



ELSEVIER

Surface Science 476 (2001) L247–L253



www.elsevier.nl/locate/susc

Surface Science Letters

Step structures and energies on monohydride-terminated vicinal Si(0 0 1) surfaces

A. Laracuate ^{*}, L.J. Whitman

Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375-5342, USA

Received 11 December 2000; accepted for publication 9 January 2001

Abstract

Scanning tunneling microscopy was used to determine the equilibrium step structures and step formation energies on monohydride-terminated silicon surfaces for the complete range of (0 0 1)-terrace-plus-step orientations, (0 0 1) to (1 1 4). Compared with the clean surfaces, hydrogen termination alters the atomic-scale step-edge structure and, in many cases, causes large-scale changes in the surface morphology. The structural modifications result directly from a change in the relative energies of the possible single- and double-layer step configurations. These results should prove useful for developing high-fidelity models of film growth and surface processing on silicon substrates in complex gaseous environments. © 2001 Published by Elsevier Science B.V.

Keywords: Scanning tunneling microscopy; Silicon; Single crystal surfaces; Hydrogen atom; Chemisorption; Surface structure, morphology, roughness, and topography; Surface energy; Equilibrium thermodynamics and statistical mechanics

The crystallographic step edge is arguably the most important structure governing epitaxial film growth on surfaces [1,2]. The step-edge energies, in concert with the kinetics and thermodynamics of adsorption, diffusion, and desorption, ultimately determine a film's growth mode and the resulting surface morphology. It is well known that foreign adsorbates can alter the equilibrium step structure, and often have a dramatic effect on film growth [3,4]. Given that most semiconductor devices are fabricated in hydrogen-rich environments on silicon substrates – via chemical vapor deposition (CVD), for example Ref. [5,6] – a comprehensive

understanding of how hydrogen affects Si step energies is essential to the development of accurate models of semiconductor growth and processing. Here we describe the effects of the simplest adsorbate, atomic hydrogen, on the step edges of one of the most studied materials, Si(0 0 1) and its vicinals.

Clean Si(0 0 1)-(2 × 1) and its vicinal surfaces have been well characterized by both experiment and theory [7,8], and the step formation energies determined [9–11]. Using gas-phase atomic hydrogen, a monohydride Si(0 0 1) surface can be readily made that essentially preserves the (2 × 1) dimer reconstruction by terminating the lone dangling bond on each surface Si atom with one H atom [4]. Hydrogen may cause little change in the reconstruction, but its presence on the surface significantly affects film growth during both molecular beam epitaxy (MBE) and CVD [4,6,12–15].

^{*} Corresponding author. Tel.: +1-202-767-2519; fax: +1-202-767-3321.

E-mail address: laracuen@stm2.nrl.navy.mil (A. Laracuate).

Although the microscopic mechanisms underlying these effects are a subject of ongoing debate, one recent theoretical study predicted that hydrogen affects growth in part by changing the step structure and step energies [16]. In this Letter, we report the equilibrium step structures and formation energies for the whole range of H-terminated (001)-terrace-plus-step surfaces, confirming some of the theoretical predictions, and explain how the step energies control the surface morphology.

Our experiments were performed in ultra-high vacuum using silicon wafers oriented between (001) and (114). Clean surfaces were prepared by repeated heating in vacuum to ~ 1450 K followed by long anneals at 615 K. Monohydride-terminated surfaces were then prepared by annealing for at least 2 min more in the presence of atomic hydrogen ($\sim 2 \times 10^{-6}$ Torr H_2 , with a hot W filament ~ 1 cm from the surface). Sample temperatures were determined based on the sample heating power, which was calibrated using both an infrared pyrometer and thermocouple measurements, and are estimated to be accurate to $\pm 25^\circ$ below 800 K and $\pm 10^\circ$ above. Filled-state scanning tunneling microscopy (STM) images were acquired at room temperature.

To prevent etching the surface with H, the monohydride surfaces were prepared at 615 K [17,18]. There is no evidence of step or terrace

etching at this temperature; in contrast, surfaces prepared at lower temperatures exhibit etching pits and step overhangs, and get progressively rougher with increasing exposure. We extensively confirmed that at 615 K the surface morphology does not change with further H exposure (i.e. 2 min vs. 4 or 6 min), demonstrating that under these conditions the surface reaches local equilibrium.

For silicon surfaces tilted away from (001) by up to 19.5° towards (111) – corresponding to Si (114) – the clean surface structure can be generally described in terms of a simple (001)- (2×1) terrace-plus-step morphology [8]. As illustrated in Fig. 1, it is the convention to label the steps on these surfaces according to whether they have a single-(S) or double-layer (D) height, and whether they are “A-” or “B-type”. The B-type steps are further distinguished by whether they are rebonded or non-rebonded, with a rebonded step having two extra atoms per dimer along the step. These additional atoms reduce the dangling bond density at the step edge, lowering the surface energy of the rebonded S_B (r- S_B) and rebonded D_B (r- D_B) steps with respect to the corresponding non-rebonded structures. On clean surfaces oriented from about 4° to 11.4° away from (001) (corresponding to (117)), only r- D_B steps are observed. However, beyond (117), both rebonded and non-rebonded D_B steps coexist [8,19].

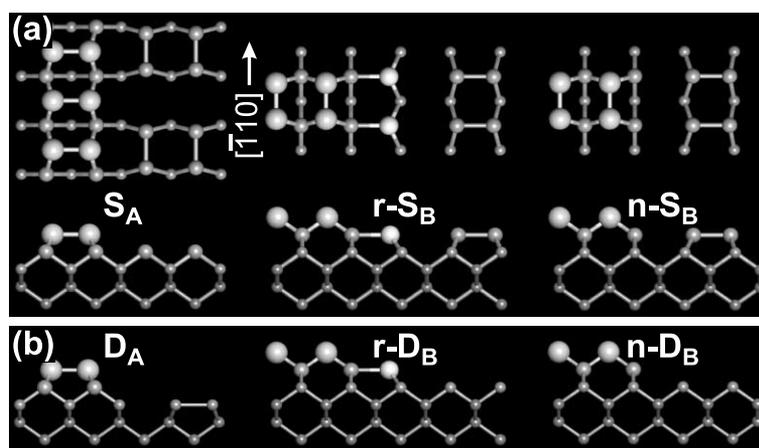


Fig. 1. Ball-and-stick models of rebonded (r) and non-rebonded (n) single- (S) and double-layer (D) step structures on vicinal Si(001) surfaces. (a) Both top and side views are shown for the single-layer steps, where the (001)- (2×1) dimers rotate from one terrace to the next. (b) For the double-layer steps (side views only), all dimers are oriented in the same direction.

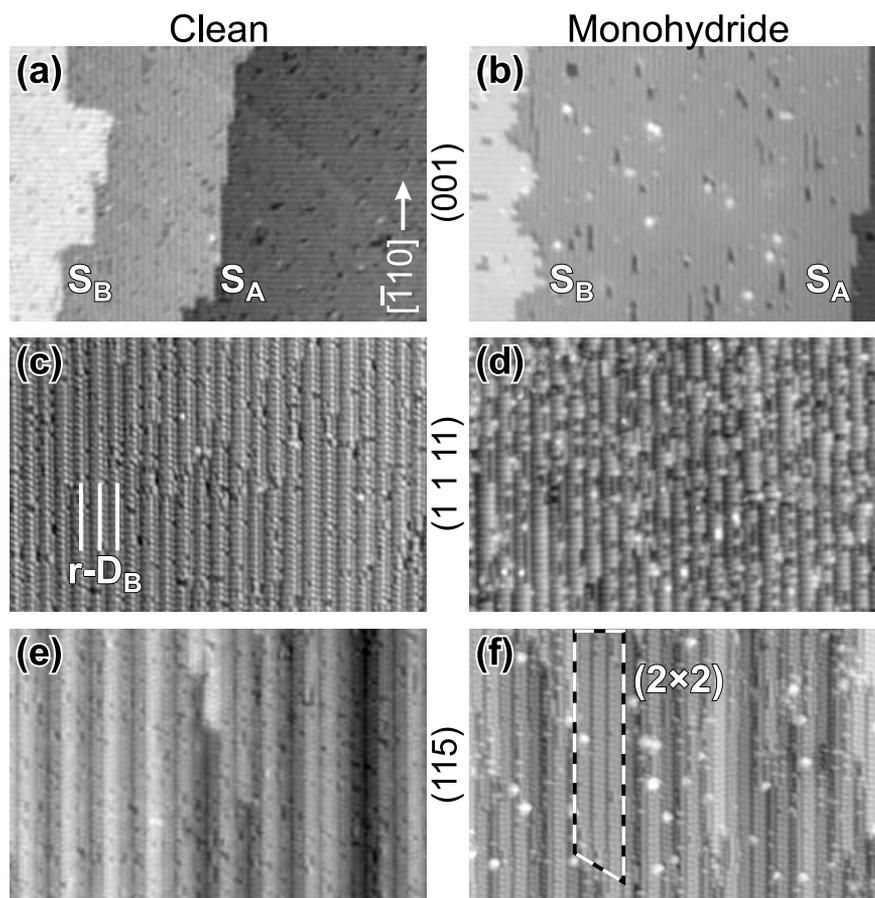


Fig. 2. STM images, 50 nm wide, showing the equilibrium morphology of clean and H-terminated Si(001), (1111), and (115). In (a) and (b) the S_A and S_B steps are indicated. Periodic rebonded D_B steps are observed on clean Si(1111), a nearly “ideal” vicinal surface. Multi-unit cell (2×2)-reconstructed regions are observed on Si(115) only when hydrogen terminated.

We find that the transformation in the equilibrium surface morphology caused by H-termination is a distinctive function of orientation (Fig. 2). The general nature of the changes can be categorized into three different regimes delineated by the types of steps present on the clean surfaces. For surfaces close to (001), the subtle changes in morphology are confined to the S_B steps. Notice that the H-terminated surface has a larger number of kinks along the S_B step edges than the clean surface, giving these steps a rougher morphology (Fig. 2(a) vs. (b)). Whereas the clean surface exhibits relatively straight edges, with segments up to eight dimers long observed without a kink, long S_B

segments rarely occur on the H-terminated surface. On vicinal surfaces from about 4° – 11° off (001), such as (1111), H-termination has a much more pronounced effect on the morphology (Fig. 2(c) vs. (d)). Clean surfaces in this range have a nearly ideal vicinal structure – an ordered, periodic array of (001)-(2×1) terraces separated by $r-D_B$ steps – but the hydrogen-terminated surfaces are rougher and much more disordered. Because the roughness is associated primarily with changes in the step configuration (described below), the H-induced roughening and disorder increases with step density, with maximal effect on Si(117) (not shown).

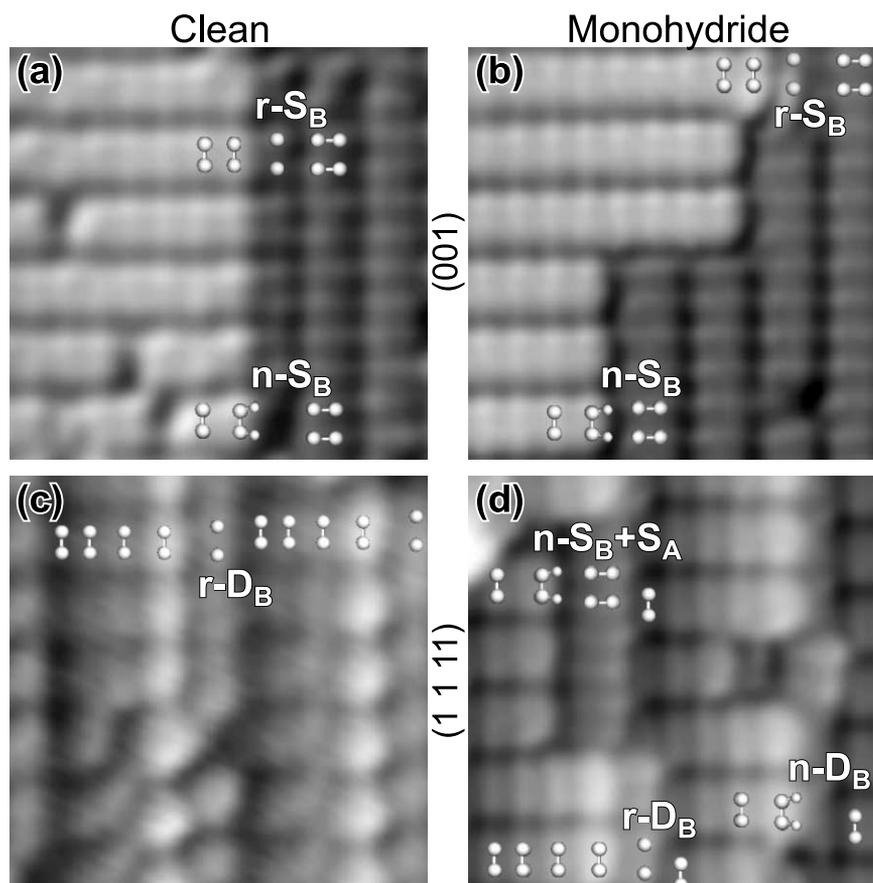


Fig. 3. Atomic-resolution images, $5 \times 5 \text{ nm}^2$, of clean and H-terminated Si(001) and (111). H-termination has little effect on how the individual Si dimers and step-edge structures appear in filled-state STM images. Models identifying the various step structures are superimposed on the images, but only the Si atoms are shown; the surface H atoms, one per Si atom in (b) and (d), are omitted for clarity.

In contrast to the rougher surfaces observed following H-termination of the $r\text{-D}_B$ -stepped surfaces, smoother morphologies are observed following H-termination of surfaces oriented approximately between (117) and (114) ($\sim 11^\circ$ – 19°). This effect is quite apparent on Si(115) (Fig. 2(e) vs. (f)). The clean surface has a saw-tooth-like morphology with of a complex mixture of (117)-, (115)-, and (114)-like segments and a typical surface roughness of 0.14 nm rms. On the monohydride surface, $\sim 10 \text{ nm}$ -wide (115)-(2×2) domains are seen, a structure never observed on the clean surface. These domains effectively smooth the surface, reducing the surface roughness to

$< 0.1 \text{ nm}$. The (001)-like dimer-plus-step morphology ends at Si(114), which has a stable planar clean surface reconstruction [19]; surprisingly, the morphology of this surface is essentially unchanged by H-termination [20].

The changes in overall surface morphology induced by hydrogen can be linked directly to distinct atomic-scale changes in the step-edge configurations (Fig. 3). Even when every Si atom on the surface becomes a Si–H, the atomic-scale geometry of the various step structures is generally preserved, and they retain a similar appearance to their clean analogues in filled-state STM images [16]. What changes is the distribution of the dif-

ferent structures on each surface. For the single-layer-stepped surfaces, the B-type step edges are almost completely non-rebonded after H-termination (Fig. 3(a) vs. (b)). Rebonded S_B steps are easily identified in atomic-resolution images, because the individual rebonding atoms are clearly visible as a single row of protrusions along the step edge, and when they are absent, a dimer row is observed instead. Statistically, we find that 90% of the dimers along S_B steps are rebonded on the clean surface; in contrast, 95% are non-rebonded on the H-terminated surface (~ 1000 step-edge dimers were examined for each case). Despite the many experimental studies of H-terminated Si(001), to our knowledge this is the first report that the equilibrium step-edge structure differs from that of the clean surface, confirming the recent theoretical prediction [16].

The rougher surface morphology observed on monohydride surfaces within the second orientation regime ($4\text{--}11^\circ$) can also be correlated with changes in the step-edge configuration. For example, on Si(111), each (001)-like terrace on the clean surface is uniformly four dimers wide with a rebonded D_B step (Fig. 3(c)). In comparison, on the monohydride surface a disordered mixture of all the different single and double-layer step structures is observed (Fig. 3(d)). The most surprising feature is the frequent occurrence of single-layer steps. Statistically, about 27% of the step edges are composed of a ($n\text{-}S_B + S_A$) step combination, with almost all the remaining step edges being D_B . However, in contrast to the monohydride S_B steps, which are basically all non-rebonded, a third of the monohydride D_B steps remain rebonded. The two different D_B step structures can be distinguished in the STM images by the distinct row of rebonded atoms observed along the step edge [16].

For surfaces within the third orientation regime, between (117) and (114), the changes in surface morphology are not caused by the introduction of additional step structures, but simply by a change in the relative distribution of rebonded vs. non-rebonded D_B steps. For instance, the complex structure of clean Si(115) has a ratio of $r\text{-}D_B:n\text{-}D_B = 3:2$ [8]. Because hydrogen apparently lowers the energy of the non-rebonded D_B

steps relative to the rebonded structure, the rebonded and non-rebonded steps occur with equal likelihood on Si(115):H, stabilizing a simpler, inherently flatter, (2×2) structure with alternating $r\text{-}D_B$ and $n\text{-}D_B$ steps (not shown). This change in the relative $r\text{-}D_B/n\text{-}D_B$ step energies also explains our earlier discovery that the Si(114)-(2×1) structure, already composed of alternating $r\text{-}D_B$ and $n\text{-}D_B$ steps, is essentially unaffected by H-termination [20].

Although the atomic-scale changes in the step configurations provide a phenomenological explanation for the different equilibrium morphologies of the clean vs. monohydride surfaces, these changes are ultimately a reflection of altered step energies. To determine the energies of the single-layer steps, we have analyzed their shapes using the terrace-step-kink model of Burton, Cabrera, and Frank (BCF) [1]. Within the BCF framework, the first- and second-nearest neighbor interaction potentials, ϕ_1 and ϕ_2 can be determined from the full kink probability distribution along a step, as follows:

$$\frac{\phi_1}{k_B T} = \ln \left(\frac{n_{+1}n_{-1}}{q^2} \right), \quad (1)$$

$$\ln \left(\frac{n_{\pm r}}{q} \right) = r \left(\ln \frac{n_{\pm 1}}{q} - \frac{\phi_2}{k_B T} \right) + \frac{\phi_2}{k_B T}, \quad (2)$$

where q is the probability that at any given position along the step edge there are no kinks, and $n_{\pm r}$ is the probability that there is a positive or negative kink of length r . Note that the formation energy of an A-type step is determined by the interaction energies across a B-type step, $\epsilon_A = \phi_1^B/4 + \phi_2/2$, and vice versa. We have analyzed the full kink distribution for both the clean and monohydride surfaces (within regions of constant azimuthal step angle [10]). The values of ϕ_1 were then determined from Eq. (1) and those of ϕ_2 from linear least-squares fits of $\ln(n_{\pm r}/q)$ vs. r (Eq. (2)) using the equilibrating surface temperature, 615 K. The step formation energies follow from ϕ_1 and ϕ_2 (Table 1).

Our formation and interaction energies for the clean single-layer steps are in good agreement with those previously reported [11]. Surprisingly, we

Table 1

Measured formation energies, ε , and first and second neighbor interaction energies, ϕ_1 and ϕ_2 , and their standard errors for A- and B-type single-layer steps on clean and monohydride (shaded) Si(001) ($a_0 = 0.384$ nm)

	ε (meV/ a_0)	ϕ_1 (meV/ a_0)		ϕ_2 (meV/ a_0)	
	Clean	Clean	H	Clean	H
S _A	24 ± 5	350 ± 13	334 ± 15	-70 ± 10	-18 ± 9
S _B	58 ± 5	210 ± 9	29 ± 6	-51 ± 4	41 ± 9

find that on the monohydride surface the value of ϕ_2 depends on the type of step (A vs. B). This result is unexpected within the simple BCF model, where the second neighbor interaction is independent of step orientation. One possible explanation is that there is an S_A step–step interaction which only shows up on the rougher monohydride S_B steps, where the many kinks create many small S_A step edges separated by only one or two unit cells. Addition of such an interaction to the BCF theory, required to extract the step formation energies from the monohydride results, is beyond the scope of this letter and will be discussed in a future publication.

Although the formation energies are important in understanding growth or etching, the interaction energies account for the step roughness on equilibrium vicinal substrates. The energy necessary to create a kink one dimer long on an S_B step (i.e. a two dimer-wide S_A step) is $\phi_1^B/2$; so, kink creation requires 105 meV on the clean surface, but only 15 meV on a monohydride surface. This large decrease in the kink energy causes the jagged shape of the S_B step edges on H-terminated Si(001) surfaces.

We have analyzed the equilibrium populations of the five step structures/combinations on Si-

(111):H, D_A, n-D_B, r-D_B, (r-S_B + S_A), and (n-S_B + S_A), for ~1500 step-edge sites, as reported in Table 2. We also report the formation energies calculated using simple Maxwell–Boltzmann statistics, with an energy scale relative to the n-D_B formation energy. Although there are significant limitations to this simple energy analysis (most notably the neglect of any interactions between step structures), it is a first step to determining the energetic landscape on monohydride vicinal Si surfaces.

It is interesting to consider the connection between the atomic-scale structure of the steps and their relative energies. In a simple picture, the rebonding atoms along clean S_B steps reduce the dangling bond density, which more than compensates energetically for any additional surface stress they create. Because H-termination can passivate these dangling bonds without introducing strained Si–Si bonds, it makes sense that the non-rebonded step becomes the lower energy structure. But why do some rebonded double-layer steps remain after H-termination? On monohydride surfaces, S_B and D_B steps have about the same energy when non-rebonded, but when rebonded, S_B steps are much higher in energy (Table 2). However, in both cases the local geometry of a S_B and D_B step is the same except for the row of dimers adjacent to the S_B step on the lower terrace (with dimer bonds oriented perpendicular to the step edge; Fig. 1). We propose that the relatively high energy of the rebonded S_B step is caused by forces between the rebonded atoms and these adjacent dimers, perhaps related to the well-known strain anisotropy of the dimer structure. Without this interaction, much less energy is saved by “unrebonding” a double-layer step, accounting for the relative stability of r-D_B steps on the H-terminated surfaces.

Table 2

Populations and formation energies for the step structures on monohydride Si(111)

Structure	Population (%)	ε (eV/ a_0)
D _A	0.5 ± 0.2	0.25
(r-S _B + S _A)	0.8 ± 0.2	0.23
r-D _B	20.6 ± 1.2	0.05
(n-S _B + S _A)	27.2 ± 1.4	0.03
n-D _B	50.9 ± 1.8	–

The energies were determined using simple Maxwell–Boltzmann statistics, with an energy scale relative to the n-D_B energy.

The step structure and step energy differences between clean and H-terminated vicinal Si(001) surfaces help to explain some of the previously reported effects of H on film growth. During Si homoepitaxy by either MBE or CVD, hydrogen increases the island density and reduces the island shape anisotropy [12,14]. It was initially proposed that H-termination causes these effects by decreasing the Si adatom diffusion rate [12]. More recently, kinetic Monte Carlo simulations were used to show these changes can be more accurately accounted for if H somehow “poisons” the S_B step edges, inhibiting Si adatom attachment [13]. In light of our results, a simple atomistic explanation becomes clear: on H-terminated surfaces, the S_B steps are non-rebonded, and attaching a Si adatom to the step edge is tantamount to converting it to a higher-energy rebonded step.¹ This simple mechanism could also account for similar effects of hydrogen on Ge and SiGe film growth [6,15,21]. Similarly, our results may explain the spontaneous step formation observed on Si(001) annealed in H_2 under extreme conditions (~ 1 atm, 1200°C) [22].

Our discovery that hydrogen termination completely disrupts the surface morphology on most double-layer-stepped surfaces will be important for understanding growth on high-index substrates; clearly, any models based on a simple periodic terrace-plus-step structure are unlikely to be accurate. Although we have focused on the effects of H on film growth, we expect the step edges to be modified in similar ways during the etching of silicon by halogen gases. These are just a few examples of how knowledge of the actual step structures and their energies should prove useful for developing high-fidelity models of silicon growth and processing.

Acknowledgements

This work was funded by ONR.

References

- [1] W.K. Burton, N. Cabrera, F.C. Frank, *Philos. Trans. R. Soc. London Ser. A* 243 (1951) 299.
- [2] Z. Zhang, M.G. Lagally, *Science* 276 (1997) 377.
- [3] H.-C. Jeong, E.D. Williams, *Surf. Sci. Rep.* 34 (1999) 171.
- [4] K. Oura, V.G. Liftshits, A.A. Saranin, A.V. Zotov, M. Katayama, *Surf. Sci. Rep.* 35 (1999) 1.
- [5] J.J. Boland, *Phys. Rev. B* 44 (1991) 1383.
- [6] M. Copel, R.M. Tromp, *Appl. Phys. Lett.* 58 (1991) 2648.
- [7] J.A. Kubby, J.J. Boland, *Surf. Sci. Rep.* 26 (1996) 61.
- [8] A.A. Baski, S.C. Erwin, L.J. Whitman, *Surf. Sci.* 392 (1997) 69.
- [9] B.S. Swartzentruber, Y.-W. Mo, R. Kariotis, M.G. Lagally, M.B. Webb, *Phys. Rev. Lett.* 65 (1990) 1913.
- [10] E.R. Heller, D.E. Jones, J.P. Pelz, Y.H. Xie, P.J. Silverman, *J. Vac. Sci. Technol. A* 17 (1999) 1663.
- [11] H.J.W. Zandvliet, *Rev. Mod. Phys.* 72 (2000) 593.
- [12] J.E. Vasek, Z. Zhang, C.T. Salling, M.G. Lagally, *Phys. Rev. B* 51 (1995) 17207.
- [13] P. Smilauer, K. Mizushima, D.D. Vvedensky, *Phys. Rev. Lett.* 81 (1998) 5600.
- [14] P.-H. Wu, D.-S. Lin, *Phys. Rev. B* 57 (1998) 12421.
- [15] H. Kim, N. Taylor, T.R. Bramblett, J.E. Greene, *J. Appl. Phys.* 84 (1998) 6372.
- [16] S. Jeong, A. Oshiyama, *Phys. Rev. Lett.* 81 (1998) 5366.
- [17] S.M. Gates, R.R. Kunz, C.M. Greenlief, *Surf. Sci.* 207 (1989) 364.
- [18] A. Dinger, C. Lutterloh, J. Kupperts, *Chem. Phys. Lett.* 320 (2000) 405.
- [19] S.C. Erwin, A.A. Baski, L.J. Whitman, *Phys. Rev. Lett.* 77 (1996) 687.
- [20] A. Laracuente, S.C. Erwin, L.J. Whitman, *Appl. Phys. Lett.* 74 (1999) 1397.
- [21] S.-J. Kahng, Y.H. Ha, J.-Y. Park, S. Kim, D.W. Moon, Y. Kuk, *Phys. Rev. Lett.* 80 (1998) 4931.
- [22] L. Zhong, A. Hojo, Y. Matsushita, Y. Aiba, K. Hayashi, R. Takeda, H. Shirai, H. Saito, J. Matsushita, J. Yoshikawa, *Phys. Rev. B* 54 (1996) R2304.

¹ Note that our explanation contradicts the prediction in Ref. [16] that a non-rebonded step should be a sink for adatoms, a prediction that seems at odds with their calculated surface energies (the rebonded step is higher in energy).