The role of strain in Si (111)7×7 and related reconstructed surfaces

I. K. Robinson
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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X-ray diffraction measurements of the sputter-annealed Si(111) 7×7 surface have been made at the National Synchrotron Light Source, Brookhaven. Technical advances have improved the reliability of such data significantly. The 120 structure factor intensities agree with the widely accepted structural model of Takayanagi at the 4σ level, but can be made to show complete agreement if the atomic coordinates of this model are allowed to relax. In this way, 15 of the 17 possible two-dimensional positional coordinates in three layers have been determined to an accuracy of ~0.02 Å. The displacement pattern can be simply interpreted as a superposition of strain fields around the adatoms, in the dimers, and within the triangular island regions. These new observations of strain are discussed in the light of theoretical calculations of the local strain fields around adatoms, observations of reconstructed states of surfaces prepared under external strain, and theoretical attempts to understand the origin of strain.

I. STRAIN AND RECONSTRUCTION

Strain is an important concept in the understanding of the stability and electronic properties of thin film semiconductors. Frank and van der Merwe[1] outlined a simple theory to predict the regions of stability and morphology of lattice-matched epitaxial films of one material upon a thick crystalline substrate of another. Such a film is in mechanical equilibrium only if it is sufficiently thin that the strain energy arising from mismatch of the lattice constants is less than the free energy of the interfacial dislocations that would form if the film relaxed to its own bulk lattice constant. This leads to the concept of a "critical thickness" which depends on the material properties and which becomes a fundamental limitation in the engineering of lattice-matched materials, such as superlattices. Experimental results for Ge_xSi_{1-x}/Si(100) (Ref. 2) have supported the concept however, with considerably larger values of the critical thickness permitted, because of metastability; the relevant energy is found to be the energy of *nucleation* of the dislocations instead.

The strain model may also be applied to a single monolayer with certain approximations and assumptions. Furthermore, because the top layer of a crystal of a single material is electronically different from the rest and has different physical properties, it may be considered to be a monolayer epitaxial film upon itself, or a *homoepitaxial* layer. If the surface is not reconstructed, its lateral bonds would be under tensile or compressive stress. This situation may be untenable in the Frank and van der Merwe sense discussed above, [1] in which case dislocations will form in the surface. The result is a particular kind of surface reconstruction in which an array of dislocations separates strained regions of crystal. The strain, as well as the dislocations, should be readily observable in the surface structure. We argue here that the Si(111) 7×7 surface is such an example.

Experimental results for related reconstructed surfaces supported the idea of a strain role, even before knowledge of the detailed structure was available. Examination of a range of thin Ge(111) films grown epitaxially on Si(111), so that they were strained compressively by up to 0.4%, revealed that the surface was 7×7 for strains >0.3%.[3] Less strained films had the normal $c2\times8$ reconstruction. The low-energy electron diffraction (LEED) patterns for Ge and Si(111) 7×7 were essentially the same, indicating the same structure. The general conclusion was that the 7×7 structure is energetically favored over the $c2\times8$ at large compressive strain, and therefore its structure is more efficient at accommodating the strain.

Another experimental approach to continuous control of strain is chemical substitution. Annealing of submonolayer depositions of Sn on Ge(111) is found to produce the 7×7 structure and also, at higher coverage, a 5×5 structure.[4] If we assume that Sn substitutes for Ge in the surface layer by alloying, then we expect strain to be induced in proportion to the lattice constants of the homologous bulk structures, which differ by 15%. The 5×5 is presumably a more strained analog of the 7×7. This trend is also consistent with the observation of a 5×5 upon substitution of Ge in Si(111).[5]

II. STRUCTURAL MODEL OF Si(111) 7×7

This paper examines the results of a recent detailed structure determination of the Si(111) 7×7 surface using x-ray diffraction at the National Synchrotron Light Source (NSLS) at Brookhaven National Lab.[6] The data and early part of the analysis followed the work of Takayanagi *et al.*,[7] arriving at a very similar Patterson function as shown in Fig. 1. We immediately concluded that the dimer–adatom–stacking-fault (DAS) model was correct by analogous reasoning to Ref. 7. Improved accuracy of the x-ray measurements, however, allowed us to interpret our data further by least-squares refinement of in-plane atomic coordinates starting from the schematic DAS model.[7] Fifteen of the possible 17 in-plane positional coordinates, three Debye–Waller factors, and a scale factor were derived from 120 observed intensities. The displacements from the ideal DAS model are shown in Fig. 2. The positional accuracy was 0.02 Å and the final mean square residual was 1.6. Details are given in Ref. 6.

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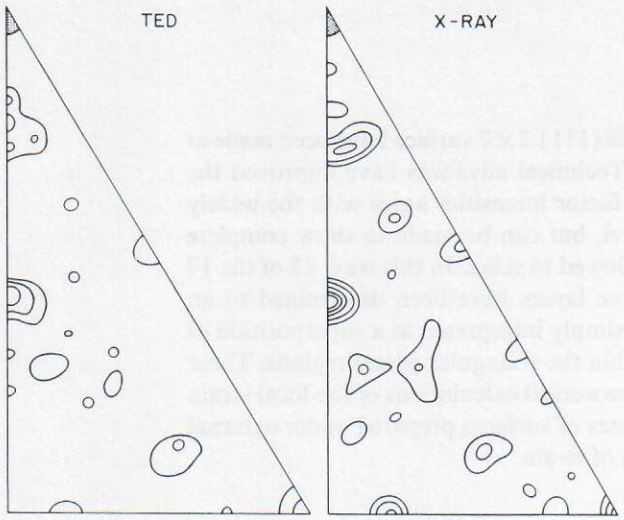

FIG. 1. Positive contours of Patterson functions showing the pair correlation of electron density in the Si(111) 7×7 crystallographic asymmetric unit. On the left-hand side is the result of the transmission electron diffraction experiment of Takayanagi *et al.*[7] On the right-hand side is our result using 120 x-ray diffraction intensities measured at NSLS.[6]

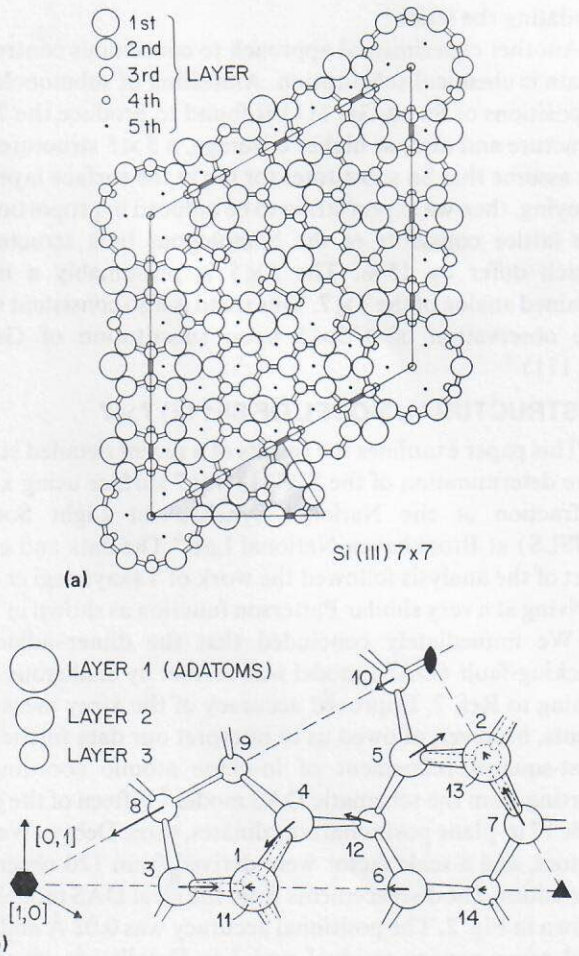

FIG. 2. (a) Full unit cell of the Takayanagi model of Si(111) 7×7 with one asymmetric unit shaded. (b) Blowup of the asymmetric unit with atomic displacements marked by arrows (exaggerated ×10).

Because the structure obtained is only a two-dimensional (2D) projection of the full structure, we cannot examine bond length and bond angle variations directly. However, the arguments concerning the role of strain in reconstruction above refer to mismatch of lattice parameter parallel to the surface also, so the information is in a useful form. The projected bond length information is given in Table I. For reference a bulk interatomic separation is 2.35 Å and its projection (tilted 19° to the plane) onto the (111) plane in the diamond lattice is 2.22 Å. We discuss the local strains in the dimers (D), around the adatoms (A), and within the stacking-fault islands (S) one by one.

A. Dimers

The most straightforward measure of bond strain comes from the dimers because they are very close to lying in the plane of the surface, so that the projected bond length is the same as the interatomic separation. Two representatives appear in the crystallographic asymmetric unit, as listed in Table I. The average length of 2.49 Å is 6% ± 2% longer than the bulk bond length of 2.35 Å. This demonstrates the presence of tensile strain directly.

B. Adatom clusters

The choice of "closed" (T_4) adatom site directly above a third-layer atom (1 above 11 and 2 above 13 in Fig. 2) was a surprising feature of the Takayanagi model when it was announced[7] because of the very short length of the bond between these layers. Previous models containing adatoms had expected an open (H_3) site in the center of the hexagonal hole in the second and third layers.[8] Northrup considered the total energy of the two alternatives within model $\sqrt{3}\times\sqrt{3}$ unit cells, allowing structural relaxation.[9] The closed site was indeed found to be favored by 0.64 eV per adatom. This was only possible because of a lateral relaxation of the three second-layer atoms toward the cluster axis by 0.15 Å (see

TABLE I. Bond distances between the atoms as marked in Fig. 2. Distances were obtained after least-squares refinement of the atomic coordinates against 120 x-ray intensity measurements. All values are projections onto the (111) plane.

Type	Atoms	Length (Å)	Average (Å)
Dimers	8–9	2.51	2.49
	10–10′	2.48	
Adatom cluster	3–1	2.07	2.11(2)
	4–1	2.13	
	5–2	2.12	
	7–2	2.11	
Rest atom	6–12	2.25	2.29(4)
	6–14	2.25	
Adatom cluster neighbor	4–12	2.23	
	5–12	2.35	
	7–14	2.30	
Dimer neighbor	3–8	2.33	
	4–9	2.32	
	5–10	2.28	

Fig. 3). This enlarges the adatom to third-layer distance to 2.49 Å, avoiding unfavorable close contact and suggesting the presence of backbonding to improve the coordination of the adatom.

We also observe this lateral relaxation in our Si(111) 7×7 structure. There are four independent representatives of the adatom cluster radius in the bond length table (Table I) with an average of 2.11 ± 0.02 Å compared with 2.22 Å in the ideal DAS model. The 0.11-Å relaxation may differ from the 0.15-Å theoretical value because the adatoms are more closely packed in the (abstracted) $\sqrt{3}\times\sqrt{3}$ unit cell than the 7×7.

Without knowing the perpendicular coordinates, we can attempt to estimate the backbond distance (adatom to third layer) by triangulation in Fig. 3. Without any relaxation the ideal DAS model has a backbond distance of 1.57 Å and a very distorted second-layer bond angle of 39° instead of the tetrahedral 109°. Assuming the measured lateral relaxation value and a bulk bond length the backbond becomes 2.08 Å and the angle 52°. However, if we use our dimer bond length of 2.49 Å as an estimate of the surface bond length (to account for the effects of strain) we obtain a backbond of 2.64 ± 0.13 Å and an angle of 64°. Thus we find it necessary to incorporate stretched surface bonds in the adatom complex (Fig. 3) to avoid an unreasonably short backbond.

C. Stacking-fault islands

The homoepitaxy theme developed above, based on the theory of Frank and van der Merwe, is useful in examining the stacking-fault islands. The two triangular islands of 21 second-layer atoms (Fig. 2) per unit cell have opposite stacking sequence with respect to the bulk: one is "normal," the other "faulted." The spacing between atoms in adjacent islands is larger than the bulk by a fraction of a unit cell spacing, making an apparent high-order commensurate superlattice 14% less dense than a complete layer. Each island atom has the normal tetrahedral bonding locally to a good approximation, yet the structure is less dense overall. This is expected in the van der Merwe theory in the "hard domain wall" limit[10] when the substrate–overlayer interactions are much stronger than overlayer–overlayer ones, as is the case for Si on Si(111). The "domain walls" are dislocation lines between the islands, which can be identified with the dimers of the Takayanagi model.[7] At the intersection of the lines of dimers are the corner holes (Fig. 2) consisting of a 12-member ring in layers 2 and 3 surrounding a dangling bond in layer 4.

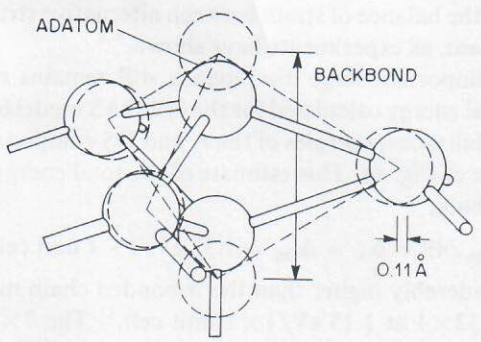

FIG. 3. Ball and stick model of the adatom cluster showing the relaxation radial to the axis and how this relieves the bond length of the backbond between the first and third layers.

The residual strain associated with this domain wall/island arrangement is seen in the atomic positions: there is a radial expansion of the islands toward the walls. The coordinate displacements can be parametrized into a radial component of the neighbors toward each adatom plus an overall radial component Δr outwards from the center of the triangular islands. Δr is found to be proportional to the radius r with a corresponding strain $\epsilon_1 = \Delta r/r = 0.8\% \pm 0.4\%$.

Bond lengths also reveal the presence of strain in the islands. Table I shows that the average projected bond length for all atoms not in the dimers or adatom clusters is 2.29 Å instead of 2.22 Å. The bond strain $\epsilon_2 = 3\% \pm 2\%$ (standard deviation) indicated is different from ϵ_1 for an interesting reason. The adatom clusters are contracted *inward* as discussed above. All other surface bonds (in projection) want to be *longer* by an amount of order ϵ_2 (3%), so a balance is reached with a net strain which is only of order ϵ_1 (1%). Thus most of the strain is absorbed in the adatom clusters, the remainder in the domain-wall/island arrays. Adatoms act to relieve strain; a Si(111) surface with no adatoms would be much more strained and would have to introduce a much higher density of dislocations to accommodate. It is interesting to speculate that Ge(111), which probably has adatoms[11] but not stacking faults,[12] might be different from Si only by a difference of order 30% in the amount of surface bond strain.

III. THEORETICAL UNDERSTANDING OF Si(111) 7×7

Since the announcement of the Takayanagi structural model[7] considerable progress has been made toward understanding the energetics and hence the mechanism of formation of the Si(111) 7×7. We will discuss here just two approaches that have been applied recently.

The fully electronic, local density approximation (LDA) pseudopotential wave function calculations have the advantage that they calculate the total system energies to an arbitrary accuracy (set by the size of the calculation) but are expensive in computer time, and at present prohibitively so for more than a dozen atoms. For the time being calculations can be done for pieces of the 7×7 but not the whole system. Work of this kind has been done by Northrup[9,13] and Vanderbilt.[14]

The other approach that has been important is the semiempirical elastic relaxation method originally pioneered by Keating[15] and applied to Si(111) 7×7 by Qian and Chadi[16] and Vanderbilt.[17] Here the calculations are easy even for a large structure but require careful choice of potential parameters representing the elastic constants for bond bending and stretching. One weakness of the method is that it does not account for changes of equilibrium bond lengths for the lower coordinated surface atoms. It can be expected to account fairly well for the *distribution* of elastic strain between the components of the 7×7, but less well for the total energy of the system.

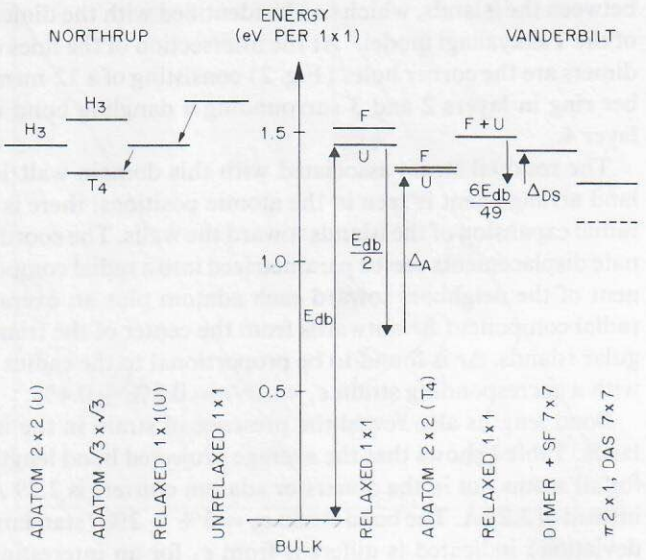

FIG. 4. Total energies calculated for components of the Si(111) 7×7 surface by Northrup (Refs. 9 and 13) and Vanderbilt (Refs. 14 and 17). All structures have the coordinates relaxed except where shown. The energies are derived from electronic LDA calculations except for the two 7×7 structures which are bootstrapped from Keating elasticity models. The dashed line is the π-bonded chain model of metastable Si(111) 2×1 due to Pandey (Ref. 18). Symbols used are F = faulted; U = unfaulted; H_3 = open adatom site; T_4 = closed adatom site; E_{db} = dangling bond energy; and Δ_A, Δ_{DS} = strain energies for adatom cluster and dimer/island structure.

These recent results are summarized in Fig. 4. Northrup's calculations[9,13] show the excess energy of formation of dangling bonds when the surface is formed, a lowering of energy due to relaxation and a further lowering by the addition of an adatom in the T_4(= closed) site mentioned above. The H_3(= open) site is considerably higher in energy for both $\sqrt{3}\times\sqrt{3}$ and 2×2 unit cells.

Vanderbilt's calculations[14] are a little more comprehensive and in excellent agreement with Northrup's. Distinction is made between faulted (F) and unfaulted (U) stacking sequences and small energy differences are seen. The energy of the adatom in the correct 2×2 T_4 (closed) site is found to be as low (per 1×1 surface unit cell) as the $\sqrt{3}\times\sqrt{3}$ T_4 adatom, indicating that the relaxation of the 2×2 site must be even more efficient. Since the formation of the 2×2 adatom structure involves the elimination of 2 of the 4 dangling bonds, the energy can be divided into a gain of $E_{db}/2$ compensated by a positive adatom strain energy Δ_A as shown. The dangling bond energy E_{db} is known because it is simply the energy of formation of the relaxed 1×1 surface (Fig. 4).

Vanderbilt[17] also used the Keating method to estimate the energy gain associated with formation of the dimers and stacking-fault islands. He omitted the adatoms, which the Keating method handles very badly, using the justification that the adatom energy was relatively small. Qian and Chadi[16] obtained very similar results with a different method of handling the adatoms. The value Δ_{DS} was obtained for the strain energy. This is offset by $6E_{db}/49$ for the six dangling bonds eliminated per 7×7 by the formation of the dimers as shown in Fig. 4.

If we make the assumption that the formation of adatoms and of stacking-fault island/dimer structures are independent of each other, we can simply add the two energy gains to obtain a final value for the DAS model in the last column of Fig. 4. There is clearly a problem here because the energy of the π-bonded chain model of Si(111)2×1[18] (dashed line) falls considerably below the DAS model. Clearly the adatoms and the stacking fault/dimers are not independent and a considerable fraction of the strain energy $\Delta_A + \Delta_{DS}$ will be regained when these components are mixed together.

Finally, Vanderbilt[17] was also able to calculate the Nielsen–Martin[19] stress forces in each of the LDA calculations performed and to evaluate the stress (strain derivative of energy) for the Keating models. He found that the relaxed 1×1 structure contains slight compressive stress, but that *both* the 2×2 adatom structures *and* the dimer/stacking-fault structure experience tensile stress.

IV. DISCUSSION

Our structural coordinates show clear evidence of two important strain fields in Si(111) 7×7[6]: the contraction of 0.11 Å of the cluster of neighbors around each adatom and the 0.8% dilation of the stacking-fault islands. The latter strain gives rise to a general increase of bond lengths which is also directly seen.

Corresponding strain energy terms are also seen directly in the results of total energy calculations of Vanderbilt[17] shown in Fig. 4. Both formation of adatoms (A) and of dimer/island (DS) structures are energetically favored, in each case with an energy gain due to elimination of dangling bonds compensated by a strain energy almost as large: Δ_A = 0.61 eV/1×1 unit cell and Δ_{DS} = 0.13 eV/1×1 unit cell. The relaxed coordinates obtained by energy minimization agree very well with the experimental values as well.[6,16]

The question of driving force for reconstruction is harder to answer. Although the Frank–van der Merwe theory nicely explains the formation of dislocation lines (dimers) in the DAS model and the observation of strain in the triangular islands, it cannot be considered to be a driving force because that would presuppose a large compressive stress in the unrelaxed surface which is not found.[17] Figure 4 shows that dangling bonds dominate the energetics, and that their elimination is a more likely driving force. Strain, however, contributes almost as large an energy with the opposite sign, and so the balance of strain between alternative structures is important, as experiments have shown.[3–5]

An important large discrepancy still remains regarding the total energy calculated for the full DAS model by adding the stabilization energies of the A and DS components (last column of Fig. 4). This estimate of the total energy relative to the bulk,

$$19E_{db}/49 + \Delta_A + \Delta_{DS} = 1.31 \text{ eV}/1\times1 \text{ unit cell}$$

is considerably higher than the π-bonded chain model[18] of Si(111)2×1 at 1.15 eV/1×1 unit cell.[17] The 7×7 is well known to be more stable than this metastable structure. This large discrepancy is not just due to inaccuracy of the estimates of Keating elastic energy because it remains even if Δ_{DS} is set to zero. The >0.16 eV discrepancy must corre-

spond to a relief of strain when A and DS are mixed together. The stress calculations[17] mentioned above do not help to resolve the issue, as both components are found to be under tension. Our x-ray coordinates show the same thing: the adatoms draw in the neighboring atoms, yet the islands show an overall spreading out of the atoms. The explanation probably lies in the detailed interaction of adatoms and dimers. Figure 2 shows that dimer pairing and the adatom cluster relaxation are approximately parallel motions: the local strain in bonds 3–8, 4–9, and 5–10 is therefore *reduced* by formation of the adatom clusters, whereas in the 2×2 unit cell used to estimate Δ_A surrounding bonds are stretched considerably. A 25% reduction in Δ_A is needed to resolve the difficulty. The smallest unit cell that can be used to test for dimer–adatom interaction in a fully electronic LDA total energy calculation is 3×3. We look forward to the day that this is feasible.

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