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Are the argon metastables important in high power impulse magnetron sputtering discharges?

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We use an ionization region model to explore the ionization processes in the high power impulse magnetron sputtering (HiPIMS) discharge in argon with a titanium target. In conventional dc magnetron sputtering (dcMS), stepwise ionization can be an important route for ionization of the argon gas. However, in the HiPIMS discharge stepwise ionization is found to be negligible during the breakdown phase of the HiPIMS pulse and becomes significant (but never dominating) only later in the pulse. For the sputtered species, Penning ionization can be a significant ionization mechanism in the dcMS discharges, while in the HiPIMS discharge Penning ionization is always negligible as compared to electron impact ionization. The main reasons for these differences are a higher plasma density in the HiPIMS discharge, and a higher electron temperature. Furthermore, we explore the ionization fraction and the ionized flux fraction of the sputtered vapor and compare with recent experimental work. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935402>]

I. INTRODUCTION

The high power impulse magnetron sputtering (HiPIMS) discharge is an ionized physical vapor deposition (IPVD) technique that has attracted much interest during the last decade.¹ The HiPIMS discharge was derived from studies of high power pulsing of a discharge created between plane parallel electrodes² and later in a transverse magnetic field.³ In HiPIMS, high power is applied to the magnetron target in short (10–500 μ s) unipolar pulses at low duty cycle and low repetition frequency (50–5000 Hz) while keeping the average power about 2 orders of magnitude lower than the peak power.¹ This results in a high plasma density, and very high ionization fraction of the sputtered vapor. The high ionization fraction improves the control of the film growth as it is possible to control the energy and direction of the deposition species, which is a significant advantage over conventional dc magnetron sputtering (dcMS) where the sputtered vapor consists mainly of neutral species.

To study the ionization as well as other key features of the HiPIMS discharge, an ionization region model (IRM)⁴ was developed to capture the main features of the plasma behavior during an HiPIMS pulse and the afterglow. The main characteristic of the model is that an ionization region (IR) is defined next to the race track formed in the sputtering target, in which the temporal behavior of the volume averaged density of all species is determined for a given applied power and pressure. This type of a global model provides a

flexible tool to explore the ionization processes, the temporal variations of the ionized fractions of the working gas and the sputtered vapor, and the electron density and temperature. The model has previously been applied to study gas rarefaction and refill processes,^{4,5} the properties of both short⁴ and long pulses,⁵ the loss in deposition rate,⁶ the electron heating mechanism,⁷ and the onset of self sputtering,⁸ for a discharge with Al target, and the temporal behavior of the argon metastables for a discharge with Ti target.⁹ For the latter study, a version of the IRM was developed that included detailed treatment of the kinetics of the metastable states of the argon atom Ar^m . This version will from now on be referred to as m-IRM. The m-IRM was demonstrated to accurately follow the time development of the metastable density and the results were validated against measurements taken by tunable diode laser absorption spectroscopy (TD-LAS).¹⁰

For the purpose of investigating ionization processes, Kudryavtsev and Skrebov¹¹ developed a model to study the initial stages of the plasma discharge and the build up of electron density. They recognized two possible cases of the growth of electron density in the plasma. In the first case, the primary role is played by stepwise ionization via a metastable state. In this case, the growth of the electron density at an initial stage is very slow, due to the fact that first there is an accumulation of metastable atoms. Subsequently, when a certain density of metastable atoms is reached, the ionization from the metastable state becomes predominant, causing an abrupt increase in the electron density to the value in the quasi-stationary regime. In the second case, the mechanism determining the increase in the electron and ion density is

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dominated by direct ionization of argon from the ground state. The growth of the electron density in this case occurs without a marked jump in the electron density. For a magnetron sputtering discharge in argon at 1.33–133 Pa, magnetic field density up to 0.3 T, and pulse voltage amplitude up to 3 kV, the second mechanism is the one realized in practice.¹² Recent experimental studies of the HiPIMS discharge in argon with a titanium target include the recording of the temporal density variation of Ti, Ti⁺, Ar, and Ar⁺ along with metastable states using resonant absorption spectroscopy¹³ and 2D mapping of the Ti, Ti⁺, and Ar^m using laser induced fluorescence (LIF),¹⁴ determination of the electron density and electron temperature,^{15,16} and ionized flux fraction,^{13,20} and determination of the titanium ionization fraction.^{13,20} Here, we study the role of the argon metastables using the m-IRM for HiPIMS discharges, in particular, how much of the ionization goes through stepwise ionization and what is the role of Penning ionization for the ionization of the sputtered species. We will also discuss the temporal behavior of the various species as well as the ionization fraction and the ionized flux fraction for titanium and argon and compare with the experimental findings.

II. THE IONIZATION REGION MODEL

In the magnetron sputtering discharge, it is well known that a high density brightly glowing torus shaped plasma hovers next to the target surface and extends a few cm from the cathode target and is embedded in a lower density plasma bulk. Based on this, the IR is defined as an annular cylinder with outer radii r_{c2} and inner radii r_{c1} which extends from z_1 to z_2 axially away from the target. Geometrical effects are included indirectly as loss and gain rates across the boundaries of this annular cylinder to the target and the bulk plasma.⁴ The temporal development is defined by a set of ordinary differential equations giving the first time derivatives of the electron energy and the particle densities for all the species. The electron density is found assuming quasi-neutrality of the plasma. The model assumes only volume-averaged values over the whole IR volume for the electron, ion, and neutral densities. For simplification, we assume a Maxwellian electron energy distribution function (EEDF) while calculating the rate coefficients but we have by separate calculations verified that the Ar^m density is only marginally changed if the EEDF contains 0.01% hot (100–500 V) electrons which is a typical fraction in a pulse.²¹

The main reactions we will address in this work are the electron impact ionization of titanium,

and the set of reactions shown in Fig. 1. The most important of these is excitation from the ground state argon atom to the metastable levels denoted by Ar^m

where we assume that Ar^m represents both the metastable levels in the 3s²3p⁵4s shell (³P₀ and ³P₂) at energies 11.72 and 11.55 eV, respectively. The rate coefficient we use for

FIG. 1. An energy level diagram for the main processes involving the argon metastable Ar^m levels. Electron induced reactions are marked by solid arrows and radiative transitions by curvy lines. (a) The complete reaction scheme, including de-excitation from Ar^m to the ground state via the resonant Ar^r levels. (b) A simplified reaction scheme in which the quenching reaction (R5), and the Ar^r reactions R7a to R10, are combined to an effective de-excitation reaction R5*.

reaction (R2) also takes into account the higher lying 4p levels that cascade to the metastable levels Ar^m as discussed by Stancu *et al.*⁹ We include direct ionization of argon by electron impact from the ground state

and ionization from the metastable levels Ar^m

Transitions from Ar^m to the ground state can go by two routes as illustrated in Fig. 1. The first route is by electron impact quenching (superelastic) collisions

The second route is de-excitation from Ar^m by coupling to the resonant levels Ar^r. The involved reactions (not written out here) are numbered R7a to R10 in Fig. 1(a). The reactions considered in the complete reaction scheme are listed in Table I. Electron-impact induced transitions between the Ar^m and Ar^r levels (reactions R7a and R7b) will, at high enough plasma density, populate these levels according to their statistical weights. The two resonant levels have very large radiative rates (reaction R9) to the ground state, 5.1×10^8 Hz and 1.2×10^8 Hz, respectively. This opens up an additional loss channel from Ar^m to the ground state (reactions R7a + R9). The

TABLE I. The reactions considered in the more detailed model shown in Figure 1(a).

Reactions	Nos.	Process
$e + \text{Ti} \rightarrow \text{Ti}^+ + 2e$	R1	Titanium ionization
$e + \text{Ar} \rightarrow \text{Ar}^m + e$	R2	Metastable excitation
$e + \text{Ar} \rightarrow \text{Ar}^+ + 2e$	R3	Argon ionization
$e + \text{Ar}^m \rightarrow \text{Ar}^+ + 2e$	R4	Ionization of metastable
$e + \text{Ar}^m \rightarrow \text{Ar} + 2e$	R5	Electron quenching of metastable
$\text{Ar}^m + \text{Ti} \rightarrow \text{Ar} + \text{Ti}^+ + e$	R6	Penning ionization
$e + \text{Ar}^m \rightarrow \text{Ar}^r + e$	R7a	Metastable to resonant level
$e + \text{Ar}^r \rightarrow \text{Ar}^m + e$	R7b	Resonant to metastable level
$e + \text{Ar} \rightarrow \text{Ar}^r + e$	R8	Resonant level excitation
$\text{Ar}^r \rightarrow \text{Ar} + h\nu$	R9	Resonant state decay
$\text{Ar} + h\nu \rightarrow \text{Ar}^r$	R10	Resonant self absorption

effectiveness of this channel, however, is reduced by the absorption of the resonant radiation (reaction R10) which re-populates the Ar^r levels. For typical pressures in magnetron discharges, the resonant radiation has escape factors in the range of 10^{-4} – 10^{-2} which partially, but not totally, blocks this loss channel. The net effect of reactions R7a to R10 in Fig. 1(a) thus depends both on the plasma density (through reactions R7a, R7b, and R8) and the argon gas density (through reaction R10), and must be individually modeled for each discharge for accurate results. The extreme cases of zero and complete level mixing, and of zero and complete imprisonment, were, however, analyzed by Stancu *et al.*⁹ Based on their results we replace, in our m-IRM runs, the quenching reaction (R5) by an effective de-excitation reaction R5^* as shown in Fig. 1(b). The rate coefficient for R5^* lies in the range from $k_{\text{R5}^*} = k_{\text{R5}}$ for complete imprisonment to $k_{\text{R5}^*} = k_{\text{R5}} + k_{\text{R7a}}$, for zero imprisonment. These limits also hold, as extreme values, independent of the degree of Ar^m – Ar^r level mixing. We will herein assume the mean value of these extremes $k_{\text{R5}^*} = (k_{\text{R5}} + 0.5 \times k_{\text{R7a}})$, and use the simplified level diagram of Fig. 1(b) to illustrate the results. We also include Penning ionization of Ti

a process with a relative importance that depends very much on the plasma density. The rate coefficients used in the model calculations are discussed and evaluated by Stancu *et al.*⁹

The m-IRM follows the time development in the discharge volume by solving the coupled differential equations for the (volume averaged) densities of the various species. Of special interest, here is the rate equation for the metastable density

$$\begin{aligned} \frac{dn_{\text{Ar}^m}}{dt} = & n_{\text{Ar}} n_e k_{\text{R2}} - n_{\text{Ar}^m} [n_e (k_{\text{R4}} + k_{\text{R5}^*}) + n_{\text{Ti}} k_{\text{R6}}] \\ & - u_{z,\text{Ar}^m} \frac{dn_{\text{Ar}^m}}{dz}, \end{aligned} \quad (1)$$

where the indices on the rate coefficients correspond to the reaction numbers above and the mean rate has been used. Here, n_{Ar^m} is the metastable atom density, n_{Ar} is the density of argon atoms in the ground state, n_{Ti} is the titanium atom density, and n_e is the electron density. The generic last term in Eq. (1) represents diffusion (which is calculated as described in Raadu *et al.*⁴) and u_{z,Ar^m} is a velocity due to diffusional outflow (or refill) of Ar^m . A term corresponding to sputter wind kick-out (see Raadu *et al.*⁴) is negligible for the metastable level.

III. RESULTS AND DISCUSSION

We will focus on two dimensionless ratios that reflect two roles which the metastable level can play in the discharge. One ratio is the fraction of Penning ionization of the sputtered target material,

$$\frac{R_{\text{Penning},\text{iz}}}{\sum_i R_{\text{Ti},\text{iz},i}} = \frac{\text{rate of Penning ionization to create Ti}^+}{\text{total rate for the creation of Ti}^+}. \quad (2)$$

The other ratio is the fraction of stepwise ionization (through the metastable states) of the argon working gas

$$\frac{R_{\text{stepwise},\text{iz}}}{\sum_i R_{\text{Ar},\text{iz},i}} = \frac{\text{rate of stepwise ionization through Ar}^m}{\text{total rate for the creation of Ar}^+}. \quad (3)$$

A case of special interest is when the metastable population is at equilibrium, and when also convection across the boundaries of the studied volume can be neglected. Under these two conditions, the fraction of the total ionization that goes through the metastable level is independent of n_e , and can be directly obtained from the involved rate coefficients and depends only on the electron temperature T_e

$$\left(\frac{R_{\text{stepwise},\text{iz}}}{\sum_i R_{\text{Ar},\text{iz},i}} \right)_{\text{eq}} = \frac{k_{\text{R2}} k_{\text{R4}}}{k_{\text{R4}} + k_{\text{R5}^*}} \bigg/ \left(k_{\text{R3}} + \frac{k_{\text{R2}} k_{\text{R4}}}{k_{\text{R4}} + k_{\text{R5}^*}} \right). \quad (4)$$

This expression has been evaluated as a function of T_e and the result is shown as a solid (red) line in Fig. 2. The dashed (blue and green) curves represent the extreme cases of zero and complete imprisonment, and the thin dashed dotted lines show the results when 0.01%, 0.1%, and 1% of the electrons are assumed to be hot (400 V).

In real discharges, there are both convective terms (sputter wind kick-out and diffusion) and, in HiPIMS pulses, there are in the breakdown phase large departures from equilibrium. We therefore use the m-IRM, which includes these effects, to explore the HiPIMS discharges. The IRM is a semi-empirical model in the sense that it uses a measured discharge current waveform as a main input parameter, as described in detail elsewhere.⁹

In the present work, we investigate experimentally recorded 200 μs long pulses with 0.5 A, 40 A, and 70 A peak current, corresponding to an average peak current density over the cathode surface of 0.006, 0.7 (average power of 100 W), and 0.9 A/cm², and a gas pressure of 1.33 Pa. The target was a titanium disc of 10 cm diameter and the pulse

FIG. 2. The relative importance of stepwise ionization of Ar via the metastable state in equilibrium and without convections from Eq. (4), the thick solid (red) line shows the result for the effective average $k_{\text{R5}^*} = k_{\text{R5}} + 0.5 \times k_{\text{R7a}}$, and the thick dashed lines show the extremes $k_{\text{R5}^*} = k_{\text{R5}}$ (complete imprisonment (green)) and $k_{\text{R5}^*} = k_{\text{R5}} + k_{\text{R7a}}$ (zero imprisonment (blue)) assuming Maxwellian EEDF. The dashed dotted lines show the results when 0.01%, 0.1%, and 1% of the electrons are assumed to be hot (400 V). The * symbol shows the results of the m-IRM calculation for HiPIMS at time t_2 in Figure 3 for 0.5 A, 40 A, and 70 A peak current.

repetition frequency was 50 Hz.⁹ The key parameters for the three cases are listed in Table II. The 0.5 A peak current case is included as the current is roughly two orders of magnitude lower than the other two cases and thus is dcMS like. The 0.5 A peak current case only reaches electron densities expected in dcMS while the 40 and 70 A cases give electron densities typical for a HiPIMS discharge. The parameter β listed in Table II is the probability that an ionized species of the sputtered vapor returns to the target and is a fitting parameter in the model.⁶ We note that β is small (15%) for the 0.5 A peak current case, and it increases with increasing peak current and over 50% of the ions of the sputtered vapor return to the target for the 70 A peak current case. Figure 3 shows the temporal variation of the electron temperature $T_e(t)$, and the relative weights of the two reaction paths during the pulse for the three cases explored. The rise with time up to 25 μ s is associated with the time it takes to build up an equilibrium metastable population.⁹ Particularly during the early breakdown phase (the mark $t_1 = 10 \mu$ s in Fig. 3) stepwise ionization through the metastable level plays only a minor role (0.3%–7% at 1.33 Pa). A flow chart illustration for the 40 A peak current case is given in Fig. 4(a), with the widths of the arrows taken at the time t_1 in the simulation run. At this time, the electron density is $3.4 \times 10^{17} \text{ m}^{-3}$. Stepwise ionization via the metastable state plays, at most, a marginal role in the ignition of this HiPIMS pulse. After 25 μ s, the metastable density is close to the equilibrium population with respect to the ground state. A flow chart illustration of this case at 150 μ s is shown in Fig. 4(b). Here, the contribution from stepwise ionization of argon is 15%, significant but not dominating. For 0.5 A peak current, stepwise ionization contributes roughly 10% (Fig. 3(a)) but for 70 A peak current it contributes 15% (Fig. 3(c)), 150 μ s into the pulse. These values from the m-IRM run have been marked onto Fig. 2 with a star and deviate only slightly from the simple estimate at equilibrium (Eq. (4)).

In steady state, and neglecting the small diffusion and kick-out terms, the rate equation for the titanium ions (not shown) gives

$$\frac{R_{\text{Penning,iz}}}{\sum_i R_{\text{Ti,iz},i}} = \frac{n_{\text{Ar}^m} k_{\text{R6}}}{n_{\text{Ar}^m} k_{\text{R6}} + n_e k_{\text{R1}} + n_{\text{Ar}^+} k_{\text{cx}}}, \quad (5)$$

TABLE II. The cases explored and numerical values of selected plasma parameters for argon discharge with a titanium target.

Case	p (Pa)	$I_{\text{D,peak}}$ (A)	t (μ s)	T_e (eV)	n_e (m^{-3})	β	Stepwise (%)	Penning (%)
HiPIMS	1.33	0.5	10	7.4	1.6×10^{16}	0.15	0.3	3.8
HiPIMS	1.33	0.5	150	6.7	1.5×10^{17}	0.15	9.9	12.1
HiPIMS	1.33	0.5	205	0.7	4.6×10^{16}	0.15	100	76.2
HiPIMS	1.33	40	10	5.7	3.4×10^{17}	0.4	5.1	2.5
HiPIMS	1.33	40	150	5.6	2.0×10^{18}	0.4	14.8	0.5
HiPIMS	1.33	40	205	1.5	4.1×10^{17}	0.4	99	37.7
HiPIMS	1.33	70	10	5.9	6.3×10^{17}	0.51	6.5	1.8
HiPIMS	1.33	70	150	4.3	1.0×10^{18}	0.51	15.4	0.9
HiPIMS	1.33	70	205	1.7	2.6×10^{17}	0.51	96.9	35.9

FIG. 3. The process weights of direct ionization and stepwise ionization of Ar via the metastable extracted from an m-IRM model run for a 200 μ s long HiPIMS pulse at 1.33 Pa, (a) 0.5 A peak current, (b) 40 A peak current, and (c) 70 A peak current. After pulse cutoff, the electron temperature and density drop rapidly. The direct ionization drops towards zero, and the high weight of the stepwise ionization at point t_3 shall be understood as a large fraction of an extremely small value.

where n_{Ar^+} is the argon ion density and k_{cx} is the rate coefficient for charge exchange between Ar^+ and Ti.

The ratios of Penning ionization for the HiPIMS discharges investigated are summarized in Table II. During the HiPIMS pulse (the 40 A and 70 A cases) they are very low, typically $R_{\text{Penning,iz}}/\sum_i R_{\text{Ti,iz},i} < 1\%$ (and consequently is not shown). The reason for the low contribution of Penning ionization for HiPIMS is the much higher plasma density, the

FIG. 4. A flow chart illustration of the two main ionization paths of argon where the widths of the arrows are proportional to the reaction rates extracted from the model for the 40 A peak current case. The ionization paths for HiPIMS discharge (a) at the time t_1 in Fig. 3, in the rising flank of the current, and (b) at equilibrium, time t_2 in Fig. 3. At t_1 (a), the Ar^m level population is far below the equilibrium value which is indicated by a dashed line and stepwise ionization is negligible. Hence, only a small fraction of the ionization is stepwise. At equilibrium (b) the fraction of ionization that is stepwise is larger, but still small.

peak electron density ($2.1 \times 10^{19} \text{ m}^{-3}$ at 70 A peak current) is roughly two orders of magnitude higher than for the 0.5 A case ($1.5 \times 10^{17} \text{ m}^{-3}$). This density enters the denominator of Eq. (5). This agrees with the findings of Britun *et al.*^{13,14} which by comparing the temporal behavior of the various species in an argon discharge with titanium target conclude that Penning ionization is negligible in the HiPIMS discharges. It is clear from Eq. (5), given that $k_{\text{cx}} n_{\text{Ar}^+} \ll k_{\text{R6}} n_{\text{Ar}^m}$, that in the limit of low n_e , Penning ionization can become the dominant ionization route for the sputtered species. For 0.5 A peak current, the electron density at equilibrium (150 μs into the pulse) is $1.5 \times 10^{17} \text{ m}^{-3}$ and Penning ionization has about 12% contribution. This is consistent with early findings in rf-sputtering glow discharges^{22,23} and with the global model calculation of Hopwood and Qian,²⁴ for a magnetron sputtering discharge with a secondary inductively coupled discharge. Hopwood and Qian²⁴ stated that for low electron density ($\ll 10^{17} \text{ m}^{-3}$), Penning ionization is the dominant ionization path and for high electron densities ($\gg 10^{17} \text{ m}^{-3}$), electron impact ionization plays the dominant role in ionization of the sputtered vapor. Sometimes the HiPIMS discharge is operated in the pre-ionized mode. Then a low voltage is maintained between the high power pulses. Such an arrangement of an argon discharge with aluminum target was explored by Vitelaru *et al.*²⁵ who found that the steady state metastable density between the high power pulses is up to 10% of the maximum metastable density in the pulse. The same order of magnitude was found independently by Britun *et al.*,¹⁴ however without pre-ionization. Thus, we made a separate test of the 0.5 A and 40 A cases with seed densities lying from 0.1% to 10% of the maximum argon metastable density. The presence of metastables before the high voltage pulse application only helps to reach the maximum value faster, compressing the period t_1 described by Stancu *et al.*,⁹ but it does not affect the absolute value of the maximum. Therefore, these seed metastable densities lead to negligible changes, particularly on the direct versus stepwise ionization, and only a very small change in T_e ($< 3\%$), and all the other densities remain essentially the same. Thus, the results are robust against the changes in the initial metastable density.

The fractional ionization of the sputtered vapor is given by $n_{\text{M}^+}/(n_{\text{M}^+} + n_{\text{M}})$, where n_{M^+} is the density of the ions of the sputtered vapor (metal) and n_{M} is the density of the neutral sputtered vapor. For the 0.5 A peak current, the ionization fraction for titanium is low, reaches roughly 3% towards the end of the pulse as seen in Figure 5(a). This ionization fraction is similar to what has been reported for the $[\text{Ti}^+]/[\text{Ti}]$ density

FIG. 5. The ionization fraction and ionized flux fraction for argon and titanium as a function of time for (a) 0.5 A peak current, (b) 40 A peak current, and (c) 70 A peak current, for a 200 μs long HiPIMS pulse at 1.33 Pa.

ratios in the dcMS discharge where for pressures below 6.67 Pa $[\text{Ti}^+]/[\text{Ti}] < 2\%$.²⁶ Furthermore, it is found that the $[\text{Ti}^+]/[\text{Ti}]$ density ratio increases with increased distance from the target and increased discharge pressure and the $[\text{Ti}^+]/[\text{Ti}]$ density ratio is higher for an argon discharge than for a krypton or a xenon discharge.²⁷ Also, Nafarizal *et al.*^{26,27} concluded that Penning ionization cannot be the dominant mechanism for ionization of titanium in dcMS. For the higher peak current, the metal ionization fraction is high and peaks at 81.7% 80 μs into the pulse and is 45% at 150 μs into the pulse for 40 A peak current but reaches 89% 62 μs into the pulse for 70 A peak current as seen in Figures 5(b) and 5(c), respectively. This is somewhat lower ionization fraction than that reported by Bohlmark *et al.*²⁰ or about 80%–90% for a 100 μs long pulse with repetition frequency of 50 Hz, pulse energy in the range of 2–12 J (average power 100–600 W) and 1.33 Pa argon pressure, using optical emission spectroscopy, a line of sight averaged method. Britun *et al.*¹³ measured the temporal evolution of the absolute Ti and Ti^+ densities for a 20 μs long pulse at 1 kHz (supplied energy per pulse 0.26 J) and at pressure of 2.7 Pa. They found that the ionization fraction is difficult to determine during the pulse on time but state that it reaches 40% in the off time. Note that these short pulses only capture the initial stages of the pulse, the current rise phase. This value agrees well with the ionization fraction for the 40 and 70 A cases which reaches roughly 40% 20 μs into the pulse as seen in Figures 5(b) and 5(c), respectively.

The metal ion flux fraction is defined as $\Gamma_i/(\Gamma_i + \Gamma_n)$ where the ion flux to the substrate scales as $\Gamma_i \sim \sqrt{T_e}$ and the neutral flux scales as $\Gamma_n \sim \sqrt{T_g}$. It is important to note that in a weakly ionized discharge $T_e \gg T_g$ so that the metal ion flux fraction is larger than the fraction of ionized metal in the plasma. Thus, it is not necessary to completely ionize the sputtered metal to create a highly ionized flux to the substrate.²⁸ This can be seen in Figure 5 where the ionized flux fraction is significantly higher than the ionization fraction for both Ti^+ and Ar^+ -ions. For the 0.5 A peak current, the ionized flux fraction for Ti^+ peaks at about 23% towards the end of the pulse. The time averaged ionized flux fraction for Ti^+ over 250 μs is 18% for 0.5 A peak current, 71% for 40 A peak current, and 72% for 70 A peak current. The time averaged ionized flux fraction for Ar^+ over 250 μs is much lower or 1.5% for 0.5 A peak current, 35% for 40 A peak current, and 38% for 70 A peak current. Lundin *et al.*¹⁶ used a gridless ion meter to determine the ionized flux fractions of the sputtered material. They found the ionized flux fraction for titanium to be 60% for 2.0 A/cm² current density and increases with increasing current density but decreases slightly with increasing the pressure in the range of 0.5–2.0 Pa.^{16,19} For current density of 1.0 A/cm², the ionized flux fraction is in the range of 41%–49%. Poolcharuansin *et al.*¹⁸ reported ionized metal flux fraction in the range of 30%–50% and decreasing with increasing average power of 300–1300 W. Kudláček *et al.*¹⁷ reported that argon ions are the predominant ions in the total ion flux. They found that the ionization flux fraction of titanium is in the range of 60%–99% at 0.5 Pa, average pulse current of 60 A, and 200 μs long pulse at 1 kHz. Note that these measured values

are time averaged values and are mostly somewhat lower than that predicted by m-IRM.

Figure 6 shows the temporal variations of the densities of the various species included in the model. For the 0.5 A peak current case, there is a small gas rarefaction, at most 6% at 200 μs into the pulse, as seen in Fig. 6(a). However, we see that there is a much more significant drop in the neutral argon density due to gas rarefaction and ionization for

FIG. 6. The densities of the various species included in the model as a function of time for (a) 0.5 A peak current, (b) 40 A peak current, and (c) 70 A peak current, for a 200 μs long HiPIMS pulse at 1.33 Pa.

the higher peak currents 40 and 70 A as seen in Figs. 6(b) and 6(c), respectively. The drop in neutral argon density is 80% at 40 A, and the minimum in the neutral argon density occurs 102 μs into the pulse. For the 70 A case, the drop in pressure is 89% and it occurs 85 μs into the pulse. Vlček *et al.*²⁹ used optical emission spectrometry that encountered almost an order of magnitude decrease in the density of atomic argon but slightly less dramatic decrease in the density of argon ions roughly 50–70 μs into a 200 μs long pulse of 50 A average current during the pulse, while sputtering a Cu target. There is also a similar drop in the Ar^m density which is discussed in detail elsewhere.^{9,10} The density of neutral titanium atoms and Ti^+ -ions reaches the values in the range of few times 10^{17} m^{-3} and agrees well with the measurements of Britun *et al.*¹³ but with 20 μs long pulses at 1 kHz (supplied energy per pulse 0.26 J) at 2.6 Pa. For the 40 A peak current, the argon ion density peaks roughly 70 μs into the pulse and the Ti^+ -density peaks a few μs later. We note that for the 0.5 A peak current the Ar^m density is higher than the electron density while at 40 A peak current the electron density and the Ar^+ -ion density are significantly higher than the Ar^m density. The Ti^+ -ion density is always lower than the Ar^+ -ion density. Lundin *et al.*¹⁶ reported that the electron density in the range of $2\text{--}40 \times 10^{17} \text{ m}^{-3}$ and electron temperature in the range of 2.9–4.1 eV for pressure 0.5–2.0 Pa at 4 cm from the target, which is somewhat lower than that reported by Bohlmark *et al.*¹⁵ or few times 10^{19} m^{-3} next to the target (2 cm) at 2.66 Pa. The model gives somewhat higher values for the peak electron density as the IR is closer to the target than is allowed to measure using a Langmuir probe. Also, as these calculations are based on the volume averaged densities it should be kept in mind that there is certainly a strong spatial variation in the species densities as has been demonstrated by Langmuir probe measurements¹⁵ and by LIF measurements.¹⁴ The latter measurements show that the ions are localized in the race track vicinity while the neutrals are mainly located in the target center. This translates also onto the metastable density. Thus, we would expect spatial variation in the role of the argon metastables with regard to stepwise ionization and Penning ionization. Also, as we move away from the target there is a decrease in the electron density and electron temperature, so the role of stepwise ionization and Penning ionization may vary from what we observe here for the IR. Under the conditions of low electron density ($n_e \ll 10^{17} \text{ m}^{-3}$), Penning ionization is found to be the dominant ionization path²⁴ and is consistent with the accepted ionization mechanism for conventional diode sputtering. When high electron densities are generated, however, electron impact ionization plays a significant role. In our case, we clearly see that Penning ionization becomes more important in the 0.5 A case. A similar situation with a lower plasma density applies in the bulk plasma and will likely generate similar results.

IV. CONCLUSION

In diode sputtering and dcMS, Penning ionization can be an important ionization mechanism for the sputtered

species but the degree of ionization is small. In HiPIMS, the sputtered species ionization is high, up to 89% for the case of an argon discharge with a titanium target is investigated here. Penning ionization is always negligible. The main reason is the higher electron density, but also a higher electron temperature in the HiPIMS contributes. Stepwise ionization through the Ar^m level is always negligible during the breakdown phase in the HiPIMS pulses, and plays a significant (but never dominating) role only later in the pulse. The model predicts a time averaged ionized flux fraction of roughly 70% for titanium, which is a slightly higher value than observed experimentally.

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