New adatom model for Si(111) 7×7 and Si(111)-Ge 5×5 reconstructed surfaces

D. J. Chadi

Palo Alto Research Center, Xerox Corporation, 3333 Coyote Hill Road, Palo Alto, California 94304

(Received 29 May 1984)

A new adatom structure with significantly less angular strain than the simple adatom geometry is proposed. The model involves a rebonding of $\simeq \frac{1}{8}$ of surface atoms to the substrate in a manner similar to that occurring in the π -bonded-chain structure for the Si(111) 2×1 surface. The interference between adatom and substrate reconstructions *forces* the smallest threefold-symmetric unit cells to be 5×5 and 7×7 in size. The proposed reconstructed-adatom model gives rise to structural features in good agreement with experiment. In particular, the inhomogeneous corrugation of the two halves of the 7×7 unit cell seen in vacuum-tunneling microscopy and the apparent need for stacking fault sequences in ion-channeling experiments are accounted for. The results of surface energy and structure calculations on 2×2, 3×3, 5×5, and 7×7 adatom models are presented.

I. INTRODUCTION

The first real-space imaging of the 7×7 reconstructed Si(111) surface by Binnig et al.¹ has generated new interest in the precise nature of the atomic bonding at this surface. Vacuum-tunneling microscopy¹ reveals 12 maxima in the unit cell and deep holes at the corners and sides of the unit cell with a corrugation as large as 2.8 Å. Except for a corner site, the lateral positions of the maxima coincide with the adatoms of Harrison's model² and the vacancies of the Lander model.³ Binnig et al.¹ suggested that the deep and inhomogeneous corrugations of the surface should be explainable by a simple relaxation or modification of the Harrison adatom model. The nature of the modifications to be made has remained unclear, however, because tunneling microscopy does not provide direct information on the surface bonding geometry even though it vields valuable information on the surface corrugation.

Despite the fact that the adatom model gives the best agreement of any simple structure with the vacuumtunneling results, it has not received universal acceptance as the correct structure for the 7×7 surface. This is primarily because it is presently unclear whether this model is consistent with other experimental data or with theoretical considerations. For example, complementary information on the surface atomic structure from a recent analysis⁴ of Rutherford backscattering experiments^{5,6} indicates that the ··· ABCABC ··· stacking sequence, characteristic of face-centered-cubic crystals, may be broken at the surface. Additional evidence for stacking faults or surface dislocations has been deduced from lowenergy-electron diffraction (LEED) data,⁴ and from transmission electron microscopy.⁷ Several models⁸⁻¹⁰ which incorporate stacking fault sequences in the unit cell and have structural features consistent with the observations of Binnig et al.¹ have been proposed recently and will be examined in this paper.

The acceptance of the adatom model for the 7×7 surface appears difficult also from theoretical considerations. The surface energy of the thermodynamically stable 7×7 surface should be lower than that of the metastable cleaved 2×1 surface. In particular, the 7×7 surface should have a lower surface energy than the π -bondedchain structure.^{11,12} In going from a chain to an adatom structure, the favorable energy lowering from π bonding is presumably lost and, in addition, a significantly larger lattice strain is introduced. The recent calculations of Northrup and Cohen¹³ for a 2×2 adatom model indicate, however, that the lowering of the dangling-bond density by a factor of 2 is sufficient to compensate for most of this energy loss. The 2×2 adatom model is found to be 0.19 eV (per 1×1 unit area) higher in energy than the π bonded structure. This energy, although comparable in size to the magnitude of typical surface reconstruction energies, is sufficiently small that it makes further investigations of the adatom model necessary.¹³

In addition to constraints from vacuum-tunneling microscopy,¹ ion-channeling,⁴ and surface-energy considerations the model for the annealed (111) surfaces of Si and Ge has to account for a large body of other experimental data. These include nucleation of the 7×7 structure at steps;¹⁴ the appearance of stable 5×5 and 7×7 periodicities¹⁵ for Sn on Ge(111) and¹⁶ for Ge on Si(111) surfaces; the similarities and differences in the photoemission¹⁷⁻¹⁹ and optical-absorption^{20,21} spectra of 2×1 and 7×7 surfaces; evidence for unique surface and subsurface hydrogen chemisorption sites on the 7×7 surface;²² the possibility of magnetic ordering at low temperatures;²³ and a unique physisorption site geometry²⁴ for Xe and Kr.

In this paper the structural and energetic aspects of the 7×7 and 5×5 reconstructions are examined via totalenergy calculations on a variety of models and on unit cells ranging from 2×2 to 7×7 in size. Large unit cells were used to eliminate uncertainties regarding the influence of unit-cell dimensions on the magnitude of the relaxation energy for any particular model, and because for the adatom geometry proposed in this paper, the minimum unit cell size is 5×5 .

The paper is organized as follows. The results of energy-minimization calculations for the conventional

30 4470

type of adatom model are discussed in Sec. II. For the particular case of a 2×2 rectangular lattice, the results are compared with those from *ab initio* self-consistent pseudopotential calculations of Northrup and Cohen.¹³ The surface energy for this structure is taken as a reference for comparing the differences between various structures discussed in this and subsequent sections.

The possibility of substrate reconstruction involving a rebonding of atoms (as opposed to simple atomic relaxation) is discussed in Sec. III. The motivation for this is the reduction of the large angular strains present in the conventional adatom model. The smallest structure for which this is possible is a rectangular 2×2 lattice. For this lattice, the results are found to be only marginally better than the old rectangular adatom model. Surprisingly, as shown in this section, it is found that as a result of the interference between the adatom and substrate reconstructions, hexagonal 2×2 , 4×4 , and 6×6 periodic structures are not possible for the new geometry. If the structure is required to have threefold symmetry, then the smallest hexagonal $n \times n$ unit cells are 5×5 and 7×7 . A 3×3 structure lacking the threefold symmetry is calculated to have a much higher surface energy than the conventional adatom model. The reduced surface energy of larger unit cells is not primarily a result of the rotational symmetry but arises from a removal of constraints inherent in smaller lattices.

The results of calculations on the new 5×5 adatom geometry and a discussion of experimental results on the 5×5 and 7×7 structures are presented in Sec. IV where it is shown that the model gives the following.

(i) A surface corrugation consistent with that observed in vacuum-tunneling experiments.¹ It provides an explanation for the inhomogeneous corrugation of the surface by having different relaxations and reconstructions on the two halves of the unit cell.

(ii) Structural elements *resembling* those arising from stacking faults at the surface.⁴ These come about directly as a consequence of the rebonding occurring in the substrate layer and are in good agreement with structural features deduced from ion channeling.

(iii) A lowering of the surface energy making the new structure energetically competitive with the π -bonded-chain model^{11, 12} for the 2×1 surface.

(iv) An explanation for the striking similarity in polarization and angular dependence of normal photoemission spectra for the surface states at $\simeq 0.8$ eV below the Fermi energy E_F in both the 2×1 and 7×7 surfaces.^{17,18} Measured relative to the valence-band maximum¹⁹ instead of E_F , this state is $\simeq 0.3$ eV more bound in the 2×1 surface than in the 7×7 surface. The new adatom model provides a simple explanation for this energy difference.

(v) Specific surface sites where hydrogen chemisorption is most likely to occur. It is proposed that hydrogen chemisorption at these sites leads to a large decrease of the surface energy.

(vi) A greatly enhanced interaction among distant dangling bonds as compared to the simple adatom model. This suggests that a magnetic ordering of spins should make a small but non-negligible contribution to the stability of 5×5 and 7×7 structures. The results of calculations for Himpsel's trimer model⁸ are discussed in Sec. V. The tight-binding-based method of calculation²⁵ is reviewed briefly in Sec. VI.

II. SIMPLE ADATOM MODELS

A. Angular strains

Two adatom models with rectangular and hexagonal 2×2 unit cells are shown in Fig. 1. In the "ideal" configuration where *all* bond lengths are equal to those in the bulk, the adatom is one interlayer spacing ($\simeq 0.78$ Å in Si) above the substrate. The large angular strains in this simple adatom configuration can be appreciated by considering the distributions of angles θ at the fourfold-coordinated surface atoms capped by the adatom. At each one of these second-layer atoms, there are three angles with the values of

$$\theta_1 = 180^\circ$$
 and $\theta_2 = \theta_3 = 70.53^\circ$ (1)

which deviate sharply from the ideal tetrahedral angle of 109.47°.

The adatom models shown in Fig. 1 are for the situation where the adatom is on a "hollow" site. If the adatom is placed on a site above a second-layer atom, then larger angular strains in addition to large bond-length



FIG. 1. Top views of simple adatom models with rectangular and hexagonal 2×2 periodicities are shown in (a) and (b). In the unrelaxed geometry, the adatom falls on the intersection of the three straight lines joining surface atoms to second-layer atoms. The resulting 180° angles go to $160^{\circ}-165^{\circ}$ after relaxation. strains develop. The surface energy of the top-site geometry is sufficiently higher than the hollow-site configuration¹³ that it will not be considered in this paper. The top-site geometry is also inconsistent with the results of vacuum-tunneling microscopy.¹

It may be argued that relaxation of surface atoms will result in a large decrease of the angular strain energy. However, the present calculations for lattices from 2×2 to 7×7 in size show that the angles in Eq. (1) relax at best to values of 160° and 81°, respectively. The angular relaxation is achieved at the cost of increasing the adatomsubstrate bond length by $\simeq 4.5\%$ over the bulk bond length. For a 2×2 hexagonal lattice, the reduction in total energy resulting from relaxation is about 1.4 eV per adatom.

Considerations based on the angular strain energy of the adatom model suggest that this energy can be decreased appreciably if the equilibrium adatom-substrate bond length is larger than the underlying bulk bond length. A larger bond length prevents the adatom from falling on a straight line with surface and second-layer atoms, thus decreasing θ_1 from 180°. For the Ge(111)-Sn and Si(111)-Ge systems where the Ge-Sn and Si-Ge bond lengths are both larger than substrate bond lengths, other possibilities for the optimization of the angular distributions exist if an intermixing of the different atomic species takes place. The Ge(111)-Sn adatom model is discussed below in Sec. C. The role of misfit strain energies in the reconstruction of annealed surfaces has been discussed by Phillips.²⁶

B. Surface energy of the rectangular 2×2 adatom model from tight-binding and pseudopotential calculations

Northrup and Cohen¹³ have recently calculated the total-energy and atomic structure of a rectangular 2×2 adatom model [see Fig. 1(a)] using the self-consistent pseudopotential method. They find that the relaxed adatom geometry has a surface energy lower by 0.17 eV/ $(1 \times 1 \text{ unit cell})$ relative to the unrelaxed ideal 1×1 surface and higher by 0.19 eV/(1×1 unit cell) as compared to Pandey's π -bonded-chain geometry.^{11,12} The removal of the lateral strains and frustrations inherent in the rectangular 2×2 lattice, which can be achieved, for example, by going to a hexagonal lattice, was proposed to lead to an even more stable adatom geometry. The present calculations, as described in more detail below, confirm this picture and show that a reduction of 0.05 eV/(1×1 unit cell) occurs in going from the rectangular to the hexagonal adatom geometry.

The atomic and electronic structure of the adatom geometry obtained from the two calculations are in generally very good agreement. However, the tight-binding calculations presented here for various adatom geometries predict the *relative* surface-energy differences between various adatom geometries more accurately than the differences between dissimilar geometries such as the ideal surface and the adatom geometry. This is because the limited sp^3 basis set used in the calculations is too small to adequately account for the large angular strains present in adatom models. Compared to pseudopotential calculations,¹³ the energy of the optimized rectangular adatom model is calculated to be 0.03 eV/(1×1 cell) higher than that of the unrelaxed ideal surface instead of 0.17 eV/(1×1 cell) lower. Despite this problem of the tightbinding method in underestimating the binding energy of an adatom, it is expected to be more useful and accurate in comparing the relative energy differences between similar types of adatom structures considered in this paper. Defining γ as

$$\gamma = \text{surface energy (in eV/1 \times 1 unit cell)}$$
 (2)

and taking the rectangular 2×2 lattice as reference, in the following sections the changes $\Delta \gamma$ in surface energy relative to the value for this lattice are given. On the basis of Northrup and Cohen's calculations,¹³ a decrease in γ of greater than 0.19 eV/(1×1 cell) should make the adatom geometry more favorable than the π -bonded-chain model.

C. Results of calculations on Si(111) adatom models

1. Rectangular 2×2 cell

The adatom and three substrate layers were allowed to relax. The optimum atomic geometry was calculated from a minimization of Hellmann-Feynman forces.²⁵ In the unrelaxed geometry the adatom is approximately 0.78 Å above the surface layer. After relaxation, the adatom moves away from the surface by an extra 0.39 Å. This is in good agreement with the 0.33 Å calculated by Northrup and Cohen.¹³ The present tight-binding calculations give a bond-length stretching of 4.9% at the surface as compared to 3.4% obtained previously.¹³ Some angular distributions, with the pseudopotential values given in parentheses, are

$$\theta = 94.7^{\circ}, 94.7^{\circ}, 97.5^{\circ} (98^{\circ})$$
 (3)

about the adatom, and

$$\theta = 163^{\circ}, 165^{\circ}, 81^{\circ}, 78^{\circ} (165^{\circ}, 169^{\circ}, 79^{\circ}, 79^{\circ})$$
 (4)

around the surface atoms capped by the adatom. Much smaller maximal angular deviations of $+12^{\circ}$ and -5° from the ideal tetrahedral value occur about atoms on the second and third layers at the surface, respectively. The rectangular lattices lead to lateral strains and frustrations which are expected to be less severe in the hexagonal 2×2 cell discussed below.

2. Hexagonal 2×2 cell

The use of a hexagonal instead of a rectangular cell is calculated to lead to an energy lowering of 0.2 eV/adatom or equivalently to a change in surface energy of

$$\Delta \gamma = -0.05 \text{ eV}/(1 \times 1 \text{ unit cell}) .$$
 (5)

This can be attributed to a slight decrease of the angular and bond-length strains on this surface. The adatomsurface bond length is stretched by $\simeq 4.4\%$ (as compared to $\simeq 4.9\%$ before) and the angular distributions are

$$\theta = 95^{\circ}$$
 (6)

about the adatom, and

<u>30</u>

$$\theta = 160.4^{\circ}, 81.4^{\circ}$$

(7)

around the surface atoms capped by the adatom. Smaller deviations of $+10^{\circ}$ and -4° from the ideal tetrahedral value are also found in the second and third layers below the surface.

The 0.05-eV drop per 1×1 unit cell in the energy of the 2×2 hexagonal cell relative to the rectangular geometry brings the energy of this structure to within 0.14 eV/atom of the π -bonded-chain structure. The question, therefore, arises as to whether the use of larger unit cells will lead to a further reduction of this energy.

3. Ge(111)-Sn: 2×2 adatom model

The addition of a fraction of a monolayer of Sn to the Ge(111) surface is known²⁷ to result in a metastable 2×2 structure before the formation of stable 5×5 and 7×7 patterns.^{15,27} The larger covalent radius of Sn compared to Ge reduces the angular strains. For the optimum hexagonal 2×2 geometry, the Sn adatoms are calculated to be 1.6 Å above the Ge surface. The optimization of structure leads to a Sn–Ge bond length of 2.73 Å which is 4% larger than the sum of the respective covalent radii. The angular distributions are

$$\theta = 88.6^{\circ} \tag{8}$$

on the adatoms, and

$$\theta = 157.3^{\circ}, 83.2^{\circ}$$
 (9)

on the substrate atoms capped by Sn. As shown in Sec. IV, a reconstruction of the subsurface leads to a lowering of the energy and results in a larger unit cell. This is consistent with the observed²⁷ metastability of the 2×2 reconstructed Ge(111)-Sn structure.

4. 5×5 and 7×7 adatom models

Simple adatom models with 5×5 and 7×7 unit cells, with, respectively, 6 and 12 adatoms per cell, were examined to test whether the greater degrees of freedom for atomic relaxation would lead to a lower surface energy. No restrictions on the atomic displacements were imposed. Each surface atom was moved in the direction of the Hellmann-Feynman forces²⁵ acting on it by an amount proportional to the force. New forces were then calculated and the process was repeated. The most extensive tests were made on 5×5 lattices. The adatoms as well as the first three atomic layers at the surface (i.e., a total of 81 atoms per cell) were allowed to relax. After many iterations, the surface energy of the 5×5 adatom structure was calculated to be $\simeq 0.04 \text{ eV/atom}$ lower than that of the hexagonal 2×2 structure. About 10 iterations were also made for the 7×7 structure. Because of the large size of the unit*cell, only the 12 adatoms and the first surface layer were allowed to relax. From the magnitude of the Hellmann-Feynman forces acting on the atoms, it can be estimated that the structure and surface energy of the 7×7 lattice will be nearly the same as that of the 5×5 lattice. It appears that an increase in unit-cell size will not result in a sufficiently large decrease in the

surface energy of the adatom model to explain the occurrence of such superstructures on annealed surfaces. For the simple adatom model, a 4×4 unit cell should be nearly as likely to occur as a 5×5 , 6×6 , or a 7×7 cell.

III. NEW ADATOM MODEL

A. Rectangular 2×2 cell

The simple adatom model leads to three highly strained 180° angles per adatom in the ideal structure where all bond lengths are equal to the bulk value. As shown in Sec. II, atomic relaxations lead to somewhat reduced angular strains and to values of around 160° for these angles. A reconstruction mechanism that leads to a further reduction in the strain energy resulting in angles of $\simeq 135^{\circ}$ is demonstrated in Fig. 2 for the case of a rectangular 2×2 lattice. The reconstruction involves a rebonding of the "rest" atom (i.e., the surface atom not capped by the adatom) to the substrate in a manner similar to that occurring for the π -bonded-chain model.^{11,12} The reconstruction results in a reversal of the coordinations of the rest atom and a second-layer atom: The rest atoms become fourfold coordinated by becoming, in essence, a secondlayer atom bonded to a third-layer atom, and the secondlayer atom becomes like a threefold-coordinated first-layer atom. The top views of the ideal and reconstructed surface are depicted schematically in Figs. 2(a) and 2(b); the corresponding side views are shown in Figs. 2(c) and 2(d). It can be seen that the reconstruction improves the values of two out of three $\simeq 180^\circ$ angles at the surface. There does not appear to be any simple way of reducing all the strains via reconstruction. The reconstruction shown in Fig. 2(b) improves the bonding of the adatom to the substrate by forcing two of the dangling bonds to become better aligned with the adatom. An optimization of the structure also shows reduced bond-length strains. The adatom substrate bond length is calculated to be $\simeq 3.5\%$ longer than the bulk value (instead of $\simeq 4.9\%$ before the reconstruction). The model has mirror reflection symmetry through a plane passing through the adatom.

The constraints on atomic relaxations inherent in a rectangular 2×2 rectangular lattice are found to limit the energy reduction from rebonding to $\simeq 0.06 \text{ eV/adatom}$. The energy of the new structure is, therefore, still $\simeq 0.14$ eV/adatom higher than that of the simple hexagonal 2×2 adatom structure discussed in Sec. II. One reason for the relatively high energy of the new structure is that the release of the strains at the surface creates additional stress at subsurface layers. The 2×2 lattice does not allow a satisfactory relaxation of these layers that will lead to a significant reduction of the surface energy. The new adatom geometry leads to an enhanced interaction between the dangling bonds on adatoms and rest atoms. For the particular case of the rectangular 2×2 geometry, this does not lead to a lowering of the electronic energy because the term involving this interaction has a zero sum over the two-dimensional Brillouin zone. The predicted higher surface energy of rectangular versus relaxed or reconstructed hexagonal 2×2 cells is consistent with the



FIG. 2. Arrows in (a) show the top view of the directions of surface atomic displacements leading to a reconstruction of the simple 2×2 rectangular adatom model. The resulting structure is shown in (b). The rebonding is similar to that occurring in the π -bonded-chain reconstruction of the Si(111) 2×1 surface. It transforms $\frac{2}{3}$ of the $\simeq 165^{\circ}$ angles to $\simeq 135^{\circ}$. The corresponding side views of the ideal and reconstructed surfaces are shown in (c) and (d).

experimental observation²⁷ of only the latter periodicity for the Ge(111)-Sn 2×2 system.

B. Hexagonal 2×2 , 4×4 , and 6×6 cells

The new reconstructed type of adatom model, surprisingly, rules out hexagonal 2×2 , 4×4 , or even 6×6 unit cells. This results from the requirement that the adatom should always be kept threefold coordinated. As shown in Fig. 3 for the hexagonal 2×2 case, this condition is incompatible with the periodicity of the unit cell. The rebonding of the rest atom (i.e., atom 3 in Fig. 3) to the substrate does not lead to relaxation of any of the $\simeq 180^{\circ}$ angles created by the adatom. To reduce these angles, it is necessary to rebond a type-1 atom to the substrate. This, however, would result in the adatom becoming twofold coordinated, raising the surface energy considerably. It is simply not possible to keep the adatom threefold coordinated and, simultaneously, relax the angular strains in a hexagonal 2×2 lattice. Exactly the same type of problem persists for the larger 4×4 , 6×6 , and possibly other $2n \times 2n$ hexagonal cells. This aspect of the new adatom model is in sharp contrast to the conventional adatom geometry where $2n \times 2n$ periodicities can be easily achieved.

C. Hexagonal 3×3 lattice

The smallest hexagonal $n \times n$ lattice for the reconstructed adatom model is 3×3 in size, as shown in Fig. 4. The directions of surface atomic displacements leading to the reconstruction of the substrate are indicated by arrows in Fig. 4(a) and the resulting structure is shown in Fig. 4(b). The optimized structure is calculated to have a surface energy 0.5 eV/(3×3 unit cell) higher than for the relaxed but unreconstructed adatom geometry. One reason for this is the extremely large bond-length strains ($\simeq 6.4\%$ and 5.7%) at the surface resulting from reconstruction. These are the largest strains for any of the adatom models examined. Another reason for the high surface energy is that reconstruction transforms only $\frac{2}{9}$ of the 160°–180° angles to $\simeq 135^\circ$ as opposed to $\frac{2}{3}$ of such angles in the rectangular 2×2 case. In addition, the reconstructed 3×3 adatom model cannot be made to have the threefold symmetry of the underlying substrate.



FIG. 3. This top-view figure illustrates that a rebonding of atoms, of the type shown in Fig. 2 for the rectangular 2×2 cell, is not possible for the hexagonal 2×2 cell. In order to get a reduction in the angular strain energy, it would be necessary to move atom 1 in the direction shown and make it a second-layer atom while making atom 2 a first-layer atom. This would result in the adatom becoming twofold coordinated, leading to an increase in the surface energy. It can be seen that the rebonding of "rest" atom 3 does not lead to any lowering of the strain energy.

IV. 5×5 AND 7×7 RECONSTRUCTED (111) SURFACES

A. Reconstructed adatom model

The smallest unit cells for which the reconstruction of the adatom model can be made to have threefold rotational symmetry are 5×5 and 7×7 in size. The presence of this symmetry is accompanied by the removal of frustrations encountered in smaller unit cells. The directions of motion of surface-layer atoms (i.e., rest atoms) which bond to the substrate to form the modified adatom model are shown by arrows in Figs. 5(a) and 6(a). The fraction of surface atoms participating in the reconstruction of the adatom model is nearly $\frac{1}{8}$ in both the 5×5 and 7×7 structures. The rebonding of each atom transforms two 160°-180° angles into \simeq 134° angles. The lateral positions of the adatoms on the left triangular region of the 5×5 structure are calculated to be modified by $\simeq 0.05$ Å relative to their ideal values as a result of this rebonding. No such change occurs on the right triangular section.

The requirement that every adatom should be close to a boundary of the unit cell (such that a reconstruction of the underlying surface similar to those for the 5×5 and 7×7 surfaces can occur) rules out adatom models with marginally larger (e.g., 9×9) unit cells. For the 5×5 and 7×7 structures, the short diagonal of the unit cell is equivalent to a boundary line of the cell as a result of threefold rotational symmetry. All the adatoms within these structures are, therefore, adjacent to a boundary. For larger cells, a number of adatoms would be forced to the interior of the unit cell and away from the boundaries.



FIG. 4. Top views of the Si(111) 3×3 surface are shown. The reconstructed 3×3 adatom model has a mirror plane going through the long diagonal but it lacks threefold rotational symmetry. The directions of atomic motions leading to a reconstruction of the substrate is shown in (a) and the resulting structure is shown in (b). Only one $\simeq 165^\circ$ angle is transformed to a $\simeq 135^\circ$ angle for each rebonding, as opposed to twice as many in 5×5 and 7×7 lattices. The atomic designations are the same as in Figs. 1-3.

This would raise the surface energy since comparable reconstruction of the substrate could not occur for these atoms.

The release of strain energy associated with the reconstruction of the substrate is calculated to be large locally. Each rebonding is calculated to release $\simeq 0.7$ eV in energy. This value is obtained by comparing the total energy for the optimized conventional 5×5 adatom model with that obtained for the new 5×5 structure. The latter has a surface energy which is lower than the *reference* rectangular 2×2 lattice (see Sec. II) by

$$\Delta \gamma \simeq -0.14 \text{ eV}/(1 \times 1 \text{ unit cell}) . \tag{10}$$

The simple reconstruction of just the left half of the 5×5 lattice goes a long way towards the $\simeq -0.19$ eV/atom needed to make the adatom model competitive with the chain model for the 2×1 cleaved surface. Because of the depth of the reconstruction, it is not presently feasible to do any meaningful calculations on the new 7×7 structure. It is assumed here that the results of the calculations on the 5×5 surface are applicable for the most part to the 7×7 surface.



FIG. 5. A top view of the ideal 5×5 adatom model is shown in (a). The directions of atomic motions leading to a reconstruction of the substrate are indicated by arrows. The resulting reconstructed structure is shown in (b), and the point of large stress in the right triangular region is indicated by an arrow. The atomic designations are the same as in Figs. 1–3.

The 5×5 and 7×7 structures shown in Figs. 5(b) and 6(b) have a reconstructed adatom geometry on the left half of the cell and a conventional type of adatom structure on the right half. The presence of an adatom at the corner of the unit cell is energetically unfavorable since it leads to a locally $\sqrt{3} \times \sqrt{3}$ structure. Adatom structures with this periodicity have a higher surface energy than those with a 2×2 lattice. From Figs. 5(b) and 6(b) it can be seen that the relation of equivalent sets of adatoms in the 5×5 and 7×7 lattices [e.g., the adatoms in the left half of the unit cells in Figs. 5(b) and 6(b)] with respect to the centers of their respective triangular regions is reversed in the two structures.

Several possibilities for the reconstruction of the right triangular section of the unit cell, as well as for the corner, were considered. Three of the reconstructions for the corner are shown in Fig. 7. The last two reconstructions preserve the threefold symmetry of the unit cell, whereas the first one breaks this symmetry. For the 5×5 lattice, none of these reconstructions is found to lower the energy; in fact, they all result in an increase of the total energy. Other types of atomic rearrangements at the corner cannot be ruled out. A comparison of the calculated structural and electronic properties of the 5×5 structure with the available experimental data is given in the following sections.



FIG. 6. Ideal and reconstructed adatom models for the 7×7 surface are shown in (a) and (b), respectively. The arrows in (a) give the directions of atomic displacements leading to the rebonding. The points of high stress in the left and right triangular regions are indicated by arrows in (b). As discussed in the text, hydrogen chemisorption at these sites would enhance the stability of the structure. The atomic designations are the same as in Figs. 1–3.

B. Vacuum-tunneling microscopy

The presence of two different adatom structures on each triangular half of the cell is consistent with results from vacuum-tunneling measurements^{1,28} on the Si(111)- 7×7 surface. The present calculations on a 5×5 surface show that the adatoms on the two halves of the unit cell differ in their heights relative to a reference (111) plane by $\Delta z \simeq 0.19 \pm 0.03$ Å, with the adatoms on the left half being higher. This is reversed for the conventional adatom model, where the difference is calculated to be -0.03 Å for the 5 \times 5 surface and -0.02 Å for the 7 \times 7 surface. Recent tunneling measurements²⁸ indicate a difference of ≈ 0.3 Å. The sign of the difference is in agreement with that calculated for the new adatom geometry. The atomic rebonding occurring along the boundaries of the unit cell leads to depressions along the edges and the short diagonal of the unit cell which are consistent with those observed in tunneling microscopy.

The maximum difference between the height of an adatom to a second-layer atom at the corner is calculated to be $\approx 1.9\pm 0.3$ Å. The experimental¹ value of the corrugation is $\approx 2.8\pm 0.3$ Å. The rest atoms at the corner would have to relax more deeply towards the bulk for the measured corrugation to be this large. For the particular case of the rectangular 2×2 lattice, the tight-binding method (as compared to the pseudopotential method¹³) may un-



FIG. 7. Three possible modes of atomic displacements at the corner of a 5×5 or a 7×7 unit cell are shown in (a), (b), and (c). The corresponding structures resulting from reconstruction are shown in (d), (e), and (f), respectively. Structures (b) and (c) preserve the threefold symmetry of the unit cell whereas (a) breaks this symmetry but maintains mirror reflection symmetry. All three types of reconstruction are found to result in an increase in energy. The atomic designations are the same as in Figs. 1–3.

derestimate this inward relaxation. Applying the results of the calculations for the 5×5 lattice to the 7×7 structure, the height difference between adatoms on the left (right) and the central atom of the left (right) triangular region is 1.55 ± 0.2 Å (0.94 ± 0.2 Å) as compared to the values of 1.2 ± 0.3 Å (0.7 ± 0.2 Å) from vacuum tunneling.¹ With the possible exception of the corner where further atomic relaxations may occur, the modified adatom provides a satisfactory overall description of the experimental results on the 7×7 surface corrugation.

C. Rutherford backscattering

The proposed 5×5 and 7×7 structures have structural features, arising from reconstruction, resembling those from stacking faults at the surface. On the ideal (111) surface, the projection of the three bonds made by a surface atom with its three nearest-neighbor second-laver atoms onto a (111) plane forms either a Y pattern or an "inverted" Y pattern which is rotated by 180° from it. If stacking fault sequences occur at the surface,⁴ then both patterns are simultaneously present. The modified adatom model demonstrates that such a feature can also arise as a result of reconstruction even in the absence of stacking faults. The rebonding of a surface atom to the substrate causes a reversal of the Y pattern next to it. An examination of the calculated atomic structure and lattice spacings of the modified adatom model shows it to be in good agreement with the structural features deduced by Bennett et al.⁴ from recent Rutherford backscattering experiments.^{5,6} The new adatom model is expected to be consistent with the results of impact-collision ion spectroscopy of Aono *et al.*²⁹ which give evidence for an adatom geometry but, at the same time, rule out the conventional, unreconstructed adatom model.

D. Magnetic ordering

The reconstruction of the simple adatom model greatly enhances the interactions between neighboring dangling bonds by bringing them much closer together. The interaction between the dangling bonds on the 5×5 surface is estimated to make a small $[\simeq 0.05 \text{ eV}/(1 \times 1 \text{ unit cell})]$ but non-negligible contribution to the lowering of the total energy. This is in contrast to the situation for the 2×1 π -bonded chain structure where second-nearest-neighbor interactions make no contribution to the stabilization of the structure because the phase constraint on the wave function resulting from the Bloch condition leads to a $\cos(ka)$ term in the electronic energy with a zero integral over the Brillouin zone. For the proposed 5×5 and 7×7 structures spin-polarization effects similar to those considered previously $^{30-32}$ for smaller lattices are also expected to make a further (≈ 0.04 eV/interacting dangling bond) contribution to the stability of the structure. Possible evidence for a magnetic ordering on the 7×7 surface resulting in a very small gap in the electronic excitation spectrum has been obtained recently from lowtemperature measurements.²³

E. Photoemission

Strong indirect evidence for the adatom reconstruction proposed in this paper is provided by normal photoemission spectra¹⁷⁻¹⁹ on Si(111) 2×1 and 7×7 reconstructed surfaces. These measurements show a surface state at 0.8 eV below the Fermi energy E_F on both surfaces with nearly identical polarization and angular dependence of photoemission intensity at normal emission.^{17,18} Measured relative to the bulk valence-band maximum instead of E_F , the two states lie at -0.7 eV and -0.4 eV for the 2×1 and 7×7 surfaces, respectively.¹⁹ The present calculations of the electronic structure for the 5×5 structure shown in Fig. 5(b) and for the 2×1 reconstructed π bonded-chain model^{11,12} predict a binding-energy difference of 0.24 eV and show the common origin of the two states. The sharply localized and multiply degenerate state at -0.4 eV for the 5×5 surface is calculated to arise primarily from the dangling bonds of the threefoldcoordinated surface atoms that were initially second-layer atoms before the (2×2) -like reconstruction. The lower binding energy of this state relative to the one on the 2×1 surface is a consequence of the absence of nearestneighbor π bonding on the 7×7 surface. The reduced emission intensity for the 7×7 surface is consistent with the smaller density of these type of atoms on this surface. The similarity between the 2×1 and 7×7 surfaces is expected to hold only near normal emission where the phase of the wave function is invariant over all equivalent dangling bonds on the 2×1 surface.

F. LEED

Additional strong evidence in favor of some 2×1 -type reconstruction on the 7×7 surface is provided by LEED. Defining the effective " $\frac{1}{2}$ -order" spectra of the 7×7 surface to be the average of the $\frac{3}{7}$ and $\frac{4}{7}$ fractional-order spectra, Yang and Jona³³ have found remarkable similarities in the $\frac{1}{2}$ spectra of the 2×1 and 7×7 surfaces. They have also shown that the 7×7 surface possesses at least one mirror plane along the doubling direction of the 2×1 surface. These results of LEED are in agreement with the modified adatom model proposed in this paper. The question of whether the 7×7 surface possesses only one mirror plane or three such planes leading to threefold rotational symmetry was also raised by the LEED measurements. Surface reconstruction leading to a reduced symmetry can lead, in principle, to a reduction in the total energy. The present calculations show that the removal of threefold symmetry on the 5×5 surface, by additional 2×1 -like reconstructions at the corner atoms, Figs. 7(a) and 7(b), which still maintain mirror symmetry along the $[2\overline{1}]$ direction, results in an increase in the surface energy. The present calculations indicate that the threefold symmetry of the 7×7 LEED pattern is intrinsic and not the result of an averaging over three single domain patterns.

G. Hydrogen chemisorption

The 5×5 and 7×7 unit cells contain points of high stress at the positions of second-layer atoms marked by

arrows in Figs. 5(b) and 6(b). The stress is caused by the passage of three $\simeq 180^\circ$ angles through these sites. The surface minimizes its energy by exerting a large outward force on these second-layer atoms which moves them up by $\simeq 0.35$ Å, reducing the 180° angles to $\simeq 163^\circ$. The large stress at these points increases the probability of bond rupture upon exposure to hydrogen. The breaking of the second- to third-layer bonds at these points, together with the chemisorption of one hydrogen atom at each of the resulting dangling bonds, should lead to a very large decrease in energy. The recent high-resolution infrared spectroscopy of Chabal et al.²² on Si(111) 7×7 surfaces covered by a few percent of a monolayer of hydrogen has provided evidence for unique chemisorption sites at the surface and the subsurface. For the 7×7 model proposed here [Fig. 6(b)] this would suggest a greater probability for hydrogen chemisorption on the left half of the unit cell (at the position of the arrow) than on the right triangular region.

Evidence for the formation of SiH₂ and SiH₃ complexes in the early stages of hydrogen chemisorption on the Si(111) 7×7 surface has been obtained by Wagner *et al.*³⁴ from electron-energy-loss studies. The most probable atomic sites to form such complexes are the adatoms where the strained adatom-surface bonds are most likely to break upon exposure to atomic hydrogen. Hydrogen chemisorption leads to a lowering of the surface energies of 5×5 and 7×7 adatom structures. Experimentally, it is known³⁵ that hydrogen chemisorption does not remove the seventh-order periodicity of the Si(111) surface.

H. Optical absorption

In the energy range of $\simeq 0.4 - 1.0$ eV, the strength of optical absorption between surface states on the Si(111) 7×7 surface is at least an order of magnitude smaller than on the 2×1 surface. For the latter case, two recent optical studies^{36,37} have provided strong evidence for the π -bonded-chain model.¹¹ For this structure, the magnitude of the optical transition matrix element can be shown to be proportional to the nearest-neighbor π -bonding interaction between dangling bonds. The weakness of the optical-absorption intensity on the 7×7 surface is related to the more distant and much weaker hopping matrix element between dangling bonds. The calculations for the 5×5 structure show narrow empty sp_z -symmetry surface-state bands at 0.13-0.28 eV and at 0.39-0.45 eV at above the valence-band maximum (VBM) which are strongly localized on the adatoms. The highest filled surface states are calculated to be $\simeq 0.4$ eV below the VBM. These states are also sp_z in character and are localized on the fourfold atoms which become threefold coordinated as a result of reconstruction. Transitions between these states are expected to be very weak as a result of the small hybridization between the orbitals. At higher excitation energies (1-3 eV), differential external reflectivity measurements³⁸ show a surface-state transition at 1.76 eV.

I. Nucleation at steps

A study of the phase transition between the Si(111) 7×7 and 1×1 structures at $T_c \simeq 830$ °C via reflection elec-

tron microscopy¹⁴ reveals that the 7×7 structure nucleates preferentially at steps. From the observation that the shapes of the steps change spontaneously and continuously above T_c , it was concluded that the 7×7 reconstruction involved an ordering of either adatoms or vacancies.¹⁴ In the context of the new adatom model for the 7×7 surface, the role of steps in the nucleation process is to force initially a linear ordering of adatoms along the step. If the binding energy of adatoms near the step is larger than that of adatoms on the terrace so that they remain effectively pinned at the step while the other adatoms can move, then a two-dimensional ordering of atoms should eventually result. A greater binding energy near a step is reasonable because of the greater freedom for atomic relaxation at such a site. The 7×7 to 1×1 order-disorder transition³⁹ probably results when all adatoms become mobile. At lower temperatures ($T \le 425$ °C), where surface atomic mobilities are smaller, steps tend to increase the 2×1 to 7×7 transition temperature.⁴⁰

J. Adsorption of closed-shell atoms

Recent studies^{24,41} of Ar, Kr, and Xe adsorption on the Si(111) 7×7 surface have provided useful information on the atomic structure of this surface. The measurements provide evidence for a unique chemisorption site at the surface which is most probably associated with the deep hole at the corner of the unit cell seen in tunneling microscopy. By measuring the amount of adsorbed Kr and Xe as a function of temperature at fixed pressure, Conrad and Webb²⁴ were able to demonstrate inadequacies in nearly all the structural models that have been proposed for this surface. More recently Demuth and Schell-Sorokin⁴¹ have reported ultraviolet photoemission measurements of the coverage-dependent electron binding energies of adsorbed Ar and Xe on Si(111) surfaces. Their results favor the Harrison-Binnig^{1,2} type of adatom model for the 7×7 surface to the exclusion of most other structural models. The three types of adsorption sites inferred from the measurements are indicative, however, of a structure more complex than the simple adatom geometry. This is consistent with vacuum-tunneling results¹ and with the reconstructed adatom model presented in this paper.

V. TRIMER MODEL

In addition to adatom models, Himpsel's trimer model⁸ for the 7×7 reconstruction was examined in detail. The model is similar to the π -bonded-chain model for the Si(111) 2×1 surface except that only one-half as much rebonding of atoms is required to create it. Furthermore, in common with the models proposed by McRae⁹ and Bennett,¹⁰ stacking-fault sequences are explicitly included in the structure. This leads to bonding between second-layer atoms along the boundaries of the unit cell leading to a $\simeq 16\%$ reduction in dangling-bond density from the 1×1 surface. It was suggested⁸ that the reduction in the number of broken bonds together with π bonding would stabilize the trimer model against the 2×1 chain model.

Using a 5×5 lattice, the atomic structure of the trimer model was fully optimized. The calculations show that

the model has a higher surface energy than either the ideal 1×1 surface or the simple adatom model. The surface energy is calculated to be $\simeq 0.3 \text{ eV}/1 \times 1$ unit cell higher than the reconstructed adatom model. The π bonding in the trimer model is found to be not as effective as in the 2×1 chain model. Calculations for an optimized 2×2 trimer model (which replaces the large strains associated with the stacking-fault sequences of the 5×5 structure with other unavoidable strains) give an identical surface energy when corrections for a 16% lower dangling-bond density are made. For 5×5 and 7×7 lattices, the results of the calculations indicate that the bonding between second-layer atoms which is required in stacking-fault models of the surface reconstruction leads to large strains which are energetically unfavorable.

VI. METHOD OF CALCULATION

The use of the empirical tight-binding method in force and energy-minimization calculations is discussed in detail in Ref. 25. In this section, the approach employed in calculating the surface energies for the large unit cells discussed above is examined.

As in previous calculations, a slab geometry infinitely periodic in two dimensions was used. The criterion for choosing the thickness of the slab is that the relaxations or reconstructions on the two ends of the slab should remain independent of each other. To reduce the need for a large number of layers in the present calculations, the dangling bonds on one end of the slab were eliminated by the addition of hydrogen for all the surfaces studied. To account for the effects of hydrogenation on the total energy, an additional calculation in which hydrogen was added to both ends of an ideal slab had to be made. One-half of the total energy of the latter geometry was subtracted from the energy of the structure with hydrogen on only one side of it, to determine the total energy E_{tot} of the remaining N atoms. The surface energy γ was then calculated by dividing the energy

$$\Delta E = E_{\text{tot}}(N) - NE_0 \tag{11}$$

by the area of the surface unit cell. In Eq. (11), E_0 is the binding energy per atom in the crystalline, diamond-structure environment.

The calculations on 5×5 adatom geometries were done with a 131-atom unit cell consisting of six adatoms, four complete (111) layers (100 atoms), and 25 hydrogen atoms. The hydrogen layer and the Si layer adjacent to it were held fixed in nearly all the calculations. The remaining 81 atoms were allowed to relax. The relaxed atomic geometries were determined by moving each atom along the direction of the Hellmann-Feynman force acting on it. The calculation of this force within the tight-binding method is straightforward and has been previously discussed.²⁵ The modified adatom model proposed in this paper leads to a relaxation extending deeper into the bulk than is the case for the simple adatom model. For this reason, it was not possible to test the new adatom model for the 7×7 surface. For the conventional adatom model. however, a calculation of the atomic structure was made. In these calculations, a 159-atom unit cell consisting of 12

adatoms, two full (111) layers (98 atoms), and 49 hydrogen atoms was used.

VII. CONCLUSIONS

A new adatom model differing from the conventional model by a reconstruction of the substrate is proposed. The new adatom structure provides an explanation for the 7×7 and 5×5 size of the unit cells seen on annealed Si(111) and Si(111)-Ge surfaces, respectively. The model is consistent with structural information from vacuumtunneling microscopy. It also provides simple explana-

- ¹G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).
- ²W. A. Harrison, Surf. Sci. 55, 1 (1976).
- ³J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2298 (1963); J. J. Lander, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1965), Vol. II, p. 26.
- ⁴P. A. Bennett, L. C. Feldman, Y. Kuk, E. G. McRae, and J. E. Rowe, Phys. Rev. B 28, 3656 (1983).
- ⁵R. J. Culbertson, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. 45, 2043 (1980).
- ⁶R. M. Tromp, E. J. van Loenen, M. Iwami, and F. W. Saris, Solid State Commun. **44**, 971 (1982).
- ⁷P. M. Petroff and R. J. Wilson, Phys. Rev. Lett. 51, 199 (1983).
- ⁸F. J. Himpsel, Phys. Rev. B 27, 7782 (1983).
- ⁹E. G. McRae, Phys. Rev. B 28, 2305 (1983).
- ¹⁰P. A. Bennett (unpublished). This model involves adatoms, stacking-fault sequences, and dimers at the surface.
- ¹¹K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981); 49, 223 (1982).
- ¹²J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. 49, 1349 (1982); J. Vac. Sci. Technol. 21, 333 (1982).
- ¹³J. E. Northrup and M. L. Cohen, Phys. Rev. B 29, 1966 (1984).
- ¹⁴N. Osakabe, Y. Tanishiro, K. Yagi, and G. Honjo, Surf. Sci.
 109, 353 (1981); N. Osakabe, K. Yagi, and G. Honjo, Jpn. J.
 Appl. Phys. 19, L309 (1980).
- ¹⁵T. Ichikawa and S. Ino, Solid State Commun. 27, 483 (1978).
- ¹⁶H. J. Gossmann, J. C. Bean, L. C. Feldman, and W. M. Gibson, Surf. Sci. 138, L175 (1984).
- ¹⁷D. J. Chadi, R. S. Bauer, R. H. Williams, G. V. Hansson, R. Z. Bachrach, J. C. Mikkelsen, F. Houzay, G. M. Guichar, R. Pinchaux, and Y. Petroff, Phys. Rev. Lett. 44, 799 (1980).
- ¹⁸F. Houzay, G. M. Guichar, R. Pinchaux, and Y. Petroff, J. Vac. Sci. Technol. 18, 860 (1981).
- ¹⁹F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B 24, 2003 (1981); F. J. Himpsel, D. E. Eastman, P. Heimann, and B. Reihl, Phys. Rev. B 24, 1120 (1981).
- ²⁰G. Chiarotti, P. Chiaradia, and S. Nannarone, Surf. Sci. 49, 315 (1975).

tions for stacking-fault-type features expected from Rutherford backscattering experiments and for similarities in the LEED and photoemission spectra of 2×1 and 7×7 surfaces.

ACKNOWLEDGMENTS

I am grateful to Dr. John Northrup for many stimulating discussions. This work is supported in part by the U. S. Office of Naval Research through Contract No. N00014-82-C-0244.

- ²¹G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B **4**, 3398 (1971).
- ²²Y. J. Chabal, G. S. Higashi, and S. B. Christman, Phys. Rev. B 28, 4472 (1983); Y. J. Chabal, Phys. Rev. Lett. 50, 1850 (1983).
- ²³J. E. Demuth, B. N. J. Persson, and A. J. Schell-Sorokin, Phys. Rev. Lett. **51**, 2214 (1983).
- ²⁴E. Conrad and M. B. Webb, Surf. Sci. 129, 37 (1983).
- ²⁵D. J. Chadi, Phys. Rev. B 29, 785 (1984).
- ²⁶J. C. Phillips, Phys. Rev. Lett. **45**, 905 (1980).
- ²⁷S. B. DiCenzo, P. A. Bennett, D. Tribula, P. Thiry, G. K. Wertheim, and J. E. Rowe (unpublished).
- ²⁸G. Binnig and H. Rohrer, J. Vac. Sci. Technol. (to be published).
- ²⁹M. Aono, R. Souda, C. Oshima, and Y. Ishizawa, Phys. Rev. Lett. **51**, 801 (1983).
- ³⁰R. Del Sole and D. J. Chadi, Phys. Rev. B 24, 7431 (1981); D. J. Chadi and R. Del Sole, J. Vac. Sci. Technol. 21, 319 (1982).
- ³¹J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. **47**, 1910 (1981).
- ³²M. Lannoo and G. Allan, Surf. Sci. 115, L137 (1982); G. Allan and M. Lannoo, *ibid.* 63, 11 (1977).
- ³³W. S. Yang and F. Jona, Solid State Commun. 48, 377 (1983).
- ³⁴H. Wagner, R. Butz, U. Backes, and D. Bruchmann, Solid State Commun. 38, 1155 (1981).
- ³⁵T. Sakurai and H. D. Hagstrum, Phys. Rev. B 12 5349 (1975).
- ³⁶P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. 52, 1145 (1984).
- ³⁷M. A. Olmstead and N. M. Amer, Phys. Rev. Lett. **52**, 1148 (1984).
- ³⁸P. E. Wierenga, A. Van Silfhout, and M. J. Sparnaay, Surf. Sci. 87, 43 (1979).
- ³⁹M. B. Webb and P. A. Bennett, Surf. Sci. 31, 104 (1981); J. Vac. Sci. Technol. 18, 847 (1981).
- ⁴⁰P. P. Auer and W. Monch, Jpn. J. Appl. Phys. Suppl. 2, Pt. 2, p. 397 (1974).
- ⁴¹J. E. Demuth and A. J. Schell-Sorokin, J. Vac. Sci. Technol. A 2, 808 (1984).