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NEW ADATOM MODEL FOR Si(111) 7X7 AND  
Si(111)Ge 5X5 RECONSTRUCTED SURFACES

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D.J. Chadi

Palo Alto Research Center  
Xerox Corp.  
Palo Alto, California 94304

A new adatom structure with significantly less angular strain than the simple adatom geometry is proposed. The model involves a rebonding of  $\approx 1/8$  of surface atoms to the substrate in a manner similar to that occurring in the  $\pi$ -bonded-chain structure for the Si(111) 2X1 surface. The interference between adatom and substrate reconstructions forces the smallest threefold-symmetric unit cells to be 5X5 and 7X7 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 7X7 unit cell seen in vacuum-tunneling microscopy and the apparent need for stacking fault sequences in channeling experiments are accounted for. The results of surface energy and structure calculations on 2X2, 3X3, 5X5, and 7X7 adatom models are presented.

## I. INTRODUCTION

The first real space imaging of the 7X7 reconstructed Si(111) surface by Binnig *et al.*<sup>1</sup> has generated new interest in the precise nature of the atomic bonding at this surface. Vacuum-tunneling microscopy<sup>1</sup> 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 model<sup>2</sup> and the vacancies of the Lander model.<sup>3</sup> Binnig *et al.*<sup>1</sup> 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 yields valuable information on the surface corrugation.

Despite the fact that the adatom model gives the best agreement of any simple structure with the vacuum-tunneling results, it has not received universal acceptance as the correct structure for the 7X7 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 analysis<sup>4</sup> of Rutherford backscattering experiments<sup>5,6</sup> 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 low-energy electron diffraction (LEED) data,<sup>4</sup> and from transmission electron microscopy.<sup>7</sup>

Several models<sup>8-10</sup> which incorporate stacking fault sequences in the unit cell and have structural features consistent with the observations of Binnig et al.<sup>1</sup> have been proposed recently and will be examined in this paper.

The acceptance of the adatom model for the 7X7 surface appears difficult also from theoretical considerations. The surface energy of the thermodynamically stable 7X7 surface should be lower than that of the metastable cleaved 2X1 surface. In particular, the 7X7 surface should have a lower surface energy than the  $\pi$ -bonded-chain structure.<sup>11,12</sup> In going from a chain to an adatom structure, the favorable energy lowering from  $\pi$  bonding is presumably lost and, in addition, a significantly larger lattice strain is introduced. The recent calculations of Northrup and Cohen<sup>13</sup> for a 2X2 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 2X2 adatom model is found to be 0.12 eV (per 1X1 unit area) higher in energy than the  $\pi$ -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.<sup>13</sup>

In addition to constraints from vacuum tunneling microscopy,<sup>1</sup> ion-channeling<sup>4</sup> 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 7X7 structure at steps;<sup>14</sup> the appearance of stable 5X5 and 7X7 periodicities<sup>15</sup> for Sn on Ge(111) and<sup>16</sup> for Ge on Si(111) surfaces; the similarities and differences in the photoemission<sup>17-19</sup> and optical-absorption<sup>20,21</sup> spectra of 2X1 and 7X7 surfaces; evidence for unique surface and subsurface hydrogen chemisorption sites on the 7X7 surface;<sup>22</sup> the possibility of magnetic ordering at low temperatures;<sup>23</sup> and a unique physisorption site geometry<sup>24</sup> for Xe and Kr.

In this paper the structural and energetic aspects of the 7X7 and 5X5 reconstructions are examined via total-energy calculations on a variety of models and on unit cells ranging from 2X2 to 7X7 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 5X5.

The paper is organized as follows. The results of energy-minimization calculations for the conventional type of adatom model are discussed in Sec. II. For the particular case of a 2X2 rectangular lattice, the results are compared with those from ab initio self-consistent pseudopotential calculations of Northrup and Cohen.<sup>13</sup> 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 2X2 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 2X2, 4X4, and 6X6 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 5X5 and 7X7. A 3X3 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 5X5 adatom geometry and a discussion of experimental results on the 5X5 and 7X7 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.<sup>1</sup> It provides an explanation for the inhomogeneous corrugation of the surface by having different relaxations and reconstructions in the two halves of the unit cell.

(ii) Structural elements resembling those arising from stacking faults at the surface.<sup>4</sup> These come about directly as a consequence of the re-bonding 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  $\pi$ -bonded-chain model<sup>11,12</sup> for the 2X1 surface.

(iv) An explanation for the striking similarity in polarization and angular dependence of normal photoemission spectra for the surface states at  $\approx 0.8$  eV below the Fermi energy  $E_F$  in both the 2X1 and 7X7 surfaces.<sup>17,18</sup> Measured relative to the valence-band maximum<sup>19</sup> instead of  $E_F$ , this state is  $\approx 0.3$  eV more bound in the 2X1 surface than in the 7X7 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 5X5 and 7X5 structures.

The results of calculations for Himpsel's trimer model<sup>8</sup> are discussed in Sec. V. The tight-binding-based method of calculation<sup>25</sup> is reviewed briefly in Sec. VI.

## II. SIMPLE ADATOM MODELS

### A. Angular strains

Two adatom models with rectangular and hexagonal 2X2 unit cells are shown in Fig. 1. In the "1" configuration where all bond lengths are equal to

those in the bulk, the adatom is one interlayer spacing ( $\approx 0.78 \text{ \AA}$  in Si) above the substrate. The large angular strains in this simple adatom configuration can be appreciated by considering the distributions of angles  $\theta$  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

$$\theta = 180^\circ \text{ and } \theta_2 = \theta_3 = 70.53^\circ \quad (1)$$

which deviate sharply from the ideal tetrahedral angle of  $109.47^\circ$ .

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 strains develop.

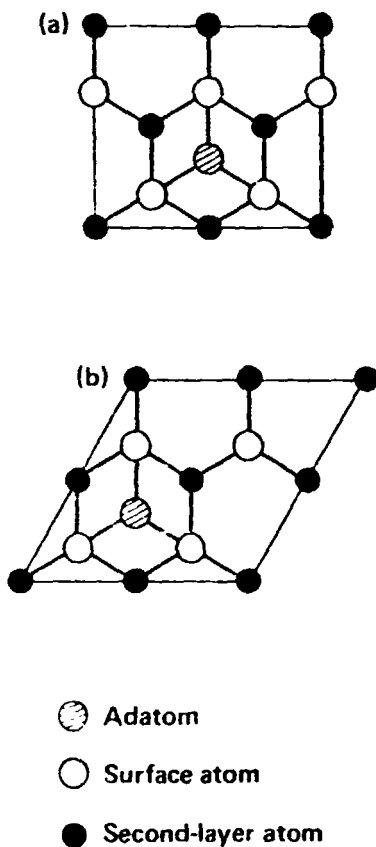


Fig. 1. Top views of simple adatom models with rectangular and hexagonal  $2 \times 2$  periodicities are shown in (a) and (b). In the unrelaxed geometry, the adatom falls at the intersection of the three straight lines joining surface atoms to second-layer atoms. The resulting  $180^\circ$  angles go to  $160^\circ$ - $165^\circ$  after relaxation.

The surface energy of the top-site geometry is sufficiently higher than the hollow-site configuration<sup>13</sup> that it will not be considered in this paper. The top-site geometry is also inconsistent with the results of vacuum-tunneling microscopy.<sup>1</sup>

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 2X2 to 7X7 in size show that the angles in Eq. (1) relax at best to values of  $160^\circ$  and  $81^\circ$ , respectively. The angular relaxation is achieved at the cost of increasing the adatom-substrate bond length by  $\approx 4.5\%$  over the bulk bond length. For a 2X2 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  $\theta_1$  from  $180^\circ$ . 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.<sup>26</sup>

#### B. Surface energy of the rectangular 2X2 adatom model from tight-binding and pseudopotential calculations

Northrup and Cohen<sup>13</sup> have recently calculated the total-energy and atomic structure of a rectangular 2X2 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/(1X1 unit cell) relative to the unrelaxed ideal 2X2 surface and higher by 0.19 eV/(1X2 unit cell) as compared to Pandey's  $\pi$ -bonded chain geometry.<sup>11,12</sup> The removal of the lateral strains and frustrations inherent in the rectangular 2X2 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/(1X1 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,<sup>13</sup> the energy of the optimized rectangular adatom model is calculated to be 0.03 eV/(1X1 cell) higher than that of the unrelaxed ideal surface instead of 0.17 eV/(1X1 cell) lower. Despite this problem of the tight-binding 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  $\gamma$  as

$$\gamma = \text{surface energy (in eV/1X1 unit cell)} \quad (2)$$

and taking the rectangular 2X2 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 calculation,<sup>13</sup> a decrease in  $\gamma$  of greater than 0.19 eV/(1X1 cell) should make the adatom geometry more favorable than the  $\pi$ -bonded-chain model.

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

#### 1. Rectangular 2X2 cell

The adatom and three substrate layers were allowed to relax. The optimum atomic geometry was calculated from a minimization of Hellmann-Feynman forces.<sup>25</sup> 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.<sup>13</sup> The present tight-binding calculations give a bond-length stretching of 4.9% at the surface as compared to 3.4% obtained previously.<sup>13</sup> Some angular distributions, with the pseudopotential values given in parentheses, are

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

about the adatom, and

$$\theta = 163^\circ, 165^\circ, 81^\circ, 78^\circ (155^\circ, 169^\circ, 79^\circ, 79^\circ) \quad (4)$$

around the surface atoms capped by the adatom. Much smaller maximal angular deviations of  $+12^\circ$  and  $-5^\circ$  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 2X2 cell discussed below.

#### 2. Hexagonal 2X2 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

$$\Delta\gamma = -0.05 \text{ eV}/(1X1 \text{ unit cell}). \quad (5)$$

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

$$\theta = 95^\circ \quad (6)$$

about the adatom, and

$$\theta = 160.4^\circ, 81.4^\circ \quad (7)$$

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

The 0.05-eV drop per 1X1 unit cell in the energy of the 2X2 hexagonal cell relative to the rectangular geometry brings the energy of this structure to within 0.14 eV/atom of the  $\pi$ -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: 2X2 adatom model

The addition of a fraction of a monolayer of Sn to the Ge(111) surface is known<sup>27</sup> to result in a metastable 2X2 structure before the formation of stable 5X5 and 7X7 patterns.<sup>15,27</sup> The larger covalent radius of Sn compared to Ge reduces the angular strains. For the optimum hexagonal 2X2 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

$$\theta = 88.6^\circ \quad (8)$$

on the adatoms, and

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

on the substrate atoms capped by Sn. As shown in Sec. IV, a reconstruction of the surface leads to a lowering of the energy and results in a larger unit cell. This is consistent with the observed<sup>27</sup> metastability of the 2X2 reconstructed Ge(111)-Sn structure.

### 4. 5X5 and 7X7 adatom models

Simple adatom models with 5X5 and 7X7 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 forces<sup>25</sup> 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 5X5 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 5X5 adatom structure was calculated to be  $\approx 0.04$  eV/atom lower than that of the hexagonal 2X2 structure. About 10 iterations were also made for the 7X7 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 7X7 lattice will be nearly the same as that of the 5X5 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 4X4 unit cell should be nearly as likely to occur as a 5X5, 6X6, or a 7X7 cell.

### III. NEW ADATOM MODEL

#### A. Rectangular 2X2 cell

The simple adatom model leads to three highly strained  $180^\circ$  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  $160^\circ$  for these angles. A reconstruction mechanism that leads to a further reduction in the strain energy resulting in angles of  $\approx 135^\circ$  is demonstrated in Fig. 2 for the case of a rectangular 2X2 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  $\pi$ -bonded chain model.<sup>11,12</sup> 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 second-layer atom bonded to a third-layer atom, and the second-layer atoms 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  $\approx 180^\circ$  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  $\approx 3.5\%$  longer than the bulk value (instead of  $\approx 4.9\%$  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 2X2 rectangular lattice are found to limit the energy reduction from rebonding to  $\approx 0.06$  eV/adatom. The energy of the new structure is, therefore, still  $\approx 0.14$  eV/adatom higher than that of the simple hexagonal 2X2 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 2X2 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 2X2 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 2X2 cells is consistent with the experimental observation<sup>27</sup> of only the latter periodicity for the Ge(111)-Sn 2X2 system.

#### B. Hexagonal 2X2, 4X4, and 6X6 cells

The new reconstructed type of adatom model, surprisingly, rules out hexagonal 2X2, 4X4, or even 6X6 unit cells. This results from the requirement that the adatom should always be kept threefold coordinated. As shown in Fig. 3 for the hexagonal 2X2 case, this condition is incompatible with the



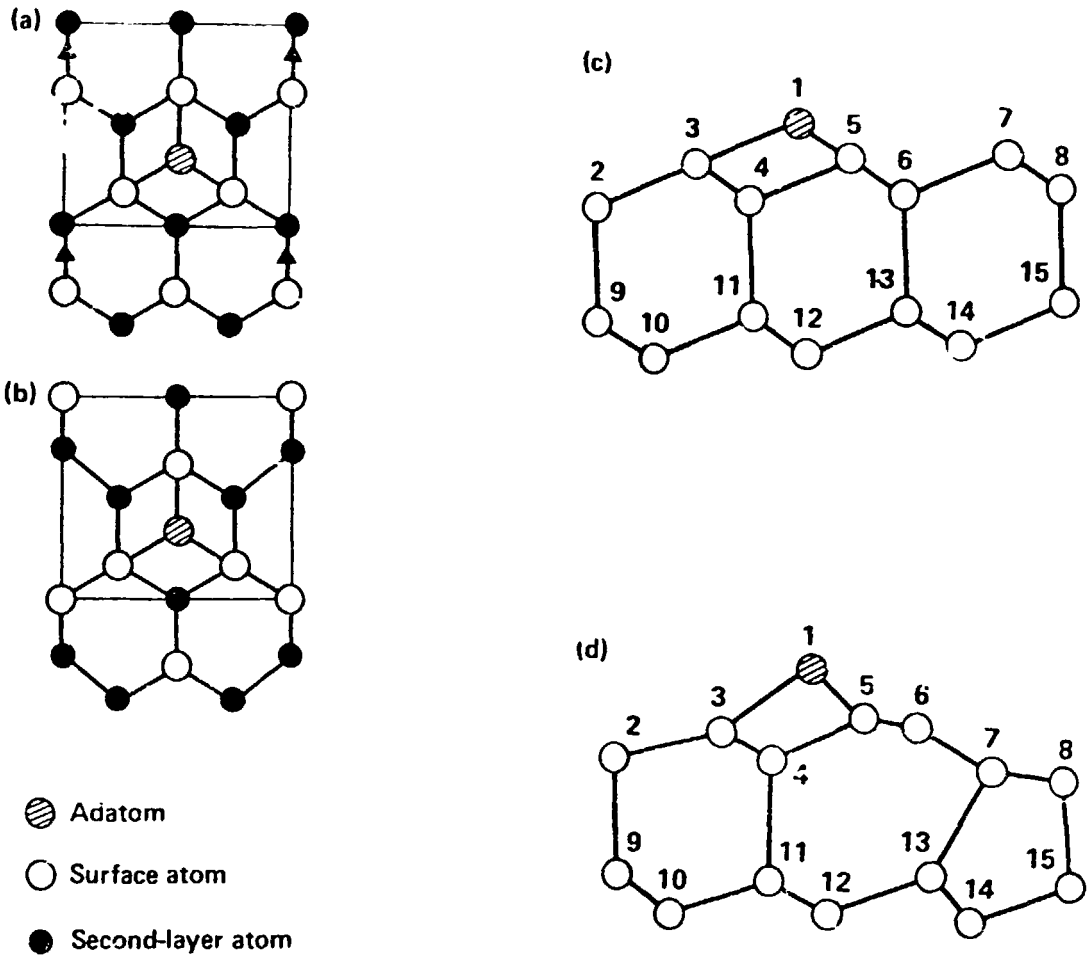


FIG. 2. Arrows in (a) show the top view of the directions of surface atomic displacements leading to a reconstruction of the simple 2X2 rectangular adatom model. The resulting structure is shown in (b). The rebonding is similar to that occurring in the  $\pi$ -bonded-chain reconstruction of the Si(111) 2X1 surface. It transforms  $2/3$  of the  $\approx 165^\circ$  angles to  $\approx 135^\circ$ . The corresponding side views of the ideal and reconstructed surfaces are shown in (c) and (d).

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  $\approx 180^\circ$  angles created by the adatom. To reduce these angles, it is necessary to rebond 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 2X2 lattice. Exactly the same type of problem persists for the larger 4X4, 6X6, 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.

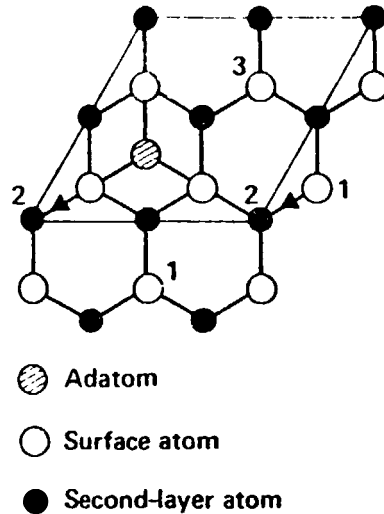


FIG. 3. This top-view figure illustrates that a rebonding of atoms, of the type shown in Fig. 2 for the rectangular 2X2 cell, is not possible for the hexagonal 2X2 cell. In order to get a reduction in the angular strain energy, it would be necessary to move atom 1 in the direction shown and make it a 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.

### C. Hexagonal 3X3 lattice

The smallest hexagonal  $n \times n$  lattice for the reconstructed adatom model is 3X3 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/(3X3 unit cell) higher than for the relaxed but unreconstructed adatom geometry. One reason for this is the extremely large bond-length strains ( $\approx 6.4\%$  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 reconstructions transform only 2/9 of the  $160^\circ$ - $180^\circ$  angles to  $\approx 135^\circ$  as opposed to 2/3 of such angles in the rectangular 2X2 case. In addition, the reconstructed 3X3 adatom model cannot be made to have the threefold symmetry of the underlying substrate.

## IV. 5X5 AND 7X7 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 5X5 and 7X7 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

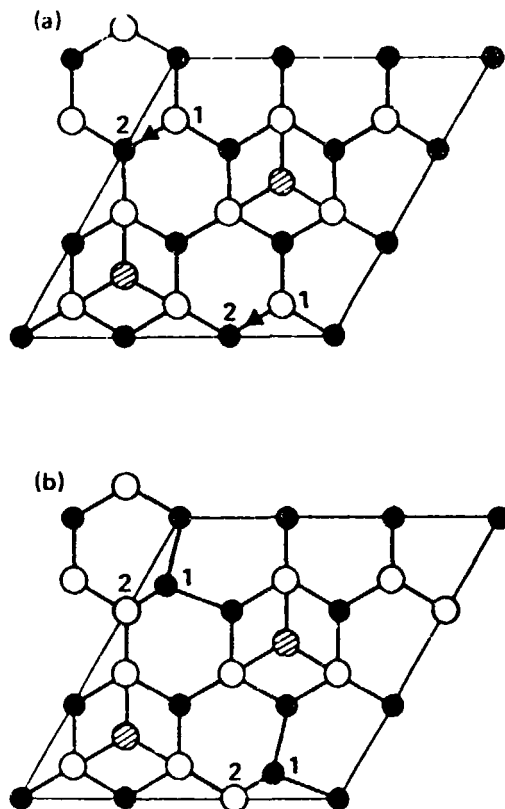


FIG. 4. Top views of the Si(111) 3X3 surface are shown. The reconstructed 3X3 adatom model has a mirror plane going through the long diagonal but it lacks threefold rotational symmetry. The directions of atomic motions leading to a reconstruction of the substrate is shown in (a) and the resulting structure is shown in (b). Only one  $\approx 165^\circ$  angle is transformed to a  $\approx 135^\circ$  angle for each rebonding, as opposed to twice as many in 5X5 and 7X7 lattices. The atomic designations are the same as in Figs. 1-3.

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 1/8 in both the 5X5 and 7X7 structures. The rebonding of each atom transforms two  $160^\circ$ - $180^\circ$  angles into  $\approx 134^\circ$  angles. The lateral positions of the adatoms on the left triangular region of the 5X5 structure are calculated to be modified by  $\approx 0.05 \text{ \AA}$  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 5X5 and 7X7 surfaces can occur) rules out adatom models with marginally larger (e.g., 9X9) unit cells. For the 5X5 and 7X7 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. 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  $\approx 0.7$  eV in energy. This value is obtained by comparing the total energy for the optimized conventional  $5 \times 5$  adatom model with that obtained for the new  $5 \times 5$  structure. The latter has a surface energy which is lower than the reference rectangular  $2 \times 2$  lattice (see Sec. II) by

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

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

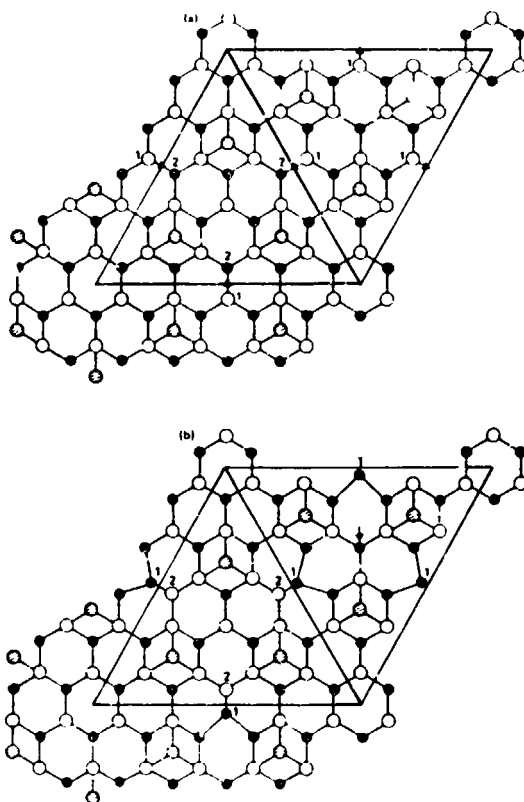


FIG. 5. A top view of the ideal  $5 \times 5$  adatom model is shown in (a). The directions of atomic motions leading to a reconstruction of the substrate are indicated by arrows. The resulting reconstructed structure is shown in (b), and the point of large stress in the right triangular region is indicated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

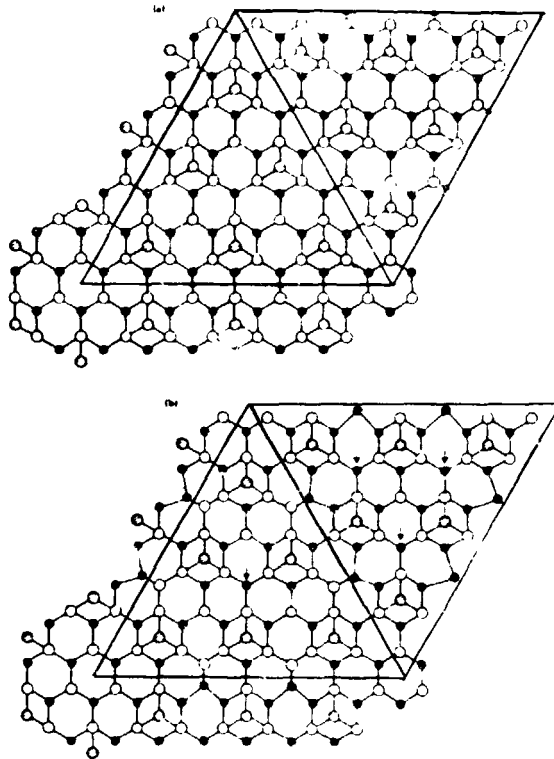


FIG. 6. Ideal and reconstructed adatom models for the 7X7 surface are shown in (a) and (b), respectively. The arrows in (a) give the directions of atomic displacements leading to the rebonding. The points of high stress in the left and right triangular regions are indicated by arrows in (b). As discussed 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.

The 5X5 and 7X7 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  $\sqrt{3X\sqrt{3}}$  structure. Adatom structures with this periodicity have a higher surface energy than those with a 2X2 lattice. From Figs. 5(b) and 6(b) it can be seen that the relation of equivalent sets of adatoms in the 5X5 and 7X7 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 cell 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 5X5 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 5X5 structure with the available experimental data is given in the following sections.

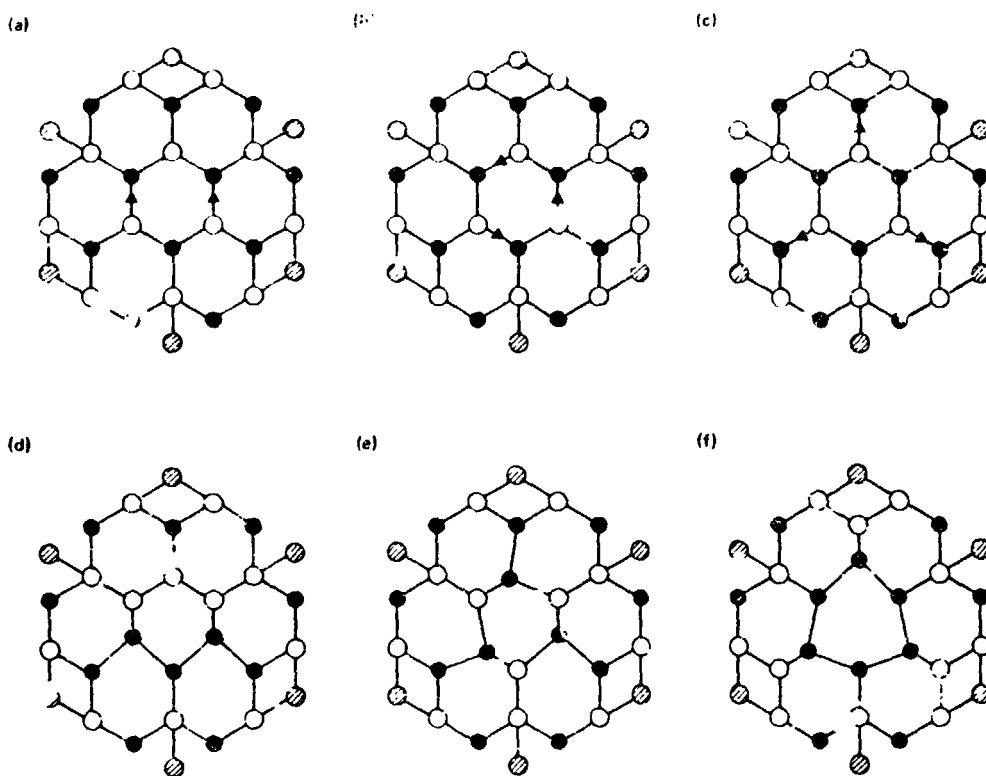


FIG. 7. Three possible modes of atomic displacements at the corner of a 5X5 or 7X7 unit cell are shown in (a), (b), and (c). The corresponding structures resulting from reconstruction are shown in (d), (e), and (f), respectively. Structures (b) and (c) preserve the threefold symmetry of the unit cell 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.

### 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<sup>1,28</sup> on the Si(111)-7X7 surface. The present calculations on a 5X5 surface show that the adatoms on the two halves of the unit cell differ in their heights relative to a reference (111) plane by  $\Delta z \approx 0.19 \pm 0.03 \text{ \AA}$ , with the adatoms on the left half being higher. This is reversed for the conventional adatom mode<sup>1</sup> where the difference is calculated to be  $-0.05 \text{ \AA}$  for the 5X5 surface and  $-0.02 \text{ \AA}$  for the 7X7 surface. Recent tunneling measurements<sup>28</sup> indicate a difference of  $\approx 0.3 \text{ \AA}$ . 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  $\approx 1.9 \pm 0.3 \text{ \AA}$ . The experimental<sup>1</sup> value of the corrugation is  $\approx 2.8 \pm 0.3 \text{ \AA}$ . 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 2X2 lattice, the tight-binding method (as compared to the pseudopotential method<sup>13</sup>) may underestimate this inward relaxation. Applying the results of the calculations for the 5X5 lattice to the 7X7 structure, the height difference between adatoms on the left (right) and the central atom of the left (right) triangular region is  $1.55 \pm 0.2 \text{ \AA}$  ( $0.94 \pm 0.2 \text{ \AA}$ ) as compared to the values of  $1.2 \pm 0.3 \text{ \AA}$  ( $0.7 \pm 0.2 \text{ \AA}$ ) from vacuum tunneling.<sup>1</sup> 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 7X7 surface corrugation.

### C. Rutherford backscattering

The proposed 5X5 and 7X7 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-layer atoms onto a (111) plane forms either a Y pattern or an "inverted" Y pattern which is rotated by  $180^\circ$  from it. If stacking fault sequences occur at the surface,<sup>4</sup> 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.<sup>4</sup> from recent Rutherford backscattering experiments.<sup>5,6</sup> The new adatom model is expected to be consistent with the results of impact-collision ion spectroscopy of Aono et al.<sup>29</sup> 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 5X5 surface is estimated to make a small [ $\approx 0.5 \text{ eV}/(1X1 \text{ unit cell})$ ] but non-negligible contribution to the lowering of the total energy. This is in contrast to the situation for the 2X1  $\pi$ -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  $\cos(\underline{k}\underline{a})$  term in the electronic energy with a zero integral over the Brillouin zone. For the proposed 5X5 and 7X7 structures spin-polarization effects similar to those considered previously<sup>30-32</sup> for

C. - }

smaller lattices are also expected to make a further ( $\approx 0.04$  eV/interacting dangling bond) contribution to the stability of the structure. Possible evidence for a magnetic ordering on the  $7\times 7$  surface resulting in a very small gap in the electronic excitation spectrum has been obtained recently from low-temperature measurements.<sup>23</sup>

### E. Photoemission

Strong indirect evidence for the adatom reconstruction proposed in this paper is provided by normal photoemission spectra<sup>17-19</sup> on Si(111)  $2\times 1$  and  $7\times 7$  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.<sup>17,18</sup> 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  $2\times 1$  and  $7\times 7$  surfaces, respectively.<sup>19</sup> The present calculations of the electronic structure for the  $5\times 5$  structure shown in Fig. 5(b) and for the  $2\times 1$  reconstructed  $\pi$ -bonded-chain model<sup>11,12</sup> 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  $5\times 5$  surface is calculated to arise primarily from the dangling bonds of the threefold-coordinated surface atoms that were initially second-layer atoms before the ( $2\times 2$ )-like reconstruction. The lower binding energy of this state relative to the one on the  $2\times 1$  surface is a consequence of the absence of nearest-neighbor  $\pi$  bonding on the  $7\times 7$  surface. The reduced emission intensity for the  $7\times 7$  surface is consistent with the smaller density of these type of atoms on this surface. The similarity between the  $2\times 1$  and  $7\times 7$  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  $2\times 1$  surface.

### F LEED

Additional strong evidence in favor of some  $2\times 1$ -type reconstruction on the  $7\times 7$  surface is provided by LEED. Defining the effective "1/2-order" spectra of the  $7\times 7$  surface to be the average of the  $3/7$  and  $4/7$  fractional-order spectra, Yang and Jona<sup>33</sup> have found remarkable similarities in the  $1/2$  spectra of the  $2\times 1$  and  $7\times 7$  surfaces. They have also shown that the  $7\times 7$  surface possesses at least one mirror plane along the doubling direction of the  $2\times 1$  surface. These results of LEED are in agreement with the modified adatom model proposed in this paper. The question of whether the  $7\times 7$  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  $5\times 5$  surface, by additional  $2\times 1$ -like reconstructions at the corner atoms, Figs. 7(a) and 7(b), which still maintain mirror symmetry along the  $[2\bar{1}1]$  direction, results in an increase in the surface energy. The present calculations indicate that the threefold symmetry of the  $7\times 7$  LEED Pattern is intrinsic and not the result of an averaging over three single domain patterns.



### G. Hydrogen chemisorption

The 5X5 and 7X7 unit cell 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  $\approx 180^\circ$  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  $\approx 0.35 \text{ \AA}$ , reducing the  $180^\circ$  angles to  $\approx 163^\circ$ . 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.*<sup>22</sup> on Si(111) 7X7 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 7X7 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  $\text{SiH}_2$  and  $\text{SiH}_3$  complexes in the early stages of hydrogen chemisorption on the Si(111) 7X7 surface has been obtained by Wagner *et al.*<sup>34</sup> 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 5X5 and 7X7 adatom structures. Experimentally, it is known<sup>35</sup> that hydrogen chemisorption does not remove the seventh-order periodicity of the Si(111) surface.

### H. Optical absorption

In the energy range of  $\approx 0.4$ – $1.0 \text{ eV}$ , the strength of optical absorption between surface states on the Si(111) 7X7 surface is at least an order of magnitude smaller than on the 2X1 surface. For the latter case, two recent optical studies<sup>36,37</sup> have provided strong evidence for the  $\pi$ -bonded-chain model.<sup>11</sup> For this structure, the magnitude of the optical transition matrix element can be shown to be proportional to the nearest-neighbor  $\pi$ -bonding interaction between dangling bonds. The weakness of the optical-absorption intensity on the 7X7 surface is related to the more distant and much weaker hopping matrix element between dangling bonds. The calculations for the 5X5 structure show narrow empty  $sp_z$ -symmetry surface-state bands at  $0.13$ – $0.28 \text{ eV}$  and at  $0.39$ – $0.45 \text{ eV}$  at above the valence-band maximum (VBM) which are strongly localized on the adatoms. The highest filled surface states are calculated to be  $\approx 0.4 \text{ eV}$  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 ( $1$ – $3 \text{ eV}$ ), differential external reflectivity measurements<sup>38</sup> show a surface-state transition at  $1.76 \text{ eV}$ .

### I. Nucleation at steps

A study of the phase transition between the Si(111) 7X7 and 1X1

structures at  $T_c \approx 830^\circ\text{C}$  via reflection electron microscopy<sup>14</sup> reveals that the 7X7 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 7X7 reconstruction involved an ordering of either adatoms or vacancies.<sup>14</sup> In the context of the new adatom model for the 7X7 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 7X7 to 1X1 order-disorder transition<sup>39</sup> probably results when all adatoms become mobile. At lower temperatures ( $T < 425^\circ\text{C}$ ), where surface atomic mobilities are smaller, steps tend to increase the 2X1 to 7X7 transition temperature.<sup>40</sup>

#### J. Adsorption of closed-shell atoms

Recent studies<sup>24,41</sup> of Ar, Kr, and Xe adsorption on the Si(111) 7X7 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 Webb<sup>24</sup> were able to demonstrate inadequacies in nearly all the structural models that have been proposed for this surface. More recently Demuth and Schell-Sorokin<sup>41</sup> 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<sup>1,2</sup> type of adatom model for the 7X7 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 results<sup>1</sup> and with the reconstructed adatom model presented in this paper.

#### V. TRIMER MODEL

In addition to adatom models, Himpfel's trimer model<sup>8</sup> for the 7X7 reconstruction was examined in detail. The model is similar to the  $\pi$ -bonded-chain model for the Si(111) 2X1 surface except that only one-half as much rebonding of atoms is required to create it. Furthermore, in common with the models proposed by McRae<sup>9</sup> and Bennett,<sup>10</sup> 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  $\approx 16\%$  reduction in dangling-bond density from the 1X1 surface. It was suggested<sup>8</sup> that the reduction in the number of broken bonds together with  $\pi$  bonding would stabilize the trimer model against the 2X1 chain model.

Using a 5X5 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 1X1 surface or the simple adatom model. The surface energy is calculated to be  $\approx 0.3$  eV/1X1 unit cell higher than the reconstructed adatom model. The  $\pi$  bonding in the trimer model is found to

be not as effective as in the 2X1 chain model. Calculations for an optimized 2X2 trimer model (which replaces the large strains associated with the stacking-fault sequences of the 5X5 structure with other unavoidable strains) give an identical surface energy when corrections for a 16% lower dangling-bond density are made. For 5X5 and 7X7 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  $\gamma$  was then calculated by dividing the energy

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

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 5X5 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.<sup>25</sup> 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 7X7 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 7X7 and 5X5 size of the unit cells seen on annealed Si(111) and Si(111)-Ge surfaces, respectively. The model is consistent with structural information from vacuum-tunneling microscopy. It also provides simple explanations for stacking-fault-type features expected from Rutherford backscattering experiments and for similarities in the LEED and photoemission spectra of 2X1 and 7X7 surfaces.

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## DISCUSSION

**RAO:** I believe you said as part of your talk that these bonds have residual ionic charges. What is the effect of ionic charges? Can you get compensation in these charges by other atoms moving in? What is the physical manifestation of this?

**KAZMERSKI:** The physical manifestation is an increase in the work function at the surface. You can actually predict that there should be about 0.5 eV increase in the work function. Measured, the work function increases about 0.35 eV. You can get rid of most of these things by hydrogen ion. You get an increase in the work function because of the way the atoms are oriented. You can tell which end is negative and which one is positive, and then calculate the work function increase.

**DYER:** This work has very far-reaching, important considerations for many uses of silicon, and I compliment you and your workers on this. I have a question that arises in my mind right away. Supposing you were dissolving away silicon or melting away silicon, do you visualize that these structures would occur instantaneously or would they take some time to come up?

**CHADI:** The reason is, for the activation barrier to go to the annealed silicon 7 x 7 structure you can measure the activation energy by going to the following experiment: You take the [100] surface, which is 2 x 1, and you keep it at, let's say, 200°C. When this has been done, then you wait, and measure the time that you have to wait to get the 7 x 7, and you do that at 300°C, 400°C, and so on. From the time that is required to transform the 2 x 1 to the 7 x 7 surface, you get an activation energy of about one-half eV per atom, to go from the 2 x 1 to the 7 x 7 structure. But if the temperature is high, if you are close to 800°C, then the structure appears spontaneously. The atomic mobilities are very large at 800°C. The Japanese have shown by beautiful microscopy measurements that the 7 x 7 structure nucleates at steps. I believe the reason it nucleates at steps is that you get a one-dimensional ordering of the atoms along the steps, which eventually lead to a three-dimensional ordering over the entire surface.

**SAH:** I would like to ask you if you could give us the implication of the results you find on oxidized silicon? How does that affect the interface states recombination velocity? On oxidized silicon at high temperature?

**CHADI:** I have done some work on silicon oxide interfaces that I did not mention here. This work has been done mostly on clean surfaces with no oxide. I have done some work on hydrogenated silicon [111] and [100] surfaces. If you add hydrogen to these surfaces, then all the reconstruction goes away. You end up with a much lower surface energy if you have essentially an ideal surface with every dangling bond saturated by hydrogen. The 7 x 7 surface, however, is known to be an extremely stable surface. A Japanese group reported that they exposed it to hydrogen and oxygen and to air for several days and they were still seeing 7th-order spots in their leads. It is a very stable structure.

GRUNTHANER: I have two questions. One is: are you familiar with a recent paper that Linus Pauling put out, looking at your asymmetric dimer situation on <100>?

CHADI: I forgot to mention that there was some controversy with the silicon <100>. The chemists, particularly Goddard at Caltech, suggested that asymmetry was not reasonable, that it should remain symmetric. I heard that in a conference where Pauling was present; Pauling took issue with Goddard. I later wrote this paper in the Physical Review suggesting giving chemical arguments why silicon <100> should have asymmetric dimer structure. In fact, they found the structure very close to mine, using very simple chemical arguments. His idea was that, essentially, there were two configurations, covalent configuration and ionic configuration, and these two configurations had roughly similar energies -- that they would mix in two different configurations that gave asymmetry.

GRUNTHANER: The thought that was quite fascinating that came out of that was these incredibly simple arguments that he has developed out of atomic orbital theory. He comes up with disgustingly close numbers in terms of what you were able to get out.

CHADI: I had the same ideas after I did the calculations. In fact, I had the angles on the viewgraph. If you look at what happens when you go from the symmetric to the asymmetric dimer: in the symmetric dimer you still have all  $190^\circ$  angles. Very close to tetrahedral. Whereas when you go to the asymmetric dimer, one of the bonds becomes  $SP^2$ -bonded, essentially. The angles can relax to close to  $120^\circ$ . The  $SP^2$  bond is very strong; much stronger than the  $SP^3$  bond. The other one becomes P-bonded and the P bonding is close to the  $SP^3$  bond. So you gain energy that way, and that is essentially Pauling's argument.

GRUNTHANER: That is what brings up the second question. When you did this calculation of the effective grain boundary in silicon material, I assume that out of the calculation you get the chemical implication of bonding and antibonding states, and of the energy distances between those. For the grain boundary in silicon, buried down in the silicon in your slab, you essentially get something like a bonding-antibonding splitting in there that I assume you can compare with what you can get for the normal  $SP^3$  bonding in silicon. So the question is, was there any difference in gap implied in that rehybridization in the 5- and 7-membered rings? And then the second part of that: was there any indication of the change in hybridization? Namely, is the S contribution to bonding really following the kind of orbital electro-negativity ideas that are being developed now?

CHADI: As I am sure that you are aware, the grain boundary I considered was a continuous grain boundary. There were no dangling bonds. It was a perfect bonding at every site.

GRUNTHANER: But the geometry is quite different around the silicon site. I am wondering whether there is an application for that in the gap.



CHADI: I looked at the static charge distribution at the grain boundary and I found, amazingly, that most of the atoms were neutral to within 200ths of an electron. However, there were a few atoms at the boundary that had deviations from neutrality of  $\pm 0.1$  electrons. As far as the electronic states -- I looked at those; whenever you have five or seven full rings, there is a very characteristic state that is forbidden essentially for even numbers of rings of atoms, and these states occur at two well-defined positions where you have pseudo-gaps. If you look at the four bands of density state then there is one of these pseudo-gaps at about 0.08 eV below the valence band. This is a very sharp state. There is also sharp state in the conduction band, I don't know at what energy, but there is nothing in the band gap. The band gap is free of any defect state associated with the grain boundary.

MILSTEIN: After Grunthaner's comment about Linus Pauling discussing this, I am not sure that I have anything further to say. The issue I was looking at was the matter where you described the thermodynamic transformation, and the argument that crossed my mind is that in the carbon system, diamond is not thermodynamically stable, although we have all seen such objects, and they stand around for quite some time. I think the issue I would raise is that this should be viewed from the point of view of the bonding of Period 4 elements. In that sense, I think, when you go from carbon to silicon the transformations occur more readily, clearly, but when you talk about a pi-bonded system, it's a straight organic system. That is where it comes from.

CHADI: That's right. However, this might be easy for you to say, but the chemist, I know Goddard for example, believes that the pi-bonding of silicon is very weak and I think it is weak, it is much, much -- by a factor of three -- weaker in magnitude than the pi-bonding in carbon. However, it does occur. Some would argue that pi-bonding should not exist in silicon, whereas there is strong evidence now, at least on the silicon surface, that pi-bonding does exist, and it is very, very weak. As I mentioned, absorption between surface states, with the polarization dependence of the absorption. The only structure that agrees with that measurement and also photon emission is the chain structure. So you have to convince the chemists. I believe, at the surface at least, there is pi-bonding, and it makes a contribution to the stability of the surface. The question is: how strong is it? The chemists say it is very weak.

MILSTEIN: Obviously, it has to be very weak. I don't think there is any argument about that.

CHADI: It is much stronger than carbon.

MILSTEIN: That probably also explains why diamond exists, because thermodynamically it ought not to. You have a big enough activation energy to get over it to change it to graphite.

CHADI: Yes. The activation energy is very big there.

HANOKA: I would like to pursue this thing about the hydrogen on the surface again. That was for a [111] surface, is that right?

CHADI: For the [111] surface it goes to an ideal, yes, the reconstruction goes away and also for the [100], if you add hydrogen; it first saturates the dangling bonds, and it stays  $2 \times 1$ , but then if you add more hydrogen then it breaks the silicon-silicon dimer bond and you get a dihydride on the [100] surface.

HANOKA: That is interesting, because there is IR spectroscopic evidence of an  $\text{SiH}_2$  being formed at the surface. Of course, there you have much higher concentrations. That is what I was going to ask you about.

CHADI: In fact, if you put water on the silicon [100] you get both silicon hydrogen and silicon OH modes, you get the association. There is a lot of work in IR with oxygen, hydrogen and water on the silicon surfaces.

KAZMERSKI: We want to thank you very much, D.J. I will point out that this is an ideal case for the experimentalists, where D.J. won the Peter Mark Award and got \$500 for his work, and I just saw that Benig and Rohr got the King Faisal Award at considerably more money, almost like a Nobel Prize.