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ABSTRACT

In the present study, we investigate the impact of pulse power (P_{pulse}) on the ion flux and the properties of TiN films using reactive high-power impulse magnetron sputtering. P_{pulse} was adjusted in the range of 5–25 kW, while keeping the total average power constant through regulating the pulsing frequency. It is found that the required N2 flow, to produce stoichiometric TiN, decreases as P_{pulse} is increased, which is due to a decrease in the deposition rate. The plasma conditions when stoichiometric TiN is formed were investigated in detail. In situ ion mass spectrometry measurements of the ion energy distribution functions reveal two distinct ion populations, ions originating from sputtered atoms (Ti+, Ti2+, and N+) and ions originating from the working gas (Ar+, Ar2+, and N2+). The average ion energies (E_{ave}) of the sputtered ions show an increase with increasing P_{pulse}, while E_{ave} for the gas ions remains almost unaffected. The relative flux intensity Ti2+/Ti+ showed an increasing trend, from 0.28 to 0.47, as P_{pulse} was increased from 5 to 25 kW. The ion flux changes affect the growth of the TiN film such that 111-textured films are grown for low P_{pulse} while higher P_{pulse} results in mixed orientations. In addition, the hardness of the deposited film increases with increasing P_{pulse}, while the compressive film stress increases significantly at a higher P_{pulse}. In this way, optimum deposition conditions were identified at P_{pulse} = 8.3 kW, where a relatively low compressive stress of 0.89 GPa and high hardness of 22.67 GPa were measured.

I. INTRODUCTION

High-power impulse magnetron sputtering (HiPIMS) is a deposition technique initially introduced by Kouznetsov et al.1 as a way to deposit dense coatings inside via-structures. High power and high current densities, of several kW/cm² and several A/cm², are supplied to the cathode in pulses of low duty cycles resulting in a time-averaged power comparable to dc magnetron sputtering (dcMS), but with electron densities up to 10^{19} m^{-3}.2,3 The result is a flux of ionized material from the cathode (target) with an ionization fraction vastly superior to dcMS and with a broader ion energy distribution.4–9 These discharge properties have been shown to result in smooth and dense coatings, control over their phase composition and microstructure, as well as enhanced mechanical and electrical properties.10–14

Despite the potential of HiPIMS for growing high quality thin films, there are examples in the literature demonstrating the adverse effects of using high-power pulses due to the development of high film stress.15–18 Grezynski et al.19 measured compressive stresses up to 6 GPa when using HiPIMS on the Ti target during deposition of Ti1−xAlxN coatings in a hybrid HiPIMS/dcMS co-sputtering setup. An even higher compressive stress (11 GPa) was measured by Hovsepian et al.20 when depositing TiN using two HiPIMS sources combined with a negative substrate bias of 75 V. More recently, Viloan et al.18 deposited TiN coatings without the use of substrate bias but still yielding a relatively high...
compressive stress of 2.1 GPa. The compressive stress further increased when a reversed, positive, pulse (150 V) was applied to the target after the HiPIMS pulse, resulting in a compressive stress reaching 4.7 GPa.

These deposition processes, where a Ti target is operated using HiPIMS, are commonly characterized by a metal ion flux having a significant fraction of Ti\textsuperscript{2+} due to a second ionization potential (\(\varphi_{\text{iz, Ti}} = 13.57 \text{ eV}\)) lower than that of the first ionization potential of Ar (\(\varphi_{\text{iz, Ar}} = 15.75 \text{ eV}\)).\textsuperscript{17,21} Strictly speaking, one should compare the electron impact cross sections for the relevant ionizing reactions, although the ionization potential serves as a good indicator of the ionization probability.\textsuperscript{22} A large amount of Ti\textsuperscript{2+} ions in the HiPIMS discharge can present a problem during film growth, especially in combination with substrate biasing, wherein the average energy gain due to the applied substrate bias scales with the charge state of the ion species. Even without applying a substrate bias, a significant fraction of Ti\textsuperscript{2+} ions can obtain an energy that exceeds the kinetic threshold for creating sub-top-layer defects, which can ultimately lead to high defect densities and high levels of compressive stresses.\textsuperscript{23,24} It is, therefore, of interest to find a way to reduce the contribution of doubly charged ions while keeping the singly charged ion fraction of metal ions as high as possible in the total flux reaching the substrate.

One approach proposed by Grenczynski et al.\textsuperscript{21} is to use noble gases with \(\varphi_{\text{iz, Xe}} < \varphi_{\text{iz, Ti}}\) to tune the average charge state of Ti ions incident at the growing film during a HiPIMS process. By changing the nature of the carrier gas, it was shown that the flux intensity ratio of Ti\textsuperscript{2+}/Ti\textsuperscript{+} was reduced when using Xe (\(\varphi_{\text{iz, Xe}} = 12.12 \text{ eV}\)) and Kr (\(\varphi_{\text{iz, Kr}} = 13.99 \text{ eV}\)) or a combination of Xe/Ar and Kr/Ar due to a reduction of the population of energetic electrons. However, these gases are considerably more expensive. Another practical approach was recently reported by Cemin et al.\textsuperscript{27} that by reducing the peak current density of the HiPIMS discharge from 0.36 to 0.19 A/cm\textsuperscript{2}, a significant reduction of the film compressive stress from 11 to 1 GPa was obtained. The effect was attributed to the reduction of the amount of doubly charged species at lower peak currents as shown by Ross et al.\textsuperscript{7} using optical emission spectroscopy.

Still, few attempts have been made at quantifying the combined effects of doubly charged metal ions and ion energy on the resulting film properties, which is likely due to the rather complex nature of the HiPIMS process, as one needs to consider, e.g., frequency, duty cycle, pulse width, type of biasing, etc. In the present study, we investigate in detail the correlation between the pulse power (\(P_{\text{pulse}}\)) and the presence of Ti\textsuperscript{2+} ions in a reactive HiPIMS discharge of Ti in an Ar–N\textsubscript{2} atmosphere. A wide range of operating frequencies are scanned at a constant average power (\(P_{\text{avg}}\)) resulting in a change of \(P_{\text{pulse}}\) (5–25 kW) and the peak current density (0.10–0.43 A/cm\textsuperscript{2}). Ion mass spectrometry is utilized to confirm changes in the relative ion intensities by recording ion energy distributions for all species involved in the process. TiN films are subsequently deposited to observe the differences in the properties of the TiN films.

II. EXPERIMENTAL DETAILS

All depositions and ion energy distribution function (IEDF) measurements are performed in a cylindrical high vacuum system that is 44 cm in diameter and 75 cm in height (base pressure of \(\sim 4 \times 10^{-4} \text{ Pa}\)) with a weakly unbalanced sputtering cathode on which a Ti target (152 mm in diameter, 99.9% purity) is mounted. Sputtering is carried out using Ar (99.9997% purity) at a flow rate of 115 sccm resulting in a pressure of 0.4 Pa and using a reactive gas, N\textsubscript{2} (99.9995% purity), with a flow rate in the range of 0–13 sccm. Si (001) substrates are rinsed in successive ultrasonic baths of acetone and isopropanol and then blow dried using N\textsubscript{2} gas before mounting on an electrically isolated stage 120 mm from the target surface. The cathode is connected to a HiPSTER 6 pulsing unit (Ionautics AB) that is fed with negative potential by an SR1KV–6KW power supply (Technix High Voltage Company). The pulsing unit is set to deliver 200 \(\mu\text{A}\) long pulses with \(P_{\text{avg}}\) maintained at 1.5 kW by changing the discharge voltage (\(U_{\text{d}}\)) and the pulse repetition frequency (\(f\)) in the range of 300–1500 Hz, which results in \(P_{\text{pulse}}\) of 5–25 kW, where \(P_{\text{pulse}}\) is defined as the integral of the instantaneous power over the entire pulse duration divided with the pulse on-time. For each of the \(P_{\text{pulse}}\) values investigated, the deposition time is varied to achieve a film thickness of \(\sim 1 \mu\text{m}\). Guided by the example shown by Shimizu et al.\textsuperscript{26} for process stabilization during H\textsubscript{2}N deposition, the N\textsubscript{2} flow (\(Q_{\text{N}}\)) vs peak current (\(I_{\text{pk}}\)) are plotted for each \(f\) to obtain the appropriate \(Q_{\text{N}}\) flow for the process to be in the transition region.

In situ mass and energy spectroscopy analyses of the ion fluxes are carried out using a PSM003 mass spectrometer (Hiden Analytical Ltd.). The IEDFs of Ar\textsuperscript{+} (40 amu), Ar\textsuperscript{2+} (40 amu), Ti\textsuperscript{+} (48 amu), Ti\textsuperscript{2+} (48 amu), N\textsuperscript{+} (14 amu), and N\textsubscript{2} (28 amu) are recorded for the different \(P_{\text{pulse}}\) values with an energy step size set to 0.1 eV while the acquisition per data point is set to 200 ms. The sampling orifice has an opening of 300 \(\mu\text{m}\) in diameter and is grounded during the measurements. Due to geometrical limitations, the mass spectrometer is mounted from the side of the chamber (Fig. 1) in the same manner as previously studied where the IEDF and ion content of a HiPIMS discharge from a Ti target were measured.\textsuperscript{7} In this geometry, the IEDFs recorded are not exactly identical when the mass spectrometer orifice is placed at the substrate position due to the angular distribution of sputtered species. However, when comparing the results from the studies done by Bohmark et al.\textsuperscript{26} and Hecimovic and Ehsanian\textsuperscript{27} for the same target and using the same mass spectrometer, the trends of the measured IEDFs are the same even with the difference in the experimental geometries. As such, the current setup should still give a good representation of the trends in the
IEDFs at the substrate position. It is also noted that the exact shapes of the IEDFs are not crucial in the present work but instead the study focuses on the trends between different $P_{\text{pulse}}$ values.

The texture and stress of the TiN films are investigated using x-ray diffraction (XRD) in the $\theta$–$2\theta$ Bragg–Brentano geometry (PANanalytical X’Pert PRO system) and using the sin$^2\psi$ method (Philips X’Pert MRD system), respectively. The in-plane stress is calculated from the lattice spacing derived from the 200 peak at different substrate tilts, $\psi$ (the angle between the sample surface normal and the diffraction plane containing the incoming and diffracted x-ray beams). The x-ray source in both diffractometers is operated at 45 kV and 40 mA and emits CuK$\alpha_1$ radiation ($\lambda = 1.540597 \text{ Å}$). Prior to the measurements, the diffractometer is aligned to the Si (100) peak at 69.13°. Finally, the hardness of the films is evaluated using a CSIRO UMIS nanoindenter (Fischer-Cripps Laboratories) operated in a constant force mode of 5.5 mN in order to keep the penetration depth to within 10% of the film thickness to minimize any substrate effects on the measurements. The indentation curves are analyzed using the method suggested by Oliver and Pharr$^{28}$ for a minimum of ten indentations per sample.

**III. RESULTS**

**A. Identification of operating point**

The influence of the reactive gas supplied to the process is illustrated in Fig. 2 where $Q_{N_2}$ first is increased and then decreased, and the resulting $I_{pk}$ is plotted for different constant $P_{\text{pulse}}$ values. All curves exhibit similar behavior in that a steep increase in $I_{pk}$ is observed after a critical $Q_{N_2}$ ($Q_{crit}$) is reached. For decreasing $Q_{N_2}$, the same trend is seen but with a small offset to higher $I_{pk}$ values. It can be noted that a slightly higher $Q_{N_2}$ (0.2–0.5 sccm) than the $Q_{crit}$ values are giving stoichiometric TiN thin films as judged from the typical golden color of the coating and are thus used as operating points for the film growth studies and mass spectrometry measurements in this work.

The $I_{pk}$ values plotted in Fig. 2 are obtained from the collection of the discharge current waveforms for the different process conditions. As an example, the set of curves for $P_{\text{pulse}} = 25 \text{ kW}$ is shown in Fig. 3. Here, the repetition frequency is kept constant while $U_{d}$ have been slightly adjusted to maintain the set $P_{\text{pulse}}$ value. For low $Q_{N_2}$, the discharge current initially rises faster than for high $Q_{N_2}$, but it also levels off earlier, and even decreases at the end of the pulse. For higher $Q_{N_2}$, the current pulse becomes increasingly more triangular in shape, which is commonly seen in several reactive HiPIMS processes,$^{29}$ giving rise to a rapid increase in $I_{pk}$ and is the reason for the kink in the curves seen in Fig. 2.

The resulting values of identified operating points in terms of $Q_{N_2}$ and pulse repetition frequency for $P_{\text{pulse}}$ investigated are summarized in Fig. 4(a). These discharge conditions are used during the deposition and ion mass spectrometry studies. The corresponding current waveforms generated by varying $P_{\text{pulse}}$ of the discharge at the identified operating points are shown in Fig. 4(b). The applied voltage pulses are square-shaped (not shown) and adjusted monotonically (from $-456 \text{ V}$ for $P_{\text{pulse}} = 5 \text{ kW}$ to $-536 \text{ V}$ for $P_{\text{pulse}} = 25 \text{ kW}$) to keep $P_{\text{avg}}$ constant. With the selected pulse length, the peak current is always reached at the end of the pulse. The peak current densities (peak current averaged over the target surface, $J_{pk}$) are also given in the figure.

The deposition rate as a function of $P_{\text{pulse}}$ for the chosen operating points is shown in Fig. 5(a). The rate decreases monotonically with increasing power and only 50% of the rate remains at 15 kW (20 nm/min) as compared to 5 kW (40 nm/min). The value given for 25 kW is unreliable due to film delamination. An apparent linear relationship between $Q_{N_2}$ used for growing the film and the calculated deposition rate is observed. From this, we estimate the deposition rate for a film deposited using $P_{\text{pulse}} = 25 \text{ kW}$ to be around 11.2 nm/min, which is close to what was measured (10.5 nm/min) when examining the cross section of the film material that did not peel off the substrate.

**FIG. 2.** $I_{pk}$–$Q_{N_2}$ curves generated by first stepwise increasing and then decreasing $Q_{N_2}$ for different $P_{\text{pulse}}$ settings of 5–25 kW. In all cases, the $P_{\text{avg}}$ was kept constant at 1.5 kW by adjusting the pulse repetition frequency in the range of 300–1500 Hz.

**FIG. 3.** Current waveforms generated for different $Q_{N_2}$ using a HiPIMS discharge with $P_{\text{pulse}} = 25 \text{ kW}$ ($f = 300 \text{ Hz}$).
B. Mass spectrometer study

Time-averaged IEDFs of Ti+, Ti2+, Ar+, Ar2+, N+ and N2+ ions for the discharge conditions identified in Sec. III A are shown in Fig. 6. All IEDFs exhibit significant amounts of low-energy ions (<10 eV). However, the IEDFs of Ti+, Ti2+, and N+ also show distinct high-energy populations with high-energy tails reaching up to the upper energy limit of the instrument (100 eV for singly charged ions). The same trends have been observed in other studies\(^7,8,30–32\) of HiPIMS discharges and are discussed in more detail by Čada et al.\(^33\) It is also noted that the high-energy tail of Ti+ and Ti2+ increases in intensity at the expense of the low-energy population when \(P_{\text{pulse}}\) is increased.

Integrating the time-averaged IEDF with respect to energy enables an estimate of the total ion flux from a species. We use these flux estimates to visualize the trend of charge state of Ti and Ar as a function of applied \(P_{\text{pulse}}\), which are presented in Fig. 7. Due to an unknown transfer function of the mass spectrometer and differences in the acceptance angle for low and high ion energies, these results should be seen as trends rather than absolute values.\(^33\) However, the acceptance angle decreases with ion energy and, therefore, the presented trends are likely an underestimation. The trends shown in Fig. 7 show a clear increase in Ti2+ and Ar2+ ion population when \(P_{\text{pulse}}\) is increased, which is in line with other observations. See, for example, an optical emission study by Ross et al.\(^25\) Also shown in Fig. 7 is the estimated ratio between N+ and N2+ ions demonstrating a strong increase of N+ relative to N2+ for increasing \(P_{\text{pulse}}\).

Figure 8 shows the estimated average ion energies (\(E_{\text{ave}}\)) calculated from the IEDF data presented in Fig. 6 for different \(P_{\text{pulse}}\) values. The Ar+, Ar2+, and N2+ ions did not exhibit a significant change in \(E_{\text{ave}}\) while the Ti+, Ti2+, and N+ ions show an increase in \(E_{\text{ave}}\) with \(P_{\text{pulse}}\). The observed increase of \(E_{\text{ave}}\) for the latter group of ions reflects the previously discussed increase in range and intensity of the high-energy tail of these species with increasing \(P_{\text{pulse}}\) (Fig. 6).

C. Film properties

Figure 9 shows the \(\theta–2\theta\) XRD scans of the deposited TiN films. All samples exhibit a mixed orientation with the dominating diffraction peaks corresponding to 111 and 200 orientations. Minor peaks, attributed to the 220, 311, and 222 orientations, were also detected (not shown). For films grown using \(P_{\text{pulse}} \leq 8.3\) kW, a 111 texture is dominant, while for \(P_{\text{pulse}} \geq 10.7\) kW, the films are of a mixed texture. With increasing \(P_{\text{pulse}}\), there is a shift in peak position toward larger lattice parameters, corresponding to a lattice expansion of 0.74% for \(P_{\text{pulse}} = 25\) kW (as calculated from the shift of the 111 peak).

The full width at half maximum (FWHM) measured from the (111) and (200) peaks are shown in Fig. 10 where an increase in the FWHM is observed with an increase in \(P_{\text{pulse}}\) signifying a decrease in the crystallite size based on the Scherrer equation.\(^34\) Being aware of the fact that peak broadening in XRD is complex\(^35\) and depends on several factors, the trend is, however, clear with the FWHM that initially decreases with increasing \(P_{\text{pulse}}\) up to 6.8 kW after which the FWHM increases with \(P_{\text{pulse}}\). SEM plan view images (Fig. 11) of the films deposited at \(P_{\text{pulse}} = 5, 8.3, 15,\) and 25 kW further confirms the decreasing trend in the crystallite size, where a clear decrease in the crystallite size with increasing \(P_{\text{pulse}}\).
(>8.3 kW) is observed. The SEM images, shown in Fig. 11, also reveal faceted grains for the lower \( P_{\text{pulse}} = 5 \) and 8.3 kW with an approximate size of 50–100 nm. These types of facets are often seen for 111 textured TiN films.\(^{36-38}\) A clear change in the crystal appearance is observed for \( P_{\text{pulse}} = 15 \) and 25 kW, which also corroborates well with the mixed texture observed by XRD.

Measured film stress (compressive) and film hardness are presented as a function of \( P_{\text{pulse}} \) in Fig. 12. It was not possible to conduct measurements on the films deposited at \( P_{\text{pulse}} = 25 \) kW due to film delamination caused by high stresses. The compressive stress, calculated using a Poisson’s ratio of 0.22\(^{39}\) and elastic modulus values in the range of 337–360 GPa from the hardness measurements, is maintained at a relatively low level of less than 1 GPa for \( P_{\text{pulse}} = 5–8.3 \) kW. An increase of \( P_{\text{pulse}} \) to 10.7 and 15 kW increases the compressive stress to 1.3 and 2.1 GPa, respectively. The hardness shows an increasing trend as \( P_{\text{pulse}} \) is increased, except for a possible decrease at \( P_{\text{pulse}} = 10.7 \) kW. The measured hardness values, 19.1–24.1 GPa, are typical values for TiN films.\(^{39}\)

### IV. DISCUSSION

#### A. Process characteristics

It is evident from the results presented in Sec. III A that there is a clear transition in the process as the reactive gas flow reaches a critical level (Fig. 2). This transition coincides with the alteration of the current peak shape (Fig. 3) and that stoichiometric TiN films are synthesized. It is well known that stoichiometric compound thin films are synthesized in, or close to, the transition between a mode where the target surface is metallic and a mode where the target surface is fully reacted with the reactive...
The transition between the two modes is often associated with hysteresis in process parameters and can often be unstable. In the present setup, however, only a small hysteresis can be observed, and a stable point of operation can be achieved. While keeping $P_{\text{avg}}$ constant by adjusting $f$, the transition between the modes, as well as the point at which stoichiometric TiN is synthesized, is shifted to lower $Q_{\text{N}_2}$ as $P_{\text{pulse}}$ increases [Fig. 4(a)]. This shift to lower $Q_{\text{N}_2}$ values occurs since the deposition rate decreases as a consequence of an increased ionization and return of the deposition material to the target. It is interesting to note that there is a linear relation between the deposition rate and the $Q_{\text{N}_2}$ used for the deposition of films [Fig. 5(b)]. From this, we can draw the conclusion that there is no significant change in reactivity between $N_2$ and Ti as $P_{\text{pulse}}$ is altered within the studied range and that the consumption of $N_2$ in the process is only dependent on the amount of Ti made available for $N_2$ to react with. Similar results have, qualitatively, been shown by Capek and Kadlec and through simulations by Kubart et al.

From the recorded discharge current characteristics in Fig. 3, one can observe that the shape of the current waveforms changes from a half-parabola to a triangular current rise with increasing $Q_{\text{N}_2}$. The shape change of the discharge current is related to the different process modes, due to the influence of the reactive gas, as earlier demonstrated in the works of Shimizu et al. for Hi-F-N and Benzeggouta et al. for Ru-O. In particular, it is connected to significant recycling of either ionized sputtered Ti (at low $Q_{\text{N}_2}$ typical for the metal mode), so-called self-sputter recycling, or mainly ionized Ar gas (at higher $Q_{\text{N}_2}$ typical for the transition and poisoned modes), so-called working gas recycling, as described in detail by Gudmundsson et al. and Brenning et al. These two recycling mechanisms lead to ions being drawn back to the cathode, which amplifies the discharge current. In Fig. 3, the continuously increasing current at $Q_{\text{N}_2} \geq 4$ sccm to significantly higher peak currents compared to the metal mode is thereby a consequence of predominantly recombined gas ions that return from the target during the pulse and subsequently become ionized and drawn back to the target, which allows a very effective amplification of the discharge current through gas recycling. For our purposes, it is, therefore, concluded that the change in the current waveform, and specifically the peak current, is a good indicator of the state of the target during reactive HiPIMS deposition and can be used to determine specific process windows for stabilizing the reactive HiPIMS process.

Let us now address the recorded IEDFs presented in Fig. 6. Based on these, we can identify two distinct sets of ions. The first set exhibits a pronounced energetic tail, as seen for Ti$^+$, Ti$^{2+}$, and N$^+$, while the other set exhibits a considerable drop in the recorded intensity for energies $>10$ eV, as seen for Ar$^+$, Ar$^{2+}$, and N$_2^+$. The
same observations were also reported in previous studies of transition metal nitride deposition using HiPIMS. The difference between these two sets of ions is due to the different origins, as described in detail by Cada et al. and can be summarized as follows. Ti+, Ti2+, and N+ originate from the target, as sputtered species and the gas leading to a reduced thermalization of the Ti+, Ti2+, and N+ ions and a higher average energy. For these ions, the high-energy tail is related to the original energy distribution of the sputter process. The Ar+, Ar2+, and N2+ ions do not have their origin at the target (not sputtered) but instead a result of ionization of the neutral gases (here Ar and N2) present in the ionization region. The background working gas is often considered to be in thermal equilibrium due to collisions within the gas and with the walls of the vacuum chamber. As such, these ions are expected to have energies <1 eV. However, the peak in the IEDF for these ions is shifted, to higher energies, by a few eV. This is due to (positive) ions being accelerated by the potential difference between the plasma potential and the grounded mass spectrometer. It is also seen in Fig. 8 that the average energy of the working gas ions is less affected by the change of the applied $P_{\text{pulse}}$. In contrast, the average energies of the sputtered species increases as $P_{\text{pulse}}$ are increased. The latter is likely due to the influence of gas rarefaction of the working gas, especially during the end of the pulses, where $P_{\text{pulse}}$ is at its peak and gas rarefaction is pronounced. A strong reduction of the working gas density, typically 50% or more, reduces the amount of collisions between the sputtered species and the gas leading to a reduced thermalization of the Ti+, Ti2+, and N+ ions and a higher average energy.

The nature of the ions in the HiPIMS discharge is affected by the variation in $P_{\text{pulse}}$ such that more doubly ionized species are produced (Ti2+ and Ar2+) when $P_{\text{pulse}}$ is increased (Fig. 7). This is in line with observations by Greeczynski and Hultman, who estimated using mass spectrometry data that the number of doubly charged Cr2+ ions increased almost linearly with increased pulse energy in an Ar/N2 discharge with a Cr target. Doubly ionized species of Ti and Ar are produced from their singly ionized counterparts by electron impact ionization, and as such, the generation of Ti2+ and Ar2+ acts as a loss term on the population of Ti+ and Ar+ ions, respectively, as $P_{\text{pulse}}$ is increased. It is also clear, from the ratio of N+ and N2+ in Fig. 7 that an increase in $P_{\text{pulse}}$ also increases the amount of N+ relative to N2+. The reason for this trend is likely due to increased gas rarefaction with increasing $P_{\text{pulse}}$ in the region close to that target, where ions are produced, which affects the N2+ population but less so the N+ population, since the latter mainly originates from the target. From reactive HiPIMS modeling, it is known that an increase in $P_{\text{pulse}}$ reduces the amount of molecular gas, here N2, which in turn reduces the probability of generating N2+ ions.

**B. Film properties**

Increasing $P_{\text{pulse}}$ has a substantial effect on the texture of the deposited films, as seen in Fig. 9. (111)-textured films are deposited for $P_{\text{pulse}} \leq 8.3$ kW while a shift to mixed-textured films is seen for $P_{\text{pulse}} > 8.3$ kW. There have been many studies conducted on the texture evolution of TiN under different energetic ion bombardment conditions. In many of these studies, dc magnetron sputtering has been the method of choice and, therefore, the ions in the discharge are dominated by Ar+ and N2+ ions. This is not the case in the present study wherein we utilize HiPIMS, which, from the results shown in Fig. 6, has a significant portion of the ion flux dominated by metal ions even for the lowest $P_{\text{pulse}}$. From previous studies, increased ion bombardment flux changes the texture from (111) to (002) due to the enhancement of Ti adatom mobility by momentum transfer from low-energy N2+ ions. This effect is more pronounced using HiPIMS in which Ti ions are more abundant resulting in a more efficient momentum transfer to the growing film due to higher mass and higher energy compared to N2+ ions. Cemin et al. reported a shift to (111)-textured TiN films when increasing the peak current densities, which translates to an increase in the Ti2+ ion fraction. They attributed the (111) texture to strain energy minimization due to an increase in the

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**FIG. 12.** The measured compressive stress and hardness for TiN thin films deposited using $P_{\text{pulse}} = 5–15$ kW.
amount of Ti\(^{2+}\) ion bombardment. This is contrary to what we report here, an increase in stress, and thus strain energy minimization is likely not the underlying mechanism for the change in texture. The significant factor that we observe to increase with increasing \(P_{\text{pulse}}\) is the doubly charged ions and an increase in their energy with \(P_{\text{pulse}}\). An increasing ion energy has been demonstrated to alter the growth preference of TiN films from (111) to (001) orientation due to the ion channeling effect on the crystallographic directions.\(^{19,20}\) This particular phenomenon affects the easiest channeling direction, [001] for TiN. Therefore, the plane orthogonal to it, [001], will have the lowest sputter yield thus surviving the ion irradiation process. In the case of the present study, although \(E_{\text{ave}}\) does not exceed 30 eV for the highest \(P_{\text{pulse}}\) (Fig. 8), there is a significant portion of the ion population (see Fig. 6), with higher energies especially from Ti\(^{2+}\) wherein the ion energy scales by the charge state. This particular portion of the ion population should be sufficiently energetic to change the texture from (111) to mixed.

Finally, let us turn to the measured hardness and film stress. The amount of doubly charged ions and the ion energies increase when \(P_{\text{pulse}}\) is increased. These parameters clearly affect the film compressive stress and the hardness. Greczynski et al.\(^{19,20}\) measured the stress of Ti-based (Ti\(_1-x\)Al\(_x\)N and Ti\(_1-x\)Si\(_x\)N) coatings and found high compressive stress values (6.2 GPa and 7 GPa, respectively) when using HiPIMS on the Ti target due to the increased amount of Ti\(^{2+}\) ions. The increase in the amount of Ti\(^{2+}\) is due to the lower ionization potential of Ti\(^{2+}\) when compared with Ar\(^+\) (\(\phi_{\text{Ar}},\text{Ti}^{2+} < \phi_{\text{Ar}},\text{Ar}^{+}\)), as discussed in the Introduction. The ion energy scales by the cation charge state, which gives rise to the creation of more film defects. Due to the high stress, the films were found to have high hardness reaching values as high as 27 GPa for Ti\(_1-x\)Al\(_x\)N and 45 GPa for Ti\(_1-x\)Si\(_x\)N films. Increasing ion energy was also shown to increase the compressive stress of TiN films deposited with HiPIMS. By applying a substrate bias of \(-125\) V, Machunze et al.\(^{28}\) measured a compressive film stress of \(-4\) GPa. Also, Viloan et al.\(^{18}\) have shown, using bipolar HiPIMS, that increasing ion energies result in TiN films with increasing compressive stress (up to \(-4.7\) GPa), although the increase in ion energies lead to densification of the film, which ultimately results in an increase in the film hardness. The increase in \(I_{\text{pk}}\) (and \(J_{\text{pk}}\)), signifying an increase in the Ti\(^{2+}\) ions, has earlier been shown to correlate well with the increase in the hardness of TiN films due to the densification of the film.\(^{25}\) Our measured values of stress and hardness agree well with previous studies as discussed above. We note that N\(^+\) ions exhibit an increase in energy, but it is likely that it does not influence the properties of the film as much as the Ti ions due to the difference in mass and the occurrence of doubly charged ions (Ti\(^{2+}\)). From the measured hardness and film compressive stress, it is clear that there is an optimum in \(P_{\text{pulse}}\) for which we achieve high hardness and more importantly a film with a low compressive stress. Using \(P_{\text{pulse}} = 8.3\) kW, the flux intensity ratio is reduced (Ti\(^{2+}\)/Ti\(^+\) = 0.3) and a good compromise between the hardness (22.67 GPa) and stress (0.89 GPa) is achieved.

V. CONCLUSION

The effects of \(P_{\text{pulse}}\) on the ion flux and the properties of TiN films deposited by HiPIMS have been systematically investigated by first showing that the process window signifying the transition from metallic to compound sputtering modes can be determined by monitoring the \(I_{\text{pk}}\) of the HiPIMS discharge. For the identified operating points, the measured IEDFs clearly indicate two sets of ions: (1) Ti\(^+\), Ti\(^{2+}\), and N\(^+\) originating from the target and ionized in the magnetic trap; (2) Ar\(^+\), Ar\(^{2+}\), and N\(^2+\) originating from the working gas and ionized in the magnetic trap. The first set of ions exhibit a high-energy tail typical of sputtered species and their corresponding \(E_{\text{ave}}\) increases with \(P_{\text{pulse}}\), while the latter set of ions does not exhibit such an energy tail and their \(E_{\text{ave}}\) remains almost unaffected even when \(P_{\text{pulse}}\) is increased. Furthermore, by analyzing the IEDFs in detail, we have shown that the amount of Ti\(^{2+}\) ions can be modulated such that the flux intensity ratio of Ti\(^{2+}\)/Ti\(^+\) can be adjusted between 0.28 and 0.47 by changing \(P_{\text{pulse}}\).

Using \(P_{\text{pulse}} \leq 8.3\) kW (Ti\(^{2+}\)/Ti\(^+\) ≤ 0.3) resulted in films with a 111 texture and a compressive stress below 1 GPa, while in the same power range, the hardness increased with \(P_{\text{pulse}}\) reaching a maximum of 22.67 GPa. For \(P_{\text{pulse}} \geq 10.7\) kW (Ti\(^{2+}\)/Ti\(^+\) ≥ 0.33), a mixed texture was obtained and the stress and hardness level increased with \(P_{\text{pulse}}\) to 2.1 GPa and 24.1 GPa, respectively, at \(P_{\text{pulse}} = 15\) kW (Ti\(^{2+}\)/Ti\(^+\) = 0.39). An even higher compressive stress was likely achieved at \(P_{\text{pulse}} = 25\) kW (Ti\(^{2+}\)/Ti\(^+\) = 0.47), but quantification was not possible due to film delamination.

It is evident from our results that the nature of the ion flux, i.e., type of ions and energy, in a HiPIMS discharge is an effective way to tailor the film properties. However, caution should be taken in order to attain the right compromise with respect to the resulting properties, i.e., hardness and stress.

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