Growth of dense, hard yet low-stress Ti_{0.40}Al_{0.27}W_{0.33}N nanocomposite films with rotating substrate and no external substrate heating

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Growth of dense, hard yet low-stress $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ nanocomposite films with rotating substrate and no external substrate heating

Running title: Growth of dense, hard yet low-stress nanocomposite films using W^+ irradiation

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W^+ irradiation of TiAlN is used to demonstrate growth of dense, hard, and stress-free refractory nitride coatings with no external heating during reactive magnetron sputtering. $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ nanocomposite films are deposited on $\text{Si}(001)$ substrates using hybrid high-power impulse and dc magnetron co-sputtering (HiPIMS and DCMS) in an industrial sputtering system employing substrate rotation during film growth from six cathodes. Two W targets powered by HiPIMS, serve as a pulsed source of energetic W^+ ions, with incident fluxes analyzed by *in-situ* time- and energy-resolved mass spectroscopy, while the remaining four targets (two elemental Ti targets and two Ti plates with Al plugs) are operated in DCMS mode (W-HiPIMS/TiAl-DCMS) to provide a continuous flux of metal atoms and sustain a high deposition rate. A negative substrate bias V_s is applied only in synchronous with the W^+ -ion-rich portion of each HiPIMS pulse

in order to provide film densification by heavy-ion irradiation of the TiAlN layers deposited between W^+ -ion exposures. W is selected for densification due to its high mass and relatively low reactivity with N_2 , thus minimizing target poisoning while enhancing gas rarefaction. Dense $Ti_{0.40}Al_{0.27}W_{0.33}N$ alloy films, grown with no external substrate heating (substrate temperature T_s lower than 150 °C due to heat load from the plasma) and $V_s = 500$ V, exhibit a nanoindentation hardness of $H = 23.1$ GPa and an elastic modulus of $E = 378$ GPa, which are, respectively, 210% and 40% higher than for reference underdense DCMS $Ti_{0.58}Al_{0.42}N$ films grown under the same conditions, but without W^+ irradiation. The W ion bombardment does not affect the film stress state, which is compressive and low at 1.2 GPa.

I. INTRODUCTION

The growth of dense thin films by magnetron sputtering under a noble-gas-based plasma condition, typically requires elevated substrate temperatures T_s to ensure sufficient adatom mobilities.¹ Films grown with no external substrate heating are columnar and underdense, as demonstrated by open inter- and intra-columnar voids visible in cross-sectional transmission electron microscopy images and by X-ray reflectivity results.²⁻⁵ Thus, these layers exhibit low nanoindentation hardness and elastic modulus values. Applying ion bombardment during film growth is often used to enhance densification by providing continuous near-surface ion mixing and enhancing adatom mean-free paths.^{6,7} However, this generally leads to trapping of noble-gas ions, as well as recoiled surface atoms in interstitial sites, which, in turn, results in high compressive stress.⁸

Recently, we presented a novel approach for the growth of dense, hard, yet low stressed thin films with no external substrate heating.⁹⁻¹⁰ In those experiments, TiN was used as a model materials system and we employed hybrid high-power impulse and dc magnetron co-sputtering (HiPIMS/DCMS)¹¹ to grow $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$ and $\text{Ti}_{0.41}\text{Al}_{0.51}\text{Ta}_{0.08}\text{N}$ films. The Ta target was powered by HiPIMS and served as a pulsed source of heavy Ta ions, while a high deposition rate was sustained by a continuous flux of Ti or Ti and Al atoms from DCMS-driven targets. A substrate bias was applied in synchronous with the metal-ion-rich portion of the Ta-HiPIMS pulse.¹² We demonstrated that tuning the incident Ta^+ energy by varying the V_s amplitude provides means of controlling film density and allows for effective elimination of both inter- and intra-columnar porosity characteristic for films grown with no external substrate heating. Nanoindentation hardness H and elastic modulus E of $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$ films exhibited a strong dependence on the incident energy of Ta^+ ions, controlled by the pulsed substrate bias V_s . H varied from 14.4 GPa at $V_s = -20$ V to 26.1 GPa at $V_s = -160$ V, while E increased from 345 to 497 GPa. These values were compared with $H = 7.8$ GPa and $E = 248$ GPa obtained for DCMS TiN reference layers grown with no external substrate heating. The use of high-mass-metal ion-irradiation was shown to be essential for densification and obtaining superior mechanical properties. Lower-mass Ti^+ -ion irradiation with the same flux and ion energy had a minimal effect. Fully-dense $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$ layers grown with no external heating perform well as diffusion barriers between Cu metallization layers and Si(001) substrates.¹³

The above experiments were carried out using a stationary sputtering configuration in which the position of each substrate was fixed with respect to the targets

during film growth. This approach provided the means to investigate the basic phenomena and revealed mechanisms responsible for film densification. However, requirement of precise control over metal-ion times-of-flight from the target to the substrate implies significant challenges for industrial implementations of metal-ion synchronized HiPIMS/DCMS growth scenario due to the fact that in the typical setup the target-to-substrate distance varies continuously, while substrates rotate in the planetary motion scheme in front of several sputtering sources. Thus, substrates are exposed to the energetic metal-ion flux only for a short fraction of the total deposition time, when they pass in front of the HiPIMS-operated magnetron, which is very different from the experiments conducted in the stationary configuration described above.

Here, we investigate densification effects due to heavy-metal ion-irradiation under more typical industrial conditions, that is, in a multi-cathode configuration with the substrate rotating in front of six targets during film growth. $\text{Ti}_{1-x}\text{Al}_x\text{N}$, a widely used wear-protective layer on cutting tools, exhibiting both high hardness and excellent high-temperature oxidation resistance, is used as a model material system. W^+ irradiation is selected based on previous ion mass spectrometry studies performed at the substrate position, which showed severe Ar rarefaction during HiPIMS pulses, while sputtering in Ar/ N_2 gas mixtures to such extent that the time- and energy-integrated metal/gas ion ratio during W-HiPIMS pulse was ~ 100 .¹⁴⁻¹⁵ Such conditions imply large flexibility in the choice of bias pulse offset and pulse length as both Ar^+ and N_2^+ ion fluxes are essentially eliminated during the time period of several hundred μs following the ignition of the HiPIMS pulse. This allows efficient W^+ irradiation of the growing film surface, while minimizing Ar^+ incorporation, even when the substrate-target separation is continuously

changing during substrate rotation, by using relatively long bias pulses. $\text{Ti}_{1-x-y}\text{Al}_x\text{W}_y\text{N}$ alloy films deposited with $T_s \leq 150$ °C (due to plasma heating) exhibit hardness and elastic modulus values which are comparable to those obtained for layers grown at high temperatures (400–500 °C).¹⁶⁻¹⁸

II. EXPERIMENTAL

$\text{Ti}_{1-x-y}\text{Al}_x\text{W}_y\text{N}$ and $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films are grown in a CC800/9 CemeCon AG magnetron sputtering system equipped with six cast rectangular 8.8×50 cm² targets. The target configuration, shown schematically in Fig. 1, includes two-each elemental Ti and W targets together with two TiAl targets consisting of Ti plates with 60 pieces of 1-cm-diameter Al plugs distributed along the racetrack. Si(001) substrates, 3×1 cm², are mounted on a substrate table which rotates sequentially under all targets at three revolutions per minute. As a result, the target-to-substrate distance varies continuously during film growth with the lower limit of 7.5 cm. The system base pressure is 3.8×10^{-7} Torr (0.05 mPa).

Fig. 1. Schematic diagram of HiPIMS/DCMS co-sputtering deposition system for TiAlWN film.

The substrates are cleaned sequentially in acetone and isopropyl alcohol and mounted with clips such that their long axis is parallel to the long axis of the targets. Prior to film growth, the system is degassed using two resistive heaters, each operated at 1.5 kW for 0.5 h, resulting in a temperature of 150 °C at the substrate position. The power is then switched off and T_s is allowed to decrease to ~120 °C prior to initiating films growth. No external substrate heating is applied during deposition and T_s , monitored with a calibrated thermocouple bonded to a dummy substrate, asymptotically reaches a maximum of ~150 °C due to plasma heating during 40 min film deposition. The Ar flow is set at 350 sccm, while the N₂ flow is controlled by an automatic pressure regulator via a feedback loop to maintain the total pressure constant during deposition at 3 mTorr (0.4 Pa).

A hybrid target power scheme is employed in which the two magnetrons equipped with W targets are operated in HiPIMS mode, while the other four are operated as conventional dc magnetrons. The average power to each W-HiPIMS target is 1.0 kW (10 J/pulse, 100 Hz, 110 µs pulse length) resulting in peak target current densities of ~0.5 A/cm². The DCMS power is 2.0 kW for each target. During growth of reference TiAlN layers, only the four DC-powered targets are used. For all film growth experiments, the deposition time is constant at 40 min.

A pulsed substrate bias $V_s = -500$ V is applied synchronously with 110-µs-HiPIMS pulses, based upon time- and energy-resolved mass spectroscopy analyses performed at the substrate position, which revealed the time- and energy-integrated W⁺/(Ar⁺ + N₂⁺) ion ratio during W-HiPIMS pulse as high as ~100.¹⁵ The bias offset is set

at 20 μs , which corresponds to the transit time for most energetic W^+ ions at the shortest target-substrate separation. The bias pulse length is set at the maximum available value of 200 μs to ensure energetic W^+ bombardment even at the longest target-substrate distance. V_s is intentionally selected at a high value in order to extend the W^+ penetration range throughout the TiAlN layers grown during the time when the substrate is passing in front of the DCMS targets (see Fig. 1). At all other times, the substrate is at floating potential. The offset time accounts for the average metal-ion time-of-flight to the substrate.

Ion-energy distribution functions (IEDFs) $I_{\text{W}^{n+}}(E_i)$ are recorded in HiPIMS mode for W^{n+} ($n = 1, 2, \dots$) and gas ions during 100 consecutive pulses such that the total acquisition time per data point is 1 ms. The ion energy is scanned in 0.5 eV steps from $E_i = 1$ to 80 eV. In order to obtain the plasma composition at the substrate plane, where the orifice of the mass spectrometer is positioned, rather than at the detector, data are corrected for ion times-of-flight through the instrument using the approach described in Ref. 19. Additional details regarding the IEDFs measurements are given in Ref. 20.

Film compositions are determined via Rutherford backscattering spectrometry (RBS) and times-of-flight elastic recoil detection analysis (ToF-ERDA) carried out in a 5-MV NEC-5SDH-2 pelletron tandem accelerator. For RBS, 2-MeV $^4\text{He}^+$ ions incident at 45° with respect to the sample surface normal are detected at a scattering angle of 170° . ToF-ERDA results are detected at a 45° angle between the 36-MeV $^{127}\text{I}^{8+}$ primary beam incident at 67.5° and a gas ionization chamber detector. Elemental depth profiles are acquired from ToF-ERDA time and energy coincidence spectra using the software packages. The stopping power data required for both RBS and ERDA simulations are retrieved from an open access software, SRIM 2013.

Ti 2p, Al 2p, N 1s, and W 4f core-level X-ray photoelectron spectroscopy (XPS) spectra are acquired in a Kratos Axis Ultra DLD instrument with a base pressure of 1.1×10^{-9} Torr (1.5×10^{-7} Pa). Monochromatic Al K_{α} radiation ($h\nu = 1486.6$ eV) is used with an anode power of 150 W. All spectra are collected orthogonal to the sample surface. In order to avoid uncertainties related to using the C 1s signal from adventitious carbon as the energy reference,²¹ the binding energy (BE) scale is referenced to the Fermi energy cut-off of a sputter-cleaned polycrystalline Ag film, resulting in an Ag 3d_{5/2} peak position of 368.3 eV. The analyzer pass energy is set to 20 eV, which yields a full-width at half maximum intensity of 0.55 eV for the Ag 3d_{5/2} peak. Prior to spectra acquisition, all surfaces are sputter-etched for two minutes with 4.0 keV Ar⁺ ions, incident at an angle of 70° with respect to the sample normal, while the beam is rastered over a 3×3 mm² area. The Ar⁺ ion energy is then lowered to 0.5 keV for another 10 min to minimize the influence of beam effects on core-level spectra.²²⁻²⁴ The area analyzed by XPS is 0.3×0.7 mm² and centered in the middle of the ion-etched crater. Spectra deconvolution and quantification is performed using the Casa XPS software package and sensitivity factors supplied by the instrument manufacturer.

θ -2 θ X-ray diffraction (XRD) scans and $\sin^2\psi$ analyses for residual stress σ_{re} determinations are carried out.²⁵ Three sets of $\sin^2\psi$ measurements on different areas of the samples are performed to obtain the average residual stress values and deviations. With the $\sin^2\psi$ technique, film strain ε is evaluated by measuring the position of a Bragg reflection to obtain the corresponding film interplanar spacing d as a function of the tilt angle ψ between the sample normal and the scattering plane defined by the incoming and diffracted X-ray beams. The film strain ε as a function of the tilt angle ψ , defined with

respect to the substrate normal, is equal to the normalized difference between d and the relaxed interplanar spacing d_0 ,

$$\varepsilon(\psi) = \frac{d - d_0}{d_0}, \quad (1)$$

Measured $\varepsilon(\psi)$ values are used to determine the residual stress σ_{re} through Hooke's law of linear elasticity as:

$$\varepsilon(\psi) = \frac{1+\nu}{E} \sigma_{re} \sin^2 \psi - \frac{2\nu}{E} \sigma_{re}, \quad (2)$$

in which ν is the Poisson ratio. Experimentally, the in-plane stress is extracted from the slope of $\varepsilon(\psi)$ vs. $\sin^2 \psi$. Tilt angles ψ are set to 0° , 18.4° , 26.6° , 33.2° , 39.2° , 45.0° , 50.8° , 56.8° , 63.4° , and 71.6° , corresponding to $\sin^2 \psi$ values of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9, respectively. Relaxed TiAlWN lattice constants a_0 are determined from θ - 2θ scans acquired at the strain-free tilt angle ψ^* , defined by setting $\varepsilon = 0$ in Eq. (2):

$$\psi^* = \arcsin \left(\sqrt{\frac{2\nu}{1+\nu}} \right), \quad (3)$$

Here, we use $\nu = 0.19$ for cubic TiAlN and TiAlWN which yields $\psi^* = 34.4^\circ$.²⁶

Plan-view transmission electron microscopy (TEM) and cross-sectional TEM (XTEM) specimens are prepared by mechanical polishing, followed by Ar^+ ion milling at 5 kV with an 8° incidence angle and sample rotation. During the final thinning stages, the ion energy and incidence angle are reduced to 2.5 kV and 5° . Film microstructure is analyzed in a FEI Tecnai G² TF 20 UT transmission electron microscope operated at 200 kV.

Nanoindentation measurements are performed in an IBIS nanoindenter equipped with a sharp Berkovich diamond probe calibrated using a fused silica reference sample. A

minimum of 25 indents is made in each specimen with maximum loads of 15 mN and indentation depths not exceeding 10% of the film thickness in order to minimize substrate effects. Film hardness H and elastic modulus E are determined using the method described by Oliver and Pharr.²⁷

III. RESULTS AND DISCUSSION

A. Result

Fig. 2 shows W^+ , W^{2+} , Ar^+ , N_2^+ , and N^+ IEDFs at the substrate plane during 300- μ s time intervals, beginning with the ignition of 110 μ s HiPIMS pulses, while sputtering a W target in Ar/ N_2 at a peak current density $J_{t,peak} = \sim 0.5$ A/cm². Metal IEDFs exhibit broad Sigmund-Thompson type sputtered-species energy distributions, with high-energy tails extending up to 80 eV and beyond.²⁸⁻²⁹ This indicates that the sputter-ejected atoms undergo few collisions between the target and substrate plane due to highly-efficient plasma rarefaction.³⁰ The effect is particularly strong for W due to its high-mass ($m_W = 183.84$ amu), high self-sputter yield,³¹⁻³² and low nitride heat of formation $\Delta H_m^\ominus = -0.2$ eV/atom (-3.4 eV/atom for TiN)³³ which minimizes target poisoning and results in a high temporal flux of sputter-ejected atoms in reactive mode.

Fig. 2. Ion energy distribution functions (IEDFs) from W target operated in HiPIMS mode. For HiPIMS, the IEDFs correspond to a peak target current density of 0.5 A/cm².

Thermalized IEDF peaks, typically observed for Group IVb TMs, are absent in Fig. 2, not only for metal ions, but also for both Ar⁺ and N₂⁺. $I_{N^+}(E_i)$ differs significantly from $I_{N_2^+}(E_i)$, and closely follows the shape of W⁺ IEDFs. This indicates that N⁺ ions originate from the target, in agreement with previous reports.¹³ The source of N⁺ is a combination of sputter-ejected N atoms and reflected N atoms arising from dissociative N₂⁺ collisions at the target surface. The W²⁺ flux accounts for only 3% of the total metal-ion flux, due to the second ionization potential of W ($IP_W^2 = 17.68$ eV) being higher than the first ionization potential of Ar ($IP_{Ar}^1 = 15.75$ eV),³⁴ the primary sputtering gas. The

strong dominance of the singly-charged W ion over gas-ion irradiation is highly beneficial as it allows for more precise control over the incident energy of metal-ions without affecting Ar^+ and N_2^+ ion energy.

Fig. 3 shows time-dependent intensities of energy-integrated primary-ion fluxes W^+ , W^{2+} , Ar^+ , N_2^+ , and N^+ , recorded while reactively sputtering a W target in Ar/ N_2 with $J_{t,peak} = \sim 0.5 \text{ A/cm}^2$. Results are plotted with a 10- μs resolution. Zero on the time axis corresponds to the onset of the cathode voltage pulse; each data point at time t represents the number of ions collected during the interval from $t-5$ to $t+5 \mu\text{s}$. The energy and time-integrated metal/gas ion ratio $N_{\text{W}^+} / N_{\text{g}^+}$, defined as $\int F_{\text{W}^+}(t)dt / \int F_{\text{g}^+}(t)dt$ (in which $F_{\text{W}^+}(t)$ is the metal-ion flux and $F_{\text{g}^+}(t)$ is the total gas-ion flux including Ar^+ , N_2^+ , and N^+) with the integral extending between $t = 0$ and $300 \mu\text{s}$, is ~ 38 . Since a lower peak target current density ($J_{t,peak} = \sim 0.5 \text{ A/cm}^2$) is used in the present work, resulting in a lower metal/gas ion ratio compared to the approach described in Ref. 15, i.e. $J_{t,peak} = 1.0 \text{ A/cm}^2$. The high value is due to strong gas-rarefaction effects, which scale with increasing metal/gas atom mass ratio. That is, the metal/gas collision cross-section increases with increasing sputtered atom mass, resulting in shorter metal-atom mean free paths, increased momentum transfer, and hence more effective gas heating.

Fig. 3. Time evolution of the energy-integrated W^+ , W^{2+} , N^+ , N_2^+ , and Ar^+ ion fluxes incident at the substrate plane during and after HiPIMS pulses while sputtering a W target in Ar at 0.4 Pa (3 mTorr) with 100 μs HiPIMS pulses. The peak target current density $J_{t, peak}$ is maintained constant at ~ 0.5 A/cm². Target current pulse J_t , shown in black line, are scaled to match the ion fluxes in order to facilitate comparison.

An independent evidence for severe rarefaction during W-HiPIMS sputtering in Ar/N₂ gas mixtures is presented in Fig. 4 showing time-resolved $I_{W^+}(E_i)$ IEDFs recorded during consecutive 50 μs time intervals throughout, and following 110 μs HiPIMS pulses. Clearly, $I_{W^+}(E_i)$ IEDFs are preserved throughout the entire measurement period up to 370 μs , i.e., they do not collapse into low-energy thermalized peaks. Instead, there is a

gradual loss in intensity and even ions arriving after the HiPIMS pulse, $t \geq 110 \mu\text{s}$, have an average energy that is significantly higher than thermal.

Fig. 4. (Color online) W^+ IEDFs acquired with $100 \mu\text{s}$ pulses, during HiPIMS sputtering of a W target in Ar at 0.4 Pa (3 mTorr). The target power is 1 kW with a 100 Hz pulse frequency. Times indicated in the legends correspond to the number of microseconds from the onset of the HiPIMS pulse at which the IEDF was acquired.

Low gas-ion fluxes during HiPIMS pulses make W an ideal candidate for the present experiments involving substrate rotation under targets with different target-substrate separations since precise synchronization of the bias pulse to the metal-ion-rich portion of the ion flux at the substrate is not necessary. Instead, relatively long bias pulses

(200 μ s) can be used to efficiently densify the growing film without risking significant Ar implantation.

The average composition of the films determined by a combination of ToF-ERDA and RBS analyses is $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ for the DCMS reference sample and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ for the alloy films deposited by the hybrid HiPIMS/DCMS technique. Argon concentrations are 0.4 and 1.3 at.% for $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$, respectively, with oxygen concentrations of 7.8 and 1.0 at.%. RBS also provides the areal density $n_b \cdot t$ of metal atoms, where n_b is the bulk density [at/cm³] and t is the film thickness [cm]. The results are given in Table 1. As a result of W^+ ion irradiation, Ti and Al area densities decrease by 2.3% and 10.3% from $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ to $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$, respectively, indicating a larger resputtering rate for the lighter Al atoms compared to that of Ti.

TABLE 1. Area density of metal atoms in films determined by RBS.

Samples	Areal density of metal atoms [10^{18} at/cm ²]		
	Ti	Al	W
$\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$	1.750	1.265	-
$\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$	1.710	1.135	1.410

Fig. 5 shows θ - 2θ scans recorded as a function of the tilt angle ψ for (a) $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and (b) $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films. In both cases, the only reflections detected in the 2θ range from 30° to 50° are NaCl structure 111 and 002 TiN peaks, consistent with single-phase films. The $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ layer (Fig. 5(a)) has a strong 111 texture. The residual stress σ obtained from $\sin^2\psi$ analyses is -1.1 GPa. For the $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ film grown with W^+ ion irradiation (Fig. 5(b)), the peaks are broader than for the reference

$\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ sample indicating a decreased grain size due to the heavy-ion bombardment.¹³ The film has a slight 002 texture and the residual stress is -1.2 GPa, essentially the same as that of the reference layer grown without W^+ bombardment. The relaxed lattice parameters a_0 of $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films are calculated 4.195 and 4.242 Å, respectively.

Fig. 5. θ - 2θ scanning patterns at different tilt angles Ψ for (a) $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and (b) $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films. The reference marked by dashed lines is TiN (JCPDS No. 38-1420).

Fig. 6 presents XTEM overview images of (a) $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and (b) $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films together with higher magnification insets of the top portions of both films. The thickness of the $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ layer is $\sim 0.76 \mu\text{m}$. The film has a columnar structure with faceted column tops. The low deposition temperature ($T_s/T_m \leq 0.14$), hence low adatom mobility, results in a columnar porosity best seen in the inset of Fig. 6(a). $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ layer is thicker, $\sim 0.94 \mu\text{m}$, due to the additional flux from the two

W targets. The effects of W^+ ion irradiation are clear in Fig. 6(b): the average column width increases from 35 ± 4 nm for the reference $Ti_{0.58}Al_{0.42}N$ to 85 ± 10 nm for $Ti_{0.40}Al_{0.27}W_{0.33}N$, columnar porosity disappears, and the column tops become rounded with much shallower grooves.

Fig. 6. Cross-sectional TEM images of (a) $Ti_{0.58}Al_{0.42}N$ and (b) $Ti_{0.40}Al_{0.27}W_{0.33}N$ films together with higher magnification insets of the top of the same samples in.

A cross-sectional Z-contrast lattice-resolution image of $Ti_{0.40}Al_{0.27}W_{0.33}N$ film is shown in Fig. 7, revealing a 3.6-nm-thick multilayer structure. Each layer is composed of 3.2-nm-thick bright contrast sublayers containing heavy W atoms and 0.4-nm-thick darker areas comprised predominantly $TiAlN$. The image also shows coherent lattice fringes extending across all nanolayers indicating local epitaxy within columns.

Fig. 7. STEM image from the upper part of $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ sample. A self-organized nano-multilayer architecture can be observed in the film.

Ti 2p, Al 2p, N 1s, and W 4f XPS spectra obtained from $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films are shown in Fig. 8. The Ti 2p spectra (Fig. 8(a)) consist of a spin-orbit-split doublet $2p_{3/2}$ - $2p_{1/2}$ with peaks at 455.3 and 461.1 eV, respectively. The peak positions are essentially the same for both films. There are satellite features on the high BE sides of the primary peaks, shifted by ~ 2.7 eV, in agreement with previously-reported XPS data recorded *in-situ* during growth of polycrystalline TiN layers.³⁵⁻³⁶ The origin of the satellite peaks is still unclear, suggestions include a decrease in the screening probability of the core hole created during photoionization of Ti 3d electrons,³⁷⁻³⁸ and $t_{1g} \rightarrow 2t_{2g}$ intraband transitions between occupied and unoccupied electron states near the Fermi level (shake-up events).³⁹⁻⁴⁰ The Al 2p spectra in Fig. 8(a) contain a single peak at 74.5 eV, which is assigned to Al atoms incorporated in $\text{Ti}_{1-x}\text{Al}_x\text{N}$, the peak position is the same for both films. The higher background in the case of the spectrum obtained from

$\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ film is due to a broad W 5s signal.⁴¹ In contrast, the N 1s spectra (Fig. 8(c)) from the W-containing layer is shifted by ~ 0.4 eV, from 397.1 eV for $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ film to 397.5 eV for $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$. This is due to a significant contribution to the latter spectrum from N incorporated in WN layers, in agreement with previous XPS analyses of WN, which revealed the N 1s peak at 397.9 eV.²⁸ W 4f spectra shown in Fig. 8(d) show a $4f_{7/2}$ - $4f_{5/2}$ doublet in the case of $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ which is superimposed on a lower-intensity Ti 3p peak. The latter is clearly seen in the case of the $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ reference sample which does not contain W. The $4f_{7/2}$ - $4f_{5/2}$ doublet is symmetric toward the low BE side and the spectrum can be fitted with two pairs of peaks, one for metallic W and one for WN with the $4f_{7/2}$ components at 31.4 and 32.2 eV, respectively.

Fig. 8. (a) Ti 2p, (b) Al 2p, (c) N 1s, and (d) W 4f XPS spectra of $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films.

The mechanical properties of the reference $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ films are significantly improved by W^+ ion bombardment. The results are shown in Table 2. Nanoindentation hardness increases from 10.9 to 23.1 GPa for the $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ film, while the elastic modulus increases from 272 to 378 GPa. The effect is a consequence of the reduced porosity combined with the presence of nanolayers. The H^3/E^2 ratio, a qualitative indication of wear resistance,⁴² increases from 0.02 for $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ to 0.09 GPa for $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$.

TABLE 2. Indentation hardness H , elastic modulus E , and H^3/E^2 ratios of $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films.

Samples	H [GPa]	E [GPa]	H^3/E^2 [GPa]
$\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$	10.9	272	0.02
$\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$	23.1	378	0.09

B. Discussion

In previous experiments with Ti-DCMS/Ta-HiPIMS $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$ and Ta-HiPIMS/Ti-DCMS/Al-DCMS $\text{Ti}_{0.41}\text{Al}_{0.51}\text{Ta}_{0.08}\text{N}$ growth performed in a stationary multi-target configuration,⁹⁻¹⁰ irradiation by heavy-metal ions from the HiPIMS target was very effective in densifying the growing film in the absence of substrate heating. This was primarily due to the fact that the zone of intense near-surface intermixing of 0.16-0.19 nm, determined by the collision-cascade range of the 160 eV Ta^+ ions, was much larger than the DCMS layer thickness deposited between successive HiPIMS pulses. Thus, under such conditions both the primary Ta^+ metal ions and the recoiled Ta lattice atoms penetrate deep into the near-surface region to dynamically fill residual vacancies resulting

from very-low-temperature growth with no external substrate heating. Given that Ta atoms are 8% of the metal constituents in the films, we can obtain an estimate for the energy per deposited metal atom, E_D , assuming that the fraction of ionized Ta species is between 30-80%, i.e., in the range typically cited in the HiPIMS literature.⁴³⁻⁴⁴ Under the conditions of Refs. 9 and 10, dense $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$ and $\text{Ti}_{0.41}\text{Al}_{0.51}\text{Ta}_{0.08}\text{N}$ films were obtained with E_D values of 4-10 eV/metal atom.

In the present experiments, the situation is different. Instead of continuous film deposition, the substrate rotation results in deposition from each DCMS target to a thickness of a few nm before the film is exposed to the intense W^+ ion flux from the adjacent HiPIMS target. This, together with target-substrate separation varying continuously, make the film densification process much more challenging. Thus, we selected W^+ instead of Ta^+ to further enhance sputter gas rarefaction,¹⁵ as both have very close atomic numbers, but the former target has lower reactivity towards N_2 , which allows for (i) better separation of metal and gas ion fluxes at the substrate, and (ii) high sputtering rate and, hence, high metal-gas collision rate. A multilayer structure is obtained in $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films deposited with substrate rotation, as evidenced by mass-contrast in W-rich areas and is caused by the substrate rotation during film growth such that two periods in the image of Fig. 7 correspond to one full revolution of the substrate. W^+ ions are incorporated into the TiAlN layers when exposed to the W targets and provide a template for further growth of the W-rich film during the time substrate is facing HiPIMS magnetrons.

In addition, a high substrate bias $V_s = -500$ V is used in order to increase the W^+ ion penetration range. A TiAlN layer deposited during a substrate pass under a TiAl

target is then subjected to W^+ ion irradiation as it passes in front of the adjacent W target. The thickness of the TiAlN layer deposited per pass under a TiAl target is ~ 3.0 nm based on deposition rate calibrations. The projected range of 500-eV- W^+ ions in $Ti_{0.58}Al_{0.42}N$ is ~ 2.5 nm with a straggle of 0.4 nm. As W is implanted the projected ranges drops to ~ 1.9 nm with straggling of 0.7 nm and the total thickness of the nano period layer increases to 3.6 nm. Thus, a two-layer structure is formed, a thin (~ 0.4 nm) W-deficient and a W-rich layer of 3.2 nm. The intermittent W^+ irradiation creates a large number of recoils to ensure film densification.

From the RBS areal density (N_t) of the Al and Ti atoms for the $Ti_{0.58}Al_{0.42}N$ vs. the thickness of the films t , we calculate the density of the metal atoms— $N = 4.25 \times 10^{22}$ at/cm³. The ideal bulk density of metal atoms comprising a B1-NaCl transition-metal nitride (four metal atoms per unit cell) with a lattice constant of 4.20 Å is 5.40×10^{22} at/cm³. Thus, the $Ti_{0.58}Al_{0.42}N$ film density is 73%, a similar estimate for $Ti_{0.40}Al_{0.27}W_{0.33}N$ films yields a density of 95%, which represents a 30% increase in film density.

The good matching of the collision cascade range, predicted by TRIM calculations, with the thickness of the W-rich layer indicates that the latter can be controlled by varying the amplitude of the synchronous bias pulse. For example, TRIM simulations indicate that ion energy of 100 eV would yield approximately equal thicknesses of both nanolayers, while energy of ~ 600 -650 eV would eliminate the W-deficient layer and produce a nearly uniform TiAlWN film.

Another point of discussion is the amount of W^+ ion needed to achieve densification. Under the conditions of our experiments, W^+ irradiation yields energy per

deposited atom values E_D (estimated in the way described above) in the range of 50-130 eV/metal atom. These values are an order of magnitude higher than what is sufficient to produce dense $\text{Ti}_{0.92}\text{Ta}_{0.08}\text{N}$ and $\text{Ti}_{0.41}\text{Al}_{0.51}\text{Ta}_{0.08}\text{N}$ films.⁹⁻¹⁰ This fact suggests that it is possible to reduce the W^+ ion flux by tuning the peak target current during the HiPIMS discharge and thus achieving dense films even with significantly lower content of W.

The present work indicates the succession of growing dense, hard, and stress-free refractory thin films with no external heating, by using W^+ irradiation. Since a low growth temperature is used for the $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ deposition, nonsufficient adatom mobilities produce a high porosity and thus make film softer, i.e. $H = 10.9$ GPa. Ion bombardment with high energy and Ar trapping favors the precipitation of wurtzite-structure AlN (*w*-AlN).^{12, 26} These negative effects of noble gas ion bombardment are eliminated during film growth with W^+ irradiation. First, high mass of W^+ ions together with low reactivity with N_2 helps to enhance gas rarefaction, especially for Ar, as evidenced by ion mass spectrometry results collected during W-HiPIMS at the substrate position. Second, in contrast to conventional DCMS processing, the high-amplitude bias is applied with low duty cycle which reduces resputtering effects. Moreover, the low-temperature deposition produced high porosity provides the ability to release a high intrinsic stress when exposed to a high-energy W^+ ion irradiation. Furthermore, it is important to note that no signals corresponding to *w*-AlN are found in the XRD patterns (Fig. 5). All of the above factors help achieve 30% increase in film density and obtain superior mechanical properties ($H = 23.1$ GPa, $E = 378$ GPa) together with low stress (-1.2 GPa) in low- T_s -deposition of $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films performed with rotating substrates.

IV. SUMMARY AND CONCLUSIONS

Cubic-structure $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ and $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films with no external substrate heating are deposited in an industrial system with substrate rotation. A comparative investigation on elemental compositions, microstructure, and mechanical properties of films against W^+ ion irradiation is conducted. W^+ ion irradiation is generated by 110- μs -HiPIMS pulses and selectively accelerated to reach ~ 500 eV at the substrate. The results show that W^+ ion irradiation powered by HiPIMS with synchronized bias effectively densifies the $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films, whereas a porous microstructure evolves in $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$. In addition, the highly-energetic W^+ ion bombardment has only a slight impact on residual stress of $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ films which is essentially the same as for the $\text{Ti}_{0.58}\text{Al}_{0.42}\text{N}$ layers, and amounts to -1.1 and -1.2 GPa, respectively. The latter advantage is due to the bias synchronization to the W^+ -rich portions of HiPIMS pulses which enables us to lower concentrations of interstitial Ar known for increasing residual stresses. $\text{Ti}_{0.40}\text{Al}_{0.27}\text{W}_{0.33}\text{N}$ exhibits 30% increase in film density and mechanical properties $H = 23.1$ GPa and $E = 378$ GPa, which are typical for layers grown at high temperatures. The here demonstrated new processing route allows to grow high-quality ceramic layers at temperatures below 150 °C, thus expands the application range to temperature-sensitive substrates.

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