[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 processing[3] and can either be a contaminant or a surfactant.[3] Recently, hydrogen implantation experiments[4] 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 ($T \lesssim 250$ K) the (4×2) reconstruction[6] 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 suspected[8] that the (1×1) phase is made up of disordered (3×1) units, the (1×1) phase has been seen[9] 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 Tokumoto[11] showed strong evidence of the existence of the (1×1) phase. However, Morita and Tokumoto[11] 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 (1sH07.f73 (12p8tely)]5-62uTf 0.333 0 TD (001)Tj11 Tf 0.33-rppe.844 15" 195.t3tD

[12] dictate the relative stability of several important step structures. The steric force[12] 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 m_{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).

~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 m_H. In Fig. 1, the highest value of m_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!#

formation energy of $S_\perp^* \uparrow S_\perp^*$ to estimate $\beta(S_\perp^*) \simeq -0.27$ 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 β as $\beta_{steric} + \beta_{bare}$. 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 $\beta(S_\parallel^*)' \beta_{bare}(S_\parallel^*)' 0.8$ eV. On the other hand, the difference $\beta(S_\parallel^*) - \beta(S_\perp^*)' 1.0$ eV/a reflects approximately $-\beta_{steric}(S_\perp^*)$ @since the steric repulsion is absent at the $S_\perp^*$ edge, row a in Fig. 2~a!#. This $-\beta_{steric}(S_\perp^*)' 1.0$ 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 surfaces[10] ~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 $S_\perp^* \uparrow S_\parallel^*$ 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 $S_\perp^* \uparrow S_\perp^*$.

Figure 2~c! shows the $D_\perp^*$ step with a dihydride configuration similar to $S_\perp^*$ @see row a in Figs. 2~c! and 2~a!#. In contrast to $S_\perp^*$, we find that $\beta(D_\perp^*) . 0$. 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 $\beta_{bare}(D_\perp^*)$ is close to twice $\beta_{bare}(S_\parallel^*)$. ~ii! The structure used to calculate $D_\perp^*$ does not involve the partition of the dimer rotation angles seen in $S_\perp^* \uparrow S_\perp^*$. ~iii! On the $D_\perp^*$

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