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Original Publication:

Davide Sangiovanni, A. B. Mei, Lars Hultman, Valeriu Chirita, Ivan Petrov and Joseph E Greene, Ab Initio Molecular Dynamics Simulations of Nitrogen/VN(001) Surface Reactions: Vacancy-Catalyzed N-2 Dissociative Chemisorption, N Adatom Migration, and N-2 Desorption, 2016, The Journal of Physical Chemistry C, (120), 23, 12503-12516.

<http://dx.doi.org/10.1021/acs.jpcc.6b02652>

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Postprint available at: Linköping University Electronic Press

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***Ab initio* Molecular Dynamics Simulations of Nitrogen/VN(001) Surface Reactions:
Vacancy-Catalyzed N₂ Dissociative Chemisorption, N Adatom Migration, and N₂ Desorption**

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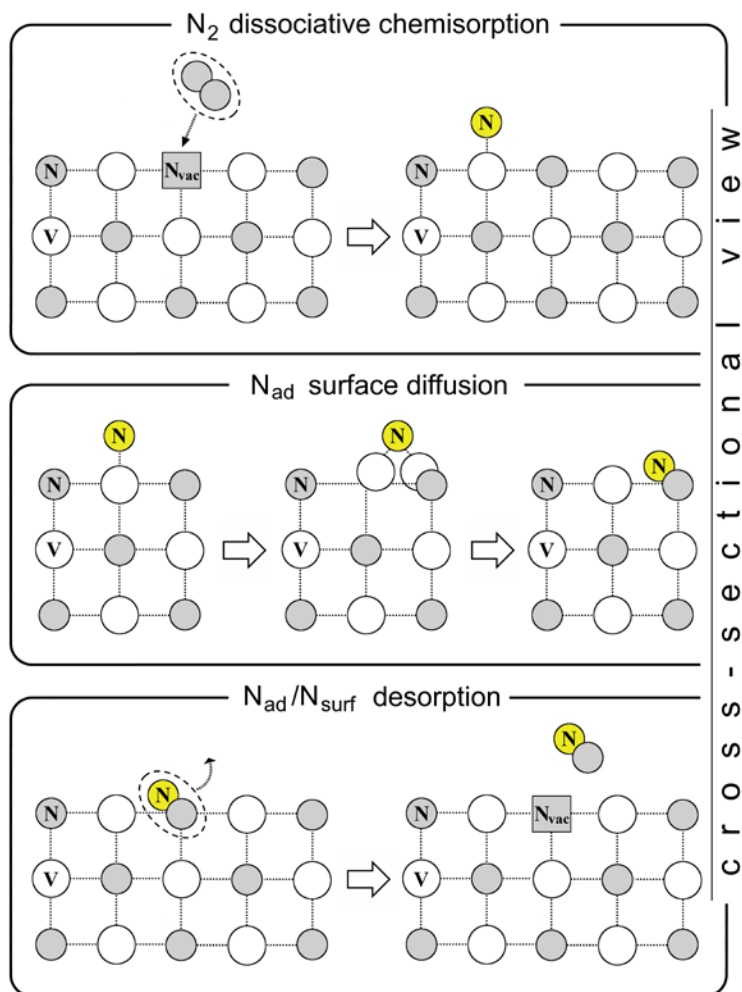
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Abstract

We use density-functional *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_{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 \rightarrow FFH \rightarrow atop-V jumps, isolated N adatoms bond strongly with an underlying N surface (N_{surf}) atom. Frequent N_{ad}/N_{surf} pair exchange reactions lead to N_2 desorption, which results in the formation of an anion surface vacancy. N vacancies rapidly migrate via in-plane $\langle 110 \rangle$ jumps and act as efficient catalysts for the dissociative chemisorption of incident N_2 molecules. During exposure of VN(001) to incident atomic N gas atoms, N_{ad}/N_{ad} recombination and desorption is never observed, despite a continuously high N monomer surface coverage. Instead, N_2 desorption is always initiated by a N adatom removing a N surface atom or by energetic N gas atoms colliding with N_{ad} or N_{surf} atoms. Similarities and differences between N/VN(001) vs. previous N/TiN(001) results, discussed on the basis of temperature-dependent *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)^{38, 39} and low-energy electron microscopy.⁵³ Thus, complementary computational investigations are necessary for detailed interpretation of experimental observations.

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.⁵⁴⁻⁵⁷ Diffusion rates can then be extrapolated to finite temperatures by transition-state theory^{58, 59} employing 0 K energy barriers and Arrhenius prefactors. This approximation, however, is not applicable to materials systems, such as NaCl-structure VN,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.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.^{62, 63}

Very few theoretical studies have considered the interaction of TM nitride surfaces with gases and metal adatoms via *ab initio* molecular dynamics (AIMD).^{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 ,⁶³ by both *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.⁶²

Similar to our observations for N adatom behavior on $TiN(001)$,⁶² previous *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.⁷¹⁻⁷⁶ In contrast, DFT results,^{72, 73, 77-79} supported by experimental observations,^{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 *both* TFS and metal-atom atop

sites, with no distinct preference. For the pseudobinary $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$ surface, which has a valence electron concentration (VEC) of 8.5 (less than that of TiN and VC, both with VEC = 9), AIMD simulations⁶⁴ and x-ray photoelectron spectroscopy⁸¹ 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 $\text{ECAS} \leq 14$ (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 $\text{ECAS} > 14$ (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 $\text{N}_{\text{ad}}/\text{N}_{\text{ad}}$ recombination and desorption is considerably less likely than $\text{N}_{\text{ad}}/\text{N}_{\text{surf}}$ desorption due to the high activation energy (~ 2 eV) required to overcome long-range $\text{N}_{\text{ad}}/\text{N}_{\text{ad}}$ 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 $\text{N}_{\text{ad}}/\text{VN}(001)$, with ECAS = 15, as a model system to probe N_{ad} surface kinetics and compare the results with the previously reported behavior of $\text{N}_{\text{ad}}/\text{TiN}(001)$,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 $N_{\text{ad}}/\text{VN}(001)$ vs. $N_{\text{ad}}/\text{TiN}(001)$. 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 code¹⁰⁰ 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 Γ -point in the Brillouin zone. Thermally-induced electronic excitations are accounted for by employing $k_{\text{B}}T$ electron-smearing energies. The visual molecular dynamics (VMD) software¹⁰³ 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 $N_{ad}/TiN(001)$ [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 $d_{NN//}$ in the simulation slab is obtained as a function of temperature, accounting for the experimental NaCl-structure VN average thermal expansion coefficient, $9.7 \times 10^{-6} \text{ K}^{-1}$,¹⁰⁴ by rescaling the 0 K DFT $d_{NN//}$ value (2.06 Å). Rescaling $d_{NN//}$ as a function of temperature is necessary to avoid spurious substrate strain effects on adatom jump rates.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.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_{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 $k_{FFH \rightarrow \text{atop-V}}/k^*$ and $k_{FFH \rightarrow TFS}/k^*$, respectively, for which $k^* = (k_{FFH \rightarrow \text{atop-V}} + k_{FFH \rightarrow TFS})$.

Stoichiometric VN crystallizes in the B1 NaCl structure over the temperature range from 250 K [60] (VN is tetragonal at lower temperatures) to the decomposition temperature $T_{dec} = 2450 \text{ K}$.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

$$\ln[k_X(T)] = \ln(A_X) - \frac{E_X}{k_B T}, \quad (1)$$

for which k_B is the Boltzmann constant. Statistical uncertainties σ_k , σ_K , σ_E , and σ_A in the values of k , $\ln(k)$, E_X , and A are obtained as described previously.⁶² In brief, σ_E and σ_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 σ_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 σ_k , are in good agreement with the corresponding k_X values determined for three-layer slabs.

N adatom 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 $D_{Nvac}(T_i)$ estimated at temperatures T_i as

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

Uncertainties σ_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 σ'_E and σ'_A , 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:

$$D(T) \cdot [\sigma_D(T)]^{\pm 1} = A' \cdot (\sigma'_A)^{\pm 1} \cdot \exp \left[- \left(E'_a \mp \sigma'_E / \sqrt{2} \right) / (k_B T) \right]. \quad (3)$$

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 ($\sim 75 \times 10^3$ 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 ($0.74 \leq x \leq 1$) 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 deposition¹¹²).

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.¹¹³ 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 *frozen* atomic configurations stochastically extracted from 400 AIMD steps, with the condition that the distance of both adatoms from the original epitaxial atop- TM_{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 $\text{N}_{\text{ad}}/\text{TM}_{\text{surf}}$ hybridized states, and energy-resolved $\text{N}_{\text{ad}}/\text{TM}_{\text{surf}}$ overlap populations (OP)^{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_{ad} and TM_{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_{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_{surf}) to which it is most-strongly bonded toward the FFH site and attracts the opposite V_{surf} nearest-neighbor (Fig. 1[(b), (f)]). The $\text{V}_{\text{surf}}\text{-N}_{\text{ad}}\text{-V}_{\text{surf}}$ transition-state quickly evolves into a stable configuration; N_{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_{surf} atoms returning to their initial positions.

N_{ad} transition rates [$\text{atop-V} \rightarrow \text{FFH}$] and [$\text{FFH} \rightarrow \text{TFS}$] follow Arrhenius relationships over the temperature range investigated (see Fig. 2). Between 1600 and 2300 K, $k_{\text{atop-V} \rightarrow \text{FFH}}$ values are one to two orders of magnitudes larger than $k_{\text{FFH} \rightarrow \text{TFS}}$. Note, however, that $k_{\text{FFH} \rightarrow \text{TFS}}$ 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 $A_{\text{atop-V} \rightarrow \text{FFH}} = 4.82(\times 2.6^{\pm 1}) \times 10^{13} \text{ s}^{-1}$ and $A_{\text{FFH} \rightarrow \text{TFS}} = 52(\times 60^{\pm 1}) \times 10^{13} \text{ s}^{-1}$. The large error bars for $k_{\text{FFH} \rightarrow \text{TFS}}$ rates are due to low statistics for these events.

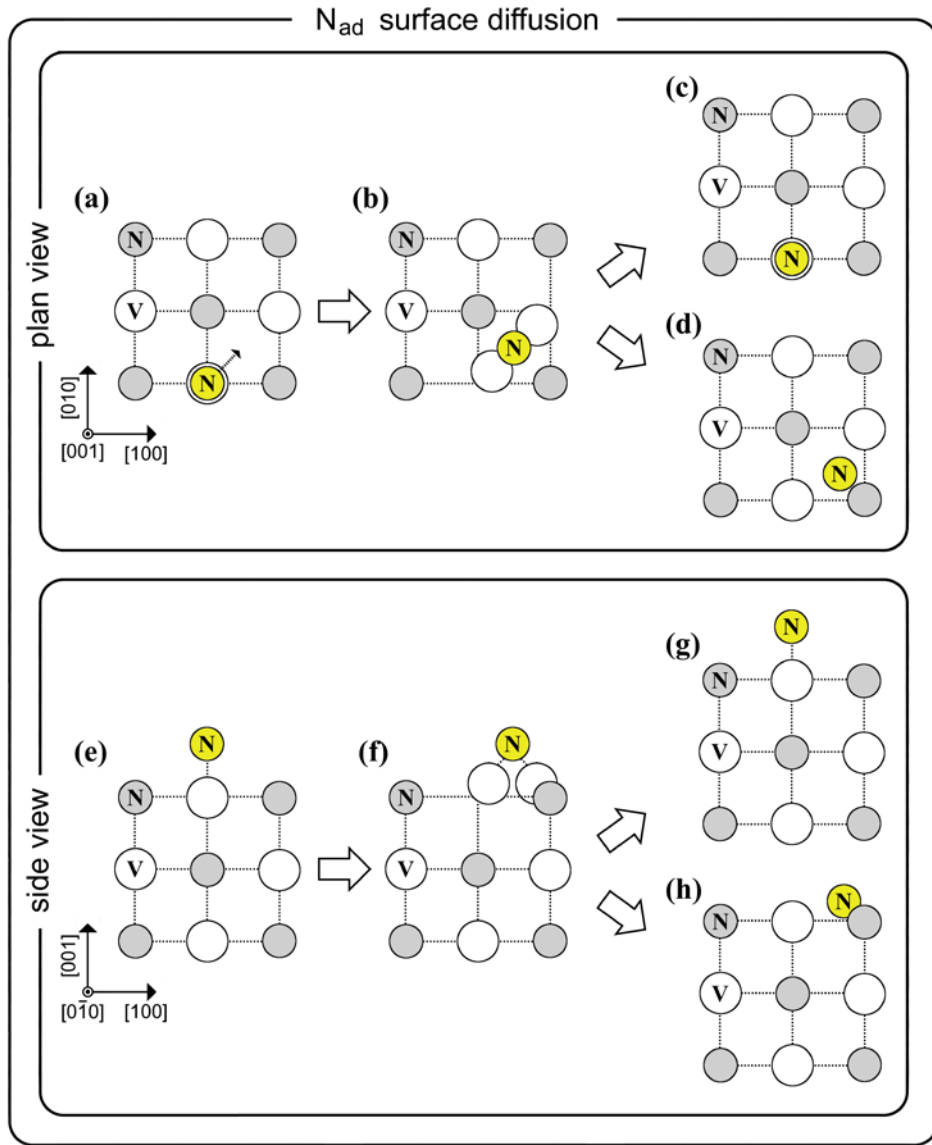


Figure 1. Schematic representation of $N_{\text{ad}}/\text{VN}(001)$ surface diffusion in (a-d) plan views and (e-h) side views. [(a), (e)] The favored site for N_{ad} adsorption is the epitaxial atop-V position. [(b), (f)] N_{ad} surface migration occurs via FFH transition states. From a FFH site, N_{ad} 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.

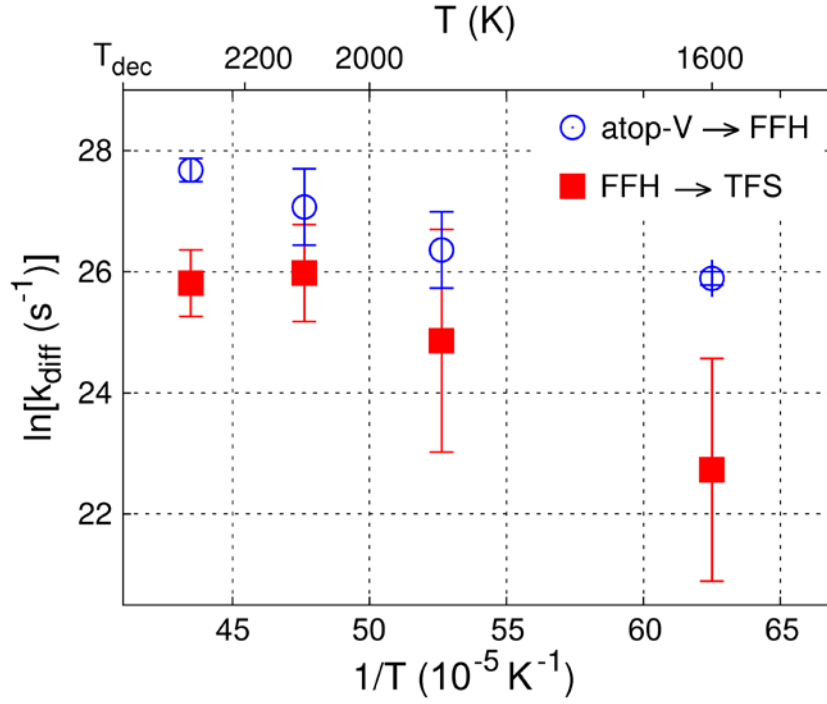


Figure 2. N_{ad} diffusion jump rate k_{diff} on VN(001) as a function of temperature T . Red filled squares correspond to adatom migration from FFH sites to TFS positions along $\langle 110 \rangle$ directions. Blue open circles correspond to the rate of $\langle 110 \rangle$ N_{ad} migration from atop-V 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 ad molecule, 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 ad molecule diffusion on TiN(001) terraces and islands.^{67, 69}

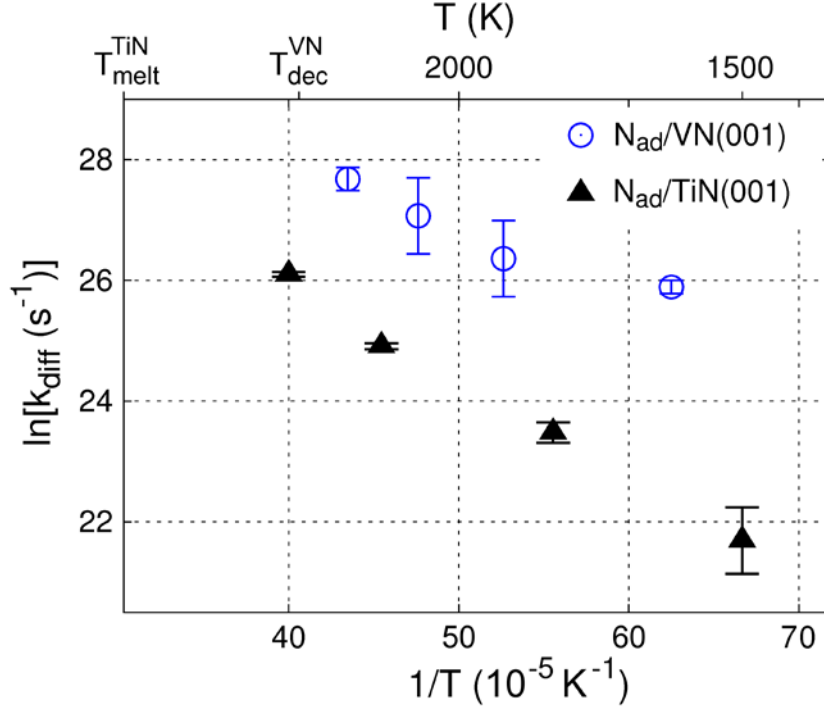


Figure 3. $N_{\text{ad}}/\text{VN}(001)$, blue open circles, and $N_{\text{ad}}/\text{TiN}(001)$, black filled triangles, jump rates k_{diff} as a function of temperature T . The VN decomposition temperature $T_{\text{dec}}^{\text{VN}}$ is ~ 2450 K and the TiN melting point $T_{\text{melt}}^{\text{TiN}}$ is ~ 3200 K.

3.2. $N_{\text{ad}}/\text{VN}(001)$ and $N_{\text{ad}}/\text{TiN}(001)$ electronic structures. In Section 1, we proposed an empirical rule based on adatom/surface electron densities, $\text{ECAS} = \text{substrate VEC} + \text{adatom valence-electron number}$, which systematizes in a consistent manner the present AIMD results, as well as previous experimental and *ab initio* results, for preferred non-metal adatom adsorption sites on TM nitride and carbide (001) surfaces. In adsorption reactions for which $\text{ECAS} \leq 14$, non-metal adatoms adsorb at TFS positions, strongly-bonded to the nearest-neighbor non-metal surface atom. However, with $\text{ECAS} > 14$, 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 positions⁶² as both FFH and atop- Ti_{surf} sites are saddle-points in the $N_{\text{ad}}/\text{TiN}(001)$ adsorption-energy landscape,¹¹⁷ consistent with an ECAS value of 14. In contrast, on VN(001) ($\text{ECAS} = 15$), N adatoms travel

primarily among atop-V surface epitaxial sites, also in agreement with the empirical prediction, and the formation of N_{ad}/N_{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_{ad}/TM_{surf} hybridized states for VN(001) and TiN(001) with a N adatom placed at atop- TM_{surf} positions.

DOS curves calculated for $N_{ad}/VN(001)$ and $N_{ad}/TiN(001)$ 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 $N_{ad}/VN(001)$, Fig. 4(a), and $N_{ad}/TiN(001)$, Fig. 4(b), derive mainly from $\sigma N_{ad}(p_z)-TM_{surf}(d_z^2)$ 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 $\pi N_{ad}(p_x+p_y)-TM_{surf}(d_{xz}+d_{yz})$ orbitals, centered at approximately -1.8 eV for VN and -0.4 eV for TiN.

For both VN(001) and TiN(001) surfaces, $(p_z)-(d_z^2)$ and $(p_x+p_y)-(d_{xz}+d_{yz})$ N_{ad}/TM_{surf} orbital overlap, schematically illustrated in Fig. 5(a), produce bonding σ and π states, respectively, as evidenced by the OP vs. energy curves in Fig. 5(b) remaining positive. A comparison of the magnitude of $N_{ad}/VN(001)$ vs. $N_{ad}/TiN(001)$ OP values demonstrates that σ and π N_{ad}/TM_{surf} bonds are both much stronger for VN(001) (Fig. 5(b)). The shift in adatom surface states to lower energies, together with N_{ad}/V_{surf} bonds being significantly stronger than N_{ad}/Ti_{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_{ad}/TM_{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_{ad}/TM_{surf} bonds (see insets in Fig. 4) range from -1.6 to -1.3 eV for σ bonds and from -2.0 to -1.6 eV for π bonds on VN(001) and from -0.3 eV to the Fermi level for σ bonds and from -0.7 to -0.3 eV for π

bonds on TiN(001). The electron distributions in Fig. 6 confirm that both σ and π $N_{\text{ad}}/\text{TM}_{\text{surf}}$ bonds are much stronger for VN than for TiN due to higher electron densities between N_{ad} and V_{surf} atoms.

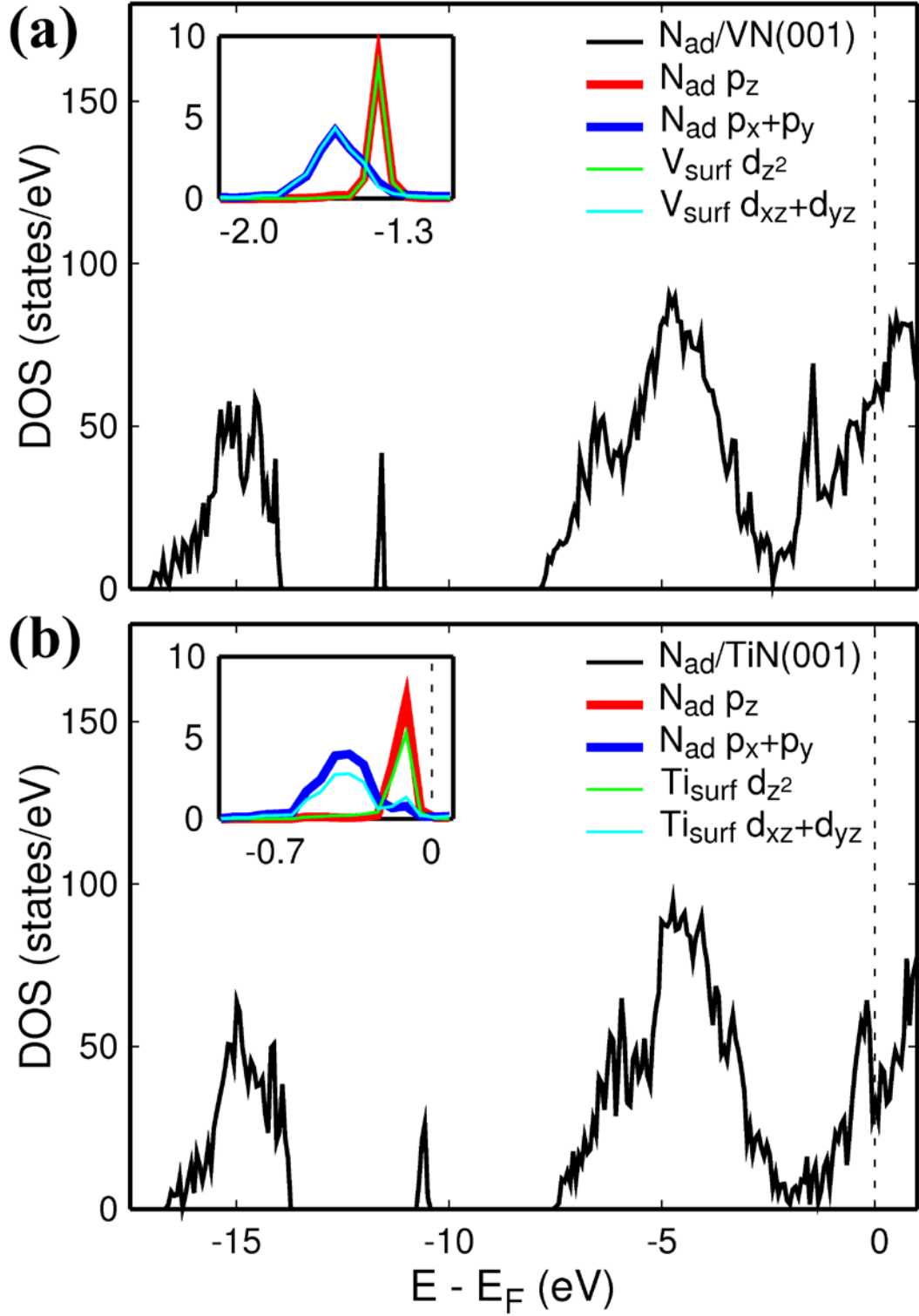


Figure 4. Density of states projected onto spherical harmonics centered at atomic positions for (a) VN(001) and (b) TiN(001) with a N adatom at an atop-TM_{surf} site at 300 K. The insets are enlarged views of N_{ad}/TM_{surf} hybridized states.

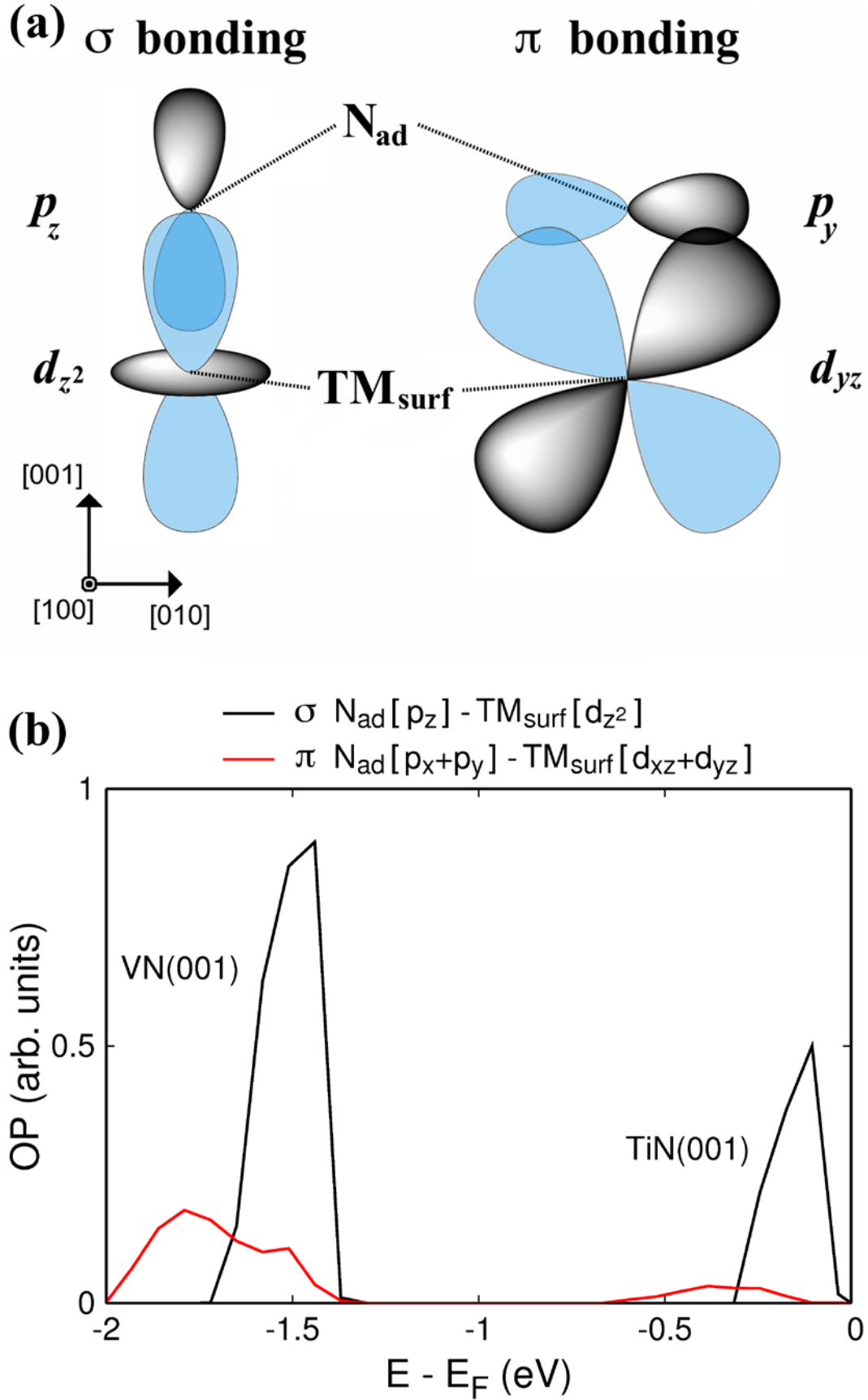


Figure 5. N_{ad}/TM_{surf} bonding on VN(001) and TiN(001). (a) Schematic representation of N_{ad}/TM_{surf} orbital overlap. (b) Overlap population (OP) for N_{ad}/TM_{surf} bonding states near the Fermi level.

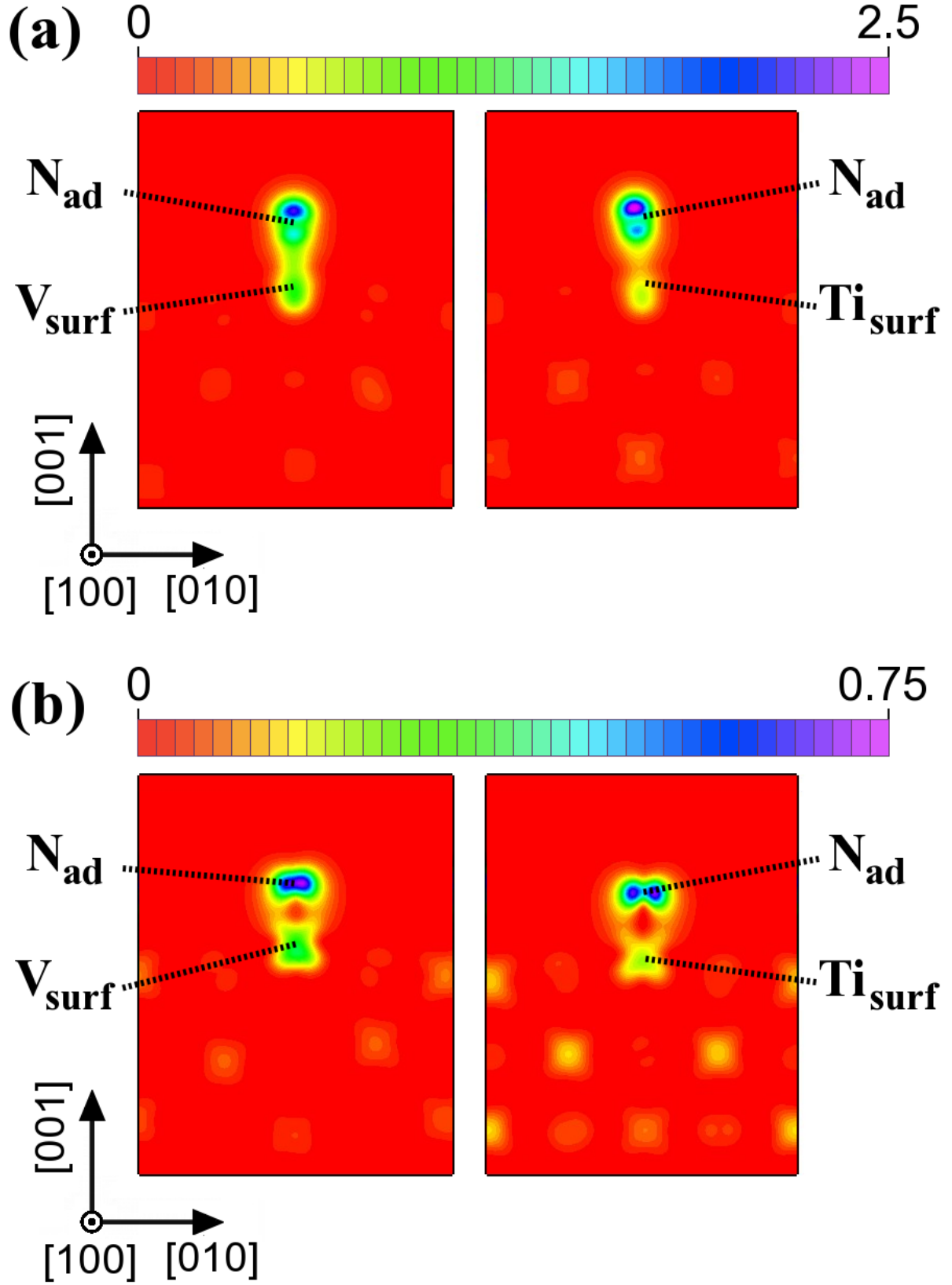


Figure 6. Energy-resolved charge densities for N adatoms at atop- TM_{surf} positions on TiN(001) and VN(001) at 300 K. (a) $N_{ad}(p_x)-TM_{surf}(d_z^2)$ and (b) $N_{ad}(p_x+p_y)-TM_{surf}(d_{xz}+d_{yz})$ bonding states

(see schematic orbital representations in Fig. 5(a)). (a) The energy intervals used for $N_{ad}/VN(001)$ and from -1.7 to -1.3 eV for $N_{ad}/VN(001)$ and from -0.3 to 0 eV for $N_{ad}/TiN(001)$. (b) The energy intervals used for $N_{ad}/VN(001)$ and from -0.7 to -0.3 eV for $N_{ad}/TiN(001)$. The red to violet color scales are in units of electrons/Å³.

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 $\langle 111 \rangle$, but frequently changes from $\langle 111 \rangle$ to $\langle 110 \rangle$ to $\langle 1\bar{1}1 \rangle$, 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 $A_{exch} = 2.26(x1.9^{\pm 1}) \times 10^{13} \text{ s}^{-1}$, respectively. On $TiN(001)$, N_{ad}/N_{surf} exchange occurs less frequently, $E_{exch} = 0.69 \pm 0.09$ eV and $A_{exch} = 1.00(x1.7^{\pm 1}) \times 10^{13} \text{ s}^{-1}$,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 $A_{des} = 3.51(x12^{\pm 1}) \times 10^{13} \text{ s}^{-1}$ 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) ($A_{\text{des}} = 4.65(\times 12^{\pm 1}) \times 10^{13} \text{ s}^{-1}$ and $E_{\text{des}} = 1.00 \pm 0.40 \text{ eV}$) is overall much more frequent than from TiN(001) ($A_{\text{des}} = 3.37(\times 5^{\pm 1}) \times 10^{13} \text{ s}^{-1}$ and $E_{\text{des}} = 1.37 \pm 0.30 \text{ eV}$)⁶² (see inset in Fig. 8).

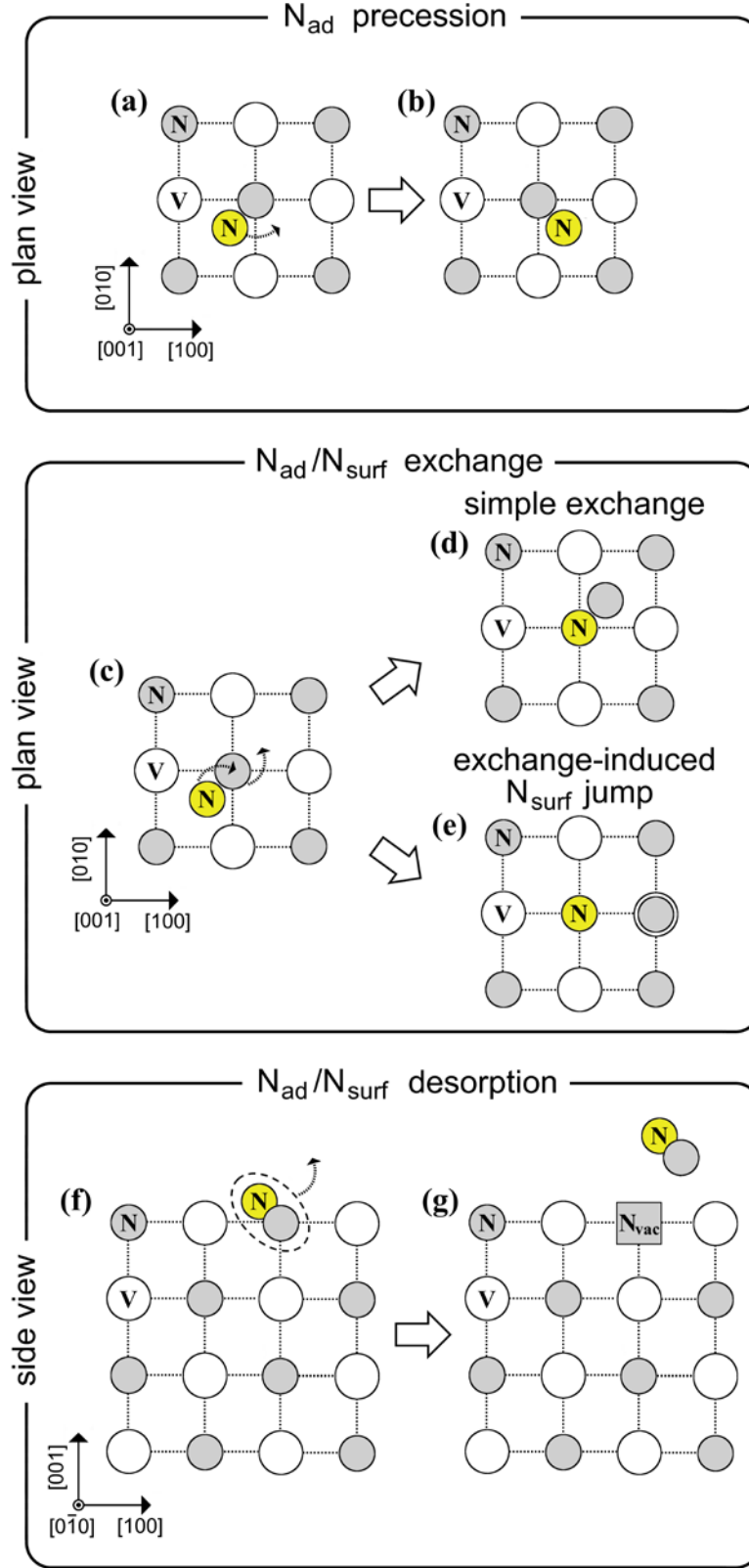


Figure 7. Schematic representation of VN(001) surface reactions initiated by N_{ad} adsorbed in TFS positions. (a), (b) N adatom precession among TFS positions in adjacent surface unit cells. (c) The exchange of a N adatom with a N surface atom (in which N_{ad} takes the position of N_{surf}) can result

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 $N_{\text{ad}}/N_{\text{surf}}$ exchange reactions, the $N_{\text{ad}}/N_{\text{surf}}$ -pair desorbs, leaving (g) an anion surface vacancy (N_{vac}).

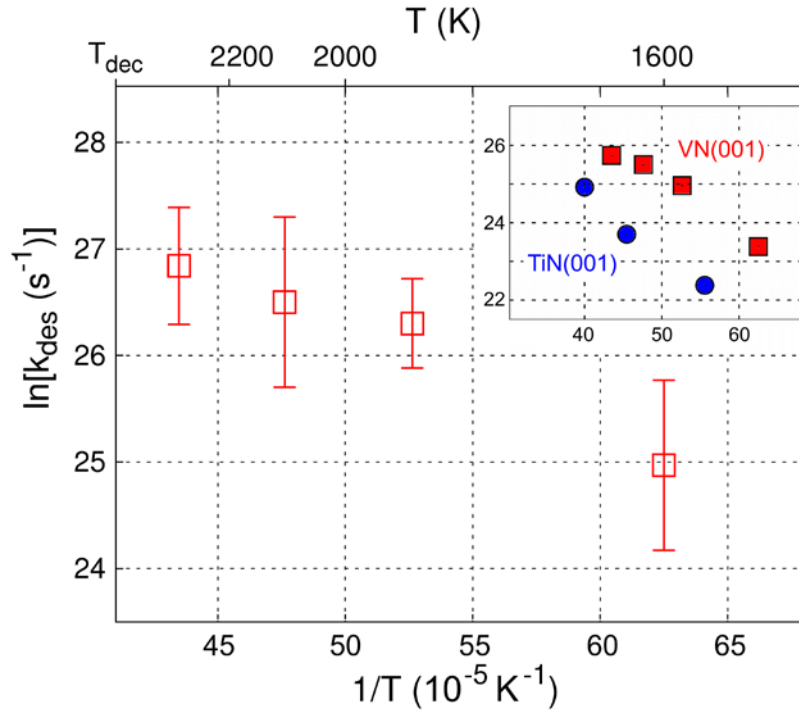


Figure 8. $N_{\text{ad}}/N_{\text{surf}}$ desorption rates k_{des} from VN(001) as a function of temperature T . The inset compares the $N_{\text{ad}}/N_{\text{surf}}$ desorption rate from VN(001) to that from TiN(001) accounting for N_{ad} surface migration times among epitaxial sites prior to $N_{\text{ad}}/N_{\text{surf}}$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

The ratio $k_{\text{diff}}(T)/k_{\text{des}}(T)$ of N_{ad} diffusion rates k_{diff} to $N_{\text{ad}}/N_{\text{surf}}$ desorption rates k_{des} quantifies N_{ad} mean surface migration events as a function of T (Fig. 9). For TiN(001), $k_{\text{diff}}(T)/k_{\text{des}}(T) = 3.53 \cdot \exp[-0.02 \text{ eV} / (k_{\text{B}} T)]$, 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 temperature¹¹⁹ and the melting point. In contrast, $k_{\text{diff}}(T)/k_{\text{des}}(T)$ varies significantly with T for N_{ad} on VN(001): $k_{\text{diff}}(T)/k_{\text{des}}(T) = 0.96 \cdot \exp[0.21 \text{ eV} / (k_{\text{B}} T)]$. At 600 K, N_{ad} jumps among VN(001) epitaxial sites approximately one hundred times prior to $N_{\text{ad}}/N_{\text{surf}}$ desorption; for T approaching the VN decomposition temperature, 2450 K, the adatom performs very few jumps, ~ 3 , before leaving the surface as a $N_{\text{ad}}/N_{\text{surf}}$ 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 $k_{diff}(T)/k_{des}(T)$ 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}

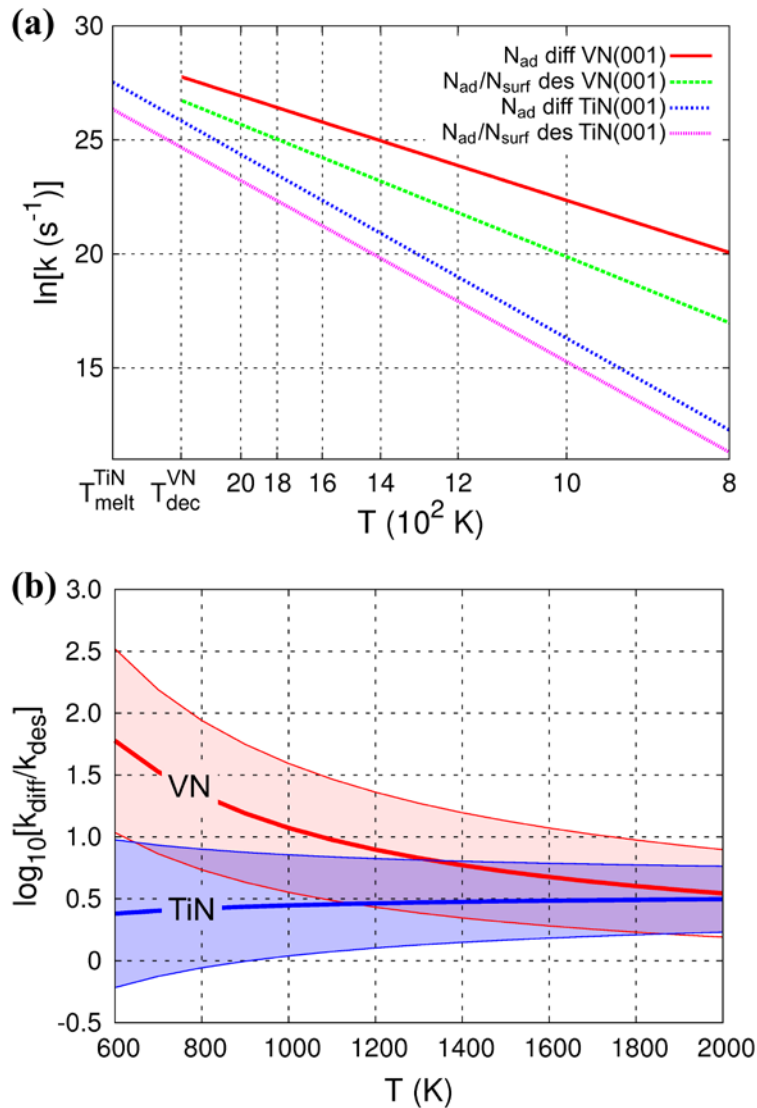


Figure 9. (a) Comparison of N_{ad} migration rates k_{diff} on, and N_{ad}/N_{surf} desorption rates k_{des} from, VN(001) and TiN(001) as a function of temperature T . (b) Temperature-dependent ratio of the N_{ad} migration rate to the N_{ad}/N_{surf} desorption rate for the two surfaces. The shaded 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 \rightarrow FFH \rightarrow 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.

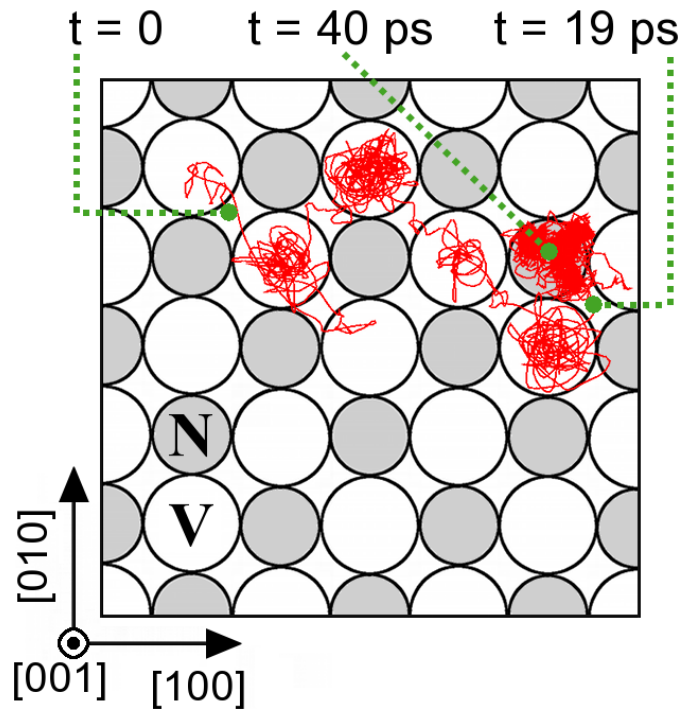


Figure 10. AIMD N_{ad} migration pathway (solid red line) during 40 ps on VN(001) at 1600 K. The N adatom is initiated ($t = 0$) at a FFH site. Between 0 and 19 ps, N_{ad} migrates among V-atop sites (six $\langle 110 \rangle$ diffusion events) by passing through FFH positions. At $t = 19$ ps, the adspecies 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 N₂ dissociative chemisorption.

N_{ad}/N_{surf} desorption results in the formation of nitrogen surface vacancies N_{vac} which give rise to relatively frequent N_{vac}/VN(001) intralayer migration events at all temperatures investigated (1600 – 2300 K). In contrast, N_{vac} intralayer migration was never observed in AIMD simulations of N_{vac}/TiN(001) dynamics at temperatures up to 2500 K [62] due to stronger metal-N bonds in TiN than in VN. N_{vac} surface migration requires one of the four neighboring N_{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 $A_{N_{vac}} = 0.31(x1.4^{\pm 1}) \times 10^{13} \text{ s}^{-1}$ and activation energies $E_{N_{vac}} = 0.25 \pm 0.05 \text{ eV}$ (Fig. 12), yielding diffusivities (Eqs. 2 and 3) with prefactors $A'_{N_{vac}} = 7.25(x1.3^{\pm 1}) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and activation energies $E'_{N_{vac}} = 0.26 \pm 0.03 \text{ eV}$.

N_{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.^{63, 121}

Due to the use of periodic boundary conditions, desorbed N_{ad}/N_{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 N₂ molecular dissociation on VN(001), as observed previously for TiN(001).⁶² N₂ dissociation is never observed for gas molecules incident at defect-free VN(001) surface regions. Occasionally, however, a N₂ molecule lands proximate to an anion surface vacancy. In each of these cases, one of the N₂ 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 O₂ dissociation on TiO₂(110).¹²² AIMD movies also show that N₂ dissociation on VN(001) can be directly followed by a N_{ad}/N_{surf} desorption reaction promoted by momentum transfer to the surface from the incident gas molecule.

Overall, N_2 dissociative chemisorption on $\text{VN}(001)$ occurs every time a N_2 molecule is incident at the surface within approximately one interatomic distance $d_{\text{NN} //}$ from an anion vacancy (five events in total), from which we infer that anion vacancies on NaCl-structure $\text{VN}(001)$ are efficient catalytic agents.

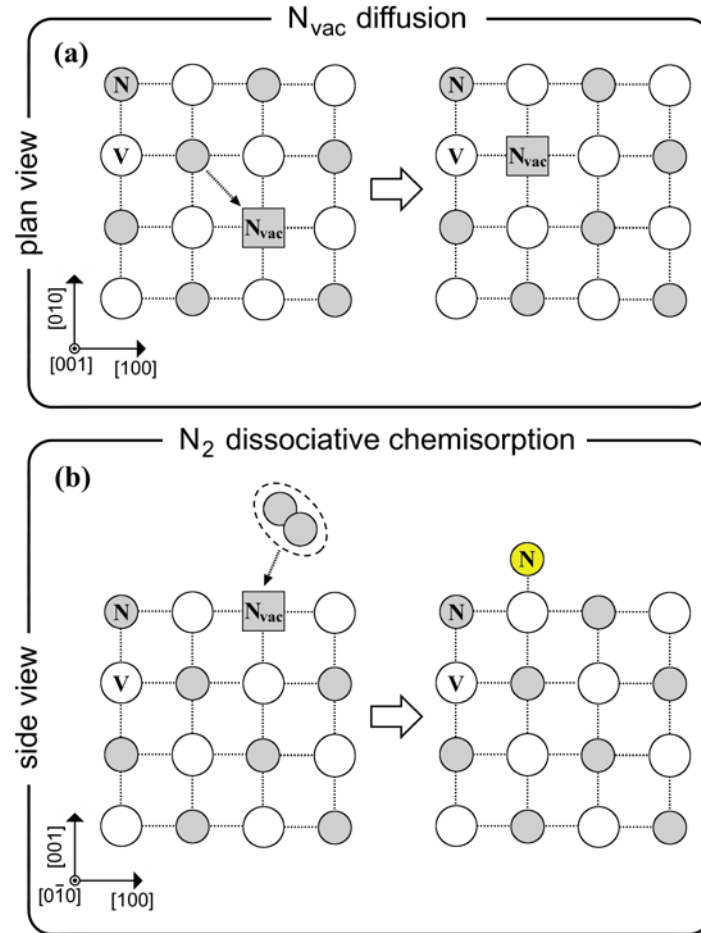


Figure 11. (a) N vacancy migration along $\langle 110 \rangle$ requires one of the four neighboring N_{surf} atoms to jump into the empty surface anion site. (b) During N_2 dissociative chemisorption at surface anion vacancies, one N atom fills the vacancy site while the other becomes a free adatom.

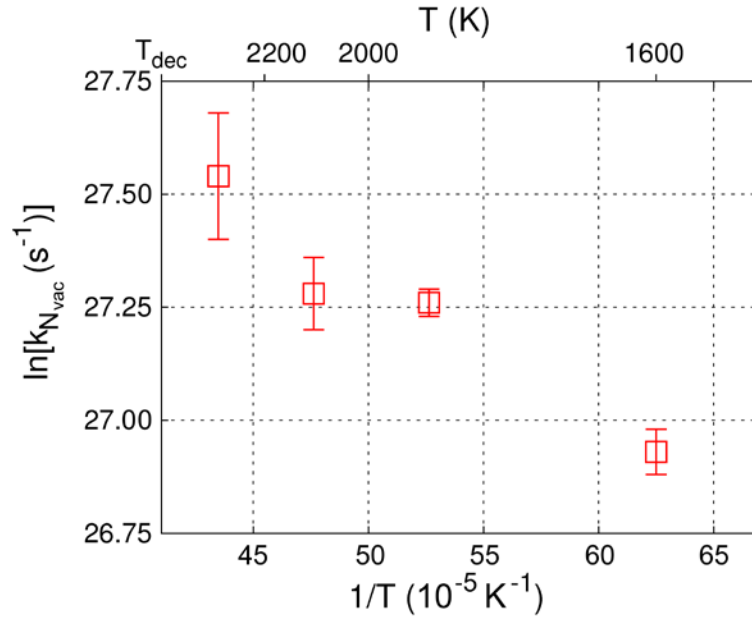


Figure 12. $N_{\text{vac}}/\text{VN}(001)$ in-plane jump rate $k_{N_{\text{vac}}}$ as a function of temperature T . N_{vac} is a N surface vacancy and $T_{\text{dec}} \sim 2450$ K is the VN decomposition temperature.

3.5 N gas reactions on VN(001). In recent AIMD and DFT investigations, we have shown that $N_{\text{ad}}/N_{\text{ad}}$ recombination on, and subsequent desorption from, $\text{TiN}(001)$ is much less likely than $N_{\text{ad}}/N_{\text{surf}}$ desorption ($E_{\text{des}} = 1.4$ eV) due to $N_{\text{ad}}/N_{\text{ad}}$ repulsive energies which rapidly increase to 2 eV as adatom/adatom separation decreases to 1.5 \AA .⁶² The probability of $N_{\text{ad}}/N_{\text{ad}}$ recombination on $\text{TiN}(001)$ is further reduced because of the extremely short average distances travelled by isolated N adatoms prior to $N_{\text{ad}}/N_{\text{surf}}$ desorption.⁶² The 0 K phonon instability of cubic VN [⁶¹] does not allow for quantification of adatom/adatom attractive/repulsive potential-energy pathways on $\text{VN}(001)$ via DFT. Thus, here we carry out AIMD simulations to probe the interaction of N gas atoms on $\text{VN}(001)$ at 1900 K, well above 250 K, at which the cubic phase becomes stable,⁶⁰ in order to provide direct insight as to whether $N_{\text{ad}}/N_{\text{ad}}$ recombination and desorption is more or less likely to occur than $N_{\text{ad}}/N_{\text{surf}}$ pair formation and desorption (see Section 2.2 for computational details).

Figure 13 shows four images extracted from $N_{\text{gas}}/\text{VN}(001)$ AIMD movies. Due to the complexity of $N_{\text{gas}}/\text{VN}(001)$ 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_{gas} reflections out of a total of approximately 40 $N_{\text{gas}}/\text{VN}(001)$ surface collisions, yielding a capture probability of

~97%. N gas atoms are adsorbed on VN(001) with approximately equal probability at atop-V and TFS positions.

Calculated average N_{ad}/N_{surf} desorption rates from VN(001), $1.0(\times 3.0^{\pm 1}) \times 10^{12} \text{ s}^{-1}$ (note desorbed N_{ad}/N_{surf} molecules in Fig. 13(b)), correspond to N adatom lifetimes of approximately 0.5 ps. Although N_{ad} surface coverages in these experiments range up to 0.2 ML, N_{ad}/N_{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_{ad}/N_{surf} pair formation followed by exchange reactions and desorption. This suggests that N_{ad}/N_{ad} long-range interactions on VN(001) are strongly repulsive, similar to the case for $N_{ad}/\text{TiN}(001)$.⁶²

In addition to establishing that N_{ad}/N_{surf} desorption is much more likely than N_{ad}/N_{ad} recombinative desorption on VN(001), AIMD movies show that N_2 desorption can also be initiated by gas/surface collisions. The vibrational amplitude of N_2 gas molecules is perturbed and enhanced by the presence of N gas atoms. Occasionally, this leads to N–N bond breakage,¹²³ which produces energetic (approximately 10 eV) N_{gas} atoms. If an energetic N_{gas} species is incident at a N adatom or a N surface atom, it forms, with ~100% probability, N_2 molecules which immediately desorb.

The creation of surface anion vacancies due to N_{ad}/N_{surf} , N_{gas}/N_{surf} , and N_{gas}/N_{ad} desorption leads to an average steady-state VN(001) surface stoichiometry of $\text{VN}_{0.96}$. In most cases, N surface vacancies are promptly filled by itinerant N adatoms or by impinging N_{gas} atoms (note, for example, the N_{gas} atoms (shown in yellow) occupying anion positions in the VN(001) surface in Fig. 13(c)). During the $N_{gas}/\text{VN}(001)$ simulation, we also detect the dissociation of N_2 gas molecules which happen to collide proximate to N_{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_{gas} atom from a V_{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_{ad} species pulls up a V_{surf} atom to form a second VN admolecule which bonds to the adjacent initial VN, thus producing an L-shape V_2N_2 cluster with all atoms in epitaxial

positions. Next, an incident N_{gas} atom bonds to the V_2N_2 cluster to form a V_2N_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_2N_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_{vac} and an additional, isolated, N_{vac} .

Experimental results for epitaxial growth of $TiN_x(001)$ [33, 88], as well as $TaN_x(001)$ [34, 124] and HfN_x ,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_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.

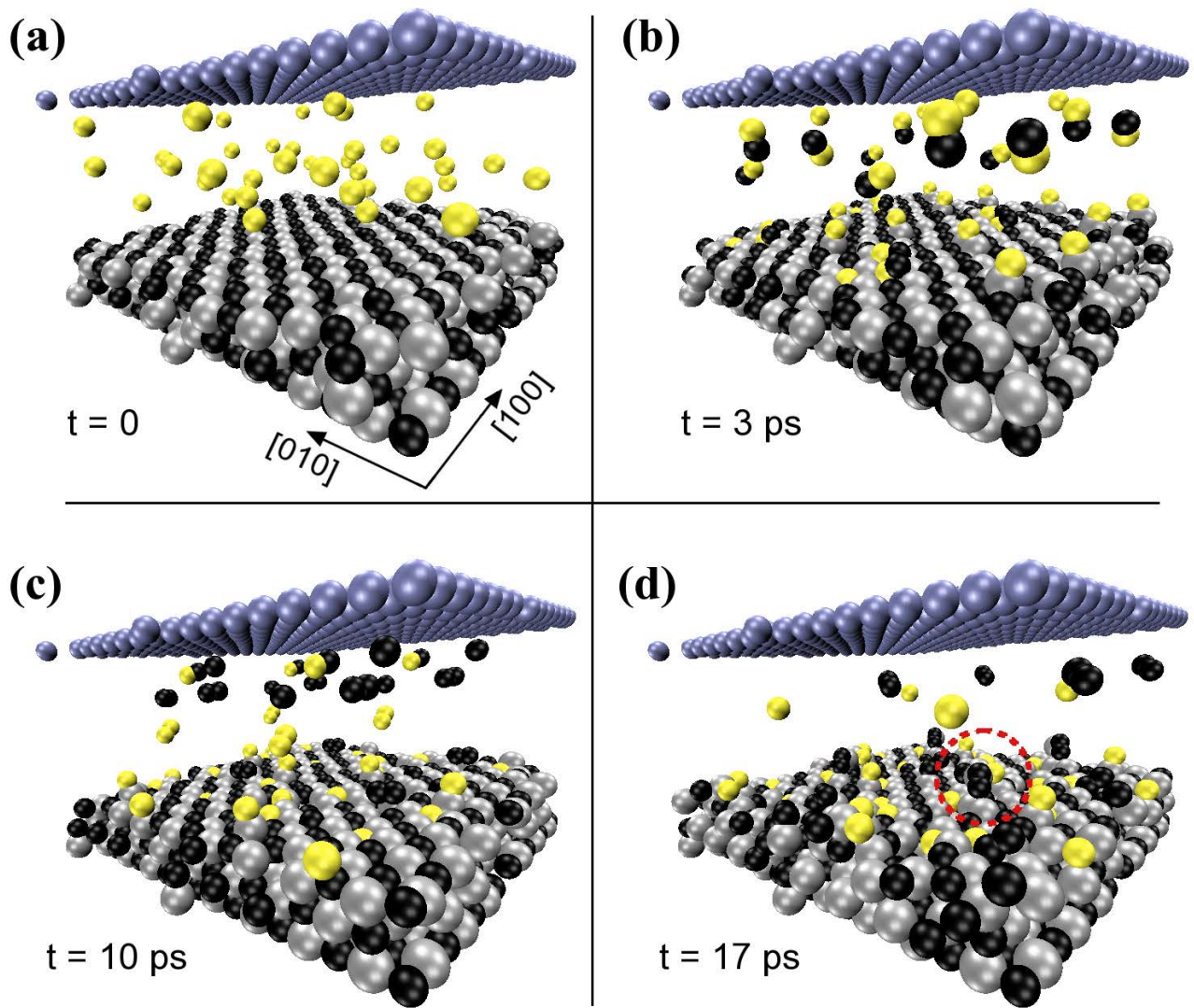


Figure 13. Images from AIMD movies of a pristine VN(001) surface exposed to N gas atoms at 1900 K. Color legend: yellow = N_{gas} , black = N_{surf} , silver = V_{surf} , blue = He barrier atoms. Each panel shows four simulation-cell replicas. The dashed red circle in panel (d) indicates the formation of an epitaxial V_2N_3 island. See Sec. 3.5 and Fig. 14 for further explanation.

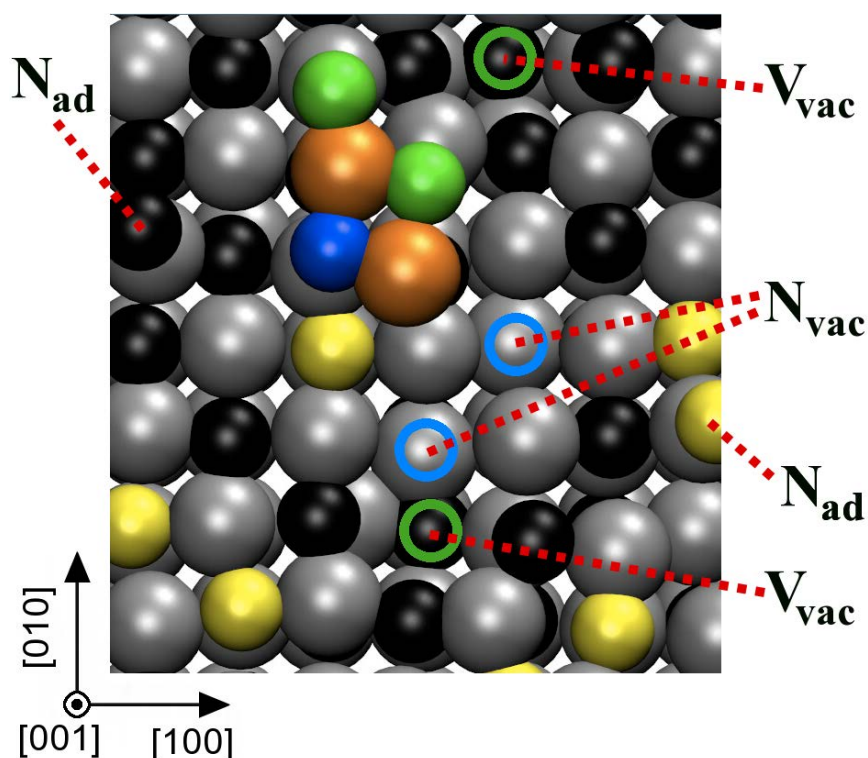


Figure 14. Images from an AIMD movie of VN(001) exposed to N gas atoms. Color legend: yellow = N_{gas} , black = N_{surf} , silver = V_{surf} , orange = V island atom, green = N island atom (originally N_{gas}), blue = N island atom (originally N_{surf}), open blue circle = N_{vac} , and open green circle = V_{vac} . N_{vac} and V_{vac} indicate anion and cation surface vacancies, respectively. N_{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,⁶² 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) surfaces⁵¹ 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 simulations⁶² and by the considerably larger N adatom adsorption energies in TFS than in FFH or atop- Ti_{surf} positions.¹¹⁷ Strong $N_{\text{ad}}/N_{\text{surf}}$ bonds do not favor N_{ad} hydrogenation and release of ammonia. N_{ad} species in TFS positions on VN(001) are also

highly stable due to the strong N_{ad}/N_{surf} bond; however, the formation of N_{ad}/N_{surf} pairs on VN(001) is kinetically hindered, as demonstrated by adatom surface migration rates being much higher than N_{ad}/N_{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 *ab initio* electronic structures demonstrating that an additional valence electron in VN vs. TiN strengthens both σ $N_{ad}(p_z)$ - $TM_{surf}(d_z^2)$ and π $N_{ad}(p_x+p_y)$ - $TM_{surf}(d_{xz}+d_{yz})$ bonding (Sec. 3.2), yields N_{ad} surface migration rates which are considerably higher than N_{ad}/N_{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_{ad}/N_{surf}) molecules ($ECAS \leq 14$) to chemically-reactive N adatoms ($ECAS > 14$).

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_{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_{ad}/N_{surf} pairs which, after several N_{ad}/N_{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_{ad} surface coverages (e.g., two, or even three, N adatoms located on adjacent TFS or atop-V positions), N_{ad}/N_{ad} recombination and desorption is never observed. Instead, N_2 loss occurs by N_{ad}/N_{surf} desorption and by energetic N_{gas} atoms colliding with N_{ad} or N_{surf} species to form molecules which immediately desorb. The formation of metastable VN admolecules, due to an itinerant N_{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.

Acknowledgments

This research was carried out using resources provided by the Swedish National Infrastructure for Computing (SNIC), on the Gamma, Triolith, Matter, and Kappa Clusters located at the National Supercomputer Centre (NSC) in Linköping, and on the Beskow cluster located at the Center for High Performance Computing (PDC) in Stockholm, Sweden. W. Olovsson and P. Münger at NSC, and H. Leskelä and J. Vincent at PDC are acknowledged for assistance with technical aspects. We gratefully acknowledge financial support from the Knut and Alice Wallenberg Foundation (Isotope Project No. 2011.0094), the Swedish Research Council (VR) Linköping Linnaeus Initiative LiLi-NFM (Grant No. 2008-6572) and Project Grants No. 2014-5790 and 2013-4018, and the Swedish Government Strategic Research Area Grant in Materials Science on Advanced Functional Materials

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