First-principles studies of hydrogenated Si(111)-7×7

D. R. Alfonso

Department of Chemistry and Condensed Matter and Surface Sciences Program, Ohio University, Athens, Ohio 45701-2979

C. Noguez

Department of Physics and Astronomy and Condensed Matter and Surface Sciences Program, Ohio University, Athens, Ohio 45701-2979
and Instituto de Física, Universidad Nacional Autónoma de Mexico, Apartado Postal 20-364,
01000 México Distrito Federal, Mexico

D. A. Drabold and S. E. Ulloa

Department of Physics and Astronomy and Condensed Matter and Surface Sciences Program, Ohio University, Athens, Ohio 45701-2979

The relaxed geometries and electronic properties of the hydrogenated phases of the Si(111)-7×7 surface are studied using first-principles molecular dynamics. A monohydride phase, with one H per dangling bond adsorbed on the bare surface, is found to be energetically favorable. Another phase where 43 hydrogens saturate the dangling bonds created by the removal of the adatoms from the clean surface is found to be nearly equivalent energetically. Experimental scanning tunneling microscopy and differential-reflectance characteristics of the hydrogenated surfaces agree well with the calculated features. [S0163-1829(96)02236-9]

The identification of the fascinating 7×7 reconstruction on the (111) surface of silicon has motivated continued interest in its structural and electronic properties over the years. The Si(111)-7×7 surface is perhaps the system that best exemplifies the important interplay between structure and electronic properties in surface physics. The work of Binnig *et al.* using scanning tunneling microscopy[1] (STM) led Takayanagi *et al.* to propose their dimer-adatom-stacking (DAS) fault model, whose structure is consistent with many experiments.[2] The geometric and electronic properties of the 7×7 surface are well known through a combination of experiments[1–5] and realistic calculations, in particular the first-principles investigations of Stich *et al.*[6] and Brommer *et al.*[7] using large supercells in state-of-the-art approaches.

The structure of the hydrogenated phases of this important surface are not as well understood. Studies of this surface reaction and associated reconstruction are of technological relevance in the chemisorption processes of H, NH_2,[4] and hydrocarbons.[8] In addition, the hydrogenated surface can be used as reference in clarifying the optical response of the bare 7×7 substrate and it is then important to have a better understanding of its structural and dynamical properties.[9,10] From a computational standpoint, Si(111)-7×7:H surfaces are challenging due to the large-size unit cells.

The adsorption of hydrogen on Si(111)-7×7 results in a complex process that depends on the amount of hydrogen present in the surface. Very recently, Borensztein and co-workers have realized real-time *in situ* differential-reflectance measurements and semiempirical microscopic calculations that show the evolution of the surface upon hydrogen adsorption[10,11]. They observe that for small amounts of hydrogen [less than 80 L (1 L=10^{-6} Torr s)], the surface still displays a 7×7 structure, and two mechanisms have been identified as responsible for the main optical signatures: dangling-bond saturation or/and H-induced breaking of the backbonds. They also find that for larger amounts of hydro-

gen an intermediate 7×1:H diagram is displayed before the 1×1:H pattern can be identified at very high hydrogen exposures (at about 20 000 L). While the 1×1:H surface is now well characterized both experimentally and theoretically,[12,13] the 7×1:H geometry has not been explored as well. Indeed, although the latter surface has been studied using several experimental techniques,[14,15] little is known theoretically. In the present work, we study the initial stages of the hydrogenation process, where the surface still shows a 7×7 symmetry, the hydrogen is saturating all dangling bonds, and important structural changes have occurred.

As mentioned earlier, experimental evidence suggests that the initial state of the adsorption of hydrogen on Si(111)-7×7 should occur in a two-step process.[10,11,15,16] The first step likely occurs when only the 19 dangling bonds (DB's) per unit cell are saturated, corresponding to those of the 12 adatoms (AD's), six rest atoms (RA's) and a corner hole atom (CHA) of the DAS model, to form Si(111)-7×7:19H. The second step occurs when the adatom layer is missing and hydrogen saturates the corresponding 43 DB's to form Si(111)-7×7:43H.[15] These findings have resulted in several unresolved issues, such as whether the DAS structure remains unchanged when the surface is terminated by H atoms, which of the two hydrogenated phases is more stable, and what are the main electronic properties of the Si(111)-7×7 surface after passivation with hydrogen. To date, the efforts to address these issues theoretically have been limited to different reconstructions of this surface[9,10] and first-principles studies of the surface upon H and NH_2 adsorption (using a cluster model for the substrate).[17] An alternative and more reliable approach is to perform molecular-dynamics supercell calculations that realistically model the surface using the full unit cell of the hydrogenated phase, combined with the accuracy of an *ab initio* treatment of the interatomic interactions.

Here we present *ab initio* studies to characterize the Si(111)-7×7:19H and :43H systems using large supercell geometries approaching 400 atoms. Application of this method to elucidate the structural and electronic properties of the clean 7×7 surfaces yields results in good agreement with previous work. We find that H adsorption on the clean surfaces leads preferentially to a monohydride structure [Si(111)-7×7:19H] and is accompanied by considerable surface relaxation, in agreement with experiments. The other hydrogenated phase identified, the Si(111)-7×7:43H surface, is found to approach energetically the :19H phase, explaining the possible coexistence reported in experiments. Moreover, we find that the electronic density of states of these H-passivated surfaces exhibits no surface states in the gap, while still showing strong contributions from backbonding states at low H coverage, in agreement with STM and differential-reflectance measurements.[10,16]

Our computational scheme uses molecular-dynamics simulations based on density-functional theory in the local-density approximation (LDA), using the Harris functional, Hamann-Schlüter-Chiang pseudopotentials,[18] and a minimal s-p basis representation. The major approaches of the method are (i) substitution of the total energy functional by one that calculates changes of the electron density from that of a sum of neutral-atom densities only to first order and (ii) solution of the Hohenberg-Kohn-Sham equations by a linear combination of slightly excited pseudoatomic orbitals. A comprehensive discussion of this scheme, the approximations used, and a description of various tests can be found in Ref. 19. In silicon, the π-bonded (2×1) reconstruction of the (111) surface, the 2×1, $p(2×2)$, and $c(4×2)$ phases of the (100) surfaces, as well as the 5×5 DAS structure of Si(111), have all been studied by this technique with great success.[20]

As a test, we started applying this approach to investigate the structural properties of clean Si(111)-7×7. The substrate is represented by a supercell with ten Si layers plus the adatoms on the slab surface (the initial coordinates of adatoms and the three uppermost Si layers were those of Ref. 7. The model system contains all the features of the DAS configuration [see Fig. 1(a)]. Periodic boundary conditions are imposed parallel to the surface and the bottom Si layer is terminated by H atoms to passivate dangling bonds. The equilibrium structure of the 543-atom slab is then obtained with a dynamical quenching minimization technique. All the atoms, except for the bottom Si layer, were allowed to relax until the forces on them converged to less than 0.1 eV/Å. Only the Γ point of the small Brillouin zone of the supercell is used to sample the electronic states. The calculated bond lengths of AD's with the first-layer atoms are found to be stretched from 3% to 6% with respect to a typical Si-Si bond length (2.35 Å). The average distance between the AD's and the second-layer atoms directly beneath them is about 2.44 Å, except for two adatoms on the faulted region of the unit cell [shown as 1 and 2 in Fig. 1(a)], which have a distance 8% larger than the typical value. The bond lengths between RA's and second-layer atoms are stretched by 4%, as they are 0.5 Å away from the first layer. The relative heights of AD's 3 to 6 are 0.069, 0.055, 0.0, and 0.025 Å, respectively. These values are in qualitative agreement with those from low-energy electron diffraction (LEED), 0.12, 0.08, 0.0, and 0.04 Å.[21] The second- and third-layer atoms directly below
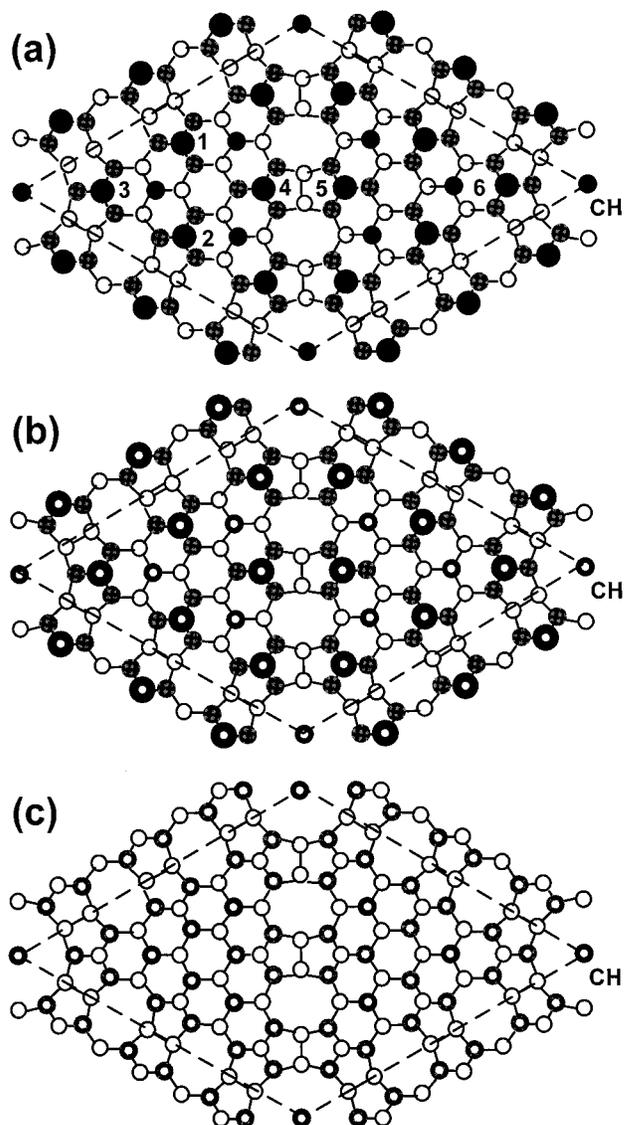

FIG. 1. Top view of (a) the DAS model for the Si(111)-7×7 bare surface [big gray, black, and small gray circles represent adatoms, rest atoms, and corner hole atom (CH), and first-layer atoms, respectively; (b) the :19H coverage (small white circles denotes H atoms); and (c) the :43H coverage surface. The faulted portion of the outlined unit cell is on the left. The unit cell is shown by dashed lines.

AD's move ~0.5 Å towards the bulk and their bond lengths are ~2% shorter than the bulk Si-Si bond length. A comparison of our relaxed atomic positions with those from the Car-Parrinello work[7] shows nearly identical geometry.[22] We adopted these equilibrated positions for the geometry of the clean surface, as it is in general agreement with values reported in previous work,[7,21,23,22] and then proceed to saturate dangling bonds.

A second set of tests were performed in order to support the reliability of our method for the hydrogenated cases. We have considered the unreconstructed and hydrogen-terminated 1×1:H surface. This has been extensively studied given its simple atomic structure and small unit cell, and is ideal for complex theoretical approaches (see Ref. 13 and

references therein). We modeled the system with a 12-layer Si slab terminated on both sides with hydrogen. We employed 78 points in the irreducibile part of the Brillouin zone to relax the surface. The calculated structure and electronic properties are in good agreement with those found in the literature[12,13,24]. We find that the silicon atoms on the first layer move inward to the bulk by 0.023 Å and a Si-H bond length of 1.54 Å, both values comparable with previous theoretical findings.[13,24] We also tested the SiH$_4$ molecule, where a Si-H bond length of 1.46 Å was found, slightly shorter than the ideal value of 1.48 Å. We also investigated the electronic states of the 1×1:H surface. We found surface states at the K point due to the presence of H at −4.3, −5.5, and −9.2 eV and at the M point at −4.2 eV, all with respect to the top of the valence band. These calculated results are in agreement with previous self-consistent first-principles calculations and experimental measurements,[12,13,24] taking into account a systematic shift of the energy of about +0.5 eV. These systematic differences in the electronic structure are expected within the context of our method since no quasiparticle effects or local-field effects are taken into account[12,13].

The Si(111)-7×7:19H is modeled by terminating all the silicon DB's of the bare surface with H atoms [see Fig. 1(b)] and all atoms, except for the bottom Si layer, of the 366-atom supercell are allowed to relax (for computational speed, we take only six Si layers here plus adatoms and chemisorbed hydrogens).[25] The positions of the surface Si atoms change when the 19 DB's are terminated by H atoms and the heights of AD's become nearly similar. Relative to the clean surface, adatoms and first-layer atoms move away from the bulk layer, while RA's, CHA's, and AD's 1 and 2 move towards the slab, leaving a nearly flat top layer.[22] The AD's backbond lengths with first-layer atoms are slightly shorter (~1%) than in the clean substrate, while those of the RA with second-layer atoms are comparable to the bare surface. The calculated Si-H bond distances are 1.54 Å, nearly 8% larger than the sum of the covalent radii of Si and H (1.43 Å) and comparable to the value obtained from the 1×1:H and other calculations (1.502–1.520).[13,17] The dimer atoms and second- and third-layer atoms directly below AD's remain in their clean-surface positions.

Now we want to know how stable the Si(111)-7×7:19H surface is compared to Si(111)-1×1:H. We define the "binding energy" of the 1×1:H reconstruction as

$$\Delta E_{1\times1:H} = E_{1\times1:clean} + E_{H_2} - E_{1\times1:H}, \qquad (1)$$

and for 7×7:19H as

$$\Delta E_{7\times7:19H} = \frac{1}{19}\{E_{7\times7:clean} + 19E_{H_2} - E_{7\times7:19H}\}. \qquad (2)$$

Then we obtain the energy difference $\Delta E_{7\times7:10H} - \Delta E_{1\times1:H}$ per Si-H bond. Notice that the energy of the H$_2$ molecule has been canceled and does not enter in our calculation of the relative stability. This calculation yields that the 7×7:19H surface is only 0.31 eV/(Si-H bond) less favorable than the 1×1:H. This indicates that the formation of the monohydride phase on Si(111)-7×7 is fairly stable, in agreement with experiments.[10,15,16,27]

The Si(111)-7×7:43H surface has been suggested to coexist with :19H, based on STM observations.[16] The first two
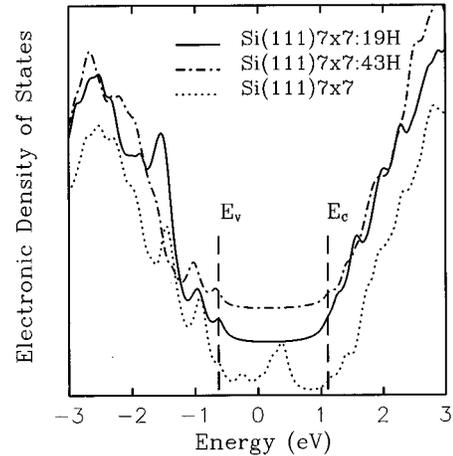

FIG. 2. Electronic density of states for the clean Si(111)-7×7 surface, as well as for the two hydrogenated surfaces studied with 19 and 43 H atoms per cell. All energies refer to the Fermi level, the level broadening used is 0.1 eV, and the curves are displaced vertically for clarity.

layers of the surface atoms in :43H (including surface H), both on the faulted and the unfaulted half of the unit cell, are found to resemble the hydrogenated bulk terminated Si(111)-1×1 surface. As in the :19H monohydride phase, dimers on the second layer and a corner hole atom are also present [see Fig. 1(c)]. Although AD removal is found to have a considerable activation barrier, it is easily compensated by the formation of Si-H bonds.[16] This surface is modeled by removing the AD's from the clean slab model and passivating the resulting 43 DB's with H, allowing this 378-atom supercell to relax. The equilibrated structure shows Si-H bonds directed normal to the surface and bond lengths comparable to the :19H phase. The uppermost Si atoms are threefold coordinated to the atoms directly below, with bond lengths stretched by 1–2 % relative to the normal Si-Si bond, comparing well with LDA results of the hydrogenated 1×1 surface.[17] The RA's and CHA's move towards the bulk by about 0.5 Å, with respect to the clean surface, while the second- and third-layer atoms, originally directly below AD's, move away from the slab and reach their typical bulk positions. The Si(111)-7×7:43H phase is found to be merely 0.12 eV/(Si-H bond) more stable than the :19H monohydride phase, indicating that these two structures are almost energetically equivalent.[27] This result suggests that energetics alone indeed allows these two phases to coexist, as reported in Ref. mortensen. Comparing with 1×1:H, the 7×7:43H surface is only 0.19 eV/(Si-H bond) less stable, so that the "binding energies" are ordered as $\Delta E_{7\times7:19H} < \Delta E_{7\times7:43H} < \Delta E_{1\times1:H}$. This indicates that 7×7:43H could be a possible intermediate surface during the 7×7→1×1 phase transition discussed above.

The calculated electronic density of states (EDOS) also contains important information on these systems. The clean Si(111)-7×7 surface contains midgap states that we can clearly identify with surface dangling bonds (see Fig. 2). These EDOS features, lying above 0.19 eV and from 0 to
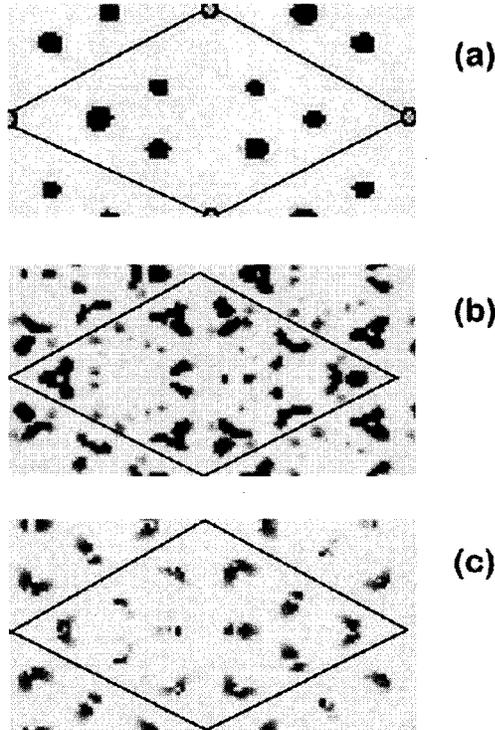
FIG. 3. Simulated STM images in the Si(111)-7×7 system. (a) RA-CH levels (at ~ −1 eV in Fig. 2), and (b) AD backbond states (~ −1.4 eV) for the clean surface. (c) AD backbond states in the monohydride :19H phase (~ −1.2 eV in Fig. 2). The faulted portion of the outlined unit cell is on the right.

−0.29 eV, arise from the empty and filled AD DB's, respectively. (Energies are referred to the Fermi level, which is 0.64 eV above the valence-band edge E_v, in close agreement with the experimental value of 0.6 eV in Ref. 3.) The dangling bond states are localized at various sites with a predominant p_z character. Between −0.88 and −0.98 eV, we find states resonant with the valence band that involve rest atom DB's, while AD backbonds lie between −1.38 and −1.44 eV. Corner hole states appear at −1.08 and −1.24 eV. Our results are in good agreement with several experiments that have reported occupied AD and RA dangling bonds at −0.25 and −0.85, AD backbonds and corner hole states at −1.8 eV, and AD back-antibonds at 0.55 eV.[5]

Figures 3(a)–3(c) exhibit simulated STM images according to the scheme of Tersoff and Hamann,[28] with the electronic states obtained in our calculation. The panels display constant charge density plots ($\rho \sim 0.01$ eV/Å^3) showing surface states at various energies below the Fermi level. Over a wide range of low bias values, for energies close to the Fermi level, we see a clear asymmetry between the faulted and unfaulted portions of the unit cell (not shown here), in agreement with low-bias STM measurements.[5] Figure 3(a) exhibits its states between −0.88 and −1.08 eV, corresponding to DB's of RA's and CHA's, while Fig. 3(b) exhibits backbond states lying between −1.38 and −1.40 eV, arising from p_x and p_y orbitals of the AD bonded to p_z orbitals of the first-layer atoms. The general features of our calculated STM im-

ages for various RA's/CHA's and AD's are in excellent agreement with those obtained by Hammers *et al.*[5]

In marked contrast to the clean surface, the EDOS of Si(111)-7×7:19H has no midgap states, as shown in Fig. 2. This is intuitively expected, as the DB's responsible for these states in the bare surface are passivated by H atoms. This finding corroborates EDOS measurements in Refs. 16 and 17, where features due to DB's on the bare surface disappear as the substrate is dosed with hydrogen. (Also, theoretical STM images of states near E_v yield featureless isodensity plots.) Moreover, we find that states lying between −0.74 eV and E_v are extended and show no contribution from the surface H and AD's states. Notice, however, that backbond states associated with the surface adatoms are still present and lie between 1.07 and 1.21 eV below the Fermi level and yield the STM image shown in Fig. 3(c). This finding supports the interpretation of recent differential-reflectance experiments,[10] as discussed below[9].

The EDOS of the Si(111)-7×7:43H also contains no midgap states (see Fig. 2). A clear reduction of the density of states in the region below E_v and in the conduction band is produced by the disappearance of AD's states. (Notice in particular the absence of a sharp feature at ~ −1.6 eV.) Our results agree quite well with the local tunneling spectroscopy experiment of Mortensen *et al.*,[16] who find no high density of states near the Fermi level for the :43H coverage. Only extended states due to surface and bulk Si were found between −0.8 eV and the valence-band edge E_v, as all the dangling bonds are fully saturated.

We should notice that a more accurate calculation of the optical gap requires the inclusion of self-energy corrections to the quasiparticle excitations, while within the LDA picture such a gap is usually underestimated.[12,13] While the method used here is based on the LDA approach, the minimal basis set (sp^3) employed overestimates the so-called LDA bulk gap. Notice that, although it has been proven that an extended basis that includes d orbitals leads to the LDA gap,[29] this is irrelevant for the molecular dynamics in the present work since only the valence states play an important role in the relaxation process. One must keep in mind that the combination of the LDA plus the minimal sp^3 basis set produces in general a good optical gap.

Our findings also provide strong support for the interpretation of differential-reflectance (DR) measurements by Roy and Borensztein,[10] who employ this powerful technique to explore the evolution of the surface electronic states under various chemisorption processes. In particular, at zero and low H coverage, a strong DR feature at 1.6 eV is identified as coming from transitions involving the backbond states of adatoms, as supported by tight-binding calculations of model structures.[9] As the H coverage increases, however, this feature saturates and higher-energy transitions dominate the DR spectra. This behavior is consistent with the disappearance of the backbond states as the higher coverage is reached and the :43H phase forms. Notice that the saturation of the 1.6-eV feature is accompanied in experiments by a strong reconstruction of the surface, as probed by LEED and as expected from the relaxation pattern shown in Fig. 1(c).[15] Finally, we should also notice that an empirical-parameter calculation of the optical response of this surface using our fully relaxed

atomic positions yields excellent agreement with the DR experiments, as discussed elsewhere.[11]

In summary, we obtained significant geometrical relaxation arising from H adsorption on the clean 7×7 surface, accompanied by strong shifts of the character and energies of the electronic states. These changes are found to be in excellent agreement with STM, differential reflectance, and LEED experiments and provide the basis for detailed comparisons with new experimental measurements.

[1] G. Binnig *et al.*, Phys. Rev. Lett. **49**, 57 (1982).

[2] K. Takayanagi *et al.*, Surf. Sci. **164**, 367 (1985).

[3] J.E. Demuth *et al.*, Phys. Rev. Lett. **51**, 2214 (1983).

[4] R. Wolkow and Ph. Avouris, Phys. Rev. Lett. **60**, 1049 (1988).

[5] J.M. Layet *et al.*, Phys. Rev. B **30**, 7355 (1984); P. Martensson *et al.*, *ibid*. **36**, 5974 (1987); R.J. Hammers *et al.*, Phys. Rev. Lett. **56**, 1972 (1986).

[6] I. Stich *et al.*, Phys. Rev. Lett. **68**, 1351 (1992).

[7] K. D. Brommer *et al.*, Phys. Rev. Lett. **68**, 1355 (1992).

[8] M.N. Piancastelli *et al.*, Phys. Rev. B **48**, 17 892 (1993).

[9] C. Noguez, A.I. Shkrebtii and R. Del Sole, Surf. Sci. **318**, 342 (1994); **331-333**, 1349 (1995).

[10] M. Roy and Y. Borensztein, Surf. Sci. **331-333**, 453 (1995); (private communication).

[11] C. Noguez, C. Beitia, W. Preyss, A.I. Shkrebtii, M. Roy, Y. Borensztein, and R. Del Sole, Phys. Rev. Lett. (to be published).

[12] K. Hricovini *et al.*, Phys. Rev. Lett. **70**, 1992 (1993).

[13] X. Blase, X. Zhu, and S.G. Louie, Phys. Rev. B **49**, 4973 (1994).

[14] E. Landemark, C.J. Karlsson, and R.I.G. Uhrberg, Phys. Rev. B **44**, 1950 (1991).

[15] C.J. Karlsson *et al.*, Phys. Rev. B **41**, 1521 (1990).

[16] K. Mortensen *et al.*, Phys. Rev. B **43**, 1816 (1991).

[17] L. Ye *et al.*, Phys. Rev. B **48**, 11 107 (1993).

[18] D.R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[19] O.F. Sankey and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989).

[20] O.F. Sankey *et al.*, Superlatt. Microstruct. **10**, 407 (1991); G.B. Adams and O.F. Sankey, Phys. Rev. Lett. **67**, 867 (1991).

[21] H. Huang *et al.*, Phys. Lett. A **130**, 166 (1988).

[22] G. Qian and D.J. Chadi, Phys. Rev. B **35**, 1288 (1987).

[23] X.P. Li, and D. Vanderbilt, Phys. Rev. Lett. **69**, 2543 (1992).

[24] The only large difference between our bare surface results and those of Brommer's involves the heights of adatoms 1 and 2 on the faulted region of the supercell. These adatoms are displaced towards the vacuum by ~ 0.18 Å, relative to other adatoms. Calculations for slabs with different thickness and for the 5×5 reconstruction geometry show that as the slab becomes larger, the displacements of these two adatoms decreases. We have also explored the type of slab used in Refs. 6 and 7 consisting of two reconstructed surfaces. In this case only one of the adatoms in question is ~ 0.2 Å higher than other adatoms. Moreover, we find an energetically equivalent configuration where the relative heights of adatoms on the faulted region of the unit cell are nearly equal and the features in the EDOS near the Fermi level shift only slightly. This difference in the clean surfaces is, however, of no significance for the hydrogenated surfaces we study, as the relaxation occurring after chemisorption reduces the differences between adatoms (in the :19H surface), as discussed in the text.

[25] For completeness, we have also studied a slab with eight Si layers capped by two reconstructed surfaces, one on each side, where the 19 DB's ($\times 2$) have been saturated with hydrogen. After relaxation, no significant differences have been found between this and the model reported in the text, consisting of six Si layers plus H adatoms. As the six-layer model has two more layers (per face) than the slab with the two reconstructed surfaces, the atoms in the former system are displaced in general between 0.01 and 0.04 Å with respect to those in the two-surface system, as one would expect for a somewhat smaller slab system.

[26] A expression similar to Eq. (2) was used to calculated the energy difference per Si-H bond.

[27] T. Sakurai *et al.*, J. Vac. Sci. Technol. A **8**, 259 (1990).

[28] J. Tersoff and D.R. Hamann, Phys. Rev. B **31**, 805 (1985).

[29] R.W. Jansen and O.F. Sankey, Phys. Rev. B **36**, 6520 (1987).