



Ab initio and classical molecular dynamics simulations of N₂ desorption from TiN(001) surfaces



D.G. Sangiovanni^{a,*}, D. Edström^a, L. Hultman^a, I. Petrov^{a,b}, J.E. Greene^{a,b}, V. Chirita^a

^a Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden

^b Departments of Materials Science, Physics, and the Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL 61801, USA

ARTICLE INFO

Article history:

Received 5 December 2013

Accepted 17 January 2014

Available online 24 January 2014

Keywords:

N₂ desorption

Surface diffusion

Nitrides

Molecular dynamics simulations

Density functional theory

Vacancy formation

ABSTRACT

Ab initio molecular dynamics simulations based on density functional theory show that N adatoms are chemisorbed in threefold sites close to a N surface atom and between the two diagonally opposed neighboring Ti surface atoms on TiN(001). The most probable N adatom reaction pathway, even in the presence of nearby N adatoms, is for the N adatom and N surface atom pair to first undergo several exchange reactions and then desorb as a N₂ molecule, resulting in a surface anion vacancy, with an activation barrier E_{des} of 1.37 eV and an attempt frequency $A_{des} = 3.4 \times 10^{13} \text{ s}^{-1}$. E_{des} is essentially equal to the N adatom surface diffusion barrier, $E_s = 1.39 \text{ eV}$, while A_s is only three to four times larger than A_{des} , indicating that isolated N adatoms migrate for only short distances prior to N₂ desorption. The probability of N₂ desorption via recombination of N adatoms on TiN(001) is much lower due to repulsive adatom/adatom interactions at separations less than $\sim 3 \text{ \AA}$ which rapidly increase to $\sim 2 \text{ eV}$ at a separation of 1.5 \AA . We obtain good qualitative and quantitative agreement with the above results using the modified embedded atom method potential to perform classical molecular dynamics simulations.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Due to remarkable physical properties including high hardness and mechanical strength [1–3], chemical inertness [4–6], thermal stability [7], and electrical conductivity which varies from metallic to semiconducting [8–10], transition-metal (TM) nitride thin films are used in a wide range of applications: from wear-resistant protective coatings for cutting tools and engine components [11,12] to diffusion barriers in electronic devices [13]. The actual properties achieved by a given TM nitride film depend in large part on surface and microstructural evolution during reactive growth. That is, the properties depend on the reaction kinetics of nitrogen on the film surface during growth in excess N₂ partial pressure. Here, we use TiN as a model system and focus on nitrogen desorption pathways and kinetics on TiN(001).

Several *ab initio* studies [14–19], with only a few performed using *ab initio* molecular dynamics (AIMD) [20,21], have considered the interaction of TM nitride surfaces with environmental gases such as oxygen, nitrogen, hydrogen, and carbon dioxide. Density functional theory (DFT) is commonly used to calculate adsorbate potential-energy landscapes, minimum energy paths, and diffusion barriers on static surfaces. These calculations require knowledge of stable system configurations. Moreover, lattice vibrations at finite temperature will affect the magnitude of diffusion barriers. Molecular dynamics (MD) simulations, which model atomic motion and vibrations as a function of temperature, can reveal the existence of unexpected system

configurations and reaction pathways. Highly computationally intensive MD based on DFT is the most accurate computational tool presently available for resolving the dynamics and kinetics of atomistic material processes.

DFT calculations, which provide a good compromise in terms of reliability vs. computational time, are widely applied in condensed matter physics. However, DFT has several limitations [22]. The approximations used in DFT for estimation of electron exchange and correlation energy are optimized to describe three-dimensional lattices. This means that the abrupt changes which occur in the electron density at surfaces can result in under- or over-estimation of surface/adsorbate bond strengths, and hence incorrect adsorption energies [23]. This, in turn, results in incorrect predictions for the relative stabilities of different adsorption sites [24] and, in DFT-based AIMD simulations of surface kinetics, in incorrect predictions of preferred adsorbate diffusion pathways and jump rates. However, if AIMD simulation results are consistent with those obtained from MD simulations based on empirical potentials, which do not consider electron–electron interactions, it is reasonable to assume that the agreement is not accidental, and that the theoretical predictions are reasonable representations of actual physical phenomena.

Several studies indicate that atoms adsorbed on a solid surface have a long-range oscillatory interaction, which, as function of decreasing separation changes from attractive to repulsive to attractive. This was first suggested by Grimley [25], who used *ab initio* calculations to probe the behavior of two hydrogen atoms chemisorbed on metallic surfaces. Einstein et al. [26], based upon a tight-binding analysis, showed that the oscillatory interaction between two adatoms adsorbed on a solid surface is a general phenomenon. Subsequent field-ion

* Corresponding author. Tel.: +46 13282478; fax: +46 13137568.

E-mail address: davsan@ifm.liu.se (D.G. Sangiovanni).

microscope experiments, carried out by Tsong [27] and by Watanabe and Ehrlich [28], verified the theoretical prediction for Re–Re, Re–Pd, W–Pd, and Ir–Ir metal-atom pairs adsorbed on W(110). Later, Lau and Kohn [29,30] reported that these interactions are repulsive or attractive depending on the nature of the adsorbate atoms and on the filling of surface electronic bands. Knowledge of the transition from, and absolute values of, repulsive to attractive lateral interactions between Sb adatom pairs on Si(001), based upon modulated-beam mass spectrometry and thermally stimulated desorption experiments, was found to be essential for understanding antimony dopant desorption kinetics during Si(001) molecular-beam epitaxy [31]. Repp et al. [32] demonstrated, using scanning tunneling microscopy to probe the dynamics of Cu adatoms on Cu(111) surfaces, that an accurate quantification of adatom/adatom interaction strength as a function of separation is necessary to understand the role of such effects on crystal growth.

It is generally assumed that N₂ loss during thin-film growth of TM nitrides such as TiN(001) occurs by adatom/adatom associative desorption [33–37]. However, N-adatom/N-adatom (N_{ad}/N_{ad}) pair-interactions on TiN(001) have not been rigorously assessed. Based upon DFT calculations, Graciani et al. [34] reported that N adatoms can recombine by overcoming a barrier of 0.11 eV. This value was determined by fixing the position of one N adatom atop a Ti terrace atom, while moving the other N adatom progressively closer by steps corresponding to second-neighbor distances (~3 Å). DFT calculation results by Gall et al. [33,38], however, showed that the minimum energy path for N diffusion on TiN(001) is along <110> via atop N-terrace positions, not crossing over Ti terrace atoms. This indicates that N adatom associative recombination is unlikely to occur following the pathway suggested by Graciani and coworkers.

Here, we determine stable adsorption sites, diffusion pathways, and migration rates of N adatoms, together with reaction pathways leading to the associative formation and desorption of N₂ molecules on TiN(001). We perform both *ab initio* and classical molecular dynamics (AIMD and CMD) simulations as a function of temperature *T*, in which interatomic forces are obtained from DFT and the modified embedded atom method (MEAM) potential optimized for TiN bulk and surface properties [39]. We find that the most stable sites for N adatoms on TiN(001) are threefold positions at the center of a triangle formed by a terrace N atom, with which the adatom forms a covalent bond, and the two neighboring Ti terrace atoms. Anchored to underlying N terrace atoms, N adatoms are significantly less mobile than Ti adatoms on TiN(001) [33,40], and migrate between threefold sites along <110> channels which requires breaking the bond with the initial N terrace atom and reforming it with the diagonally opposite terrace atom.

Strong N-adatom/N-surface-atom (N_{ad}/N_{surf}) bonding hinders N_{ad} surface diffusion, but favors N_{ad}/N_{surf} exchange. As observed in AIMD and CMD simulations, only three to four N_{ad} diffusion hops on TiN(001) are observed prior to N_{ad}/N_{surf} desorption as N₂ molecules with *E*_{des} = 1.37 eV, thus producing vacant anion sites in the TiN(001) surface. Moreover, we show that N₂ formation by N_{ad}/N_{ad} associative recombination is considerably less likely, with *E*_{des} = 2 eV. We obtain good qualitative and quantitative agreement between *ab initio* and classical predictions which allows us to determine the probabilities of N_{ad} diffusion, N_{ad}/N_{surf} exchange, and N_{ad}/N_{surf} molecular desorption, with corresponding activation energies and prefactors acquired from Arrhenius plots of the rate constant as a function of temperature for each event.

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 [41]. Standard Verlet algorithms are used to integrate Newton's equations of motion at time intervals of 1 fs for both CMD and AIMD runs. CMD simulations are carried out by

describing atomic interactions with the second-neighbor modified embedded atom method [42] potential as implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) [43]. We use the TiN MEAM parameters from our previous publications [39,44,45], which were shown to yield adatom formation energies, diffusion barriers, and Ehrlich step-edge barriers that are consistent with experimental values [36,46,47]. AIMD simulations are accomplished with the VASP code [48], using the generalized gradient approximation (GGA) [49], and the projector augmented wave (PAW) [50] method. The Brillouin zone is sampled with 3 × 3 × 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.

N adatom dynamics on TiN(001) terraces 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. 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 <d_{NN//}> in the simulation slab is obtained accounting for the experimental TiN thermal expansion coefficient, 9.35 × 10⁻⁶ K⁻¹ [7], by rescaling the 0 K <d_{NN//}> value, 2.127 Å for DFT + GGA [51] and 2.121 Å for MEAM [39]. Rescaling of <d_{NN//}> as a function of temperature is necessary to avoid spurious substrate strain effects on the adatom jump rate [52]. Prior to initiating each MD run, thermal oscillations in the adatom-free simulation slab are allowed to stabilize for five ps, a time interval sufficient to equilibrate the phonon modes in the system.

AIMD runs are performed at temperatures *T* = 1200, 1500, 1800, 2200, and 2500 K for a total simulation time of ~1 ns. With CMD, we perform ten runs each at *T* = 1200, 1500, 1800, 2000, 2300, and 2500 K. All results are stored in video files with a time resolution of 10 fs. Each CMD run is continued for the time required to observe N₂ desorption. From the combination of AIMD and CMD runs, we extract pathways, kinetic barriers, and attempt frequencies for N_{ad} diffusion among threefold surface sites, N_{ad}/N_{surf} exchange events, and N_{ad}/N_{surf} desorption.

We calculate average attempt frequencies \bar{A} and activation energies \bar{E}_a from linear interpolation of the logarithm of the rate coefficient \bar{k} (average rate coefficients \bar{k} are obtained from MD runs) as a function of the inverse temperature using the Arrhenius equation: $\ln(\bar{k}(T)) = \ln(\bar{A}) - \bar{E}_a/(k_B T)$. Data scatter κ , for which $\kappa = \ln[k(T_i)]$, is characterized at each temperature *T_i* by a normalized Gaussian distribution function *f*, with maximum at $\bar{\kappa} = \ln(\bar{k})$, and width σ_κ (standard deviation): $f(\kappa, \bar{\kappa}, \sigma_\kappa) = [1/(\sigma_\kappa \sqrt{2\pi})] \exp\left\{-\left[(\kappa - \bar{\kappa})/(\sqrt{2}\sigma_\kappa)\right]^2\right\}$.

The uncertainty σ_κ is estimated using the formula reported in reference [53]: $\sigma_\kappa = [\ln(\bar{k}/k^{\min}) + \ln(k^{\max}/\bar{k})]/2$, for which *k_{min}* and *k_{max}* are the extreme values for the rate coefficient *k*. Rate coefficients outside the range [*k^{min}*, *k^{max}*] occur with negligible probability. The uncertainties σ_E and σ_A for calculated values of the average activation energy \bar{E}_a and attempt frequency \bar{A} correspond to the widths of the normal distributions $f(E_a, \bar{E}_a, \sigma_E)$ and $f(A, \bar{A}, \sigma_A)$. The latter are obtained from a linear interpolation of a large number of stochastically created { $\kappa(T_i)$ } data sets, { $\kappa(T_i)$ } = { $\ln[k(T_1)]$, $\ln[k(T_2)]$, ..., $\ln[k(T_n)]$ }; at each temperature *T_i*, a $\kappa(T_i)$ value is selected with probability $f(\kappa, \bar{\kappa}, \sigma_\kappa)$. Accordingly, in the results and discussion section, predicted values of *E_a* and *A* are expressed as $\bar{E}_a \pm \sigma_E$, and $\bar{A} \pm \sigma_A$.

To assess the probability for N₂ molecule formation via associative adatom recombination, we carry out additional MD tests: ten 0.5-ns-runs with CMD, at each of the temperatures listed above, for a total

Download English Version:

<https://daneshyari.com/en/article/5422225>

Download Persian Version:

<https://daneshyari.com/article/5422225>

[Daneshyari.com](https://daneshyari.com)