

Hydrogen-induced instability on the flat Si(001) surface via steric repulsion

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The exposure of the miscut Si(001) surface to H gives rise to a rich sequence of stable step structures as a function of the H chemical potential. First-principles calculations of step-formation energies show that the formation of steps on the (2×1) reconstructed surface requires energy, but that on the (1×1) surface, steps form exothermically. This explains surface roughness at high H chemical potentials.

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I. INTRODUCTION

Due to their high chemical activity, surface defects (point or extended alike) often interact strongly with chemisorbed atoms. These interactions are particularly important in nanodevices because they determine the growth and etching of semiconductor surfaces and the quality of semiconductor devices. Among all semiconductor surfaces, Si(001) is by far the most studied,¹ because it is the starting point for chip fabrication. Among the surface defects, the structure evolution of steps on Si(001) has been a subject of intensive research.² Hydrogen is the smallest and simplest chemisorbate and has been routinely used in device processing³ and can either be a contaminant or a surfactant.³ Recently, hydrogen implantation experiments⁴ showed the appearance of internal H-terminated surfaces that ultimately lead to cracking of the silicon surface in (001) planes. This phenomenon is the basis of a promising new silicon-on-insulator technology known as “smart cut.”⁵

The clean Si(001) surface exhibits at low temperatures ($T \approx 250$ K) the (4×2) reconstruction⁶ whose tilted Si-Si dimers reduce the density of unsatisfied surface (“dangling”) bonds, thus chemically stabilizing the surface.¹ Hydrogen chemisorption changes the surface electronic structure by reducing the need for Si-Si dimers via direct capping of the dangling bonds. This replaces the (4×2) reconstruction by (2×1) ,⁷ (3×1) ,⁸ and at the highest H concentration by the (1×1) reconstruction.^{9,10} While some have suspected⁸ that the (1×1) phase is made up of disordered (3×1) units, the (1×1) phase has been seen⁹ by scanning tunneling microscopy measurements in samples exposed to hydrogen plasma. However, the (1×1) structure is blurred by the simultaneous presence of roughness.⁹ More recently, Raman spectra measurements by Weldon *et al.*⁴ on H-implanted Si(001) showed evidence of the appearance of (001) (1×1) *internal* surfaces before cracking occurs. Moreover, ultraclean surface preparation experiments by Morita and Tokumoto¹¹ showed strong evidence of the existence of the (1×1) phase. However, Morita and Tokumoto¹¹ also found that small concentration OH ions immediately leads to surface roughness and faceting. Despite progress in other areas, the cause of surface roughness^{9,11} at high concentration of H on Si(001) has remained a challenge for the past ten years.

In this paper, we study the consequences of H-surface interactions as a function of the H chemical potential μ_H .

We find that “steric repulsions”¹² dictate the relative stability of several important step structures. The steric force¹² between two H [hereby denoted as $(\text{SiH} \cdots \text{HSi})$] is a short-range repulsive force acting when two H atoms, already bonded to Si atoms, become too close to each other.^{10,12} We find the following. (i) In the (1×1) phase, the step energetics is controlled by the $\text{H} \cdots \text{H}$ steric repulsion, and the formation energy of the fully hydrogenated single step (S_{\perp}^*) becomes negative with respect to the flat surface, resulting in spontaneous roughening of the surface. (ii) In the (2×1) phase, we find that all steps have *positive* formation energies. (iii) In the (2×1) phase, the single step (S_{\perp}) has lower energy than all other steps. When μ_H increases, the edge of the S_{\perp} becomes dihydrided (S_{\perp}^*) and the steric interaction starts to determine the stability of the surface.

II. METHOD OF CALCULATION

Formation energies were calculated using the local-density approximation.¹³ We used the plane-wave pseudopotential total-energy and force method.¹⁴ Details are given in Ref. 15. The pseudopotentials were generated from the method of Troullier and Martins.¹⁶ The exchange correlation is given by the parametrization of Perdew and Zunger.¹⁷ We use an energy cutoff of 16 Ry and a theoretical lattice constant of $a_o = a\sqrt{2} = 5.3891$ Å. Hydrogenated (001) flat surfaces were calculated using 11, 22, and 33 Si atom supercells for the (1×1) , (2×1) , and (3×1) reconstructions, respectively. Isolated single-steps were calculated on nominal (001) surfaces. The formation energies of single step pairs and double steps were calculated on Si(1,1,11) slabs with a thickness of seven atomic layers. The supercells were repeated periodically in the (001) direction separating the surfaces by 4.4 monolayers of vacuum, which is enough to give results independent of surface separation.¹⁸ Two Si layers on the bottom of the supercell were fixed at their bulk positions. The bottom surfaces were passivated with H atoms. In order to avoid systematic errors, the Si bulk chemical potential (μ_{Si}) was determined for each supercell family using a cell growth method.¹⁹ This set of parameters reproduces a number of clean surface step energies.^{2,20}

Surface formation energy is defined as the energy cost per surface atom required to create the surface with respect to the bulk crystal. The formation energy per unit length $a = a_o/\sqrt{2}$ of a step S [λ (S)] is calculated as the energy difference between the (001) surface with step S and a flat

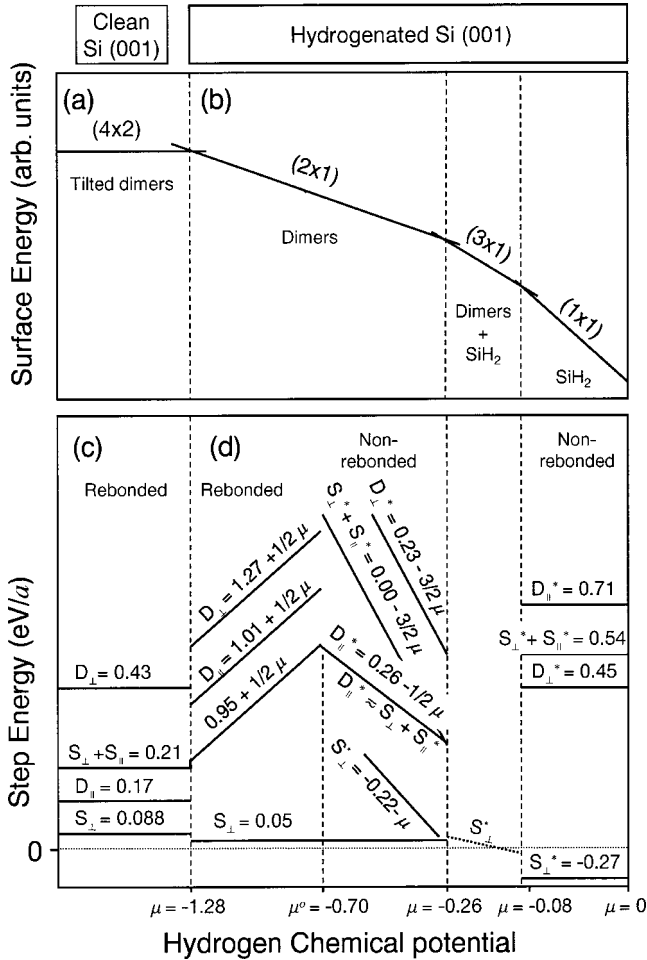


FIG. 1. Schematic representation of the formation energies of surface reconstructions and steps on Si(001): (a) Clean (4×2) phase, (b) hydrogenated (2×1) , (3×1) , and (1×1) phases, (c) steps on clean Si(001) as reported in Ref. 20, and (d) steps on the (2×1) and (1×1) phases. The dotted line corresponding to S_{\perp}^* in the (3×1) phase is an estimate. On miscut surfaces of the type $(11n)$, single steps must occur in $S_{\perp} + S_{\parallel}$ pairs. On flat surfaces with terraces, no such restriction is required and isolated single steps can exist.

(001) surface having the same projected (001) area. Because the concentration of H is different in each phase, and because steps can introduce a local change of the H density with respect to the flat surface, both the surface and step formation energies are functions of the H chemical potential μ_{H} . In Fig. 1, the highest value of μ_{H} (taken here as zero) is that at which H extracts without energy cost Si atoms from the surface, forming the SiH_4 molecules.²¹

III. FLAT SURFACE

Figure 1 shows schematically calculated surface formation energies of clean Si(001) [Fig. 1(a)] and hydrogenated Si(001) [Fig. 1(b)], as well as the step formation energies of clean^{2,22,23,20} Si(001) [Fig. 1(c)] and hydrogenated Si(001) surfaces [Fig. 1(d)].

In agreement with earlier calculations by Northrup,¹⁰ we see from Figs. 1(a) and 1(b) that upon chemisorption the (4×2) reconstruction transforms first to (2×1) , which contains only (untilted) Si-Si dimers, then to (3×1) , which contains both dimers and SiH_2 , and finally to (1×1) , which has only SiH_2 .

IV. STEPS ON THE DIFFERENT PHASES OF Si(001)

Chadi²² classified steps according to the orientation of the Si dimers with respect to the steps: Single steps are called here S_{\perp} or S_{\parallel} (previously denoted as S_A and S_B) if the dimers on the upper terrace are, respectively, perpendicular or parallel to the step. Similarly, double steps are denoted D_{\perp} and D_{\parallel} (previously²² denoted as D_A and D_B). On the clean (4×2) phase, steps can be rebonded or nonrebonded²² depending on whether the Si atoms at the step edge participate in dimer formation (see below). We will use an asterisk to denote unrebonded steps. While, in general, the formation of steps in the clean (4×2) phase of the Si(001) surface requires energy, rebonded steps have the smallest formation energies.²² Figure 1(c) shows the steps formation energies of rebonded steps in the clean (4×2) phase as calculated in Ref. 20.

A. Steps in the hydrogenated (1×1) phase

H-H steric effects have important consequences in the (1×1) phase where H atoms are closely packed into dihydrides. Indeed, Northrup¹⁰ found that a rotation of the dihydrides from the symmetric position (see, e.g., Fig 2) increases the distance of neighboring H atoms, thus gaining energy. On the (1×1) phase, all stable steps are nonrebonded. The density of H atoms is the same as the flat surface. Therefore, step formation energies are independent of μ_{H} . The rotation plane of the dihydrides can be either parallel or perpendicular to the step direction (see Fig. 2), but it is always parallel to the direction that the Si dimers would have had on the (2×4) phase. Therefore, we will use a notation for these steps similar to that defined for clean (4×2) surfaces (see Fig. 2).

Since in the saturated (1×1) phase the energetics of the flat surface is dominated by H steric effects, one might suspect the same for the formation energies of *steps*. Figure 2(a) shows a schematic structure of an $S_{\perp}^* + S_{\parallel}^*$ pair on miscut (001) surfaces. On the upper terrace of S_{\parallel}^* , the rotation of the dihydrides is in a plane parallel to the steps. Thus, although the step could affect the elastic energy of the rotation, the S_{\parallel}^* does not modify the steric energy of the dihydrides. The step S_{\perp}^* at the upper terrace [see Fig. 2(a), row α] is qualitatively different from S_{\parallel}^* . The dihydrides at row α gain energy, because the dihydrides rotate toward empty space so the $\text{SiH} \cdots \text{HSi}$ repulsion is eliminated. Also, the dihydrides at rows β and γ lower their energies by benefiting from the free rotation of the dihydrides at row α .

In order to determine separately the energies of S_{\parallel}^* and S_{\perp}^* we calculated the structure shown in Fig. 2(b), which we will call $S_{\perp}^* + S_{\perp}^*$. It corresponds to a terrace of width $4a$ terminated by two S_{\perp}^* steps on the flat surface. We use the

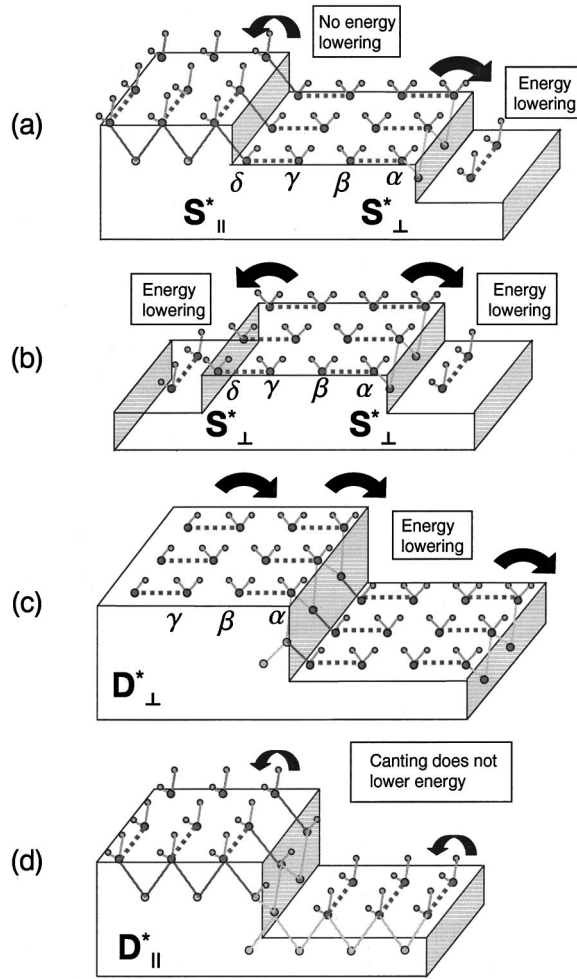


FIG. 2. Schematic representation of step structures on the (1×1) dihydrided phase of Si(001): (a) $S_A^* + S_B^*$ pair, (b) $S_A^* + S_A^*$ terrace, (c) D_A^* , and (d) D_B^* . The following steps on the (2×1) monohydride phase can be obtained by forming dimers at the dotted lines: (a) rebonded $S_A^* + S_B^*$ pair, (b) rebonded $S_A^* + S_A^*$ terrace, (c) rebonded D_A^* , and (d) nonrebonded D_B^* .

formation energy of $S_{\perp}^* + S_{\perp}^*$ to estimate $\lambda(S_{\perp}^*) = -0.27$ eV/a. The reasons for a negative formation energy of S_{\perp}^* are twofold: (i) Steric energy reductions at the step edge: One may write the step energy λ as $\lambda_{\text{steric}} + \lambda_{\text{bare}}$. At the upper terrace of the S_{\parallel}^* step, the steric repulsion is approximately the same as in the flat surface. Therefore, in this case $\lambda(S_{\parallel}^*) \approx \lambda_{\text{bare}}(S_{\parallel}^*) \approx 0.8$ eV. On the other hand, the difference $\lambda(S_{\parallel}^*) - \lambda(S_{\perp}^*) \approx 1.0$ eV/a reflects approximately $-\lambda_{\text{steric}}(S_{\perp}^*)$ [since the steric repulsion is absent at the S_{\perp}^* edge, row α in Fig. 2(a)]. This $-\lambda_{\text{steric}}(S_{\perp}^*) \approx 1.0$ eV/a translates into 1.0 eV/at at the step, which can be compared to the energy gain (0.18 eV/at) due to the rotation of dihydrides on flat surfaces¹⁰ (which is a *partial* steric energy gain minus the elastic cost of the rotation). When the *full* steric energy is removed from the S_{\perp}^* step, its formation energy becomes negative. (ii) Note in Fig. 2(b) that at the center of the terrace, the rotation of the dihydrides is parted into two regions. This division creates extra space that also

reduces the steric energy. This effect is not present at the $S_{\perp}^* + S_{\parallel}^*$ structure [see Fig. 2(a)]. Accordingly, the formation energy of the *isolated* S_{\perp}^* might be one-tenth of an eV higher than the one estimated here from $S_{\perp}^* + S_{\perp}^*$.

Figure 2(c) shows the D_{\perp}^* step with a dihydride configuration similar to S_{\perp}^* [see row α in Figs. 2(c) and 2(a)]. In contrast to S_{\perp}^* , we find that $\lambda(D_{\perp}^*) > 0$. Since the upper terraces of D_{\perp}^* and S_{\perp}^* have similar structures, one might wonder why the energy costs of the steps are so different. The reasons are the following. (i) The estimated $\lambda_{\text{bare}}(D_{\perp}^*)$ is close to twice $\lambda_{\text{bare}}(S_{\parallel}^*)$. (ii) The structure used to calculate D_{\perp}^* does not involve the partition of the dimer rotation angles seen in $S_{\perp}^* + S_{\perp}^*$. (iii) On the D_{\perp}^* step, all the dihydrides rotate in the same direction, while on the $S_{\perp}^* + S_{\perp}^*$ and $S_{\parallel}^* + S_{\perp}^*$ structures, the rotation direction alternates. Such alternation is known²⁵ to reduce the long-range elastic energy of stepped surfaces.

Figure 2(d) shows the structure of D_{\parallel}^* , which appears to be similar to S_{\parallel}^* . However, there are important differences. At the step edge of D_{\parallel}^* , there is a row of monohydrides that is absent at S_{\parallel}^* . These H atoms are not too far away from the H atoms at the next dihydride rows (at 2.43 Å and 3.13 Å, respectively) as compared with the H-H distance on the flat surface (2.12 Å). D_{\parallel}^* is thus an example of partial reduction of the steric interaction: $\lambda(D_{\perp}^*) < \lambda(D_{\parallel}^*)$ because some steric repulsion remains in D_{\parallel}^* , but $\lambda(D_{\parallel}^*) < \lambda(S_{\parallel}^*) = 0.8$ eV where all steric repulsion remains. Note in Fig. 1(c) that the order of the corresponding energies is different in the case of the clean (4×2) phase when steric interactions are absent.

B. Stability of the (1×1) phase

The energetics of steps has important consequences on the structure of the (001) surface in the (1×1) phase. Because $\lambda(S_{\perp}^*)$ is negative, the flat (1×1) phase is thermodynamically unstable against the formation of steps S_{\perp}^* [i.e., terraces like the one shown in Fig. 2(b) will form spontaneously]. Because $\lambda(S_{\perp}^*)$ is independent of μ_{H} , this instability holds for the entire μ_{H} range where the (1×1) phase was assumed in the past.¹⁰ Although the formation of trihydrides might cost low energy for very high μ_{H} ,¹⁰ our results imply that the H-rich surface is rough on the atomic scale due to dihydrides, which are the building blocks of the steps. However, since the formation of the terraces and steps requires a massive rearrangement of the Si atoms, the metastable (1×1) structure might still exist regionally, as observed in the experiments of Boland⁹ and Morita and Tokumoto.¹¹ As the surface instability develops, the surface may evolve via a hydrogenated vacancy mechanism¹⁸ from a stepped surface into a faceted surface in order to minimize the steric interactions further. The (111) facets have larger H-H separation than the (001) steps and have been seen experimentally.^{26,11} Clearly, the experiments of Morita and Tokumoto show that the (1×1) phase is unstable and suggest that OH ions catalyze the movement of Si atoms allowing the formation of (111) facets.

C. Steps in hydrogenated (2×1) phase

A rebonded S_{\parallel} step can be constructed using Fig. 2(a), if the Si atoms at row γ form dimers with the Si atoms at row δ . A nonrebonded step S_{\parallel}^* can be constructed instead if the Si atoms at row γ form dimers with the next Si at row β . When a dimer forms, two dihydrides are converted into monohydrides and an H_2 molecule is released. On the terrace, far from the step edge, the above two possibilities differ only by a translation along the (110) direction of the dimers with no energy cost. But the nonrebonded step S_{\parallel}^* has one extra H per a with respect to the rebonded step S_{\parallel} . Moreover, in the rebonded case, the Si atom at the step [row δ in Fig. 2(a)] is backbonded to a third Si atom in the upper terrace. Thus, rebonded steps cost more elastic energy than nonrebonded steps.^{22,23} However, nonrebonded steps have to pay the price of steric repulsion between neighboring $\text{SiH}\cdots\text{HSi}$ groups at the step edge.

We considered here also other steps on the (2×1) phase. For example, the Si atom β at the upper terrace of S_{\perp}^* of (1×1) [see Fig. 2(a)] can “choose” to form a dimer either with the atom α at the step edge (forming S_{\perp}) or with atom γ leaving dihydrides at the α row (forming and hydrogenated step S_{\perp}^*). Again, in this case the structure of the terrace is not modified, but the H concentration and bonding structure are different at the step.

D. Energetics of the rebonded and nonrebonded steps in the (2×1) phase

In general, rebonded or nonrebonded is decided by the balance between the chemical energy of the Si-H bonds, the $\text{SiH}\cdots\text{HSi}$ steric repulsion, and the strain energy due to stretched bonds. This balance changes with μ_{H} . Jeong and Oshiyama²⁴ recently calculated steps in hydrogenated (2×1) phase. They found a crossing in the formation energies between rebonded and nonrebonded steps as a function of the chemical potential. In addition, they report that the nonrebonded D_{\parallel}^* as well as the S_{\parallel}^* steps have negative formation energies at chemical potentials below the (2×1) to (3×1) phase transition. Jeong and Oshiyama²⁴ calculations imply that the nonrebonded D_{\parallel}^* as well as the S_{\parallel}^* steps will form *spontaneously* on the high chemical potential side of the (2×1) phase. It is interesting to double check Jeong and Oshiyama²⁴ calculations because the local structures of the D_{\parallel}^* as well as the S_{\parallel}^* steps are the same in the (3×1) and (2×1) surfaces. Accordingly, the results of Jeong and Oshiyama²⁴ cast doubts on the stability of the flat (3×1) surface against step formation.

(i) Rebonded steps. Similar to the (4×2) case, in the (2×1) phase, the smallest step formation energy corresponds to the isolated S_{\perp} . This is because the dimers at the lower terrace are parallel to the S_{\perp} step [Fig. 2(a)]. Therefore, one does not have to pay the price of elastic energy for rebonding,²² whereas the D_{\parallel} , S_{\parallel} , and D_{\perp} steps have stretched bonds due to rebonding. An important difference between the (2×1) and (4×2) reconstructions is that

$\lambda(S_{\parallel}+S_{\perp}) < \lambda(D_{\parallel})$ in the former, but the order reverses in the latter. On the (2×1) phase, single-step pairs are more stable than double steps even for (1,1,11) surfaces with miscut angles as large as 7.3° . This is not the case in clean (4×2) surfaces.^{22,23,20}

(ii) Nonrebonded steps. The formation energies of the nonrebonded steps in the (2×1) phase are also shown in Fig. 1(d). Nonrebonded steps have more H than the rebonded ones. Therefore, there are changes in the slopes of the formation energies in Fig. 1.²⁴ The condition $\lambda(S_{\parallel}+S_{\perp}) = \lambda(S_{\parallel}^*+S_{\perp})$ determines $\mu_{\text{H}}^0 = -0.70$ eV, at which the rebonded to nonrebonded transition occurs. Despite the fact that hydrogenation of single dangling bonds becomes exothermic at $\mu_{\text{H}} = -1.28$ eV, and that, in addition, the structure is noticeably relaxed in the nonrebonded configuration, the rebonded step remains stable up to $\mu_{\text{H}} = -0.70$. This structural transition “delay” can only be accounted for by the steric $\text{SiH}\cdots\text{HSi}$ interaction, which penalizes the shorter H-H distances at the nonrebonded steps. This structural transition was also reported by Jeong and Oshiyama but the delay was not discussed. We did not find, however, *negative* formation energies for the nonrebonded steps in the (2×1) phase. We used a 16-Ry cutoff for the plane-wave expansion while Ref. 24 used 8 Ry.

For high μ_{H} , near the transition between (2×1) and (3×1) ($\mu_{\text{H}} = -0.27$) we find that $\lambda(S_{\perp}) = \lambda(S_{\perp}^*)$. At this point dihydrides can be incorporated at the edge of the S_{\perp}^* step (see row α in Fig. 2). A complete row of dihydrides first forms at the upper edge of the S_{\perp}^* step where the dihydrides are perpendicular to the step edge facing empty space. However, at D_{\parallel}^* or S_{\parallel}^* , steric repulsion hinders such a change before the (3×1) to (1×1) transition occurs. On the (3×1) phase, $\lambda(S_{\perp}^*)$ depends on the chemical potential as $-\frac{1}{3}\mu_{\text{H}}$. Assuming that $\lambda(S_{\perp}^*)$ is similar on the (2×1) and (3×1) surfaces at the phase transition, one might argue that the (3×1) phase would be stable against roughness for low μ_{H} . But the $-1/3\mu_{\text{H}}$ dependence of $\lambda(S_{\perp}^*)$ raises the possibility that $\lambda(S_{\perp}^*)$ becomes negative before the (3×1) to (1×1) transition occurs.

V. SUMMARY

We find that hydrogenation drastically changes the topology of steps of flat and miscut Si(001) surfaces as compared to clean surfaces. An important effect is that, in the (1×1) phase, the H-H steric interaction destabilizes the flat surface against the formation of steps that leads to surface roughness. This effect is caused by the steric repulsion of the H atoms at the surface. However, the (1×1) surface is metastable because the formation of steps and facets requires the movement of a large number of silicon atoms. Our quantitative results explain the experimental instability of the (1×1) phase and the observation of facets and roughness. We verify in the (2×1) phase the crossings between the formation energies of rebonded and not rebonded steps as a function of the H chemical potentials reported earlier by Jeong and Oshiyama.²⁴ However, in contradiction with Jeong and

Oshiyama, we find that in the (2×1) phase all steps have positive formation energies, which implies that the flat surface is stable against step formation in the (2×1) phase. But our results suggest that the same might not be true for the (3×1) phase for H chemical potentials close to the transition to the (1×1) phase.

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