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Effect of Al substitution on Ti, Al, and N adatom dynamics on TiN(001), (011), and (111) surfaces

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Abstract

Substituting Al for Ti in TiN(001), TiN(011), and N- and Ti-terminated TiN(111) surfaces has significant effects on adatom surface energetics which vary strongly with the adatom species and surface orientation. Here, we investigate Ti, Al, and N adatom surface dynamics using density functional methods. We calculate adatom binding and diffusion energies with both a nudged elastic band and grid-probing techniques. The adatom diffusivities are analyzed within a transition-state theory approximation. We determine the stable and metastable Ti, Al, and N binding sites on all three surfaces as well as the lowest energy migration paths. In general, adatom mobilities are fastest on TiN(001), slower on TiN(111), and slowest on TiN(011). The introduction of Al has two major effects on the surface diffusivity of Ti and Al adatoms. First, Ti adatom diffusivity on TiN(001) is significantly reduced near substituted Al surface atoms; we observe a 200% increase in Ti adatom diffusion barriers out of fourfold hollow sites adjacent to Al surface atoms, while Al adatom diffusivity between bulk sites is largely unaffected. Secondly, on TiN(111), the effect is opposite; Al adatoms are slowed near the substituted Al surface atom, while Ti adatom diffusivity is largely unaffected. In addition, we note the importance of magnetic spin polarization on Ti adatom binding energies and diffusion path. These results are of relevance for the atomistic understanding of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloy and $\text{Ti}_{1-x}\text{Al}_x\text{N}/\text{TiN}$ multilayer thin-film growth processes.

Keywords: surface diffusion, titanium nitrides, first principles, TiAlN

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1. Introduction

The $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloy system has long attracted significant attention. Since alloying TiN with AlN can be used to improve properties such as hardness[1–6] and oxidation resistance,[7–9] $\text{Ti}_{1-x}\text{Al}_x\text{N}$ thin films currently enjoy a wide range of applications, from wear-resistant coatings for high-speed cutting tools[10] to use as bio-implant coatings.[11]

$\text{Ti}_{1-x}\text{Al}_x\text{N}$ is a metastable alloy which can be synthesized by low-temperature kinetically-limited physical vapor deposition, in which phase separation is hindered by lack of bulk diffusion and limited surface diffusion. However, when subjected to high temperatures, e.g., during high-speed cutting-tool operations, such metastable coatings separate into TiN and either NaCl- or wurtzite-structure AlN as bulk diffusion becomes active.[12–15] This is believed to be responsible in part for the improved wear resistance of TiAlN coatings which has been extensively studied both experimentally[12, 13, 15] and theoretically.[12, 15–18] During growth, limited short-range clustering is likely to occur[19] and must be taken into account in order to obtain a complete atomistic understanding of these materials.

Atomic-scale simulation is necessary in order to understand the dynamics of micro- and nano-structural evolution in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ thin films. Knowledge of adatom dynamics is difficult to obtain experimentally due to the short time scales involved. Instead, first-principles calculations, often within transition state theory (TST),[20, 21] have been extensively used to provide valuable insight into the surface kinetics of elemental metals,[22–24] binary compounds such as TiC,[25, 26] and the parent compounds of $\text{Ti}_{1-x}\text{Al}_x\text{N}$, TiN[26–30] and AlN.[31] Going beyond static approximations, *ab initio* and classical molecular dynamics have proven valuable to elucidate mechanisms of adspecies migration[32, 33] and to model thin-film growth.[34] With the knowledge from such computational investigations, experimental results based upon, for example, variable-temperature scanning tunneling microscopy (STM)[35–39] and synchrotron x-ray scattering,[40] can be better understood.

When investigating an alloy system such as $\text{Ti}_{1-x}\text{Al}_x\text{N}$, an additional degree of complexity, the configurational effects of Ti and Al cation site disorder can dramatically influence adatom kinetics. Previous modeling work on alloy diffusion, e.g., in bulk Li_xCoO_x by Van der Ven et al. and on the CuSn(111) surface by Chen et al., has provided methods for modeling configurational disorder.[41–44]

Recently, we showed that Ti adatoms experience considerably slower migration rates on disor-

dered $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$ compared to the binary $\text{TiN}(001)$ surface.[45] However, the effect on Al adatoms was found to be small. Disorder effects on cation diffusion on other low-index $\text{Ti}_{1-x}\text{Al}_x\text{N}$ surfaces and the role of N adatoms are still unknown.

The aim of this study is to extend the understanding of cation diffusion on (001) , (011) , and (111) $\text{Ti}_{1-x}\text{Al}_x\text{N}$ surfaces, and to compare Ti, Al, and N adatom dynamics on both pure TiN and AlN-substituted TiN surfaces. By focusing, in this work, on the dilute Al limit, we isolate the impact on diffusion energetics, due to Al cations, from configurational disorder effects and elucidate both the magnitude and range of the effects of Al surface atoms on adatom diffusion. We show results for Ti, Al, and N adatoms on all three low-index TiAlN surfaces, determine the impact of Al surface atoms on adatom kinetics, and discuss the consequences for TiAlN nanostructural evolution during film growth.

2. Methodology

Density functional theory[46] (DFT) calculations are performed with the Vienna Ab-initio Simulation Package[47, 48] (VASP). The standard projector augmented wave[49] (PAW) approach[50] is used together with the Perdew-Burke-Ernhofer generalized gradient approximation[51, 52] (PBE-GGA) for the exchange correlation (XC) functional where the Ti 3p semi-core states are treated as valence electrons. The calculations are implemented with a $3 \times 3 \times 3$ Monkhorst-Pack[53] k-mesh grid.

The TiN surfaces are modeled with 108-atom supercells, 6 layers for (001) , and (011) slabs and 9 layers for the polar (111) slab. To define the surface, a vacuum slab of 25 Å is added above the supercells (see Fig. 1). The supercells are 3×3 unit cells in-plane, all layers are allowed to fully relax, and the surface energies of $\text{TiN}(001)$ and $\text{TiN}(011)$ are converged for up to 8 layers, $\text{TiN}(111)$ is converged for odd numbers of layers up to 17.

The choice of approximation for exchange and correlations effects influences the quantitative values of calculated surface energies and adsorption energetics. Semi-local GGA-type XC functionals tend to overestimate adsorption energies and underestimate the surface energy, while the local density approximation (LDA) tends to do the opposite. [54] Advanced methods, such as hybrid functionals or explicit many-body theory frameworks, which describe surface effects at a higher level of accuracy, are still too computationally intensive to be a reasonable choice for the present study focusing on adatom dynamics on large disordered surface slabs. Thus, we began by performing a

Figure 1: (Color online) Supercells used to model TiN surfaces: (a) TiN(001), (b) TiN(011), and (c) TiN(111).

benchmark test of the influence of different exchange-correlation approximations on the energetics of adatom migration by comparing LDA [55] and GGA-PBE approximations, which are expected to bracket the influence on calculated structural properties due to differences in how the techniques treat exchange and correlation effects. A comparison of the lowest energy pathway for a Ti adatom, from one fourfold hollow site to another on TiN(001) using a 3x3x3 supercell, is shown in Fig. 2. As can be seen, there are no qualitative differences between the curves; however, LDA yields stronger adsorption energies and higher diffusion barriers. Even though the relative differences are small, they enter exponentially into the jump probability expression. This underlines the fundamental difficulty in obtaining accurate quantitative values of diffusion coefficients directly from theoretical calculations regardless of the method applied to modeling atomic migration. In this study, we are primarily interested in qualitative mechanistic comparisons, e.g., differences in adatom mobilities on different crystal surfaces and the effects caused by configurational disorder. Thus, the level of uncertainty caused by the XC-approximation is not crucial.

In addition, we have taken adatom magnetic degrees of freedom into account. Fig. 2 shows that the Ti adatom adsorption energy at, and close to, a bulk site is dramatically different with magnetism included. The effect on the energetics are largest when using PBE-GGA. Neglecting spin polarization at specific positions on the surface can be detrimental for understanding even the

Figure 2: (Color online) Ti adatom diffusion paths from a stable fourfold site to a metastable bulk site atop N (see Fig.3 for site descriptions) on TiN(001) calculated using PBE-GGA and LDA, with and without magnetic degrees of freedom. E_{ad} is the Ti adatom adsorption energy, E_0^{TiN} is the adsorption energy at the stable fourfold hollow site, and nm is non-magnetic.

qualitative adatom migration path, not just quantitative barrier values, as will be discussed in the section on Ti adatoms below, Sec. 4.1.

The surface energy, E_s , is defined as

$$E_s = \frac{E_{slab} - E_{bulk}}{2A}, \quad (1)$$

in which E_{slab} is the energy of the slab, E_{bulk} is the bulk energy for the corresponding number of atoms, A is the surface area, and the factor two accounts for the bottom as well as the top surface of the supercell. For the (111):N surface, the additional n_N N atoms in the top N layer are accounted for by subtracting $n_N \cdot E_{N_2}/2$ from E_{slab} , where $E_{N_2}/2$ is half the N_2 bond energy.

The adatom calculations are performed with the lower six substrate layers (two N and two Ti layers for (111)) fixed at bulk positions. The (111) is a polar direction for TiN, in which the surface termination layer is composed of only one atomic species, Ti or N. Therefore, we use TiN(111):N termination for investigating cation surface diffusion and TiN(111):Ti termination for anion diffusion.

Two approaches are employed to investigate surface diffusion energetics. The first is to probe the TiN surfaces with adatoms positioned at each point of a specified surface grid and calculate adsorption energies. Adatoms are maintained at fixed positions within the plane and allowed to

Figure 3: (Color online) Schematic representation of relevant binding sites on (a) TiN(001), (b) TiN(011), and (c) TiN(111):N. For the TiN(111):Ti surface (not shown), the N and Ti atomic positions are exchanged compared to the TiN(111):N surface in (c).

relax normal to the plane. The surface atoms are allowed to relax in all three orthogonal directions. Points in the surface grid are separated by $0.15 \text{ \AA}$ in x and y directions, and the origin is at the Al substitution site. The shape of the grid is chosen with respect to the surface symmetry, minimizing the number of required calculations. This methodology, similar to that used previously,[45] provides a rapid overview of stable and metastable adsorption sites on each surface. The second approach employs the nudged elastic band method to determine the minimum energy path between surface binding sites, thus providing quantitative values of adatom diffusion energy barriers.[56–58]

The adatom adsorption energy is calculated as

$$E_{ad} = E_{config} - (E_{slab} + E_{atom}^{vacuum}), \quad (2)$$

in which E_{config} is the energy of the atomic configuration being investigated and E_{atom}^{vacuum} is the adatom energy in vacuum.

We define the surface diffusion path as the minimum energy path for an adatom migrating between stable adsorption sites. The diffusion path results in Section 4 present energies which are referenced to the strongest binding site on the corresponding clean TiN surface. In-plane distances are measured from the point on the diffusion path that is closest to an Al surface atom. The

primary adatom binding sites are shown schematically in Fig. 3.

The diffusion barrier ΔE is defined as

$$\Delta E = E_{ad}^{saddle-point} - E_{ad}^{binding-site}, \quad (3)$$

the difference between E_{ad} at the binding site and at the saddle point between binding sites. In cases where there are multiple pathways, each having separate diffusion barriers on a surface, we define the barrier limiting long-range surface diffusion as the activation barrier ΔE_{act} .

For the simple case where all binding sites are equal, the diffusivity D of an adatom is related to ΔE and the diffusion prefactor D_o according to

$$D = D_o \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (4)$$

with D_o defined as

$$D_o = \nu_0 l^2, \quad (5)$$

for which ν_0 is the attempt frequency and l is the jump length. The exponential term in Eq. (4) is the success probability of a migration attempt. To obtain an estimate of the adatom jump attempt frequency, we use the harmonic oscillation approximation,

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{\partial^2 E / \partial x^2}{m}}, \quad (6)$$

in which $\partial^2 E / \partial x^2$ is the second derivative of the binding site adsorption energy with respect to the distance along the diffusion path and m is the mass of the adatom. Details associated with calculating the jump frequencies are presented in Appendix [Appendix A](#).

3. Surface energies for TiN (0 0 1), (0 1 1), and (1 1 1)

Surface energy is an important factor governing the growth of thin films, where the lowest surface energy is thermodynamically preferred. Therefore, it is important that our supercells provide accurate surface energies. Calculated energies for relaxed TiN(001), (011), and (111) surfaces are presented in Table 1. For TiN(001), we obtain $E_s^{(001)} = 81 \text{ meV}/\text{\AA}^2$, identical to the results reported earlier by [Gall et al.\[27\]](#), and within 1 meV of the results by [Marlo and Milman.\[59\]](#) We note that we use a larger supercell and vacuum slab than those in previous reports, thus providing

increased accuracy. The relaxed TiN(0 1 1) and TiN(1 1 1):N surface energies, $E_s^{(0 1 1)} = 167 \text{ meV}/\text{\AA}^2$ and $E_s^{(1 1 1)} = 92 \text{ meV}/\text{\AA}^2$, are 11 $\text{meV}/\text{\AA}^2$ [Ref. [59]] and 7 $\text{meV}/\text{\AA}^2$ [Ref. [27]] higher, respectively, than previous results.

TiN(001) and (111):N surface energies differ by only 11 $\text{meV}/\text{\AA}^2$, with $E_s^{(0 1 1)}$ being much higher; this explains why TiN films nucleate on amorphous substrates with approximately equal probability of forming (001) and (111) oriented islands and essentially no (011) islands, as observed experimentally.[60, 61] The closeness of these surface energies also underlines the importance of kinetic factors determining the competitive nanostructural evolution pathways of growing films for this material system.[62]

Table 1: Surface energies E_s of relaxed (001), (011), and (111) TiN surfaces. Results from Gall et al.[27] and Marlo and Milman[59] are also tabulated for reference.

	This work	Gall et al.	Marlo and Milman
$E_s^{(0 0 1)}$ [meV/ $\text{\AA}^2$]	81	81	80
$E_s^{(0 1 1)}$ [meV/ $\text{\AA}^2$]	167	-	178
$E_s^{(1 1 1)}$ [meV/ $\text{\AA}^2$]	92	85	-

4. Adatom surface site energetics

Sec. 4 is divided into three subsections describing the dynamics of Ti, Al, and N adatoms, in which we focus on migration energies and determine diffusion barriers. We also determine the effects on adatom migration energetics of substituting surface Al at a cation site, Al_{Ti} .

Readers interested in the implications of our results on adatom diffusion on all three surfaces – TiN(001), TiN(011), and TiN(111):(N,Ti) – are referred to Sec. 5, where we also discuss the role of Al_{Ti} substitution on adatom diffusion properties.

4.1. Ti adatom migration energetics

Ti adatom adsorption energy landscapes are presented in Fig. 4 for TiN(001), (011), and (111) surfaces. A larger absolute magnitude of the negative adsorption energy represents stronger adatom binding to the surface. Adatom diffusion is restricted to the low-energy valleys of the surface. We find that the preferred Ti adatom binding site on TiN(001) is the fourfold hollow site, and the bulk epitaxial site atop N is metastable (see Fig. 4(a)). On the TiN(011) surface, shown in Fig. 4(b), the stable binding site for a Ti adatom is the bulk epitaxial position atop a N surface atom; there

Figure 4: (Color online) Ti adatom adsorption energy landscapes for: (a) TiN(001), (b) TiN(011), and (c) TiN(111):N. Each contour line corresponds to a 0.5 eV difference in adsorption energy E_{ad} referenced to a single Ti atom in vacuum.

are no significant metastable sites. The stable positions on the N-terminated TiN(111) surface is also the bulk site, with a metastable site atop a second-layer Ti atom.

There are large differences in Ti adatom adsorption energies among the three surface orientations, see Table 2. The fourfold hollow site on TiN(001), $E_{ad} = -3.41$ eV, and the bulk epitaxial site on (011), $E_{ad} = -6.80$ eV, and (111) surfaces, $E_{ad} = -9.92$ eV, are the strongest binding sites. Surface diffusion barriers are presented in Table 3. Here, we see that the activation barriers also differ significantly for the three surface orientations, ranging from $\Delta E_{act} = 0.36$ eV on TiN(001), to 1.66 eV on TiN(111), to 2.31 eV on TiN(011).

Fig. 4 provides, in addition, an overview of the favored diffusion paths on the three surfaces. The pathway on TiN(001) is from the stable fourfold hollow site to an adjacent metastable bulk site. From there, the adatom can move to any of four fourfold hollow sites between two Ti surface atoms, while the fourfold site, in turn, is only connected to two adjacent bulk sites. On the TiN(011) surface, there are two distinct diffusion paths from the stable bulk site. One is across a saddle point atop a N surface atom in the $\langle 0\bar{1}1 \rangle$ direction. The other pathway is in the $\langle 100 \rangle$ direction, across a saddle point between two surface Ti atoms. The Ti adatom diffusion path on the TiN(111):N surface follows a hexagonal pattern, where each stable bulk site is connected to three metastable atop Ti sites separated by 120° from each other, and each atop Ti site is hexagonally connected to three bulk sites. The sites are all separated by identical saddle points located between adjacent N surface atoms.

The Ti adatom adsorption energy, is plotted topographically in Fig. 5 as a function of distance

Figure 5: (Color online) Ti adatom diffusion path on TiN(001) between the stable fourfold hollow and metastable bulk sites, with and without an Al atom substituted on a cation surface sublattice site. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis corresponds to the fourfold hollow site closest to the Al_{Ti} substitution position.

along TiN(001) surface diffusion paths with and without an Al_{Ti} substitution. The path connects the stable fourfold hollow site and the metastable epitaxial bulk site with the energy normalized to E_{ad} at the fourfold hollow site on a pure TiN(001) surface. The diffusion activation barrier on this surface is $\Delta E_{act} = 0.36$ eV corresponding to a saddle point between the fourfold hollow site and the epitaxial bulk site with $E_{ad} = -3.05$ eV.

Al_{Ti} substituted in a TiN(001) surface cation position has a large effect on the migration energetics of Ti adatoms as shown in Fig. 5. The Ti adsorption energy in fourfold hollow sites adjacent to Al_{Ti} is increased by 0.24 eV to $E_{ad} = -3.65$ eV. However, the change in E_{ad} at metastable bulk sites is insignificant, see Table 2. The effect of Al_{Ti} on Ti adatom binding in fourfold hollow sites is confined primarily to within the first coordination shell, although minor changes in adsorption energy, less than 0.05 eV, are observed even in the fourth coordination shell about the Al_{Ti} atom.

We find that accounting for the magnetic spin of the Ti adatom has a significant effect on local adsorption energies. The most important effect is stronger binding at the metastable bulk site on TiN(001). The adsorption energy at this site increases by 0.14 eV, raising the diffusion barrier for a Ti adatom to migrate from a bulk site to a fourfold hollow site by almost a factor of four, from 0.05 to 0.17 eV, when magnetism is included. In addition, the barrier for Ti adatom jumps from the stable fourfold hollow site into the bulk site is slightly lower, decreasing from 0.38 eV to 0.36

eV, when magnetism is included. Although the barrier difference in this case is small, the stronger binding at the bulk site increases the occupation time at this site enough to significantly alter Ti adatom diffusion dynamics on TiN(001).

Figure 6: (Color online) Ti adatom diffusion path on TiN(011) between bulk sites, with and without an Al atom substituted on a cation surface sublattice site. The diffusion path in the $\langle 0\bar{1}1 \rangle$ direction is presented in the left side of the figure, and the path along the $\langle 100 \rangle$ direction in the right side. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis is the position on the diffusion path closest to the Al_{Ti} substitution position.

The TiN(011) surface consists of parallel rows, comprised of alternating Ti and N atoms, along $\langle 100 \rangle$ (see Fig. 4), for which the barrier for Ti adatom diffusion along the rows is 4.26 eV. The rows are separated by 3.01 Å in the $\langle 0\bar{1}1 \rangle$ direction. The bulk site is located between N surface atoms in adjacent $\langle 100 \rangle$ rows. The diffusion path from bulk to bulk sites in the $\langle 0\bar{1}1 \rangle$ direction, with a saddle point atop a N surface atom, has a diffusion activation barrier of 2.31 eV. ΔE_{act} in this case is five times higher than the activation barrier on the TiN(001) surface. The saddle point along $\langle 0\bar{1}1 \rangle$ is located atop a N surface atom and diffusion is one-dimensional. From bulk to bulk site in the $\langle 100 \rangle$ direction, the barrier is $\Delta E = 4.26$ eV, with a saddle point located between two Ti surface atoms.

Introducing an Al_{Ti} atom strengthens Ti adatom adsorption along the diffusion path in the $\langle 0\bar{1}1 \rangle$ direction adjacent to the Al_{Ti} atom, similar to the case for the (001) surface. The difference is that the barriers for Ti adatom diffusion are much higher on the (011) surface, such that the relative change due to Al_{Ti} substitution is smaller. There are two effects: the adsorption energy at the saddle point closest to the Al_{Ti} atom decreases and the Ti adsorption energy at the closest

bulk sites increases from -6.80 to -6.98 eV. The combination leads to a decreased diffusion barrier, from 3.31 to 2.00 eV. Although the absolute change in energy is twice that on the (001) surface, 0.31 eV, this is only a 14% relative change due to the much higher barriers on $\text{TiN}(011)$. For the diffusion path in the $\langle 100 \rangle$ direction on (011) , the effect is the opposite; there is an increase in the diffusion barrier, from 4.26 to 4.77 eV, also a small change compared to the magnitude of the diffusion barrier.

Figure 7: (Color online) Ti adatom diffusion path on $\text{TiN}(111)$ between stable bulk sites and metastable atop Ti sites, with and without an Al atom substituted on a cation surface sublattice site. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis corresponds to the atop Al_{Ti} site.

Fig. 7 shows the adsorption energy along the most favorable diffusion path on the $\text{TiN}(111):\text{N}$ surface. The adsorption energies at the stable and metastable binding sites are -9.92 and -8.97 eV. The saddle point in this path is located between adjacent N surface atoms; and the adsorption energy at this point is $E_{ad} = -8.26$ eV. This corresponds to a barrier $\Delta E_{act} = 1.66$ eV from the bulk site to the atop Ti site, with $\Delta E = 0.71$ eV for the reverse transition.

Introducing Al_{Ti} affects both Ti adatom adsorption energies and diffusion barriers on $\text{TiN}(111):\text{N}$. At the metastable binding site atop the Al_{Ti} atom, the adsorption energy increases by 0.27 eV to -9.24 eV. Adsorption energies at the closest bulk sites decrease by 0.14 eV to -9.78 eV, resulting in a corresponding increase in the diffusion barrier between the bulk site and the first atop Ti site.

Another effect of Al_{Ti} substitution in the $\text{TiN}(111):\text{N}$ surface is that an Al atom introduced at a Ti position in the layer beneath the N-termination will relax upward into the N layer, leaving a cation vacancy (see Fig. 8). However, as soon as a Ti or Al adatom migrates close to the Al_{Ti} atom,

Al relaxation in TiN(111)

Figure 8: (Color online) The relaxed TiN(111):N surface with substituted Al_{Ti} . Relaxation results in migration of the Al atom into the N termination layer.

it moves back to the upper metal layer. Therefore, care must be taken when adsorption energies are calculated for positions close to the Al_{Ti} surface atom on (111). We evaluate the energy path for both starting configurations, a fully-relaxed slab and one with the Al_{Ti} atom in the upper metal layer.

Table 2: Adsorption energies E_{ad} for Ti adatoms on TiN(001), TiN(011) and TiN(111):N surfaces with and without a surface Al_{Ti} substitution. Stable sites are denoted with (s), and metastable sites with (m).

Binding position	$E_{ad,\text{TiN}}$ [eV]	$E_{ad,\text{Ti(Al)N}}$ [eV]
TiN(001)		
Bulk site (m)	-3.22	-3.25
Fourfold hollow site (s)	-3.41	-3.65
TiN(011)		
Bulk site (s)	-6.80	-6.98
TiN(111):N		
Bulk site (s)	-9.92	-9.78
Atop Ti site (m)	-8.97	-9.24

4.2. Al adatom migration energetics

Al adatom adsorption energy landscapes on TiN(001), TiN(011), and TiN(111):N are presented in Fig. 9. Al adatoms, in contrast to Ti adatoms bind exclusively at bulk sites on TiN(001) and TiN(011). On TiN(001), the Al adsorption energy $E_{ad} = -2.45$ eV, while on TiN(011), $E_{ad} = -4.71$ eV. The TiN(111) surface has on Al adatom metastable site atop Ti in addition to the stable bulk site, the former with an adsorption energy $E_{ad} = -5.39$ eV, and the latter with

Table 3: Diffusion barrier energies ΔE for Ti adatoms on TiN(001), TiN(011) and TiN(111):N surfaces with and without a surface Al_{Ti} substitution. The diffusion activation barrier for each surface is denoted with (act). Diffusion barriers in alternate directions from the same site are given within parenthesis.

Binding position	ΔE_{TiN} [eV]	$\Delta E_{\text{Ti(Al)N}}$ [eV]
TiN(001)		
Bulk site	0.17	0.20
Hollow site	0.36 (act)	0.43
TiN(011)		
Bulk site $\langle 100 \rangle$	4.26	4.77
Bulk site $\langle 0\bar{1}1 \rangle$	2.31 (act)	2.00
TiN(111):N		
Bulk site	1.66 (act)	1.40
Atop Ti site	0.71	0.86

Figure 9: (Color online) Al adatom adsorption energy landscapes for: (a) TiN(001), (b) TiN(011), and (c) TiN(111):N. Each contour line correspond to a 0.5 eV difference in adsorption energy E_{ad} referenced to a single Al atom in vacuum.

$E_{ad} = -5.84$ eV. A summary of Al adatom adsorption energies is presented in Table 4.

Two general aspects should be noted regarding Al adatoms. First, in Fig. 9 we see that the Al adsorption energy at stable bulk sites increases from TiN(001), to TiN(011), to TiN(111). Secondly, Table 5 shows that surface diffusion activation barriers are considerably lower on the (001) surface, $\Delta E_{act} = 0.42$ eV, than on the (011) and (111) surfaces with, $\Delta E_{act} = 1.16$ and 0.91 eV. In these respects, the results are similar to those for Ti adatoms; however, there are also significant differences.

An overview of Al adatom diffusion paths is shown in Fig. 9. Al adatoms follow the same paths as Ti adatoms, with the important exception that Al does not bind at the fourfold hollow site on TiN(001). On TiN(011), there are two distinct diffusion paths with different saddle points, one

atop the N surface atom between bulk sites in the $\langle 0\bar{1}1 \rangle$ direction, with $\Delta E_{act} = 1.16$ eV, and the other, with a diffusion barrier of 2.67 eV, between Ti surface atoms in the $\langle 100 \rangle$ direction. The Al adatom diffusion pathways on the TiN(111):N surface follow the same hexagonal pattern as the Ti adatoms, where each bulk site has three equally distant neighboring metastable atop Ti sites separated by 120° and each atop Ti site has three neighboring bulk sites separated by 120° . Saddle points are located between N surface atoms.

Figure 10: (Color online) Al adatom diffusion path on TiN(001) between stable bulk sites, with and without an Al atom substituted on a cation surface sublattice site. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis corresponds to the position on the diffusion path closest to the Al_{Ti} substitution position.

The primary effect of Al_{Ti} substitution on Al adatom diffusion on TiN(001), Fig. 10, is a reduction in the saddle point closest to the Al_{Ti} atom; since the adsorption energy E_{ad} increases from -2.04 to -2.10 eV. In addition, the bulk site adsorption energy decreases from -2.45 to -2.43 eV, and the energy of the second-closest saddle points decreases from $E_{ad} = -2.04$ eV to -2.01 eV, lowering the diffusion barrier to $\Delta E = 0.33$ eV. Diffusion of Al adatoms is less affected than that of Ti adatoms by Al_{Ti} substitution, the largest change in the Ti adatom adsorption energy is 0.24 eV, while that of Al adatoms is only 0.06 eV.

The effect of Al_{Ti} on Al adatom diffusion barriers on TiN(001) is largest within the first coordination shell, with minor effects observable to the third shell, somewhat shorter range than the case for Ti adatoms. However, the nature of the effects are very much different for Al than for Ti adatoms, as discussed in Sec. 5.1.

Al adatom diffusion pathways on the (011) surface, shown in Fig. 11, are identical to those

Figure 11: (Color online) Al adatom diffusion path on TiN(011) between stable bulk sites, with and without an Al atom substituted on a cation surface sublattice site. The diffusion path in the $\langle 0\bar{1}1 \rangle$ direction is presented in the left side of the figure, and the path along the $\langle 100 \rangle$ direction in the right side. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis is the position on the diffusion path closest to the Al_{Ti} substitution position.

for Ti adatoms, but with lower adsorption energies and diffusion barriers. Al adatoms migrate from bulk to bulk sites along the $\langle 0\bar{1}1 \rangle$ direction over a saddle point, $\Delta E_{\langle 0\bar{1}1 \rangle}^{\text{Al}} = 1.16$ eV, atop a N surface atom, and in the $\langle 100 \rangle$ direction with a saddle point, $\Delta E_{\langle 100 \rangle}^{\text{Al}} = 2.67$ eV, between Ti surface atoms.

The substitution of an Al_{Ti} atom into the surface layer has relatively little influence on (011) diffusion barriers. Saddle point adsorption energies closest to the Al_{Ti} atom increase by 0.06 eV in the $\langle 0\bar{1}1 \rangle$ direction and 0.09 eV in the $\langle 100 \rangle$ direction. Adsorption energies at bulk sites decrease from $E_{ad} = -4.71$ to -4.67 eV. The second-closest set of saddle points also exhibit stronger adsorption; in the $\langle 0\bar{1}1 \rangle$ directions, E_{ad} increases from -3.55 to -3.62 eV, and from -2.04 to -2.13 eV, respectively. This lowers the corresponding diffusion barriers to $\Delta E = 1.06$ eV in the $\langle 0\bar{1}1 \rangle$ direction and $\Delta E = 2.54$ eV in the $\langle 100 \rangle$ direction.

Fig. 12 is plotted as $(E_{ad} - E_0^{\text{TiN}})$ vs. distance along the Al adatom diffusion path on the TiN(111):N surface. The pathway extends from the atop Ti site to the closest bulk site, and then to the next atop Ti site. The saddle points are between adjacent N surface atoms. There are two diffusion barriers on this surface, one from a metastable site to a stable bulk site ($\Delta E = 0.46$ eV), and a larger one from the stable site to the next atop Ti site ($\Delta E = 0.91$ eV).

As was the case for Ti adatoms, introducing Al_{Ti} into the TiN(111):N surface layer increases

Figure 12: (Color online) Al adatom diffusion path on TiN(111):N between stable bulk sites and metastable atop Ti sites, with and without an Al atom substituted on a cation surface sublattice site. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis corresponds to the metastable atop Al_{Ti} site.

the Al adatom adsorption energy E_{ad} in the metastable site atop Al_{Ti} , from -5.39 to -5.54 eV, while adsorption at bulk sites adjacent to the Al_{Ti} atom decreases from -5.84 to -5.79 eV. The adsorption energy at the saddle point between the first metastable site and the first bulk site is essentially unchanged. Therefore, the barrier from the metastable site is increased by 0.18 eV to $\Delta E = 0.64$ eV, while ΔE for the reverse barrier remains approximately the same at 0.88 eV. However, the second saddle point, between the nearest-neighbor bulk site and the second metastable site is strongly affected, the adsorption energy decreases from $E_{ad} = -4.93$ to -4.40 eV, thus increasing the diffusion barrier by 0.25 eV to $\Delta E = 1.16$ eV; the barrier in the opposite direction is increased to $\Delta E = 0.85$ eV.

Table 4: Adsorption energies E_{ad} for Al adatoms on TiN(001), TiN(011), and TiN(111):N surfaces with and without a surface Al_{Ti} substitution. Stable sites are denoted with (s), and metastable sites with (m).

Binding position	$E_{ad, \text{TiN}}$ [eV]	$E_{ad, \text{Ti(Al)N}}$ [eV]
TiN(001)		
Bulk site (s)	-2.45	-2.43
TiN(011)		
Bulk site (s)	-4.71	-4.67
TiN(111):N		
Bulk site (s)	-5.84	-5.79
Atop Ti site (m)	-5.39	-5.54

Table 5: Diffusion barrier energies ΔE for Al adatoms on TiN(001), TiN(011) and TiN(111):N surfaces with and without a surface Al_{Ti} substitution. The diffusion activation barriers are denoted with (act). Diffusion barriers in alternate directions from the same site are given within parenthesis.

Binding position	ΔE_{TiN} [eV]	$\Delta E_{\text{Ti(Al)N}}$ [eV]
TiN(001)		
Bulk site	0.42 (act)	0.33
TiN(011)		
Bulk site $\langle 100 \rangle$	2.67	2.54
Bulk site $\langle 0\bar{1}1 \rangle$	1.16 (act)	1.06
TiN(111):N		
Bulk site	0.91 (act)	0.88 ¹ (1.19) ²
Atop site	0.46	0.64 (0.85) ³

4.3. N adatom migration energetics

Figure 13: (Color online) N adatom adsorption energy landscape for: (a) TiN(001), (b) TiN(011), and (c) TiN(111):Ti. Each contour line correspond to a 0.5 eV difference in the adsorption energy E_{ad} referenced to a single N atom in vacuum, and in parenthesis, with respect to half of the N_2 bond energy.

N adatom adsorption energy landscapes, referenced to a single N atom in vacuum, are presented in Fig. 13. Note that with respect to N desorption as N_2 , the adsorption energy is 5.19 eV lower, as shown by the values in parenthesis. Thus, the adsorption energy is positive on the (001) surface, which means that N favors desorption as N_2 given the opportunity. However, the N adsorption energy is negative at the stable positions on both the TiN(011) and the TiN(111):Ti surfaces. Fig. 13, shows that the N adatom adsorption energy at stable binding sites on the three TiN surfaces increase from TiN(001) to TiN(011) to TiN(111), in agreement with results for the metal adatoms. N binding energies are listed in Table 6.

As shown in Fig. 13(a), the preferred binding site on TiN(001) is the threefold site located in

the middle of the triangle formed by a N and two Ti surface atoms and near the N surface atom with $E_{ad} = -4.15$ eV. The fourfold hollow site is metastable, with $E_{ad} = -3.48$ eV. The saddle point located between threefold sites has an adsorption energy $E_{ad} = -3.85$ eV, and the saddle point located between a threefold site and a fourfold hollow site corresponds to $E_{ad} = -3.32$ eV. Adsorption at N bulk sites, $E_{ad} = -2.95$ eV, is much weaker than at the stable threefold site. Therefore, diffusion paths through N bulk sites on TiN(001) are highly improbable.

On the (011) surface, Fig. 13(b), the N bulk site is the stable site for a N adatom with $E_{ad} = -6.12$ eV, and the bridge site, located at the bond center between adjacent Ti and N surface atoms, is metastable with $E_{ad} = -4.93$ eV. The saddle point between them has an adsorption energy $E_{ad} = -4.22$ eV, and E_{ad} for the saddle point between two bridge sites is -3.59 eV. The (111):Ti surface landscape in Fig. 13(c) shows that the bulk site is the stable binding site, $E_{ad} = -7.99$ eV, and the atop Ti site is metastable with $E_{ad} = -7.37$ eV. The saddle point between the two sites corresponds to $E_{ad} = -7.13$ eV.

The N diffusion barriers are presented in Table 7. Diffusion activation barriers for the three surfaces are $\Delta E_{act} = 0.83$ eV for TiN(001), $\Delta E_{act} = 1.90$ eV for TiN(011), and $\Delta E_{act} = 0.86$ eV for TiN(111):Ti. Thus, the lowest diffusion activation barriers are on TiN(001) and TiN(111):Ti. Nevertheless, ΔE_{act} for N adatoms on TiN(001) is much higher than ΔE_{act} of Ti and Al adatoms.

Compared to Ti and Al adatoms, N adatom diffusion pathways on TiN(001) and TiN(011) are more complex since N adatoms can access narrower adsorption sites, including the threefold site on (001) and the bridge site on TiN(011), both close to N surface atoms. The difference is most notable on TiN(001), where N adatoms on TiN(001) do not follow a diffusion path connecting N bulk sites, instead they primarily move by rotating among threefold sites around N surface atoms, occasionally migrating across a fourfold hollow site. On TiN(011), the N adatom diffusion path extends from bulk sites, which are located between Ti surface atoms, to the next bulk site via a path around Ti surface atoms. Along this path, there is a metastable bridge site between adjacent Ti and N surface atoms. On the TiN(111):Ti surface, N adatom diffusion paths follow a hexagonal pattern which is identical to those for Ti and Al adatoms. The path connects bulk sites to metastable atop N sites, with saddle points located between Ti surface atoms.

The N adatom diffusion path on TiN(001) is shown in Fig. 14. Overcoming the barrier between two nearest-neighbor threefold sites via precession requires much less energy, 0.30 eV, than migrating across the barrier, 0.83 eV, between a threefold site to the fourfold hollow site. Note, however, that

Figure 14: ((Color online) N adatom diffusion path on TiN(001) between stable threefold and the metastable fourfold hollow sites, with and without an Al atom substituted on a cation surface sublattice site. The adsorption energy E_{ad} is evaluated relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis corresponds to the fourfold hollow site closest to the Al_{Ti} substitution position.

precession does not lead to net diffusion.

Substituting an Al_{Ti} atom into the TiN(001) surface eliminates N adsorption at nearest-neighbor bulk sites, and significantly reduces the possibility to bind at the fourfold hollow site. The path from threefold to threefold sites across the fourfold hollow has a barrier of 0.92 eV. The barrier for precession between neighboring threefold sites is reduced by 0.05 eV to 0.25 eV.

Fig. 15 is a plot of $(E_{ad} - E_0^{TiN})$ as a function of N position on TiN(011) for diffusion in both the $\langle 0\bar{1}1 \rangle$ and $\langle 100 \rangle$ directions. In $\langle 0\bar{1}1 \rangle$, the saddle point, with $\Delta E = 1.90$ eV, between the bulk site and the bridge site is located half-way between the bulk site and the nearest-neighbor N surface atom. The diffusion path in the $\langle 100 \rangle$ direction, between bridge sites across a N surface atom, has a 1.34 eV diffusion barrier.

Incorporating an Al_{Ti} atom in the TiN(011) surface decreases the N adatom adsorption energy at neighboring bridge sites by 0.15 eV to $E_{ad} = -4.87$ eV, while adsorption at the bulk site decreases E_{ad} by 0.59 eV to -5.53 eV. The saddle point between the two sites corresponds to $\Delta E = -4.13$ eV, a decrease of 0.08 eV. This, in turn, decreases the barrier between the bulk site and the bridge site in the $\langle 0\bar{1}1 \rangle$ direction by 0.5 eV to 1.40 eV. ΔE decreases to 0.73 eV for migration from the bridge to the bulk site. The diffusion barrier from the bridge to the bulk is 0.01 eV lower, at 4.47 eV. In the $\langle 100 \rangle$ direction, the presence of an adjacent Al_{Ti} increases the diffusion barrier by 0.64 eV to 3.2 eV. Note that the nearest bulk and the bridge sites on TiN(011) are at approximately the

Figure 15: (Color online) N adatom diffusion path on TiN(011) between stable bulk and metastable bridge sites, with and without an Al atom substituted on a cation surface sublattice site. The diffusion path in the $\langle 0\bar{1}1 \rangle$ direction is presented in the left side of the figure, and the path along the $\langle 100 \rangle$ direction in the right side. The energy is relative to the lowest energy binding site on pure TiN. Zero on the x-axis corresponds to the bridge site closest to the Al_{Ti} substitution position.

same distance to the Al surface atom, see Fig. 9(b). Substituting an Al_{Ti} atom into the TiN(011) surface has a significant effect only within the first correlation shell.

Fig. 16 is a plot of $(E_{ad} - E_0^{\text{TiN}})$ as a function of distance along the N adatom diffusion path on TiN(111):Ti. The nearest bulk sites and atop N sites are at the same distance from the substituted Al_{Ti} atom. Thus, there are three diffusion paths of interest. Figs. 16(a), 16(b), and 16(c) show the pathway leading from a bulk site adjacent to the Al_{Ti} atom, the path connecting the bulk site and atop N sites, and the path from an atop N site away from the Al_{Ti} atom to the next bulk site.

Al_{Ti} in the (111):Ti surface decreases the N adatom adsorption at the bulk site by 0.43 eV to -7.56 eV. E_{ad} at the closest metastable atop N site decreases by 0.24 eV to -7.11 eV. The second-neighbor bulk and atop N sites are much closer in energy to those on pure TiN(111):Ti. The adsorption energy increases by 0.17 eV to -8.16 eV, and by 0.06 eV to -7.43 eV, respectively. The adsorption energy at the saddle points between the bulk-site closest to Al_{Ti} and atop N sites decreases to -7.01 eV for the path in Fig. 16(a), -6.81 eV in Fig. 16(b), and -6.97 eV in Fig. 16(c).

5. Comparison of adatom dynamics on TiN and implications of Al_{Ti} substitution on adatom surface diffusion

Adatom surface diffusivities are dependent on both the exponential $-\Delta E/k_B T$ term and the diffusion prefactor D_o (Eq. (4)). The main focus of this study has been on changes in ΔE for Ti,

Figure 16: (Color online) N adatom diffusion paths on TiN(111), with and without an Al atom substituted on a cation surface sublattice site: (a) the path away from a bulk site adjacent to the Al_{Ti} atom; (b) the path between a bulk site and an atop N site, both next to the Al_{Ti} atom; and (c) the path from an adjacent atop N site away from the Al_{Ti} atom. The adsorption energy E_{ad} is relative to the lowest energy binding site E_0^{TiN} on pure TiN. Zero on the x-axis corresponds to the bulk and atop N sites adjacent to the Al_{Ti} substitution position.

Al, and N adatoms on TiN(001), (011), and (111) with and without the presence of substituted Al_{Ti} surface atoms. For the discussion in this section, we use a fixed temperature $T = 800$ K, a reasonable value for TiN and TiAlN film growth, and also investigate the changes in D_o , using a harmonic approximation, when an Al_{Ti} atom is substituted into the three TiN surfaces. The details of the diffusion prefactor calculations are presented in Appendix [Appendix A](#). Although the Al_{Ti} atom affects both the diffusion prefactor and the diffusion barrier, adatom diffusivity is much less affected by the change in D_o than the change in ΔE ; the dominate factor is the exponential term which determines the success probability of a migration attempt.

5.1. Adatom diffusion on pure and Al_{Ti} -substituted TiN(001)

Ti, Al, and N adatom diffusion activation barriers on pure TiN(001) are within 0.47 eV of each other. Ti adatoms have the lowest activation barrier, $\Delta E_{\text{act}} = 0.36$ eV; the Al and N adatom activation barriers are 0.42 eV and 0.83 eV. Thus, N adatoms are the slowest diffusing species on TiN(001).

Based upon the diffusion activation barriers alone, Ti adatoms would be the fastest diffusing species. The Ti activation barrier is 0.06 eV lower than that of Al, however, Ti adatoms have three times as many adsorption sites. Although the differences in sites provide an extra complexity when comparing the adatom mobilities, we have taken this into account and come to the conclusion that, at $T = 800$ K, the Ti adatom jump frequency is $2.70\times$ higher than the Al adatom jump frequency.

Table 6: Binding energies E_{ad} for N adatoms on TiN(001), TiN(011), and TiN(111):Ti surfaces with and without a surface Al_{Ti} substitution. Stable sites are denoted with (s), and metastable sites with (m).

Binding position	$E_{ad, \text{TiN}}$ [eV]	$E_{ad, \text{Ti(Al)N}}$ [eV]
TiN(001)		
Bulk site (m)	-2.95	-
Fourfold hollow site (m)	-3.48	-3.26
Threefold site (s)	-4.15	-4.13
TiN(011)		
Bulk position (s)	-6.12	-5.53
Bridge site (m)	-4.93	-4.87
TiN(111):Ti		
Bulk site (s)	-7.99	-7.56
Atop N site (m)	-7.37	-7.11

Table 7: Diffusion barrier energies ΔE for N adatoms on TiN(001), TiN(011), and TiN(111):Ti surfaces with and without a surface Al_{Ti}. The diffusion activation barriers are denoted with (act). Diffusion barriers in alternate directions from the same site are given within parenthesis.

Binding position	ΔE_{TiN} [eV]	$\Delta E_{\text{Ti(Al)N}}$ [eV]
TiN(001)		
Fourfold hollow site	0.16	0.07
Threefold site ⁴	0.83 (act)	0.94
Threefold site ⁵	0.30	0.25
TiN(011)		
Bulk site	1.90 (act)	1.40 ⁶ (1.94) ⁷
Bridge site	0.73 (1.34) ⁸	0.72 (1.99) ^e
TiN(111):Ti		
Bulk site	0.86 (act)	0.55
Atop N site	0.24	0.26

However, the $2\times$ longer jump length for Al corresponds to a $4\times$ higher diffusivity. Taken together, Al adatoms diffuse 48% faster than Ti adatoms at 800 K. This is consistent with the results of Alling et al.[45]

The substitution of Al_{Ti} into the TiN(001) surface has a stronger effect on Ti than on Al and N adatoms. Alling et al.[45] determined Ti adatom adsorption energies at different fourfold hollow sites on Ti_{0.5}Al_{0.5}N(001), between Ti and Ti, Al and Al, and Ti and Al surface atoms. They found that the Ti adsorption energy is strongest between surface Ti and Al on Ti_{0.5}Al_{0.5}N(001). Consistent with these results, we find that the Ti adsorption energy at the fourfold hollow sites closest to the Al_{Ti} atom increases by 0.24 eV, 67% of $\Delta E_{act}^{\text{Ti}}$. This creates a Ti trap at the fourfold hollow and the two adjacent bulk sites. Ti must perform a double jump via the bulk site adjacent

to the Al_{Ti} atom in order to escape. However, the barrier from the bulk site back to the Al_{Ti} atom is only 0.03 eV which makes a jump back to the fourfold hollow site much easier than a jump away from it. Therefore, we can instead approximate the double hop as a single jump over an effective barrier of 0.60 eV, 167% of $\Delta E_{act}^{\text{Ti}}$. At $T = 800$ K, the escape success rate from a trap site is only 2% compared to the success rate at a fourfold hollow site on pure $\text{TiN}(001)$. However, even if a Ti adatom successfully escapes the trap and reaches the neighboring fourfold hollow site, from that site a jump back into the trap is just as likely as a jump to a next-neighbor bulk site; the barrier into the trap-site is as large as ΔE_{act} . Thus, during film growth, a Ti adatom will be considerably delayed by the trap-sites increasing the probability that additional adatoms can reach the surface and react with it before it reaches a grain boundary.

The diffusivity of Al adatoms on the (001) surface is less affected than Ti adatoms by Al_{Ti} substitution. The diffusion barrier between bulk sites adjacent to Al_{Ti} decreases by 0.09 eV. A jump attempt over this barrier is $3\times$ more likely to succeed than an attempt to jump over the activation barrier $\Delta E_{act}^{\text{Al}}$. Thus, an Al adatom will stay longer at bulk sites adjacent to an Al_{Ti} atom longer. However, the time spent there is much shorter than the time spent at a trap site.

Similar to the case for Al adatoms, the N adatom diffusivity on (001) is not strongly affected by Al_{Ti} surface substitution. The diffusion barrier between threefold and fourfold hollow sites is increased by 0.11 eV. At 800 K, an attempt to migrate across this barrier is less likely to succeed than an attempt to migrate across the N diffusion activation barrier $\Delta E_{act}^{\text{N}}$. For 28 successful attempts to migrate past the barrier between threefold and fourfold hollow sites adjacent to an Al_{Ti} atom, 100 attempts will successfully migrate over $\Delta E_{act}^{\text{N}}$.

5.2. Adatom diffusion on pure and Al_{Ti} -substituted $\text{TiN}(011)$

The surface energy, $E_s^{(011)} = 167 \text{ meV}/\text{\AA}^2$, is approximately twice that of the (001) and (111) surfaces. This makes $\text{TiN}(011)$ much less thermodynamically favored than the other two surface orientations. Therefore, it is important to understand Ti, Al, and N diffusion in order to optimize $\text{TiN}(011)$ and $\text{TiAlN}(011)$ film growth.

Adatom diffusion on $\text{TiN}(011)$ is the slowest of the three surfaces due to the high diffusion activation barriers: $\Delta E_{act}^{\text{Al}} = 1.16 \text{ eV}$, $\Delta E_{act}^{\text{N}} = 1.90 \text{ eV}$, and $\Delta E_{act}^{\text{Ti}} = 2.31 \text{ eV}$. Ti is the slowest diffusing species on this surface, Al atoms the fastest. Diffusion is primarily one-dimensional in the $\langle 0\bar{1}1 \rangle$ direction for both Ti and Al adatoms, with barriers in the orthogonal $\langle 100 \rangle$ directions of 4.26 eV for Ti adatoms and 2.67 eV for Al adatoms, twice those in the $\langle 0\bar{1}1 \rangle$ direction.

None of the adatom species on TiN(0 1 1) are significantly affected by changes in barriers caused by Al_{Ti} substitution which has only small effects on Ti and Al adatom migration. The Al adatom diffusion barrier closest to the Al_{Ti} atom is lowered by 0.1 eV, and the Ti adatom diffusion barrier is decreased by 0.31 eV. The changes in diffusion barrier values are small compared to those on (0 0 1) and (1 1 1) surfaces. Similarly, while the decrease in the N adatom diffusion barrier adjacent to Al_{Ti}, 0.56 eV, is large compared to those of the metal adatoms, it is still a relatively small fraction of the N adatom diffusion activation barrier. None of the changes in Ti, Al, and N adatom adsorption energies are large enough for (0 1 1) to become a competitive surface orientation during TiAlN growth.

5.3. Adatom diffusion on pure and Al_{Ti}-substituted TiN(1 1 1)

The Al and Ti diffusion activation barriers on the (1 1 1):N surface are $\Delta E_{act}^{Al} = 0.91$ eV and $\Delta E_{act}^{Ti} = 1.66$ eV. On the Ti-terminated (1 1 1) surface, the N adatom diffusion activation barrier, ΔE_{act}^N , is 0.86 eV. Overall, diffusion barriers on TiN(1 1 1) are higher than on (0 0 1), and lower than on (0 1 1). Ti is the slowest diffusing adatom species on the TiN(1 1 1):N surface, with an activation barrier which is 0.75 eV higher than that of Al. Thus, at 800 K Al is 53000× more likely than Ti to succeed with a jump attempt.

Substituting Al_{Ti} into the TiN(1 1 1) surface introduces a trap for Al adatoms. The trap will confine the Al adatom to the atop Al_{Ti} site and the adjacent neighboring bulk sites. Unlike the Ti adatom trap-site on TiN(0 0 1), the diffusion barrier into the Al adatom trap is 0.39 eV higher than in the reverse direction. Although the increased barrier into the trap makes it less accessible, the barrier is lower than ΔE_{act}^{Al} . From within the trap, the escape barrier is 0.28 eV higher than the activation barrier; this means that the probability to escape is only 2% of the probability to migrate from across the activation barrier. Therefore, an Al adatom trapped at this position is unlikely to escape before additional adatoms reach the surface.

The primary effect of Al_{Ti} substitution on Ti/TiN(1 1 1) surface migration is an increased adsorption energy at the metastable atop Al_{Ti} site. E_{ad} is increased by 0.27 eV, which increases the diffusion barrier from the atop Al_{Ti} to an adjacent bulk site by 0.15 eV to 0.86 eV. However, this is still only 52% of the Ti activation barrier. Thus, Ti adatom migration is not significantly affected by Al_{Ti} substitution on TiN(1 1 1).

N adatoms on the Ti-terminated TiN(1 1 1) surface experience weaker adsorption energies close to the Al_{Ti}. Although the diffusion barriers leading away from the adjacent bulk and atop N sites

are lower than the ones towards them, they are all lower than the activation barrier. Thus, as for Ti adatoms, N adatoms are not significantly affected by Al_{Ti} substitution on $\text{TiN}(111)$.

5.4. Implications for TiN and TiAlN film growth

Our results show that E_s , the energy per unit area (Sec. 3), of relaxed $\text{TiN}(001)$ and $\text{TiN}(111):\text{N}$ surfaces, 81 and 92 $\text{meV}/\text{\AA}^2$, respectively, are similar and both are much lower than E_s for $\text{TiN}(011)$, 162 $\text{meV}/\text{\AA}^2$. This is consistent with experimental observations showing that nucleation of TiN on amorphous (i.e., non-orientationally biased) substrates is dominated by approximately equal number densities of (001) and (111) islands with almost no (011) islands detected.[60, 62]

The considerably higher Ti adatom mobility, hence chemical potential, of Ti adatoms on $\text{TiN}(001)$ compared to (111) surfaces (see Sec. 4.1) implies that Ti adatoms have a higher chance of moving off (001) islands compared to low-potential-energy, low-surface-diffusivity, (111) islands. Thus, we would expect that $\text{TiN}(001)$ islands would exhibit a higher probability of expanding laterally, while (111) islands would tend to grow more three dimensionally. This is also consistent with experimental results for TiN/SiO_2 film deposition carried out under conditions of minimal intrinsic growth stress.[60, 62] However, once island coalescence occurs, the effect is reversed. Since Ti adatoms have longer residence times on (111) than (001) surfaces, adatoms deposited near grain boundaries have a much higher probability of being captured on (111) grains. Thus, with continued deposition, (111) grains slowly and inexorably overgrow (001) grains in a competitive growth mode leading to increasingly strong (111) preferred orientation as observed by x-ray diffraction studies as a function of film thickness and cross-sectional transmission electron microscopy analyses.[60, 62]

We find that Al adatoms also have a higher mobility on $\text{TiN}(001)$ than on $\text{TiN}(111)$ (Sec. 4.2). However, the kinetic advantage for Al adatoms contributing to the development of (111) texture is less than for Ti adatoms due to the lower Al diffusion activation barrier on $\text{TiN}(111)$, $\Delta E_{act} = 0.91$ eV vs. $\Delta E_{act}^{\text{Ti}} = 1.66$ eV, while the activation barriers are similar on $\text{TiN}(001)$, 0.36 eV for Ti and 0.42 eV for Al.

As AlN is substituted into the TiN surface layer, strong local traps appear for Ti adatoms near Al_{Ti} sites on $\text{TiN}(001)$ and Al adatoms near Al_{Ti} sites on $\text{TiN}(111)$; Al on $\text{TiN}(001)$ and Ti on $\text{TiN}(111)$ are not as strongly affected. Moreover, in the presence of Al_{Ti} , the chemical-potential advantage for (111) texture formation decreases. Overall, extrapolating from our results predicts that for growth of metastable NaCl-structure TiAlN films, (001) grains will tend to be more TiN

rich than the average film composition, while (1 1 1) grains will be more AlN rich, with a decrease in the degree of (1 1 1) preferred orientation.

Although our results provide explanations for the experimentally observed shift from (1 1 1) toward (0 0 1) texture[6, 40] with increasing AlN content, and higher AlN content in (1 1 1) compared to (0 0 1) grains during TiAlN growth,[40] not all observations can be explained from these results alone. Clearly, additional studies of the effect of AlN substitution on, for example, mass transport over step edges and adatom migration on TiAlN surfaces, and N concentration effects are necessary to develop a fuller understanding of surface diffusion processes controlling morphological evolution during TiAlN film growth. However, the insights gained in this work on Ti and Al adatom migration energetics, with and without Al_{Ti} surface substitution in all three low index cubic planes, should help to provide an initial foundation for future research in this area.

6. Conclusions

Using first-principles calculations, we have investigated Ti, Al, and N adatom diffusion on pure and Al_{Ti}-substituted TiN(0 0 1), TiN(0 1 1), and TiN(1 1 1):(N,Ti) surfaces. We determine surface energies, adsorption energy landscapes, and diffusion paths. Surface energies are $E_s^{(001)} = 81$ meV/Å², $E_s^{(011)} = 167$ meV/Å², and $E_s^{(111)} = 92$ meV/Å². Substituting Al_{Ti} into the TiN surface is found to affect adatom diffusion near Al_{Ti} primarily due to changes in diffusion barriers; changes in the diffusion prefactor are small.

Ti adatoms on TiN(0 0 1) favor the stable fourfold hollow sites and metastable bulk sites atop N. Accounting for magnetic spin relaxation increases E_{ad} at metastable sites by 0.14 eV to -3.22 eV. Al binds exclusively at bulk positions, while N binds at stable threefold and metastable fourfold hollow sites. The N adsorption energy at bulk sites is very weak compared to the fourfold hollow and threefold sites. The stable Ti, Al, and N adatom sites on TiN(0 1 1) are the corresponding epitaxial bulk sites; N adatoms also have a metastable bridge site. Ti, Al, and N adatoms on TiN(1 1 1) all prefer their stable bulk sites and metastable atop Ti sites; Ti and Al on the N-terminated (1 1 1) surface, and N on Ti-terminated (1 1 1).

The primary Ti adatom diffusion path on TiN(0 0 1) are in the $\langle \bar{1}10 \rangle$ and $\langle 110 \rangle$ directions between stable fourfold hollow sites, $E_{ad} = -3.41$ eV, and metastable bulk sites, $E_{ad} = -3.22$ eV, with a diffusion activation barrier, $\Delta E_{act} = 0.36$ eV. Al adatoms on TiN(0 0 1) also migrate in the $\langle \bar{1}10 \rangle$ and $\langle 110 \rangle$ directions, but between bulk sites, $E_{ad} = -2.45$ eV, with an activation

barrier $\Delta E_{act} = 0.42$ eV. N adatoms primarily migrate between neighboring threefold hollow sites, $E_{ad} = -4.15$ eV, with a saddle point adsorption energy of -3.85 eV. The precession motion around a surface N atom results in no net diffusion. Net diffusion occurs by migration from threefold to fourfold hollow to threefold site over an activation barrier $\Delta E_{act} = 0.83$ eV.

The primary Ti and Al adatom diffusion paths on TiN(011) is in the $\langle 0\bar{1}1 \rangle$ direction between bulk sites for which $E_{ad}^{Ti} = -6.80$ eV and $E_{ad}^{Al} = -4.71$ eV. Saddle points are atop N surface atoms with diffusion activation barriers $\Delta E_{act}^{Ti} = 2.31$ eV and $\Delta E_{act}^{Al} = 1.16$ eV. In the $\langle 100 \rangle$ direction, diffusion is limited by a much higher saddle point, $E_{ad}^{Ti} = -2.54$ eV and $E_{ad}^{Al} = -2.04$ eV, between neighboring Ti surface atoms. N adatoms primarily migrate between a stable bulk site, $E_{ad} = -6.12$ eV, and a metastable bridge site, $E_{ad} = -4.93$ eV, limited by a diffusion activation barrier $\Delta E_{act} = 1.90$ eV. A secondary diffusion path exists between bridge sites over a saddle point located atop a N surface atom with $E_{ad} = 3.59$ eV.

The Ti, Al, and N adatom diffusion paths on TiN(111) (N-terminated for Al and Ti, and Ti-terminated for N) are between stable bulk sites ($E_{ad}^{Ti} = -9.92$ eV, $E_{ad}^{Al} = -5.84$ eV, and $E_{ad}^N = -7.99$ eV), and metastable atop Ti sites ($E_{ad}^{Ti} = -8.97$ eV, $E_{ad}^{Al} = -5.39$ eV, and $E_{ad}^N = -7.37$ eV); with the diffusion activation barriers $\Delta E_{act}^{Ti} = 1.66$ eV, $\Delta E_{act}^{Al} = 0.91$ eV, and $\Delta E_{act}^N = 0.86$ eV located between nearest-neighbor surface atoms. Each stable site is connected to three metastable sites via symmetrically identical diffusion paths, and each metastable site is connected to three stable sites, which together forms a hexagonal-shaped pattern of diffusion paths.

A substitutional Al_{Ti} atom in TiN(111):N will migrate from the second layer into the N-termination layer. Only when an adatom is at a bulk site adjacent to the Al_{Ti} atom, will it move back to its second layer position.

The addition of Al_{Ti} has two important effects on the diffusivity of Ti and Al adatoms. First, on TiN(001), Ti adatom diffusion is slowed because of trap sites created at the fourfold hollow sites adjacent to the Al_{Ti} atom. Secondly, Al adatoms on TiN(111) surfaces are slowed because of a trap zone that is introduced between atop Al_{Ti} and nearest-neighbor bulk sites.

In summary, the results of this investigation are intended to provide insights into effects regarding Ti, Al, and N adatom migration on both pure and Al-substituted TiN(001), (011), and (111) surfaces.

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- [1] G. Beensh-Marchwicka, L. Król-Stepniewska, and W. Posadowski. Structure of thin films prepared by the cosputtering of titanium and aluminium or titanium and silicon. *Thin Solid Films*, 82(4):313–320, 1981.
- [2] H. A. Jehn, S. Hofman, V. E. Rückborn, and W. D. Münz. Morphology and properties of sputtered (Ti,Al)N layers on high speed steel substrates as a function of deposition temperature and sputtering atmosphere. *J. Vac. Sci. Technol. A*, 4(6):2701, November 1986.
- [3] O. Knotek, M. Böhmer, and T. Leyendecker. On structure and properties of sputtered Ti and Al based hard compound films. *J. Vac. Sci. Technol. A*, 4(6):2695, November 1986.
- [4] O. Knotek, W. D. Münz, and T. Leyendecker. Industrial deposition of binary, ternary, and quaternary nitrides of titanium, zirconium, and aluminum. *J. Vac. Sci. Technol. A*, 5(4):2173, July 1987.
- [5] P. C. Jindal, A. T. Santhanam, U. Schleinkofer, and A. F. Shuster. Performance of PVD TiN, TiCN, and TiAlN coated cemented carbide tools in turning. *Int. J. Refract. Met. Hard Mater.*, 17(1):163–170, 1999.
- [6] A. Hörling, L. Hultman, M. Oden, J. Sjöln, and L. Karlsson. Mechanical properties and machining performance of Ti_{1-x}Al_xN-coated cutting tools. *Surf. Coat. Tech.*, 191(2-3):384–392, February 2005.
- [7] W. D. Munz. Titanium aluminum nitride films: A new alternative to TiN coatings. *J. Vac. Sci. Technol. A*, 4(6):2717, November 1986.

- [8] D. McIntyre, J. E. Greene, G. Hakansson, J. E. Sundgren, and W. D. Munz. Oxidation of metastable single-phase polycrystalline Ti_{0.5}Al_{0.5}N films: Kinetics and mechanisms. *J. Appl. Phys.*, 67(3):1542, 1990.
- [9] Y. C. Chim, X. Z. Ding, X. T. Zeng, and S. Zhang. Oxidation resistance of TiN, CrN, TiAlN and CrAlN coatings deposited by lateral rotating cathode arc. *Thin Solid Films*, 517(17):4845–4849, 2009.
- [10] T. Leyendecker, O. Lemmer, S. Esser, and J. Ebberink. The development of the PVD coating TiAlN as a commercial coating for cutting tools. *Surf. Coat. Tech.*, 48(2):175–178, 1991.
- [11] B. Subramanian, C. V. Muraleedharan, R. Ananthakumar, and M. Jayachandran. A comparative study of titanium nitride (TiN), titanium oxy nitride (TiON) and titanium aluminum nitride (TiAlN), as surface coatings for bio implants. *Surf. Coat. Tech.*, 205(21-22):5014–5020, 2011.
- [12] P. H. Mayrhofer, A. Horling, L. Karlsson, J. Sjolen, T. Larsson, C. Mitterer, and L. Hultman. Self-organized nanostructures in the TiAlN system. *Appl. Phys. Lett.*, 83:2049, 2003.
- [13] A. E. Santana, A. Karimi, V. H. Derflinger, and A. Schütze. Thermal treatment effects on microstructure and mechanical properties of TiAlN thin films. *Tribol. Lett.*, 17(4):689–696, November 2004.
- [14] R. Rachbauer, S. Massl, E. Stergar, D. Holec, D. Kiener, J. Keckes, J. Patscheider, M. Stiefel, H. Leitner, and P. H. Mayrhofer. Decomposition pathways in age hardening of Ti-Al-N films. *J. Appl. Phys.*, 110:023515, 2011.
- [15] A. Knutsson, J. Ullbrand, L. Rogstrom, N. Norrby, L. J. S. Johnson, L. Hultman, J. Almer, M. P. Johansson Joesaar, B. Jansson, and M. Oden. Microstructure evolution during the isostructural decomposition of TiAlN combined in-situ small angle x-ray scattering and phase field study. *J. Appl. Phys.*, 113(21):213518, June 2013.
- [16] B. Alling, A. V. Ruban, A. Karimi, O. E. Peil, S. I. Simak, L. Hultman, and I. A. Abrikosov. Mixing and decomposition thermodynamics of c-Ti_{1-x}Al_xN from first-principles calculations. *Phys. Rev. B*, 75:045123, 2007.

- [17] B. Alling, A. Karimi, and I. A. Abrikosov. Electronic origin of the isostructural decomposition in cubic $M_{1-x}Al_xN$ ($M=Ti, Cr, Sc, Hf$): A first-principles study. *Surf. Coat. Tech.*, 203(5-7): 883–886, December 2008.
- [18] B. Alling, M. Oden, L. Hultman, and I. A. Abrikosov. Pressure enhancement of the isostructural cubic decomposition in $Ti_{1-x}Al_xN$. *Appl. Phys. Lett.*, 95(18):181906, 2009.
- [19] L. J. S. Johnson, M. Thuvander, K. Stiller, M. Odén, and L. Hultman. Spinodal decomposition of $Ti_{0.33}Al_{0.67}N$ thin films studied by atom probe tomography. *Thin Solid Films*, 520(13): 4362–4368, 2012.
- [20] H. Eyring. The Activated Complex in Chemical Reactions. *J Chem. Phys.*, 3(2):107, February 1935.
- [21] G. H. Vineyard. Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids*, 3(1-2):121–127, 1957.
- [22] A. Bogicevic, J. Strömquist, and B. I. Lundqvist. Low-Symmetry Diffusion Barriers in Homoepitaxial Growth of $Al(111)$. *Phys. Rev. Lett.*, 81(3):637–640, 1998.
- [23] M. Mantina, Y. Wang, R. Arroyave, L. Q. Chen, Z. K. Liu, and C. Wolverton. First-Principles Calculation of Self-Diffusion Coefficients. *Phys. Rev. Lett.*, 100(21):215901, May 2008.
- [24] G. Antczak and G. Ehrlich. *Surface Diffusion: Metals, Metal Atoms, and Clusters*. Cambridge University Press, Cambridge, first edition, 2010. ISBN 9780521899833.
- [25] C Ruberto and B. I. Lundqvist. Nature of adsorption on $TiC(111)$ investigated with density-functional calculations. *Phys. Rev. B*, 75(23):235438, 2007.
- [26] C. Ruberto, A. Vojvodic, and B. I. Lundqvist. Nature of versatile chemisorption on $TiC(111)$ and $TiN(111)$ surfaces. *Solid State Commun.*, 141(1):48–52, 2007.
- [27] D. Gall, S. Kodambaka, M. A. Wall, I. Petrov, and J. E. Greene. Pathways of atomistic processes on $TiN(001)$ and (111) surfaces during film growth: an ab initio study. *J. Appl. Phys.*, 93(11):9086–9094, 2003.
- [28] C. V. Ciobanu, D. T. Tambe, and V. B. Shenoy. First-principles calculations of step formation energies and step interactions on $TiN(001)$. *Surf. Sci.*, 582(1-3):145–150, 2005.

- [29] J. Graciani, J. Fdez Sanz, T. Asaki, K. Nakamura, and J. A. Rodriguez. Interaction of oxygen with TiN(001):NO exchange and oxidation process. *J. Chem. Phys.*, 126(24):244713–244718, 2007.
- [30] S. Sanyal, U. V. Waghmare, and J. A. Ruud. Adsorption of water on TiN (100), (110) and (111) surfaces: A first-principles study. *Appl. Surf. Sci.*, 257(15):6462–6467, 2011.
- [31] T. Akiyama, K. Nakamura, and T. Ito. Ab initio-based study for adatom kinetics on AlN(0001) surfaces during metal-organic vapor-phase epitaxy growth. *Appl. Phys. Lett.*, 100(25):251601, 2012.
- [32] D. Music and J. M. Schneider. Ab initio study of Ti_{0.5}Al_{0.5}N(001)residual and environmental gas interactions. *New J. Phys.*, 15(7):073004, July 2013.
- [33] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene. Dynamics of Ti, N, and TiN_x (x=13) admolecule transport on TiN(001) surfaces. *Phys. Rev. B*, 86(15):155443, 2012.
- [34] Z. H. Xu, L. Yuan, D. B. Shan, and B. Guo. A molecular dynamics simulation of TiN film growth on TiN(001). *Comp. Mater. Sci.*, 50(4):1432–1436, 2011.
- [35] S. Kodambaka, V. Petrova, A. Vailionis, P. Desjardins, D. G. Cahill, I. Petrov, and J. E. Greene. TiN(001) and TiN(111) island coarsening kinetics: in-situ scanning tunneling microscopy studies. *Thin Solid Films*, 392(2):164–168, 2001.
- [36] S. Kodambaka, S. V. Khare, V. Petrova, A. Vailionis, I. Petrov, and J. E. Greene. Absolute orientation-dependent TiN(001) step energies from two-dimensional equilibrium island shape and coarsening measurements on epitaxial TiN(001) layers. *Surf. Sci.*, 513(3):468–474, 2002.
- [37] S. Kodambaka, V. Petrova, A. Vailionis, and I. Petrov. In situ high-temperature scanning tunneling microscopy studies of two-dimensional TiN island coarsening kinetics on TiN(001). *Surf. Sci.*, 526:85–96, 2003.
- [38] M. A. Wall, D. G. Cahill, I. Petrov, D. Gall, and J. E. Greene. Nucleation kinetics during homoepitaxial growth of TiN(001) by reactive magnetron sputtering. *Phys. Rev. B*, 70(3):35413, 2004.

- [39] M. A. Wall, D. G. Cahill, I. Petrov, D. Gall, and J. E. Greene. Nucleation kinetics versus nitrogen partial pressure during homoepitaxial growth of stoichiometric TiN(001): A scanning tunneling microscopy study. *Surf. Sci.*, 581(2-3):L122–127, 2005.
- [40] M. Beckers, N. Schell, R. M. S. Martins, A. Mücklich, and W. Möller. In situ x-ray diffraction studies concerning the influence of Al concentration on the texture development during sputter deposition of TiAlN thin films. *J. Vac. Sci. Technol. A*, 23(5):1384, 2005.
- [41] A. Van der Ven, G. Ceder, M. Asta, and P. D. Tepesch. First-principles theory of ionic diffusion with nondilute carriers. *Phys. Rev. B*, 64(18):184307, 2001.
- [42] Z. Chen, N. Kioussis, K. N. Tu, N. Ghoniem, and J. M. Yang. Inhibiting Adatom Diffusion through Surface Alloying. *Phys. Rev. Lett.*, 105(1):15703, 2010.
- [43] A. Van der Ven, J. C. Thomas, Q. Xu, and J. Bhattacharya. Linking the electronic structure of solids to their thermodynamic and kinetic properties. *Math. Comput. Simulat.*, 80(7):1393–1410, 2010.
- [44] A. Van der Ven, H. C. Yu, G. Ceder, and K. Thornton. Vacancy mediated substitutional diffusion in binary crystalline solids. *Prog. Mater. Sci.*, 55(2):61–105, 2010.
- [45] B. Alling, P. Steneteg, C. Tholander, F. Tasnádi, I. Petrov, J. E. Greene, and L. Hultman. Configurational disorder effects on adatom mobilities on Ti_{1-x}Al_xN(001) surfaces from first principles. *Phys. Rev. B*, 85(24):245422, 2012.
- [46] W. Kohn and L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.*, 140(4A):A1133–A1138, 1965.
- [47] G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.*, 6(1):15–50, 1996.
- [48] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54(16):11169–11186, 1996.
- [49] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50(24):17953–17979, December 1994.

- [50] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59(3):1758, 1999.
- [51] J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77(18):3865–3868, October 1996.
- [52] J. P. Perdew, K. Burke, and M. Ernzerhof. Erratum: Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 78:1396, October 1997.
- [53] H. J. Monkhorst and J. D. Pack. Special points for Brillouin-zone integrations. *Phys. Rev. B*, 13(12):5188–5192, June 1976.
- [54] L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse. Accurate surface and adsorption energies from many-body perturbation theory. *Nat. Mater.*, 9(9):741–744, September 2010.
- [55] J. P. Perdew and A. Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, 23(10):5048, 1981.
- [56] G. Mills, H. Jónsson, and G. K. Schenter. Reversible work transition state theory: application to dissociative adsorption of hydrogen. *Surf. Sci.*, 324(2-3):305–337, 1995.
- [57] G. Henkelman, B. P. Uberuaga, and H. Jónsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.*, 113(22), 2000.
- [58] D. Sheppard, R. Terrell, and G. Henkelman. Nudged elastic band method for finding minimum energy paths of transitions. *J. Chem. Phys.*, 128(13):134106, April 2008.
- [59] M. Marlo and V. Milman. Density-functional study of bulk and surface properties of titanium nitride using different exchange-correlation functionals. *Phys. Rev. B*, 62(4):2899, 2000.
- [60] J. E. Greene, J. E. Sundgren, L. Hultman, I. Petrov, and D. B. Bergstrom. Development of preferred orientation in polycrystalline TiN layers grown by ultrahigh vacuum reactive magnetron sputtering. *Appl. Phys. Lett.*, 67(20):2928, 1995.
- [61] F. H. Baumann, D. L. Chopp, T. Díaz de la Rubia, G. H. Gilmer, J. E. Greene, H. Huang, S. Kodambaka, P. O’Sullivan, and I. Petrov. Multiscale Modeling of Thin-Film Deposition: Applications to Si Device Processing. *MRS Bull.*, 26(03):182–189, 2001.

- [62] L. Hultman, J. E. Sundgren, J. E. Greene, D. B. Bergstrom, and I. Petrov. High-flux low-energy (20 eV) N+2 ion irradiation during TiN deposition by reactive magnetron sputtering: Effects on microstructure and preferred orientation. *J. Appl. Phys.*, 78(9):5395, November 1995.

Appendix A. Adatom surface diffusion prefactor, D_o

Calculating adatom surface diffusivities requires knowledge of both diffusion prefactors and diffusion barriers. The diffusion prefactor can be calculated from the attempt frequency ν_0 and jump distance l according to Eq. (5). ν_0 and l can, in principle, be obtained using molecular dynamics. However, for alloys, such methods are currently limited either by accuracy at the quantum level, including features such as magnetism, or short time frames which are unable to capture all migration events. Within density functional theory, it is possible to approximate the surface energetics contribution to the diffusion prefactor for specific diffusion mechanisms with good accuracy using the harmonic approximation in Eq. (6) and the jump lengths obtained from the diffusion path calculations.

Jump length l for TiN(001), TiN(011), and TiN(111) surfaces are listed in Table A.8. Distances follow from the crystal structure. The Ti adatom jump length on TiN(001), 1.50 Å, is the distance between the fourfold hollow site and the bulk site, while the Al and N adatoms jump length, 3.01 Å, is the distance between bulk sites. Ti and Al adatom jump lengths on TiN(011) are the distances between bulk sites in the $\langle 0\bar{1}1 \rangle$ direction, 3.01 Å, and in the $\langle 100 \rangle$ direction, 4.26 Å. Thus, Ti and Al diffusion on the (011) surface is primarily in the $\langle 0\bar{1}1 \rangle$ direction. The N adatom jump length, 2.05 Å, is the distance between the N bulk site and the bridge site. On TiN(111), Ti, Al, and N adatom jump lengths are 1.74 Å, the distance between the stable bulk site and the nearest-neighbor metastable atop site.

Changes in local jump lengths near substituted Al_{Ti} are small enough that we ignore the minor differences. Thus, changes in D_o are due to Al_{Ti} effects on the attempt frequency ν_0 . However, even a large difference in ν_0 produces only a small change in the diffusivity; small differences in the diffusion energy barrier are much more significant due to the exponential term.

The attempt frequencies calculated using Eq. (6) are presented in Tables A.9-A.11. We are aware that the harmonic approximation within the transition state theory is a simplification which ignores

anharmonicity and collective lattice vibrations effects. However, dilute Al_{Ti} substitution will not significantly influence such effects. Thus, the harmonic approximation provides qualitative insights into attempt frequency differences vs. adatom type, surface orientation, and Al_{Ti} substitution.

Changes in the Ti, Al, and N attempt frequencies due to Al_{Ti} substitution are all very small. The largest change is to ν_0^{Ti} which is reduced by 33% reduction from $2.03 \times 10^{12} \text{ s}^{-1}$ at bulk sites on $\text{TiN}(001)$ adjacent to Al_{Ti} ; all other ν_0^{Ti} changes are less than 10%. ν_0^{Al} is at most affected by a 20% decrease at the bulk site on $\text{TiN}(111)$, and 13% on average. The N adatom is most affected by Al_{Ti} ; the largest ν_0^{N} changes are increases of 122% and 105% at the bridge site on $\text{TiN}(011)$ and the threefold site on $\text{TiN}(001)$ respectively; the average effect at other N sites is only $\pm 16\%$ depending on the site.

Taken together, the differences in Ti and Al attempt frequencies are at most 33%, which, at 800 K, would give the same change in D as a change in the diffusion barrier by 0.076 eV. Thus, the primary effect of Al_{Ti} substitution on adatom surface diffusion is due to changes in E_{act} , not ν_0 .

Table A.8: Jump length l for Ti, Al, and N adatoms on $\text{TiN}(001)$, (011) , and (111) surfaces. Values for the $\langle 100 \rangle$ direction on $\text{TiN}(011)$ are given within parenthesis.

Adatom species	$l_{(001)} [\text{\AA}]$	$l_{(011)} [\text{\AA}]$	$l_{(111)} [\text{\AA}]$
Ti	1.50	3.01(4.26)	1.74
Al	3.01	3.01(4.26)	1.74
N	3.01	2.05(1.60)	1.74

Table A.9: Attempt frequencies ν_0 for Ti adatom migration on $\text{TiN}(001)$, $\text{TiN}(011)$ and $\text{TiN}(111):\text{N}$ surfaces with and without a substituted Al_{Ti} surface atom.

Binding site	$\nu_{0,\text{TiN}} [s^{-1}]$	$\nu_{0,\text{Ti(Al)N}} [s^{-1}]$
(001)		
Bulk site	2.03×10^{12}	1.36×10^{12}
Hollow site	3.93×10^{12}	3.54×10^{12}
(011)		
Bulk site ⁹	4.42×10^{12}	4.83×10^{12}
Bulk site ¹⁰	5.47×10^{12}	5.45×10^{12}
(111):N		
Bulk site	6.03×10^{12}	5.62×10^{12}
Atop Ti site	5.09×10^{12}	5.39×10^{12}

Table A.10: Attempt frequencies ν_0 for Al adatom migration on TiN(001), TiN(011) and TiN(111):N surfaces with and without a substituted Al_{Ti} surface atom.

Binding site	$\nu_{0,\text{TiN}} [s^{-1}]$	$\nu_{0,\text{Ti(Al)N}} [s^{-1}]$
(001)		
Bulk site	3.27×10^{12}	2.93×10^{12}
(011)		
Bulk site ¹¹	5.05×10^{12}	5.40×10^{12}
Bulk site ¹²	6.42×10^{12}	5.81×10^{12}
(111):N		
Bulk site	8.03×10^{12}	6.50×10^{12}
Atop Ti site	1.03×10^{13}	8.34×10^{12}

Table A.11: Attempt frequencies ν_0 for N adatom migration on TiN(001), TiN(011) and TiN(111):Ti surfaces with and without a substituted Al_{Ti} surface atom.

Binding site	$\nu_{0,\text{TiN}} [s^{-1}]$	$\nu_{0,\text{Ti(Al)N}} [s^{-1}]$
(001)		
Fourfold hollow site	1.26×10^{13}	1.34×10^{13}
Threefold site	7.59×10^{12}	1.72×10^{13}
(011)		
Bulk	8.35×10^{12}	6.67×10^{12}
Bridge site	3.62×10^{12}	8.03×10^{12}
(111):Ti		
Bulk site	9.28×10^{12}	1.18×10^{13}
Atop N site	9.00×10^{12}	9.83×10^{12}