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

C. V. Ciobanu[1,2]*, D. T. Tambe[1] and V. B. Shenoy[1]

[1]Division of Engineering, Brown University, Providence, Rhode Island 02912, USA
[2]Division of Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

February 2, 2008

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.

---

*Corresponding author

Titanium nitride thin films have attracted sustained interest for diverse technological application partly because of fast diffusion characteristics on the (001) surfaces. Although there have been a large number of experimental reports 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 different groups have recently employed density functional total-energy methods to study the structure and energies of low index TiN surfaces [1, 2, 3], as well as the diffusion barriers on these surfaces [3]. To our knowledge, similar studies for the stepped surfaces have not yet been attempted. Motivated by recent experimental work [4, 5, 6, 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 here the structure and energetics of monatomic steps on TiN(001). While the [001] step edge is made of alternating Ti and N atoms, 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 [100] steps, and suggest that the steps along [110] direction are N-terminated.

The density functional calculations were 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, $a = 4.24$Å; for this lattice constant, bulk calculations with an eight-atom unit cell and 35 k points yielded a bulk energy per pair of $e_b = -19.2747$ eV. For surface calculations, the Brillouin zone was sampled using a Γ-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. The ions 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 250eV (18.37 Ry) throughout this study. Before discussing the stepped surfaces, we compare the results for the flat TiN(001) surface obtained using the above model parameters with other recent theoretical studies [1, 2, 3]. It is well known (see, e.g., Ref. [1]) that this surface exhibits a so-called rumpling reconstruction, where the N atoms relax outwards the surface and the Ti atoms are pulled inwards. Although somewhat different computational parameters are used in Refs. [1, 2, 3] than in the present study, our results for the displacements of the first and second surface layer agree with previously reported values (refer to Table 1). In terms of surface energy of TiN(001), we obtained $\gamma_{(001)}$=80.6 meV/Å^2, which is also very close to the value of 81 meV/Å^2 given in Refs. [2, 3].

In this work we are considering 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 of only one type of atoms, either N or Ti. Fig. 1 illustrates the step structures considered here, and also shows

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 supercell, respectively. The dimension L_y is taken equal to 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 8 atomic layers (16.96 Å) and a vacuum thickness of 12Å.

Similar to our recent work [11], the energetics of steps is studied starting from the ledge energy, defined as [10]

$$\lambda = (E - N_p e_b - 2\gamma_{(001)}A)/2L_y \ , \tag{1}$$

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 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), case in which Eq. (1) will give the average ledge energy between 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: in this non-stoichiometric situation, the ledge energy can be written as

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

where N_N (N_{Ti}) and μ_N (μ_{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 $(\mu_N + \mu_{Ti} = e_b)$, the chemical potential of (e.g.) the N atoms is not known, which leads to ambiguities in the values of the formation energies of each of the two types of [110] steps. We will continue with the analysis of ledge energies, but return to this issue in later paragraphs.

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

$$\lambda = \Lambda + \frac{\pi^2}{6}\frac{G}{L_x^2} \quad , \tag{3}$$

where Λ is the formation energy of a step and G is the strength of the repulsive interaction between two isolated steps. The factor $\pi^2/6$ arises since we treat a periodic array of steps, rather than two individual ones. Similar to Ref. [11], we compute the fitting parameters Λ and G in Eq. (3) and give the results for the stoichiometric case in Table 2. For the [100]-oriented steps we found 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 Ti(001) layers [4]. The interaction strength G, which has not been reported so far, is found here to be 548 meVÅ; the result is similar to the repulsive strength (607 meV/Å) recently determined for single-height steps on TaC(001) [11]. The structure of the step edges along [100] (shown in Fig. 2(a)) is also similar to the one reported for steps on TaC(001) [11], with the metal atoms undergoing larger displacements than the N atoms.

While it is notable to have found that the calculated formation energy for [100] steps agrees with experiments [4], this agreement ceases in the case of [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 lies at the step edges, and, furthermore, it is in 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.

Although we do not consider the smallest possible step separations when fitting the ledge energies to Eq. (3), it is worth noting that for those separations ($L_x = a\sqrt{2}/4$) the two faces of the slab assume the (111) facet orientations. For the N- and Ti-terminated (111) facets, the surface energies have been reported recently by Gall and coworkers [3], which we will now compare with our own results in the limit of smallest terrace width. Recalling that these surface energies depend on the value chosen for chemical potential of either N or Ti (but not both), we start by choosing a value of μ_N that exactly reproduces the value of 85 meV/Å^2 given in Ref. [3]. Under this condition ($\mu_N = -7.49$ eV), the surface energy that we computed for the Ti-terminated (111) was 373 meV/Å^2, an 8% difference from the value of 346 meV/Å^2 given in [3]. This difference is perhaps due to the larger number of layers (thirteen) used in Ref. [3], which in principle allows for a better relaxation.[1] Since we are studying supercells with different terrace widths (different sizes in the x- direction), in order to keep calculations tractable with our current computational resources we used a maximum of 9 layers. While the convergence of the surface energy for (111) facets might not have been fully reached for 9 layers, the results reported here are consistent: the average of $\gamma_{N-(111)}$=85 meV/Å^2 and $\gamma_{Ti-(111)}$=373 meV/Å^2 (which have been obtained from independent odd-layer calculations) differs by only 1.6 meV/Å^2 from the result of a separate, even-layer calculation which gives $\overline{\gamma}_{(111)}$=227.4 meV/Å^2 (Table 2).

With this preamble on the surface energies of (111) facets, the formation energies obtained for the N- and Ti- terminated [110] steps are -14 meV/Å^2 and 846 meV/Å^2, respectively. These values indicate that it is much more energetically favorable to create N- terminated steps

---

[1]Other contributing factors could be differences in the vacuum size, the kinetic energy cut-off for the plane waves, and the k- space sampling

than it is to form Ti-terminated ones. Since the chemical potential is not directly controlled or measured in experiments, we are cautious about interpreting the minus sign of the formation energy of the N-terminated steps, as that sign can change with the choice of μ_N. We can, however, report that for a range of the chemical potential, -8 eV $\leq \mu_N \leq -5$ eV, the relative formation energy $\Lambda_{Ti} - \Lambda_N$ of the two types of edge terminations is positive, and lies in the range 689 meV/Å$< \Lambda_{Ti} - \Lambda_N <$ 1690 meV/Å. This reinforces the conclusion that the N-terminated steps have a much lower formation energy, and are therefore expected to be present in experiments such as the ones described in [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. 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 implies breaking only three bonds N-Ti bonds, the formation of a Ti step requires 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 counteracted 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 0.27Å. 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 also calculated inward horizontal (vertical) relaxations of 0.2Å (~ 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. A better way of identifying the step termination could perhaps be STM, since the electron localization 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. Such local maxima of the electron localization function 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, which supports 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 reports [4]. While a direct comparison with the experiments was 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 showed 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.

References

[1] K. Kobayashi, Jpn. J. Appl. Phys. **39**, 4311 (2000); *ibid.* Surf. Sci. **493**, 665 (2001).

[2] M. Marlo and V. Milman, Phys. Rev. B **62**, 2899 (2000).

[3] D. Gall, S. Kodambaka, M.A. Wall, I. Petrov, J.E. Greene, J. Appl. Phys. **93**, 9086 (2003).

[4] S. Kodambaka, S.V. Khare, V. Petrova, A. Vailionis, I. Petrov, J.E. Greene, Surf. Sci. **513**, 468 (2002).

[5] S. Kodambaka, V. Petrova, S.V. Khare, D. Gall, A. Rocket, I. Petrov, J.E. Greene, Phys. Rev. Lett. **89**, 176102 (2002).

[6] S. Kodambaka, V. Petrova, S.V. Khare, D.D. Johson, I. Petrov, J.E. Greene, Phys. Rev. Lett. **88**, 146101 (2002).

[7] S. Kodambaka, S.V. Khare, V. Petrova, D.D. Johnson, I. Petrov, J.E. Greene, Phys. Rev. B **67**, 035409 (2003).

[8] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996); *ibid.*, Comput. Mater. Sci. **6**, 15 (1996).

[9] J. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[10] T.W. Poon, S. Yip, P.S. Ho and F.F. Abraham, Phys. Phys. Rev. B **45**, 3521 (1992).

[11] V.B. Shenoy and C.V. Ciobanu, Phys. Rev. B **67**, 081402(R) (2003).

[12] V. I. Marchenko and Y. A. Parshin, Sov. Phys. JETP **52**, 129 (1980).

[13] C. Jayaprakash, C. Rottman and W. F. Saam, Phys. Rev. B **30**, 6549 (1984).

	d_N^1	d_{Ti}^1	d_N^2	d_{Ti}^2	r_1	r_2
Ref. [1]	0.134	-0.074			0.21	0.005
Ref. [2]					0.179	
Ref. [3]	0.12	-0.06			0.18	
This work	0.113	-0.066	0.040	0.028	0.179	0.012

Table 1: Rumpling relaxation of TiN(001) compared with previous reports. 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.

			Present work	Previous reports
[100] steps:	$\Lambda_{[100]}$	(meV/Å)	238	250±50 [4]
	$G_{[100]}$	(meVÅ)	548	—
[110] steps:	$\overline{\Lambda}_{[110]}$	(meV/Å)	410	210±50 [4]
	$\overline{G}_{[110]}$	(meVÅ)	445	—
surfaces:	$\gamma_{(001)}$	(meV/Å^2)	80.6	81 [2, 3]
	$\overline{\gamma}_{(111)}$	(meV/Å^2)	227.4	216 [3]

Table 2: Step formation energies and interaction strengths obtained from ab initio density functional calculations. 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].
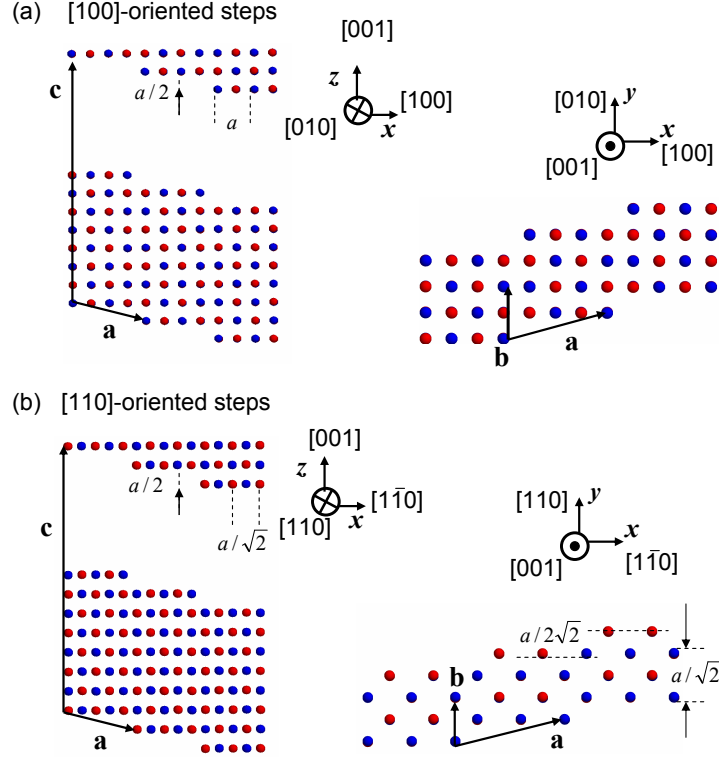
Figure 1: Typical configurations of stepped TiN(001) surfaces, with (a) steps along [100], and (b) steps oriented along [110]. The periodic vectors of the computational cell are indicated by **a**, **b**, and **c**. The steps oriented in the [100] direction are made of alternating N (blue) and Ti (red) 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 fig. (b).

(a)   [100]-oriented steps

$\Delta_1 = -0.133\mathbf{x} + 0.127\mathbf{z}$
$\Delta_2 = -0.241\mathbf{x} - 0.026\mathbf{z}$
$\Delta_3 = 0.050\mathbf{x} + 0.094\mathbf{z}$
$\Delta_4 = 0.137\mathbf{x} + 0.133\mathbf{z}$

Δ_1
Δ_2
Δ_3 Δ_4

[001]
[010] [100]

(b)   [110]-oriented steps

$\Delta_1 = -0.272\mathbf{x} - 0.013\mathbf{z}$
$\Delta_2 = 0.108\mathbf{x} + 0.208\mathbf{z}$

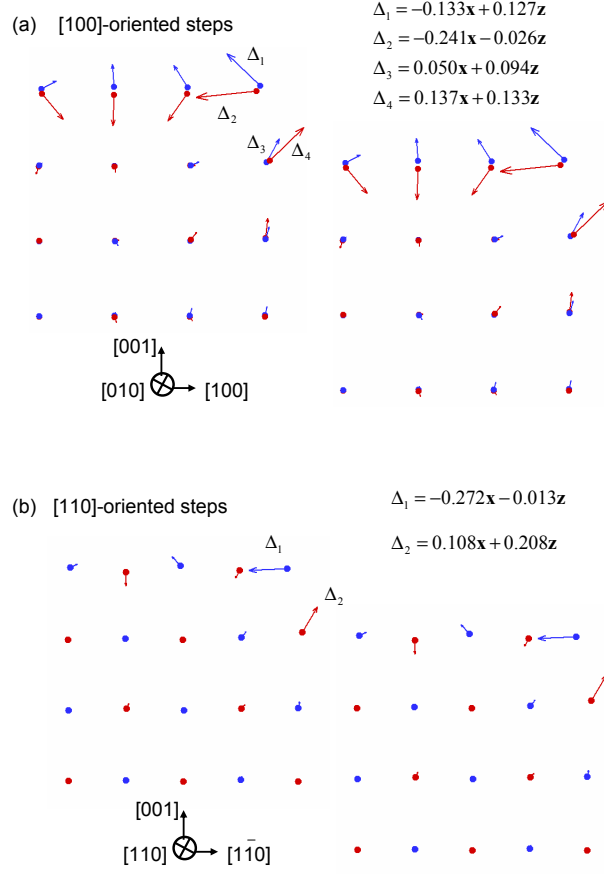Δ_1
Δ_2

[001]
[110] [1$\bar{1}$0]

Figure 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.

9
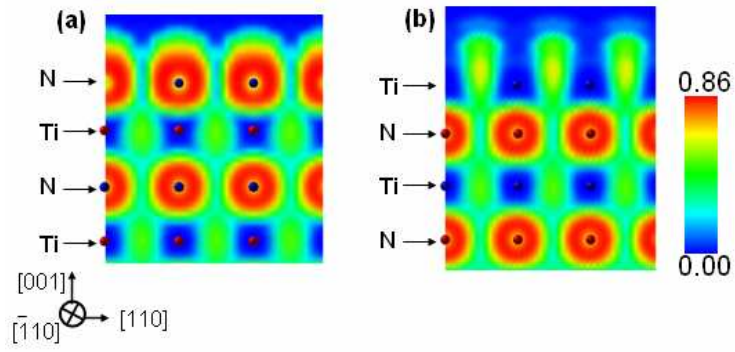
Figure 3: Electron localization function (arbitrary units) in an (110) plane passing through a [110]-oriented step. In this plane, the nature of the atomic rows alternates starting with N atoms on the top row (step edge) (a), or with Ti atoms (b).