I. INTRODUCTION

Transition-metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, and high temperature stability. As a result, they are widely studied and have become technologically important for applications such as hard wear-resistant coatings, diffusion barriers, and optical coatings. In most cases, the layers are grown by reactive magnetron sputter deposition. B1-NaCl-structure δ-TaN$_x$ has received considerable interest over the past several years for use as adhesion and diffusion-barrier layers in Cu-metallized integrated circuits and as mask layers for x-ray lithography. However, little is known about the physical properties of δ-TaN. Unlike the well-studied TM nitride system Ti–N, for which the only two compound phases are Ti$_2$N and TiN, the Ta–N system is extensive with 12 reported equilibrium and metastable phases.\textsuperscript{1–5} δ-TaN$_x$, which has a very wide single-phase field extending from $x \approx 0.94$ to $1.37$,\textsuperscript{6} only exists in equilibrium at temperatures above 1750 °C.\textsuperscript{1}

Published lattice constants, resistivities, and hardnesses of polycrystalline δ-TaN$_x$ layers range from 0.433 to 0.442 nm\textsuperscript{3,5,7} 200 to $>1000$ μΩcm,\textsuperscript{3,4,3,8} and 25–42 GPa,\textsuperscript{9} respectively. While these large differences are presumably due to corresponding variations in film composition and microstructure, the layers are generally poorly characterized. In addition, data interpretation is hampered by the fact that the fundamental properties of single-crystal δ-TaN$_x$ are unknown due to difficulties in obtaining fully dense phase-pure epitaxial layers of this material. In an initial study of δ-TaN$_x$(001) epitaxy,\textsuperscript{6} we demonstrated that controlling the film growth temperature $T_s$ during magnetron sputter deposition in mixed Ar/N$_2$ discharges is not sufficient to obtain fully dense single crystal layers. Epitaxial δ-TaN$_x$ ($x = 0.94–1.37$) films grown on MgO(001) at $T_s = 550–650$ °C contain a network of nanopipes due to low adatom surface mobilities, while increasing $T_s > 650$ °C leads to the emergence of the equilibrium phase, hexagonal $\varepsilon$-TaN.

In this article we explore the possibility of obtaining high-quality dense stoichiometric epitaxial δ-TaN(001) layers using low-energy, high flux, ion irradiation during film growth. The layers were deposited at $T_s = 600$ °C by ultrahigh vacuum (UHV) magnetically unbalanced magnetron sputter deposition in Ar+N$_2$ mixtures with N$_2$ fractions $f_{N_2} = 0.100–0.275$ at a total pressure of 20 mTorr. The incident ion energy $E_i$ was varied from 8.4 to 65 eV while the ion-to-Ta flux ratio $J_{i}/J_{Ta}$ was maintained at 11 with 0.100 $\leq f_{N_2} \leq 0.200$ and 15 with 0.250 $\leq f_{N_2} \leq 0.275$. The film microstructure and microchemistry were characterized using a
combination of x-ray diffraction (XRD), high-resolution x-ray diffraction (HRXRD), transmission electron microscopy (TEM), and Rutherford backscattering spectrometry (RBS).

We obtained stoichiometric single-phase epitaxial $\delta$-TaN layers with $f_{N_2}$=0.125 and $E_i$ between 8.4 and 40 eV. However, the use of $E_i$>40 eV resulted in multiphase polycrystalline films while films grown with $E_i$<20 eV were underdense. Fully dense stoichiometric phase-pure epitaxial $\delta$-TaN(001) layers were grown with $E_i$=30 eV. The measured room-temperature resistivity ($\rho$), hardness (H), elastic modulus (E), and relaxed lattice constant ($a_o$) for these layers are $\rho$=185±18 $\mu$Ω cm, $H=32.9±0.9$ GPa, $E=435±15$ GPa, and $a_o=0.4351±0.0002$ nm, respectively.

II. EXPERIMENTAL PROCEDURE

All $\delta$-TaN layers were grown in a load-locked multichamber UHV magnetically unbalanced stainless-steel dc magnetron sputter deposition system described in detail in Refs. 10 and 11. The pressure in the sample introduction chamber was reduced to less than $5\times10^{-6}$ Torr ($7\times10^{-6}$ Pa), using a 50 l/s turbomolecular pump (TMP), prior to initiating substrate exchange into the deposition chamber which has a base pressure of $5\times10^{-10}$ Torr ($7\times10^{-8}$ Pa), achieved using a 500 l/s TMP. A water-cooled 6.35 cm diameter Ta target with a purity of 99.97% was mounted 10 cm from the substrate holder. Sputter deposition was carried out at a constant power of 150 W and a total pressure of 20 mTorr (2.67 Pa) in mixed atmospheres consisting of Ar (99.999% pure) and N$_2$ (99.999%). The N$_2$ fraction $f_{N_2}$ was varied from 0.100 to 0.275, resulting in discharge voltages of 312–330 V and film growth rates of 4.8–3.0 nm min$^{-1}$. During deposition, the pressure was monitored by a capacitance manometer and maintained constant with automatic mass-flow controllers.

A pair of external Helmholtz coils with Fe pole pieces were utilized to create a uniform axial magnetic field $B_{ext}=180$ G in the region between the target and the substrate. $B_{ext}$ has a strong effect on the ion flux incident at the substrate, with only minor effects on the target atom flux, and provides a high ion-to-metal flux ratio $J/I_{Ta}$. 11

The substrates were polished 10×10×0.5 mm$^3$ MgO(001) wafers cleaned with successive rinses in ultrasonic baths of trichloroethylene, acetone, ethanol, and deionized water and blown dry with dry N$_2$. The wafers were then mounted on resistively heated Ta platens using Mo clips and inserted into the sample introduction chamber for transport to the growth chamber where they were thermally degassed at 800°C for 1 h, a procedure shown to result in sharp MgO(001)11×1 reflection high-energy electron diffraction patterns. 12 Immediately prior to deposition, the target was sputter etched for 5 min with a shutter shielding the substrate. All TaN layers were grown at $T_s$=600°C, including the contribution due to plasma heating, $T_p$, was measured with a pyrometer calibrated by a thermocouple bonded to a dummy TaN-coated MgO substrate. Following deposition, the samples were allowed to cool below 100°C before transferring them to the load-lock chamber, which was then vented with dry N$_2$. All TaN films were grown to a thickness of 0.5 μm.

Electrostatic probes were used to determine plasma characteristics in the vicinity of the substrates during film growth by following the procedure described in Ref. 11. The probe for measuring the ion flux $J_i$ incident at the growing film surface is a 6-mm-diameter stainless-steel disk mounted in a through-hole drilled in the center of a special substrate platen. The surface of the probe is coincident with the substrate surface and is electrically isolated from the platen by a 0.25 mm vacuum gap. To minimize edge effects, the probe and substrate platen were maintained at the same potential with respect to the grounded chamber. The plasma potential $V_p$ and floating potential $V_f$ were obtained from the current–voltage characteristics of a smaller cylindrical probe, 5 mm long by 0.4 mm in diameter, situated 6 mm above the substrate surface. The Ta deposition flux $J_{Ta}$ was determined as a function of $f_{N_2}$ from a combination of film composition and growth rate measurements using RBS and cross-sectional scanning electron microscopy (SEM), respectively.

The microstructure and microchemistry of as-deposited samples were characterized by RBS, XRD, SEM, atomic force microscopy (AFM), TEM, and cross-sectional TEM (XTEM) analyses. The RBS probe beam consisted of 2 MeV He$^+$ ions incident at an angle of 22.5° relative to the sample surface normal with the detector set at a 150° scattering angle. The total accumulated ion dose was 100 μC. Back-scattered spectra were analyzed using the RUMP simulation program. 13 The uncertainty in reported N/Ta ratios is less than ±0.03.

$\omega$–2θ and glancing angle XRD (GAXRD) 2θ scans with $\omega$=2° were carried out in the powder diffraction mode using incident slit divergences of 0.05° and 1°, respectively, resulting in resolutions of 0.01° and 0.1° 2θ for $\omega$–2θ and 2θ scans with Cu $K_a$ radiation ($\lambda=0.15418$ nm). For epitaxial layers, lattice constants $a_u$ along the growth direction, in-plane lattice constants $a_i$, and residual strains were obtained from high-resolution reciprocal lattice maps (HRRLMs) around 113 asymmetric reflections. A series of $\omega$–2θ scans was acquired at different $\omega$ offsets. The measurements were performed in a Philips X-Pert MRD diffractometer using Cu $K_a$ radiation ($\lambda=1.540597$ Å) from a four-crystal Ge(220) monochromator. A two-crystal Ge(220) analyzer was placed in front of the detector providing an angular divergence of $<12$ arcsec with a wavelength spread $\Delta\lambda/\lambda=7\times10^{-5}$. TEM and XTEM analyses were carried out in a Philips CM12 microscope operated at 120 kV. Plan-view samples were first mechanically thinned from the backside to a thickness of 30 μm. Final thinning to electron transparency was accomplished by ion milling using a 5 keV Ar$^+$ ion beam incident at 12°. Cross-sectional specimens were prepared by gluing two samples film-to-film and then cutting vertical sections which were ground and ion-milled following a procedure similar to that used for the plan-view samples, except that they were thinned from both sides.

A Hitachi S4700 microscope with a field-emission source
Table I. Plasma potential (V_p), floating potential (V_f), ion saturation flux (J_i), Ta atom flux (J_Ta), and the ratio J/\mu J_Ta as a function of N_2 fraction f_{N_2} in the discharge during reactive magnetron sputter deposition of δ-TaN_x layers in mixed N_2/Ar atmospheres.

<table>
<thead>
<tr>
<th>f_{N_2}</th>
<th>V_p (V)</th>
<th>V_f (V)</th>
<th>J_i \left(10^{15} \text{ cm}^{-2}\text{s}^{-1}\right)</th>
<th>J_Ta \left(10^{15} \text{ cm}^{-2}\text{s}^{-1}\right)</th>
<th>J/\mu J_Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>−17.1</td>
<td>−25.4</td>
<td>3.6</td>
<td>3.3</td>
<td>11.0</td>
</tr>
<tr>
<td>0.150</td>
<td>−17.4</td>
<td>−26.0</td>
<td>3.2</td>
<td>3.0</td>
<td>10.7</td>
</tr>
<tr>
<td>0.200</td>
<td>−17.8</td>
<td>−25.8</td>
<td>3.0</td>
<td>2.6</td>
<td>11.5</td>
</tr>
<tr>
<td>0.250</td>
<td>−17.0</td>
<td>−26.2</td>
<td>2.9</td>
<td>2.0</td>
<td>14.7</td>
</tr>
<tr>
<td>0.275</td>
<td>−17.0</td>
<td>−26.3</td>
<td>2.9</td>
<td>1.9</td>
<td>15.3</td>
</tr>
</tbody>
</table>

was used for cross-sectional SEM analyses of cleaved samples. Surface roughnesses were quantified by AFM using a Digital Instruments Nanoscope II instrument operated in the contact mode. Several 1×1 μm² areas were scanned on each sample using oxide-sharpened Si$_3$N$_4$ tips with radii of 5–40 nm. Nanoindentation responses of TaN films were determined using a Hysitron TriboScope instrument attached to the AFM. Epitaxial TiN(001) layers, also grown on MgO(001) and having the same thickness as the TaN samples, served as references for calibration purposes. The triangular Berkovich diamond tip was calibrated following the procedure described in Ref. 15. At least three indents were made in each sample using a multiple loading cycle with peak loads of 1, 2, 3, 5, 7, and 9 mN and unloading to 10% of the peak value between. In the final unloading segment, a hold of 100 s was included at 10% of the peak load in order to allow system drift to be measured and corrected for. Hardness H and elastic modulus E values were calculated from each unloading segment. Room-temperature resistivities were obtained from four-point probe measurements.

III. RESULTS AND DISCUSSION

A. Plasma characterization

Table I lists the plasma potential V_p, the substrate floating potential V_f, the Ta flux J_Ta, and the energy E_i and flux J_i of ions incident at the substrate during reactive sputtering of Ta as a function of f_{N_2}. From previous glow discharge mass spectroscopy measurements during magnetron sputtering of Ti in Ar/N$_2$ mixtures, the primary ions incident at the substrate over the N$_2$ partial pressure range f_{N_2}=0.100–0.275 are Ar$^+$ (≈92%–94%), ArN$_2^+$ (3% to 4%) and N$_2^+$ (2%–5%). For all gas mixtures, sputtered species represent less than 1% of the total ion population.

The vast majority of the ions incident at the growing film experience the full substrate sheath potential E_s=ε(V_s−V_p), where V_s is the negative substrate bias (V_s=V_f when no bias is applied), since the mean free path for Ar$^+$ and N$_2^+$ charge exchange collisions, from the Child–Langmuir equation to be 0.2–0.5 mm. Table I shows that the incident ion-to-Ta flux ratio J_i/J_Ta, with the external magnetic field $B_{ext}=180$ G, is 11±0.5 when 0.100≤f_{N_2}≤0.200 and 15±0.3 when 0.250≤f_{N_2}≤0.275. On electrically floating substrates, E_i is 8.4±0.3 eV, independent of f_{N_2}.

B. δ-TaN_x(001) layers grown with $E_i$=8.4 eV as a function of f_{N_2}

All layers, irrespective of f_{N_2}, grown on MgO(001) at $T_s=600^\circ$C with E_i=8.4 eV are epitaxial single-phase δ-TaN_x as judged by a combination of XRD φ-2θ, XRD φ scans, and HRRLMs. However, GAXRD scans, which are sensitive to the presence of small volume fractions of randomly oriented grains, reveal the presence of misoriented regions in layers grown with f_{N_2}=0.100–0.150. Typical GAXRD scans, presented in Fig. 1, show that δ-TaN_x layers grown with f_{N_2}=0.100 (corresponding to $x=0.94$), 0.125 ($x=1.00$), and 0.150 ($x=1.13$) contain (111), (002), (022), and (113) δ-TaN peaks. GAXRD patterns from films grown with f_{N_2} values between 0.175 ($x=1.17$) and 0.275 ($x=1.37$) are featureless indicating, in agreement with TEM results presented below, that these layers are single crystals.

Figure 2 shows typical XTEM and plan-view TEM micrographs with selected-area electron diffraction (SAED) patterns from 500-nm-thick single-crystal δ-TaN_x films, in this case for a layer with $x=1.22$ (f_{N_2}=0.200). The SAED patterns contain only symmetric single crystal reflections. The [100] zone axis cross-sectional pattern in Fig. 2(b), obtained with a 0.4 μm aperture centered at the film/substrate interface, consists of two sets of diffraction spots arising from TaN and MgO. The reflections, indexed in the simulated pattern in Fig. 2(c), reveal a cube-on-cube epitaxial relationship: (001)δ-TaN//(001)MgO and [100]δ-TaN//[100]MgO. The separations between matching TaN and MgO reflections correspond to a 2.9% lattice constant mismatch between TaN and MgO.

The micrographs in Fig. 2 were obtained with an underfocus of 200 nm in order to enhance the contrast of regions with lower density. The XTEM image in Fig. 2(a) clearly shows that the layer is underdense, containing nanopipes.
While the film/substrate interface is abrupt, the surface is quite rough [see, for example, the higher magnification XTEM image in Fig. 2(e)] and composed of mound structures which are characteristic of kinetic roughening as observed previously in semiconductor,19–21 metal,22 and TM nitride23,24 films grown at low homologous temperatures. The primary origin of kinetic roughening is the presence of Ehrlich barriers,25–28 and/or deep traps at step edges,29 to the migration of adatoms over down-steps on growing surfaces. This leads to a divergence in adatom flux and, hence, increased nucleation on terraces which, in turn, gives rise to surface roughening with increasing film thickness. The large non-normal distribution of deposition flux inherent to sputtering30 exacerbates the rate of kinetic surface roughening and results in the subsequent formation of deep surface cusps.

AFM images show that the mounds adjoin along ⟨100⟩ directions. The deposition rate is reduced at the bottoms of cusps between adjacent mounds due to atomic shadowing and leads, in combination with limited adatom mobility, to the formation of the nanopipes. Analyses of XTEM images of the $E_f=8.4$ eV, $f_{N_2}=0.200$ sample in Fig. 2 shows that the surface width $w$, equivalent to the root-mean-square (rms) roughness, is $\approx 2$ nm with a lateral mound-to-mound correlation length $d$ (obtained from plan-view TEM images) of $12 \pm 3$ nm. This is in good agreement with results from large-area AFM analyses yielding $w \approx 1.7$ nm and $d \approx 14$ nm. The number density of nanopipes, $\approx 5.1 \times 10^3 \, \mu m^{-2}$, correlates well with the average mound spacing.

Cross-sectional TEM and SEM analyses of the microstructure of $\delta$-TaN$_x$ layers with $x=0.94–1.13$ ($f_{N_2}=0.100–0.150$), exhibiting polycrystalline peaks in GAXRD scans [e.g., Figs. 1(a)–1(c)], show that the films are initially highly perfect single crystals and then develop randomly oriented grains at thicknesses $t \approx 120$ nm. Figure 3 contains typical plan-view TEM/XTEM images and SAED patterns from a 500-nm-thick $\delta$-TaN$_x$ layer with $x=1$ ($f_{N_2}=0.125$). The [001] zone axis SAED pattern consists of, in addition to strong symmetric single-crystal reflections from the epitaxial portion of the film, weak reflections emanating from randomly oriented $\delta$-TaN grains. The dark-field plan-view TEM image in Fig. 3(a), obtained by selecting a portion of the (111) and (002) diffraction rings, but excluding the epitaxial reflections, is composed of misoriented grains, appearing in bright contrast, embedded in the epitaxial matrix.

Figure 3(b) is a dark-field XTEM micrograph imaged using the epitaxial 002 $\delta$-TaN and MgO reflections in the SAED pattern [Fig. 3(c)] obtained with a 0.7-μm-diameter selected-area aperture centered at the film/substrate interface. Both the substrate and the epitaxial component of the film appear bright while misoriented grains are dark. The film initially grows epitaxially until secondary nucleation leads to the formation of incommensurate misoriented $\delta$-TaN grains which grow in competition with the epitaxial region. The misoriented grains, shown in dark contrast, have an inverted cone shape and originate at distances of 120–270 nm from

along the [001] growth direction. The majority of nanopipes originate at a film thickness $t$ of approximately 5 nm and extend to the film surface. Figure 2(d) is a plan-view micrograph from the layer in Fig. 2(a). The nanopipes tend to be rectangular in cross section, with areas of $\approx 1 \times (1–15)$ nm$^2$, and are predominantly aligned along orthogonal ⟨100⟩ directions.

![Fig. 2. (a) Bright-field XTEM image with corresponding (b) experimental and (c) calculated SAED patterns together with (d) a bright-field plan-view TEM image and SAED pattern from an epitaxial $\delta$-TaN layer grown on MgO(001) at $T_s=600$ °C with $f_{N_2}=0.200$ and $E_i=8.4$ eV. (e) A higher-resolution XTEM micrograph showing the near-surface region from the same sample.](image-url)
the film/substrate interface. These values were confirmed over larger sampling volumes using SEM images (see, for example, Fig. 4) from fracture cross sections.

We find, based upon analyses of SEM images obtained from nine cross sections from three different samples grown under the same conditions, that the initial 120 nm grows essentially defect free before the onset of local epitaxial breakdown. The misoriented grains, which grow at the expense of the surrounding epitaxial matrix, shown in Fig. 3, as well as in the higher-magnification bright-field XTEM image [Fig. 3(d)] obtained from the upper portion of the film, have an open voided structure. Figure 3(d) also shows that the columnar grains extend to heights of up to 20 nm above the epitaxial portion of the film. The number density of mis-oriented grains, obtained from large-area AFM analyses, is \( \approx 32 \, \mu \text{m}^{-2} \) with diameters ranging from 15 to 70 nm.

Epitaxial breakdown occurs only in films grown with \( f_{N_2} \approx 0.150 \). Thus, we propose that nucleation of polycrystalline \( \delta \)-TaN columns within epitaxial layers occurs due to local surface regions stochastically encountering an insufficient N supply to sustain epitaxial growth. This results in, for example, Ta adatoms forming close-packed N-deficient islands which, when covered with adsorbed N atoms, represents the initiation of a 111-oriented grain. The fact that there exists a critical thickness for the nucleation of the polycrystalline grains suggests that kinetic surface roughening, which increases with film thickness, enhances the probability for nonepitaxial island nucleation. Surface roughening, as well as the formation of misoriented grains, is suppressed, as discussed in Sec. III c, during growth with \( E_i = 20 \, \text{eV} \), corresponding to higher-steady-state N surface coverages.

The (001) surface of \( \delta \)-TiN, and presumably isostructural \( \delta \)-TaN, has the lowest surface energy. Thus, misoriented grains, once nucleated, expose higher-energy surfaces to the growing flux and experience enhanced growth rates, as reported previously for TiN, and \( \text{Ti}_{1-x}\text{Al}_x\text{N} \) and ScN (Ref. 36) growth and in Monte Carlo simulations of fcc film deposition. In each of these cases, the effect can be explained as being due to anisotropies in surface diffusivities and adatom potential energies. That is, the average adatom residence time is significantly higher at lattice sites on low diffusivity versus high diffusivity surfaces. Thus, adatoms which are stochastically deposited near grain boundaries and, through surface diffusion, sample sites on both sides of the boundary, have a higher probability of finally being incorporated at the low-diffusivity surface which provides the more stable, lower potential energy sites.

Conversely, adatoms on high diffusivity planes have larger mean free paths with correspondingly higher probabilities to move off the plane and become trapped on adjacent grains. Thus, at low deposition temperatures, grains with low surface diffusivities grow at the expense of their neighbors. Once a misoriented grain protrudes above the epitaxial TaN\(_x\)(001) layer, its growth rate is further enhanced.
due to atomic shadowing resulting from the large non-normal component of the sputtered flux. The protruding grains collect an increased fraction of the incident deposition flux relative to the 002-oriented epitaxial region of the film. Thus, at low homologous temperatures, $T_s/T_m=0.3$ (where $T_m$ is the film melting point expressed in K), grains with low surface diffusivities will slowly but inexorably expand at the expense of the surrounding matrix as we observe in XTEM and cross-sectional SEM micrographs.

C. $\delta$-TaN(001) layers grown with $f_{N_2}=0.125$ as a function of $E_i$

As demonstrated in Sec. III B, all $\delta$-TaN$_x$ layers grown with $E_i=8.4$ eV are underdense, independent of the nitrogen partial pressure. In an attempt to obtain dense stoichiometric epitaxial $\delta$-TaN(001) layers, we varied $E_i$ from 8.4 to 65 eV with $J_i/J_{Ta}=11$. $f_{N_2}$ was maintained at 0.125, the value at which stoichiometric layers are obtained with $E_i=8.4$ eV. RBS analyses show that the film composition remains constant with $N/Ta=1.00\pm0.03$, irrespective of $E_i$, for 8.4 $\leq E_i \leq 40$ eV. At higher ion energies, $N/Ta$ progressively decreases to 0.92 with $E_i=55$ eV and 0.90 with $E_i=65$ eV due to N loss by preferential resputtering.

GAXRD 2θ scans ($\omega=2^\circ$) from a series of 500-nm-thick $\delta$-TaN films grown as a function of $E_i$ are presented in Fig. 5. The scan from the layer grown with $E_i=8.4$ eV exhibits pronounced (111), (002), (022), and (113) $\delta$-TaN peaks at $2\theta=35.84, 41.55, 60.34$, and 72.21°, respectively. Increasing $E_i$ to 20 eV [Fig. 5(b)] significantly decreases the intensities of the nonepitaxial diffraction peaks; only very small misoriented (111) and (002) features are resolvable. GAXRD 2θ scans obtained from layers grown with higher $E_i$, 30–55 eV, are featureless, indicating that these layers are single crystals. The $E_i=65$ eV scan contains several second-phase hexagonal $\gamma$-TaN peaks.

Figure 6 shows a typical [001] plan-view TEM image, with a corresponding SAED pattern, from a $\delta$-TaN(001) layer grown with $E_i=20$ eV. The film is underdense with a network of nanopipes similar to those observed with $E_i=8.4$ eV. The SAED pattern consists only of symmetric single crystal reflections. Although the film is still underdense, the nucleation rate of nonepitaxial grains was dramatically reduced. The surface width $w$ of the epitaxial region is $\approx1.2$ nm with $d=23$ nm while the number density of misoriented grains, obtained from large area AFM analyses, is $\approx0.03 \mu m^{-2}$. Thus, increasing $E_i$ from 8.4 to 20 eV results in the suppression of nonepitaxial grain nucleation, by a factor of 4, and smoother surfaces. This is comparable to the effect caused by increasing $f_{N_2}$ from 0.125 to 0.175 with $E_i=8.4$ eV (see Fig. 1). $E_i=20$ eV is sufficient for the collisional dissociation of $N_2^+$ ions, which have a molecular binding energy of 9.8 eV at the growing surface. This process represents an additional source of adsorbed surface N which, as discussed below, suppresses the nucleation of misoriented grains.

Figures 7(a) and 7(b) are plan-view and XTEM brightfield images, with corresponding SAED patterns as insets, from a $\delta$-TaN(001) layer grown with $E_i=30$ eV. In agreement with results from XRD (not shown) and GAXRD (Fig. 5) analyses, the SAED patterns show that the film is a single crystal. Moreover, the micrographs reveal a fully dense microstructure indicating that high-flux 30 eV ion irradiation provides sufficient adatom surface mobilities to reduce kinetic roughening during film growth and, thus, eliminate the nanopipes.

The weak streaking along (110) directions in the plan-view SAED pattern [Fig. 7(a)] and the related dark contrast regions in the bright-field images show that the $E_i=30$ eV
layers, while fully dense, contain extended planar defects. These features are also present, but at very much higher density, in films deposited with $E_i=40$ eV as shown in the [001] bright-field plan-view TEM image in Fig. 8(a). The corresponding SAED pattern exhibits extensive (110) streaking. The planar defects giving rise to these features were found, using a series of two-beam dark- and bright-field images along different zone axis, as well as by lattice-resolution imaging, to be stacking faults. Tilting the sample 45° from the [001] to the [011] zone axis, as shown in Fig. 8(b), renders the streaks in the diffraction pattern nearly continuous along (111) directions while the dark contrast features appear as line defects indicating that the stacking faults are viewed edge on. Schematic illustrations of the stacking fault geometry, deduced from the TEM analyses, are presented in Fig. 8(c). {111} stacking faults appear as bands along orthogonal [011] directions when viewed in the [001] zone axis, while they appear as lines intersecting at an angle of 70.53° [the angle between {111} planes] when viewed along the [011] zone axis.

TEM micrographs from δ-TaN$_{0.92}$ layers grown with $E_i=55$ eV contain not only single {111} stacking faults, but also {111} platelets. Figure 9(a) is a [011] bright-field plan-view image with a corresponding SAED pattern. The latter consists of, in addition to the streaks along (111) directions, two 109.47°-rotated coherent hexagonal γ-Ta$_2$N patterns which are shown more clearly in the calculated SAED pattern in Fig. 9(b). The orientation relationship between the cubic δ-TaN and hexagonal γ-Ta$_2$N planes is (111)$_{\delta\text{-TaN}}$||(0001)$_{\gamma\text{-Ta}_2\text{N}}$ and [110]$_{\delta\text{-TaN}}$±[110]$_{\gamma\text{-Ta}_2\text{N}}$. The half-order δ-TaN spots in the Fig. 9(a) inset are forbidden reflections which appear because of the breakdown in long-range periodicity due to the presence of a commensurate second phase. γ-Ta$_2$N(0002) and δ-TaN(111) planes have identical two-dimensional symmetry and good lattice constant match along equivalent close-packed directions for which the misfit is only 0.77% with intraplanar separations $d_{\delta\text{-TaN}}=0.3068$ nm and $d_{\gamma\text{-Ta}_2\text{N}}=0.3045$ nm.

Figure 9(c) is an [011] dark-field XTEM micrograph, imaged using the γ-Ta$_2$N reflection in the inset of Fig. 9(c), showing that the 111 platelets form immediately upon initiating film growth. γ-Ta$_2$N diffraction features are not observed in the GAXRD scan in Fig. 5(e) since γ-Ta$_2$N is coherent with δ-TaN.

TEM investigations of layers grown with $E_i=65$ eV, which contain several γ-Ta$_2$N peaks in GAXRD 2θ scans [see Fig. 5(f)], reveal that film growth initially proceeds as with the $E_i=55$ eV layers, resulting in coherent γ-Ta$_2$N platelets in epitaxial δ-TaN. However, epitaxy eventually breaks down locally with the nucleation and growth of polycrystalline γ-Ta$_2$N columns. We attribute this to the high irradiation energy leading to the agglomeration of residual ion-induced defects produced near the growing film surface, similar to the case of TiN(001) growth at 300–900 °C with $E_i=200$ eV. 39

The γ-Ta$_2$N platelets observed in understoichiometric TaN layers grown with $E_i=55$ and 65 eV can be viewed as a modified δ-TaN phase in which the (111) N planes are only 50% occupied due to ion-irradiation-induced ordering of N vacancies with adjacent Ta planes arranged in a hexagonal stacking sequence. The stacking faults observed in stoichiometric $E_i=30–40$ eV layers can then be described as incipient γ-Ta$_2$N phase platelets with N vacancies accumulated on (111) planes.

The in-plane $a_{||}$ and out-of-plane $a_{\perp}$ lattice constants, as well as the degree of in-plane relaxation $R_L$ in epitaxial δ-TaN(001) layers grown as a function of $E_i$ between 8.4 and 40 eV, with $f_{N_2}=0.125$ and $f_{Ta}=11$, were determined from HRRLM analyses. A typical HRRLM about the asymmetric 113 reflection for the layer grown with $E_i=30$ eV is shown in Fig. 10. Diffracted intensity distributions are plotted as

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Fig. 7. Bright-field (a) plan-view TEM and (b) XTEM images with corresponding SAED patterns from an epitaxial δ-TaN layer grown on MgO(001) at $T_s=600$ °C with $f_{N_2}=0.125$ and $E_i=30$ eV.
isointensity contours as a function of the reciprocal lattice vectors $k_\parallel$ parallel and $k_\perp$ perpendicular to the surface. For a 113 reflection from an 001-oriented NaCl-structure sample, $a_\parallel = \sqrt{2}/k_\parallel$ and $a_\perp = 3/k_\perp$. Analyses of the results in Fig. 10...
yields $a_1 = 0.4315$ nm and $a_\perp = 0.4376$ nm, respectively. Measured $a_1$ and $a_\perp$ values for epitaxial $\delta$-TaN(001) layers grown with $E_i$ ranging from 8.4 to 40 eV are plotted as a function of $E_i$ in Fig. 11(a).

The relaxed bulk lattice constant $a_0$ of stoichiometric $\delta$-TaN is determined from $a_1$ and $a_\perp$ values through the relationship

$$a_0 = a_\perp \left(1 - \frac{2\nu(a_\perp - a_1)}{a_\perp(1 + \nu)}\right),$$

where $\nu = 0.25$ is the Poisson ratio of $\delta$-TaN. From the above HRRLM results, we obtain $a_0 = 0.4349 \pm 0.0004$ nm for all layers. This corresponds to a film/substrate lattice constant misfit of $3.3 \pm 0.9\%$.

The degree of in-plane layer relaxation $R_L$ is defined as

$$R_L = \frac{a_1 - a_\perp}{a_0 - a_\perp},$$

where $a_\perp = 0.42112$ nm is the MgO substrate lattice constant. $R_L$ values determined for epitaxial $\delta$-TaN(001) layers grown with $E_i = 8.4 - 40$ eV are plotted as a function of $E_i$ in Fig. 11(b). $R_L$ decreases from 93% (nearly fully relaxed) with $E_i = 8.4$ eV to 74% with $E_i = 30$ eV to 68% with $E_i = 40$ eV as shown in Fig. 11(b).

Room-temperature resistivities $\rho$ of stoichiometric $\delta$-TaN(001) layers are plotted in Fig. 12(a) as a function of $E_i$. $\rho$ decreases continuously from 221 $\mu\Omega$ cm with $E_i = 8.4$ eV to 162 $\mu\Omega$ cm with $E_i = 40$ eV. This corresponds to an overall decrease of only 27% which can be attributed to ion-irradiation-induced changes in film microstructure. The electron mean free path obtained from our measured resistivities using an estimated Fermi velocity of $2 \times 10^8$ cm s$^{-1}$ (Ref. 43) is $\approx 2$ nm, more than an order of magnitude less than both the average nanopipe separation in layers with $E_i \leq 20$ eV and the average stacking fault spacing in layers with $E_i \geq 30$ eV. Thus charge scattering from extended defects does not significantly affect electron transport. However, the presence of nanopipes, which act as insulating inclusions in metallic $\delta$-TaN, do increase the total path for current flow and, hence, indirectly increase the measured resistivity. Nevertheless, we expect the dominant mechanism controlling $\rho$ to be charge scattering from point defects including cation and anion vacancies and antisites. $\rho(E_i)$ decreases with increasing $E_i$ due to a decrease in the residual point defect density caused by ion-irradiation-induced enhancement of adatom surface mobilities.

The hardness $H$ and elastic modulus $E$ of $\delta$-TaN(001) layers were determined from nanoindentation measurements carried out as described in detail in Ref. 44. $H$ values were extracted from data corresponding to maximum displacements of less than 80 nm. At larger displacements, substrate effects influence the results giving rise to lower $H$ values due...
to the relatively low hardness of MgO, 9.0±0.3 GPa. Figure 12(b) shows that the hardness of δ-TaN(001) layers grown with $E_i\leq 20$ eV is 29.0±1.5 GPa, while $H$ increases to 32.9±0.9 GPa with $E_i=30$ eV and 35.4±1.2 GPa with $E_i=40$ eV. The increase in $H$ with increasing $E_i$ is due to the corresponding decrease in the number density of nanopipes which can act as centers for dislocation formation. Similar results were reported for epitaxial CrN layers grown on MgO(001) by reactive magnetron sputtering. In the case of δ-TaN, an additional contributing effect is the increased density of stacking faults which inhibit dislocation glide. The elastic modulus $E$ remains approximately constant for all layers, independent of $E_i$; at 433±26 GPa [Fig. 12(b)]. Thus, $E$ is unaffected by the presence of both nanopipes and stacking faults. This is expected since $E$, in contrast to $H$, is a purely elastic property and the total volume fraction occupied by nanopipes and stacking faults is always less than 2% with $E_i=8.4–40$ eV.

IV. CONCLUSIONS

Epitaxial δ-TaN$_x$(001) layers were grown on MgO(001) at 600 °C by magnetically unbalanced UHV reactive magnetron sputtering of Ta in mixed Ar/N$_2$ discharges as a function of the N$_2$ fraction $f_{N_2}$ (0.100≤$f_{N_2}$≤0.275) and incident ion energy $E_i$ (8.4≤$E_i$≤65 eV). The ion-to-Ta flux ratio $J_i/J_{Ta}$ at the growing film was 11±0.5 with 0.10≤$f_{N_2}$≤0.20 and 15±0.3 with 0.250≤$f_{N_2}$≤0.275. Films deposited with $E_i=40$ eV exhibit a cube-on-cube epitaxial relationship with the substrate, (001)$_{\delta}$-TaN|$||$(001)MgO and [100]$_{\delta}$-TaN|$||$[100]MgO, and have N/Ta ratios which range from 0.94 with $f_{N_2}=0.100$ to 1.37 with $f_{N_2}=0.275$. However, all δ-TaN$_x$(001) layers grown with $E_i\leq 20$ eV are underdense with an array of 1-nm-wide nanopipes self-organized predominantly along orthogonal [100] directions. The nanopipes, which are first observed at film thicknesses of ≈5 nm and extend to the final surface, result from atomic shadowing near the bottom of a periodic array of surface cusps which form due to kinetic roughening. $E_i\leq 20$ eV layers grown with low $f_{N_2}$ ($f_{N_2}=0.150$) also contain misoriented δ-TaN grains whose nucleation can be suppressed by either increasing $f_{N_2}$ ($f_{N_2}=0.175$) or $E_i$. Fully dense stoichiometric epitaxial δ-TaN(001) films were obtained with $E_i=30$ eV and $f_{N_2}=0.125$. Increasing $E_i$ to 40 eV results in a high density of [111] stacking faults. Films grown with even higher ion energies, 40≤$E_i$≤65 eV, contain large concentrations of residual extended defects as well as second-phase hexagonal γ-Ta$_2$N inclusions.

In summary, stoichiometric fully dense single crystalline δ-TaN(001) layers are only obtained over a narrow range in growth parameters: $f_{N_2}=0.125$ with $E_i=30–40$ eV. These layers have a relaxed lattice constant of 0.4351±0.0007 nm and an elastic modulus of 437±19 GPa. The highest crystalline quality layers were obtained with $E_i=30$ eV for which $\rho_{300} = 185±15 \mu \Omega \text{cm}$ and $H = 32.9±0.9$ GPa.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Materials Science, under Grant No. DEFG02-91ER45439 through the University of Illinois Frederick Seitz Materials Research Laboratory (MRL). The authors also appreciate the use of the facilities of the MRL Center for Microanalysis of Materials, which is partially supported by the DOE, at the University of Illinois. C.S.S. is partially supported by Hynix Semiconductor Inc., Ichon, Korea. N.H. acknowledges the support from the Swedish Foundation for International Cooperation in Research and Higher Education (STINT).

7 Inorganic Index to Powder Diffraction File (Joint Committee on Powder Diffraction Standards, Swarthmore, PA, 1997); Card No. 32-1283.
30 Sputter deposition typically results in a cos(θ) sin(θ) distribution, with θ being the polar angle, of the incoming atom flux. The highest flux, therefore, is at an azimuthal angle of 45° as shown in Ref. 37.
41The Poisson ratio \( \nu \) for TaN is not known. However, \( \nu \) values for related cubic transition-metal nitrides vary only from 0.211 for TiN [J. O. Kim, J. D. Achenbach, P. B. Mirkarimi, M. Shinn, S. A. Barnett, J. Appl. Phys. 72, 1805 (1992)] to 0.29 for CrN [U. Wiklund, M. Bromark, M. Larsson, P. Hedenqvist, S. Hogmark, Surf. Coat. Technol. 91, 57 (1997)]. We used an average value of 0.25 for the calculation of \( a_0 \). The uncertainty in \( a_0 \) introduced by \( \nu_{\text{TaN}} \) is only \( \pm 0.00011 \) nm (0.02%).