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Time and energy resolved ion mass spectroscopy studies of the ion flux during high power pulsed magnetron sputtering of Cr in Ar and Ar/N₂ atmospheres

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ABSTRACT

Mass spectroscopy was used to analyze the energy and composition of the ion flux during high power pulsed magnetron sputtering (HIPIMS/HPPMS) of a Cr target in an industrial deposition system. The ion energy distribution functions were recorded in the time-averaged and time-resolved mode for Ar⁺, Ar²⁺, Cr⁺, Cr²⁺, N₂⁺ and N⁺ ions. In the metallic mode the dependence on pulse energy (equivalent of peak target current) was studied. In the case of reactive sputtering in an Ar/N₂ atmosphere, variations in ion flux composition were investigated for varying N₂-to-Ar flow ratio at constant pressure and HIPIMS power settings. The number of doubly charged Cr ions is found to increase linearly with increasing pulse energy. An intense flux of energetic N⁺ ions was observed during deposition in the reactive mode. The time evolution of ion flux composition is analyzed in detail and related to the film growth process. The ionization of working gas mixture is hampered during the most energetic phase of discharge by a high flux of sputter-ejected species entering the plasma, causing both gas rarefaction and quenching of the electron energy distribution function. It is suggested that the properties (composition and energy) of the ion flux incident on the substrate can be intentionally adjusted not only by varying the pulse energy (discharge peak current), but also by taking advantage of the observed time-variations in the composition of ion flux.

keywords: high power pulsed magnetron sputtering; HPPMS; high power impulse magnetron sputtering; HIPIMS; ion mass spectroscopy; ion energy distribution; plasma diagnostics; ion flux

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INTRODUCTION

High power pulsed magnetron sputtering (HIPIMS/HPPMS) is a sputtering technique that has drawn much attention from the academia in the recent years as indicated by a growing number of publications [1]. The method has been promoted by Kouznetsov et al. [2] and principles are described in detail elsewhere [1]. Recently commercial solutions have become available indicating that the potential of this new technology has also been realized by the coating industry. The feature that is most appealing is the high temporal electron density in the plasma that results in an effective ionization of sputtered material. In addition, the ion-to-neutral flux ratio may to some extent be controlled by the applied pulse voltage. As such HIPIMS appears as an attractive alternative to conventional DC sputtering for thin film deposition. Since the influence of ion bombardment during film growth on properties of resulting coatings is well proven [3-5] it is of primary importance to understand what factors affect the ion energy distribution function (IEDF) in the case of HIPIMS processing. The correlation is expected to be even more pronounced since film-forming ions are available in concentrations that significantly exceed standards of DC sputtering, and in some cases, even dominate the ion flux incident on the substrate.

The first mass spectroscopy measurements of HIPIMS plasma were reported by Bohlmark *et al.* [6] for a Ti target sputtered in Ar. The Ti^+ ion energy distribution was shown to be composed of ions with low energy that produces a high intensity peak and more energetic ions that produce a high-energy tail, significantly broader than for the DC

discharge (with ~50% of the ions having energies larger than 20 eV). Using the time-resolved experiments, authors were able to show that these energetic metal ions are generated during the pulse, when the target current reaches its maximum. After the pulse is turned off, the IEDF quickly narrows down as a result of energy exchange with filling gas atoms (process known as “thermalization”) giving rise to the low energy peak.

The origin and the time evolution of IEDF in the case of HIPIMS Cr plasma has been studied by Hecimovic *et al.* [7,8] for laboratory-scale Cr targets sputtered in Ar atmosphere. The authors found that the IEDF of both metal and argon gas ions can be fitted with two Maxwellian distributions (describing low and high energy components), what in the former case is claimed to be caused by an effective thermalization of the sputtered metal atoms. The high energy component of the metal IEDF was found to scale monotonically with a peak value of the target current, whereas the low energy peak (owing to completely thermalized ions) remained constant. Metal and gas ions could be detected in the after glow plasma on the ms time scales, thus long after the current pulse was turned off.

When it comes to the reactive sputtering of Cr in Ar/N₂ gas mixtures to our best knowledge there is no report on measurements of IEDF performed during HIPIMS. The closest published results deal with modulated pulse power magnetron sputtering where longer pulses (>1ms) and lower current levels are used resulting in less pronounced high energy tails of ionized species [9].

In the present paper, the results of mass spectroscopy studies during Cr target sputtering in both, metallic (Ar only), as well as, reactive mode (Ar/N₂) are reported. The IEDFs for a number crucial species, including Ar⁺, Ar²⁺, Cr⁺, Cr²⁺, N₂⁺, N⁺ and CrN⁺, were recorded in the time-averaged and time-resolved mode. The first part of the paper is focused on the metallic mode of operation laying the grounds for interpretation of data recorded in the reactive mode. The dependence on pulse energy (equivalent of peak target current) is studied in the metallic mode. For sputtering in an Ar/N₂ atmosphere, variations in ion flux composition are investigated for varying N₂-to-Ar flow ratio at a constant pressure and HIPIMS power settings. The measured IEDFs have implications for growth of chromium and chromium nitride thin films.

EXPERIMENTAL

All measurements were performed in an industrial CC800/9 coating system manufactured by CemeCon AG in Germany upgraded with the HIPIMS technology. The relevant details of the system configuration can be found on the manufacturer's web site [10]. This system offers the possibility to simultaneously operate two cathodes and substrate table in the HIPIMS mode. The base pressure in the vacuum chamber after the overnight bake-out was 4×10^{-5} Pa. For the purpose of this work, a single rectangular chromium target of dimensions 88×500 mm² was sputtered in Ar or Ar/N₂ atmosphere at the total pressure of 0.4 Pa. The cathode was operated in the frequency range between 100 Hz and 300 Hz. The average power was between 500 W and 4500 W, and the pulse duration was 200 μ s. In order to facilitate reliable plasma analysis with mass spectrometry, the cathode was dismounted from its original location (chamber door) and placed flat on the substrate table with target facing upwards. The mass spectrometer head was then introduced through the port on top of the deposition chamber so that in the resulting configuration the entrance of the spectrometer was facing the center of the target from the distance of 21 cm. Under these experimental conditions sputtered atoms with an average energy of 10-30 eV are expected to make several collisions (get thermalized) on the way to the mass spectrometer entrance [11,12]. Therefore, time-averaged data are expected to be dominated by the thermalized ions.

The ion energy distribution functions (IEDFs) were measured both in time-averaged and time-resolved mode with commercially available mass spectrometer

PSM003 (from Hiden Analytical, UK), that has been described in details elsewhere [6]. The spectrometer is equipped with a quadrupole mass analyzer that allows for mass discrimination up to 300 amu with a 0.01 amu resolution. The orifice of the spectrometer was grounded and aligned along the target surface normal. Using the same settings (in order to enable relative ion content estimates) the IEDFs for the following ions were measured: Ar^+ , Ar^{2+} , Cr^+ and Cr^{2+} . In addition, while sputtering in the reactive mode, IEDFs for N_2^+ , N^+ and CrN^+ were also acquired. The IEDF were often recorded for more than one isotope of a given ion in order to eliminate the risk of detector saturation. Table 1 presents the complete list of measured isotopes along with the relevant properties. To facilitate comparison, data presented in this paper are scaled by the abundance values.

Due to the fact that quadrupole mass analyzers transmit more at low mass than at high mass, the $1/\text{mass}$ transmission function is often assumed [13]. Here, we follow the same procedure even though the data quantification in the absolute terms is not attempted due to the fact that the energy-dependent transmission function of our mass spectrometer is not known. For the same reason, any reliable fitting of recorded ion energy distribution functions is not meaningful and as such not attempted here. Data are instead presented as acquired (as far as the energy dependence is concerned) and all conclusions are drawn from the outlined trends in the relative ion content in the plasma with varying process parameters.

Keeping in mind the relatively high deposition rates of industrial coaters, special care has been taken to account for a potential signal drop caused by sputter-deposited

material on the spectrometer orifice. Control scans were thus performed with approximately equal time intervals. The target was sputtered for 60 s. in pure Ar prior to such control scans. Following that, Cr^+ and Ar^+ spectra were recorded. These spectra were then used to scale the data accordingly whenever a signal drop was detected. It should also be mentioned that the total signal drop after performing all measurements did not exceed a factor of 2, indicating that these corrections are rather minor.

In cases of time-averaged measurements, the detector dwell time was chosen such that data were collected from at least 20 pulses for each energy data point (the lowest frequency and dwell time used were 100 Hz and 200 ms, respectively). The particular value of the dwell time was determined by the count rate for a given ion and is listed in Table 1. The scanned energy range for singly charged ions was between 0 eV and 100 eV in 0.5 eV steps (for doubly charged ions correspondingly 0 eV to 50 eV in 0.25 eV steps).

For time-resolved measurements, the mass spectrometer unit was triggered by the signal from the Tektronix DPO4054 500 MHz bandwidth digital oscilloscope that was also used for recording current and voltage waveforms. The detector gate window was in this case set to 10 μs and a delay time with respect to the onset of the voltage pulse to the cathode was varied from 20 μs up to 240 μs in 10 μs intervals. The total acquisition time per data point was 1ms, implying that data were collected during 100 consecutive pulses. Due to the fact that time-resolved measurements are significantly more time consuming the scanned energy range was shortened with respect to time-averaged measurements. For singly charged ions, the ion energy was scanned between 0 eV and 50 eV in 1 eV

steps, for doubly charged ions correspondingly 0 eV to 25 eV in 0.5 eV steps. In order to obtain the plasma composition at the front end of the mass spectrometer rather than at the detector, all data were compensated for the time-of-flight (TOF) of ions through the instrument using the same approach as described in [6]. The calculated corrections to the time axis obtained in this way are listed in Table 1. The TOF correction for a given ion is obviously dependent on the initial kinetic energy. However, as has already been pointed out [6] for ions in the energy range between 0 and 100 eV, the TOF does not vary more than 10%. It is therefore justified to use the average values.

RESULTS AND DISCUSSION

Current and voltage waveforms

In the case of industrial-size targets like in the present work, the exact shape of current and voltage waveforms is to a great extent determined by the size of the capacitor bank used in the powering unit. A set of current and voltage waveforms recorded with pulsing frequency, f , of 100 Hz for different values of pulse energy (E_p) is shown in Fig.1. The corresponding average power levels are easily obtained according to $\langle P \rangle = f E_p$. As can be seen in Fig. 1b, the voltage is not constant throughout the pulse, but rather drops from the peak value (reached right at the beginning of the pulse before any current flows, cf. Fig. 1a) as the charge is withdrawn from the capacitor bank after plasma

Fig. 1 Recorded waveforms: a) target current and b) target voltage for different values of pulse energy. Inset in a) shows the DC-like phase of discharge that follows after the high current (HIPIMS) stage is passed.

ignition. The resulting target current is thus proportional to the rate at which the voltage drops according to $i(t) = Cdu(t)/dt$, where C stands for capacitance, $i(t)$ and $u(t)$ are the

target current and target voltage, respectively. Two different regimes can be clearly distinguished here: between 0 μs and 100 μs discharge operates at typical HIPIMS conditions with large dynamic changes in both current and voltage, that later stabilize in the second phase (100 μs to 200 μs) to resemble that of DC sputtering (cf. inset in Fig. 1a). Closer comparison to the actual I-V characteristics of DC sputtering recorded under the same conditions reveals, however, that current levels achieved during the second phase constitute only a fraction of typical DC currents for a corresponding target voltage. This observation clearly indicates that this, DC-like discharge, operates under Ar-depleted conditions owing to the severe gas rarefaction [14] taking place during the HIPIMS phase of the discharge. As was pointed out in [15] the refill with thermal speed of Ar (at RT) over the characteristic distance of 2 cm has a time constant that significantly exceeds typically used pulse lengths. Authors reported that not even a 750 μs long pulse-off time (after high current pulse) was enough to completely restore the initial conditions. This is consistent with the observation that the DC-like current stays low (or slightly increases in case of 15 J and 20 J) at least up to 200 μs . Additional evidence that speaks in favor of this interpretation is that the drop in the DC-like current (measured in the second phase) with respect to the corresponding DC current increases with increasing pulse energy. At 10 J per pulse (cf. red curve in Fig. 1a) the current after the HIPIMS mode saturates at a level that corresponds to $\sim 70\%$ of the DC current (at the same voltage), whereas for 15 J pulses the saturation level is set at only 40 %. Eventually, at 25 J per pulse only 30% of the typical DC current is reached. This trend is expected due to the fact that the amount of sputtered metal atoms increases with increasing pulse energy leading to more effective heating of the filling gas. In fact, it has been shown for

conventional DC discharges that the density of filling gas in front of the target decreases as the inverse of the square root of discharge current due to energy exchange with sputtered metal atoms [14,16,17].

Since the energy released during the DC-like phase constitutes a small fraction of the total pulse energy (apart from really low E_p values, like, e.g., 5 J per pulse where the HIPIMS to DC transition smears out) the potential effects on the film growth will be determined by ion flux generated during the HIPIMS phase. It should be also emphasized that the observed drop in the target current that ends the HIPIMS phase of the discharge is not ascribed exclusively to gas rarefaction effects, but rather to the combination of decaying cathode voltage and a lowered density of the argon gas.

Sputtering in metallic mode: time-averaged measurements and dependence on pulse energy

Figure 2a-c) shows the IEDFs of Cr^+ , Cr^{2+} and Ar^+ ions, respectively, for different values of pulse energy. Doubly charged Ar ions were also recorded, but are omitted here due to their low intensity. The contribution of Ar^{2+} to the total ion signal is below 2 %, owing to the very high second ionization potential of 27.76 eV (for comparison: 2nd ionization potential for Cr is 16.57 eV). This is in agreement with previously reported measurements of similar type performed for a Ti target [6]. The IEDFs of singly and doubly charged Cr ions comprises low energy peaks and very pronounced high-energy tails that completely dominate the ion energy spectrum for energies larger than 5 eV. The

Fig. 2 Time-averaged IEDFs for a) Cr^+ , b) Cr^{2+} and c) Ar^+ ions. The evolution of ion energy spectra with increasing pulse energy is presented. Data were scaled up according to abundance numbers, in order to facilitate relative comparison.

low-energy peak can be assigned to the sputtered atoms that have lost their initial kinetic energy in numerous collisions with filling gas atoms (thermalization) and become post-ionized. The high intensity of this peak is in qualitative agreement with the results of theoretical simulations [11] that predict ~90 % reduction of the original energy flux under the present conditions (pressure-distance product of 84 [mmPa] and mean atomic mass of colliding species equal to 46). The high energy tail that develops with increasing E_p represents primarily the original distribution function of sputter-ejected metal atoms (so-called Sigmund-Thompson distribution [18,19]) convoluted with (i) the probability function for electron impact ionization (which is the dominant ionization mechanism in HIPIMS discharge [20]), (ii) the probability function for collisions of metal ions with Ar neutrals, and finally (iii) the energy transmission function of the spectrometer [21]. In parallel, a contribution from the back-reflected metal ions (i.e., ions that were trapped by the negative potential at the cathode and accelerated towards the target) to the high energy tail is also expected. This is so since the commonly observed drop in HIPIMS deposition rate (with respect to DC sputtering at corresponding average power) indicates that a large portion of the Ar-sputtered metal flux does not leave the cathode fall region. The contribution from the back-reflected Cr ions may be two-fold: the Cr ions that arrive at the target with sufficiently high energy can kick out another Cr atom (self-sputtering) or get neutralized and reflected (essentially preserving kinetic energy gained during acceleration). Due to this complexity only the relative changes in IEDF of metal ions (upon varying process conditions) are addressed in this paper. It can also be seen that the number of ions in the high energy portion of the IEDFs increases with increasing E_p (and thus increasing peak current) what is consistent with previously reported results [8].

In the low energy portion of the IEDF ascribed to thermalized ions, the Cr^+ signal in Fig. 2a) shows a very intense peak that gains intensity (a factor of three) with increasing E_p and moves towards lower energy (from 1.3 eV to 0.5 eV). Since the orifice of the mass spectrometer was grounded, the position of this low energy peak reflects the value of plasma potential in the region where ions were created, averaged over the entire time period of the pulse ($T=1/f$). Due to the fact that the plasma potential varies quite substantially during the relatively short voltage pulse (ca. 100 μs in the present case) and tends to saturate in the long post-discharge phase on the millisecond scale [8], the position of the low energy peak in time-averaged measurements is determined by the plasma potential in the post-discharge phase, denoted here by V_{pd} . Therefore, one can conclude that the typical value of V_{pd} decreases with increasing pulse energy (or, alternatively, the peak current). In fact, this agrees with reported measurements [8] where V_{pd} was shown to decrease from 1.7 V to 0.9 V upon increasing the peak current density from 0.32 A/cm² to 0.91 A/cm². In the present study V_{pd} decreases from 1.2 V to 0.6 V when the peak current density increases from 0.23 A/cm² (5 J/pulse) to 1.5 A/cm² (25 J/pulse).

In addition, there is also a shoulder visible on the high energy side of the intense peak, at the energy range between 3 eV and 4 eV (E_p dependent), the origin of which will be explained by time-resolved measurements, as is presented in the next section.

In contrast to the Cr^+ signal, the low energy portion of the Cr^{2+} IEDF possesses two well-resolved peaks, see Fig. 2b). The lower energy one is assigned to thermalized ions and appears at twice the value of the plasma potential (moving from 2.6 eV to 1.0 eV) due to a double charge of the ions under consideration. The origin of the second peak, at around 5.5 eV to 6 eV (E_p dependent) is discussed in the next section.

The IEDF of Ar^+ ions in Fig. 2c) reveals that the majority of ions are thermalized and reside in the low energy portion that comprises the intense peak with a shoulder on the high energy side, at 2-3 eV. The position of the main peak moves in a similar fashion to the corresponding peak in IEDF of Cr^+ (from 1.3 eV down to 0.5 eV) while its intensity remains roughly constant (in contrast to Cr^+). The contribution from ions with somewhat higher energy ($E > 10$ eV) are detected for pulse energies of 12 J and above (forming a hump extending to 15 eV), however, they are by far less energetic than the Cr ions. These higher energy Ar^+ ions are thought to originate either from momentum transfer in collisions with sputtered species (followed by immediate ionization) or from Ar ions that after being accelerated towards the cathode got reflected as energetic neutrals to undergo post-ionization in the next stage [22,23]. It is worth to point out here that, apart from these high-energy ions that do not constitute a significant fraction of the total Ar^+ flux, the intensity of Ar^+ signal is independent of the pulse energy. This, at first contradictory result, can be rationalized if one takes into account that ions contributing to this spectral feature are created in the post-discharge phase (after the pulse is turned off) and as such do not necessarily reflect the Ar gas density in the DC-like phase of the discharge. The time-resolved data presented in the next section support this explanation.

As was mentioned above the number of Cr^+ and Cr^{2+} ions in the high energy portion of the IEDFs increases with increasing E_p . This effect may be ascribed to a higher probability of electron-impact ionization caused by the fact that the maximum plasma density reached during the most energetic phase of the discharge increases with increasing E_p (discharge current). This will have a direct effect on the fraction of ionized metal flux reaching the detector. The present results are in this respect in a good agreement with previously reported *in situ* optical emission spectroscopy measurements [24,25] that show the same trend of increasing ionized metal fraction with increasing pulse energy. The second effect of the increased plasma density is that the relative amount of back-reflected ions will also go up. This is in line with observed changes since, as was outlined above, the latter species are also thought to contribute to the high energy tail. There is experimental evidence that supports the statement about the increased amount of back-reflected metal ions. Figure 3 plots the power-normalized deposition rate of chromium, along with DC-normalized deposition rate, versus the pulse energy. A severe drop in the deposition rate is observed for increasing pulse energy. Keeping in mind that the loss of sputtered material is attributed to back-attraction of ions created within the cathode fall, the most straightforward interpretation of this trend is that the fraction of back-reflected ions increases with pulse energy. It should also be added, that not only the relative fraction of back-attracted metal ions increases, but also the average kinetic energy gained within the cathode fall should increase due to the fact that peak target voltage increases with increasing E_p . The increase of temporal plasma density with pulse energy has only a small effect on the intensity of Ar^+ signal since it is

Fig. 3 Plot of deposition rate (as estimated from cross-sectional SEM images) vs pulse energy. The left axis is power-normalized (black data points), whereas axis on the right hand side is scaled relative to DC sputtering (red data points).

dominated by the low-energy ions created on the later stage of discharge, thus when the plasma is already cooled down. For the same reason, the increase in intensity of the low energy peak of Cr^+ IEDF although noticeable, is still small compared to changes observed in the high-energy end of IEDF. Moreover, the uniform increase in the intensity of Cr^{2+} IEDF suggests that most of these ions are created during the most energetic phase of the discharge. This observation will be further verified in the next section, where the time-resolved data are discussed.

Sputtering in metallic mode: time-resolved measurements

More insight into the detailed shape of the time-averaged IEDFs discussed above can be gained by examination of the time-resolved data presented in Fig. 4 and Fig. 5. As described in the *Experimental* section, the IEDFs were recorded with 10 μs intervals. However, for the sake of clarity, in case of Fig. 4 data were summed up and are presented in 20 μs intervals. The power supply was operated at 15 J pulses and 300 Hz pulsing frequency. The zero for the time scale in all graphs presented corresponds to the onset of the voltage pulse to the target. The TOF correction has also been applied to all IEDFs. Thus, the presented data reflect the time sequence in the front end of the mass spectrometer. The top graph in Fig. 4 shows the time development of Cr^+ IEDF. The first ions are detected 35 μs after the beginning of the voltage pulse. Their distribution in the time interval between 35 μs and 55 μs (cf. red curve in Fig. 4) is quite unique in that the intensity in the low energy part of the energy spectrum (below 10 eV) is several times lower than in the high energy part. In the next time interval (55 to 75 μs) the Cr^+ ions increase tremendously in intensity to a large extent preserving the original shape of IEDF, with the highest intensity residing in the region between 10 eV and 20 eV. After that the trend is very clear: the high-energy tail loses its intensity and IEDF gradually narrows down to the low-energy portion of the spectrum. Eventually at times longer than 150 μs after the onset of the pulse, the IEDF consists of a single peak at around 3-3.5 eV, and a little bump on the high energy side is all that is left from the original high-energy tail. It is remarkable that the position of this low-energy peak does not coincide with a thermalized peak observed in time-averaged measurements (discussed above). Rather than that it fits very well to the position of the shoulder observed previously on the high-energy side of the intense peak in the time-averaged data. To understand this, one has to

Fig. 4 Time-resolved IEDFs for a) Cr^+ , b) Cr^{2+} and c) Ar^+ ions. Each individual color represents IEDF recorded during a $20 \mu\text{s}$ long time interval, as described in the legend.

Fig. 5 Plots of total ion count rate vs time (from the onset of the voltage pulse to the cathode). Each data point corresponds to IEDF recorded during 10 μs and integrated over entire energy range. Integrated intensities for Cr^+ , Ar^+ and Cr^{2+} ions are shown along with substrate current waveforms recorded for corresponding values of pulse energy, E_p .

realize that time-averaged data include also information about the plasma state after 200 μs (i.e., post-discharge phase), which is not covered here in time-resolved measurements. Taking this into consideration the low energy peak observed in time-averaged data at ~ 1 eV (for $E_p = 15$ J) is assigned to completely thermalized ions that reside in the plasma during time scales exceeding 200 μs (thus in the pulse off state), whereas a shoulder at around 3 eV is due to thermalized ions present in the plasma at the end of the pulse (corresponds to peak observed in the time-resolved data in the time interval 195-215 μs). The difference in detected energy of thermalized ions (present at 200 μs vs those detected after the pulse) is caused by the drop in plasma potential after the pulse is turned off. Hecimovic *et al.* [8] measured the variation in plasma potential up to 400 μs after the beginning of the 70 μs pulse and showed that it reaches 3-3.5 V during the pulse and then drops and saturates at around 0.9 V on the later stage (post-discharge plasma potential, V_{pd}). These numbers agree surprisingly well with the present results, even though the experimental set up was quite different. The possible explanation may be due to a similar peak current density in both cases (0.9 A/cm² vs. 0.96 A/cm² measured here for the 15 J pulses).

By analogy, the time-resolved data of Fig. 4 may be used to interpret the double peak appearing in the low energy portion of Cr²⁺ IEDF presented in Fig. 2. The low energy component forms already 135 μs after the pulse ignition (cf. yellow curve) and is centered at around 6 eV giving rise to a corresponding peak in the time-averaged spectrum. As time goes by this peak gradually moves towards lower energy (due to a dropping plasma potential) and eventually ends up at ~ 2 eV for the rest of the pulse off

time accounting for higher intensity peak (higher intensity being the result of a long time during which ions are collected with no change in the plasma potential). The comparison to the corresponding time-averaged data for Cr^+ reveals that the intensity of the low-energy peak at 2 eV is significantly lower in the case of Cr^{2+} , which is a consequence of a significantly lower probability for double-ionization events in the post-discharge plasma. A further comparison of time-resolved Cr^{2+} IEDFs to corresponding data for Cr^+ reveals that the distribution function in both cases develops in a similar fashion up to 75 μs . After that the drop in the high-energy portion of the ion spectrum is significantly faster for Cr^{2+} ions: already after 135 μs the high energy tail of Cr^{2+} ions is practically gone, whereas in the case of Cr^+ ions it does not take place until 195 μs .

It is also interesting to follow in more detail the time evolution of IEDF of Ar^+ ions shown in the bottom graph of Fig. 4 and compare it to the corresponding time-averaged data (Fig. 2). The Ar^+ ions exhibit high intensity already between 15 μs and 35 μs after the onset of the voltage pulse (cf. black curve) clearly preceding the Cr ions, as commonly observed in the case of HIPIMS discharges [6,26,27]. In the following time interval, between 35 μs and 55 μs , the IEDF increases in intensity and broadens up to 20 eV (cf. red curve) to collapse drastically in the next 20 μs (cf. green curve). After 75 μs the IEDF gradually narrows down to a single peak centered around 2.4 eV. It is this very peak that accounts for the shoulder at 2-3 eV in the time-averaged spectra. The higher energy ions that are produced during relatively short period of time (between 15 μs and 55 μs) account for a hump in the corresponding energy range of the time-averaged spectra (the intensity of this hump appears low as compared to the low energy peak since

they appear only during 40 μs). It can be noticed that a sudden drop observed after 55 μs (going from red to green IEDF) coincides with an equally dramatic increase in the number of Cr^+ and Cr^{2+} ions. This can be caused by two different phenomena that take place as soon as large amounts of metal atoms are sputtered from the target. Firstly, the density of Ar gas is reduced in the vicinity of the cathode due to effective energy exchange with high temporal flux of sputter-ejected metal neutrals [14]. Since the characteristic length for this effect (2-5 cm [16,28]) is significantly longer than the typical thickness of the cathode sheath (~ 1 mm in magnetron discharges), ions created in the affected volume may escape cathode electric field and be detected. Secondly, the observed drop in the intensity of Ar^+ signal can also result from lower ionization probability. In fact, it has been shown for ionized PVD with inductively coupled rf (RFI) plasma, that large fluxes of Al atoms may effectively cool down an Ar plasma [29,30]. Due to the fact that the ionization potential of commonly used metals is significantly lower than that of Ar, quenching of the electron temperature takes place, resulting in a less efficient ionization of the filling gas atoms. Vetushka *et al.* [31] have analyzed the plasma dynamics for a HIPIMS discharge with a Cr target, and showed that the energetic tail of electron energy distribution function decreases due to a metallic character of the plasma, causing a drop in the effective electron temperature from 2.9 eV to 1.1 eV during the pulse. It is rather impossible to distinguish between relative contributions from both effects to the observed decrease in the Ar^+ signal in the present experiments. Nevertheless, it is not an ambition of the present work to judge which effect dominates. The key result is instead, that the Ar^+ ion density is drastically reduced during the most

energetic phase of the discharge, which should significantly influence the film growth process.

In order to be able to get more insight into the time-related aspects, the recorded set of IEDFs have been integrated over the entire energy range and plotted with 10 μ s resolution in Fig. 5a-c), for different values of pulse energy. Fig. 5d) shows for reference also the corresponding table current waveforms. The substrate table current was collected with one single dummy column placed at the distance of 21 cm from the target, which is assumed to be a fair correction for the time-of-flight of the ions from the target through the deposition chamber before they reach the spectrometer entrance. The table bias was set to -150 V to ensure current saturation. Comparing this data set to the corresponding target current waveforms of Fig. 1 indicates that the time lag is of the order of 20-25 μ s, quite independent of pulse energy.

With increasing pulse energy, all peaks (including the table current) move to the left on the time axis that is caused by the fact that the discharge was operated at 100 Hz. The ignition time at this low frequency is a sensitive function of pulse energy due to the fact that density of ionized species oscillates around the break-down threshold right before ignition. With increasing frequency time between the pulses becomes short enough to ensure immediate ignition and no such effects are observed. The frequency in this experiment was limited to 100 Hz due to power restrictions for the cathode. Despite this condition it can be easily seen from the figure that the order by which ions of different kind arrive at the detector is preserved through out the whole pulse energy range

studied. The first detected species are in all cases Ar^+ ions. It is remarkable that the intensity of Ar^+ signal increases up to the point when first Cr^+ ions are detected. Increasing intensity of Cr^+ IEDF is then accompanied by a sudden drop in the Ar^+ signal, such that in all cases the maxima of Cr^+ intensity coincide with minima of Ar^+ IEDF. On the later stage (when the discharge goes into the DC-like phase, cf. first section) Cr^+ IEDF decays (with a considerably lower rate than for the Ar^+ intensity drop) and the Ar^+ IEDF slowly picks up. This peculiar behavior is believed to be caused by a combination of gas rarefaction effects and quenching of electron density (as described above) and, as can be seen, takes place over the entire pulse energy range.

A comparison of the IEDFs plotted in Fig. 4 with the corresponding data in Fig. 5 ($E_p=15$ J, green curves) reveals that the high-energy tails are associated with the rising portion (first half) of the intensity peaks (true also for Ar^+ ions). The high-energy tails drop off after the peak maximum is reached. This observation helps in the interpretation of the Cr^{2+} intensity plots also shown in Fig. 5b) that at first may seem to precede Cr^+ . It should be pointed out, however, that the amplitude of the Cr^{2+} signal is lower than that of Cr^+ . In fact, the former peak is contained within the envelope of the latter spectrum. More importantly, a closer examination reveals that the maxima of the Cr^{2+} signal coincide with the rising portions of the Cr^+ peaks meaning that doubly charged ions are most effectively produced during the time interval when single charged ions possess a very broad energy spectrum (most energetic part of the pulse where plasma density reaches its maximum, thus yielding the highest cross-section for electron impact ionization). From this perspective it is not surprising that the detected Cr^{2+} ions have a higher ratio of high-

energy ions to low-energy ions than is the case for singly charged Cr ions. After the most energetic part of the pulse is over, the production of Cr^{2+} ions goes down rapidly, whereas the production of Cr^+ ions decays with significantly longer time constant leading to gradual (not sudden, like in the case of Cr^{2+}) drop of the intensity of the high-energy tail and the formation of a more intense low-energy peak (cf. Fig. 4). The rapid decrease of Cr^{2+} intensity may be indicative of a plasma cooling effect induced by the still-increasing concentration of metal atoms (Cr^{2+} signal begins to fall before Cr^+ reaches its maximum). Since the second ionization potential of Cr (16.57 eV) is even higher than the first ionization potential of Ar (15.84 eV) any changes of the high-energy portion of the electron energy distribution function would have a strong effect on the Cr^{2+} signal intensity.

Sputtering in reactive mode: time-averaged measurement and dependence on N_2 -to-Ar flow ratio

In this section measurements of IEDF performed during sputtering of Cr target in Ar/ N_2 gas mixture are treated. The total gas pressure was kept constant at 0.4 Pa and the N_2 -to-Ar gas ratio, $f_{\text{N}_2/\text{Ar}}$, was varied between 0 (metallic mode) and 5 (sputtering in heavily poisoned mode). The HIPIMS power was delivered to the cathode in 15 J pulses with the frequency of 300 Hz. Figure 6 shows the time-averaged IEDFs of Cr^+ , Ar^+ , N_2^+ and N^+ for increasing $f_{\text{N}_2/\text{Ar}}$. The corresponding IEDFs of Cr^{2+} ions were also recorded, but are not shown due to lack of space. The signal detected at $e/m=14$ is assumed to be

Fig. 6 Time-averaged IEDFs for: a) Cr^+ , b) Ar^+ , c) N_2^+ and d) N^+ ions. Data were acquired at the constant pressure of 0.4 Pa, and the N_2 -to-Ar flow ratio, $f_{\text{N}_2/\text{Ar}}$, was varied between 0 and 5. Sputtering was done at the average power of 4.5 kW (15 J pulses, 300 Hz).

entirely dominated by N^+ ions; the contribution from N_2^{2+} ions is expected to be orders of magnitude lower due to its very high ionization potential (29.75 eV). This assumption is justified by the fact that the Ar^{2+} signal intensity (the ionization potential of 27.76 eV) is very low, even at high Ar flows.

Similar to sputtering in metallic mode, the IEDF of singly charged Cr ions for increasing $f_{N_2/Ar}$ comprises the low energy peak and very pronounced high-energy tails (see Fig. 6). With increasing N_2 content in the plasma the low energy peak moves from 1.1 eV to 0.5 eV, indicating that the post-discharge, V_{pd} , decreases (this means that increasing N_2 has a similar effect on V_{pd} as increasing E_p in metallic mode, cf. previous sections). There are also subtle variations in the high-energy portion of the IEDF that will be treated in more detail later on. The shoulder on the high-energy side of the thermalized peak (at around 3 eV) is visible up to $f_{N_2/Ar} = 0.2$ and disappears at higher N_2 flows. The IEDF of Ar^+ shows a more or less uniform increase in intensity with increasing nitrogen content in the plasma up to $f_{N_2/Ar} = 0.2$. Thereafter the count rate decreases, preserving the overall shape of IEDF, to end up at approximately half of the initial value at $f_{N_2/Ar} = 5$. The low-energy peak moves in a similar manner to the corresponding feature in the Cr^+ signal (from 1.0 eV to 0.5 eV). The overall shape of N_2^+ IEDF is similar to that of Ar^+ , especially at higher nitrogen flows. The low-energy peak moves from 0.7 eV to 0.5 eV and total intensity increases gradually (in contrast to Ar^+) with increasing $f_{N_2/Ar}$ from 0.02 to 5. Apart from N_2^+ a large flux of atomic N^+ ions is present as shown in Fig. 6d). The IEDF of N^+ is qualitatively different as it possesses the high energy tail typical for Cr^+ (or Cr^{2+}) ions and never observed for Ar^+ or N_2^+ ions. This energetic stream of monoatomic

nitrogen ions is created through the electron-impact ionization of nitrogen atoms originating from the target: either sputtered from the nitrated portion of the target or being the result of dissociation of back-attracted N_2^+ ions at the target surface. The N^+ count rate increases linearly with increasing $f_{N_2/Ar}$, while the low energy peak moves from 1.0 eV to 0.5 eV.

Sputtering in reactive mode: time-resolved measurements

Fig. 7 shows a set of IEDFs for Cr^+ , Ar^+ , N_2^+ and N^+ ions recorded in 20 μs time intervals for $f_{N_2/Ar} = 2$ (poisoned mode). Since this data were recorded at 15 J pulse energy (E_p) and 300 Hz pulsing frequency, a direct comparison to analogous data for metallic mode is possible (cf. Fig. 3). Starting with the IEDF of Cr^+ it can be seen that the high-energy tail of the most energetic distributions (between 55 μs and 95 μs) falls off faster with increasing ion energy for $f_{N_2/Ar} = 2$ than in the case of sputtering in pure Ar. Qualitatively similar changes with respect to the operation in metallic mode are also observed in the case of Ar^+ despite the fact that Ar ions are by far less energetic than Cr ions. During the most energetic phase of the discharge (35 μs to 55 μs , cf. red curves in Fig. 4 and Fig. 6), both intensity and the maximum ion energy are greatly reduced when sputtering in the poisoned mode. This is, however, accompanied by the increase in intensity on the later stage (after 135 μs) when only thermalized species are present. As was already indicated by the time-averaged data, the IEDF of N_2^+ ions is quite narrow with most energetic ions appearing between 35 μs and 75 μs , thus about the same time as for Ar^+ ions. The time-resolved IEDFs of N^+ ions shown at the bottom of Fig. 7, bring yet

Fig. 7 Time-resolved IEDFs for a) Cr^+ , b) Ar^+ , c) N_2^+ and d) N^+ ions recorded at the average power of 4.5 kW (15 J pulses, 300 Hz) and $f_{\text{N}_2/\text{Ar}} = 2$. Each color represents an IEDF recorded during a 20 μs long time interval, as described in the legend.

another evidence that supports their origin from the target; energetic ions appear at the same time interval as most energetic Cr^+ ions (55 μs to 95 μs) and with a certain delay with respect to N_2^+ ions.

Figure 8 gives further insight into the time sequence discussed above. Following the same procedure as previously for the metallic mode case, the total number of counts detected within the 10 μs window is plotted here as a function of delay time (with respect to the voltage pulse to the cathode) for increasing N_2 -to-Ar flow ratio. Independent of $f_{\text{N}_2/\text{Ar}}$ the first ions detected are always Ar^+ and N_2^+ . Both ion types gain intensity as time goes by up to the point where Cr^+ and N^+ signals start to take off, at around 50 μs (somewhat later for the highest N_2 concentrations). The increase of the Cr^+ and N^+ ion flux (that reach maximum at ca. 80 μs and 70 μs , respectively) is accompanied by a decrease in a number of Ar^+ and N_2^+ ions detected. The situation is reversed in the following time interval (after 80 μs) where Ar^+ and N_2^+ ions begin to increase again (showing an interesting dependency on $f_{\text{N}_2/\text{Ar}}$) while the Cr^+ and N^+ signals continuously decay. Finally, after reaching the second maximum at around 110 μs , the N_2^+ signal decays with a significantly lower rate than that of the Cr^+ ions. The evolution of the Ar^+ signal is similar, except for the fact that the second maximum is not that pronounced at lower $f_{\text{N}_2/\text{Ar}}$ values presumably due to the fact that it appears at later times (beyond the scale of Fig. 8). In that way the integrated intensity of Ar^+ and N_2^+ features two characteristic peaks: one at early stage of discharge associated with more energetic ions (cf. Fig. 7) and one broader bump composed of thermalized ions.

Fig. 8 Plots of total ion count rate vs time (from the onset of the voltage pulse to the cathode). Each data point corresponds to IEDF recorded during 10 μ s and integrated over entire energy range. Integrated intensities for a) Cr^+ , b) Ar^+ , c) N_2^+ and d) N^+ ions are shown for different values of N_2 -to-Ar flow ratio, $f_{\text{N}_2/\text{Ar}}$

There is a number of interesting conclusions that can be drawn from the presented temporal changes in the relative number of ions during a HIPIMS discharge. First of all, there is a perfect time synchronization of the Cr^+ and N^+ signals, that take off at the same instant (some 20-25 μ s after Ar^+ and N_2^+) and develop in a similar way, which emphasizes their common origin from the target. More detailed inspection of the relevant graphs in Fig. 8 reveals also that the intensity of Cr^+ decays with a longer time constant than that of N^+ ; the typical full width at the half-maximum (FWHM) of integrated distribution peaks are 60 μ s and 30 μ s, respectively. This phenomenon is related to the fact that after 100 μ s the character of the discharge changes from HIPIMS to DC-like, as discussed above. Furthermore, the reference measurements of the ion flux composition during the DC discharge for varying N_2 -to-Ar ratio (not shown) indicate that the relative N^+ content is 4 to 10 times lower than in the case of the HIPIMS discharge operated at the same average power. Therefore, it is understandable that a faster decay of the N^+ signal is observed upon transition into the DC-like mode of operation, as the relative ion content for delay times exceeding 100 μ s should resemble that of DC discharge. The reason for a higher N^+ content in the case of HIPIMS plasma is attributed to the fact that very high temporal energy density on the target can enhance the dissociative sputtering of CrN, as well as, lead to more effective decomposition of back-reflected N_2^+ ions. The fact that the concentration of CrN^+ ions is measured to be, in average, ~80% higher during sputtering in DC mode than in HIPIMS, may indicate that the former process dominates.

There is clear evidence that, similar to Ar ions, the number of N_2^+ ions is affected by the energetic flux of Cr atoms from the target. A perfect correlation between the overall time evolution of Cr^+ (or N^+) and Ar^+ (or N_2^+) exists: signals from the filling gas ions (Ar^+ and N_2^+) are reversely proportional to those that originate from the target (Cr^+ and N^+).

A closer inspection of the peak intensities presented in Fig. 8 reveals that, unexpectedly, the intensity of the Ar^+ and Cr^+ signals increases with decreasing Ar flow, at least for the lower values of $f_{N_2/Ar}$. In the time interval between 30 and 50 μs (thus before any Cr^+ ions appear) the Ar^+ signal increases with decreasing Ar flow up to $f_{N_2/Ar} = 0.2$ and decreases after that, whereas in the second phase (second maximum at around 120 μs) an increase is observed even up to $f_{N_2/Ar} = 1$. Correspondingly, in the case of Cr^+ ions, an increase is observed up to $f_{N_2/Ar} = 0.5$ and a slight drop after that for the highest nitrogen flows. The observation that the amount of Ar^+ and Cr^+ ions can increase with decreasing Ar gas flow into the chamber seems, at first, counterintuitive. One has to realize, however, that a varying gas composition together with related poisoning of the target surface gives a number of effects that can account for this unexpected result. In the simplest terms, higher ion content may be either due to (i) an increased volume density of species to be ionized (e.g., increased density of Ar) or to (ii) an increased probability for ionization event per each gas atom (e.g., changes of electron distribution function), and finally (iii) the plasma volume probed in experiment may change (any changes in the thickness of cathode sheath would also affect the number of ions that could escape and be

detected). In the present case certain changes of the gas density in front of the target can not be excluded, as the primary cause of gas rarefaction - energetic stream of sputtered Cr atoms - decreases with increasing $f_{N_2/Ar}$ due to the lower sputtering rate from a poisoned portion of the target (and less effective sputtering with N_2). This fact is experimentally confirmed by the observed drop in the deposition rate. A lower flux of sputter-ejected metal atoms implies also a reduced cooling effect on the high energy tail of the electron distribution function leading to an increase in the electron temperature. Apart from this, the secondary electron emission from nitrided surfaces is believed to be higher than for metals presenting another reason for the altered electron density in the plasma and, in turn, a higher ionization probability. Since all these effects occur simultaneously it is presently not possible to quantify their individual contributions to the observed intensity variations. The results of our mass spectroscopy studies are further supported by optical emission spectroscopy (not shown). Even though in the later case data were recorded in a different set up the same trends are observed: the emission from Ar^+ and Cr^+ ions increased initially to reach maximum at around $f_{N_2/Ar} = 0.2$ and fell down at higher nitrogen flows. In addition, a corresponding increase of emission from Ar neutrals was observed, whereas the line intensity from Cr neutrals decreased continuously in the entire parameter range.

Implications for film growth

Unlike the case for DC sputtering, ions available during film growth with HIPIMS may constitute a major part of the particle flux incident on the substrate. Even though precise quantification of ion-to-neutral ration is difficult, the OES measurements of Cr and Cr^+ emission performed in our laboratory [25] indicate that concentrations of both species are on a comparable level already for the peak current of 400 A (corresponding to 15 J pulses in the present case). Moreover, with a further increasing pulse energy, the emission from Cr^+ ions increases faster than that from Cr neutrals indicating that film forming ions dominate the material flux to the substrate.

When it comes to reactive gas species, (like N^+ or N_2^+ ions and neutrals), the situation becomes more complicated, as the substrates are exposed to neutrals (N_2) also between the pulses. In consequence, for cases where formation of a compound is energetically favorable even without the presence of activated species, surface reactions may continue also during the pulse off time and it has to be taken into account in any analysis of film growth processes. On the other hand, if the extra energy is required to promote compound formation, film growth will proceed mainly during the high energy pulse and analysis of ion fluxes in that phase is of particular relevance. Two examples that may illustrate this point are TiN and CrN. Ensinger *et al.* [32] have demonstrated that the reaction of an as-deposited Cr metal film with adsorbing N_2 molecules is not sufficient for a phase transformation from metal into nitride without an additional source of energy, whereas N_2 reacts spontaneously with a Ti film to form TiN. Taking this into account, it may be understood why relatively low flows of nitrogen gas are required for growth of stoichiometric TiN films with HIPIMS (as compared to conventional DC

process [33]), while in the case of CrN no dependence on the sputtering method is observed (DC or HIPIMS) [34].

Considering the energetics of the ionized flux during sputtering in the metallic mode it may be concluded that increasing the pulse energy leads to a rapid (linear) increase of a number of doubly charged metal ions (a factor of 8 when going from 3 J to 30 J), while the Cr^+ signal intensity increases 2.5 times and the intensity of Ar^+ remains constant (time-averaged data are referred to). The relative contributions to the ion flux at $E_p = 3$ J are as follows: Cr^+ - 32.3%, Ar^+ - 65.3%, Cr^{2+} - 1.2% and Ar^{2+} - 1.2% and, at $E_p = 30$ J, respectively: Cr^+ - 52.2%, Ar^+ - 41.1%, Cr^{2+} - 5.4% and Ar^{2+} - 1.3%. In the case of Cr^+ ions, additional energy available during the pulse has also a strong effect on the average ion energy that doubles upon an increase of E_p from 3 J to 30 J (as evident from the observed growing high-energy tail), whereas in the case of Cr^{2+} ions, the average ion energy increases by only 20% and it is primary the number of ions that goes up (cf. Fig. 2). Fig. 9 gives an overview of the distribution of the total energy among all ions in the ion flux upon increasing pulse energy. The Cr^+ intensity has been divided by 5 in order to facilitate comparison. It can be seen that already at 3 J per pulse it is Cr^+ ions that dominate being responsible for 55% of the total energy flux, although the Ar^+ contribution is not much smaller (~38%, respectively). With increasing E_p , the Cr^+ contribution increases linearly, whereas Ar^+ stays practically unchanged. A 10-fold increase is observed at the same time for the Cr^{2+} ions, that for the pulse energy higher than 22 J carry actually more energy than the flux of Ar^+ ions. The signal from Ar^{2+} ions stays low and does not exceed 2%. For the pulse energy of 30 J, the contributions are as

Fig. 9 Energy of ion flux entering the mass spectrometer as a function of pulse energy, E_p . Trends for all highest intensity ions (Cr^+ , Ar^+ , Cr^{2+} and Ar^{2+}) are plotted. Note that Cr^+ data are downscaled by a factor of 5 in this plot to facilitate comparison.

follows: Cr^+ - 76%, Cr^{2+} - 14%, Ar^+ - 9% and Ar^{2+} 1%. Note that all these values refer to the situation where no biasing is applied.

The fact that the number (and energy) of doubly charged Cr ions is comparable to the number of singly charged Cr ions may have dramatic consequences for the film growth process, since a high flux of doubly charged ions upon application of typical bias voltages in the range 50-100 V is energetic enough to cause high lattice defect density that may eventually lead to disruption of epitaxial growth for individual columns with resulting renucleation [5]. The films would then become denser, but exhibit high

compressive internal stress and inert gas incorporation. A solution to this potential problem is suggested by the results of time-resolved studies, as discussed below.

From the presented data it is clear that in the case of Cr sputtering with HIPIMS the composition and energy spectrum of the ion flux incident on the substrate can be varied to a large extent by tuning the pulse energy (peak current). As was indicated above, film growth performed at $E_p=3$ J would be accompanied by the ion flux composed mostly of Cr^+ and Ar^+ ions with the average energy per ion of 4.6 eV and 1.6 eV, respectively. On the other hand in the case of deposition at $E_p=30$ J more energetic Cr^+ ions would dominate (average energy per ion of 9.3 eV), in addition, a largely increased number of Cr^{2+} ions with a mean energy of 16.7 eV would be present. One can also, to some extent, selectively steer the energy of incident group of ions taking the advantage of the situation that a certain time dispersion exists between Ar and Cr ions (cf. Fig. 5). For instance, in the experimental set up used in our experiment, the application of a synchronized biasing pulse between 0 μs and 40 μs should affect the average energy of a significant portion of the Ar^+ ions, without having a noticeable effect on the energy spectrum of the Cr^+ and Cr^{2+} ions, as they arrive to the substrate at a later stage. Alternatively, one could affect predominantly Cr ions by applying a relatively short bias pulse (30-50 μs) with a certain delay (with respect to the onset of the voltage pulse) of, say, 60-70 μs . For sufficiently high bias voltage, this could result in an effective implantation of Cr ions (mainly due to doubly ionized species that would gain twice the energy of Cr^+) with limited incorporation of undesired Ar. More complex biasing scenarios, involving, e.g., short positive pulses (to repel undesired, high energy, ions) can

be imagined, nevertheless, these possibilities for working in the time domain remain to be demonstrated in practice.

Similar to sputtering in the metallic mode in the case of reactive sputter deposition (cf. Fig. 6-8), the composition of the ion flux is not uniform throughout the pulse. The ion flux to the sample up to 60 μs is dominated by Ar^+ and N_2^+ ions with the energy in the 2-10 eV range (dependent on $f_{\text{N}_2/\text{Ar}}$). This stage is followed by the 40 μs period (60-100 μs) of highly energetic flux composed of Cr ions (both Cr^+ and Cr^{2+}) along with N^+ ions. During this period significant amounts of ions arrive with an energy higher than 50 eV. After that, thermalized Ar^+ and N_2^+ ions dominate the ion flux and the average ions energy in this phase is close to 2 eV. These time variations in ion composition (and energy) open up a possibility to tweak the properties of the ion flux incident on the growing film, in a similar manner as discussed here for the metallic mode of operation. One may envision different biasing scenarios for growth of CrN_x films since, in case of Cr, nitride formation is believed to take place mainly during the time when intense plasma is present. In particular, it would be interesting to evaluate separately the roles of low energy N_2^+ ions and energetic N^+ ions in the nitride formation process.

Even though the presented data were obtained for a specific value of a pressure (0.4 Pa) and distance (21 cm), we infer that the time evolution of ion flux composition is an inherent feature of high power pulsed discharges. The ionization of working gas mixture will always suffer during the energetic portion of the pulse, when large amounts

of metal species enter the plasma causing both gas rarefaction, and quenching of the electron energy distribution function.

Figure 10 shows the contributions from different ions to the total energy flux measured during reactive sputtering in a Ar/N₂ gas mixture plotted against the N₂-to-Ar gas ratio. It can be seen that most of energy is supplied by Cr⁺ ions, independent of $f_{N_2/Ar}$. At lower N₂ flows ($f_{N_2/Ar} < 0.1$) Ar⁺ ions account for ca. 10-15% of the total energy flux. This contribution goes down rather quickly with increasing $f_{N_2/Ar}$ and already at $f_{N_2/Ar} = 0.3$ it becomes surpassed by that of N⁺ ions. These nitrogen ions constitute the second most energetic contribution for all values of $f_{N_2/Ar}$ higher than 0.3, due to the wide energy distribution. The energy carried by N₂⁺ molecular ions increases continuously with increasing $f_{N_2/Ar}$ and eventually at $f_{N_2/Ar} = 1$ it becomes higher than that of the Ar⁺ ion flux. Taking into account the fact that growth of stoichiometric CrN (under the same experimental conditions) requires a $f_{N_2/Ar}$ value higher than 0.3 [34] it may be concluded that in such case it is primary Cr⁺ and N⁺ ions that are responsible for the energy transfer to the growing film. This is, of course, provided that no more sophisticated biasing scheme is used.

Fig. 10 Energy of ion flux entering the mass spectrometer during reactive sputtering in Ar/N₂ gas mixture as a function of N₂-to-Ar flow ratio, $f_{N_2/Ar}$. Note the log scale on the X and Y axes.

CONCLUSIONS

Mass spectroscopy has been used to obtain original results for the energy and composition of the ion flux during high power pulsed magnetron sputtering of Cr target in an industrial deposition system. The time-averaged and time-resolved ion energy distribution functions were recorded while sputtering in argon gas, for different values of pulse energy (equivalent of peak current). For the first time, corresponding IEDFs were

also recorded during reactive (Ar/N₂) mode of operation for varying N₂-to-Ar ratios. The following findings are noted:

- 1) Increasing the pulse energy during sputtering in the metallic mode leads to a rapid (linear) increase of the number of doubly charged Cr ions (by a factor of 8 when going from 3 J to 30 J), while the intensity of Cr⁺ signal increases by a factor of 2.5 and the intensity of Ar⁺ signal remains constant.
- 2) The composition (and energy) of the ion flux can be significantly altered by varying the pulse energy. The film growth performed at $E_p=3$ J would thus be accompanied by the ion flux composed mostly of Cr⁺ and Ar⁺ ions with the average energy per ion of 4.6 eV and 1.6 eV, respectively. In the case of deposition at $E_p=30$ J, the ion flux would be dominated by more energetic Cr⁺ ions (average energy per ion of 9.3 eV), in addition, a largely increased number of Cr²⁺ ions with a mean energy of 16.7 eV would be present.
- 3) Low energy N₂⁺ molecular ions and energetic N⁺ ions are present while sputtering in reactive mode. The N⁺ ions constitute the primary source of nitrogen ions detected and for $f_{N_2/Ar}$ higher than 0.3 are the second highest contribution to the total energy flux. This is in contrast to the reactive DC sputtering where N₂⁺ ions dominate over N⁺.

- 4) Time-resolved studies reveal a significant variation in the composition of the ion flux throughout the pulse. The initial phase is always dominated by relatively low-energy ions of the working gas (Ar^+ or Ar^+/N_2^+). Next, intense emission from energetic sputtered species occurs (Cr^+ or Cr^+ and N^+) with a simultaneous decrease in the intensity of Ar^+ (or Ar^+/N_2^+) signal due to gas metal induced gas rarefaction and lowering of the electron temperature. Finally, thermalized ions of the working gas dominate.

- 5) The properties (composition and energy) of the ion flux incident on the substrate can be controllably adjusted not only by varying the pulse energy (discharge peak current), but also by taking advantage of the revealed time-variations in the composition of ion flux.

Finally, the time evolution of ion flux composition is proposed to be an inherent feature of the high power pulsed discharges due to the fact that the ionization of working gas mixture will always decrease during the energetic portion of the pulse, when large amounts of metal species enter the plasma causing gas rarefaction and quenching of the electron energy distribution function.

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Table 1. List of isotope ion species measured in the present work along with their properties and corresponding experimental settings.

Ion	Abundance [%]	m/e	Dwell time [ms]	TOF correction [μs]
$^{36}\text{Ar}^+$	0.337	36	400	55.3
$^{40}\text{Ar}^{2+}$	99.6	20	400	41.2
$^{50}\text{Cr}^+$	4.345	50	200	65.2
$^{50}\text{Cr}^{2+}$	4.345	25	200	46.1
$^{15}\text{N}^+$	0.366	15	600	35.7
$^{29}\text{N}_2^+$	0.73	29	400	49.6