Ab initio Molecular Dynamics Simulations of Nitrogen/VN(001) Surface Reactions: Vacancy-Catalyzed N\textsubscript{2} Dissociative Chemisorption, N Adatom Migration, and N\textsubscript{2} Desorption

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Abstract

We use density-functional \textit{ab initio} molecular dynamics to investigate the kinetics of N/VN(001) surface reactions at temperatures ranging from 1600 to 2300 K. N adatoms (N\textsubscript{ad}) on VN(001) favor epitaxial atop-V positions, and diffuse among them by transiting through fourfold-hollow (FFH) sites, at which they are surrounded by two V and two N surface atoms. After several atop-V→FFH→atop-V jumps, isolated N adatoms bond strongly with an underlying N surface (N\textsubscript{surf}) atom. Frequent N\textsubscript{ad}/N\textsubscript{surf} pair exchange reactions lead to N\textsubscript{2} desorption, which results in the formation of an anion surface vacancy. N vacancies rapidly migrate via in-plane <110> jumps and act as efficient catalysts for the dissociative chemisorption of incident N\textsubscript{2} molecules. During exposure of VN(001) to incident atomic N gas atoms, N\textsubscript{ad}/N\textsubscript{ad} recombination and desorption is never observed, despite a continuously high N monomer surface coverage. Instead, N\textsubscript{2} desorption is always initiated by a N adatom removing a N surface atom or by energetic N gas atoms colliding with N\textsubscript{ad} or N\textsubscript{surf} atoms. Similarities and differences between N/VN(001) vs. previous N/TiN(001) results, discussed on the basis of temperature-dependent \textit{ab initio} electronic structures and chemical bonding, provide insights for controlling the reactivity of NaCl-structure transition-metal nitride (001) surfaces via electron-concentration tuning.
1. Introduction

Transition-metal (TM) nitride refractory compounds possess a unique combination of properties including high hardness,1-3 toughness,4, 5 chemical inertness,6, 7 tunable optical properties,8-10 thermal stability,11 and good electrical conductivity.2, 12 Currently, these materials are widely employed as wear-resistant protective coatings on cutting tools13 and engine components,14 diffusion barrier in microelectronic devices,15-18 and active layers in energy-harvesting thermoelectric and piezoelectric devices.19, 20 Recently, refractory TM nitrides have been suggested as highly promising candidates to replace noble metals in plasmonic devices for high-temperature optoelectronic applications.21-23 In addition, they are known to exhibit high catalytic activities for important reactions including hydrogenolysis, hydrogenation, and methanation.24-27

The properties of TM nitrides ultimately depend on their nanostructure28-32 and stoichiometry.33-35 Growth and surface morphological evolution of titanium nitride (TiN), one of the first hard-coating materials,36, 37 have been extensively studied experimentally.38-45 Vanadium nitride (VN), another important TM nitride, although not as well characterized as TiN, is of interest for low-friction, hard coatings.46, 47 Moreover, supercapacitors based upon VN deliver remarkable specific capacitance with high energy and high power densities, the properties required for developing efficient energy-storage devices.48 VN and VN-based nanostructures are also promising anode materials for rechargeable lithium batteries.49, 50 Recently, NaCl-structure (cubic-B1) VN(001) has been identified as a novel electrode material for the synthesis of ammonia at room temperature and atmospheric pressure, a requirement for sustainable production of inorganic fertilizers.51, 52

Understanding fundamental processes such as dissociative N₂ chemisorption, mass transport of N and metal adatoms, and associative N₂ desorption, which together control the nucleation and growth kinetics of TM nitride layers, requires resolving surface dynamics at the picosecond time-scale. This is beyond the capabilities of atomic-scale experimental techniques such as scanning
tunneling microscopy (STM)\textsuperscript{38, 39} and low-energy electron microscopy.\textsuperscript{53} Thus, complementary computational investigations are necessary for detailed interpretation of experimental observations.

\textit{Ab initio} density functional theory (DFT) is routinely used to predict adatom and admolecule adsorption-energy landscapes, minimum energy paths, and migration energies $E_a$ on surfaces at 0 K.\textsuperscript{54-57} Diffusion rates can then be extrapolated to finite temperatures by transition-state theory\textsuperscript{58, 59} employing 0 K energy barriers and Arrhenius prefactors. This approximation, however, is not applicable to materials systems, such as NaCl-structure VN,\textsuperscript{60} which is stable at room temperature due to large vibrational entropy contributions to the Gibbs free energy of formation, but dynamically unstable with imaginary phonon frequencies at 0 K.\textsuperscript{61} Molecular dynamics (MD) inherently resolves the above issues by integrating Newton’s equations of motion for each atom. Thus, MD provides reliable diffusion rates and can reveal non-intuitive system configurations and reaction pathways at finite temperatures.\textsuperscript{62, 63}

Very few theoretical studies have considered the interaction of TM nitride surfaces with gases and metal adatoms via \textit{ab initio} molecular dynamics (AIMD).\textsuperscript{64, 65} Recently, we investigated mass transport of Ti and N adatoms, together with TiN$_x$ ($x = 1–3$) admolecules, on TiN(001) [62, 66-69] and TiN(111) [70] surfaces, and bulk diffusion in TiN,\textsuperscript{63} by both \textit{ab initio} and classical molecular dynamics. MD simulations show that isolated N adatoms (N$_{ad}$) on TiN(001) favor threefold sites (TFS) near, and strongly bonded with, nitrogen surface atoms (N$_{surf}$) and bounded by two Ti surface atoms. After several N$_{ad}$/N$_{surf}$ exchange reactions, over times corresponding to very few N$_{ad}$ surface jumps, the N$_{ad}$/N$_{surf}$ pair desorbs, thus leaving a N$_{surf}$ vacancy in the upper substrate layer.\textsuperscript{62}

Similar to our observations for N adatom behavior on TiN(001),\textsuperscript{62} previous \textit{ab initio} and experimental results indicate that oxygen adatoms on Group-IVb TM carbide (001) surfaces also adsorb in TFS positions, and then desorb as CO molecules by extracting a carbon surface atom.\textsuperscript{71-76} In contrast, DFT results,\textsuperscript{72, 73, 77-79} supported by experimental observations,\textsuperscript{76, 80} show that oxygen monomers on (001) Group-IVb and Group-Vb TM nitride surfaces, as well as Group-Vb and Group-VIb TM carbide surfaces are found to chemisorb close to \textit{both} TFS and metal-atom atop
sites, with no distinct preference. For the pseudobinary Ti$_{0.5}$Al$_{0.5}$N(001) surface, which has a valence electron concentration (VEC) of 8.5 (less than that of TiN and VC, both with VEC = 9), AIMD simulations$^{64}$ and x-ray photoelectron spectroscopy$^{81}$ results have shown that oxygen adatoms bond preferentially to metal surface atoms.

The experimental and theoretical observations described above suggest that the electron-concentration in the vicinity of the adatom-adsorption-site (ECAS = substrate VEC + adatom valence-electron number) controls the behavior of isolated non-metal adatoms on (001) TM nitride and carbide surfaces. For ECAS ≤ 14 (e.g., N$_{ad}$ on the Group-IVb TM nitride TiN with ECAS = 14), non-metal adatoms adsorb at TFS positions, strongly-bonded to the nearest-neighbor non-metal surface atom. In contrast, with ECAS > 14 (e.g., N$_{ad}$ on the Group-Vb TM nitride VN with ECAS = 15), the adsorption energies for non-metal adatoms residing close to either cation or anion surface sites are comparable.

The population of surface electronic states affects not only preferred adatom adsorption sites, but also the nature (attractive or repulsive) of adsorbate/adsorbate interactions.$^{82-87}$ For N adatoms on TiN(001), electronic-structure analyses show that associative N$_{ad}$/N$_{ad}$ recombination and desorption is considerably less likely than N$_{ad}$/N$_{surf}$ desorption due to the high activation energy (∼2 eV) required to overcome long-range N$_{ad}$/N$_{ad}$ repulsive interactions.$^{62}$

NaCl-structure TM nitride systems have wide single-phase compound fields and varying the stoichiometry ratio (N/TM) during synthesis has been used to tune electrical,$^{34, 88, 89}$ optical,$^{90-92}$ structural,$^{93-96}$ catalytic,$^{97, 98}$ and mechanical$^{33, 35, 89, 99}$ properties. Thus, elucidation of the mechanisms leading to anion-vacancy formation and N$_2$ desorption during synthesis may provide guidance for adjusting experimental conditions to tailor the material’s characteristics to meet specific requirements. Motivated by the outstanding properties of VN, we choose N$_{ad}$/VN(001), with ECAS = 15, as a model system to probe N$_{ad}$ surface kinetics and compare the results with the previously reported behavior of N$_{ad}$/TiN(001),$^{62}$ ECAS = 14. We employ density-functional-based AIMD simulations to follow the dynamics of nitrogen incorporation and surface migration on, as
well as desorption from, VN(001).

The paper is organized as follows. In Section 2.1, we describe the methodology for calculating N/VN(001) surface dynamics and surface mass transport (including migration of isolated N adatoms and surface anion vacancies) as well as $N_{\text{ad}}/N_{\text{surf}}$ exchange and desorption reaction rates from VN(001) as a function of temperature. A description of the model employed to simulate the interaction of N gas atoms with VN(001) is presented in Section 2.2, while Section 2.3 outlines the procedure used to calculate temperature-dependent electronic structures and the bonding nature of $N_{\text{ad}}$/VN(001) vs. $N_{\text{ad}}$/TiN(001). Results are presented in Section 3. Sections 3.1 and 3.2 focus on the dynamics of isolated N adatoms on VN(001) and the effects of temperature on adatom/surface electronic structures and bonding characteristics. Dynamic and kinetic results for $N_{\text{ad}}/N_{\text{surf}}$ surface exchange reactions and desorption from VN(001) are presented in Section 3.3. Section 3.4 describes results for N-vacancy migration and vacancy-catalyzed $N_2$ dissociative chemisorption. AIMD simulation results for N gas interactions with VN(001) are summarized in Section 3.5. Section 3 ends with a discussion (Section 3.6) of the implications of N/VN(001) reaction kinetics on the catalytic properties of VN(001) surfaces. Our overall findings are summarized in Section 4.

2. Theoretical methods

DFT-based AIMD simulations are carried out using the VASP code$^{100}$ implemented with the generalized gradient approximation (GGA)$^{101}$ and the projector augmented wave method.$^{102}$ The calculations are performed within the canonical ensemble NVT, integrating the equations of motion at 1 fs time intervals, and controlling temperature via the Nosè-Hoover thermostat. At each time-step, the total energy is evaluated to an accuracy of $10^{-5}$ eV/atom using a plane-wave energy cutoff of 400 eV, while sampling the $\Gamma$-point in the Brillouin zone. Thermally-induced electronic excitations are accounted for by employing $k_B T$ electron-smearing energies. The visual molecular dynamics (VMD) software$^{103}$ is used to generate images and videos of the results.

2.1. N adatom and vacancy dynamics on VN(001). N adatom diffusion pathways and
jump rates are probed as a function of temperature on 3x3 VN(001) surface unit cells. The substrate consists of three layers for a total of 108 atoms. The lateral size of the simulation cell is sufficient to avoid adatom self-interactions as shown previously for N\textsubscript{ad}/TiN(001) \cite{62}. During all runs, the bottom slab layer remains fixed. This does not affect the substrate temperature, which depends only on the atomic-motion translational degrees of freedom. The simulation boxes contain a 16.8-Å-thick vacuum layer to minimize the interaction between VN(001) surface slab replicas. The average in-plane V–N nearest-neighbor distance \( d_{\text{NN//}} \) in the simulation slab is obtained as a function of temperature, accounting for the experimental NaCl-structure VN average thermal expansion coefficient, \( 9.7 \times 10^{-6} \text{ K}^{-1} \) \cite{104}, by rescaling the 0 K DFT \( d_{\text{NN//}} \) value (2.06 Å). Rescaling \( d_{\text{NN//}} \) as a function of temperature is necessary to avoid spurious substrate strain effects on adatom jump rates.\textsuperscript{105} Prior to initiating each AIMD run, thermal oscillations in the adatom-free simulation slab are allowed to stabilize for two ps, a time interval sufficient to equilibrate the system.

On TiN(001), N adatoms migrate almost exclusively among stable TFS positions, crossing metastable FFH sites; atop-Ti sites are rarely sampled.\textsuperscript{62} In contrast, N adatoms on VN(001) due to the compound having an additional valence electron, can reside in TFS as well as atop-V sites. In order to identify the preferred N\textsubscript{ad} adsorption site, fourfold-hollow sites on VN(001) are chosen as adatom starting positions. The probabilities for N adatoms jumping from initial FFH sites to neighboring epitaxial positions (atop-V) vs. a threefold site, are proportional to jump-rate ratios \( k_{\text{FFH} \to \text{atop-V}}/k^{*} \) and \( k_{\text{FFH} \to \text{TFS}}/k^{*} \), respectively, for which \( k^{*} = (k_{\text{FFH} \to \text{atop-V}} + k_{\text{FFH} \to \text{TFS}}) \).

Stoichiometric VN crystallizes in the B1 NaCl structure over the temperature range from 250 K \cite{60} (VN is tetragonal at lower temperatures) to the decomposition temperature \( T_{\text{dec}} = 2450 \text{ K} \) \cite{106-108}. This allows us to employ high simulation temperatures and obtain well-converged rate constants. AIMD runs of 0.525, 0.3, 0.125, and 0.1 ns are performed at 1600, 1900, 2100, and 2300 K, respectively.

The rate \( k_{X} \) of thermally-activated process \( X \) is obtained by dividing the number of events \( n_{X} \) occurring during the time \( t_{X} \) the system remains in configurations from which the event \( X \) can
be initiated. Activation energies $E_X$ and attempt frequencies $A_X$ are obtained using a linear regression fit to the Arrhenius equation

$$\ln[k_X(T)] = \ln(A_X) - \frac{E_X}{k_B T},$$

(1)

for which $k_B$ is the Boltzmann constant. Statistical uncertainties $\sigma_k$, $\sigma_{\ln(k)}$, $\sigma_E$, and $\sigma_A$ in the values of $k$, $\ln(k)$, $E_X$, and $A$ are obtained as described previously. In brief, $\sigma_E$ and $\sigma_A$ correspond to the widths of the normal distributions in $E_X$ and $A$ obtained from linear interpolation of a large number of stochastically-created $\{\ln[k(T_i)]\}$ data sets. Gaussian $\ln[k(T_i)]$ distributions are characterized by standard deviations $\sigma_{\ln(k)}$. The sensitivity of surface rate constants $k_X$ to substrate thicknesses is assessed in preliminary benchmarking tests employing five-layer slabs comprised of 180 atoms. Three AIMD test runs, 20 ps each, are performed at 1900 K and other three runs of 20 ps each are carried out at 2100 K. $N_{ad}$ migration, surface anion-vacancy jump rates, and $N_{ad}/N_{surf}$ exchange rates, which are obtained with reasonably small uncertainties $\sigma_k$, are in good agreement with the corresponding $k_X$ values determined for three-layer slabs.

$N_{ad}$ atom surface migration is ultimately limited by $N_{ad}/N_{surf}$ desorption. Thus, the diffusion coefficient of isolated $N$ adatoms is negligible. Anion surface vacancies formed by $N_{ad}/N_{surf}$ desorption migrate in plane (intralayer diffusion) with diffusivities $D_{N_{vac}}(T_i)$ estimated at temperatures $T_i$ as

$$D_{N_{vac}}(T_i) = k_{N_{vac}}(T_i) \cdot d_{NN}(T_i)^2/2,$$

(2)

Uncertainties $\sigma_D$ for diffusion coefficient values are proportional to those of vacancy jump rates. Thus, activation energies $E'_a$ and diffusion prefactors $D_0$, with corresponding uncertainties $\sigma'_a$ and $\sigma'_D$, can be obtained from interpolation of the $\{D(T_i) \pm \sigma_D(T_i)\}$ data set. This leads to a general expression for temperature-dependent diffusion coefficients:

$$D(T) \left[ \sigma_D(T) \right]^{-1} = A' \cdot \left[ \sigma'_A \right]^{-1} \cdot \exp \left[ -\left( E'_a \mp \frac{\sigma'_E}{\sqrt{2}} \right)/(k_B T) \right].$$

(3)
2.2. VN(001) exposure to atomic N gas. AIMD simulations are also used to study the interaction of gas-phase N atoms with the VN(001) surface (results described in Sec. 3.5). A 20-ps simulation is carried out at 1900 K, integrating the equations of motion at 2-fs time steps. The VN(001) slab, comprised of three layers, each containing 64 atoms, is thermally equilibrated for 3 ps. Ten N gas (N_{gas}) atoms, with initial velocities assigned stochastically based upon a 1900 K Maxwell-Boltzmann distribution, are placed at random initial positions in a 10-Å-thick vacuum region beginning 5 Å above the surface. A static monolayer of 64 He atoms (with the He–He interatomic spacing set to d_{NN/}) is added in the upper part of the simulation box, at ~2 Å from the [001] supercell replica, to prevent gas adsorption at the frozen bottom slab-layer. Helium is chemically inert and allows for faster calculations compared to the use of noble gases possessing p valence electrons.

The ideal gas law provides an estimate of the nitrogen gas pressure to which the surface is exposed. The simulated nitrogen pressure, ~10 MPa (~75x10^{3} Torr), is several orders of magnitude larger than N_{2} pressures typically used during reactive magnetron sputter deposition (≤ 20 mTorr),\(^{109}\) while comparable to that employed for the synthesis of stoichiometric VN by nitridation of vanadium at temperatures ranging from 1400 to 2000 K \([104, 110]\) and for producing bulk cubic VN\(_{x}\) (0.74 ≤ x ≤ 1) samples by float-zone and zone-annealing techniques at 2300 K.\(^{111}\) High nitrogen pressures allow us to follow, over feasible simulation times, N and N\(_{2}\) gas/surface reactions (both N and N\(_{2}\) species are present in the plasma during reactive sputter deposition\(^{112}\)).

2.3. N\(_{ad}\)/VN(001) and N\(_{ad}\)/TiN(001) room-temperature electronic structures. N\(_{ad}\)/TM\(_{surf}\) bonding (TM\(_{surf}\) = surface transition-metal atom) is investigated for both VN(001) and TiN(001) directly via AIMD simulations at 300 K. Accounting for the effect of lattice vibrations on the VN(001) electronic structure is necessary due to the instability of cubic VN below 250 K.\(^{60}\) The calculations are carried out for VN(001) and TiN(001) slabs, each comprised of five layers with 4x4 atoms per layer (80 atoms) and two N\(_{ad}\) species in specular atop-TM\(_{surf}\) positions below the bottom layer and above the upper slab layer; mirroring is used in order to cancel adatom-induced slab
polarization. Six vacuum layers separate slab replicas along [001].

Representative 300 K electronic properties are determined by averaging over DFT results obtained for fifty different AIMD \textit{frozen} atomic configurations stochastically extracted from 400 AIMD steps, with the condition that the distance of both adatoms from the original epitaxial atop-TM$_{\text{surf}}$ positions is shorter than 1/8 of the metal–N in-plane spacing. For these calculations, the Brillouin zone is integrated on 5x5x1 Γ-centered k-point grids. We determine temperature-dependent density of states (DOS) projected onto spherical harmonics centered at atomic positions, charge densities resolved within energy intervals containing N$_{\text{ad}}$/TM$_{\text{surf}}$ hybridized states, and energy-resolved N$_{\text{ad}}$/TM$_{\text{surf}}$ overlap populations (OP)\textsuperscript{114,115} which are a projection of the local DOS into bonding (positive OP values) and anti-bonding (negative OP values) states. The overlap integrals are set to ±1, for which the sign depends on the relative orientation of N$_{\text{ad}}$ and TM$_{\text{surf}}$ orbitals.

3. Results and discussion

3.1. N adatom surface migration. Figure 1 provides plan- and side-view schematic illustrations of N adatom migration on VN(001). At temperatures between 1600 and 2300 K, the most probable migration path for N$_{\text{ad}}$ species starting in VN(001) FFH sites is toward epitaxial atop-V positions. N adatoms travel among epitaxial sites (Fig. 1[(a), (e)]) passing through transition-state FFH positions (Fig. 1[(b), (f)]). During migration, the N adatom pulls the V surface atom (V$_{\text{surf}}$) to which it is most strongly bonded toward the FFH site and attracts the opposite V$_{\text{surf}}$ nearest-neighbor (Fig. 1[(b), (f)]). The V$_{\text{surf}}$-N$_{\text{ad}}$-V$_{\text{surf}}$ transition-state quickly evolves into a stable configuration; N$_{\text{ad}}$ species can jump to an epitaxial atop-V site (including back to the previous one, (Fig. 1[(c), (g)])) or, more rarely, to one of the neighboring TFS positions, (Fig. 1[(d), (h)]), with the two V$_{\text{surf}}$ atoms returning to their initial positions.

N$_{\text{ad}}$ transition rates [atop-V $\rightarrow$ FFH] and [FFH $\rightarrow$ TFS] follow Arrhenius relationships over the temperature range investigated (see Fig. 2). Between 1600 and 2300 K, k$_{\text{atop-V $\rightarrow$ FFH}}$ values are one to two orders of magnitudes larger than k$_{\text{FFH $\rightarrow$ TFS}}$. Note, however, that k$_{\text{FFH $\rightarrow$ TFS}}$ accounts only
for the time spent by a nitrogen adatom in FFH positions (see Sec. 2.1), which is a small fraction of the total surface-migration time. From the dependence of \( \ln(k_{\text{diff}}) \) on \( 1/T \), we extract activation energies \( E_{\text{atop-V} \rightarrow \text{FFH}} = 0.79 \pm 0.13 \) eV and \( E_{\text{FFH} \rightarrow \text{TFS}} = 1.5 \pm 0.9 \) eV, with attempt frequencies \( \Lambda_{\text{atop-V} \rightarrow \text{FFH}} = 4.82(\times2.6^{\pm1}) \times 10^{13} \text{ s}^{-1} \) and \( \Lambda_{\text{FFH} \rightarrow \text{TFS}} = 52(\times60^{\pm1}) \times 10^{13} \text{ s}^{-1} \). The large error bars for \( k_{\text{FFH} \rightarrow \text{TFS}} \) rates are due to low statistics for these events.

**Figure 1.** Schematic representation of \( N_{\text{ad}}/\text{VN}(001) \) surface diffusion in (a-d) plan views and (e-h) side views. [(a), (e)] The favored site for \( N_{\text{ad}} \) adsorption is the epitaxial atop-V position. [(b), (f)] \( N_{\text{ad}} \) surface migration occurs via FFH transition states. From a FFH site, \( N_{\text{ad}} \) can migrate to either [(c), (g)] an atop-V site or [(d), (h)] a TFS position, close to a N surface atom. FFH = fourfold hollow and TFS = threefold site.
Figure 2. \( N_{ad} \) diffusion jump rate \( k_{diff} \) on VN(001) as a function of temperature \( T \). Red filled squares correspond to adatom migration from FFH sites to TFS positions along <110> directions. Blue open circles correspond to the rate of <110> \( N_{ad} \) migration from atop-V to FFH. The VN decomposition temperature \( T_{dec} \) is \(~2450\) K. FFH = fourfold hollow and TFS = threefold site.

\( N_{ad} \) in a TFS position bonds strongly to the underlying nearest-neighbor \( N_{surf} \); it is therefore unlikely that a free \( N \) monomer reforms (see Sec. 3.3 below) after \( N_{ad} \) [FFH \( \rightarrow \) TFS] migration. Thus, \( N \) adatom migration on VN(001) occurs preferentially along atop-V \( \rightarrow \) FFH \( \rightarrow \) atop-V pathways. In contrast, on TiN(001), \( N_{ad} \) species move almost exclusively among TFS, through FFH, by breaking and reforming highly energetic \( N_{ad}/N_{surf} \) bonds.\(^{62}\) This results in significantly higher \( N_{ad} \) mobilities on VN(001) than on TiN(001) at all temperatures (Fig. 3). Nevertheless, as described below, the \( N_{ad} \) surface mobility is ultimately limited, for both VN(001) and TiN(001), by \( N_{ad}/N_{surf} \) desorption rates.

AIMD simulations at 1900 K also reveal an unexpected \( N_{ad}/VN(001) \) reaction. On one occasion, a \( N \) adatom pulls a V surface atom onto the surface to form a VN admolecule, while a second-layer V atom moves into the vacated upper-layer cation site, indicating relatively strong V-V bonds in VN.\(^{116}\) After a few VN dimer rotations, the V dimer-atom displaces a V surface atom which fills the second-layer cation vacancy. Rotation of TiN\( _x \) (\( x = 1-3 \)) species was previously
observed during classical molecular dynamics simulations of admolecule diffusion on TiN(001) terraces and islands.\textsuperscript{67,69}

Figure 3. $N_{\text{ad}}$/VN(001), blue open circles, and $N_{\text{ad}}$/TiN(001), black filled triangles, jump rates $k_{\text{diff}}$ as a function of temperature $T$. The VN decomposition temperature $T_{\text{dec}}^{\text{VN}}$ is $\sim2450$ K and the TiN melting point $T_{\text{melt}}^{\text{TiN}}$ is $\sim3200$ K.

3.2. $N_{\text{ad}}$/VN(001) and $N_{\text{ad}}$/TiN(001) electronic structures. In Section 1, we proposed an empirical rule based on adatom/surface electron densities, ECAS = substrate VEC + adatom valence-electron number, which systematizes in a consistent manner the present AIMD results, as well as previous experimental and \textit{ab initio} results, for preferred non-metal adatom adsorption sites on TM nitride and carbide (001) surfaces. In adsorption reactions for which ECAS is $\leq 14$, non-metal adatoms adsorb at TFS positions, strongly-bonded to the nearest-neighbor non-metal surface atom. However, with ECAS $> 14$, the adsorption energies for non-metal adatoms residing close to either cation or anion surface sites are comparable (see literature survey in Sec. 1).

On TiN(001), N adatoms adsorb and migrate exclusively among TSF positions\textsuperscript{62} as both FFH and atop-Ti$_{\text{surf}}$ sites are saddle-points in the $N_{\text{ad}}$/TiN(001) adsorption-energy landscape,\textsuperscript{117} consistent with an ECAS value of 14. In contrast, on VN(001) (ECAS = 15), N adatoms travel
primarily among atop-V surface epitaxial sites, also in agreement with the empirical prediction, and the formation of N\textsubscript{ad}/N\textsubscript{surf} pairs is kinetically hindered.

Room-temperature electronic properties explain the role of the additional valence electron for VN(001) vs. TiN(001) in stabilizing N adatoms at surface epitaxial sites. Figs. 4, 5, and 6 are plots of densities of states, overlap populations, and electron densities in N\textsubscript{ad}/TM\textsubscript{surf} hybridized states for VN(001) and TiN(001) with a N adatom placed at atop-TM\textsubscript{surf} positions.

DOS curves calculated for N\textsubscript{ad}/VN(001) and N\textsubscript{ad}/TiN(001) exhibit very similar shapes. However, due to VN having a higher electron density than TiN, the DOS of VN is shifted to lower energies. The sharp DOS peaks near the Fermi energies of N\textsubscript{ad}/VN(001), Fig. 4(a), and N\textsubscript{ad}/TiN(001), Fig. 4(b), derive mainly from $\sigma$ N\textsubscript{ad}(p\textsubscript{z})–TM\textsubscript{surf}(d\textsubscript{z\textsuperscript{2}}) states. For VN, these states are located at binding energies which are ~1.3 eV higher than for TiN (see insets in Fig. 4(a) and (b)). A secondary adatom/surface electronic interaction stems from $\pi$ N\textsubscript{ad}(p\textsubscript{x+y})–TM\textsubscript{surf}(d\textsubscript{xz}+d\textsubscript{yz}) orbitals, centered at approximately -1.8 eV for VN and -0.4 eV for TiN.

For both VN(001) and TiN(001) surfaces, (p\textsubscript{z})–(d\textsubscript{z\textsuperscript{2}}) and (p\textsubscript{x+y})–(d\textsubscript{xz}+d\textsubscript{yz}) N\textsubscript{ad}/TM\textsubscript{surf} orbital overlap, schematically illustrated in Fig. 5(a), produce bonding $\sigma$ and $\pi$ states, respectively, as evidenced by the OP vs. energy curves in Fig. 5(b) remaining positive. A comparison of the magnitude of N\textsubscript{ad}/VN(001) vs. N\textsubscript{ad}/TiN(001) OP values demonstrates that $\sigma$ and $\pi$ N\textsubscript{ad}/TM\textsubscript{surf} bonds are both much stronger for VN(001) (Fig. 5(b)). The shift in adatom surface states to lower energies, together with N\textsubscript{ad}/V\textsubscript{surf} bonds being significantly stronger than N\textsubscript{ad}/Ti\textsubscript{surf} bonds, explains the gain in N adatom stability at epitaxial sites provided by the additional valence electron in VN.

The latter finding is supported by results for charge densities resolved within energy intervals containing primarily N\textsubscript{ad}/TM\textsubscript{surf} electronic states. While specific chemical bonds are not easily distinguishable in the total electron density of a solid, the partial charge density technique allows visualization of the chemical bond of interest. The energy intervals used to map N\textsubscript{ad}/TM\textsubscript{surf} bonds (see insets in Fig. 4) range from -1.6 to -1.3 eV for $\sigma$ bonds and from -2.0 to -1.6 eV for $\pi$ bonds on VN(001) and from -0.3 eV to the Fermi level for $\sigma$ bonds and from -0.7 to -0.3 eV for $\pi$
bonds on TiN(001). The electron distributions in Fig. 6 confirm that both $\sigma$ and $\pi$ $N_{ad}/TM_{surf}$ bonds are much stronger for VN than for TiN due to higher electron densities between $N_{ad}$ and $V_{surf}$ atoms.
Figure 4. Density of states projected onto spherical harmonics centered at atomic positions for (a) VN(001) and (b) TiN(001) with a N adatom at an atop-TM$_{\text{surf}}$ site at 300 K. The insets are enlarged views of N$_{\text{ad}}$/TM$_{\text{surf}}$ hybridized states.
Figure 5. $N_{ad}/TM_{surf}$ bonding on VN(001) and TiN(001). (a) Schematic representation of $N_{ad}/TM_{surf}$ orbital overlap. (b) Overlap population (OP) for $N_{ad}/TM_{surf}$ bonding states near the Fermi level.

Figure 6. Energy-resolved charge densities for N adatoms at atop-$TM_{surf}$ positions on TiN(001) and VN(001) at 300 K. (a) $\sigma_{N_{ad}(pz)}-TM_{surf}(dz^2)$ and (b) $\sigma_{N_{ad}(px+py)}-TM_{surf}(dxz+dyz)$ bonding states.
bonding orbitals for $N_{ad}/VN(001)$ and from -0.3 to 0 eV for $N_{ad}/TiN(001)$. The red to violet color scales are in units of electrons/Å$^3$.

### 3.3. $N_{ad}/N_{surf}$ surface exchange reactions and desorption

The bond strength and vibrational frequency of $N_{ad}/N_{surf}$ pairs on VN(001) are similar to those of isolated $N_2$ gas molecules. The preferred bond-axis orientation of $N_{ad}/N_{surf}$ pairs is along $<111>$, but frequently changes from $<111>$ to $<110>$ to $<111>$, resulting in $N_2$ dimer rotation. Analogous behavior was reported for $N_{ad}/N_{surf}$ pairs on TiN(001),$^{62}$ as well as for $N$-interstitial/N-lattice dimers in bulk TiN and CrN.$^{63,118}$

The most probable $N_{ad}/N_{surf}$ rotation event on VN(001) is precession, with the $N$ adatom migrating among TFS sites in adjacent surface unit cells, while remaining anchored to the same $N_{surf}$ atom, Figs. 7(a) and (b). Rotation can also occur by $N_{ad}/N_{surf}$ exchange. In this case, $N_{ad}$ takes the position of $N_{surf}$ (Fig. 7(c)) which is pushed upward into the diagonally-opposite TFS position (Fig. 7(d)). Calculated $N_{ad}/N_{surf}$ exchange activation energies and attempt frequencies are $E_{exch} = 0.46 \pm 0.11$ eV and $A_{exch} = 2.26 \times 10^{13}$ s$^{-1}$, respectively. On TiN(001), $N_{ad}/N_{surf}$ exchange occurs less frequently, $E_{exch} = 0.69 \pm 0.09$ eV and $A_{exch} = 1.00 \times 10^{13}$ s$^{-1}$ $^{62}$, reflecting stronger metal–N bonds than for VN(001). Occasionally (three observations at 2300 K and two at 2100 K), $N_{ad}/N_{surf}$ exchange on VN(001) provides sufficient kinetic energy for $N_{surf}$ to break the $N_{ad}/N_{surf}$ bond and move to a neighboring epitaxial position (Fig. 7(e)) as a free $N$ adatom. Exchange-induced $N_{surf}$ jumps were also observed in AIMD simulations of $N_{ad}/TiN(001)$ migration.$^{62}$ In the latter case, however, $N_{surf}$ moves to a metastable TiN(001) FFH position.

The most probable reaction, after several $N_{ad}/N_{surf}$ exchange events, is $N_{ad}/N_{surf}$ molecular desorption, Fig. 7(f), which results in the creation of an anion vacancy in the VN(001) surface (Fig. 7(g)). $N_{ad}/N_{surf}$ desorption rates on VN(001), calculated considering only the time spent by $N$ adatoms in TSF positions, correspond to attempt frequencies $A_{des} = 3.51 \times 10^{13}$ s$^{-1}$ and activation energies $E_{des} = 0.84 \pm 0.40$ eV (Fig. 8). Even accounting for the time spent by $N$ adatoms in migrating among atop-V sites, which lowers $N_{ad}/N_{surf}$ desorption rates, $N_{ad}/N_{surf}$ desorption from
VN(001) ($A_{\text{des}} = 4.65 \times 10^{13} \text{ s}^{-1}$ and $E_{\text{des}} = 1.00 \pm 0.40 \text{ eV}$) is overall much more frequent than from TiN(001) ($A_{\text{des}} = 3.37 \times 10^{13} \text{ s}^{-1}$ and $E_{\text{des}} = 1.37 \pm 0.30 \text{ eV}$)\(^\text{62}\) (see inset in Fig. 8).

**Figure 7.** Schematic representation of VN(001) surface reactions initiated by N\(_{\text{ad}}\) adsorbed in TFS positions. (a), (b) N\(_{\text{ad}}\) adatom precession among TFS positions in adjacent surface unit cells. (c) The exchange of a N\(_{\text{ad}}\) adatom with a N surface atom (in which N\(_{\text{ad}}\) takes the position of N\(_{\text{surf}}\)) can result
in: (d) simple exchange, with N_{surf} moving into the diagonally opposite TFS position, or (e) an exchange-induced N_{surf} jump, with N_{surf} moving onto the adjacent epitaxial atop site. (f) After several N_{ad}/N_{surf} exchange reactions, the N_{ad}/N_{surf}-pair desorbs, leaving (g) an anion surface vacancy (N_{vac}).

**Figure 8.** N_{ad}/N_{surf} desorption rates k_{des} from VN(001) as a function of temperature T. The inset compares the N_{ad}/N_{surf} desorption rate from VN(001) to that from TiN(001) accounting for N_{ad} surface migration times among epitaxial sites prior to N_{ad}/N_{surf} bond formation.

The ratio k_{diff}(T)/k_{des}(T) of N_{ad} diffusion rates k_{diff} to N_{ad}/N_{surf} desorption rates k_{des} quantifies N_{ad} mean surface migration events as a function of T (Fig. 9). For TiN(001), $k_{diff}(T)/k_{des}(T) = 3.53 \cdot \exp\left[-0.02 \text{eV}/(k_B T)\right]$ indicating that the average number of N_{ad} surface migration events prior to N_{2} desorption is three or four, independent of T between room temperature and the melting point. In contrast, k_{diff}(T)/k_{des}(T) varies significantly with T for N_{ad} on VN(001): $k_{diff}(T)/k_{des}(T) = 0.96 \cdot \exp\left[0.21 \text{eV}/(k_B T)\right]$. At 600 K, N_{ad} jumps among VN(001) epitaxial sites approximately one hundred times prior to N_{ad}/N_{surf} desorption; for T approaching the VN decomposition temperature, 2450 K, the adatom performs very few jumps, ~3, before leaving the surface as a N_{ad}/N_{surf} molecule.
The fact that the kinetics of N$_{ad}$ migration on, and N$_{ad}$/N$_{surf}$ desorption from, VN(001) (ECAS = 15) approaches, with increasing temperatures, that observed for TiN(001) (ECAS = 14) is attributed to progressively stronger vibrational effects which effectively cancel out the atop-V stability-gain derived from the additional valence electron. The $k_{\text{diff}}(T)/k_{\text{des}}(T)$ ratio results described above imply that, during (001) layer growth, the VN$_x$ nitrogen fraction $x$ is more sensitive to temperature than that of TiN$_x$. The fact that relatively low deposition temperatures delay N$_2$ desorption with respect to surface diffusion on VN(001) is consistent with experimental results for epitaxial layers grown by magnetron sputter deposition. High-quality single-crystal fully-dense cubic VN(001) thin films have been synthesized at ~700 K.$^{109}$ For comparison, the optimum temperature range for growth of dense epitaxial TiN(001) layers is ~1000-1200 K.$^{88,120}$
Figure 9. (a) Comparison of $N_{ad}$ migration rates $k_{diff}$ on, and $N_{ad}/N_{surf}$ desorption rates $k_{des}$ from, VN(001) and TiN(001) as a function of temperature $T$. (b) Temperature-dependent ratio of the $N_{ad}$ migration rate to the $N_{ad}/N_{surf}$ desorption rate for the two surfaces. The shaded areas indicate uncertainty ranges.

Figure 10, summarizing the above described surface reactions, illustrates a typical diffusion pathway for $N_{ad}$ on VN(001) at 1600 K. Within a fraction of a ps, the adatom migrates from its starting FFH position, labeled as time $t = 0$, to a stable atop-V epitaxial site. The adatom trajectory during the initial 19 ps of the simulation reveals that $N_{ad}$ spends relatively long times at atop-V epitaxial positions, while moving rapidly through FFH sites. At $t = 19$ ps, following six atop-V→FFH→atop-V surface transitions, the N adatom migrates from a FFH to a TFS site, in which it remains as part of a $N_{ad}/N_{surf}$ pair for an additional 21 ps. The $N_{ad}/N_{surf}$ dimer exchanges positions 17 times before desorbing as $N_2$ at $t = 40$ ps.

Figure 10. AIMD $N_{ad}$ migration pathway (solid red line) during 40 ps on VN(001) at 1600 K. The N adatom is initiated ($t = 0$) at a FFH site. Between 0 and 19 ps, $N_{ad}$ migrates among V-atop sites (six <110> diffusion events) by passing through FFH positions. At $t = 19$ ps, the adspecies jumps from a FFH to a TFS position, in which it bonds strongly to a $N_{surf}$ atom. During the remaining 21 ps, 17 $N_{ad}/N_{surf}$ exchange reactions are recorded. At $t = 40$ ps, the $N_{ad}/N_{surf}$ pair desorbs, leaving a N surface vacancy. Color legend: $V_{surf} =$ open circles, $N_{surf} =$ gray filled circles.
3.4. N-vacancy surface migration and vacancy-catalyzed N\textsubscript{2} dissociative chemisorption.

N\textsubscript{ad}/N\textsubscript{surf} desorption results in the formation of nitrogen surface vacancies N\textsubscript{vac} which give rise to relatively frequent N\textsubscript{vac}/VN(001) intralayer migration events at all temperatures investigated (1600 – 2300 K). In contrast, N\textsubscript{vac} intralayer migration was never observed in AIMD simulations of N\textsubscript{vac}/TiN(001) dynamics at temperatures up to 2500 K \cite{62} due to stronger metal-N bonds in TiN than in VN. N\textsubscript{vac} surface migration requires one of the four neighboring N\textsubscript{surf} atoms to migrate along <110> and fill the vacant anion site (Fig. 11(a)). In-plane diffusion of isolated N vacancies occurs with attempt frequencies $\Lambda_{N\text{vac}} = 0.31(\pm 1) \times 10^{13} \text{ s}^{-1}$ and activation energies $E_{N\text{vac}} = 0.25 \pm 0.05 \text{ eV}$ (Fig. 12), yielding diffusivities (Eqs. 2 and 3) with prefactors $\Lambda'_{N\text{vac}} = 7.25(\pm 1) \times 10^{-4} \text{ cm}^{2} \text{ s}^{-1}$ and activation energies $\Xi_{N\text{vac}} = 0.26 \pm 0.03 \text{ eV}$.

N\textsubscript{vac} interlayer diffusion in VN(001) is observed only once during a total simulation time of 40 ps, and only at the highest temperature, 2300 K, as a second-layer N atom fills a vacant anion surface site. This indicates that anion surface vacancies are highly stable, as expected for all TM nitrides; strong TM–N bonds hinder N diffusion.\textsuperscript{63, 121}

Due to the use of periodic boundary conditions, desorbed N\textsubscript{ad}/N\textsubscript{surf} molecules rebound from the bottom layer of the overlying slab replica to return to the upper layer of the slab from which they desorbed. AIMD simulations show that the presence of N vacancies catalyzes N\textsubscript{2} molecular dissociation on VN(001), as observed previously for TiN(001).\textsuperscript{62} N\textsubscript{2} dissociation is never observed for gas molecules incident at defect-free VN(001) surface regions. Occasionally, however, a N\textsubscript{2} molecule lands proximate to an anion surface vacancy. In each of these cases, one of the N\textsubscript{2} nitrogen atoms moves into the vacant anion site, while the other remains on the surface as a free adatom (Fig. 11(b)). This is analogous to the mechanism proposed, based upon STM experiments, for O\textsubscript{2} dissociation on TiO\textsubscript{2}(110).\textsuperscript{122} AIMD movies also show that N\textsubscript{2} dissociation on VN(001) can be directly followed by a N\textsubscript{ad}/N\textsubscript{surf} desorption reaction promoted by momentum transfer to the surface from the incident gas molecule.
Overall, N₂ dissociative chemisorption on VN(001) occurs every time a N₂ molecule is incident at the surface within approximately one interatomic distance d_{NN//} from an anion vacancy (five events in total), from which we infer that anion vacancies on NaCl-structure VN(001) are efficient catalytic agents.

**Figure 11.** (a) N vacancy migration along <110> requires one of the four neighboring N_{surf} atoms to jump into the empty surface anion site. (b) During N₂ dissociative chemisorption at surface anion vacancies, one N atom fills the vacancy site while the other becomes a free adatom.
In recent AIMD and DFT investigations, we have shown that \( \text{N}_{\text{ad}}/\text{N}_{\text{ad}} \) recombination on, and subsequent desorption from, TiN(001) is much less likely than \( \text{N}_{\text{ad}}/\text{N}_{\text{surf}} \) desorption (\( E_{\text{des}} = 1.4 \text{ eV} \)) due to \( \text{N}_{\text{ad}}/\text{N}_{\text{ad}} \) repulsive energies which rapidly increase to 2 eV as adatom/adatom separation decreases to 1.5 Å\textsuperscript{62}. The probability of \( \text{N}_{\text{ad}}/\text{N}_{\text{ad}} \) recombination on TiN(001) is further reduced because of the extremely short average distances travelled by isolated N adatoms prior to \( \text{N}_{\text{ad}}/\text{N}_{\text{surf}} \) desorption\textsuperscript{62}. The 0 K phonon instability of cubic VN \textsuperscript{[61]} does not allow for quantification of adatom/adatom attractive/repulsive potential-energy pathways on VN(001) via DFT. Thus, here we carry out AIMD simulations to probe the interaction of N gas atoms on VN(001) at 1900 K, well above 250 K, at which the cubic phase becomes stable\textsuperscript{60} in order to provide direct insight as to whether \( \text{N}_{\text{ad}}/\text{N}_{\text{ad}} \) recombination and desorption is more or less likely to occur than \( \text{N}_{\text{ad}}/\text{N}_{\text{surf}} \) pair formation and desorption (see Section 2.2 for computational details).

Figure 13 shows four images extracted from \( \text{N}_{\text{gas}}/\text{VN}(001) \) AIMD movies. Due to the complexity of \( \text{N}_{\text{gas}}/\text{VN}(001) \) reactions, it is difficult to accurately determine the fraction of incident N gas atoms reflected from the surface. We estimate that there are one or two N\textsubscript{gas} reflections out of a total of approximately 40 N\textsubscript{gas}/VN(001) surface collisions, yielding a capture probability of
N gas atoms are adsorbed on VN(001) with approximately equal probability at atop-V and TFS positions.

Calculated average N\textsubscript{ad}/N\textsubscript{surf} desorption rates from VN(001), 1.0\(\times\)3.0\(\times\)10\textsuperscript{12} \text{ s}^{-1} (note desorbed N\textsubscript{ad}/N\textsubscript{surf} molecules in Fig. 13(b)), correspond to N adatom lifetimes of approximately 0.5 ps. Although N\textsubscript{ad} surface coverages in these experiments range up to 0.2 ML, N\textsubscript{ad}/N\textsubscript{ad} recombination is never observed. Even when three N adatoms are located at adjacent TSF positions and/or atop-V sites, the most probable reaction pathway is N\textsubscript{ad}/N\textsubscript{surf} pair formation followed by exchange reactions and desorption. This suggests that N\textsubscript{ad}/N\textsubscript{ad} long-range interactions on VN(001) are strongly repulsive, similar to the case for N\textsubscript{ad}/TiN(001).\textsuperscript{62}

In addition to establishing that N\textsubscript{ad}/N\textsubscript{surf} desorption is much more likely than N\textsubscript{ad}/N\textsubscript{ad} recombinative desorption on VN(001), AIMD movies show that N\textsubscript{2} desorption can also be initiated by gas/surface collisions. The vibrational amplitude of N\textsubscript{2} gas molecules is perturbed and enhanced by the presence of N gas atoms. Occasionally, this leads to N–N bond breakage,\textsuperscript{123} which produces energetic (approximately 10 eV) N\textsubscript{gas} atoms. If an energetic N\textsubscript{gas} species is incident at a N adatom or a N surface atom, it forms, with \~100% probability, N\textsubscript{2} molecules which immediately desorb.

The creation of surface anion vacancies due to N\textsubscript{ad}/N\textsubscript{surf}, N\textsubscript{gas}/N\textsubscript{surf}, and N\textsubscript{gas}/N\textsubscript{ad} desorption leads to an average steady-state VN(001) surface stoichiometry of VN\textsubscript{0.96}. In most cases, N surface vacancies are promptly filled by itinerant N adatoms or by impinging N\textsubscript{gas} atoms (note, for example, the N\textsubscript{gas} atoms (shown in yellow) occupying anion positions in the VN(001) surface in Fig. 13(c)). During the N\textsubscript{gas}/VN(001) simulation, we also detect the dissociation of N\textsubscript{2} gas molecules which happen to collide proximate to N\textsubscript{vac} surface sites. As described in Sec. 3.4, one N atom fills the vacancy, while the other remains on the surface as a free N adatom.

On one occasion out of 10–15 events, the recoil of an energetic N\textsubscript{gas} atom from a V\textsubscript{surf} atom, Fig. 13(d), lifts the latter to form a VN admolecule. The presence of the VN admolecule promotes cluster growth. A nearby N\textsubscript{ad} species pulls up a V\textsubscript{surf} atom to form a second VN admolecule which bonds to the adjacent initial VN, thus producing an L-shape V\textsubscript{2}N\textsubscript{2} cluster with all atoms in epitaxial
positions. Next, an incident N\textsubscript{gas} atom bonds to the V\textsubscript{2}N\textsubscript{2} cluster to form a V\textsubscript{2}N\textsubscript{3} epitaxial island (indicated by the red circle in Fig. 13(d)). Fig. 14, a plan view image of the final simulation frame, summarizes the effects of N gas atoms on VN(001) surface morphology. The epitaxial V\textsubscript{2}N\textsubscript{3} island forms together with four surface vacancies: a next-nearest neighbor cation surface vacancy pair in which one of the V vacancies is adjacent to a N\textsubscript{vac} and an additional, isolated, N\textsubscript{vac}.

Experimental results for epitaxial growth of TiN\textsubscript{x}(001) [33, 88], as well as TaN\textsubscript{x}(001) [34, 124] and HfN\textsubscript{x},\textsuperscript{95} indicate that plasma activation producing gas-phase atomic N is essential for forming stoichiometric layers. Our simulation results are consistent with the experimental reports and show that N\textsubscript{2} is much less reactive than atomic N since the molecular species require interaction with surface anion vacancies (see Sec. 3.4) to promote dissociative chemisorption.
Figure 13. Images from AIMD movies of a pristine VN(001) surface exposed to N gas atoms at 1900 K. Color legend: yellow = N\textsubscript{gas}, black = N\textsubscript{surf}, silver = V\textsubscript{surf}, blue = He barrier atoms. Each panel shows four simulation-cell replicas. The dashed red circle in panel (d) indicates the formation of an epitaxial V\textsubscript{2}N\textsubscript{3} island. See Sec. 3.5 and Fig. 14 for further explanation.
Figure 14. Images from an AIMD movie of VN(001) exposed to N gas atoms. Color legend: yellow = N$_{\text{gas}}$, black = N$_{\text{surf}}$, silver = V$_{\text{surf}}$, orange = V island atom, green = N island atom (originally N$_{\text{gas}}$), blue = N island atom (originally N$_{\text{surf}}$), open blue circle = N$_{\text{vac}}$, and open green circle = V$_{\text{vac}}$. N$_{\text{vac}}$ and V$_{\text{vac}}$ indicate anion and cation surface vacancies, respectively. N$_{\text{ad}}$ = nitrogen adatoms. See text, Sec. 3.5, for further discussion.

3.6. Implications for TiN(001) vs. VN(001) catalytic properties. In addition to elucidating the effects of nitrogen precursor fluxes and temperatures for controlling the stoichiometry of TM nitride (001) layers, the results described in the previous sections, demonstrate the ability of surface anion vacancies to catalyze N$_2$ dissociation on VN(001), as well as on TiN(001) surfaces, and suggest a route to tune the catalytic reactivity of these surfaces. An example is the formation of ammonia at ambient conditions.$^{51,52}$

It has been recently suggested that free N adatoms on NaCl-structure TM nitride (001) surfaces$^{51}$ promote NH$_4^+$ formation upon hydrogenation. However, this reaction requires constant availability and reactivity of N adatoms. On TiN(001), N adatoms immediately form strong bonds with N surface atoms, as shown by AIMD simulations$^{62}$ and by the considerably larger N adatom adsorption energies in TFS than in FFH or atop-Ti$_{\text{surf}}$ positions.$^{117}$ Strong N$_{\text{ad}}$/N$_{\text{surf}}$ bonds do not favor N$_{\text{ad}}$ hydrogenation and release of ammonia. N$_{\text{ad}}$ species in TFS positions on VN(001) are also
highly stable due to the strong $N_{\text{ad}}/N_{\text{surf}}$ bond; however, the formation of $N_{\text{ad}}/N_{\text{surf}}$ pairs on VN(001) is kinetically hindered, as demonstrated by adatom surface migration rates being much higher than $N_{\text{ad}}/N_{\text{surf}}$ desorption rates for $T$ below 1000 K (Fig. 9).

The relatively high stability of $N$ adatoms on epitaxial atop-V sites on VN(001), explained by means of temperature-dependent \textit{ab initio} electronic structures demonstrating that an additional valence electron in VN vs. TiN strengthens both $\sigma$ $N_{\text{ad}}(p_z)$–$\text{TMsurf}(d_z^2)$ and $\pi$ $N_{\text{ad}}(p_x+p_y)$–$\text{TMsurf}(d_{xz}+d_{yz})$ bonding (Sec. 3.2), yields $N_{\text{ad}}$ surface migration rates which are considerably higher than $N_{\text{ad}}/N_{\text{surf}}$ desorption rates at room temperature (Fig. 9). Thus, itinerant $N$ adatoms have a high probability to bond with hydrogen atoms, favoring ammonia formation and desorption at 300 K.

In summary, the reactivity of $N$ adatoms on TM nitride (001) surfaces increases with surface ECAS electron concentrations due to nitrogen species evolving from being essentially chemically-inert $N_2$ ($N_{\text{ad}}/N_{\text{surf}}$) molecules (ECAS $\leq$ 14) to chemically-reactive $N$ adatoms (ECAS $>$ 14).

\section*{4. Conclusions}

Density-functional AIMD simulations show that $N$ adatoms on VN(001), at temperatures ranging from 1600 to 2300 K, prefer epitaxial atop-V positions, and diffuse among them by transiting through fourfold hollow sites. From FFH positions, $N_{\text{ad}}$ species can also reach stable threefold sites, close to a $N$ surface atom and bounded by two V atoms. In this position, $N$ adatoms form strongly-bonded $N_{\text{ad}}/N_{\text{surf}}$ pairs which, after several $N_{\text{ad}}/N_{\text{surf}}$ exchange reactions, desorb leaving an anion surface vacancy. $N$ surface vacancies rapidly migrate in-plane via $\langle 110 \rangle$ jumps and act as efficient catalysts for the dissociative chemisorption of incident $N_2$ molecules. AIMD simulations of VN(001) exposed to gas-phase $N$ atoms reveal that even at high $N_{\text{ad}}$ surface coverages (e.g., two, or even three, $N$ adatoms located on adjacent TFS or atop-V positions), $N_{\text{ad}}/N_{\text{ad}}$ recombination and desorption is never observed. Instead, $N_2$ loss occurs by $N_{\text{ad}}/N_{\text{surf}}$ desorption and by energetic $N_{\text{gas}}$ atoms colliding with $N_{\text{ad}}$ or $N_{\text{surf}}$ species to form molecules which immediately desorb. The formation of metastable VN admolecules, due to an itinerant $N_{\text{ad}}$ pulling a
V substrate atom onto the surface, can lead to growth of larger clusters via capture of incident N gas atoms.

Comparison with our previous results for N$_{ad}$ migration on, and N$_2$ desorption from, TiN(001) show that on both VN(001) and TiN(001) surfaces, N$_2$ molecule formation and desorption is primarily initiated by N adatoms removing a N surface atom and desorbing as N$_{ad}$/N$_{surf}$ rather than by N$_{ad}$/N$_{ad}$ recombinative desorption. However, on VN(001), N$_{ad}$ species reside primarily on surface atop-V epitaxial sites rather than at TFS positions, the preferential N$_{ad}$/TiN(001) adsorption sites, due to an additional valence electron per formula unit for VN(001) vs. TiN(001) which strengthens N$_{ad}$/TM$_{surf}$ bonding. This yields, for temperatures less than 1000 K, significantly higher N$_{ad}$ average migration distances on VN(001), compared to TiN(001), prior to N$_{ad}$/N$_{surf}$ desorption.

The present findings explain why plasma activation during reactive sputter deposition plays such a crucial role for forming stoichiometric TM nitride (001) layers: gas-phase N$_2$ is much less reactive than atomic N since the molecular species require interaction with surface anion vacancies to initiate dissociation. Our results also provide direct insights for controlling the catalytic reactivity of TM nitride (001) surfaces via electron-concentration tuning.

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119. Assuming that the Arrhenius relationships continue below 1500 K, lowest simulation temperature used in Ref. [62].


123. Note that the relatively ease of N-N bond breakage in N$_2$ gas molecules may be an artifact caused by the use of canonical NVT sampling of configurational space.