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Symmetry of Si(111)7×7 at an *a*-Si interface

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The x-ray diffraction pattern of fractional-order reflections from the 7×7 structure at a Si(111)/*a*-Si interface is found to have sixfold symmetry, in contrast to the bulk. This supports the structural model of Takayanagi which has the same high symmetry. Upper limits are placed on the extent of displacements in both the reconstructed and lower, bulklike layers of this structure.

In the past two years there has been a rekindling of interest in a classical problem in surface science: the structure of the clean Si(111)7×7 reconstructed surface. This has culminated in the proposal of a structure by Takayanagi *et al.*[1] which combined the "stacking-fault" principle[2] suggested to explain general features of ion channeling[3] and low-energy electron diffraction (LEED) data with the array of 12 "adatoms" first seen in scanning tunneling microscopic (STM) images[4] and later confirmed by x-ray diffraction.[5] Takayanagi's model was derived from transmission electron diffraction (TED) data[1] and has since been found to be consistent with almost all available structural information.[6,7] Recently, total-energy calculations have shown elements of the model to be energetically favorable[8] as well as the whole 7×7 scheme.[9]

This remarkable consensus notwithstanding, there is one feature of the Takayanagi model which is paradoxical and very alarming: its point symmetry (6*mm*) is *higher* than that of the bulk crystal projected onto the (111) plane (3*m*). This is illustrated in Fig. 1 as an additional mirror plane across the short diagonal of the unit-cell rhombus. The extra symmetry is apparent in all three reconstructed layers of the model and is lost abruptly in the fourth layer which is nominally unreconstructed.[1] The matching up of the three 6*mm* layers with the 3*m* bulk implies that the stacking sequence is "faulted" on one side and "normal" on the other. Tunneling microscope images do not, in general, have the extra symmetry: the asymmetry depends strongly on tip voltage and disappears at certain potentials.[10,11] The difference between the two sides of the STM unit cell can be explained in the context of the Takayanagi model as due to the *electronic structure* of Si(111)7×7 which is sensitive to the presence or absence of the stacking fault between the third and fourth layers (Fig. 1).[10,11] Clear distinction between electronic and geometric contributions to STM images is a difficult problem in which much progress has been made,[12] but which has been limited by the lack of independent structural information. Keating-type energy-minimization calculations[13] have suggested that there may be a real height difference across the unit cell that would break the sixfold symmetry. In this paper we describe a simple test of the symmetry of the *atomic positions* in the reconstructed region alone, and conclude that, within experimental error, it is indeed 6*mm*, and therefore consistent with the Takayanagi picture.

In answering this question, we must perform an experiment which distinguishes the reconstructed part of the sample from the bulk. This is most naturally achieved by

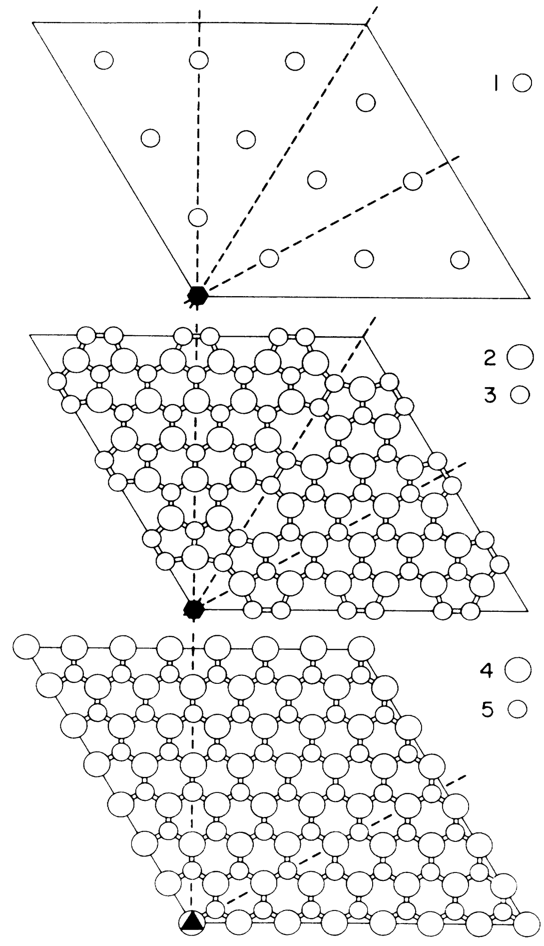

FIG. 1. Schematic diagram of the structural model of the Si(111)7×7 surface due to Takayanagi (Ref. 1). The model is sectioned into double layers, and numbered from the vacuum side. Layer 1 contains the adatoms, layer 2 the stacking fault islands, and layer 3 the dimers and the vacancy at the origin. Layers 4 and 5 and below are nominally unreconstructed. The rhombus is the unit-cell boundary. Symmetry is indicated, layer by layer, by conventional symbols: triangles for threefold axes, hexagons for sixfold axes, and dashed lines for mirror planes.

diffraction methods where the fractional-order reflections contain information only about the regions with the periodicity of the reconstruction: all other structural elements are automatically filtered out. Furthermore, we must consider diffraction with the momentum transfer *out of the plane* of the surface, since Friedel's law adds a center of symmetry which would cause a $3m$ structure to have a $6mm$ in-plane diffraction pattern. The TED (Ref. 1) and x-ray (Ref. 5) studies made previously have been exclusively in-plane measurements and have therefore always shown diffraction patterns with $6mm$ symmetry. LEED is an inadequate technique because multiple scattering will always couple with the bulk to produce $3m$ symmetry. Thus no rigorous test of the symmetry has yet been made.

The required experiment is an accurate comparison of the integrated x-ray diffraction intensities of out-of-plane reflections that would be symmetry related. This was first attempted for the clean reconstructed surface in a custom-built ultrahigh-vacuum (UHV) system,[5,14] but proved to be impossible because the data were not sufficiently reproducible. The weight of the vacuum hardware caused unacceptably large mechanical distortion of the diffractometer. Moreover, only two symmetry equivalents of each reflection could be reached through the Be window, and these repeated only to within 25%. We chose instead to measure a derivative of Si(111)7×7 made by evaporation of Si onto a clean reconstructed substrate at room temperature until an amorphous layer 50—70 Å thick had been formed.[15] This "burying" procedure is known to preserve the 7×7 periodicity[16] at the Si(111)/*a*-Si interface and has the enormous advantage that the structure is encapsulated and can be measured at ambient pressure, without a UHV enclosure. The structure is, however, modified by the disappearance of the adatoms and the ordering of two layers on the *a*-Si side of the interface.[15]

X-ray measurements were made on beam line VII-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). Focused radiation was monochromated with two parallel Si(111) crystals to produce a wavelength of 1.3 Å. The four-circle diffractometer was operated in the symmetric ($\omega=0$) mode to maximize the angles of the incident and diffracted beams with the surface.[14] Only an exit slit was used in front of the detector: this increased accuracy by ensuring that the intensity was fully integrated in the scattering angle (2θ), but at a cost of increasing background levels.[14] The highest counting rates for fractional-order reflections were 30 counts s^{-1} in the signal and 5 counts s^{-1} background. All measured points were taken as rocking-curve scans of the sample orientation angle (ω). These were integrated numerically and background subtracted to give an intensity and error bar (counting statistics in both peak and background).[14]

The dependence of the integrated intensity on out-of-plane (perpendicular) momentum transfer, l, is shown in Fig. 2 for one fractional order $(\frac{6}{7},0)$ and an integer order (1,0) reflection. We have chosen a hexagonal coordinate frame in which the c axis is along the surface-normal [111] direction;[15] the divergence of the intensity at (1,0,1) is therefore the cubic $(11\bar{1})$ Bragg reflection. Because the

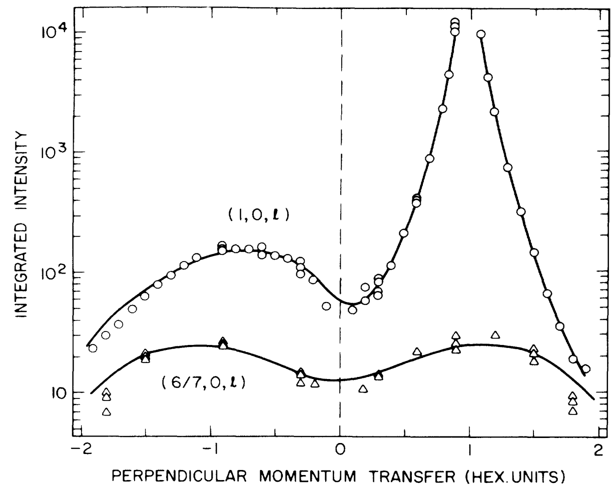

FIG. 2. Out-of-plane measurements of integer-order and fractional-order rods of diffraction from the Si(111)/*a*-Si 7×7 sample. The same vertical scale (arbitrary units) applies to both curves, although crystallographic corrections (Ref. 14) have not been applied. Reciprocal-lattice positions in this paper relate to a hexagonal choice of unit cell for Si, defined by $[100]=\frac{1}{3}[\bar{4}22]_{\text{cubic}}$, $[010]=\frac{1}{3}[\bar{2}\bar{2}4]_{\text{cubic}}$, $[001]=\frac{1}{3}[111]_{\text{cubic}}$. The hexagonal units in the abscissa are therefore fractions of [001]. The solid curve for the $(1,0,l)$ rod is from Ref. 15; that for the $(\frac{6}{7},0,l)$ rod comes from the four-layer model described in the text.

crystalline side of the sample was thick, we could only reach the 7×7 interface from the *a*-Si side and were therefore restricted to $l>0$ measurements. We obtained the $l<0$ data by use of the center of symmetry, $(1,0,l)\equiv(-1,0,-l)$, which makes no assumptions about the sample symmetry. Bulk symmetry ($3m$) equivalent measurements were also made by 120° rotations of the sample and these are included in the figure to show their reproducibility.

$6mm$ symmetry is evident in the fractional-order data as an equivalence of $(\frac{6}{7},0,l)$ and $(\frac{6}{7},0,-l)$ intensity for $l\neq0$. The same result holds for all rods tested: $(\frac{6}{7},0)$, $(1\frac{6}{7},0)$, $(1,\frac{1}{7})$ and $(\frac{6}{7},\frac{1}{7})$. It is very clearly not the case for the integer-order data because these pass through a bulk Bragg peak at $l=1$, but not at $l=-1$. The $(1,0,l)$ data have been analyzed previously and shown to consist of a crystal truncation rod,[17] a bulk feature due to the shape transform of the abruptly terminated crystal lattice, together with contributions from three ordered layers at the interface with partly reversed stacking.[15] Thus the bulk component of this rod determines its $3m$ symmetry.

We would now like to make these arguments quantitative by determining an upper limit to the extent of symmetry breaking in the 7×7 structure, for which we must use a model. First of all, we note that the ordered *a*-Si layers in the interface and the remains of clean reconstructed surface both show the higher symmetry, since either one alone could render the $(\frac{6}{7},0)$ rod unsymmetric. We do not yet have an accurate model of all the atomic coordinates in this system, but good agreement with the intensities of 65 in-plane structure factors[18] is provided by the model inferred in Ref. 15 from Ref. 1: the stacking-fault and dimer layers (numbers 2 and 3 in Fig. 1) are taken from the Takayanagi model; on top of this comes a second faulted layer, identical to No. 2, which is ordered from the *a*-Si; finally a partially ordered layer continues the diamond lattice in the two halves of the unit cell separately. The "adatom" layer (No. 1 in Fig. 1) has disappeared. Other than its $6mm$ symmetry, the details of this approximate model are unimportant to the present discussion.

We measured full sets of symmetry-equivalent intensities at $l=0.9$, close to the $l=1$ position which shows the maximum asymmetry in the integer-order rods. The integrated intensities obtained for $(\frac{6}{7},0)$ and $(1,\frac{1}{7})$ are displayed in Fig. 3. There are systematic variations among these that are larger than the statistical errors in the measurements. This is attributed to nonuniformities across the sample, and is not expected to have threefold symmetry. Indeed, the averages over threefold rotations, 322 ± 5 for $(\frac{6}{7},0,0.9)$ versus 314 ± 4 for $(\frac{6}{7},0,-0.9)$ and 346 ± 7 for $(1,\frac{1}{7},0.9)$ versus 344 ± 4 for $(1,\frac{1}{7},-0.9)$ show differences within the statistical errors, with a magnitude of less than 2.5%.

Perturbations in the model were then made to put a limit on the symmetry breaking in the structure. Deletion of an atom on one side of the unit cell and not on the other is a crude test of the symmetry of the atomic arrangement: this gave asymmetries in the intensity of $(1,\frac{1}{7},\pm0.9)$ and $(\frac{6}{7},0,\pm0.9)$ in the range 3% to 15% depending on the atom chosen. Lateral displacement of a typical atom by 0.4 Å was enough to produce a 2.5% asymmetry; vertical displacement of an atom by 0.1 Å had the same effect. Since perturbations of different atoms cause asymmetry of the diffraction in different directions, it is more important to determine the effect of correlated motions. Close inspection of the Takayanagi model[1] reveals that the most likely way for its $6mm$ symmetry to be broken under the influence of the $3m$ bulk is for the height of *all* atoms to be different on the faulted and unfaulted sides of the unit cell (Fig. 1). This would correspond to a difference in average layer spacing between cubic and hexagonal crystal forms for Si. A height difference of 0.13 Å in the model was needed to produce a 2.5% intensity asymmetry; this is therefore the maximum acceptable value that would be consistent with our data in Fig. 3.

Patterns of displacement that do not have sixfold symmetry in the fourth layer and below (Fig. 1) are also ruled out by our data. In particular, this eliminates the possibility of any displacements at all with 7×7 periodicity in layers 5–8, since these do not contain any sets of atoms related by the sixfold axis in the corner of the reconstructed unit cell, and so cannot have sixfold displacement patterns. It is a remarkable feature of the Takayanagi model that the transition from unreconstructed to reconstructed layers is so abrupt.

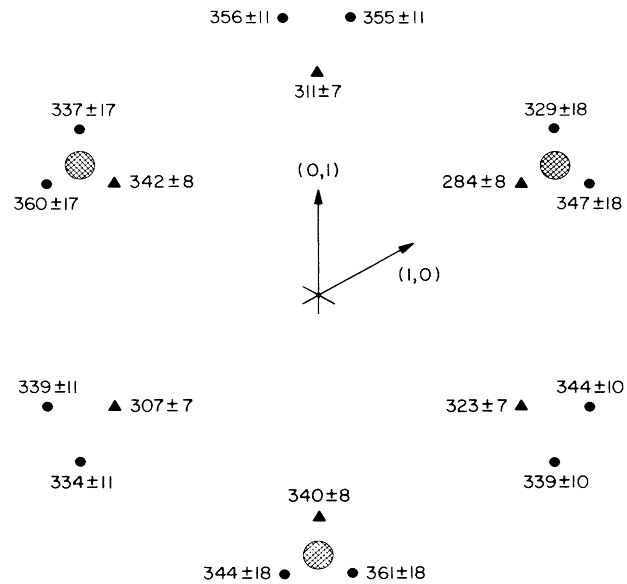

FIG. 3. Integrated intensities of fractional order $(\frac{6}{7},0,0.9)$ and $(1,\frac{1}{7},0.9)$ reflections and their symmetry equivalents displayed as triangles and circles, respectively, in a $l=0.9$ section through the reciprocal lattice. Bulk Bragg reflections at (1,0,1), (0,−1,1), and (−1,1,1) are indicated by large shaded circles and have threefold symmetry. Whether the out-of-plane fractional-order reflections have threefold or sixfold symmetry depends on the symmetry of the reconstructed part of the sample.

We summarize by restating that this is the first critical test of the symmetry, sixfold versus threefold, of the atomic positions in the Si(111)7×7 structure. Although the topmost (adatom) layer was not present in our sample, the second (stacking fault) and third (dimer) reconstructed layers, which are present at the Si(111)7×7/*a*-Si interface, are shown to have sixfold symmetry within 0.13 Å vertically. Since these layers lie closest to the bulk crystal, they are most sensitive to threefold influence. 7×7 displacements, more than a comparable amount, in layers 5 and below are ruled out. The picture is consistent with the Takayanagi model[1] and places an upper limit on the magnitude of symmetry-breaking perturbations to it. The sixfold symmetry, furthermore, is seen to extend to the ordered part of the *a*-Si evaporated layers, suggesting the beginning of epitaxial growth separately on the two halves of the unit cell.

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