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Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands

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Abstract

We use classical molecular dynamics and the modified embedded atom method to determine residence times and descent pathways of Ti and N adatoms on square, single-atom-high, TiN islands on TiN(001). Simulations are carried out at 1000 K, which is within the optimal range for TiN(001) epitaxial growth. Results show that the frequency of descent events, and overall adatom residence times, depend strongly on both the TiN(001) diffusion barrier for each species as well as the adatom island-edge location immediately prior to descent. Ti adatoms, with a low diffusion barrier, rapidly move toward the island periphery, via funneling, where they diffuse along upper island edges. The primary descent mechanism for Ti adatoms is via push-out/exchange with Ti island-edge atoms, a process in which the adatom replaces an island edge atom by moving down while pushing the edge atom out onto the terrace to occupy an epitaxial position along the island edge. Double push-out events are also observed for Ti adatoms descending at N corner positions. N adatoms, with a considerably higher diffusion barrier on TiN(001), require much longer times to reach island edges and, consequently, have significantly longer residence times. N adatoms are found to descend onto the terrace by direct hopping over island edges and corner atoms, as well as by concerted push-out/exchange with N atoms adjacent to Ti corners. For both adspecies, we also observe several complex adatom/island interactions, before and after descent onto the terrace, including two instances of Ti island-atom ascent onto the island surface.

Keywords: Nitrides, Titanium alloy, Nucleation, Growth, Diffusion, Molecular dynamics simulations

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1. Introduction

Thin film growth is a complex process controlled by the interplay between thermodynamic and kinetic driving forces. Fundamental understanding of processes governing nanostructural and surface morphological evolution during growth requires detailed information concerning the dynamics of atomic-scale transport on surfaces. State-of-the-art experimental techniques, including scanning tunneling microscopy (STM) [1-3] and low-energy electron microscopy [4-6], cannot resolve dynamics on the picosecond time-scale, necessitating the use of complementary computational studies. First-principles methods have been applied to small systems to study diffusion on static transition-metal nitride surfaces [7-9]. However, system sizes required to study dynamics are prohibitively large for methods such as density functional theory (DFT). This renders classical molecular dynamics (MD) as the primary deterministic computational method available to probe the dynamics of atomic-scale processes on compound surfaces.

Here, we report the results of a detailed study of Ti and N adatom dynamics on square, single-atom-high islands on TiN(001). Titanium nitride, one of the first hard-coating materials [10-12], serves as a model system for NaCl-structure transition-metal (TM) nitride compounds, including VN [13,14], TaN [15], ScN [16,17], and HfN [18,19], currently employed in a variety of applications based upon their unique properties: high hardness [10,20], excellent scratch and abrasion resistance [21], relatively low coefficient of friction [22], high-temperature oxidation resistance [23-25], metallic to semiconducting conductivity [26], optical absorption which can be tuned across the visible spectrum [26], and superconductivity [27,28].

Experimentally, TiN is the most extensively investigated TM nitride using, for example, in-situ variable-temperature scanning tunneling microscopy (VT-STM) to probe nucleation [7,29], growth [2,3,30,31], and microstructural and surface morphological evolution [32,33] during reactive evaporation and sputter deposition. VT-STM nucleation studies, combined with DFT calculations [7,8], have shown that the primary diffusing species during TiN(001) epitaxial growth are Ti and N adatoms and TiN_x complexes ($x = 1, 2, 3$). The dominant N-containing ad molecule on

the growth surface depends upon the incident N/Ti flux ratio, for which the N source includes plasma-dissociated N_2 , collisionally dissociated N_2^+ , and dissociatively chemisorbed N_2 [34]. In our recent paper focused on terrace surface diffusion [35], we reported that Ti adatoms have significantly higher mobilities than N adatoms on TiN(001) terraces, and that, surprisingly, TiN_2 trimers exhibit the highest mobility of the TiN_x clusters, comparable to that of Ti adatoms [35].

As the next step in our investigation of atomic-scale transport on TiN(001) during the early stages of homoepitaxial film growth, we use classical MD to study the dynamics of Ti and N adatoms on square two-dimensional 8×8 atom TiN islands with $\langle 100 \rangle$ edges on TiN(001) at 1000 K, within the optimal range for TiN(001) epitaxial growth [20,36]. Our results show that island relaxation leads to funneling toward the edges and that Ti adatoms reside for significantly shorter times than N adatoms on TiN islands, with average residence times of 1.15 ns and 1.96 ns, respectively. The long residence times of N adatoms indicate that they are the precursors leading to multilayer growth and surface roughening.

Ti adatoms are observed to descend onto TiN(001) terraces exclusively via single and double push-out/exchange mechanisms. For N adatoms, descent occurs by both push-out/exchange and direct hops onto the terrace. In addition, the location of the N adatom along the island edge immediately prior to a descent event plays a distinctively more important role than for Ti adatoms. Once descended from atop the island, adatoms are unable to diffuse along the island edge, but can easily overcome corner barriers – the opposite of what is observed on simple fcc metal surfaces [37].

2. Methodology

Classical molecular dynamics simulations are performed using the second-nearest-neighbor modified-embedded-atom method (MEAM) [38] as implemented in the large-scale atomic/molecular massive parallel simulator (LAMMPS) [39]. We employ the same set of MEAM parameters as in our previous study of adspecies diffusion on TiN(001) terraces [35,40]. The

parameters yield adatom formation energies, surface energies, step-edge formation energies, diffusion barriers, and Ehrlich barriers consistent with experimental values [1,3,29,41]. Two-dimensional TiN islands with $\langle 100 \rangle$ edges, and composed of 8×8 atoms, are placed at the center of TiN(001) terraces consisting of six layers, each comprised of 18×18 atoms, for a system total of 2008 atoms [Fig. 1].

All simulations are carried out in the standard microcanonical ensemble with a timestep of 1 fs. A constant temperature of 1000 K is maintained via a velocity rescaling algorithm. Atomic positions are recorded every 30 time steps and stored in video files for later analyses. With each adspecies, we perform 50 statistically-independent simulations of 2 ns each, with adatoms initially placed at epitaxial positions close to the island center. Due to the low number of observed N adatom descent events, 20 additional simulations of 5 ns each are performed for this adspecies. Finally, in order to analyze N adatom descent pathways in greater detail, we carry out three sets of 50 simulations, 150 runs, of 2 ns each in which the initial position of the N adatom is in a low-energy fourfold hollow-site: (i) adjacent to the island edge, (ii) close to an island Ti corner, or (iii) close to an island N corner. In each simulation, we record the dynamics of adatom migration, accumulate statistics on near-edge vs. near-corner diffusion pathways, identify descent pathways, and determine average adatom residence times τ on islands. Island diffusion coefficients D are calculated using the two-dimensional Einstein relation,

$$D = \lim_{t \rightarrow \infty} \frac{\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle}{4t}, \quad (1)$$

evaluated over the time the adatom remains on the island. In equation (1), $\vec{r}(t)$ is the adatom position at time t and D is calculated for each run and averaged over the set of runs.

We use the nudged elastic band (NEB) method [42,43], implemented in LAMMPS, to obtain energy barriers for descent pathways observed during the simulations. Each pathway is divided into 20 steps for which the first and the last steps correspond to the initial and final states of the system as observed in our MD movies. The intermediate states are automatically generated by linear

interpolation. In NEB, atoms in adjacent images are connected by spring forces to ensure that images do not overlap. The convergence criterion for force minimization at each step is set to 0.1 eV/Å. The force constant between images is set to 1.0 eV/Å².

3. Results

Before initiating the MD simulations, we allow the substrate and island to relax via static energy minimization. We find that TiN(001) square islands relax in the (001) plane by shrinking; Ti and N atoms at the center of the island edge move 0.09 Å and 0.05 Å along in-plane $\langle 100 \rangle$ directions toward the island interior respectively, while Ti and N atoms at the corners of the island move 0.12 Å and 0.07 Å along in-plane $\langle 110 \rangle$ directions, respectively.

3.1. Ti adatoms on TiN(001) islands

For Ti adatoms on TiN(001) islands, the fourfold hollow sites are energetically favored and diffusion occurs primarily via hopping between neighboring hollow sites along [100] and [010] channels, as observed on TiN(001) terraces [35]. A summary of Ti adatom island-descent pathways is given in Table I. The average residence time τ of Ti adatoms on TiN(001) islands obtained from 50 MD runs totaling 0.1 μ s simulation time is 1.15 ns. In all cases for which Ti adatoms descend onto the terrace, the process involves a push-out exchange event at the island edge, a N corner, or a Ti corner.

A typical Ti adatom push-out/exchange event at an island edge is illustrated in Fig. 2. The Ti adatom, after migration from the island center, is shown in a fourfold hollow site at an island edge [Fig. 2(a)]. The adatom then moves to an adjacent saddle point between a Ti island-edge atom and its neighboring N atom, near the center of the Ti-N bond [Fig. 2(b)]. In this process, Ti adatoms can be trapped at the saddle point for a few picoseconds due to strong interactions with adjacent N island-atoms, thus stretching the underlying Ti-N bond and slightly pushing out the Ti edge atom. When the underlying Ti-N bond is sufficiently stretched, the descent event is initiated by the Ti

adatom, which moves downward at an angle, while continuing to push the Ti edge atom onto the terrace [Fig. 2(c)]. The process is complete when the Ti adatom replaces the Ti edge atom and the original Ti edge atom is displaced to an epitaxial position along the island edge [Fig. 2(d)]. The pushed-out Ti edge atom is not observed in any of the MD runs to diffuse along the island edge or to desorb onto the terrace.

Push-out/exchange events involving Ti edge atoms are observed in 14 of 50 MD runs, and the average residence time τ for this descent pathway is 0.89 ns. Push-out/exchange events are also observed next to N corners in which one of the adjacent Ti edge atoms is pushed-out onto the terrace [Fig. 2(e)]. This type of event occurs in 18 of 50 MD runs, and the average residence time τ for Ti adatoms in this case is 1.06 ns. Push-out/exchange events occur much less frequently at Ti corners of the island. In this case, the Ti corner atom is pushed-out onto the terrace to an epitaxial position adjacent to the island corner as the adatom replaces the corner atom [Fig. 2(f)]. Ti adatoms descend in this manner in only four out of 50 MD runs, with an average residence time τ of 0.83 ns.

We observe Ti adatom double push-out/exchange events, but only at N corners. The process is initiated, as for single N-corner push-out/exchange events, with a Ti adatom pushing-out one of the two Ti edge-atoms adjacent to the N-corner atom [Fig. 3(a)]. In this case, however, the pushed-out Ti edge-atom pulls the N corner atom with it [Fig. 3(b)]. Upon completion of the descent event, both Ti edge- and N corner-island atoms occupy epitaxial positions on the terrace along the island edge, while the Ti adatom occupies the position of the pushed-out Ti edge atom leaving the N corner position empty. This configuration remains stable for the duration of the simulations. Double push-out/exchange events occur seven times during the 50 MD runs with an average Ti adatom residence time τ of 1.23 ns.

NEB calculations yield energy barriers (Table II) for Ti adatom descent via direct hops over the island edge of 1.1, 1.4, and 1.3 eV at the Ti corner, N corner, and island edge. The corresponding barriers for descent via push-out/exchange are 0.5, 0.6, and 0.6 eV. Descent via push-out/exchange at the N corner and island edge requires that the Ti adatom first move to a position on

top of the bond-center between an edge Ti atom and the interior N atom neighbor, which itself has a barrier of 0.6 eV.

Prior to Ti adatom descent, some quite unexpected adatom/island interactions are observed. In two of the MD runs for which the Ti adatom is near a N island corner, the adatom/island complex reshapes into a metastable configuration with the Ti-adatom remaining in a stable fourfold hollow site [Fig. 4(a)], while the N corner atom moves upward on top of the island and toward the Ti adatom [Fig. 4(b)]. The Ti adatom then moves to a saddle point near the center of the bond between the Ti edge atom next to the N corner and the neighboring interior N island atom, slightly pushing out the Ti edge atom [Fig. 4(c)]. The other Ti edge-atom adjacent to the corner then moves underneath the N-corner atom to an intermediate position, as shown in Fig. 4(d), in which the Ti adatom and the N corner atom are both located close to fourfold hollow sites on top of the island. The two Ti edge atoms remain in the island plane, but close to terrace hollow sites. This configuration is maintained for significant times (0.37 and 1.14 ns) in both of the MD runs for which it is observed. The two Ti edge atoms and the N corner atom then relax back to their original positions [Fig. 4(e)] as the Ti adatom moves to the corner fourfold hollow site. In the simulation for which the complex remains stable for 0.37 ns, a double push-out/exchange event, as illustrated in Fig. 3, occurs immediately after the complex relaxes. In the other case, a double push-out/exchange is observed 0.33 ns after the complex has relaxed.

Post descent, the incorporation of Ti adatoms along island edges also leads to island reconfiguration events, but only when island corner atoms are involved. Edge diffusion is never observed, due to electrostatic repulsion between atoms of the same type (see section 4). Island reconfiguration occurs in 13 of the 22 events for which push-out/exchange occurs at, or next to, an island corner. Fig. 5(a) shows a configuration equivalent to Fig. 2(e) following a push-out/exchange event at a Ti corner. Concerted motion of the Ti adatom and the original Ti corner atom diagonally along the [110] channel [Fig. 5(b)] allows the Ti corner atom to regain its initial position as the Ti adatom moves via a one-dimensional (1D) push-out event into an epitaxial position next to the

corner [Fig. 5(c)]. The island configurations in 5(a) and 5(c) are energetically identical. NEB calculations yield a 1D Ehrlich corner-barrier for this transition of 1.0 eV. In one of the cases for which this event is observed, the reverse transition is also observed after 0.49 ns.

The other common island reconfiguration pathway involving Ti adatoms occurs following single push-out/exchange events at the N corner in which an adjacent Ti edge atom is pushed-out to an epitaxial island edge site, next to a N corner, as shown in Fig. 6(a). The pushed-out Ti edge atom then moves in the $\langle 110 \rangle$ direction to the fourfold hollow site diagonally next to the N corner atom [Fig. 6(b)]. From this position, the Ti edge atom oscillates between this site and the two closest equivalent epitaxial sites adjacent to island edges. NEB calculations yield a 1D Ehrlich barrier for corner rounding by this process of only ~ 0.1 eV.

3.2. *N adatoms on TiN(001) islands*

The stable TiN(001) surface site for N adatoms on 2D islands is, as for Ti, the fourfold hollow, but the low-energy diffusion path among hollow sites is along in-plane $\langle 110 \rangle$ channels crossing metastable sites atop Ti atoms, rather than along $[100]$ and $[010]$ directions as observed for Ti. This agrees with results on TiN(001) terraces [35]. More importantly, N adatoms have significantly higher diffusion barriers, hence lower mobilities, than Ti adatoms. Consequently, N adatoms require much longer times to reach island edge positions and therefore reside much longer on TiN islands than do Ti adatoms.

A summary of observed N adatom island descent pathways is given in Table III. Due to their low mobilities, N adatoms descend in only four (8%) of the 50, 2-ns MD runs in which the adatoms are initially placed at island centers. Two of the four descents involve push-out/exchange events with N atoms next to a Ti corner; the other two are direct hops over island edges. N descent via direct hopping over an island edge is illustrated in Fig. 7. From a stable hollow site at the island edge [Fig. 7(a)], the N adatom moves atop the adjacent Ti edge atom [Fig. 7(b)] and then hops directly into an epitaxial terrace site along the island edge [Fig. 7(c)].

The pathway for N-adatom push-out/exchange descent next to Ti corner sites is analogous to that of a Ti adatom at a N corner. However, in contrast to $[110]$ migration in the island interior, N moves along $[100]$ from a fourfold hollow [Fig. 8(a)] to a saddle position almost directly above the bond center between a N edge atom and the interior Ti neighbor [Fig. 8(b)], stretching the bond and slightly pushing out the N edge atom. The descent is initiated by the N adatom moving down while pushing the N edge atom either to the nearest epitaxial position along the island edge [Fig. 8(c)] or next to the Ti corner atom [Fig. 8(d)]. In the latter case, the N edge atom oscillates between the two sites adjacent to the Ti corner atom through the intermediate fourfold hollow site.

During two of the 50, 2-ns MD runs, island atoms are observed to ascend atop the island. In Fig. 9(a), a N adatom located at an interior island hollow site, forms a strong bond with an adjacent Ti island atom (shown shaded) diagonally next to a Ti corner atom; the Ti corner-atom then moves to the shaded island atom position as the shaded atom moves on top of the island [Fig. 9(b)]. This results in the formation of a TiN dimer, in its most stable configuration, with the N atom in an epitaxial site and the Ti atom in an adjacent fourfold hollow site [Fig. 9(c)]. The newly formed TiN dimer diffuses by rotation as well as translation, as observed on infinite terraces [35]. However, due to the attractive interaction of the Ti dimer atom to N atoms along the $\langle 110 \rangle$ edge, dimer diffusion is limited to a region close to the vacant island corner. Upward migration of interior island atoms has previously been observed experimentally in field ion microscopy studies of Ir/Ir(111) islands [44].

In order to provide better statistics for N adatom descent events, we carry out 170 additional MD runs. The first set consists of 20 MD runs of 5 ns each in which N adatoms are initially placed at island centers. A summary of these results is presented in Table IV. We observe N adatom descent via direct hopping over island edges on seven occasions and two push-out/exchange events near an island Ti corner. In eight of the remaining 11 MD runs, in which the N adatoms do not descend, the adatom did not reach the island edge.

We also performed three additional sets of 50 MD runs, 2 ns each, in which the initial N adatom position is in hollow-sites which are (i) adjacent to the island edge, (ii) next to a Ti island corner, or (iii) next to a N island corner. The results are summarized in Tables V, VI, and VII.

The primary descent mechanism for N adatoms placed near the island edge is direct hopping over the edge. This is observed in 42 of the 50 MD runs (Table V). In 38 of these events, the adatom does not diffuse away from its initial site before hopping, while in four cases the adatom migrates one step, in the $[100]$ direction, as opposed to the $[110]$ as observed on the island interior, to an adjacent hollow site before hopping. In the remaining eight MD runs, N adatoms do not descend, and in two of these cases, the N adatom diffuses two and three hops, respectively, along $\langle 110 \rangle$ away from the island edge toward the island center. The average residence time τ in these runs is 0.85 ns.

For N adatoms placed next to Ti corners, we observe 47 push-out/exchange events (Table VI), all of which involve N edge atoms, such as that shown in Fig. 8. Hopping over the island edge occurs on two occasions, both times directly over the Ti corner-atom, within 0.5 ps, as illustrated in Fig. 10. The N adatom first moves along $[\bar{1}\bar{1}0]$ from the corner hollow [Fig. 10(a)] to a site atop the Ti corner-atom [Fig. 10(b)], then continues in the $[\bar{1}\bar{1}0]$ direction to hop directly into the terrace hollow site diagonally next to the Ti corner atom [Fig. 10(c)]. From this position, the adatom oscillates rapidly between the two adjacent epitaxial edge sites.

In the remaining MD run, the N adatom migrates atop a N edge island atom and does not descend for the entire duration of the simulation. The formation of a strong N-N chemical bond at the island edge, enabled by island edge relaxation, hinders further N adatom diffusion or descent. This is illustrated in Fig. 11. From the hollow site next to the Ti corner atom [Fig. 11(a)], the N adatom moves to a saddle point between the adjacent N edge atom and the interior neighbor Ti atom, close to the center of the Ti-N bond [Fig. 11(b)], and then atop the neighboring N-edge atom [Fig. 11(c)]. The two N atoms repeatedly exchange positions [Fig. 11(d)] throughout the remaining

simulation time (1.96 ns). This is not counted as a net adatom descent event. Overall, the average island residence time τ for N adatoms placed next to a Ti corner atom is 0.12 ns.

The 50 MD runs in which N adatoms are placed next to a N island corner reveal a behavior which is quite different than that described for initiation adjacent to a Ti corner atom. In this set of runs, we record 28 direct hops and 13 push-out/exchange events; the N adatom does not descend during eight of the simulations. In one of the MD runs, the N adatom initially moves atop the N corner atom with which it forms a strong N-N bond and the two N atoms repeatedly exchange positions for the remaining 1.50 ns. In all but two runs, there is no migration on the island; the adatom either remains confined to the hollow-site or descends. In the two migration events, the adatom moves one unit cell distance along the island edge, in the [100] direction as opposed to the [110] migration observed on the interior of the island, to an adjacent hollow site.

N adatom descent via direct hops close to N island corners follows the same pathway as at island edges (see Fig. 7): the N adatom moves atop a Ti edge atom then moves along a $\langle 100 \rangle$ direction into an epitaxial terrace site. For push-out/exchange events at a N corner [Fig. 12(a)], the N adatom moves along a $\langle 110 \rangle$ direction from its initial hollow site to a position atop a Ti edge atom next to the N corner [Fig. 12(b)]. It then moves toward a saddle point, near the center of the Ti-N bond between the N corner atom and the Ti edge atom, which pushes out the N corner atom toward a hollow site next to the island corner [Fig. 12(c)]. The descent event is completed when the N adatom occupies the island corner position and the initial N corner atom moves to an edge epitaxial site next to the island corner [Fig. 12(d)]. The average residence time τ for N adatoms initialized next to a N island corner is 0.90 ns.

NEB calculations yield energy barriers for N adatom descent via direct hops over the island edge of 0.4, 0.8, and 0.6 eV at the Ti corner, N corner, and island edge (Table VIII). The corresponding barriers for descent via push-out/exchange are 0.5, 1.4, and 1.7 eV (Table VIII). Descent via push-out/exchange at the N corner requires that the N adatom move on top of a Ti edge atom, which has a barrier of 0.9 eV. Push-out/exchange at the island edge or at Ti corner requires

the N adatom to move on top of the bond-center between an edge N atom and a neighboring Ti atom, yielding migration barriers of 0.9 eV at the edge and 1.0 eV at the Ti corner (Table VIII).

4. Discussion

Ti and N adatoms are energetically stable in fourfold hollow sites and adatom diffusion pathways on 8x8 islands agree with results on infinite TiN(001) terraces [35]: Ti adatoms move along $\langle 100 \rangle$ directions through bond-center saddle-points to the next hollow site and N adatoms migrate along $\langle 110 \rangle$ directions over Ti atoms to an adjacent hollow site. Compared to terraces, however, island relaxation results in shorter in-plane interatomic distances, which decreases island diffusion barriers. Relaxation is more pronounced at island corners and edges, resulting in a funneling effect in which adatoms have positive drift velocities from the center toward island corners/edges. This is consistent with the fact that the diffusion coefficient we obtain for Ti adatoms on 8x8 TiN(001) islands, $8.4 \times 10^{-5} \text{ cm}^2/\text{s}$, is significantly higher than on terraces, $5.2 \times 10^{-5} \text{ cm}^2/\text{s}$.

Ti adatoms are found to descend from atop TiN/TiN(001) islands solely by push-out/exchange with a Ti atom along island edges or adjacent to a corner atom (Table I). NEB calculations confirm that push-out/exchange is energetically favored over direct hops from atop positions along the island edge as well as at N and Ti corners (Table II). Lattice vibrations at 1000 K facilitate push-out/exchange at the island perimeter, while the higher vertical vibration amplitudes of lower-mass N edge atoms decreases the probability of Ti adatoms descending to the terrace by direct hops over N atoms.

During the 50, 2-ns runs, Ti adatoms descend 43 times (86%), all via push-out/exchange; 25 of these events occur at N corners, 18 of which are single push-outs, while seven are double push-outs. Single push-out events lead to final configurations which are indistinguishable from those that would have resulted from Ti adatom descent via direct hops, which are never observed. In contrast, double push-out events result in island corner blunting (see, for example, Fig. 3(c)).

Calculated energy barriers for Ti adatom descent are summarized in Table II. For push-out/exchange at both the island edge and next to a N corner, the adatom must overcome two barriers: the barrier to diffuse to a saddle point between a Ti island edge-atom and the neighboring N atom (0.6 eV for both cases), and the barrier to push out the Ti edge-atom (0.5 and 0.6 eV, respectively). The results of these calculations show that push-out/exchange pathways are considerably energetically favored over direct hops at all positions (hopping energy barriers range from 1.1 to 1.4 eV). This is especially the case at Ti corners where the adatom initiates the descent directly from a stable fourfold hollow position. The difference in activation barriers also explains why the residence time for push-out/exchange at the N corner is longer than at the Ti corner (1.06 vs. 0.83 ns), even though the transport of Ti adatoms is primarily directed towards N corners, as shown by descent probabilities at the two corners (Table I).

While we are unaware of any experimental or theoretical data for adatom descent from islands on compound surfaces, push-out/exchange events have been observed experimentally for W on Ir(111) islands using field-ion microscopy [45], and verified by MD simulations to be energetically more favorable than direct hopping for Pt on Pt/Pt(111) islands [46].

In contrast to Ti adatoms, N adatoms descend from TiN/TiN(001) islands by both push-out/exchange and direct hops over island edges and corners. However, due to the low mobility of N adatoms, even on small islands, very few examples of either are observed in the 50, 2-ns runs for which the adatoms are initialized at island centers. In fact, N adatoms reach the island edge in only 12 of the 50 runs. In 2-ns simulations, N adatoms typically make between one and four diffusion jumps with average migration distances of one to two unit cells. We observe a total of only four descents, two of which are accomplished by push-out/exchange at Ti corners and two via direct hops over island edges.

In the 20, 5-ns runs, we observe seven N direct hops at island edges and two instances of push-out/exchange at Ti corners. The N diffusion coefficient on relaxed 8x8 islands, $3.0 \times 10^{-5} \text{ cm}^2/\text{s}$, is slightly higher than that on TiN(001) terraces, $2.6 \times 10^{-5} \text{ cm}^2/\text{s}$. This is a much lower funneling

effect than observed for Ti adatoms in which the diffusion coefficient increases by a factor of $\sim 3\times$. The difference is primarily due to the fact that N adatoms, in 5 ns, are unlikely to reach the outer portions of the island, where the funneling effect is strongest. It is possible that further increases in the simulation times for N adatoms would lead to enhanced funneling.

In the 50 runs for which the N adatoms were initially placed at the island edge, N descends by hopping in 42 of the runs without, in the vast majority of cases, prior island migration. In two cases, however, the N adatom diffused toward the island center and did not return to the edge.

When a N adatom is initially placed in a fourfold hollow-site next to a Ti corner of the island, it descends in 49 of the 50 runs. 47 of these events occur via push-out/exchange with one of the N edge-atoms adjacent to the Ti corner-atom, while two are by direct hops over the Ti corner-atom. In the case of the two direct hops, the N adatom descends within a few picoseconds. The rapid direct hops are likely due to the initial velocity of the adatom, which is assigned randomly, being aligned along a [110] direction, thus enabling the N adatom to immediately overcome the barrier for diffusion atop the Ti corner-atom, from which it directly hops. There is no diffusion on the island in any of the runs for which the N adatom is initially placed at the Ti corner. This results in short residence times: 0.08 ns for push-out/exchange and < 10 ps for direct hops.

When a N adatom is initially placed near a N corner of the island, it descends in 41 of the 50, 2-ns runs. Of these, 28 are by direct hops and 13 are via push-out/exchange events with residence times of 0.73 ns and 0.45 ns, respectively; comparable to that of direct hops at the island-edge, 0.63 ns, but much longer than those at the Ti corner of the island.

NEB activation barrier calculations for direct hop and push-out/exchange mechanisms indicate that hopping is the favored pathway for N adatom descent (Table VIII), with barriers of 0.4, 0.8, and 0.6 eV at Ti corners, N corners, and island edges, respectively. Calculated push-out/exchange barriers are considerably higher, with corresponding values of 1.0, 1.4 and 1.7 eV. Moreover, when initiating push-out/exchange, the N adatom must first move to an island epitaxial position which itself has a high barrier, 0.9 eV at edges and N corners and 1.0 eV at Ti corners. At

higher film growth temperatures, increased in-plane oscillation of the island edge atoms will facilitate migration to the bond-center, thus increasing the probability of push-out/exchange, while enhanced out-of-of plane island atom oscillation will hinder direct hops over the island edge. Conversely, as the growth temperature is lowered, direct hops will become progressively more favored over push-out/exchange.

Adatom diffusion along island edges has a much higher barrier than corner rounding. The calculated barrier for Ti adatoms diffusing between epitaxial positions along island edges is 2.8 eV. The high barrier results from the fact that the Ti adatom must, during edge diffusion, pass by other Ti atoms. It is energetically more favorable for a Ti adatom to detach from an island edge, with a formation energy of 1.1 eV, than to diffuse along it. The same is true for N adatoms, for which the barrier for diffusion along the edge is 4.5 eV and the formation energy is 1.4 eV.

Calculated activation barriers for adatom diffusion along island edges and around corners are presented in Table IX. The relatively low barrier of 1.0 eV for Ti adatom corner migration at Ti corners via 1D push-out/exchange is consistent with the observation of this mechanism in our MD movies (see, for example, Fig. 5). The barrier for Ti adatoms rounding N corners is only 0.1 eV, and this pathway is also observed in our simulations [Fig. 6]. Analogously, the barrier for N adatoms to round Ti corners is also relatively low, 0.6 eV. However, the barrier for N corner 1D push-out/exchange is much higher, 1.7 eV. This mechanism was never observed.

That TiN is a compound surface offers insight into why adatoms pass corners of the same element by 1D push-out rather than by direct corner rounding, which is the energetically favored mechanism on fcc metal surfaces [47]. While atoms in a simple metal are electrically neutral, TiN has a strong ionic bonding character [35,48]. Thus, for corners of the same type, TiN corner rounding will be prohibited by electrostatic repulsion and 1D push-out will be favored. Cation adatoms rounding anion corners, and vice versa, is easier due to the fact that the adspecies remains coordinated to a corner species of the opposite type. Hence, on compound surfaces, the two different corners give rise to different mechanisms of corner rounding mass transport depending

upon the adatom type. These observations reveal that the cause of island roughening during growth of compounds with significant ionic bonding character is not pile-up at island corners, as for fcc metal surfaces [37], but the high barriers for adatom diffusion along island edges.

Our results show that Ti adatoms on TiN(001) have high mobilities at 1000 K, which means that Ti atoms deposited on small islands will rapidly descend onto terraces. N adatoms, however, have much lower mobilities, and are much less likely to descend from islands before encountering other adspecies, forming either a N_2 molecule, which desorbs at kinetic rates (except at island edges), or TiN_x molecules. Increasing the incident N/Ti flux ratio during film growth will increase the formation rate of TiN_x molecules which have lower mobilities on infinite TiN(001) terraces [35] and similar results are expected on TiN(001) islands, thus promoting multilayer growth. 2D island roughening, as observed by STM studies of TiN(001) growth at temperatures similar to that used here [7], is caused by the high barrier for diffusion along island edges, not by corner rounding barriers.

5. Conclusions

Investigation of the dynamic behavior of Ti and N adatoms on small two-dimensional TiN/TiN(001) islands reveals that Ti adatoms migrate along $\langle 100 \rangle$ directions, while N adatoms migrate along $\langle 110 \rangle$ passing over Ti atoms, as on infinite terraces. Ti adatoms experience a significant funneling effect on small islands, resulting in comparatively short residence times. In contrast, due to their much lower diffusion rates, N adatoms have long island residence times and thus act as precursors for multilayer formation and surface roughening during TiN film growth. At 1000 K, Ti adatoms descend from islands exclusively via a push-out/exchange mechanism, while N adatoms are observed to descend primarily via direct hops. Having descended from TiN/TiN(001) islands, both Ti and N adatoms experience large barriers for edge diffusion, which explains 2D island roughening observed during in-situ STM film-growth studies at similar temperatures. TiN(001) corner rounding barriers, however, are relatively easily overcome by 1D push-out, in the case of adatoms rounding corners of the same atom type, or by direct corner rounding, in the case of

adatoms rounding corners of the opposite type.

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Table captions

Table 1. Summary of Ti adatom descent pathways in 50, 2-ns runs initiated with the adatom at the center of 8x8 TiN/TiN(001) islands.

Ti adatom descent pathways 50, 2-ns runs initiated at island center	Number of events (percentage)	Average residence time, τ (ns)
Single push-out/exchange	36 (72%)	0.97
island edge	14 (28%)	0.89
Ti corner	4 (8%)	0.83
N corner	18 (36%)	1.06
Double push-out/exchange		
N corner	7 (14%)	1.23
No descent	7 (14%)	2.00
Total	50	1.15

Table 2. Calculated energy barriers for descent of Ti adatoms from Ti corner, N corner, and edge positions of 8x8 TiN/TiN(001) islands. Values in parentheses are the barriers for passing from fourfold hollow sites to metastable bond-center positions. Calculated formation energies for the detachment of descended Ti atoms from the island edge out onto the open terrace are also shown.

Ti adatom	Hopping barrier (eV)	Push-out/exchange barrier (eV)	Formation energy (eV)
Ti corner	1.1	0.5	1.2
N corner	1.4	0.6 (0.6)	1.0
Edge	1.3	0.5 (0.6)	1.1

Table 3. Summary of N adatom descent pathways in 50, 2-ns runs initiated with the adatom at the center of 8x8 TiN/TiN(001) islands.

N adatom descent pathways 50, 2-ns runs initiated at island center	Number of events (percentage)	Average residence time, τ (ns)
Push-out/exchange		
at Ti corner	2 (4%)	1.08
Direct hop		
at island edge	2 (4%)	1.90
No descent	46 (92%)	2.00
Total	50	1.96

Table 4. Summary of N adatom descent pathways in 20, 5-ns runs initiated with the adatom at the center of 8x8 TiN/TiN(001) islands.

N adatom descent pathways 20 5-ns runs initiated at island center	Number of events (percentage)	Average residence time, τ (ns)
Push-out/exchange at Ti corner	2 (10%)	2.60
Direct hop at island edge	7 (35%)	2.66
No descent	11 (55%)	5.00
Total	20	3.94

Table 5. Summary of N adatom descent pathways in 50, 2-ns runs initiated with the adatom at the edge of 8x8 TiN/TiN(001) islands.

N adatom descent pathways 50, 2-ns runs initiated at center of island edge	Number of events (percentage)	Average residence time, τ (ns)
Direct hop at island edge	42 (84%)	0.63
No descent	8 (16%)	2.00
Total	50	0.85

Table 6. Summary of N adatom descent pathways in 50, 2-ns runs initiated with the adatom in the fourfold hollow site next to a Ti corner of 8x8 TiN/TiN(001) islands.

N adatom descent pathways 50, 2-ns runs initiated next to Ti corner atom	Number of events (percentage)	Average residence time, τ (ns)
Push-out/exchange at Ti corner	47 (94%)	0.08
Direct hop at Ti corner	2 (4%)	0.00
No descent	1 (2%)	2.00
Total	50	0.12

Table 7. Summary of N adatom descent pathways in 50, 2-ns runs initiated with the adatom next to a N corner of 8x8 TiN/TiN(001) islands.

N adatom descent pathways 50, 2-ns runs initiated next to N corner atom	Number of events (percentage)	Average residence time, τ (ns)
Push-out/exchange at N corner	13 (26%)	0.45
Direct hop at N corner	28 (56%)	0.73
No descent	9 (18%)	2.00
Total	50	0.88

Table 8. Calculated energy barriers for descent of N adatoms from Ti corner, N corner, and island edge positions. Values in parentheses are the barriers for passing from fourfold hollow sites to metastable bond-center (descent at edge and Ti corner) or edge Ti atom (descent at N corner) positions. Calculated formation energies for the detachment of descended N atoms from the island edge out onto the open terrace are also shown.

N adatom	Hopping barrier (eV)	Push-out/exchange barrier (eV)	Formation energy (eV)
Ti corner	0.4	0.5 (1.0)	2.0
N corner	0.8	1.4 (0.9)	1.4
Edge	0.6	1.7 (0.9)	1.4

Table 9. Energy barriers for Ti and N adatoms rounding corners of 8x8 TiN/TiN(001) islands.

	Corner rounding energy barrier (eV)	
	Ti corner	N corner
Ti adatom	1.0	0.1
N adatom	0.6	1.7

Figure captions

FIG. 1. (Color online) TiN/TiN(001) simulation supercell. The blue (grey) spheres represent Ti atoms and the green (black) spheres represent N atoms comprising the island (substrate).

FIG. 2. (Color online) Typical pathways for a Ti adatom to descend from atop a TiN/TiN(001) island edge to the terrace via push-out/exchange processes. Note that only part of the 8x8 atom island is shown. (a) Ti adatom in a fourfold hollow site adjacent to the island edge, (b) the Ti adatom, above the bond-center between a Ti edge atom and its interior N island atom, (c) the Ti adatom begins pushing out the Ti edge atom, and (d) the Ti adatom descends to an epitaxial Ti island-edge position and the displaced Ti edge atom moves to an epitaxial site along the island edge. (e) Ti adatom descends next to a N corner as the displaced Ti edge atom moves to an epitaxial site along the island edge. (f) Ti adatom descends at a Ti corner and the displaced Ti corner atom moves to an epitaxial site adjacent to the Ti corner.

FIG. 3. (Color online) Pathway for a Ti adatom to descend to the terrace from atop a TiN/TiN(001) island at a N corner via a double push-out/exchange process. Note that only part of the 8x8 atom island is shown. (a) Ti adatom, above the bond-center between a Ti edge atom and an interior island N atom, begins pushing out the Ti edge atom, (b) the N corner atom is attracted by the pushed-out Ti edge atom and displaced from the corner, and (c) the Ti adatom descends to an epitaxial Ti position and the displaced Ti edge atom and N corner atom move to epitaxial sites along the island edge leaving an empty corner site.

FIG. 4. (Color online) A complex TiN/TiN(001) island reshaping process initiated by a Ti adatom occupying a first-neighbor fourfold hollow site near a N corner site. Note that only part of the 8x8 atom island is shown. (a) Ti adatom in a fourfold hollow site close to a N corner, (b) the N corner atom moves upward and toward the Ti adatom, (c) the Ti adatom moves to a position above the bond-center between a Ti edge atom next to the N corner and the closest interior island N atom, thereby displacing the Ti edge atom, (d) the other Ti edge atom adjacent to the corner moves to a position close to the hollow site next to the Ti adatom, and (e) the island atoms relax to their original positions with the Ti adatom moving to the corner fourfold hollow site.

FIG. 5. (Color online) Net Ti edge atom migration around a Ti-corner of a TiN/TiN(001) island via concerted motion of the adatom and corner atom along a $[1\bar{1}0]$ channel. Note that only part of the 8×8 atom island is shown. (a) Ti adatom has descended from the island via push-out/exchange next to the Ti corner, (b) the displaced Ti corner atom and descended Ti adatom both move in the $[1\bar{1}0]$ direction, and (c) the displaced Ti corner atom returns to the corner position and the Ti adatom moves to the opposite epitaxial position adjacent to the Ti corner.

FIG. 6. (Color online) Pathway for a Ti adatom rounding the N corner of a TiN/TiN(001) island, moving along $[110]$ through a fourfold hollow site. Note that only part of the 8×8 atom island is shown. (a) Ti adatom has descended from the island via push-out/exchange next to the N corner, displacing a Ti edge atom to an epitaxial site next to the N corner, and (b) the displaced Ti edge atom moves to the hollow site along the island diagonal, from which it oscillates between epitaxial sites adjacent to the N corner.

FIG. 7. (Color online) N adatom descent from a TiN/TiN(001) island via direct hopping over an island edge. Note that only part of the 8x8 atom island is shown. (a) N adatom in a fourfold hollow site adjacent to the island edge, (b) the N adatom moves on top of a Ti island edge atom, and (c) the N adatom descends from the island to an epitaxial position along the island edge.

FIG. 8. (Color online) Pathways for a N adatom to descend from atop a TiN/TiN(001) island via a push-out/exchange process at a Ti corner. Note that only part of the 8x8 atom island is shown. (a) N adatom in a fourfold hollow site next to a Ti corner atom, (b) N adatom above the bond-center between a N edge atom and its interior Ti neighbor, which begins pushing out the N edge atom, (c) the N adatom descends to an epitaxial N edge position and the displaced N edge atom moves to an epitaxial site along the island edge, or (d) the displaced N edge atom moves to an epitaxial site adjacent to a Ti corner atom.

FIG. 9. (Color online) N adatom pulling up a Ti island atom (shown shaded) adjacent to a Ti corner atom in a TiN/TiN(001) island. Note that only part of the 8x8 atom island is shown. (a) N adatom in an interior fourfold hollow site, (b) the Ti island atom moves on top of the island while the Ti corner atom is attracted toward the resulting vacancy, and (c) the N adatom and the ascended Ti atom form a dimer with the Ti atom in a hollow site and the N atom on top of a Ti island atom. The former Ti corner atom fills the island vacancy leaving the corner site empty.

FIG. 10. (Color online) Pathway for N adatom to descend from a TiN/TiN(001) island via a direct hop over a Ti corner atom. Note that only part of the 8x8 atom island is shown. (a) N adatom in a fourfold hollow site at a Ti corner, (b) the N adatom migrates along $[\bar{1}\bar{1}0]$ atop the Ti corner atom, and (c) the N adatom hops down onto the terrace into the fourfold hollow site diagonally adjacent to the Ti corner atom.

FIG. 11. (Color online) N adatom exchange with a N edge atom adjacent to a Ti corner atom in a TiN/TiN(001) island. Note that only part of the 8x8 atom island is shown. (a) N adatom in a fourfold hollow site at the Ti corner, (b) N adatom above the bond-center between a N edge atom and its interior Ti atom, (c) N adatom on top of a N edge atom next to the Ti corner, and (d) the N adatom and the N edge atom exchange positions.

FIG. 12. (Color online) Typical pathway for a N adatom to descend from atop a TiN/TiN(001) island to the terrace via a push-out/exchange process at a N corner. Note that only part of the 8x8 atom island is shown. (a) N adatom in a fourfold hollow site at the N corner, (b) N adatom atop a Ti edge atom next to the N corner, (c) the N adatom moves to the bond-center between the N corner atom and the nearest Ti edge atom, while pushing the N corner atom to a neighboring hollow site, and (d) the N adatom descends into the N corner position and the original N corner atom moves to an epitaxial position adjacent to the N corner.