



Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations



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ABSTRACT

Ab initio and classical molecular dynamics (AIMD and CMD) simulations reveal that Ti adatoms on TiN(001) surfaces migrate between neighboring fourfold hollow sites primarily along in-plane $\langle 100 \rangle$ and $\langle 110 \rangle$ single jumps, as well as $\langle 100 \rangle$ double jump rates, obtained directly from MD runs as a function of temperature, are used to determine diffusion activation energies E_a , and attempt frequencies A , for the three preferred Ti adatom migration pathways on TiN(001). From transition rates $A \exp[-E_a / (k_B T)]$, we determine adatom surface distribution probabilities as a function of time, which are used to calculate adatom diffusion coefficients $D_s(T)$. AIMD and CMD predictions are consistent and complementary. Using CMD, we investigate the effect on the adatom jump rate of varying the phonon wavelength degrees of freedom by progressively increasing the supercell size. We find that long-wavelength phonons significantly contribute to increasing adatom mobilities at temperatures ≤ 600 K, but not at higher temperatures. Finally, by directly tracking the Ti adatom mean-square displacement during CMD runs, we find that Ti adatom jumps are highly correlated on TiN(001), an effect that yields lower D_s values (D_s^{corr}) than those estimated from uncorrelated transition probabilities. The temperature-dependent diffusion coefficient is $D_s^{\text{corr}}(T) = (4.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}) \exp[-0.55 \text{ eV} / (k_B T)]$.
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1. Introduction

Transition-metal (TM) nitrides exhibit excellent physical and mechanical properties, including high hardness [1,2] and toughness [3], chemical inertness, and good thermal stability and electrical conductivity [4]. Thus, they are employed in a wide variety of applications ranging from wear-resistant protective coatings on cutting tools and engine components [5,6] to diffusion barriers in electronic devices [7–11]. The properties and performance of TM nitrides layers ultimately depend on their nanostructure. During thin-film deposition, nanostructural and surface morphological evolution are largely controlled by the dynamics of adatom surface migration which, in turn, determine nucleation kinetics and film growth modes. A deeper understanding of these processes may allow better control of growth dynamics, and thus the ability to tailor film properties to specific requirements.

Very little is known about either the mechanisms or the kinetics of mass transport in TM nitride systems [12–14]. For TiN, the most studied and best characterized TM nitride [15], differences in reported bulk

diffusion coefficients range over several orders of magnitude [14,16,17]. Moreover, surface mass transport properties lack experimental verification. This is due to the fact that even advanced atomic-scale experimental techniques, such as scanning tunneling microscopy [18–20] and low-energy electron microscopy [21–23], which provide important information regarding surface and nanostructure evolution, cannot provide detailed atomistic dynamics and kinetics, due to the timescales involved, that govern the initial stages of nucleation leading to film growth.

Ab initio calculations focusing on atomic diffusion on TM nitride surfaces are commonly used to determine minimum energy paths and corresponding diffusion barriers at 0 K [24–26]. Generally, this is accomplished by determining adspecies static adsorption-energy landscapes, or using algorithms such as the nudged elastic band (NEB) method [27,28]. However, the rate of thermally-activated migration events depends not only on diffusion barriers, but also on jump attempt frequencies [29]. Vineyard showed that the latter can be estimated within the harmonic approximation at 0 K from the ratio of the product of the N phonon frequencies at the starting point of the transition to the $(N-1)$ phonon frequencies of the system constrained in the transition-state saddle-point configuration [30,31].

While providing estimates of diffusion barriers and attempt frequencies, the computational approaches described above do not account for

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the fact that activation energies and pathways are affected by atomic vibrations at finite temperatures. Moreover, Arrhenius exponential prefactors estimated from 0 K phonon calculations do not accurately describe diffusion attempt-frequencies for materials characterized by large anharmonic contributions to atomic interactions. The approximation proposed by Vineyard [31] is not applicable to TM nitride compounds, such as B1 NaCl-structure vanadium nitride, which are predicted to be dynamically unstable at 0 K [32]. Molecular dynamics (MD) simulations are the most accurate and reliable approaches available to determine surface diffusion jump rates and pathways at finite temperatures.

In MD simulations, the atomic interactions can be described by first-principles or empirical formulations; both methods have advantages and disadvantages. Density functional theory (DFT) is, in principle, the most accurate methodology available to calculate interatomic forces during MD runs [33]. However, DFT has several limitations [34]. The approximations used in DFT for estimation of electron exchange and correlation energy are optimized to describe three-dimensional lattices. However, the abrupt changes which occur in the electron density at surfaces can result in under- or overestimation of surface/adsorbate bond strengths, and hence incorrect adsorption energies [35]. This, in turn, results in incorrect predictions for the relative stabilities of different adsorption sites [36] and, in DFT-based ab initio molecular dynamics (AIMD) simulations of surface kinetics, in incorrect predictions of preferred adsorbate diffusion pathways and jump rates.

Highly computationally demanding AIMD/DFT runs are also limited to the simulation of small systems (a few hundred atoms) and for short time intervals (a few nanoseconds). This does not allow investigation of the effects of phonon wavelength degrees of freedom on atomic migration, estimation of the effect of correlated jumps on diffusion coefficients, or obtaining well-converged values of rate constants for rare events. These limitations are easily overcome when, instead of DFT, empirical potentials are used for the description of interatomic forces. However, classical molecular dynamics (CMD) simulations based upon empirical potentials are less accurate than quantum-mechanical approaches. Despite their individual limitations, AIMD and CMD simulations can be used in parallel to provide complementary information. When AIMD and CMD results are consistent, it is reasonable to assume that the agreement is not accidental, and that the theoretical predictions are realistic representations of actual physical phenomena.

In this study, we probe the dynamics of Ti adatoms on TiN(001) as a function of temperature by performing both AIMD simulations based on DFT and CMD simulations in which the interatomic forces are obtained from the modified embedded atom method (MEAM) potential parameterized to reproduce TiN bulk, as well as surface, properties [37–39]. Titanium nitride, one of the first hard-coating materials [15,40,41], serves as a model to probe diffusion dynamics and kinetics on NaCl-structure TM nitride surfaces in general.

AIMD/DFT and CMD/MEAM simulations show that Ti adatoms on TiN(001) favor fourfold-hollow positions, surrounded by two Ti and two N surface atoms; adatom migration between these sites occurs primarily via in-plane $\langle 100 \rangle$ channels. We determine activation energies E_a and jump-attempt frequencies A of the most frequently observed Ti adatom diffusion pathways on TiN(001) extrapolated from jump-rate $\ln(k)$ vs. inverse temperature $1/T$ Arrhenius plots, in which k is the rate constant. We assess the effect of increasing phonon wavelength degrees of freedom by using progressively larger simulation supercells in CMD runs. Finally, the Ti adatom normal distributions on TiN(001), obtained using uncorrelated jump probabilities $A \exp[-E_a / (k_B T)]$, are employed to determine the surface diffusion coefficient D_s as a function of temperature T . The latter values are compared to those extracted directly from the adatom mean-square displacements during CMD runs to evaluate correlation between consecutive jumps. Remarkably, diffusion coefficient results obtained from AIMD and CMD are in good agreement at all temperatures.

2. Computational details

MD simulations are performed within the microcanonical ensemble NVE, while the substrate temperature is maintained constant via periodic rescaling of the atomic velocities, which mimics a canonical NVT sampling of configurational space [42]. Standard Verlet algorithms are used to integrate Newton's equations of motion at 1 fs time intervals for both CMD and AIMD runs. CMD simulations are carried out by describing atomic interactions with the second-neighbor MEAM [43] potential as implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) [44]. We use the TiN MEAM parameters from our previous publications [37–39,45], which were shown to yield diffusion barriers, Ehrlich step-edge barriers, surface formation energies, step-edge formation energies, and adatom formation energies which are consistent with experimental values [18,20,46], as well as a description of single N adatom and N adatom pair interactions on TiN(001) which are in agreement with AIMD/DFT simulation predictions [39]. Ab initio molecular dynamics simulations are carried out with the VASP code [47] implemented using the generalized gradient approximation (GGA) [48] and the projector augmented wave (PAW) [49] method. The Brillouin zone is sampled with $3 \times 3 \times 1$ k-point grids centered at the Γ point. 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.

Ti adatom diffusion pathways and jump rates are probed as a function of temperature on 3×3 TiN(001) surface unit cells. The substrate consists of three layers for a total of 108 atoms in AIMD runs, and eight layers with 288 atoms in CMD runs. The lateral size of the simulation cell is sufficient to avoid adatom self-interactions. During all MD 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. AIMD simulation boxes contain six vacuum layers to prevent interaction between TiN(001) surface slab replicas along the [001] direction. At each temperature, the average Ti–N in-plane nearest-neighbor distance $\langle d_{NN//} \rangle$ in the simulation slab is obtained, accounting for the experimental TiN thermal expansion coefficient $9.35 \times 10^{-6} \text{ K}^{-1}$ [4], by rescaling the 0 K $\langle d_{NN//} \rangle$ values, 2.127 Å for DFT + GGA [50] and 2.121 Å for MEAM [37]. Rescaling of $\langle d_{NN//} \rangle$ as a function of temperature is necessary to avoid spurious substrate strain effects on the adatom jump rate [51]. Prior to initiating each MD run, thermal oscillations in the adatom-free simulation slab are allowed to stabilize for 5 ps, a time interval sufficient to equilibrate the phonon modes in the system.

Ten statistically independent CMD runs of 10 ns are performed at temperatures T of 600, 900, 1200, and 1500 K for a total of 0.4 μs simulated time. 0.5-ns AIMD runs are performed at 1000, 1200, 1500, and 2200 K, for a total of 2 ns simulation time. All results are stored in video files with a time resolution of 10 fs. In order to further verify the reliability of our AIMD model, we vary the number of simulation slab layers from three to five (180 atoms) to test the dependence of the diffusion rate constant k on substrate thickness. Two 40-ps AIMD runs, performed at $T = 2200$ and 2500 K with the larger simulation cell, return jump-rates which are in good agreement with those calculated for three-layer slabs.

We use MEAM and DFT conjugate gradient minimizations to calculate Ti adatom adsorption energy landscapes on 4×4 atom static TiN(001) supercells consisting of five layers, by sampling the irreducible triangle of the surface unit cell on a 25-point grid. This is accomplished by relaxing the upper two TiN(001) layers and the vertical coordinates of the adspecies at each point. Adsorption energies are evaluated to an accuracy of 10^{-5} eV/atom, which in DFT is achieved by using a plane-wave cutoff of 500 eV and integrating the Brillouin zone on $15 \times 15 \times 1$ k-point meshes centered at Γ . Both quantum-mechanical and empirical results indicate that the most stable position for isolated Ti adatoms on infinite TiN(001) terraces at 0 K is in fourfold hollow sites surrounded by two Ti and two N surface atoms (Fig. 1). Considering the

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