Ab Initio Molecular Dynamical Relaxation Applied to the Silicon(111)-5×5 Surface Reconstruction

Gary B. Adams and Otto F. Sankey
Arizona State University, Tempe, Arizona 85287

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We have applied first-principles molecular dynamical relaxation to the Si(111) surface in the 5×5 dimer–adatom–stacking-fault structure. We have determined the relaxed atomic surface geometry and the corresponding electronic structure. We find that the filled adatom dangling-bond states are segregated, with the charge density residing on the faulted side of the unit cell, and that the adatoms on the faulted side are higher than the adatoms on the unfaulted side. Surprisingly, we find that, at low temperature, the adatoms on each side of the unit cell are corrugated in a variety of patterns.

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When the Si(111) surface is prepared by cleaving in vacuum, the surface reconstructs into a 2×1 unit cell. A commonly accepted model for this 2×1 reconstruction is the π-bonded chain model, first proposed by Pandey [1]. Upon annealing, the 2×1 reconstruction converts to 5×5 and 7×7 reconstructions, as first shown by Lander, Gobeli, and Morrison [2] in 1963. Recently, Feenstra and Lutz [3] have made a detailed study of this conversion process using the scanning tunneling microscope (STM). They find that the 5×5 surface plays an important intermediate role in the conversion from 2×1 to the ground state of 7×7. In pure 2×1 regions (i.e., away from domain boundaries), the initial conversion, at about 330 °C, is from 2×1 to 5×5; this can occur because the 2×1 and the 5×5 structures have the same surface atom density. In comparison, the 7×7 surface atom density is 4% larger, so that growth of the 7×7 requires extra atoms coming from the bulk or from a distant surface. The 5×5 regions are found to be stable up to about 600–650 °C, at which point the entire surface converts to 7×7. The accepted model for both the 5×5 and 7×7 reconstructions is the dimer–adatom–stacking-fault (DAS) model of Takayanagi *et al.* [4].

We report here the first *ab initio* molecular dynamical (MD) relaxation of a very large (150-atom) semiconductor surface unit cell. We determine, entirely from first principles, the relaxed atomic geometry of the Si(111)-5×5 reconstruction in the DAS model, and the energy, band structure, and charge density for this relaxed geometry. Our first-principles MD technique involves no adjustment of parameters. The electronic eigenstates are expanded as a linear combination of pseudo atomic orbitals. The electronic states, the total energy, and the forces on the atoms are evaluated within the local-density and pseudopotential approximations, and in the non-self-consistent Harris-functional approximation [5]. The atoms move according to Newton's laws. A thorough description of the method, including all approximations, as well as numerous tests, can be found in Ref. [6]. This method has been applied successfully to bulk properties [6], clusters [7], amorphous Si [8], and Si surfaces [9]. In particular, the method spontaneously forms the Si(111)-2×1 π-bonded chain reconstruction as well as the 2×1, $p(2\times2)$, and $c(4\times2)$ reconstructions of the Si(001) surface [9]. In the present calculation, we use four "special" k points in the Brillouin zone, and we dynamically relax to the ground-state atomic configuration by removing the kinetic energy whenever a potential-energy minimum is passed.

Ideally, we would like to explore the entire pathway from the 2×1 π-bonded chain reconstruction to the 5×5 DAS reconstruction. However, this is currently unrealistic. To arrive at a realistic starting point, we have elected to create the stacking fault and place the adatoms in their approximate positions before beginning the dynamical relaxation.

We begin with the bulk-terminated Si(111) surface, six layers deep, in a 5×5 unit cell [Fig. 1(a)]. The single dangling bonds of each of the sixth-layer (deepest) atoms are tied off with hydrogen atoms. These sixth-layer atoms are made infinitely massive to simulate the bulk. The first-layer (top) atoms thus become the surface of interest, and each of these 25 atoms has a single dangling bond. We create the stacking fault by moving the first-layer atoms on the right-hand side of the unit cell by the vector $(d\sin30°, d\cos30°, 0)$, where $d=(\cos19.5°)(2.35\ \text{Å})$. This creates eight dangling bonds on second-layer atoms, four along the vertical center line and four at the lower right of the unit cell. The energy of this "half-faulted" surface is 0.447 eV per 1×1 surface unit cell (SUC) *higher* than the energy of the bulk-terminated surface.

Finally, we obtain the six "adatoms" by taking them from five first-layer sites ($F_1, \ldots, F_5$) at the lower left of the unit cell and one second-layer site (S_1) at the lower center of the unit cell. Removal of the four leftmost first-layer atoms ($F_1, \ldots, F_4$) creates four second-layer dangling bonds along the lower-left boundary of the unit cell, akin to those created earlier along the center line and lower-right boundary. Removal of the remaining first-layer atom (F_5) and the second-layer atom (S_1) creates a third-layer dangling bond in a "hole" at the lower center

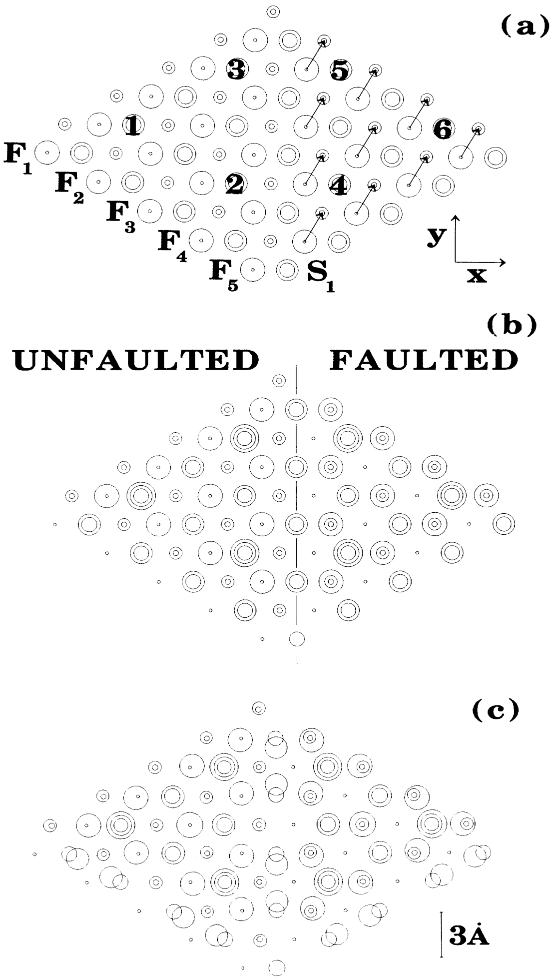

FIG. 1. (a) The bulk-terminated Si(111) surface. The z axis is out of the page. The atoms' z locations are indicated by relative size, with the smallest circles representing sixth-layer atoms. First-layer atoms on the right-hand side of the unit cell are moved by the indicated vectors to create the stacking fault. Adatoms are taken from sites labeled F_1–F_5 and S_1, and placed above the sites labeled 1–6. (b) The "half-faulted with adatoms" surface, which is the starting point for the MD relaxation. (c) The final relaxed Si(111)-5×5 DAS reconstructed surface. Note the dimerization of second-layer atoms along the lines separating faulted regions from unfaulted regions.

of the unit cell. These adatoms are placed 1.5 Å above the first layer at the sites labeled 1–6 in Fig. 1(a).

Placing the adatoms resolves eighteen (=6×3) first-layer dangling bonds, leaving two (=25−18−5) first-layer dangling bonds at the centers of the two sides. These first-layer atoms with dangling bonds are called the "rest atoms." In addition, there are now six adatom dangling bonds, twelve second-layer dangling bonds, and one third-layer dangling bond (in the hole). This "half-faulted with adatoms" surface, shown in Fig. 1(b), is the starting point for the MD relaxation. The energy of this surface is 0.280 eV per 1×1 SUC *higher* than the energy of the bulk-terminated surface.

The final state achieved by dynamical relaxation of the surface is shown in Fig. 1(c). The energy of this related 5×5 surface is 0.560 eV per 1×1 SUC *lower* than the energy of the bulk-terminated surface. (For comparison, in a 2×1 unit cell, using 32 special k points, we find −0.384 eV per 1×1 SUC for the energy of the relaxed π-bonded chain with respect to the bulk-terminated surface. A self-consistent calculation [10] for the π-bonded chain finds −0.21 eV per 1×1 SUC.) The most important energy-lowering process is the dimerization of the second-layer atoms along the boundaries between faulted and unfaulted regions. This process eliminates the twelve second-layer dangling bonds. We estimate that this dimerization process lowers the energy of the half-faulted with adatoms surface by about 0.58 eV per 1×1 SUC, or about 2.4 eV per dimer pair.

A second energy-lowering process is the relaxation (primarily in the z direction) of the atoms within the triangles, faulted and unfaulted, which make up the two sides of the unit cell. We find 0.1-Å z-direction relaxation even at the fifth of the six layers of atoms. We estimate that this relaxation process lowers the energy of the half-faulted with adatoms surface by about 0.2 eV per 1×1 SUC. During this z-direction relaxation, significant height differences develop between the faulted and unfaulted sides of the unit cell. These height differences are discussed in more detail below, as is the final energy-lowering process, "corrugation" of the adatoms within the faulted and unfaulted triangles. We estimate that the corrugation process lowers the energy of the half-faulted with adatoms surface by at most 0.02 eV per 1×1 SUC.

The nine dangling-bond bands of the final relaxed surface are displayed as solid lines in the band structure shown in Fig. 2. The lowest-energy surface band (at −3.88 eV) corresponds to the third-layer or hole dangling bond, and is doubly filled. The next two lowest-energy surface bands (at about −3.83 eV) correspond to the two first-layer dangling bonds, and are also doubly filled. The rest atoms, on which these dangling bonds are located, are at a height of about 0.55 Å (at the initial MD time step all first-layer atoms are at $z=0.00$ Å), 0.48 Å higher than the average height of the other first-layer atoms. By increasing the height of the rest atoms, the system stretches the rest-atom back bonds, making them more p-like, thus making the (doubly filled) rest-atom dangling bonds more s-like, and lower in energy. Above these three "deep-dangling-bond" bands are two bulk bands, followed by the six bands which correspond to the six adatom dangling bonds. These occur in the range from −3.25 to −2.60 eV. These six levels contain only three electrons. This fact is central to the unique, low-temperature, adatom corrugation of this surface.

On average, the adatoms on the faulted side are 0.17 Å higher than the adatoms on the unfaulted side. Since

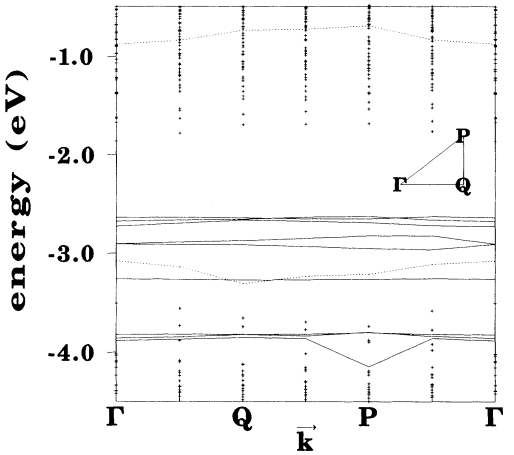

FIG. 2. Band structure of the final relaxed Si(111)-5×5 DAS reconstructed surface. Surface dangling-bond bands are indicated by solid lines. Dotted lines indicate the bulk silicon valence- and conduction-band edges for these k points. Crosses indicate bulk levels or nonlocalized surface levels in this energy range.

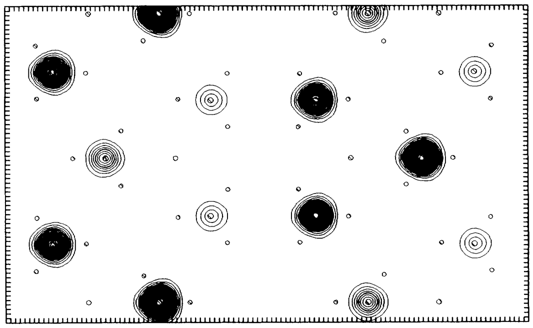

FIG. 3. Γ-point charge density of the three lowest adatom dangling-bond levels. This is an x-y plane of charge density slightly above the adatoms. Only atoms less than 2.0 Å from this plane are shown. The charge density for these levels is almost exclusively on the faulted side of the unit cell.

higher adatoms have lower-energy dangling bonds, the three electrons almost exclusively fill adatom dangling-bond states on the faulted side. The (Γ point) charge density of the filled adatom dangling-bond states is shown in Fig. 3. In Fig. 2, these are the doubly filled band at −3.25 eV and the almost degenerate bands at −2.91 eV. Conversely, since the adatoms on the unfaulted side are lower in height, the adatom dangling bonds there are more p-like and higher in energy. Thus the empty adatom dangling-bond states are preferentially on the unfaulted side of the unit cell. These findings are in excellent agreement with STM images [11] of filled and unfilled states on the Si(111)-5×5 surface.

Finally, we come to the unexpected behavior of adatom corrugation. In the simplest model, one expects to find a pair of threefold-degenerate energy levels, one threefold set for the three adatoms on the faulted side (with more s-like dangling bonds), and one threefold set for the three adatoms on the unfaulted side (with more p-like dangling bonds). However, this degeneracy can be broken by varying the heights of the adatoms *within* the equilateral triangles which make up the two sides. Our MD relaxation has automatically provided us with this symmetry-breaking distortion, and we find the adatom at site 6 to be 0.30 Å higher than the adatoms at sites 4 and 5. On the unfaulted side, with empty dangling bonds, the effect is less pronounced and we find the adatom at site 1 to be 0.04 Å higher than the adatoms at sites 2 and 3.

This adatom corrugation and the corresponding novel electronic structure of the adatom dangling bonds can be understood through a 6×6 empirical tight-binding model. Define $z_{iu}=z_i-z_u$ and $z_{if}=z_i-z_f$, where z_i is the height of the atom at site i, and z_u and z_f are the adatom heights (u stands for unfaulted, f for faulted) before corrugation begins. Then the (Γ point) Hamiltonian is

$$H=\begin{pmatrix} \epsilon_u-az_{1u} & s & s & t & t & 0 \\ s & \epsilon_u-az_{2u} & s & t & 0 & t \\ s & s & \epsilon_u-az_{3u} & 0 & t & t \\ t & t & 0 & \epsilon_f-az_{4f} & s & s \\ t & 0 & t & s & \epsilon_f-az_{5f} & s \\ 0 & t & t & s & s & \epsilon_f-az_{6f} \end{pmatrix}. \tag{1}$$

TABLE I. Computer-generated exact solutions of the 6×6 model of adatom corrugation. Degeneracies of each solution type are given in parentheses.

Type	z_{1u} (Å)	z_{2u} (Å)	z_{3u} (Å)	z_{4f} (Å)	z_{5f} (Å)	z_{6f} (Å)
I (3)	0.0103	0.0055	0.0055	0.0482	0.0482	0.2138
II (3)	0.0096	0.0036	0.0036	0.1572	0.1572	0.0002
III (6)	0.0035	0.0069	0.0037	0.2138	0.0003	0.1034

The self-energies of the adatom dangling bonds are modified by the term $-\alpha z_{iu}$ or $-\alpha z_{if}$, where α is a proportionality constant with dimension eV/Å. This height-dependent term makes higher adatoms (with more s-like dangling bonds) lower in energy. The off-diagonal element t (s) represents an indirect, effective interaction between nearest (second-nearest) neighbor adatoms. We assume a uniform spring constant k connecting the adatoms to the first layer, and from our first-principles MD results find the following parameters:

$$\epsilon_u = -2.68\ \text{eV},\quad s = +0.006\ \text{eV},\quad z_u = 1.29\ \text{Å},\quad \alpha = 1.37\ \text{eV/Å},$$

$$\epsilon_f = -2.86\ \text{eV},\quad t = -0.062\ \text{eV},\quad z_f = 1.39\ \text{Å},\quad k = 12.6\ \text{eV/Å}^2.$$

The total energy of the adatom system in this model is given by

$$E_{\text{total}} = E_{\text{band structure}} + \tfrac{1}{2} k (z_{1u}^2 + z_{2u}^2 + z_{3u}^2 + z_{4f}^2 + z_{5f}^2 + z_{6f}^2). \qquad (2)$$

We desire the displacements z_{iu} and z_{if} which minimize Eq. (2).

One approach is to set α equal to zero and solve the resulting problem exactly, then include $-\alpha z_{iu}$ and $-\alpha z_{if}$ as perturbations. However, since αz_{iu} and αz_{if} are on the order of t, the perturbation-theory results are only suggestive. A second approach is to solve the model numerically. Both approaches yield twelve solutions of three types. The exact, computer-generated solutions are presented in Table I, and both sets of solutions are diagramed in Fig. 4. All twelve perturbation-theory solutions are degenerate, while the twelve exact solutions differ in energy by at most 6 meV/atom (70 K). Both approaches can also yield the least-energy noncorrugated configuration; numerically, this is $z_{1u} = z_{2u} = z_{3u} = 0.0097$ Å, and $z_{4f} = z_{5f} = z_{6f} = 0.1006$ Å. The energy of this noncorrugated configuration is only 15 meV/atom (175 K) higher than that of the most energetic corrugated solution. Since meV is beyond the accuracy of our calculation, 175 K can only be regarded as an estimate for the onset of corrugation, but perturbation theory insures that corrugation will appear at some low temperature.

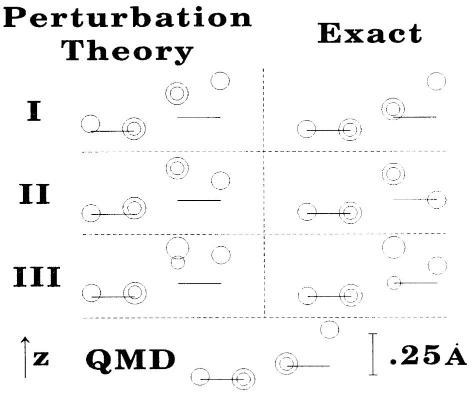

FIG. 4. Solutions to the 6×6 Hamiltonian for the adatom corrugation process. Shown is a side view (looking along the y direction of Fig. 1) of the adatoms in the 5×5 unit cell. Left to right in each six-atom diagram are sites 1, 2 and 3, 4 and 5, and 6. The two horizontal lines in each diagram represent z_u and z_f. The perturbation-theory solutions are strictly schematic. The computer-generated solutions are to scale in the z direction. Also shown to scale (neglecting corrugations in the first layer) are the adatoms from the full (150-atom) MD solution.

To summarize, in what is the largest first-principles molecular dynamical relaxation to date, we have determined the final relaxed atomic positions and corresponding electronic structure of the Si(111)-5×5 reconstruction in the dimer-adatom-stacking-fault model. We find the 5×5 reconstruction to be 0.560 eV per 1×1 SUC lower in energy than the bulk-terminated surface in the same unit cell. We find that the adatoms on the faulted side of the unit cell are higher than the adatoms on the unfaulted side. The adatom dangling-bond states are primarily filled on the faulted side, and primarily empty on the unfaulted side. At low temperature, adatoms within the faulted and unfaulted triangles (most noticeably the faulted) take on different heights and different electron occupancies.

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