

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



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ABSTRACT

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

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1. Introduction

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

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

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

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

Recently, we showed that Ti adatoms experience considerably slower migration rates on disordered $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$ compared to the

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

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

2. Methodology

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

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

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

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

In addition, we have taken adatom magnetic degrees of freedom into account. Fig. 2 shows that the Ti adatom adsorption energy at, and close to, a bulk site is dramatically different with magnetism included. The effect on the energetics is largest when using PBE-GGA. Neglecting spin polarization at specific positions on the surface can be detrimental for understanding even the qualitative adatom migration path, not just quantitative barrier values, as will be discussed in the section on Ti adatoms below, Section 4.1.

The surface energy, E_s , is defined as

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

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

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

Two approaches are employed to investigate surface diffusion energetics. The first is to probe the TiN surfaces with adatoms positioned at

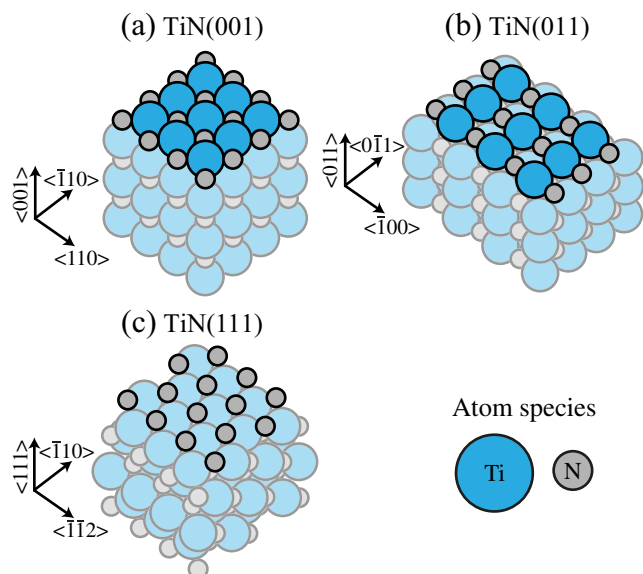


Fig. 1. Supercells used to model TiN surfaces: (a) TiN(001), (b) TiN(011), and (c) TiN(111).

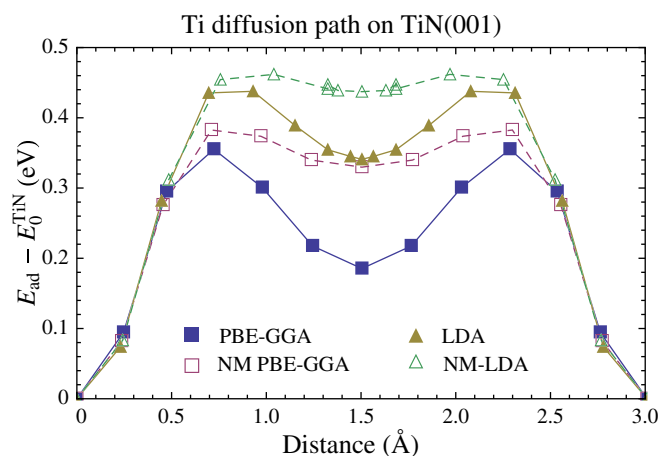


Fig. 2. Ti adatom diffusion paths from a stable fourfold site to a metastable bulk site atop N (see Fig. 3 for site descriptions) on TiN(001) calculated using PBE-GGA and LDA, with and without magnetic degrees of freedom. E_{ad} is the Ti adatom adsorption energy, E_0^{TiN} is the adsorption energy at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

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