First-principles calculations of step formation energies and step interactions on TiN(001)

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Abstract

We study the formation energies and repulsive interactions of monatomic steps on the TiN(001) surface, using density functional total-energy calculations. The calculated formation energy of [100] oriented steps agree well with recently reported experimental values; these steps are shown to have a rumpled structure, with the Ti atoms undergoing larger displacements than the N atoms. For steps that are parallel to [110], our calculations predict a nitrogen (N) termination, as the corresponding formation energy is several hundred meV/Å smaller than that of Ti-terminated steps.

Keywords: Density functional calculations; Single crystal surfaces; Surface energy; Step formation energy; Titanium nitride

Titanium nitride thin films have attracted sustained interest for diverse technological applications because of their high resistance to corrosion and wear, their good thermal and electrical conductivity, and fast surface diffusion characteristics. Although there have been a large number of experimental studies on different aspects related to thin film growth on TiN surfaces, few atomistic studies have been performed so far. Recognizing the need for accurate atomic scale properties, several groups have recently employed density functional total-energy methods to study the structure and energy of low index TiN surfaces [1–3], and diffusion barriers on these surfaces [3]. To our knowledge, similar studies for the stepped surfaces have not yet been reported. Motivated by recent experimental work [4–7] that addresses the determination of absolute step formation energy and stiffness from equilibrium shape fluctuations and decay of two-dimensional islands on TiN surfaces, we study the structure and energetics of monatomic steps on TiN(001). While the [001] step edge is made up of alternating Ti and N atoms,

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the nature (i.e. N-terminated or Ti-terminated) of the [110] oriented steps has not been elucidated. Calculations of step formation energies for the two types of edge terminations can give insight into the structure of the step. In this paper, we report the formation energies as well as the strength of repulsive interactions between the steps, and provide a description of the step structures in terms of atomic displacements. Our calculations on step energetics are consistent with the experimental results for the [100] steps, and suggest that the steps along the [110] direction are N-terminated.

The density functional calculations have been carried out with the VASP package [8], using ultra-soft pseudopotentials and the Perdew–Wang functional form for the exchange-correlation energy [9]. In all the computations we use the experimental value for the lattice constant of TiN, \( a = 4.24 \text{ Å} \); for this lattice constant, bulk calculations with an eight-atom unit cell and 35 \( k \)-points yielded a bulk energy per pair of \( e_b = -19.2747 \text{ eV} \). For surface calculations, the Brillouin zone was sampled using a \( \Gamma \)-centered \( 8 \times 8 \times 1 \) grid. This sampling yielded 15 \( k \)-points for the TiN(001) surface, and 21–25 \( k \)-points for the stepped surfaces. All atoms were relaxed via a conjugate-gradient algorithm until the total energy converged to less than 0.001 eV. The energy cutoff for the plane waves was set to 250 eV (18.37 Ry) in all the calculations. Before discussing the stepped surfaces, we compare the results for the flat TiN(001) surface obtained using the above model parameters with recent theoretical studies [1–3]. It is well known (see, e.g., Ref. [1]) that this surface exhibits the so-called rumpling reconstruction, where the N atoms relax away from the surface and the Ti atoms are pulled inwards. Although somewhat different computational parameters are used in Refs. [1–3] compared to the present study, our results for the displacements of the first and second surface layer are in agreement with previously reported values (refer to Table 1). In terms of surface energy of TiN(001), we obtain \( \gamma_{\text{TiN}(001)} = 80.6 \text{ meV/Å}^2 \), which is very close to the value of 81 meV/Å\(^2\) given in Refs. [2,3].

In this work we consider two types of steps on the TiN(001) surface, which correspond to the [100] and [110] orientations. The [100] step edge consists of alternating N and Ti atoms along the step, while the [110] steps have edges that are made up of a single atomic species, either N or Ti. Fig. 1 illustrates the step structures considered here, along with the periodic supercells used in the density functional calculations. The dimensions of the supercell are \( L_x \times L_y \times L_z \), where \( L_x \) and \( L_z \) denote the terrace width and the height of the

![Fig. 1. Typical configurations of stepped TiN(001) surfaces, with (a) steps along [100], and (b) steps oriented along [110]. The periodic vectors of the supercell are indicated by \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \). The steps oriented in the [100] direction are made of alternating N (blue) and Ti (red) atoms as depicted in (a), while the steps parallel to [110] are either N-terminated or Ti-terminated (upper and lower slab surface, respectively) as shown in (b).](https://example.com/fig1.png)

<table>
<thead>
<tr>
<th>( d_{N}^{1} )</th>
<th>( d_{N}^{2} )</th>
<th>( d_{Ti}^{1} )</th>
<th>( d_{Ti}^{2} )</th>
<th>( r_{1} )</th>
<th>( r_{2} )</th>
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<tr>
<td>Ref. [1]</td>
<td>0.134</td>
<td>-0.074</td>
<td>\text{---}</td>
<td>0.21</td>
<td>0.005</td>
</tr>
<tr>
<td>Ref. [2]</td>
<td>\text{---}</td>
<td>\text{---}</td>
<td>\text{---}</td>
<td>0.179</td>
<td>0.18</td>
</tr>
<tr>
<td>Ref. [3]</td>
<td>0.12</td>
<td>-0.06</td>
<td>\text{---}</td>
<td>0.21</td>
<td>0.179</td>
</tr>
<tr>
<td>This work</td>
<td>0.113</td>
<td>-0.066</td>
<td>0.040</td>
<td>0.028</td>
<td>0.179</td>
</tr>
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</table>

The outward displacements of the first \( (d_{N, Ti}^{1}) \) and second \( (d_{N, Ti}^{2}) \) layer surface atoms, and the rumpling amplitudes \( r_{1(2)} \equiv d_{N}^{1(2)} - d_{Ti}^{1(2)} \) are given in Å.
supercell, respectively. The dimension $L_y$ is given by the spatial period in the direction parallel to the step, which is $a$ for the [100] steps and $a\sqrt{2}/2$ in the case of [110] steps. To create the steps, we employ shifted boundary conditions [10], in which the amount of shift in the $z$-direction is the step height ($a/2$) and the shift in the $y$-direction is determined from requirements of periodicity. Most calculations on vicinal surfaces were carried out using a slab of TiN with eight atomic layers (16.96 Å) and a vacuum thickness of 12 Å.

The energetics of steps can be understood by considering the ledge energy, defined as [10]

$$\lambda = \left( E - N_p e_b - 2\gamma_{(001)} A \right) / 2L_y,$$

where $E$ is the relaxed total energy of the $N_p$ Ti–N pairs in the supercell, and $A$ is the projected area of the slab on the (001) plane. The ledge energy is the energy per unit length (along the step) of the vicinal surface in excess of the surface energy of the terraces separating the steps: in the case of [100] steps this excess energy can be uniquely defined by Eq. (1) because the system is stoichiometric irrespective of the slab thickness. For the [110] steps, the only way to preserve stoichiometry is to have an N-terminated step on one face of the slab and a Ti-terminated step on the other face (even number of layers), in which case Eq. (1) gives the average ledge energy of the two types of [110] steps. On the other hand, when the number of (001) layers in the computational cell is odd, the same kind of termination for the [110] steps will be present on both sides of the slab, so the system becomes non-stoichiometric. We simulate the non-stoichiometric slab as a system with zero net charge, which is consistent with the experimental conditions of growth [4]. There is no inconsistency between the overall charge neutrality and non-stoichiometry, since upon density functional optimization the electrons will be redistributed; no long-range electric fields occur and the calculations are convergent (also refer to the calculations in Ref. [3]). In the non-stoichiometric case, the ledge energy can be written as

$$\lambda = \left( E - N_N\mu_N - N_Ti\mu_{Ti} - 2\gamma_{(001)} A \right) / 2L_y,$$

where $N_N$ ($N_Ti$) and $\mu_N$ ($\mu_{Ti}$) are the number of N (Ti) atoms and their chemical potential, respectively. While the two chemical potentials add up to the bulk cohesion energy per pair ($\mu_N + \mu_{Ti} = \epsilon_0$), the chemical potential of (e.g.) the N atoms is not known, which leads to ambiguities in the values of the formation energies of the two types of [110] steps. We will continue with the analysis of ledge energies, but return to this issue later.

The ledge energy —as calculated by either Eq. (1) or (2), includes both the step formation and interaction energies. The interaction between the steps is caused by electrostatic and by elastic contributions, with comparable magnitudes [11]. Using the fact that both the elastic and electrostatic effects give rise to dipolar interactions [12,13], the ledge energy can be expressed as

$$\lambda = A + \pi^2 G / 6 L_y^2,$$

where $A$ is the formation energy of a step and $G$ is the strength of the inverse-square repulsive interaction between two isolated steps. The factor $\pi^2/6$ arises because we deal with a periodic array of steps, rather than with two isolated ones [14]. The parameters $A$ and $G$ obtained by fitting the results of first-principles calculations to Eq. (3) are given in Table 2. For the [100]-oriented steps we find a formation energy of 238 meV/Å, which is in very good agreement with the value of 250 ± 50 meV/Å obtained from two-dimensional equilibrium island shape and coarsening measurements on epitaxial TiN(001) layers [4]. The interaction strength $G$, which has not been reported so far, is found here to be 548 meVÅ. The structure of the step edges along the [100] direction (refer to Fig. 2(a)) is similar to the one reported for steps on TaC(001) [11], with the metal atoms undergoing larger displacements than the N atoms. This rumbled structure of the [100] step edges gives rise to effective electric dipoles of comparable magnitude with those obtained by charge spill-out at the polar [110] steps, which is reflected in the comparable magnitudes of the repulsion strengths $G$ for the two types of steps (refer to Table 2).

While we find remarkable agreement of the computed formation energy of the [100] step with [11]...
There are differences between our results and experimental values reported for the [110]-oriented steps. The discrepancy is not surprising for the following two reasons: (a) in the case of [110] steps, the value we report in Table 2 is the arithmetic mean between the formation energies of N- and Ti-terminated steps and (b) in experiments, it is not known what type atoms lie at the step edges, and, furthermore, it is unlikely that the two terminations occur with equal probability. Given this situation, we have set out to investigate further the [110] steps in order to estimate the individual formation energies of the N- and Ti-terminated steps. To this end, we have repeated the calculations using supercells with odd numbers of layers, for which steps are terminated in the same way on both faces of the slab.

Table 2

<table>
<thead>
<tr>
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<th>Present work (Theory)</th>
<th>Previous reports</th>
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<tr>
<td>[100] steps:</td>
<td>( A_{[100]} ) (meV/Å)</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>( G_{[100]} ) (meV/Å)</td>
<td>548</td>
</tr>
<tr>
<td>[110] steps:</td>
<td>( A_{[110]} ) (meV/Å)</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>( G_{[110]} ) (meV/Å)</td>
<td>445</td>
</tr>
<tr>
<td>Surfaces:</td>
<td>( \gamma_{[001]} ) (meV/Å²)</td>
<td>80.6</td>
</tr>
<tr>
<td></td>
<td>( \gamma_{[111]} ) (meV/Å²)</td>
<td>227.4</td>
</tr>
</tbody>
</table>

Absolute formation energies have been recently determined from experiments by Kodambaka et al. [4]. Surface energies of TiN(001) and TiN(111) (averaged over N- and Ti-terminated surfaces) are also given for comparison with previous first-principles studies [2,3].

Experimental work [4], there are differences between our results and experimental values reported for the [110]-oriented steps. The discrepancy is not surprising for the following two reasons: (a) in the case of [110] steps, the value we report in Table 2 is the arithmetic mean between the formation energies of N- and Ti-terminated steps and (b) in experiments, it is not known what type atoms lie at the step edges, and, furthermore, it is unlikely that the two terminations occur with equal probability. Given this situation, we have set out to investigate further the [110] steps in order to estimate the individual formation energies of the N- and Ti-terminated steps. To this end, we have repeated the calculations using supercells with odd numbers of layers, for which steps are terminated in the same way on both faces of the slab.

Before reporting the formation energies of steps on TiN(001), we note that for the smallest possible step separations, \( L_s = a\sqrt{2}/4 \), the two faces of the slab assume the (111) facet orientations. Recent theoretical work on TiN(111) [3] offers a reference for comparing surface energies of N- and Ti-terminated (111) facets. Recalling that these surface energies depend on the value used for chemical potential of either N or Ti, we choose a value of \( \mu_N \) that exactly reproduces the value of experimental work [4], the smallest step separations are not considered when fitting ledge energies to Eq. (3), because the elastic regime of step interactions Eq. (3) is not applicable when steps lose their identity by forming a (111) facet.

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Fig. 2. (a) Structure of the single-height, [100]-oriented steps that form a TiN(104) surface. (b) Structure of the N-terminated, [110]-steps that form a TiN(115) surface. The displacements of N and Ti atoms are represented by blue and red arrows (respectively), which lie in the xz plane and are magnified for clarity. For selected atoms around the step edge the components of the displacement vectors \( \Delta_i \) (i = 1, ..., 4) are given in Ångstrom.
\( \gamma_{N-(111)} = 85 \text{ meV/Å}^2 \) given in Ref. [3]. Under this condition, the surface energy computed for the Ti-terminated \((111)\) was 373 meV/Å\(^2\), which is relatively close to the value of 346 meV/Å\(^2\) reported in [3]. Our results for the surface energies of \((111)\) facets are therefore in agreement with the previous study.

For separations that are larger than \( L_x = a\sqrt{2}/4 \), the steps retain their identity and the total slab energies can be used to extract ledge energies and fit them to Eq. (3). The formation energies obtained for the N- and Ti-terminated \([110]\) steps are \( \Delta E_N = -14 \text{ meV/Å}^2 \) and \( \Delta E_T = 846 \text{ meV/Å}^2 \), respectively. These values indicate that it is much more favorable to create N-terminated steps than it is to form Ti-terminated ones. We are cautious about interpreting the negative sign of \( \Delta E_N \) as indicating the presence of steps at zero Kelvin, since the sign of this formation energy can depend on the value of chemical potential of the nitrogen atoms, which is not directly controlled in experiments. We can, however, report that for a range of the chemical potential, \(-8 \text{ eV} \leq \mu_N \leq -5 \text{ eV}\), the relative formation energy \( \Delta E_T - \Delta E_N \) of the two types of edge terminations is positive, and lies in the range \( 689 \text{ meV/Å} < \Delta E_T - \Delta E_N < 1690 \text{ meV/Å} \). This reinforces the conclusion that the N-terminated steps have a much lower formation energy, and are therefore expected to be present on \((001)\) surfaces under the conditions described in Ref. [4]. The physical reason for the large difference in the formation energies of the two types of \([110]\) steps can be understood qualitatively by considering the nature of the chemical bonding in TiN. In bulk, the N atoms bond only to their nearest neighbors, i.e. six Ti atoms. On the other hand, the titanium atoms bond not only with their six first-order neighbors, but also with their second-order neighbors, i.e. 12 Ti atoms. Therefore, while creating an N-terminated \([110]\) step requires breaking only three N–Ti bonds, the formation of a Ti step leads to the breaking of an additional seven Ti–Ti bonds. Although some directional dependence of the strength of the remaining Ti–Ti bonds may arise due to the presence of the step, the broken Ti–Ti bonds will contribute to an increase in the formation energy of the Ti steps. This effect is not compensated by atomic relaxations, which are comparable for the two types of \([110]\) steps.

The N atoms on the \([110]\) step edge undergo rather large displacements with respect to their bulk-truncated positions. As shown in Fig. 2(b), the edge moves inwards by about 0.27 Å. This value is larger than the rumpling amplitudes (refer to Table 1) of the flat TiN(001), so it is conceivable that the relaxation of the step can be observed experimentally. For the Ti-terminated steps we have also calculated the inward horizontal (vertical) relaxations of 0.2 Å (~0.1 Å). Since the horizontal displacements of the Ti steps are comparable to those of the N-terminated steps, it is unlikely that measurements of displacements can help identify the nature of the atoms on the step edges. The step termination could be unambiguously identified using STM, since the localization (of spill-out) charge is different for the two types of steps. As illustrated in Fig. 3, in the case of N-terminated steps the electron density has maxima directly above the positions of the N atoms, while for the Ti-steps these maxima lie between the Ti edge atoms. Local maxima of the electron localization function that are between the Ti atoms occur not only on the surface, but also in the bulk (Fig. 3): this indicates the presence of covalent Ti–Ti bonds, therefore supporting the above bond-counting arguments for the larger formation energy of the Ti steps.

In summary, we have studied the structure and energetics of steps on TiN(001) surface using density functional calculations. For the steps parallel to \([100]\), we have obtained quantitative agreement...
with recent experimental work [4]. While a direct comparison with the experiments is not possible in the case of [110] steps, we have argued that the step edges are N terminated—a prediction that can be experimentally verified. We have also reported the structures of the steps, and have demonstrated a rumpled configuration for the [100] steps, and large inwards relaxations for the [110] step edges. Future work aimed at determining the kink formation energies on these steps can allow for the calculation of their stiffness and for comparison with experimental estimates.

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