X-ray diffraction evidence of adatoms in the Si(111)7×7 reconstructed surface

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Synchrotron radiation has been employed to measure 73 fractional-order surface Bragg reflections from Si(111)7×7. A novel data-filtering technique is introduced to address the question of which sites in the diamond lattice are filled and which are vacant at the surface. The analysis is greatly simplified because atomic displacements are systematically nulled. Our observations agree with the principle of a "stacking fault" under half the unit cell. Difference analysis then requires 12 adatoms and one vacancy to complete the structure.

Semiconductor surfaces are believed to reconstruct by reducing the number of bond "dangling" into vacuum.[1,2] Detailed understanding of the mechanisms involved requires accurate determination of the positions of all the atoms. In many cases it is not yet known *how many* atoms are involved with the reconstruction: Beneath the issue of the exact coordinates lies one of a schematic model or "gross morphology" of a surface. In this paper we use a method of constraining x-ray diffraction data to determine the gross morphology of the Si(111)7×7 surface. By deliberately removing the finer details of the atomic displacements we can see which sites of the ideal bulk lattice are occupied and which are vacant at the surface. Si(111)7×7 is on of the earliest known reconstructed surfaces[3] and certainly the most widely studied case.[4,5] It has become the canonical example of reconstruction and yet the structure has remained unsolved for 25 years.

Morphological information about Si(111)7×7 has been provided by scanning tunneling microscopy (STM),[6] which sees an arrangement of 12 "bumps" per unit cell with twice the lateral spacing of Si. It has been speculated that each bump contains an "adatom" or cluster of adatoms,[6] even though the technique is sensitive only to some very low probability tail of the electronic wave functions and not to the atomic cores. Here we will present independent evidence for the existence of single atoms at these positions. We also find significant rearrangement of the layers below, which the STM cannot visualize.

One of the most significant experimental results regarding the Si(111)7×7 structure is the discovery, from ion channeling,[7] that there are approximately two layers (in this paper a monolayer is defined by the primitive rhombic unit cell) of the surface lattice substantially displaced from the off-normal [001] channeling direction, but with only small displacements from the normal direction. Recently it was suggested[8] that this could be due to the presence of stacking faults below the surface, rearranging the order of the layers above. The idea emerged of a stacking-fault "island,"[8,9] occupying only *half* the 7×7 unit cell, thereby reducing the total number of atoms per layer and so relieving lateral strain. Various stacking-fault models have been proposed.[8–10] Very recently, the role of strain in the stability of the 7×7 structure was directly demonstrated by thin-film experiments.[11]

We have measured the clean Si(111) surface by glancing-incidence x-ray diffraction. Focused wiggler radiation provided by the Stanford Synchrotron Radiation Laboratory (SSRL) was monochromated by parallel asymmetric-cut Ge(111) crystals and impinged on the sample via a large beryllium window brazed into the wall of our ultrahigh-vacuum cell. The cell was oriented on three axes by a four-circle diffractometer. X rays diffracted in the vertical plane (to avoid polarization effects) were collected through Soller slits by a scintillation counter. The sample was cleaned every 12 hours by direct electrical heating to 1200°C. An ion pump maintained the pressure in the 10^{-10}-torr range.

A total of 73 surface Bragg intensities were collected, close enough to the surface plane for the perpendicular momentum transfer to be negligible, but far enough away to avoid refraction artifacts. Each intensity was integrated over the sample rotation angle ω and then corrected for Lorentz factor and changes of active area.[2] The Si form factor was divided out and the resulting values are displayed in Fig. 1. A limited number of symmetry-related reflections were measured to estimate the reproducibility, which was found to be about 25%. The most intense reflection was 300 counts/sec for the $(1,\frac{3}{7})$; the background level was around 10 counts/sec. The resemblance between the pattern in Fig. 1 and published transmission electron diffraction photographs[10,12] of Si(111)7×7 is locally very good and suggests that the kinematical assumption made in the latter work is appropriate.

The data display the $6mm$ symmetry expected from the $3m$ symmetry of the bulk coupled with a center of sym-

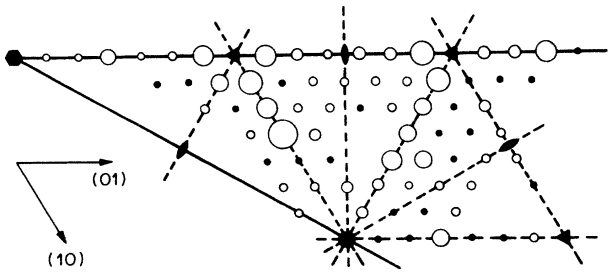

FIG. 1. Observed structure factors. The radius of each circle is proportional to the amplitude, the area to the intensity. Solid circles are reflections measured to be zero. Exact mirror lines (solid) bound the $6mm$ asymmetric repeating unit; approximate mirror lines (dashed) and conventional symbols denote the apparent pseudosymmetry.

metry because the perpendicular momentum transfer is close to zero. In addition, the diffraction pattern in Fig. 1 shows a rather striking approximate symmetry or "pseudosymmetry" indicated by the dashed lines. Thus the pattern tends to repeat itself with the same symmetry and spatial period as the bulk reciprocal lattice. Periodicity in reciprocal space is a characteristic of "lattice gas" structures, in which atoms are either present on or absent from a lattice of sites.[13] Here, the lattice is that of the bulk, so we can conclude that Si(111)7×7 has most of its atoms close to bulk sites in the two-dimensional projection onto the surface plane. This observation is in striking agreement with the basic finding of ion channeling experiments,[7] that the lateral atomic displacements from ⟨111⟩ rows are small.

The pseudosymmetry is the key to our new analysis technique: It is straightforward to show that a set of structure factors, which is *averaged* over some symmetry so that it becomes exactly periodic in reciprocal space, corresponds to a structure with all its atoms moved to the nearest lattice site. The result is exact only to first order in the displacements from the lattice positions, and is a good approximation when the displacements are small, i.e., when the pseudosymmetry is strong. It is clear how this can be used to analyze the Si(111)7×7 structure: If we average our data over the pseudosymmetry, we remove the detail of exact atomic displacements to first order and directly address the question (in a two-dimensional projection at least) of which atoms are present and which are not.

Table I gives the values of the structure factors averaged over the $6mm$ pseudosymmetry (mirror lines in Fig. 1). The list is complete because all other structure factors are generated by those pseudosymmetry operations. Since the original data were not a complete set, some error in the average is introduced from imperfect sampling; the quoted errors are from the measurements alone.

The largest structure factors in Table I are those lying on the pseudomirror lines themselves, given by $k=0$ and $h+k=1$. This is the diffraction pattern of an array of triangles[13] and immediately suggests the presence of triangular "islands" of scattering matter in Si(111)7×7 structure. To reconcile this with the ion channeling results[7] which call for stacking faults under the surface,[8] the simplest kind of stacking-fault island[10] is postulated: 21 atoms in one half of the unit cell lie in A sites that are a continuation of the face centered cubic ($ABCA$) stacking of the bulk, while 21 atoms on the other side lie in B sites that have local hexagonal stacking ($ABCB$ instead of $ABCA$). We use

$$\chi^2=\frac{1}{N}\sum\frac{(F^{\rm obs}-|F^{\rm calc}|)^2}{\sigma^2} \tag{1}$$

as a standard measure of agreement between the N calculated ($F^{\rm calc}$) and observed ($F^{\rm obs}$) structure factors. χ^2 is larger than unity for an imperfect fit, and drops to unity when the discrepancy is at the level of the experimental error. χ^2 is equal to 7.6 for the arrangement of 42 atoms in the stacking-fault-island model after adjustment of a scale factor: This shows limited agreement, with significant room for improvement of the model. Other stacking-fault-island arrangements were tried but did not work as well.

We use a difference Fourier map (Fig. 2) to analyze remaining discrepancies between the model and observation in real space. This technique is extremely powerful in locating missing atoms in a structure.[2] There are 12 large peaks in this map indicating the need for extra

TABLE I. X-ray structure factor amplitudes $F^{\rm obs}$ averaged over the pseudosymmetry of Fig. 1. The two-dimensional Miller indices refer to the surface coordinate scheme in the figure. $|F^{\rm calc}|$ are amplitudes calculated for the final model of Fig. 3, after adjustment of a scale factor only. The mean-square residual [Eq. (1)] is $\chi^2=1.8$.

h	k	$F^{\rm obs}_{hk}$	σ_{hk}	$\lvert F^{\rm calc}_{hk}\rvert$
$\frac{1}{7}$	0	0.73	0.25	1.08
$\frac{2}{7}$	0	1.12	0.23	1.25
$\frac{3}{7}$	0	3.45	0.39	2.67
$\frac{4}{7}$	0	2.29	0.37	2.94
$\frac{5}{7}$	0	2.30	0.28	2.25
$\frac{6}{7}$	0	4.40	0.33	4.05
$\frac{1}{7}$	$\frac{1}{7}$	0.91	0.83	0.44
$\frac{2}{7}$	$\frac{1}{7}$	0.80	0.58	0.87
$\frac{3}{7}$	$\frac{1}{7}$	2.08	0.52	1.34
$\frac{4}{7}$	$\frac{1}{7}$	0.42	0.36	0.87
$\frac{5}{7}$	$\frac{1}{7}$	0.40	0.75	0.44
$\frac{6}{7}$	$\frac{1}{7}$	3.95	0.22	3.99
$\frac{2}{7}$	$\frac{2}{7}$	1.80	0.72	0.55
$\frac{3}{7}$	$\frac{2}{7}$	1.10	0.78	0.55
$\frac{4}{7}$	$\frac{2}{7}$	1.46	0.45	0.87
$\frac{5}{7}$	$\frac{2}{7}$	1.73	0.23	2.06
$\frac{3}{7}$	$\frac{3}{7}$	1.78	0.43	1.34
$\frac{4}{7}$	$\frac{3}{7}$	1.71	0.44	0.32

scattering matter in the model. We therefore have direct evidence of adatoms in the Si(111)7×7 structure. These 12 positions are those occupied by the bumps in STM images of Si(111)7×7.[6] Since the averaged data only have meaningful interpretation by models with atoms at bulk lattice sites, we include extra atoms at the nearest allowed sites, marked in Fig. 2. When a Si atom is included at each site, χ^2 drops to 2.1. To determine how many adatoms are required per site, their occupancy is allowed to vary in a least-squares fit: A value 1.2±0.4 atoms results. We conclude that a *single* adatom per site is required.

The model with stacking-fault islands and adatoms comes close to agreement with observation. Improvements were attempted by systematically adding and deleting atoms on lattice sites: Deletion of any of the 54 atoms led to an increase in χ^2. Addition of a third layer vacancy at the origin of the difference Fourier map in Fig. 2 was the only change that led to an improved χ^2 of 1.8; this had been anticipated from the large negative difference peak there (not shown). The resulting model drawn in Fig. 3 gives the calculated structure factors in Table I. As a final test of this model, the errors were analyzed one more time by means of a difference map: Si atoms were then added to the model at the positions of the largest peaks, but their occupancies were found to reduce to <0.2 upon least-squares refinement. We conclude that Fig. 3 represents the gross morphology of Si(111)7×7 at the level of ±1 atom.

The idea that adatoms are involved with the Si(111)7×7 reconstruction is not new,[14] but this is the first direct evidence of their existence. A structure similar to that of Fig. 3 has already been tested[12] and shown to agree with transmission electron diffraction data better than other models; it also agrees with ion channeling results when subsurface relaxations are accounted for.[5] This structure[12] has the same number of atoms and topology as ours, but includes displacements in the third layer (dashed in Fig. 3), also proposed previously.[15] We are insensitive to these because of our symmetry averaging technique. However, if we return to test our raw data, we see a dramatic improvement in the agreement (from $\chi^2=13$ to $\chi^2=4$) when displacements of 0.6±0.15 Å are included (Fig. 3). The displaced atoms have separation of 2.6±0.3 Å suggesting the presence of a covalent "dimer" bond there (2.35 Å in bulk Si). Thus there is consensus among the experimental techniques for the three principal

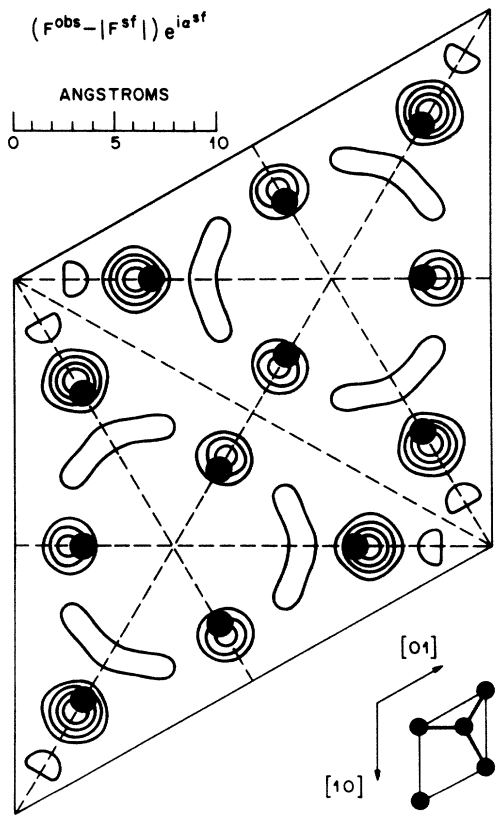

FIG. 2. Difference Fourier map of the 7×7 unit cell. Amplitudes $|F^{sf}|$ and phases α^{sf} were derived from the basic 42 atom stacking-fault-island model described in the text; F^{obs} are the observed amplitudes. Equally spaced positive contours are drawn, the lowest being omitted for clarity. A single bulk unit cell is inset to define the scale and the surface coordinate basis vectors.

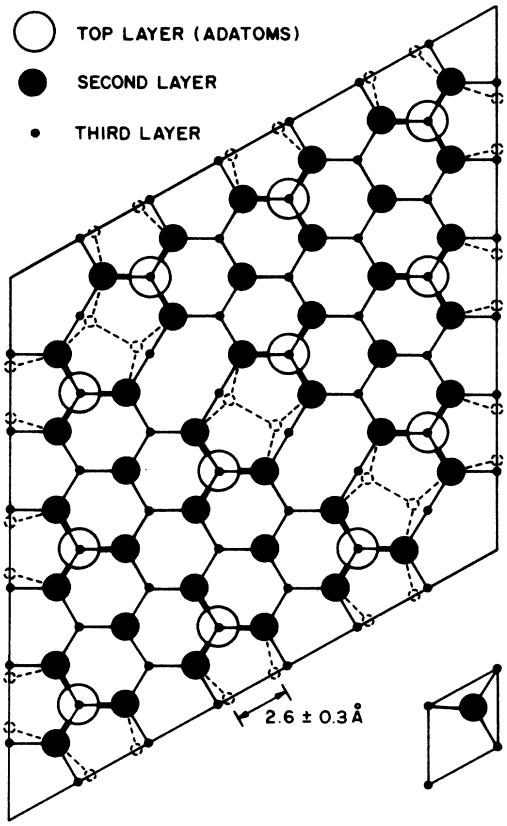

FIG. 3. Lattice model of the Si(111)7×7 reconstructed surface with all displacements removed. The projected atomic positions are uniquely derived from the x-ray data; the bonding scheme and arrangement into layers are deduced. The 42 shaded atoms in the second layer display the triangular antiphase island arrangement that appears because of a stacking fault under half the unit cell. Dashed lines denote displacements that substantially improve agreement with the 73 unaveraged measurements of Fig. 1.

components of the model in Fig. 3 (in order of importance in our analysis): stacking-fault islands, adatoms, and dimers.

In summary, we have shown how symmetry averaging of diffraction data can be used to break a surface structure problem into two sequential steps: determination of the lattice structure followed by the detailed atomic displacements. This is conceptually very important in the early stages of structural analysis because it enormously reduces the number of starting models that must be tried, particularly in the sense that all effects of subsurface strain[5] are removed. The method is expected to be generally useful for large unit-cell surface structural problems. We have shown that an antiphase triangular arrangement of faulted and unfaulted islands agrees with our diffraction data. The remaining differences are then explained by the addition of 12 adatoms and one vacancy, which reduce the total number of dangling bonds from 43 to 19 per unit cell.[12]

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