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Observation of strain in the Si(111) 7×7 surface

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X-ray diffraction intensities for 120 independent superlattice reflections of the clean reconstructed Si(111) 7×7 surface have been measured using improved sources and techniques. Starting from the Takayanagi model, we have refined a full set of in-plane structural coordinates and determined the atom positions to within 0.02 Å. Our structure clearly shows the local strain fields expected around the adatoms as well as a general dilation of the reconstructed layers showing the presence of strain.

Understanding of the 7×7 reconstruction, the equilibrium state of the Si(111) surface over a wide temperature range, has advanced dramatically over the last two years with the proposal of an atomic model by Takayanagi *et al.*[1] to explain electron diffraction data. It has been announced since that this model agrees very well with x-ray diffraction,[2] ion scattering,[3] and tunneling microscope data,[4] and so has become widely accepted. The model consists of a triangular lattice of "islands," connected to the bulk by alternately "normal" and "faulted" stacking sequences. Between the islands lies a network of "dimers" joining them together. On top of this sits an array of "adatoms" each satisfying three bonds that would otherwise dangle from the island layer. Total-energy calculations[5] have shown that this adatom configuration is energetically favorable because there is inward relaxation of the layer below. While no fully electronic total-energy calculation can yet encompass the entire 7×7 unit cell, there have been attempts to rationalize it from simple physical principles.[6–8] On the experimental front, several approaches to the question of its stability have been made: It is found that lateral compression of Ge(111) films cause the surface to adopt the 7×7 state.[9] Similarly, chemical substitution of Ge in Si(111) (Ref. 10) and Sn in Ge(111) (Ref. 11) surfaces can give rise to the 7×7. All of these experiments suggest an intimate relation between strain and reconstruction. In the present work we have been able to observe the strain in the 7×7 reconstruction *directly* be detailed x-ray crystallographic analysis of the in-plane atomic coordinates.

The argument for expecting a strain-mediated reconstruction originates with the theory of epitaxy of Frank and van der Merwe.[12] This concerns the strain energy of a thin crystalline layer of a material in contact with a crystal of different lattice spacing. When the strained layer is sufficiently thick, relief becomes energetically favorable by the formation of misfit dislocations at the interface. Here we consider the possibility that the topmost layers of an unreconstructed Si(111) surface can be strained because of structural and electronic relaxation that places its lateral bonds under compression; the bonds are constrained by the bulk crystal to have the normal projected bond length but would prefer to be longer.[13] It is also clear how chemical substitution[10,11] might lead to the same effect. Thus an *unreconstructed* Si(111) surface is strained and reconstruction is the means of strain relief. Adatoms may be considered to function this way: the adatom configuration is energetically favorable[5] because it is accompanied by considerable lateral relaxation of the three neighbors towards the axis of the cluster, thereby relieving strain outside. Further relief must be achieved in the classical way by the introduction of misfit dislocations,[12] which are the lines of dimers separating islands of opposite stacking sequence in the Takayanagi model.[1] A necessary consequence is that misfit should be visible within the islands;[12] atoms near the edges should be displaced further from their ideal sites than atoms near the center of the islands. Testing of these ideas cannot be undertaken with the present level of schematic structural models.[1–4] To pursue the question of driving mechanism further, we require accurate atomic coordinates.

Historically, the most reliable method for obtaining structural coordinates is x-ray crystallography. In recent years many advances have been made in its application to surface problems, particularly when use is made of the high intensity of synchrotron radiation sources.[2,14] The x-ray wavelength (1.3 Å) we choose is sufficiently short that the diffraction is accurately kinematical, so that linear wave-superposition methods may be used for analysis without approximation. Least-squares methods are then extremely accurate for the determination of structural coordinates. The accuracy is limited only by the reproducibility of the measurements and the number of reflections that can be reached. The diffraction pattern of a surface is a two-dimensional (2D) lattice of "rods," diffuse as a function of perpendicular momentum transfer $q_\perp$. Analysis of the intensities of the $q_\perp = 0$ section yields a projection of the structure onto the surface plane. The power of the method has been demonstrated for InSb(111) 2×2.[14]

The x-ray diffraction intensities given in Fig. 1 represent the first data obtained from the X16A beam line at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, which is customized for

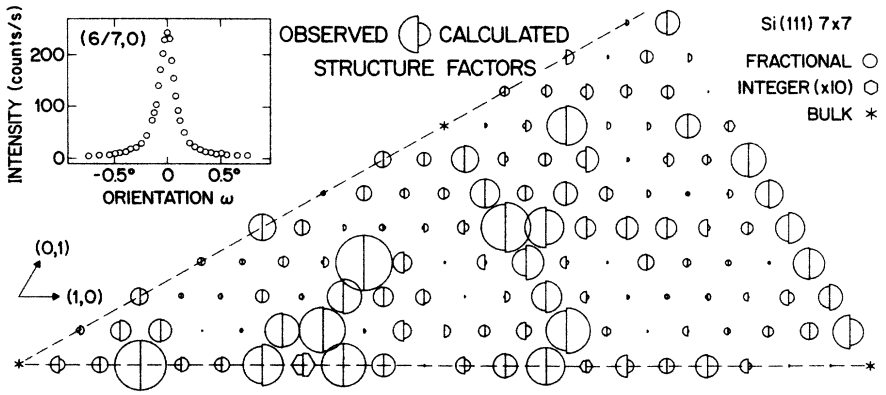

FIG. 1. Observed and calculated structure factors for Si(111) 7×7 measured close to $q_\perp = 0$. The radius of each circle is proportional to the amplitude, the area to the intensity. Dashed lines are mirrors relating equivalent reflections. The hexagonal coordinate system is the same as used for electron diffraction: the bulk reflections, indexed (1,1) and (3,0), correspond to the cubic $(\bar{2}20)$ and $(\bar{4}22)$ positions. The calculations of integer-order (1,0), (2,0), and (2,1) reflections have included the contribution of crystal truncation rods (Ref. 21). Inset is a typical rocking curve which has a characteristic Lorenzian line shape that indicates a surface coherence length of 1500 Å.

high-resolution diffraction experiments in ultrahigh vacuum.[15] The beam line uses a bent cylindrical mirror to focus bending-magnet radiation onto 1 mm^2 at the sample. The incident beam is monochromated by parallel Si(111) crystals; the diffracted beam is detected behind 2×10-mm slits placed 0.5 m away. The sample was cleaned by ion bombardment and annealing at 850 °C. Contamination (mainly C) was $<0.5\%$ and did not change during the course of the measurements, lasting 48 h at $3\times10^{-10}\tau$. The sample orientation was chosen to maintain an incident and exit angle about twice the critical angle for total reflection so that $q_\perp$ was kept small (<0.07 $Å^{-1}$) without significant distortion due to refraction. The intensities were integrated over orientation angle ω (Fig. 1, inset), background subtracted, then corrected for Lorentz factor and variation of active area.[16] Three or four symmetry equivalents of each reflection were collected and averaged together; their reproducibility determined their uncertainty which was 12% on average. The maximum signal observed was 300 counts per second under typical running conditions of 2.5 GeV and 100 mA.

We use the three-layer Takayanagi model[1] as a starting point for refinement of coordinates by the least-squares method. The 6-mm point symmetry of the model was assumed to be correct,[17] which leaves 17 positional parameters for the 14 atoms of the asymmetric unit. Of these, 15 parameters could be refined satisfactorily; separate displacements for the two adatoms (1 and 2 in Fig. 2) and the third-layer atoms immediately below (11 and 13) could not be assigned in projection, so these were allowed to move in parallel as two pairs. The displacements from the model sites, determined in this way, are given in Table I and drawn as arrows in Fig. 2. The calculated intensities are shown in Fig. 1, which gave a least-squares residual[16] of $\chi^2 = 1.6$, indicating a disagreement only 25% larger than the experimental uncertainties themselves. The starting model (no displacements) had a χ^2 of 15.2.

The bond lengths, listed in Table II, derived from the refined coordinates, can be immediately interpreted. The dimer bonds (2.49 Å) are significantly longer than the bulk Si-Si bond length of 2.35 Å. The $6\pm2\%$ stretch is the first sign of tensile strain in the surface. Second, there is the expected lateral contraction of the immediate neighbor distances surrounding the adatoms. The net inward contraction of 0.11 ± 0.02 Å compares fairly well with the value of 0.148 Å obtained by total-energy minimization,[5] especially considering that the theory applies to a $\sqrt{3}\times\sqrt{3}$ not a 7×7 unit cell. An inward contraction of 0.20 Å has also been reported for Sn/Ge(111) $\sqrt{3}\times\sqrt{3}$ with the same adatom site.[18]

After these features are taken into account by subtraction of the local dimer and adatom-cluster components from the total displacements, the remaining motions are found to fall into a simple pattern. We express the radial component Δr of the displacement of an atom at distance r from the center of the island (the threefold axis at the

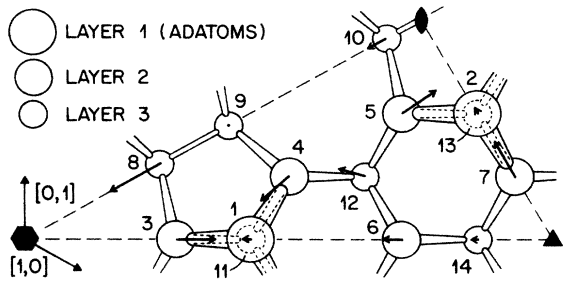

FIG. 2. Atomic model and numbering scheme of the unit cell of the Si(111) 7×7 structure. Atoms are drawn in the ideal lattice positions of the Takayanagi model. Layer 1 is the outermost one. The dimers form between atoms 8 and 9 and between atom 10 and its image. Symmetry is indicated by dashed mirror lines and conventional symbols. The hexagonal coordinate system is the reciprocal of that in Fig. 1, so that atom 8 is at [1,1], atom 3 is at $[\frac{4}{3},\frac{2}{3}]$, etc. Arrows show the directions and relative size of the displacements from the starting positions, exaggerated 10 times.

TABLE I. Observed displacements of the atoms from the ideal lattice positions of the Takayanagi model (Ref. 1). The hexagonal crystallographic coordinate system and the atom numbering conventions are explained in Fig. 2. In addition to these refined parameters we determined an arbitrary scale factor and layerwise Debye-Waller factors of 1.5 ± 0.6 Å^2 for the adatoms (1 and 2), 1.5 ± 0.6 Å^2 for atoms 3–7, and 0.0 ± 0.4 Å^2 for 8–14. The theoretical displacements refer to calculations of Qian and Chadi (Ref. 19) after conversion to our coordinate frame.

Atom	Observed displacement	Theory
1	−0.004(2) [2,1]	−0.002 [2,1]
11		0.003 [2,1]
2	−0.003(2) [1,−1]	0.004 [1,−1]
13		0.003 [1,−1]
3	0.018(5) [2,1]	0.018 [2,1]
4	[−0.025(8), −0.032(7)]	[−0.041, −0.035]
5	[0.028(7), 0.032(7)]	[0.036, 0.031]
6	−0.009(5) [2,1]	−0.014 [2,1]
7	−0.019(5) [1,−1]	−0.012 [1,−1]
8	0.151(8) [1,1]	0.163 [1,1]
9	−0.195(8) [1,1]	−0.206 [1,1]
10	0.178(7) [1,1]	0.186 [1,1]
12	[−0.023(6), −0.006(6)]	[−0.007, −0.006]
14	−0.004(4) [2,1]	−0.021 [2,1]

right of Fig. 2) as a dimensionless strain, $\epsilon_1 = \Delta r/r$. We find all motions to be directed outwards and in the range $0.35\% < \epsilon_1 < 1.3\%$, except for atom 10 which has no radial component and atom 3 which is associated with the corner "hole," the 12-membered ring around the sixfold axis. The average strain is $\epsilon = 0.8 \pm 0.4\%$ for 12 atoms, where the quoted error is just the standard deviation of the measurements.

This dilation can be seen just as clearly in the third group of bond lengths in Table II, containing the eight bonds not involved with the dimers or adatom clusters. These have an average of 2.29 Å and a standard deviation of 0.04 Å, compared with the bulk projected value of 2.22 Å. This gives a different estimate of the strain, $\epsilon_2 = 3.2 \pm 1.8\%$, related to the bonds themselves rather than absolute atomic positions. One reason ϵ_2 is larger than ϵ_1 is that it includes the effects of the strain fields around the adatoms that were subtracted out in the calculation of ϵ_1. Of course, ϵ_2 represents changes both in bond angle and interatomic separation, which we cannot distinguish in our 2D projection; however, either of these is an indication of local strain.

Finally, we have included for comparison in Table I a list of coordinates obtained recently by energy minimization of a semiempirical tight-binding functional,[19] also starting from the ideal Takayanagi model. There is generally good agreement indicating that this simplified view

TABLE II. Projected bond distances between the atoms of Fig. 2. The bulk bond length projected onto the (111) plane is 2.22 Å.

Atoms	Projected bond length (Å)	Average bond length (Å)
8–9	2.51(4)	2.49
10–10′	2.48(6)	(dimers)
1–3	2.07(4)	2.11
1–4	2.13(5)	(adatom clusters)
2–5	2.12(5)	
2–7	2.11(4)	
All others (8 bonds)		2.29

of the electronic interactions is adequate to explain the relaxation of Si(111) 7×7 at this level.

To put our results in perspective we compare the magnitude of the observed strains, $\epsilon_1 = 0.8\%$ for the dilation and $\epsilon_2 = 3.2\%$ for the projected bond length, with other experiment values. A lateral compression of 0.3% is sufficient to change the reconstruction of Ge(111) from $c(2\times8)$ to 7×7;[9] it is likely, however, that the $c(2\times8)$ state (whose structure is unknown, but probably involves adatoms[20]) already has strain-relief mechanisms at work and that a slight additional compression forces it to switch over to the misfit mechanism of the 7×7. An estimate of the local bond strain induced by the substitution of Ge in Si(111) or Sn in Ge(111) surfaces, which exhibit 5×5 and 7×7 reconstructions,[10,11] is at least 2% from covalent radius arguments.

These results support, by direct observation, the notion that strain is an important element of the reconstruction of semiconductors. By careful analysis of a large number of data, we have brought the "model" of Takayanagi *et al.*[1] to the rank of "structure" as far as the in-plane coordinates are concerned; we still lack a complete set of perpendicular coordinates, however. We find many significant deviations from the ideal model geometry, which reveal the strain. The pattern of displacements observed has been interpreted in terms of three superimposed strain fields: the dimer stretch of 6%, the adatom cluster relaxation of 0.11 Å, and the general dilation of 0.8%. These make sense in the context of a strain-relief model of the reconstruction.

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