be species that are only present during that time. The most straightforward explanation is the scattering of ionized sputtered chromium by chromium ions in the plasma and their return to the target. The efficiency of this well known return effect depends on the plasma density in the HiPIMS plasma in front of the target: in the beginning of the pulse, the plasma density is small and the scattering is negligible - high energy species are observed; in the high current phase of the pulse, the plasma density is high and the scattering re-distributes the ions in energy space; after switching off the plasma, the plasma density drops and the scattering efficiency is reduced, allowing the remaining ions to reach the MS at high energies.

This temporal varying efficiency of scattering is dominant in the case of sputtering of chromium in pure nitrogen, but apparently absent in the case of sputtering in pure argon (see Fig 4a). This might originate from the different plasma patterns when using argon instead of nitrogen as plasma gas. To test this, the ICCD images of the racetrack
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

Figure 5. IEDF of Cr\textsuperscript{+} for a HiPIMS of chromium in pure nitrogen at different times within the pulse as indicated (same data as in Fig. 4 (c). The different low energy (LE1 to LE3) and high energy (HE1 to HE3) peaks are indicated. The dashed and dotted lines are Thomson-distributions for chromium sputtering, shifted by 10 eV. For details see text.

are compared with the IEDFs for the three different plasma gas mixtures in Fig. 6 for (a) pure argon, (b) argon/nitrogen mixture, and (c) pure nitrogen. The ICCD images are shown on the left column in Fig. 6. Energy-integrated IEDFs are generated from the data shown in Fig. 4 and are shown on the right column of Fig. 6. The energy integrated IEDF yielding the temporal evolution of the ion flux for a pure argon plasma (Fig. 6a) shows a very typical behavior with an increase in the beginning, a phase and a drop off at the end. The energy integrate IEDF for the the nitrogen/argon mixture appears similar, although the metal ions flux rises later in the pulse and increase slightly during the high current phase of the pulse. The energy-integrated IEDF for the pure nitrogen case, however, shows the prominent minimum in the Cr\textsuperscript{+} flux during the high current phase within the HiPIMS pulse. Also, the rise in current is the latest, but also steepest, when the three plasma gas mixtures are compared. It seems, that the build up of the plasma density and thus the sputtered chromium ion flux in the case of the pure nitrogen case is most abrupt. In addition, directly after the build-up of the ion current flux, it is immediately reduced leading to a much smaller ion flux during the high current phase of the pulse.

The ICCD images shown in left column of Fig. 6 are very different for the three cases. In the case of a pure argon plasma, a homogeneous plasma torus is observed in Fig. 6a covering almost the complete racetrack. In the case of pure nitrogen in Fig. 6c, however, only a very narrow plasma torus along the racetrack is observed, where the ionization zones are not well defined. In case of an argon nitrogen mixture in Fig. 6b,
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

![Figure 6](image)

**Figure 6.** Left column: ICCD images of the plasma torus for different plasma mixtures ranging from (a) pure argon, (b) a mixture of nitrogen and argon as indicated, to finally (c) pure nitrogen. The target current is always 80 A. The indicated power densities varied due to varying target voltage. Right column: energy-integrated IEDFs for Cr\(^+\). The energy-integrated IEDF for the 100% case is also displayed with a factor of 10 multiplied.

A plasma emission pattern consisting of two well defined spokes is observed. All ICCD images are taken at the same absolute target currents and comparable power densities as indicated in Fig. 6.

The different appearances of plasma patterns for argon and nitrogen discharges can be explained by the different power dissipation mechanism in both cases. In the case of a molecular gas compared to an atomic gas, the electrons lose their energy more efficiently in collisions due to the higher degrees of freedoms of molecules compared to atoms. During a HiPIMS pulse, however, the electron loss mechanisms are even...
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

more complex, because the plasma consists of the plasma gas being either molecules or atoms or a combination of both, but also of sputtered metal species. This results in a complex gas mixture above the target, where the gas rarefaction by the sputter wind creates a local metal plasma surrounded by the neutral molecular or atomic sputter gas. The ionization in that complex gas mixture defines the current that is carried through the discharge. If we identify the plasma emission pattern as shown in Fig. 6 being proportional to the plasma density, one may conclude that the plasma current in the three cases argon, argon/nitrogen, or nitrogen is carried by different species and different plasma densities. Consequently it is reasonable to assume that the local plasma density in the pure nitrogen case must be significantly higher, because the plasma is much more confined, but also has to carry 80 A as in the other two cases. This is supported by the results shown in Fig. 3.

But why is the plasma pattern so strongly affected by the choice of the plasma gas? This may be explained by regarding the plasma impedance of a metal plasma above the racetrack surrounded by the ionized sputter plasma gas (argon and/or nitrogen). From a very simple electrical point of view this corresponds to a parallel circuit of two impedances connecting target and substrate. If the impedance of the ionized sputter plasma gas is much higher compared to the metal plasma, much more of the current is carried by the metal plasma rather than by the surrounding ionized sputter gas. This effect is self-amplifying and causes a strong localization of the plasma current. Apparently, this is the case for sputtering in nitrogen [15], resulting in a much stronger confinement of the plasma above the racetrack, as it is observed in the ICCD images.

In the case of pure argon as sputter gas, the current may be carried by argon ions as well as by sputtered metal ions and a much broader distribution of target current above the racetrack is observed, indicated by the broad plasma emission in the ICCD images. Summarizing, one can state that the stronger differences in plasma impedance between pure nitrogen and metals causes a localization of the plasma and therefore a high local plasma density. This in turn enhances the scattering of sputtered metal neutrals by the high density of metal ions in the localized plasma above the racetrack. It is expected that this scattering becomes dominant if the plasma density is above a certain threshold. Apparently, this threshold is not reached in pure argon, but in the case of nitrogen due to the localization of the plasma. The exactly test of this hypothesis would require a direct 3D modeling and simulation of the pulsed plasma or a direct measurement of the ion density distribution in space and time in the dynamic plasma pulse by for example laser spectroscopy. Both, simulation and experiments are facing enormous numerical and technical challenges, which is beyond the scope of this paper. Therefore, we restrict ourselves here to just present a working hypothesis on the change in plasma patterns going from the pure argon to the reactive case.

In the following the temporal variation of all species generated during reactive HiPIMS of chromium in argon/nitrogen mixture is analyzed. The IEDFs (not shown) exhibit a high energy tail for the sputtered species such as Cr$^+$, Cr$^{2+}$, and N$^+$, whereas the plasma source gas species such as Ar$^+$ and N$_2^+$ exhibit only a low energy peak.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

This is expected since the sputtered species start as neutrals following the Thompson distribution and might also gain additional energy due to the potential structure in the plasma. The plasma source gas instead is rarefied in the region of the plasma torus and ionization takes place only in the plasma bulk between target and substrate yielding an energy which corresponds only to the sheath potential in front of the substrate.

The IEDFs of Cr+, Cr2+, N+, Ar+, and N2+ are energy-integrated to yield the temporal evolution of the ion fluxes and are shown in Fig. 7 for a HiPIMS plasma with a gas mixture of nitrogen and argon. The begin and end of the pulse are marked by vertical red lines. The dynamic can be separated in 3 phases (marked in Fig. 7): in phase (I) at the onset of the pulse all ion fluxes increase simultaneously. Then, the plasma gas species Ar and N2 decrease due to gas rarefaction; in phase (II) the fluxes of the sputtered species Cr+, Cr2+, and N+ saturate, whereas the fluxes of Ar and N2 increase again. Apparently, the initial depletion is now being compensated by the stronger ionization of the rarefied gas when reaching the high current phase. Towards the end of the pulse the flux or Cr2+ increases slightly due to the increasing electron temperature and density, which shifts the ionization equilibrium form Cr+ to Cr2+. The increase in plasma temperature can also be corroborated by the slight increase in ion energy at the end of the pulse (not shown); in phase (III), all fluxes decrease simultaneously after the end of the pulse.

![Figure 7. Energy integrated IEDFs for Cr+, Cr2+, N2+, N+, Ar+ for HiPIMS of chromium in a nitrogen argon gas mixture. The begin and end of the pulse are marked by red vertical dashed lines. The data can be separated in three regimes as indicated. For details see text.](image-url)
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

The IEDFs of Cr\(^+\), Cr\(^{2+}\), N\(^+\), and N\(_2^+\) are energy-integrated to yield the temporal evolution of the ion fluxes and are shown in Fig. 8 for a HiPIMS plasma of nitrogen only. The begin and end of the pulse is marked by vertical red lines. The dynamic can be again separated in 3 phases (marked in Fig. 8): in phase (I) all fluxes increase simultaneously; in phase (II), the fluxes of the sputtered species Cr\(^+\) and Cr\(^{2+}\) decrease, whereas the flux of the plasma gas N\(_2^+\) strongly increases. This is the opposite behavior to the dynamic shown above in Fig. 7. The flux of N\(^+\) increases slowly with time and may contain contributions from the sputtered flux from the surface as well from dissociated N from the bulk plasma; in phase (III), the fluxes of nitrogen species decrease, whereas the fluxes of the chromium species go through a small maximum in flux.

This dynamic is consistent with the hypothesis of self-scattering: in phase (II), the intense self-scattering of chromium ions, causes a reduction of the flux, because scattering reduces the forward direction of the sputter flux. Furthermore, charge exchange processes between chromium ions and nitrogen gas molecules must be present to explain the strong increase in N\(^+\) and N\(_2^+\) flux. Unfortunately, no cross-sections are available up to our knowledge. Charge exchange reactions for N\(^+\) ions in N\(_2\) start to dominate above momentum transfer for energies higher than 40 eV [16]. If the situation is similar for chromium this would imply a depopulation of the high energy part of the Thomson distribution. Consequently, the current to the target is now carried by nitrogen ions, rather than by chromium ions. At the end of the pulse the scattering is again reduced due to the decrease in plasma density. The plasma becomes transparent for the transport of sputtered species, leading to a short increase in the metal ion flux.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium.

Figure 8. Energy integrated IEDFs for Cr$^+$, Cr$^{2+}$, N$_2^+$, N$^+$ for HiPIMS of chromium in a pure nitrogen gas mixture. The begin and end of the pulse are marked by red vertical dashed lines. The data can be separated in three regimes as indicated. For details see text.
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

The physics of the change in the IEDFs due to scattering are summarized by a schematic shown in Fig. 9 with the left side showing the situation for a pure argon discharge and the right side showing the situation for a pure nitrogen discharge. The cross section of the plasma torus is indicated by a light gray area and the metal dominated central part is indicated by the dark grey area. The measurements shown in Fig. 3b reveal that the extension of the plasma towards the substrate also is a factor 2 smaller for nitrogen compared to argon. The plasma emission in the case of nitrogen as plasma gas is apparently contracted laterally and normally to the target surface. Since the complete plasma current, which is identical in both cases, is carried mainly through the metallic part of the plasma, the plasma density in the case of argon as plasma gas is lower compared to nitrogen. The different local plasma densities lead to a larger contribution of collisions of sputtered metal species with metal ions in the case of nitrogen as plasma gas. This reduces the velocity of the metal ions, the cross section for charge exchange reactions of \( \text{Cr}^+ \) with the \( \text{N}_2 \) background gas increases and many of the ions reach the substrate as \( \text{N}_2^+ \) ions. This is absent in the case of argon since the sputtered ions traverse the plasma torus without significant scattering. The charge exchange cross section to argon are also much smaller, so that the growth flux consists of energetic chromium ions only.

![Figure 9](image)

**Figure 9.** Scheme for self-scattering dynamic comparing the non-reactive sputtering of chromium in argon (left) and the reactive sputtering in nitrogen (right). The different gray areas denote, the plasma bulk consisting mainly of the ionized plasma gas, the plasma torus with a central metallic part and an outer plasma gas part. For details see text.

Scattering is very efficient, if sputtered chromium ions are scattered from other chromium ions and chromium neutrals. This is different to the scattering of sputtered chromium ions from other neutrals following a Langevin cross sections, which is much smaller than for Coulomb collisions. These ion-neutral collision can be avoided by reducing the background pressure in the discharge. Consequently, typical HiPIMS
Influence of the nitrogen admixture to argon on the ion energy distribution in reactive high power pulsed magnetron sputtering of chromium

processes are operated at pressures below 0.5 Pa. The self-scattering regime, however, can inherently be formed by a localized high plasma density. Therefore, the efficiency of a HiPIMS process might not only be reduced by the return effect as the back-acceleration of ions in the electric field pointing to the cathode, but also by scattering sideways which leads to a drastic reduction of the growth flux towards the substrate. Such influence of the scattering of sputtered species by plasma species is expected in all plasmas, irrespective of the plasma gas that is used. Here, we presented a more indirect influence of the nitrogen admixture in reactive sputtering, because, according to our hypothesis, nitrogen might not directly act as a scatterer for the sputtered metals, but rather modifies the plasma pattern and the local plasma density, which then in turn acts as an efficient scatterer for the sputtered species.

4. Conclusion

The data presented indicate the existence of a self-scattering regime in HiPIMS plasmas, which can be established if the plasma density is above a certain threshold so that the scattering of the sputtered metal species, by ionized metal ions in the plasma torus becomes efficient. This self-scattering causes a re-distribution of the ion in energy space, and a reduced directed flux towards the substrate. The plasma density in turn can be varied by increasing the plasma power or by the localization of the plasma in ionization zones. This localization is enhanced in the case of reactive plasmas, because the plasma impedance of a localized metal plasma is much smaller than of a plasma from a molecular reactive gas. Therefore, a strong localization is observed leading to a high local plasma density. This in turn favors self-scattering. It is expected that the self-scattering regime has a strong influence on the deposited materials, because the energetic metal ion flux is converted into a low energy flux of reactive source gas ions. It is expected that this self-scattering regime also occurs on industrial scale HiPIMS plasma but may be overlooked so far, because the absorbed powers might have been too low, or the self-scattering regime is hidden in the large parameter space.
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References