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Strategy for tuning the average charge state of metal ions incident at the growing film during HIPIMS deposition

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Abstract

Energy- and time-dependent mass spectrometry is used to determine the relative number density of singly- and multiply-charged metal-ion fluxes incident at the substrate during high-power pulsed magnetron sputtering (HIPIMS) as a function of the average noble-gas ionization potential. Ti is selected as the sputtering target since the microstructure, phase composition, properties, and stress-state of Ti-based ceramic thin films grown by HIPIMS are known to be strongly dependent on the charge state of Ti^{n+} ($n = 1, 2, \dots$) ions incident at the film growth surface. We find that the flux of Ti^{n+} with $n > 2$ is insignificant; thus, we measure the Ti^{2+}/Ti^+ integrated flux ratio $J_{Ti^{2+}}/J_{Ti^+}$ at the substrate position as a function of the choice of noble gas -- Ne, Ar, Kr, Xe, as well as Ne/Ar, Kr/Ar, and Xe/Ar mixtures -- supporting the plasma. We demonstrate that by changing noble-gas mixtures, $J_{Ti^{2+}}$ varies by more than two orders of magnitude with only a small change in J_{Ti^+} . This allows the ratio $J_{Ti^{2+}}/J_{Ti^+}$ to be continuously tuned from less than 0.01 with Xe, which has a low first-ionization potential IP^1 , to 0.62 with Ne which has a high IP^1 . The value for Xe, $IP_{Xe}^1 = 12.16$ eV, is larger than the first ionization potential of Ti, $IP_{Ti}^1 = 6.85$ eV, but less than the second Ti ionization potential, $IP_{Ti}^2 = 13.62$ eV. For Ne, however, $IP_{Ne}^1 = 21.63$ eV is greater than *both* IP_{Ti}^1 and IP_{Ti}^2 . Therefore, the high-energy tail of the plasma-electron energy distribution can be systematically adjusted, allowing $J_{Ti^{2+}}/J_{Ti^+}$ to be controllably varied over a very wide range.

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I. Introduction

Low-energy *metal-ion* irradiation of growing films during high-power pulsed magnetron sputter deposition (HIPIMS),¹ with the substrate bias synchronized to the metal-ion-rich portion of the pulses,^{2,3} has recently been shown to provide microstructure densification and surface smoothing, without introducing the large increases in film compressive stress reported for noble-gas ion irradiation during dc magnetron sputter deposition,^{4,5} provided that the metal-ion flux incident at the substrate is primarily singly-ionized. In contrast, multiply-charged metal-ion irradiation, even at floating potential, can result in films with high defect densities and high compressive stresses.^{2,3} Synchronized-bias HIPIMS CrN films deposited in mixed Ar/N₂ atmospheres with high substrate bias and a significant doubly-charged metal-ion component, $J_{Cr^{2+}}/J_{Cr^{+}} = 0.23$, exhibit compressive stresses up to -9.6 GPa.^{6,7}

Film stress increases rapidly as the average metal-ion momentum per deposited atom $\langle p_d \rangle$ transferred to the film surface exceeds a critical value $\langle p_d \rangle^*$, which depends upon the choice of materials system and the ion flux incident at the growth surface.⁸ $\langle p_d \rangle$ is defined as $\sqrt{2m_i n_i e (V_s - V_{pl})} \times J_{ion}/J_{Me}$ in which V_{pl} is the plasma potential, m_i and n_i are the ion mass and average charge state, and J_{ion}/J_{Me} is the ratio of incident metal-ion to total metal (ion plus atom) fluxes. During deposition by HIPIMS, and hybrid techniques incorporating HIPIMS and dc magnetron co-sputtering (HIPIMS/DCMS),² $\langle p_d \rangle^*$ for growth of films with high-mass metal constituents can easily be exceeded, even with no applied substrate bias V_s . $\langle p_d \rangle$ is further increased for higher-mass metals with second-ionization potentials IP_{Me}^2 lower than the first-ionization potential IP_g^1 of the sputtering gas, leading to the production of high fluxes of multiply-charged ($n > 1$) metal ions.⁸

It is therefore of interest to systematically vary the noble-gas composition, and hence the gas ionization potential, during HIPIMS and explore the effect of the average IP_g^1 value on the

metal-ion charge state distribution. We use Ti as a model target material and employ energy- and time-dependent mass spectrometry to measure the integrated fluxes $J_{Ti^{n+}}$ ($n = 1, 2, \dots$) of metal ions incident at the substrate during Ti HIPIMS in Ar, Ne, Kr, Xe, and mixed noble-gas plasmas. The average value of IP_g^1 can be tuned by systematically adjusting mixed noble-gas compositions, thereby continuously altering the high-energy tail of the plasma-electron-energy distribution and controllably varying $J_{Ti^{2+}}/J_{Ti^{+}}$ over a wide range from 0.01 to 0.62.

II. Experimental procedure

HIPIMS experiments are carried out in a CemeCon CC800/9 magnetron sputtering system. A cast rectangular 8.8×50 cm² Ti target (99.99 % pure) is operated in HIPIMS mode with the average power $\mathcal{P}$ set to 1.0 kW, a pulsing frequency of 100 Hz (2% duty cycle), and an energy per pulse (the product of target voltage and target current integrated over the entire pulse) of $E_p = 10$ J. The total pressure of Ne, Ar, Kr, Xe, and Ar-based gas mixtures is maintained constant at $P = 0.4$ Pa (3 mTorr). For sputtering with gas mixtures, the relative noble-gas flow rate $\chi_g = f_g/(f_g + f_{Ar})$, in which f_g and f_{Ar} are mass flows, is varied from 0 to 1.

Time-dependent in-situ mass and energy spectroscopy analyses of ion fluxes incident at the substrate plane are performed using a Hiden Analytical EQP1000 instrument. The orifice of the mass spectrometer is placed at the substrate position, parallel to the target surface, and 18 cm from its center. The composition, charge state, and energy of ion fluxes incident at the substrate plane are determined as a function of χ_g . Ion-energy distribution functions $I_{Ti^{n+}}(E_i)$ (IEDFs) are recorded in HIPIMS mode for Ti^{n+} ($n = 1, 2, \dots$) metal and gas ions during 50 consecutive 200- μ s pulses such that the total acquisition time per data point is 1 ms. The ion energy is scanned in 1 eV steps from $E_i = 1$ eV to E'_i , corresponding to the energy at which the $I_{Ti^{n+}}$ flux intensity decreases

to $\leq 1\%$ of the maximum value $I_{Ti^{n+}}^{max}$. For Ar, Kr, and Xe, $I_{Ti^{+}}$ becomes $\leq 0.01 \times I_{Ti^{+}}^{max}$ at $E_i' \leq 30$ eV, while E_i' increases to > 50 eV in Ne discharges. For the case of lower-intensity Ti^{2+} ion fluxes (e.g., Ti sputtered in Kr and Xe), E_i' is set by the detection limit of the mass spectrometer. Here, for consistency, we show IEDFs plotted as a function of $1 \leq E_i \leq 30$ eV. Additional details associated with the IEDF measurements are given in Ref. 9.

III. Results

III.A. Discharge characteristics

HIPIMS target current density waveforms $j_T(t)$ acquired during sputtering of Ti in mixed noble gases -- Ne/Ar, Kr/Ar, and Xe/Ar -- with χ_g varied from 0 to 1 in each case, are shown in Figure 1. All pulse shapes are characterized by a steep rise during the first 30-50 μs , followed by a more gradual decrease during the next 80-100 μs due to depletion of the power-supply capacitor bank.

For pure noble-gas discharges, $j_T(t)$ reaches a maximum at $\tau_{max} = 63, 36, 49,$ and $57 \mu s$ into the pulse while sputtering with Ne, Ar, Kr, and Xe, respectively. Maximum $j_T(t)$ values j_{max} vary from 0.75 A/cm^2 for Xe, to $0.80, 1.05,$ and 1.06 A/cm^2 for Kr, Ne, and Ar. The onset of the $j_T(t)$ pulse occurs, following a delay, at $\tau_{on} \sim 2 \mu s$, in Ar, Kr, and Xe discharges. With Ne, τ_{on} is $\sim 25 \mu s$, more than an order of magnitude larger, due to a significantly lower electron-impact ionization cross-section σ_i (see Table 1).

For HIPIMS sputtering in Ne/Ar mixtures, Fig. 1(a), j_{max} values are essentially independent of χ_{Ne} at $1.04 \pm 0.02 \text{ A/cm}^2$. The time τ_{max} into the pulse at which $j_T(t)$ reaches a maximum ranges from $63 \mu s$ with $\chi_{Ne} = 1$ to $41, 39, 38 \mu s$ with $\chi_{Ne} = 0.75, 0.60, 0.40$, and remains essentially constant at $36 \mu s$ for $0.25 \geq \chi_{Ne} \geq 0$. The pulse onset time τ_{on} decreases sharply upon addition of Ar, from

25 μs with $\chi_{\text{Ne}} = 1$, to 8, 5, 4, 3, 2.5, and 2 μs with $\chi_{\text{Ne}} = 0.75, 0.60, 0.40, 0.25, 0.1$, and 0. The overall $j_T(t)$ peak shape does not vary significantly with χ_{Ne} .

$j_T(t)$ waveforms for Kr/Ar mixtures are plotted as a function of χ_{Kr} in Fig. 1(b). Both pulse shapes and j_{max} values are strongly dependent on the Kr fraction. As χ_{Kr} is decreased from 1 to 0.75, 0.60, 0.40, 0.25, and 0.10, $j_T(t)$ maxima gradually increase from 0.80 A/cm² to 0.86, 0.91, 0.95, 1.00, and 1.03 A/cm² with a corresponding decrease in τ_{max} from 49 μs for pure Kr to 45, 43, 40, 38, and 37 μs , respectively. The pulse onset time τ_{on} is ~ 2 μs for all χ_{Kr} values.

Xe/Ar waveform shapes as a function of χ_{Xe} , Figure 1(c), are similar to those for Kr/Ar (Fig. 1(b)). j_{max} increases and τ_{max} decreases with decreasing Xe fraction in the gas mixture. j_{max} is 0.75 A/cm² ($\tau_{\text{max}} = 57$ μs) with $\chi_{\text{Xe}} = 1$ and increases to 0.82 A/cm² (52 μs), 0.85 (48), 0.90 (45), 0.95 (42), and 0.98 A/cm² (40 μs) with $\chi_{\text{Xe}} = 0.75, 0.60, 0.40, 0.25$, and 0.10.

Figure 1 reveals a marked delay in the current pulse onset in pure Ne compared to Ar, Kr, Xe, and noble-gas mixtures. This is primarily due to the fact that Ne has a much lower electron-impact ionization cross section σ_i over the entire electron-energy range.¹⁰ Noble-gas σ_i values exhibit, by definition, a threshold at IP_g^1 and the threshold is highest for Ne (see Table 1). At electron energies $E_e > IP_g^1$, σ_i vs. E_e curves have broad maxima, which for Ne occurs at ~ 160 eV compared to 70-90 eV for the heavier noble gases. In addition, σ_{Ne} is markedly lower, by $4\times$ to $7\times$, than corresponding values for Ar, Kr, and Xe, which are grouped more closely together, for all electron energies. The small σ_{Ne} value makes it more difficult to strike a Ne discharge and thus increases τ_{on} in Fig. 1, analogous to reported observations that the low-pressure limit for striking Ne magnetron discharges is $7\times$ to $10\times$ higher than for Ar, Kr, or Xe.¹¹ Adding relatively small amounts of Ar to Ne decreases τ_{on} as the lower ionization potential of Ar facilitates plasma ignition.

III.B. Mass and energy analyses of ions incident at the substrate position

For all gas compositions, the only detected ionized sputter-ejected target atoms incident at the substrate plane are Ti^+ and Ti^{2+} . Figs. 2(a) and 2(b) are Ti^+ and Ti^{2+} IEDFs for Ne, Ar, Kr, and Xe HIPIMS plasmas. Ar, Kr, and Xe Ti^+ IEDFs exhibit similar shapes characterized by broad ion-energy distributions together with an I_{Ti^+} peak at low energy, $\sim 3\text{-}4$ eV, corresponding to sputter-ejected species which are thermalized during transport in the gas phase and hence arrive late in the HIPIMS pulse.⁹ The integrated average incident ion energy $\langle E_{\text{Ti}^+} \rangle$ is 6.4 eV for Ar, 6.8 eV for Kr, and 7.1 eV for Xe. Ti^+ IEDFs recorded while sputtering in Ne also have a broad energy distribution, but without the strong low-energy peak obtained with the other noble-gases. In addition, Ne-based Ti^+ IEDFs have a much more pronounced high-energy tail giving rise to a much higher average ion energy, $\langle E_{\text{Ti}^+} \rangle = 15.6$ eV. The integrated area J_{Ti^+} under the $I_{\text{Ti}^+}(E_i)$ curves, $J_{\text{Ti}^+} = \int_{E_i=1}^{E_i=E'_i} I_{\text{Ti}^+}(E_i) dE_i$, corresponding to the total flux of Ti^+ ions with $E_i \leq E'_i$, is 3.4×10^8 cps for Ne; J_{Ti^+} decreases with increasing noble-gas atomic number to 2.6×10^8 , 2.2×10^8 , and 1.2×10^8 cps for Ar, Kr, and Xe. The maximum range in J_{Ti^+} , from Ne to Xe, is $2.8 \times$.

The Ti^{2+} IEDFs, Fig. 2(b), are much more sensitive than Ti^+ IEDFs to the choice of sputtering gas and $I_{\text{Ti}^{2+}}(E_i)$ decreases more slowly with ion energy. Integrated areas under Ne Ti^{2+} IEDFs correspond to $J_{\text{Ti}^{2+}} = 2.1 \times 10^8$ cps. $J_{\text{Ti}^{2+}}$ decreases dramatically with increasing atomic number of the sputtering gas to 4.5×10^7 cps for Ar, 6.3×10^6 cps for Kr, and 1.2×10^6 cps for Xe. Thus, from Ne to Xe, $J_{\text{Ti}^{2+}}$ drops by a factor of $175 \times$, dramatically larger than the corresponding change in J_{Ti^+} . The average Ti^{2+} ion energy $\langle E_{\text{Ti}^{2+}} \rangle$ is also substantially higher for Ne, 25.0 eV, than for the other noble gases: 10.9 eV for Ar, 12.3 eV for Kr, and 14.0 eV for Xe.

Fig. 3 is a plot of the doubly-to-singly charged Ti ion flux ratio, $J_{\text{Ti}^{2+}}/J_{\text{Ti}^+}$, as a function of the sputtering gas composition χ_g . Of the four noble gases, $J_{\text{Ti}^{2+}}/J_{\text{Ti}^+} = 0.62$ is highest for Ne,

which has the highest first ionization potential IP_{Ne}^1 value, 21.63 eV (see Table 1). $J_{Ti^{2+}}/J_{Ti^{+}}$ decreases to 0.17 for Ar, to 0.03 for Kr, and 0.01 for Xe which has the lowest first ionization potential, $IP_{Xe}^1 = 12.16$ eV. Thus, $J_{Ti^{2+}}/J_{Ti^{+}}$ can be varied step-wise over a wide range from 0.01 to 0.62 simply by changing the sputtering gas. Controlled continuous tuning of $J_{Ti^{2+}}/J_{Ti^{+}}$ is obtained through the use of gas mixtures, as illustrated in Figure 3. For Ne/Ar, $J_{Ti^{2+}}/J_{Ti^{+}}$ ranges from 0.17 (pure Ar) to 0.62 (pure Ne); in Kr/Ar mixtures, $0.03 \leq J_{Ti^{2+}}/J_{Ti^{+}} \leq 0.17$; and for Xe/Ar, $0.01 \leq J_{Ti^{2+}}/J_{Ti^{+}} \leq 0.17$.

An alternative approach to varying the doubly-to-singly charged Ti ion flux ratio $J_{Ti^{2+}}/J_{Ti^{+}}$ is to vary the HIPIMS pulse parameters, which we explore here and compare with the above results for adjusting noble-gas mixtures. Since ionization of sputter-ejected species in HIPIMS discharges is predominantly due to electron impact,¹² $J_{Ti^{2+}}/J_{Ti^{+}}$ is strongly affected by the plasma density in front of the target, which is in turn directly proportional to the maximum target current density j_{max} .¹³ For example, while sputtering Ti in pure Ar, $J_{Ti^{2+}}/J_{Ti^{+}}$ can be varied from 0.02 to 0.17 by increasing j_{max} from 0.06 to 1.1 A/cm². This is accomplished by increasing the energy E_p per HIPIMS pulse from 1 to 10 J at a constant pulse length of 200 μ s. At the low end of the HIPIMS range, $j_{max} = 0.06$ A/cm², a current density comparable to conventional dc magnetron sputtering which is known to have a lower plasma density ($n_e \sim 10^{10}$ cm⁻³ [ref.14] compared to $n_e \sim 10^{12}$ - 10^{13} cm⁻³ for HIPIMS [ref.15]), and hence a low probability of sputter-ejected metal atom ionization (the mean ionization distance is inversely proportional to n_e).¹⁴ As a consequence, lowering $J_{Ti^{2+}}/J_{Ti^{+}}$ by reducing j_{max} has the effect of decreasing the overall degree of metal ionization.

Figure 4 compares the evolution of singly-ionized metal-ion flux $J_{Ti^{+}}$ as a function of $J_{Ti^{2+}}/J_{Ti^{+}}$ for two different types of experiments. In the lower curve, E_p (and thus j_{max}) is varied from 1 to 10 J in pure Ar discharges (filled squares), while in the upper curve χ_{Xe} is varied from 0

to 1 at a constant E_p value of 10 J (open circles). For the former case, decreasing Ti^{2+} comes at the steep price of a corresponding reduction in the singly-ionized metal-ion flux J_{Ti^+} , from 2.6×10^8 cps with $E_p = 10$ J ($j_{max} = 1.1$ A/cm², $J_{Ti^{2+}}/J_{Ti^+} = 0.17$) to 5.7×10^6 cps with $E_p = 1$ J ($j_{max} = 0.06$ A/cm², $J_{Ti^{2+}}/J_{Ti^+} = 0.02$), i.e., a decrease by a factor of 45. This indicates a dramatic reduction in the overall degree of metal ionization, as the *total* metal flux J_{Ti} to the substrate, estimated based upon film thickness obtained from cross-sectional scanning electron microscopy (SEM) images of corresponding Ti layers, decreases by only a factor of two. As a consequence, deposition conditions that correspond to $J_{Ti^{2+}}/J_{Ti^+} = 0.02$ resemble those of conventional dc magnetron sputtering for which metal ionization is negligible. In distinct contrast, varying $J_{Ti^{2+}}/J_{Ti^+}$ by tuning the gas composition while maintaining HIPIMS pulse parameters constant provides the ability to significantly decrease $J_{Ti^{2+}}$ with relatively little effect on J_{Ti^+} . $J_{Ti^{2+}}/J_{Ti^+}$ decreases from 0.17 with $\chi_{Xe} = 0$ to 0.01 with $\chi_{Xe} = 1$, while J_{Ti^+} decreases by a factor of only 2.2 $\times$, from 2.6×10^8 to 1.2×10^8 cps.

In Figure 5, the metal-ion flux ratio $J_{Ti^{2+}}/J_{Ti^+}$ incident at the substrate position is plotted as a function of the first ionization potential IP_g^1 for the four noble gases. $J_{Ti^{2+}}/J_{Ti^+}$ increases with increasing IP_g^1 , from 0.01 with Xe ($IP_{Xe}^1 = 12.16$ eV) to 0.03 for Kr ($IP_{Kr}^1 = 14.04$ eV), 0.17 for Ar ($IP_{Ar}^1 = 15.76$ eV), and 0.62 for Ne ($IP_{Ne}^1 = 21.63$ eV).

IV. Discussion

The choice of the noble gas used during sputtering of metal targets in HIPIMS mode has a profound effect on the discharge characteristics as well as on the energy distribution and average charge state of metal ions incident at the substrate and growing film. We show, using Ti as a model target material, that the metal-ion flux ratio $J_{Ti^{2+}}/J_{Ti^+}$ at the substrate can be continuously and

controllably adjusted over a wide range, $0.01 \leq J_{Ti^{2+}}/J_{Ti^+} \leq 0.62$. This provides increased capability for controlling film microstructure, and hence physical properties, while minimizing ion-bombardment-induced compressive stress (such as obtained from rare-gas ion irradiation) during HIPIMS film growth utilizing a substrate bias synchronized to the metal-ion dominated portion of the pulses.^{2,3,5} Metal, as opposed to the noble-gas, ions primarily end on lattice sites.⁵

HIPIMS discharges are complex, time-dependent, and operate far from equilibrium. In order to qualitatively describe the general trends observed in these experiments, we use time-averaged parameters (e.g., electron temperature, discharge voltage, and sputter-ejected atom thermalization distance) corresponding to steady-state plasmas.

In low-pressure, cold-cathode, steady-state discharges, each electron must produce, on average, a sufficient number of ions impacting the target that one new secondary electron is emitted. This requires a discharge voltage:¹⁶

$$V_{dis} = E_g/\gamma_g \varepsilon_i \varepsilon_e, \quad (1)$$

in which E_g is the average electron energy needed to produce an ion by electron-impact ionization, γ_g is the ion-impact secondary-electron emission coefficient at the target, ε_i is the ion collection efficiency, and ε_e is the average fraction of the primary electron energy consumed in ionizing collisions. The product $\varepsilon_i \varepsilon_e$ is close to unity in magnetrons;¹⁶ thus, V_{dis} is primarily controlled by the ratio E_g/γ_g .

Observed variations in j_{max} as a function of gas composition (see Fig. 1) arise from the fact that, with constant pulse energy and length, the average current density is inversely proportional to the average discharge voltage V_{dis} . j_{max} values for pure Ne, Ar, and Ne/Ar gas mixtures are approximately the same as shown in Fig. 1(a). The Ti secondary-electron emission coefficient γ_g is larger for Ne;¹⁷ however, because of the higher Ne ionization potential, the average energy required

to create an ion is also larger. Thus, the ratio E_g/γ_g , and therefore j_{max} , remains approximately constant as a function of χ_g in Ne/Ar mixtures. In Kr/Ar and Xe/Ar mixtures, j_{max} decreases with increasing χ_g (i.e., decreasing Ar concentration) due primarily to the correspondingly lower γ_g values.¹⁷

The Ti^+ and Ti^{2+} IEDFs are controlled by the interplay between ionization and mass transport through the gas phase. Changing the noble gas, hence the ionization potential IP_g^1 , and the electron impact ionization cross-section σ_i , affects the discharge and plasma parameters, while the mass m_g and the gas scattering cross-section of the noble gas species control metal mean free path λ and thermalization distance in the gas phase. IP_g^1 , σ_i , m_g , and λ values for Ne, Ar, Kr, and Xe are listed in Table 1 (note that σ_i corresponds to maximum values as a function of electron energy). Together, these parameters determine the shape of the Ti^+ and Ti^{2+} IEDFs shown in Fig. 2, and account for the large differences observed between $I_{Ti^{n+}}(E_i)$ curves for Ne and those obtained for the other noble gases.

IEDFs shown in Fig. 2 are plots of metal-ion energy distributions during 200- μ s-long HIPIMS pulses. In the early stages of a pulse ($\tau < 100 \mu$ s), metal-ion IEDFs resemble very broad Sigmund-Thompson sputtered-species energy distributions;^{18,19} that is, $I_{Ti^{n+}}(E_i) \propto E_i/(E_i + E_b)^3$ (in which E_b denotes the surface-atom binding energy).¹⁸ Thus, the original energy distribution of sputter-ejected atoms is preserved since these species undergo few or no collisions due to strong plasma rarefaction.¹² During the later phase of HIPIMS pulses ($\tau > 150 \mu$ s), $I_{Ti^+}(E_i)$ and $I_{Ti^{2+}}(E_i)$ IEDFs collapse to narrow, low-energy peaks as a result of thermalization, in which the sputtered species lose energy via inelastic collisions with noble-gas atoms, as the target current density and, hence, rarefaction decreases.

The thermalization distance λ_{th} for sputtered species ejected normal to the target - - i.e., the distance at which their initial velocity v_o is reduced to the thermal velocity v_{th} - - is estimated as ²⁰

$$\lambda_{th} = \lambda\eta = \lambda \ln(v_{th}/v_o)/\ln(\xi). \quad (2)$$

λ , a function of ion energy, is the average distance traveled between collisions (the mean free path), η is the number of collisions in the ejection direction required to thermalize a sputter-ejected atom, and ξ depends only on the ratio of the sputter-ejected atom mass to that of the sputtering gas. Estimates of λ_{th} based on Eq. (2) should be treated as lower limits since gas rarefaction effects, which are strong in HIPIMS due to high instantaneous sputter-ejected fluxes, further extend the thermalization distance, especially during metal-ion rich portion of the pulse. Estimated η , λ , and λ_{th} values for Ti atoms passing through Ne, Ar, Kr, and Xe discharges at 3 mTorr with an average sputter-ejection energy of 5 eV are listed in Table 1.

Based upon the η values given in Table 1, the number of collisions necessary to thermalize sputtered Ti atoms increases, as expected, with decreasing noble-gas atomic number. λ_{th} is significantly greater than the target/substrate separation only for Ne. This explains the higher average energy, and the lack of low-energy thermalization peaks, in Ti^+ and Ti^{2+} IEDFs obtained from Ne HIPIMS discharges (see Fig. 2).

Since electron impact is the primary ionization mechanism in HIPIMS plasmas,¹² the ionization rate is a strong function of the shape of the electron-energy distribution function $g(E_e)$, which for a steady-state plasma has an approximately Maxwellian form, $g(E_e) \sim \sqrt{E_e} e^{-E_e/kT_e}$, in which T_e is the electron temperature and $g(E_e)$ reaches a maximum at $E_e = T_e/2$. In plasmas for which $T_e \ll IP_g^1$, the typical case for HIPIMS with $T_e \sim 3-5$ eV,¹⁵ only electrons in the high-energy tail of the $g(E_e)$ function contribute to the ionization rate. The Thomson cross-section for electron-impact ionization is zero for $E_e \ll IP_g^1$, while for $E_e > IP_g^1$, it varies as $(E_e - IP_g^1)/IP_g^1$.²¹ Thus,

$g(E_e)$ is expected to strongly deviate from a Maxwellian distribution for $E_e > IP_g^1$. Since IP_g^1 in noble-gas plasmas increases with increasing atomic number,²² the choice of sputtering gas determines the shape of the high-energy $g(E_e)$ tail and, thus, the probability for creating multiply-ionized metal ions since IP_{Me}^2 is often comparable to IP_g^1 .

Results presented in Figures 2-4 demonstrate that the sputtering-gas composition can be used to tune the average charge state of metal ions incident at the film surface during HIPIMS deposition. For example, $J_{Ti^{2+}}$ is reduced by a factor of 37.5, while J_{Ti^+} drops by only 2.2× upon replacing Ar with Xe; no multiply-charged Ti^{n+} ions with $n > 2$ are observed. As a consequence, $J_{Ti^{2+}}/J_{Ti^+}$ decreases from 0.17 to 0.01. Such a large effect can be explained by comparing the first and second ionization energies IP_{Me}^1 and IP_{Me}^2 of sputtered species to the first ionization energy of the sputtering gas IP_g^1 . The production of doubly-ionized metal ions requires electrons with energy $E_e > IP_{Me}^2$; thus, the creation rate of doubly-ionized species strongly depends on whether IP_g^1 is larger or smaller than IP_{Me}^2 .

If $IP_{Me}^2 < IP_g^1$, as is the case for Ti sputtered in Ar ($IP_{Ti}^2 = 13.62$ eV and $IP_{Ar}^1 = 15.76$ eV), there is a significant electron population in the discharge with energies in the range $IP_{Ti}^2 < E_e < IP_{Ar}^1$, i.e., too low to ionize Ar, yet high enough to produce Ti^{2+} . The situation changes dramatically if $IP_{Me}^2 > IP_g^1$, as for Ti sputtered in Xe ($IP_{Xe}^1 = 12.16$ eV). Here, Xe ionization depletes the population of electrons with $E_e > IP_{Xe}^1$ and the Ti^{2+} creation rate decreases, as shown in Figs. 2-4. Since both IP_{Xe}^1 and IP_{Ar}^1 are significantly higher than IP_{Me}^1 ($IP_{Ti}^1 = 6.85$ eV), the impact on Ti^+ production is small. Consequently, varying χ_{Xe} has a large effect on the integrated $J_{Ti^{2+}}$ flux incident at the film growth surface, but affects J_{Ti^+} to a far smaller extent. Increasing the difference between IP_{Me}^2 and IP_g^1 , as for Ti sputtered in Ne ($IP_{Ne}^1 = 21.63$ eV), increases the population of

electrons with energy in the range $IP_{Ti}^2 < E_e < IP_{Ne}^1$, which leads to an increased production of Ti^{2+} as observed experimentally ($J_{Ti^{2+}}/J_{Ti^+} = 0.62$).

The ionization potentials of selected metallic elements with atomic numbers from 13 to 79, including groups IV, V, and VI transition metals (TM) which are relevant for HIPIMS growth of TM nitrides, carbides, and oxides, are shown in Figure 6. The horizontal lines correspond to noble-gas IP_g^1 values. In general, both IP_{Me}^1 and IP_{Me}^2 increase with decreasing atomic radius, moving from left to right across the periodic table, due to a stronger Coulomb interaction between the nucleus and outer-shell electrons. IP_{Me}^1 and IP_{Me}^2 decrease from top to bottom within columns in the periodic table, because of enhanced screening of the nuclear charge by increasing numbers of inner-shell electrons.

The average sputtered metal-ion charge state can be controllably tuned during deposition of a wide range of transition metals for which the conditions $IP_{Me}^1 < IP_{Xe}^1$ and $IP_{Xe}^1 < IP_{Me}^2 < IP_{Ne}^1$ are satisfied by adjusting mixed noble-gas compositions. Note that extending the upper limit of IP_g^1 to IP_{He}^1 (24.59 eV)²² is not practical due to extremely low He sputter yields.²³ Comparison with data in Figure 6 indicates that the approach described here is broadly applicable.

VII. Conclusions

We demonstrate a strategy for tuning the fraction of multiply-ionized metal ions incident at the growing film surface during HIPIMS deposition. This has been shown, for example, to be essential for controlling phase composition, while minimizing compressive residual stresses, in pseudobinary TM nitride thin films.^{2,3,8} The approach is based on controllably adjusting plasma electron-energy distributions $g(E_e)$ by the proper choice of sputtering-gas mixtures, since the ionization probability of sputtered metal atoms during HIPIMS is determined by the $g(E_e)$ high-

energy tail. The key parameters are the second ionization potential IP_{Me}^2 of sputter-ejected metal atoms and the first ionization potential IP_g^1 of the sputtering gas. Using Ti as a model target material sputtered in the noble gases Ar, Ne, Kr, Xe, and gas mixtures, we employ energy- and time-dependent mass spectrometry to measure the Ti^{2+}/Ti^+ flux ratio $J_{Ti^{2+}}/J_{Ti^+}$ incident at the substrate during HIPIMS (there is no measurable Ti^{n+} flux with $n > 2$). We show that $J_{Ti^{2+}}/J_{Ti^+}$ can be tuned over a wide range, from 0.01 to 0.62, for which $J_{Ti^{2+}}$ varies strongly while J_{Ti^+} remains approximately constant. This strategy should be applicable to a wide range of metal targets for which the criteria $IP_{Xe}^1 < IP_{Me}^2 < IP_{Ne}^1$ is satisfied.

VIII. Acknowledgements

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Figure captions

Fig. 1. Target current density j_T vs. time τ waveforms recorded as a function of noble-gas composition during HIPIMS sputtering of Ti in (a) Ne/Ar, (b) Kr/Ar, and (c) Xe/Ar mixtures. The average target power $\mathcal{P}$ and total gas pressure P were maintained constant at 1 kW and 0.4 Pa (3 mTorr), while gas flow rates $f_g/(f_g+f_{Ar})$, in which $g = \text{Ne, Kr, or Xe}$, are varied from 0 to 1.

Fig. 2. Ti^+ and Ti^2 ion energy distribution functions recorded during HIPIMS pulses while sputtering Ti in Ne, Ar, Kr, and Xe. The average target power $\mathcal{P}$ and total gas pressure P were maintained constant at 1 kW and 0.4 Pa (3 mTorr) respectively.

Fig. 3. The $\text{Ti}^{2+}/\text{Ti}^+$ integrated flux ratio $J_{\text{Ti}^{2+}}/J_{\text{Ti}^+}$ at the substrate position, plotted as a function of noble-gas composition for Ne/Ar, Kr/Ar, and Xe/Ar mixtures during HIPIMS sputtering of a Ti target. The average target power $\mathcal{P}$ and total gas pressure P were maintained constant at 1 kW and 0.4 Pa (3 mTorr), while gas flow rates $f_g/(f_g+f_{Ar})$ are varied from 0 to 1.

Fig. 4. Singly-charged Ti^+ ion flux J_{Ti^+} plotted as a function of the $\text{Ti}^{2+}/\text{Ti}^+$ flux ratio $J_{\text{Ti}^{2+}}/J_{\text{Ti}^+}$ incident at the substrate position during HIPIMS sputtering of a Ti target. Two different types of experiments are carried out: the target peak current density j_{max} is varied while sputtering in pure Ar (filled squares), and the composition χ_{Xe} of the Xe/Ar sputtering gas mixture is varied while maintaining HIPIMS parameters constant (open circles). In the first set of experiments, j_{max} is adjusted by varying the target power $\mathcal{P}$ from 0.1 to 1 kW with the

gas pressure P maintained constant at 0.4 Pa (3 mTorr). In the second set, χ_{Xe} is varied from 0 to 1 at a constant target power $\mathcal{P} = 1$ kW and pressure $P = 0.4$ Pa (3 mTorr).

Fig. 5. The Ti^{2+}/Ti^+ integrated flux ratio $J_{Ti^{2+}}/J_{Ti^+}$, measured at the substrate position during HIPIMS sputtering of a Ti target, plotted as a function of the first ionization potential IP_g^1 of the sputtering gas (Ne, Ar, Kr, or Xe). The average target power $\mathcal{P}$ and total gas pressure P were maintained constant at 1 kW and 0.4 Pa (3 mTorr).

Fig. 6. The ionization potentials IP of selected solid elements with atomic numbers from 13 to 79; the filled squares and circles correspond to first and second IP values, respectively. The horizontal lines indicate first ionization potentials IP_g^1 for the noble gases Ne, Ar, Kr, and Xe.

Table 1. Parameters relevant for HIPIMS sputtering of a Ti target in Ne, Ar, Kr, and Xe. Noble-gas mass m_g , atomic radii r_g ,²⁰ first ionization potential IP_g^1 ,²² and maximum electron-impact ionization cross-section σ_i ,¹⁰ the Ti ion-impact secondary-electron emission coefficient γ_{Ti} ,¹⁷ the number of collisions η required to thermalize sputtered Ti atoms ejected with 5 eV in the forward direction (see Eq. (2)); the average sputtered Ti atom mean free path λ ,²⁰ and the thermalization distance λ_{th} (Eq. (2)) for sputtered Ti atoms ejected with 5 eV in the forward direction.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

<div>Property</div> <div>Inert gas</div>	m_g [amu]	r_g [Å]	IP_g^1 [eV]	σ_i [10 ⁻¹⁶ cm ²]	γ_{Ti}	η	λ [cm]	λ_{th} [cm]
Ne	20.18	1.25	21.63	0.68	0.27	6.6	5.0	33.0
Ar	39.95	1.45	15.76	2.55	0.12	3.2	4.6	14.7
Kr	83.30	1.75	14.04	3.49	0.07	2.2	4.7	10.3
Xe	131.29	2.00	12.16	4.67	0.03	1.8	5.1	9.2

Table 1