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Effects of incident N atom kinetic energy on TiN/TiN(001) film growth dynamics: a molecular dynamics investigation

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Large-scale classical molecular dynamics (CMD) simulations of epitaxial TiN/TiN(001) thin film growth at 1200 K, a temperature within the optimal range for epitaxial TiN growth, with an incident N-to-Ti flux ratio of four, are carried out using incident N energies $E_N = 2$ and 10 eV and incident Ti energy $E_{Ti} = 2$ eV. To further highlight the effect of E_N , we grow a bilayer film with $E_N = 2$ eV initially and then switch to $E_N = 10$ eV. As-deposited layers are analyzed as a function of composition, island-size distribution, island-edge orientation, and vacancy formation. Results show that growth with $E_N = 2$ eV results in films which are globally overstoichiometric with islands bounded by N-terminated polar 110 edges, whereas films grown with $E_N = 10$ eV are flatter and closer to stoichiometric. However, $E_N = 10$ eV layers exhibit *local* N deficiency leading to the formation of isolated 111-oriented islands. Films grown by changing the incident energy from 2 to 10 eV during growth are more compact than those grown entirely with $E_N = 2$ eV and exhibit greatly reduced concentrations of upper-layer adatoms, ad molecules, and small clusters. Islands with 110 edges formed during growth with $E_N = 2$ eV transform to islands with 100 edges as E_N is switched to 10 eV.

I. INTRODUCTION

Transition-metal (TM) nitride^{1–3} coatings are employed in a wide variety of applications due to their unique combination of properties including high hardness,^{1,4–6} scratch and abrasion resistance,⁷ low coefficient of friction,⁸ high-temperature oxidation resistance,^{9–11} metallic to semiconducting electrical conductivity,^{12–15} optical absorption which is tunable across the visible spectrum,¹⁶ and superconductivity.^{12,17,18} TiN_x , with a single-phase field ranging from $x = 0.6$ to 1.0,¹⁹ was one of the first hard-coating materials and today serves as a model system for NaCl-structure TM nitride compounds and alloys. Consequently, TiN has been extensively studied experimentally in order to probe island formation,^{20,21} growth kinetics,^{22–25} and microstructure evolution.^{26–28}

Fundamental understanding of the processes governing nanostructural and surface morphological evolution during thin-film growth requires detailed information regarding the dynamics of mass transport on surfaces, nucleation, and the early stages of growth. Since surface processes occurring on the picosecond time scale cannot be

resolved with state-of-the-art atomic-scale experimental techniques, such as scanning tunneling microscopy^{22,23,29} and low-energy electron microscopy,³⁰ the use of complementary computational investigations is essential. Conversely, the system sizes and time scales required for film-growth studies are prohibitively large for *ab-initio* computational methods such as density functional theory (DFT). This renders classical molecular dynamics (CMD) as the primary computational tool for large-scale studies of film growth dynamics.

We have previously applied CMD to investigate both intralayer and interlayer mass transport of Ti and N adatoms, and TiN_x ad molecules, on $\text{TiN}(001)$ ³¹ and $\text{TiN}(111)$ terraces³² as well as on $\text{TiN}/\text{TiN}(001)$ islands.^{33,34} Ti adatom migration velocities on infinite terraces at 1000 K are nearly three times that of N adatoms.³¹ On $\text{TiN}/\text{TiN}(001)$ islands, Ti adatoms rapidly reach island step edges and descend exclusively via push-out/exchange processes, whereas N adatoms have lower mobilities and descend by both hopping over step-edges and push-out/exchange with N edge atoms.³³ Admolecule surface mobilities depend strongly on the N-content of the molecule. While TiN_2 ad molecules display remarkably high mobilities on both flat $\text{TiN}(001)$ terraces and $\text{TiN}/\text{TiN}(001)$ islands, TiN_3 ad molecules remain essentially stationary. Motivated by these results, we recently performed a large-scale MD study of $\text{TiN}/\text{TiN}(001)$ film growth using incident N/Ti ratios of N/Ti = 1, 2, and 4 to investigate the effect of the N/Ti ratio on film growth modes at 1200 K.³⁵ The results demonstrated that at low N/Ti flux ratios, both 100- and 110-bounded epitaxial islands are formed, and surface roughening occurs through nucleation of 111 islands in areas of local N deficiency via growth of 110-oriented in-plane ladder-like structures. At higher N/Ti ratios, islands with N-terminated 110 edges become dominant and surface roughening occurs due to enhanced upper-layer nucleation. Films grown with N/Ti = 2 display the smoothest surfaces.

The reaction paths of incident N and Ti atoms on $\text{TiN}(001)$ surfaces have been theoretically and experimentally shown to depend strongly on the incident kinetic energy.^{36,37} Energetic N atoms can fragment small islands and clusters, giving rise to higher adatom supersaturation. As a result of these factors, the choice of incident energy is expected to have an effect on island shapes and orientations similar to that observed with varying N/Ti ratios.³⁵ Here, we perform large-scale CMD simulations of $\text{TiN}/\text{TiN}(001)$ growth at 1200 K using incident N energies E_N of 2 and 10 eV at a flux ratio of N/Ti = 4. While previous results showed that a flux ratio of N/Ti = 2 resulted in the smoothest films at $E_N = 2$ eV,³⁵ we choose N/Ti = 4 for the present investigation since we anticipate losing additional N adatoms due to enhanced N_2 desorption and reflection with $E_N = 10$ eV.

The use of $E_N = 2$ eV corresponds approximately to the surface potential experienced by an incident N atom,³⁸ while $E_N = 10$ eV is a reasonable representation of the energy per N atom of an N_2^+ ion incident at the growing film in response to a typical floating potential, $V_f \sim -20$ V, during dc magnetron reactive sputter deposition of TiN in pure N_2 , for which N_2^+ accounts for $\sim 96\%$ of all incident ions (the remainder are N^+ ions).³⁸ To further investigate whether changing E_N during deposition will significantly affect steady-state film growth dynamics, we also grow a film in which E_N is switched from 2 to 10 eV after two-thirds of the total deposition time. In all three cases, we probe average film and island stoichiometry, island-size distributions, island-edge orientations, and vacancy formation as a function of E_N during the early stages of film growth.

Overall, our results show that increasing the incident N energy results in smoother and more stoichiometric films. TiN islands formed during deposition with $E_N = 2$ eV are predominantly bounded by N-terminated 110 edges. For growth with $E_N = 10$ eV, the islands are primarily bounded by 100 edges. Switching E_N from 2 eV to 10 eV during film growth leads to a sharp increase in 100 island edges, a decrease in the number density of small clusters, and an overall surface smoothening. The primary surface vacancies in $E_N = 2$ eV films are Ti, while N surface vacancies are obtained with $E_N = 10$ eV.

II. METHODOLOGY

We perform large-scale CMD simulations of TiN/TiN(001) film growth at 1200 K, a temperature within the optimal range for TiN(001) epitaxial growth,^{14,37} using incident N energies of 2 and 10 eV with a N/Ti flux ratio of four. In a third case study, we set the N energy to 2 eV initially, and change it to 10 eV after depositing 1.15 ML. Total film thicknesses are ~ 1.5 ML for each case. The simulations are carried out using the modified embedded-atom method (MEAM)³⁹ interatomic potential as implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)⁴⁰ with the TiN parameterization employed in references.^{31,33,34,41,42} The parameterization has been validated using DFT-based *ab-initio* molecular dynamics to determine Ti⁴¹ and N⁴² diffusion kinetics on, as well as N_2 desorption from,⁴² TiN(001) surfaces.

The simulation timestep is set to 1 fs and the NaCl-structure TiN(001) substrate is $100 \times 100 \times 6$ atoms, $212 \times 212 \times 13$ Å³, for a total of 60 000 atoms. Periodic boundary conditions are applied along in-plane directions. The atoms in the bottom layer are stationary. Atoms in the second and third lowest layers are subject to velocity rescaling at each time-step and thus act as a heat sink to maintain the temperature constant at 1200 K. The top three layers, and all deposited

atoms, are free of any constraints. Every 50 000 timesteps, or 50 ps, we sequentially add a Ti atom, followed 25 ps later by a set of 4 N atoms, all starting at random positions 10 to 12 Å from the film surface. The incident atoms are assigned a random velocity within a 30° angle from normal incidence corresponding to an average energy of 2 eV for Ti and 2 or 10 eV for N, depending on the case study. We use incidence angles ranging from normal to $\pm 30^\circ$ to approximate TiN deposition by magnetron sputtering, for which sputtered atoms are ejected with a cosine distribution with ballistic transport through the gas phase.⁴³

The coordinates of upper-layer substrate atoms as well as the deposited atoms are stored every 1000 timesteps (1 ps) in MD videos which are visualized using Visual Molecular Dynamics.⁴⁴ We simulate $\tau = 375$ ns of deposition time in which 7500 Ti atoms are incident at the substrate and growing film. This corresponds, for unity Ti incorporation probability, to a nominal Ti sublattice coverage of 1.5 ML. During the simulation, atoms are free to leave the simulation box. This is primarily an issue for N atoms, which can leave either by direct reflection or through N₂ desorption as N adatoms bond with, and remove, N surface atoms.^{36,42}

III. RESULTS AND DISCUSSION

A. TiN/TiN(001) film growth with $E_N = 2$ eV

Figure 1(a) shows the position of all deposited atoms at the end of film growth ($\tau = 375$ ns), corresponding to a total Ti coverage $\theta_{\text{tot,Ti}} = 1.41$ ML, with incident nitrogen energy $E_N = 2$ eV. All elemental coverages are normalized to their respective sublattice, i.e. $\theta_{\text{tot}} = (\theta_{\text{tot,Ti}} + \theta_{\text{tot,N}})/2$. Atoms are color-coded according to element and layer. Accounting for surface relaxation, the spacing between TiN(001) layers is ~ 2.10 Å, whereas the bulk interlayer distance is ~ 2.12 Å.³¹ Thus, we define layer numbers by intervals of 2.1 Å in the growth direction. Islands are epitaxial and bounded primarily by N-terminated 110 edges. The highest layer in which island nucleation is observed is the fourth, and there are itinerant TiN_x molecules in the fifth layer. Ti surface vacancies are prominent. The total number of condensed Ti and N atoms, n_{Ti} and n_{N} , are plotted as a function of simulation time τ and Ti first-layer coverage $\theta_{1,\text{Ti}}$ in the lower panel of Fig 1(a). $n_{\text{Ti}}(\tau)$ follows a linear behavior, whereas the N capture probability, initially linear with deposition time, decreases after $\theta_{1,\text{Ti}} \sim 0.19$ ML ($\tau = 50$ ns). The early net N capture probability, corresponding to the deposition of the initial 500 N atoms, is 0.55. During further deposition, the N capture probability decreases, primarily due to increased N₂ desorption rates with increased N coverage. For the final 500 deposited N atoms, the net N capture probability is 0.19.

FIG. 1. Positions, viewed along 001, of all deposited atoms (upper panels) during TiN/TiN(001) film growth at 1200 K with an atomic flux ratio $N/Ti = 4$. Total Ti exposures are 7500 atoms and incident N energies E_N are (a) 2 eV, (b) 10 eV, and (c) 2 eV initially, switching to 10 eV at time $\tau = 250$ ns (total deposition time is 375 ns). The substrate surface area is $212.1 \times 212.1 \text{ \AA}^2$ (100×100 atoms). Ti and N atoms are color coded by layer number as shown in the legend. The layer numbers are defined by intervals of $2.1 \text{ \AA}$ in the growth direction. The lower panels in (a), (b), and (c) are plots of the total numbers of captured Ti and N atoms (n_{Ti} and n_N) as a function of Ti coverage in the first layer $\theta_{1,Ti}$ [ML]. τ is the deposition time.

Total layer coverages θ_i^t , in which i indicates the layer number, and t is the total atom (Ti plus N) coverage, are $\theta_1^t = 0.82$, $\theta_2^t = 0.50$, $\theta_3^t = 0.24$, and $\theta_4^t = 0.07$ ML. The total film coverage θ_{tot} is 1.63 ML and the overall film composition is $\text{TiN}_{1.32}$. The islands in the first layer of the deposited film are primarily bounded by 110 oriented edges, with a total of 603 atoms along 110 edges and 172 atoms along 100 edges. The 100 edges of TiN are non-polar and the 110 edges polar; thus, the formation of N-saturated 110 edges allows excess N atoms to be accommodated. The island number density, defined as the number of islands with four or more atoms per unit area, is $8.9 \times 10^{11} \text{ cm}^{-2}$ for the first deposited layer and $4.7 \times 10^{12} \text{ cm}^{-2}$ for the second layer. The use of four atoms as a lower limit for island size is motivated by the fact that TiN_3 ad molecules are the smallest stationary clusters.³¹ The first layer of the deposited film is dominated by one island of 8137 atoms. A total of 40 Ti vacancies are formed in the substrate surface layer, and 50 residual Ti vacancies in the first layer of the deposited film; there are no N vacancies. All vacancies are counted, whether they are covered by an upper layer or reside in the exposed surface.

Figure 2(a) is a tomographic slice of a film grown with $E_N = 2 \text{ eV}$, showing only the atoms located in the first layer at the end of deposition. The islands are almost exclusively bounded by N-terminated 110 edges, and tend to form elongated structures with a high edge-length/area ratio. Defining island atoms with four nearest neighbors as interior “bulk” atoms and those with three or fewer nearest neighbors as edge atoms yields an average edge-to-bulk atom ratio $n_{\text{edge}}/n_{\text{bulk}} = 0.33$. Elemental coverages in the first layer are $\theta_{1,\text{Ti}} = 0.74$ and $\theta_{1,\text{N}} = 0.90$ ML (total film elemental coverages are $\theta_{\text{tot,Ti}} = 1.41$ and $\theta_{\text{tot,N}} = 1.85$ ML). The red ellipses in Fig. 2(a) highlight examples of island branches consisting of one row of Ti atoms bounded by N atoms.

FIG. 2. Positions, viewed along 001, of all deposited atoms in the first layer during TiN/TiN(001) film growth at 1200 K with an atomic flux ratio $N/Ti = 4$. Total Ti exposures are 7500 atoms and incident N energies E_N are (a) 2 eV, (b) 10 eV, and (c) 2 eV initially, switching to 10 eV at time $\tau = 250$ ns (total deposition time is 375 ns). The substrate surface area is $212.1 \times 212.1 \text{ \AA}^2$ (100×100 atoms). Ti and N atoms are color coded as shown in Figure 1. The black dashed ellipse in (b) highlights a 111-oriented island. The red ellipses in (a) and (c) indicate examples of island branches formed with $E_N = 2$ eV, which are suppressed when switching to 10 eV.

Figure 3(a), which shows second-layer island structures after 375 ns of deposition time, provides additional insight into nanostructural evolution. With $E_N = 2$ eV, islands grow in a dendritic fashion with extended island edges. For this layer, $n_{\text{edge}}/n_{\text{bulk}} = 0.60$. Second-layer, like first-layer, islands are also bounded primarily by N-terminated 110 edges with elemental coverages of $\theta_{2,Ti} = 0.43$ and $\theta_{2,N} = 0.57$ ML.

FIG. 3. Positions, viewed along 001, of all deposited atoms in the second layer during TiN/TiN(001) film growth at 1200 K with an atomic flux ratio $N/Ti = 4$. Total Ti exposures are 7500 atoms and incident N energies E_N are (a) 2 eV, (b) 10 eV, and (c) 2 eV initially, switching to 10 eV at time $\tau = 250$ ns (total deposition time is 375 ns). The substrate surface area is $212.1 \times 212.1 \text{ \AA}^2$ (100×100 atoms). Ti and N atoms are color coded as shown in Figure 1. The black dashed ellipse in (b) highlights a 111-oriented island.

Figure 4(a) is an island-size histogram corresponding to 375 ns of deposition. The horizontal axis corresponds to island sizes, expressed as a range in the number of atoms per island, and the vertical axis specifies the total number of atoms residing in islands of the corresponding size range. Islands in the first, second, third, and fourth layers are indicated by blue diagonal stripes, red horizontal stripes, green zig-zag, and purple checkered bars, respectively. With $E_N = 2$ eV, there is a large first-layer island of 8137 atoms, one island of 27 atoms, two islands with 4-10 atoms, and

23 adatoms and small admolecules ($x \leq 3$). In the second layer, the largest island is 1439 atoms, with four islands in the 5001-1000 atom range. In the third layer, there are five islands in the 101-500 atom range, with the largest comprised of 251 atoms. In the fourth layer, there are four islands composed of 51-100 atoms, of which the largest is 57 atoms.

FIG. 4. TiN/TiN(001) island-size distributions as a function of layer number during TiN/TiN(001) film growth at 1200 K with an atomic flux ratio $N/Ti = 4$. Total Ti exposures are 7500 atoms and incident N energies E_N are (a) 2 eV, (b) 10 eV, and (c) 2 eV initially, switching to 10 eV at time $\tau = 250$ ns (total deposition time is 375 ns). The substrate surface area is $212.1 \times 212.1 \text{ \AA}^2$ (100×100 atoms). Island-size distributions are plotted as the logarithm of the total number of atoms n_{tot} vs. island size in units of the total number of atoms per island.

Figure 5(a) compares the relative edge orientations of first-layer islands as a function of Ti coverage $\theta_{1,Ti}$. The solid blue line indicates the total length L_{100} , in atoms, of 100 edges, the dashed red line the total length $L_{110,Ti}$ of Ti-

terminated 110 edges, and the dot-dashed green line the total length $L_{110,N}$ of N-terminated 110 edges. We define the fractional length ζ of 100 and 110 edges as $\zeta_{100} = L_{100}/(L_{100}+L_{110})$ and $\zeta_{110} = L_{110}/(L_{100}+L_{110})$, where $L_{110} = L_{110,Ti} + L_{110,N}$. Initially, $L_{110} \sim L_{100}$; however, polar 110 edges rapidly dominate at coverages above $\theta_{1,Ti} \simeq 0.05$ ML in order to accommodate the excess surface N concentration (at $\tau = 50$ ns, $\theta_{1,Ti} = 0.19$ ML and $\theta_{1,N} = 0.39$ ML). As the layer fills, ζ_{110} reaches its maximum value of 0.88 at $\theta_{1,Ti} = 0.45$, after which it begins to decrease. At the end of deposition, $\theta_{1,Ti} = 0.74$ ML and $\zeta_{110} = 0.78$.

FIG. 5. Total length L , in atoms, of nonpolar 100 island edges and polar Ti- and N-terminated 110 island edges as a function of first-layer Ti coverage $\theta_{1,\text{Ti}}$ during TiN/TiN(001) film growth at 1200 K with an atomic flux ratio $N/\text{Ti} = 4$. Total Ti exposures are 7500 atoms and incident N energies E_N are (a) 2 eV, (b) 10 eV, and (c) 2 eV initially, switching to 10 eV at time $\tau = 250$ ns (total deposition time is 375 ns). The substrate surface area is $212.1 \times 212.1 \text{ \AA}^2$ (100×100 atoms). The solid blue line corresponds to L_{100} , the dashed red line to $L_{110,\text{Ti}}$, and the dot-dashed green line to $L_{110,\text{N}}$.

We also track the number of residual vacancies formed during film growth. For deposition with $E_N = 2$ eV, only Ti vacancies are obtained. Following deposition, there are 40 Ti vacancies V_{Ti} in the 100×100 atom substrate surface, corresponding to a surface vacancy number density $D_{V_{Ti}}$ on the cation sublattice of 0.008 vacancies/atom. In the first deposited layer, $V_{Ti} = 50$ with $D_{V_{Ti}} = 0.01$ vacancies/atom. There are also a few Ti vacancies in the second and third deposited layers, $V_{Ti} = 10$ and 4, respectively. The formation of Ti vacancies is due, as clearly shown in MD movies, to migrating N adatoms pulling Ti atoms out of the exposed surface layer. N vacancies formed due to N_2 desorption are rapidly replaced by the excess N in the deposition flux, thus explaining the absence of residual N vacancies.

B. TiN/TiN(001) film growth with $E_N = 10$ eV

The positions of all atoms in an $E_N = 10$ eV film with $\theta_{tot} = 1.47$ ML and $\theta_{Ti} = 1.49$ ML are shown in Fig. 1(b). Islands have nucleated in the fourth layer and there are some TiN_x molecules ($x \leq 3$) in the fifth layer. The majority of islands in all four layers are epitaxial, bounded by both 100 and 110 edges, and contain N vacancies. However, as noted below, there is one 111-oriented island. The total number of condensed atoms, plotted in the lower panel of Fig. 1(b) as a function of deposition time τ , follows a linear behavior for Ti and is close to linear for N. As mentioned in the introduction, we anticipated a reduction in retained N using $E_N = 10$ eV. This prediction is verified, as seen by comparing the total number of condensed N atoms in Figs. 1(a) and 1(b). The net N capture probability, initially significantly lower than for films grown with $E_N = 2$ eV as more nitrogen is lost by N reflection and N_2 desorption, increases from 0.14 with $\theta_{1,Ti} \leq 0.05$ ML to 0.26 for the final 500 deposited N atoms.

Total as-deposited layer coverages are $\theta_1^t = 0.95$, $\theta_2^t = 0.45$, $\theta_3^t = 0.06$, and $\theta_4^t = 0.01$ ML ($\theta_{tot} = 1.47$ ML) with an overall film composition of $TiN_{0.98}$. In contrast to films grown with $E_N = 2$ eV, residual vacancies in $E_N = 10$ eV layers reside primarily on the N sublattice. Islands in the first layer have approximately equal 100 and 110 edge lengths: 101 and 92 atoms along 100 and 110, respectively. The first layer consists of one large island; the second layer has an island number density of $3.1 \times 10^{12} \text{ cm}^{-2}$ (the corresponding number density for film growth with $E_N = 2$ eV, as noted in the previous section, is 4.7×10^{12}). There are 32 N vacancies and no Ti vacancies in the substrate surface, while in the first deposited layer there are 62 N vacancies with 5 Ti vacancies.

Figure 2(b) shows the first-layer island structure for an $E_N = 10$ eV film at the end of deposition. The layer is almost completely filled and is stoichiometric with average elemental coverages $\theta_{1,Ti} = \theta_{1,N} = 0.95$ ML. Nevertheless, a region of *local* N deficiency leads to the formation of a 111-oriented island, as Ti atoms in N-deficient areas favor

four-fold hollow sites, rather than atop N sites, and form a ladder-like structure extending along 110-directions. This is schematically illustrated in Figure 6. Such structures serve as seeds for the formation of 111 islands.³⁵ A 111 island is highlighted in Fig. 2(b) with a black dashed ellipse. Due to the nearly complete coverage of this first layer, the edge-to-bulk ratio is low, $n_{\text{edge}}/n_{\text{bulk}} = 0.08$.

FIG. 6. In-plane ladder-like structure, leading to the formation of 111-oriented islands during TiN/TiN(001) film growth at 1200 K with incident flux ratio $N/Ti = 4$ and $E_N = 10$ eV. Color code for ladder atoms: Ti = blue and N = yellow. Ti substrate atoms are black and N substrate atoms are gray.

The $E_N = 10$ eV second-layer film structure is shown in Figure 3(b). The Ti coverage in this layer, $\theta_{2,Ti} = 0.46$ ML, is similar to that of $E_N = 2$ eV films, $\theta_{2,Ti} = 0.43$ ML. However, the islands are more compact with a lower edge-to-bulk ratio: $n_{\text{edge}}/n_{\text{bulk}} = 0.38$ with $E_N = 10$ eV vs. 0.60 for $E_N = 2$ eV films. In addition, second-layer $E_N = 10$ eV islands are primarily bounded by non-polar 100 edges due to a lower N coverage, $\theta_{2,N} = 0.45$ ML, while islands in the corresponding layer of $E_N = 2$ eV films are primarily bounded by polar 111-oriented edges and have a N coverage of 0.57 ML. The 111-oriented island observed in the first layer of the $E_N = 10$ eV film (Fig. 2(a)) continues into the second layer (highlighted in Fig. 3(b) with a black dashed ellipse), as well as the third and fourth layers.

Figure 4(b) shows an island-size histogram following deposition of a complete $E_N = 10$ eV film. The first layer consists of one large island composed of 9469 atoms and one free N adatom. In the second layer, there are four islands

in the 501-1000 atom range, the largest of which is 992 atoms, as well as ten islands with between 11 and 500 atoms, and 18 itinerant adatoms and admolecules. In the third layer, the largest island is 162 atoms and there are 16 adatoms and admolecules; while the fourth layer contains only two islands, one of 113 atoms and the other of 11 atoms, with six adatoms.

The evolution of first-layer island-edge orientations is shown in Figure 5(b). Predominantly 100 edges are formed initially; however, both L_{100} and L_{110} decrease with $\theta_{1,Ti} \gtrsim 0.5$ ML as the total island edge-length decreases and the film approaches full layer coverage. We also note that $L_{110,Ti} \sim L_{110,N}$; whereas for growth with $E_N = 2$ eV, $L_{110,Ti} \sim 0$. Fig. 5(b) shows that L_{100} decreases from 570.5 atoms at $\theta_{1,Ti} = 0.50$ ML to 95.5 with $\theta_{1,Ti} = 0.95$ ML, while L_{110} ranges from 396 atoms at $\theta_{1,Ti} = 0.50$ ML to 90 with $\theta_{1,Ti} = 0.95$ ML.

As noted above, increasing E_N from 2 to 10 eV results in a reduction in the N incorporation probability. Thus, the primary vacancies in $E_N = 10$ eV films reside on the N sublattice. At the end of deposition, there is a total of 32 N vacancies in the substrate surface, $D_{V_N} = 0.006$ vacancies/atom, with no Ti vacancies. The first deposited layer contains 62 N vacancies and 5 Ti vacancies, yielding vacancy densities of $D_{V_N} = 0.012$ and $D_{V_{Ti}} = 0.001$ vacancies/atom. In the second layer, there are 28 N vacancies and 2 Ti vacancies, $D_{V_N} = 0.006$ and $D_{V_{Ti}} \sim 0$ vacancies/atom, and there is 1 N vacancy in the third layer.

C. Bilayer TiN/TiN(001) film growth: $E_N = 2$ eV for $\tau = 250$ ns, and $E_N = 10$ eV for $250 < \tau < 375$ ns.

The positions of all deposited atoms in the TiN/TiN(001) bilayer film, grown with $E_N = 2$ eV for $\tau = 250$ ns ($\theta_{1,Ti} = 0.58$ ML, $\theta_{tot,Ti} = 0.96$ ML) and $E_N = 10$ eV for the remaining 125 ns, is shown in Figure 1(c). As for the case of film growth with $E_N = 2$ eV throughout, all islands in the first four layers are epitaxial. The fifth layer contains only adatoms and small clusters. There are fewer vacancies in both the substrate surface and the first film layer than in films grown continuously with either 2 or 10 eV. As expected, the total number of condensed atoms, plotted as a function of τ in the lower panel of Fig. 1(c), initially follows the same shape as for deposition with $E_N = 2$ eV. However, at $\theta_{1,Ti} = 0.58$ ML, as E_N is switched to 10 eV, $n_N(\theta_{1,Ti})$ begins to decrease immediately. This results in a distinct kink in the $n_N(\theta_{1,Ti})$ curve, while the slope of $n_{Ti}(\theta_{1,Ti})$ remains constant. For the last 500 atoms deposited before switching E_N , the net N capture probability is 0.23, whereas for the first 500 atoms deposited immediately after the change to $E_N = 10$ eV, the probability is ~ 0 . As $E_N = 10$ eV deposition continues, the net N capture probability increases again and reaches 0.25, essentially equal to the value, 0.26, obtained for 10 eV films.

The overall composition at $\tau = 375$ ns is $\text{TiN}_{1.12}$ and total layer coverages are $\theta_1^t = 0.80$, $\theta_2^t = 0.49$, $\theta_3^t = 0.20$, and $\theta_4^t = 0.04$ ML, corresponding to $\theta_{\text{tot}} = 1.53$ ML. An important difference compared with the $E_N = 2$ eV case is that the increase in incident N energy leads to significantly fewer itinerant adatoms and small islands (of size ≤ 10 atoms) in all layers, thus resulting in a higher density film. The first layer consists of a single large island, while the second-layer island number density is $4.0 \times 10^{12} \text{ cm}^{-2}$. Residual vacancies in the bilayer film are primarily on the Ti sublattice, but their number density is significantly less than for continuous $E_N = 2$ eV growth. At the end of bilayer deposition, there are 11 Ti and 4 N vacancies in the substrate surface, with 23 Ti and 8 N vacancies in the first deposited layer. In the second layer, there are 5 Ti and 5 N vacancies, and in the third layer 1 Ti and 1 N vacancy. For comparison, in the 2 eV film, there were 40 Ti vacancies in the substrate surface, 50 in the first deposited layer, 4 in the second layer, and none in the third layer.

In Figure 2(c), we show the first-layer structure of the bilayer film at the end of deposition. First-layer islands are preferentially bounded by 100 edges; there are 453 atoms along 100 and 375 atoms along 110 edges. Compared to the film grown with $E_N = 2$ eV throughout, the total length of N-terminated 110 edges, and hence island branches consisting of 110 rows of Ti atoms bounded by N (examples are marked with red ellipses in Figs. 2(a) and 2(c)), is reduced. In addition, there are essentially no free N adatoms, whereas there were 22 N adatoms in the 2 eV film. Thus, overall, bilayer islands are slightly more compact with edge-to-bulk ratio $n_{\text{edge}}/n_{\text{bulk}} = 0.29$ compared to 0.33 for $E_N = 2$ eV films. With respect to $E_N = 10$ eV films, no 111-oriented island is formed, and bilayer films exhibit a lower total first-layer coverage $\theta_{1,\text{tot}} = 0.80$ ML ($\theta_{1,\text{tot}} = 0.95$ ML for $E_N = 10$ eV) with first-layer elemental coverages $\theta_{1,\text{Ti}} = 0.77$ ML and $\theta_{1,\text{N}} = 0.84$ ML.

The position of all second-layer atoms in the bilayer film at the end of deposition is shown in Figure 3(c). Switching E_N from 2 to 10 eV for the final one-third of the deposition time has a significant effect on both film-growth kinetics and layer composition. There are significantly fewer adatoms and small clusters than in the film grown entirely with 2 eV. The number of surface adspecies consisting of 1 to 3 atoms is 34 (a total of 36 atoms) with $E_N = 2$ eV, and 14 clusters (15 atoms) for the bilayer film. In the 4-10 atom range, there are five islands (26 atoms) with $E_N = 2$ eV and one island (9 atoms) for the bilayer film. There is also an increased tendency to form 100-oriented islands; $\zeta_{100} = 0.60$ at the end of the bilayer deposition, an increase from $\zeta_{100} = 0.35$ at the point where E_N was switched from 2 to 10 eV at $\theta_{1,\text{Ti}} = 0.58$ ML ($\tau = 250$ ns). The islands in the bilayer film are more compact with $n_{\text{edge}}/n_{\text{bulk}} = 0.55$ compared

to 0.60 for growth with $E_N = 2$ eV. The second-layer elemental coverages for the bilayer film are $\theta_{2,\text{Ti}} = 0.45$ and $\theta_{2,\text{N}} = 0.52$ ML (total film elemental coverages are $\theta_{\text{tot,Ti}} = 1.44$ and $\theta_{\text{tot,N}} = 1.61$ ML).

The bilayer-film island-size histogram is shown in Figure 4(c). The first layer contains one large island of 8008 atoms with five single adatoms. In the second layer, there are two islands with more than 1000 atoms, the largest containing 1381 atoms. There are six islands in the third layer with 101-500 atoms, of which the largest is 331 atoms. In the fourth layer, there are two islands with 58 atoms each. Compared to deposition with $E_N = 2$ eV throughout, the primary difference is the greatly reduced concentrations of adatoms, ad molecules, and small islands (≤ 10 atoms) in all layers of the film. For the bilayer film, the sum of all atoms in islands consisting of fewer than 10 atoms is 5, 24, 26, and 16 for layers 1, 2, 3, and 4. The corresponding numbers for the film grown with 2 eV are 39, 62, 118, and 147.

Figure 5(c) is a plot of the evolution of first-layer edge orientations in the bilayer film as a function of $\theta_{1,\text{Ti}}$. L_{100} and L_{110} curves follow those shown in Fig. 5(a) for $E_N = 2$ eV until E_N is switched to 10 eV at $\theta_{1,\text{Ti}} = 0.58$ ML ($\tau = 250$ ns), which results in an immediate sharp increase in L_{100} from 191 atoms ($\zeta_{100} = 0.18$) to ~ 460 atoms at $\theta_{1,\text{Ti}} = 0.65$ ML as L_{100} saturates. As a result, the final value of ζ_{110} , 0.45, is considerably lower than for films grown with $E_N = 2$ eV ($\zeta_{110} = 0.78$).

At the end of the $E_N = 2$ eV portion of the bilayer film ($\tau = 250$ ns), there are 56 Ti vacancies ($D_{\text{V,Ti}} = 0.011$ vacancies/atom) in the top layer of the film. In the first deposited layer, there are 27 Ti vacancies and 1 N vacancy ($D_{\text{V,Ti}} = 0.005$, $D_{\text{V,N}} \sim 0$ vacancies/atom). After setting $E_N = 10$ eV for the remaining 125 ns of film growth, the number of Ti vacancies at the end of deposition has decreased to 11 in the top substrate layer and the number of N vacancies has increased to 4 ($D_{\text{V,Ti}} = 0.002$, $D_{\text{V,N}} \sim 0$ vacancies/atom). In the first deposited layer, $V_{\text{Ti}} = 23$ and $V_{\text{N}} = 8$. The increased incident N energy results in a reduced N concentration and the formation of residual N vacancies. The reduced N coverage gives rise, in turn, to fewer Ti atoms being dragged up to the surface from underlying layers and, hence, fewer total Ti vacancies.

We have shown previously that N adatoms are much less mobile on both TiN(001) terraces and small TiN/TiN(001) islands.^{31,33} In the present film-growth results, we find that excess N surface concentrations lead to the formation of polar N-terminated islands bounded by 110 edges. Increasing E_N from 2 to 10 eV decreases the N adatom concentration by both reflection and N_2 desorption. This, in turn, destabilizes islands with 110 edges in favor of forming islands which are more compact and predominantly bounded by non-polar 100 edges. In the case for which

E_N was switched from 2 to 10 eV after deposition of two-thirds of the film, energetic bombardment led to a dramatic decrease in the number density of free N adatoms which reduced the probability of forming stable immobile TiN_3 nuclei. In addition, 10 eV N irradiation may result in the breaking of small clusters into smaller units and adatoms which are more mobile and can be captured by larger islands. Overall, we observe that switching from 2 to 10 eV N irradiation yields lower island nucleation rates and larger average island sizes. This is consistent with previous experimental results for the epitaxial growth of Si/Si(001)⁴⁵ and InAs/Si(001)⁴⁶ which showed that increased incident kinetic energies suppress three-dimensional island formation and yield smoother surfaces. Finally, we note that our results are also consistent with STM analyses of epitaxial TiN(001) films showing that nitrogen irradiation during growth leads to smoother films⁴⁷ and that increased nitrogen partial pressures during film growth results in smaller characteristic island sizes and hence rougher films.²¹ The simulation results presented here demonstrate similar results for TiN/TiN(001) growth, while focusing on atomic-scale mechanisms during deposition under well-controlled conditions.

IV. CONCLUSIONS

Our CMD results demonstrate significant atomic-scale effects due to incident N energy during TiN/TiN(001) film growth. At an incident flux ratio of $N/Ti = 4$, growth with $E_N = 2$ eV results in globally overstoichiometric films with islands primarily bounded by N-terminated 110 edges and rapid upper-layer nucleation leading to surface roughening. With $E_N = 10$ eV, small islands are continuously dissociated into smaller clusters and adatoms leading to higher upper-layer supersaturation, and resulting in smoother films with compositions close to stoichiometric. Incident energetic N atoms also give rise to increased nitrogen desorption and reflection. However, *local* N deficiency results in the formation of 111-oriented islands. Changing the incident energy from 2 to 10 eV during growth has a large and immediate effect on film nanostructure and stoichiometry. The films are more compact than those grown entirely with $E_N = 2$ eV, and exhibit greatly reduced concentrations of adatoms, admolecules, and small islands. The reduced concentration of N adatoms destabilizes island edges composed of a single row of Ti atoms bounded by N atoms and favor the formation of islands which display an increased tendency to be bounded by 100 edges. As in the case of $E_N = 2$ eV films, no 111-oriented islands are observed.

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REFERENCES

- ¹ H. Ljungcrantz, M. Odén, L. Hultman, J.E. Greene, and J.-E. Sundgren, *J. Appl. Phys.* **80**, 6725 (1996).
- ² J.-E. Sundgren, *Thin Solid Films* **128**, 21 (1985).
- ³ J.E. Greene, J.-E. Sundgren, L. Hultman, I. Petrov, and D.B. Bergstrom, *Appl. Phys. Lett.* **67**, 2928 (1995).
- ⁴ T. Reeswinkel, D.G. Sangiovanni, V. Chirita, L. Hultman, and J.M. Schneider, *Surf. Coat. Technol.* **205**, 4821 (2011).
- ⁵ C.-S. Shin, D. Gall, N. Hellgren, J. Patscheider, I. Petrov, and J.E. Greene, *J. Appl. Phys.* **93**, 6025 (2003).
- ⁶ H. Kindlund, D.G. Sangiovanni, J. Lu, J. Jensen, V. Chirita, I. Petrov, J.E. Greene, and L. Hultman, *J. Vac. Sci. Technol. Vac. Surf. Films* **32**, 30603 (2014).
- ⁷ P. Hedenqvist, M. Bromark, M. Olsson, S. Hogmark, and E. Bergmann, *Surf. Coat. Technol.* **63**, 115 (1994).
- ⁸ T. Polcar, T. Kubart, R. Novák, L. Kopecký, and P. Široký, *Surf. Coat. Technol.* **193**, 192 (2005).
- ⁹ A.S. Ingason, F. Magnus, J.S. Agustsson, S. Olafsson, and J.T. Gudmundsson, *Thin Solid Films* **517**, 6731 (2009).
- ¹⁰ D. McIntyre, J.E. Greene, G. Håkansson, J.-E. Sundgren, and W.-D. Münz, *J. Appl. Phys.* **67**, 1542 (1990).
- ¹¹ L.A. Donohue, I.J. Smith, W.-D. Münz, I. Petrov, and J.E. Greene, *Surf. Coat. Technol.* **94–95**, 226 (1997).
- ¹² A.B. Mei, A. Rockett, L. Hultman, I. Petrov, and J.E. Greene, *J. Appl. Phys.* **114**, 193708 (2013).
- ¹³ H.-S. Seo, T.-Y. Lee, J.G. Wen, I. Petrov, J.E. Greene, and D. Gall, *J. Appl. Phys.* **96**, 878 (2004).
- ¹⁴ C.-S. Shin, S. Rudenja, D. Gall, N. Hellgren, T.-Y. Lee, I. Petrov, and J.E. Greene, *J. Appl. Phys.* **95**, 356 (2004).
- ¹⁵ D. Gall, I. Petrov, N. Hellgren, L. Hultman, J.E. Sundgren, and J.E. Greene, *J. Appl. Phys.* **84**, 6034 (1998).
- ¹⁶ D. Gall, I. Petrov, and J.E. Greene, *J. Appl. Phys.* **89**, 401 (2001).
- ¹⁷ H.-S. Seo, T.-Y. Lee, I. Petrov, J.E. Greene, and D. Gall, *J. Appl. Phys.* **97**, 83521 (2005).
- ¹⁸ C.-S. Shin, D. Gall, Y.-W. Kim, P. Desjardins, I. Petrov, J.E. Greene, M. Odén, and L. Hultman, *J. Appl. Phys.* **90**, 2879 (2001).
- ¹⁹ J.E. Sundgren, B.O. Johansson, A. Rockett, S.A. Barnett, and J.E. Greene, in *Phys. Chem. Prot. Coat.*, edited by J.E. Greene, W.D. Sproul, and J.A. Thornton (American Institute of Physics, New York, NY, 1986).
- ²⁰ M.A. Wall, D.G. Cahill, I. Petrov, D. Gall, and J.E. Greene, *Phys. Rev. B* **70**, 35413 (2004).
- ²¹ M.A. Wall, D.G. Cahill, I. Petrov, D. Gall, and J.E. Greene, *Surf. Sci.* **581**, L122 (2005).
- ²² S. Kodambaka, V. Petrova, A. Vailionis, P. Desjardins, D.G. Cahill, I. Petrov, and J.E. Greene, *Thin Solid Films* **392**, 164 (2001).
- ²³ S. Kodambaka, V. Petrova, A. Vailionis, I. Petrov, and J.E. Greene, *Surf. Sci.* **526**, 85 (2003).
- ²⁴ F.H. Baumann, D. I. Chopp, T.D. de la Rubia, G.E. Gilmer, J.E. Greene, H. Huang, S. Kodambaka, P. O’Sullivan, and I. Petrov, *MRS Bull.* **26**, 182 (2001).
- ²⁵ S. Kodambaka, S.V. Khare, V. Petrova, A. Vailionis, I. Petrov, and J.E. Greene, *Surf. Sci.* **513**, 468 (2002).
- ²⁶ C.-S. Shin, D. Gall, Y.-W. Kim, N. Hellgren, I. Petrov, and J.E. Greene, *J. Appl. Phys.* **92**, 5084 (2002).
- ²⁷ U. Helmersson, J.-E. Sundgren, and J.E. Greene, *J. Vac. Sci. Technol. A* **4**, 500 (1986).
- ²⁸ B.W. Karr, I. Petrov, D.G. Cahill, and J.E. Greene, *Appl. Phys. Lett.* **70**, 1703 (1997).
- ²⁹ S. Kodambaka, V. Petrova, A. Vailionis, P. Desjardins, D.G. Cahill, I. Petrov, and J.E. Greene, *Surf. Rev. Lett.* **7**, 589 (2000).
- ³⁰ F. Watanabe, S. Kodambaka, W. Swiech, J.E. Greene, and D.G. Cahill, *Surf. Sci.* **572**, 425 (2004).
- ³¹ D.G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J.E. Greene, *Phys. Rev. B* **86**, 155443 (2012).
- ³² D.G. Sangiovanni, F. Tasnádi, L. Hultman, I. Petrov, J.E. Greene, and V. Chirita, *Surf. Sci.* **649**, 72 (2016).
- ³³ D. Edström, D.G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J.E. Greene, *Thin Solid Films* **558**, 37 (2014).
- ³⁴ D. Edström, D.G. Sangiovanni, L. Hultman, I. Petrov, J.E. Greene, and V. Chirita, *Thin Solid Films* **589**, 133 (2015).

- ³⁵ D. Edström, D.G. Sangiovanni, L. Hultman, I. Petrov, J.E. Greene, and V. Chirita, J. Vac. Sci. Technol. Vac. Surf. Films **34**, 41509 (2016).
- ³⁶ Z. Xu, Q. Zeng, L. Yuan, Y. Qin, M. Chen, and D. Shan, Appl. Surf. Sci. **360**, Part B, 946 (2016).
- ³⁷ L. Hultman, S.A. Barnett, J.-E. Sundgren, and J.E. Greene, J. Cryst. Growth **92**, 639 (1988).
- ³⁸ I. Petrov, A. Myers, J.E. Greene, and J.R. Abelson, J. Vac. Sci. Technol. Vac. Surf. Films **12**, 2846 (1994).
- ³⁹ B.-J. Lee and M.I. Baskes, Phys. Rev. B **62**, 8564 (2000).
- ⁴⁰ S. Plimpton, J. Comput. Phys. **117**, 1 (1995).
- ⁴¹ D.G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J.E. Greene, and V. Chirita, Surf. Sci. **627**, 34 (2014).
- ⁴² D.G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J.E. Greene, and V. Chirita, Surf. Sci. **624**, 25 (2014).
- ⁴³ J.A. Thornton and J.E. Greene, in *Depos. Technol. Films Coat.*, edited by R.F. Bunshah (Noyes Publications, Park Ridge, NJ, 1994), p. 249.
- ⁴⁴ W. Humphrey, A. Dalke, and K. Schulten, J. Mol. Graph. **14**, 33 (1996).
- ⁴⁵ N.-E. Lee, G.A. Tomasch, and J.E. Greene, Appl. Phys. Lett. **65**, 3236 (1994).
- ⁴⁶ C.-H. Choi, L. Hultman, and S.A. Barnett, J. Vac. Sci. Technol. A **8**, 1587 (1990).
- ⁴⁷ B.W. Karr, D.G. Cahill, I. Petrov, and J.E. Greene, Phys. Rev. B **61**, 16137 (2000).