

### Total energy of the adatom and pyramidal-cluster models for Si(111)

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The total energy is calculated for a Si(111)-(2×2) adatom geometry with a local bonding topology which is similar to the models of Harrison and Binnig *et al.* for the structure of the Si(111)-(7×7) surface. This 2×2 model is found to be higher in energy than the Pandey chain geometry by about 0.2 eV/(surface atom). The energy of a 2×2 pyramidal-cluster model is also calculated, and is found to be higher than the chain surface by about 0.9 eV/(surface atom). The activation energy for diffusion on the ideal surface is estimated.

Harrison<sup>1</sup> first proposed that adatoms could be an important feature of the Si(111)-7×7 reconstruction. Recently, the scanning tunneling microscopy (STM) experiments performed by Binnig *et al.*<sup>2</sup> have greatly increased our knowledge of this complex system and have renewed interest in the adatom model. These authors interpreted their measurements in terms of a modified Harrison model with 12 adatoms per unit cell and a possible 13th adatom site unoccupied. We feel it is of interest to study the energetics of these adatoms and also determine whether their presence is consistent with photoemission experiments.<sup>3-6</sup> Although the large size of the 7×7 unit cell precludes a direct calculation of the total energy, much information can be gained by studying a 2×2 lattice in which the adatoms have a local environment which is

similar to the proposed model.

We have also considered the pyramidal-cluster model proposed by Aono *et al.*<sup>7</sup> This model gives the best agreement with the results of helium-ion scattering experiments. The pyramidal cluster is very similar in structure to a model proposed recently by Snyder.<sup>8</sup>

The total energy is calculated for a 2×2 rectangular lattice of adatoms using the pseudopotential method and the local-density-functional formalism. In the threefold hollow site geometry, which we denote  $H_3$ , an adatom is placed in one of the four hollow sites in each 2×2 unit cell. This results in a coverage of  $\frac{1}{4}$ , which is similar to the adatom coverage of  $\frac{12}{49}$  for the proposed 7×7 adatom model. Each adatom is bonded to the three surface atoms below, resulting in a reduction of two dangling bonds per adatom. Dangling-bond reduction is the principal motivation for the adatom model.<sup>1</sup> A schematic illustration of the  $H_3$  geometry is shown in Fig. 1.

A supercell approach<sup>9</sup> with eight layers of Si atoms separated by vacuum is employed in the calculation. The distance across the vacuum between adatoms in neighboring cells is  $\sim 14$  a.u. Inversion symmetry is imposed on the system. Self-consistent calculations are carried out in momentum space,<sup>10</sup> and the solutions to the Kohn-Sham equations<sup>11</sup> are expanded in a symmetrized plane-wave basis. Plane waves with kinetic energies up to 5 Ry are included in the basis set. This corresponds to approximately 1250 plane waves. More plane waves than this are necessary for guaranteed convergence of energy differences to within 0.1 eV/(surface atom). Calculations of the energy difference between the Si<sub>2</sub> molecule and isolated atoms are converged to within  $\sim 0.1$  eV/(atom) with a plane-wave cutoff of 5 Ry.<sup>12</sup> A norm-conserving pseudopotential<sup>13</sup> for silicon is generated, and the Perdew and Zunger parametrization<sup>14</sup> of the Ceperley and Alder<sup>15</sup> exchange correlation energy functional is used.

To compute the energy of the 2×2 adatom geometry relative to the ideal topology surface, calculations must be performed for the adatom geometry, for the ideal geometry, and for the bulk. Comparisons must be made between systems with the same total number of atoms. To create an ideal surface with the same number of atoms as in the adatom system we assume that the adatoms can be

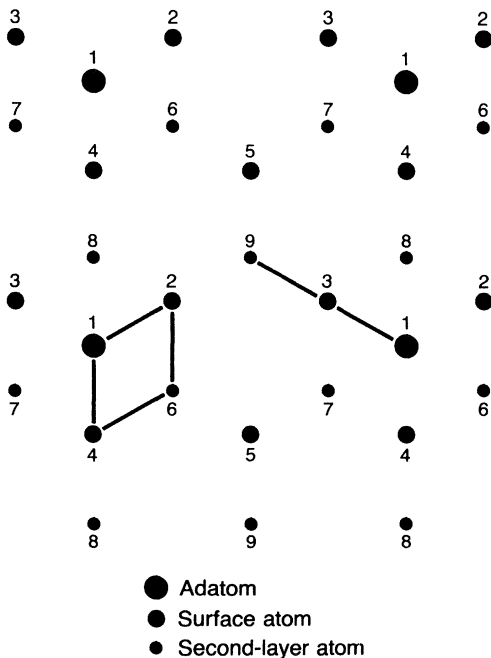


FIG. 1. Top view of the rectangular 2×2 adatom geometry  $H_3$ . The adatom is bonded to three surface atoms (2, 3, and 4). The solid lines show an example of a fourfold ring of bonds (1-2-6-4) and a 180° bond angle (1-3-9).

TABLE I. Deviations of the atomic positions from the ideal positions in a.u. Atom numbers refer to Fig. 1. Atoms 10, 11, 12, and 13 are directly below atoms 6, 7, 8, and 9, respectively. The  $x$  direction is parallel to the line through atoms 4 and 5; the  $y$  direction is parallel to the line through atoms 4 and 1.

	Atom	$\Delta x$	$\Delta y$	$\Delta z$
Adatom	1	0.0	0.0	0.63
	2	-0.15	-0.09	-0.10
Surface layer	3	0.15	-0.09	-0.10
	4	0.0	0.22	-0.10
	5	0.0	0.10	-0.10
Second layer	6	0.09	-0.05	-0.20
	7	-0.09	-0.05	-0.20
	8	0.0	0.20	-0.03
Third layer	9	0.0	-0.02	0.32
	10	0.0	0.0	-0.10
	11	0.0	0.0	-0.10
Third layer	12	0.0	0.0	-0.06
	13	0.0	-0.08	0.13

grouped together to form a macroscopic bilayer on the ideal surface. The number of surface atoms for this system is the same as on the completely flat surface, but if  $L$  adatoms are grouped together in a bilayer, then the system contains  $L$  more *bulk* atoms. Thus the energy difference per surface atom between the adatom system and the ideal topology system is given by

$$\frac{1}{n_s} \{N_A E_A - [N_I E_I + (N_A - N_I) E_B]\},$$

where  $E_A$ ,  $E_I$ , and  $E_B$  are the total energies per atom for the adatom, ideal, and bulk systems, respectively,  $N_A$  is the number of atoms per supercell for the adatom system,  $N_I$  is the number of atoms in the ideal supercell, and  $n_s$  is the number of surface atoms in each supercell. In our calculations  $N_A = 34$ ,  $N_I = 32$ ,  $n_s = 8$ .

For each  $H_3$  geometry tested, the forces on the atoms were calculated and used to find geometries with successively lower total energy. For the most stable geometry obtained, the deviations from the ideal positions are shown in Table I. The vertical distance between the adatom (atom 1) and the undisturbed surface atom (atom 5) changes from 1.48 a.u. (for bulk bond lengths and no relaxation) to 2.21 a.u. for the  $H_3$  geometry with lowest energy. The magnitudes of the lateral distortions are 0.22 a.u. or less. These types of displacements should be taken into account in experimental tests of the adatom model. The distortions are understood as a compromise between bond-angle and bond-length changes. The ideal bond angles and the relaxed angles are shown in Table II. The adatom moves upward by  $\sim 0.6$  a.u. and pulls the surface atoms to which it is bonded (2, 3, and 4) under itself to reduce the bond angles 1-2-9, 1-3-9, and 1-4-8 from the initial values of  $180^\circ$  to  $\sim 165^\circ$ , which is closer to the tetrahedral angle ( $109^\circ$ ). The angles 2-1-3, 3-1-4, and 2-

TABLE II. Bond angles for the ideal  $2 \times 2$  adatom geometry and for the relaxed  $2 \times 2$  adatom geometry ( $H_3$ ). Atom numbers refer to Fig. 1.

Bonds	Ideal	$H_3$
1-2-9	$180^\circ$	$165^\circ$
1-4-8	$180^\circ$	$169^\circ$
1-2-6	$70^\circ$	$79^\circ$
1-4-6	$70^\circ$	$79^\circ$
2-1-4	$109^\circ$	$98^\circ$
2-1-3	$109^\circ$	$98^\circ$

1-4 become closer to  $90^\circ$ . This suggests that the adatom does not develop complete  $sp^3$  hybridization. Atoms 1-2-6-4, etc., form fourfold rings of bonds with bond angles of  $70^\circ$  for 1-2-6, 1-4-6, etc. These angles increase from  $70^\circ$  to  $79^\circ$  as the forces are reduced. The opening of this angle forces atoms 6, 7, and 8 down and away from the adatom. On the other hand atoms 8 and 9 are forced upwards to reduce the angles 1-2-9, 1-3-9, and 1-4-8 from  $180^\circ$  to  $165^\circ$ . Notice that atom 9 moves up by  $\sim 0.3$  a.u. while atom 8 is only displaced by a small amount. This reflects a frustration effect inherent in this rectangular  $2 \times 2$  adatom geometry. Atom 8 lies between two adatoms; one forces it downwards and the other forces it upwards. This frustration would not occur in a triangular  $2 \times 2$  adatom model.

We find that a relaxed  $H_3$  geometry has a total energy which is 0.17 eV/(surface atom) lower than the unrelaxed ideal surface. This energy is similar to the relaxed  $1 \times 1$  surface.<sup>16</sup> The energy of the Pandey<sup>17,18</sup>  $2 \times 1$   $\pi$ -bonded chain geometry has been calculated to be  $\sim 0.36$  eV/(surface atom) below the ideal surface.<sup>19,20</sup> This energy is, at present, an upper bound on the energy of the true  $7 \times 7$  reconstruction. Although the present calculation indicates that the  $2 \times 2$  adatom model is too high in energy by at least 0.19 eV/(surface atom), we believe that *the energy is low enough so that less restrictive adatom models should not be discounted* on the basis of total-energy considerations. The presence of the lateral strains and frustration suggests that the removal of the rectangular  $2 \times 2$  periodicity requirement could result in a significant reduction in the energy.

The valence charge density for the  $2 \times 2$  adatom model is shown in Fig. 2. A reasonably large bond charge between the adatom (atom 1) and the surface atom (atom 4) has formed in spite of the nontetrahedral bond angle. The maximum of the charge density in this bond occurs above the bond center. This may be because of the tendency for charge to be attracted to the dangling-bond region above atom 4. The formation of reasonably strong bonds between the adatom and the three surface atoms is necessary if the adatoms, in fact, lead to a surface with low energy.

Experimentally,<sup>3-6</sup> for the  $7 \times 7$  surface, there are three surface states near the top of the valence band. The uppermost of these states is sensitive to the long-range order of the surface (3) and its existence appears to depend on the special nature of the  $7 \times 7$  unit cell. The two lower states are the most prominent, and are insensitive to the

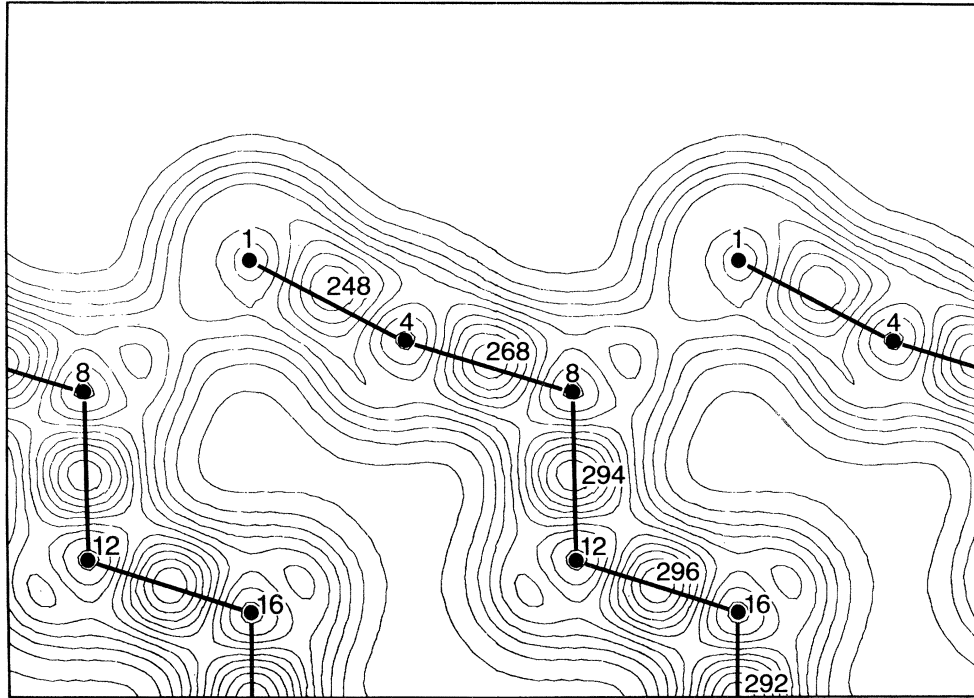


FIG. 2. Contour plot of the charge density in the plane containing atoms 1, 4, and 8 for the  $H_3$  geometry. The numbering of the atoms corresponds to Fig. 1. The contour interval is 25 in units of electrons/ $(3376a_B^3)$ .

long-range order. Of these two, the uppermost one is thought to be an  $sp_z$  dangling-bond state. The energy of this state is near to the top of the valence band. The lowermost state is thought to have substantial  $p_x$  and  $p_y$  character, and its energy is approximately 0.9 eV below the dangling-bond state. In our calculations we find a dangling-bond surface state near the top of the valence band. This state is localized mainly on the free surface

atom but has some amplitude on the adatom. We also find a new type of back-bond surface resonance. The character of this resonance is illustrated in Fig. 3. The state has  $sp_z$  character relative to the surface atom, and  $p_y$  character relative to the adatom. The energy of this state is about 1.1 eV below the dangling-bond states. Thus the adatom model can account for the existence of the two most prominent surface states on Si(111)-(7 $\times$ 7).

We have also studied the geometries where the adatom is placed in a threefold site above a second-layer atom ( $T_3$ ); in a twofold bridge site ( $B_2$ ) or in a onefold top site above a surface atom ( $T_1$ ). In the  $T_3$  geometry the adatom is above atom 8 and bonded to the three surface atoms (2, 3, and 4). In the  $B_2$  geometry the adatom is bonded to two surface atoms (2 and 3). In the  $T_1$  geometry the adatom is directly above the surface atom 4. The energies of these geometries, relative to the energy of  $H_3$ , are shown in Table III. Clearly the adatom prefers the threefold sites over the twofold or onefold coordinated sites. From these energies we can make an estimate of the activation energy for diffusion of an adatom on an ideal

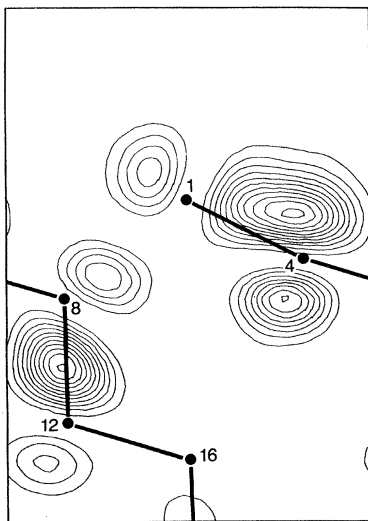


FIG. 3. Contour plot of the charge density corresponding to a back-bond surface resonance. The same plane as in Fig. 2 is plotted.

TABLE III. Energies (relative to  $H_3$ ) of four types of  $2 \times 2$  adatom geometries.

Surface	Energy (eV/adatom)
$H_3$	0.0
$T_3$	0.37
$B_2$	0.83
$T_1$	2.20

substrate. Diffusion may take place via the path  $H_3-B_2-T_3-B_2-H_3$ . The activation energy for this process is  $\sim 0.8$  eV. This corresponds to the energy required to move the adatom from the  $H_3$  position to the  $B_2$  site which is a saddle point on the adatom energy surface. One bond is broken in the process.

The pyramidal-cluster structure<sup>7</sup> has as its building block a four-atom pyramidal cluster with one atom at the apex and three atoms at the base. Each basal atom is two-fold coordinated; it is bonded to a substrate atom and to the apical atom. Each apical atom is bonded to three basal atoms. In the original model,<sup>7</sup> the bond angles and lengths of the apical and basal atoms are equal to the ideal values. Twelve of these clusters are distributed over the  $7 \times 7$  unit cell in the pattern determined by the STM experiment. This leaves 13 free surface atoms without bonds to any basal atom. In our calculations, we have considered a  $2 \times 2$  cell with one cluster and one free surface atom per cell. Total energy calculations were performed for two different sets of positions for the apical and basal atoms. In the first case the apical atom is positioned 1.04 a.u. above the basal plane. The energy of this geometry is 1.02 eV/(surface atom) higher than the chain geometry. In the second case the apical atom is 0.44 a.u. above the basal plane and the basal atoms are displaced la-

terally by about 0.3 a.u. The energy of this geometry is 0.88 eV/(surface atom) above the chain geometry. We do not think further optimization of the structure will lower the energy by more than a few tenths of an eV. Hence, based on total-energy considerations, the pyramidal-cluster model seems implausible.

In summary, we believe that the present calculations show that the  $2 \times 2$  rectangular adatom geometry is sufficiently low in energy so that, in general, adatom models should not be excluded on the basis of total-energy considerations. We find that both prominent types of surface states observed experimentally can be accounted for by the adatom model. On the other hand a pyramidal-cluster model is found to be very high in energy and therefore is unlikely. In addition we have calculated the activation energy for self-diffusion on an ideal topology substrate.

#### ACKNOWLEDGMENTS

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