Consensus on Silicon Surface Structure Near

Experiment and theory support a recent Japanese model of the elusive structure of a clean silicon surface, thereby bringing a journey of a quarter century close to its end

"FIVE years ago, no one thought the structure would ever be known. Now we can see the details," says John Northrup of Arizona State University, reflecting the satisfaction of surface scientists as they savor the apparent end of a 27-year journey in search of a satisfactory model for the atomic structure of a silicon surface. In the jargon, it is the silicon (111) 7×7 reconstructed surface that is the cause of all the excitement.

Reconstructed means that, in an effort to minimize the extra energy associated with broken bonds at a surface, atoms there assume a different arrangement from that in the crystal interior. As for the 7×7, the lattice spacings of the surface unit cell are seven times that in the interior. Finally, the nature of the reconstruction depends on the crystallographic orientation of the surface. The (111) surfaces correspond to those exposed by diagonally slicing open silicon's cubic crystal structure normal to the line from one corner to the far opposite one.

Because silicon is the key material in the microelectronics industry and because fabrication of integrated circuits depends largely on processes taking place at surfaces, reseachers have a natural interest in silicon surfaces. But the large unit cell with more than 100 atoms makes the notoriously difficult problem of surface structure determination even more so in the case of the 7×7 reconstruction. Accurate calculations of atomic positions from the intensities of spots in its low-energy electron diffraction (LEED) pattern are prohibitively time-consuming on any computer, for example.

Since the 1959 LEED experiments in which the 7×7 reconstruction first turned up, investigators proposed dozens of models for the arrangement of atoms in this surface. It is only in the last few years, however, that new experimental techniques have begun to reveal the crucial clues leading toward a resolution of the surface structure. Finally, in a series of conference presentations and publications from 1982 to the present, a group from the Tokyo Institute of Technology led by Kunio Takayanagi worked out the essentials of what at last seems to be the correct structure.

Takayanagi, Yasumasa Tanishiro, Masaetsu Takahashi, and Shigeki Takahashi derived their 7×7 reconstruction from transmission electron diffraction data. The proposed structure has three key elements, which give it its name, the dimer-adatom-stacking fault (DAS) model, but most surface scientists call it the Takayanagi model. Confirming evidence for its correctness comes from recent scanning tunneling microscopy, grazing-angle x-ray diffraction, and medium-energy ion-scattering experiments.

The Tokyo group tested more than 100 models, says Takayanagi.

Moreover, with a specific structural model to work from, theorists can calculate the electronic structure of the surface with more confidence. Matching the theory with peaks in the existing body of photoemission spectra makes it possible to associate surface quantum states and their energies with specific features of the surface structure.

As a routine tool used in conjunction with transmission electron microscopy, transmission electron diffraction is not in itself new and, as usually practiced, is not surface-sensitive, since almost all the diffracted intensity comes from the interior of a sample. However, in contrast to surface-sensitive electron techniques, such as LEED, it has an important advantage.

As in x-ray diffraction, a high-energy electron interacts with much less than one atom as it passes through the sample. This single-scattering feature makes calculation of the intensities of spots in a diffraction pattern relatively simple. Techniques such as LEED are surface-sensitive precisely because they use low-energy electrons that interact strongly and thereby with many atoms; in effect, the electrons never make it to the interior. However, the resulting multiple-scattering calculations are formidable.

To make transmission electron diffraction surface-sensitive, Takayanagi and his Tokyo colleagues did two things, as did Pierre Petroff of AT&T Bell Laboratories and Robert Wilson (now at the IBM Almaden Laboratory), who also studied the silicon (111) 7×7 reconstructed surface but reached different conclusions. First, they used an ultrahigh-vacuum chamber, quite a novelty until recently for transmission electron microscopy, which has not been widely used for surface studies. Surface scientists have a well-worked out ritual for ensuring that a surface is clean and well characterized, and maintaining a sample in an ultrahigh vacuum is part of it.

Second, they took advantage of what both Japanese and American electron and x-ray researchers were beginning to appreciate; namely, with a reconstructed surface, surface-diffracted beams are scattered into the regions between spots that make up the normal diffraction pattern of the material with enough intensity to be recorded. These extra spots constitute the surface diffraction pattern.

With only diffraction intensities, it is not possible to derive the structure by the technique of Fourier synthesis, which requires both amplitudes (square root of intensity) and phases. However, a trial-and-error procedure is feasible if some guidance is available. As their next step, Takayanagi and his colleagues generated a Patterson map (inverse Fourier transform of the intensities in the diffraction pattern). Peaks in the Patterson map provide clues to the kinds of structural features that are present. From model structures based on these hints, they then calculated the corresponding diffraction patterns. The correct structure was presumed to be the one whose diffraction pattern agreed best with the experimental data.

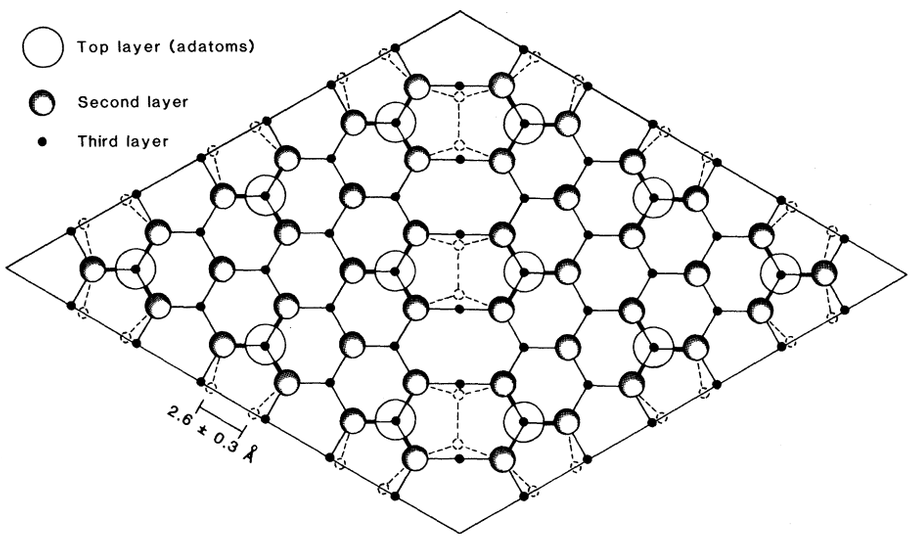
The Tokyo group tested more than 100 model structures in this way, according to Takayanagi, a procedure made feasible by the single-scattering or kinematic diffraction theory that applies to transmission electron diffraction through thin samples only a few hundred angstroms thick. Takayanagi told *Science* he is confident that the lateral or projected positions of the atoms in the DAS model are approximately correct. However, the diffraction data do not yield vertical positions. Moreover, detailed assignments of all atomic coordinates remain to be worked out.

As it happens, each of the three key structural elements were already known, although no one had assembled them in the way the Tokyo group did. To see how they work together, start with the normal silicon structure, which is called diamond cubic. Looked at from the perspective of a (111) crystallographic plane, the structure is generated from a stack of double atomic layers.

As indicated in the drawing, each double layer comprises a honeycomb-like network of buckled hexagons with each silicon atom at a vertex bonded to its three nearest neighbors. Not shown in the drawing are the bonds between double layers needed to complete silicon's tetrahedral covalent bonding geometry.

When a (111) surface is formed by, for example, cleaving a crystal, the bonds between double layers are broken; that is, one electron of the pair that makes up a covalent bond is removed. The missing electrons increase the energy of the surface atoms relative to those in the interior. In the 7×7 unit cell before reconstruction, there are 98 atoms in the outer double layer with 49 unit cell is necessary to maintain reasonably normal bonding between the remaining atoms in the double layer. Stacking fault refers to a change in the orientation of the buckled hexagons in successive double layers. Since only one double layer is shown in the drawing, in which the bonds match as in the interior, it is not possible to tell which is the faulted half. However, the boundary between faulted and unfaulted material, which is called a partial dislocation, is clearly visible.

It runs across the short diagonal of the unit cell and can be seen in two ways. One is by the mirror symmetry across the boundary between faulted and unfaulted material. The other is to look at a row of medium shaded



I. Robinson, AT&T Bell Laboratories

7×7 reconstruction

Top view of the unit cell of the DAS model showing three layers of atoms, the adatom and underlying double layer.

broken bonds located on the atoms in the upper half of the double layer.

In an effort to reduce the energy, the unpaired electrons flow back into the surface, where they try to form so-called back bonds. The resulting interaction is complex, involving a balance between energy reduction due to bond formation and energy gain due to compressive forces arising from the desire of the surface to expand while the underlying crystal lattice constrains it. To accommodate the forces and reduce the associated strain energy, the surface stretches, as it were, by removing eight surface atoms.

In the drawing, there are only 42 medium shaded circles, a loss of seven atoms in the upper half of the double layer, and there are 48 small solid circles (circles on the boundary are shared by two cells and thus count as one-half), a loss of one in the bottom half of the double layer.

A stacking fault within one-half of the circles parallel to the edge of the unit cell. The jog in what should be a straight line marks the boundary. The edges of the unit cell are also boundaries of this type.

The idea of incorporating a stacking fault is generally credited to Peter Bennett of Arizona State University, who, along with several co-workers from Bell Labs, published the idea in 1983. The motivation was to reconcile the 1980 results of medium-energy ion-scattering experiments at Bell Labs by Robert Culbertson (now at Oak Ridge National Laboratory), Leonard Feldman, and Paul Silverman with the results of LEED experiments. From the variation in the intensity of reflected ions, such as hydrogen or helium bombarding the surface at about 100,000 electron volts, with the direction of the incoming and outgoing beams, one can deduce some features of surface structure.

One problem with the removal of atoms and the creation of a stacking fault is that the atoms in the lower half of the double layer that lie along the boundary between unfaulted and faulted material now have broken bonds of their own. To complete these bonds, dimers, represented in the drawing by the linked, small dotted circles, form. The net reduction in broken bonds due to the removal of surface atoms, creation of the stacking fault, and formation of the dimers is six. An additional important role of the nine dimers in each unit cell (once again those on the unit cell boundary count only as one-half) is to stitch together the unfaulted and faulted regions with minimum strain energy. Eion McRae of Bell Labs emphasized the importance of dimers in the early 1980's in his interpretations of LEED patterns.

One can appreciate the importance of strain energy by considering one other way to reduce the number of broken bonds in the upper half of the double layer, namely, by the addition of adatoms, as represented by the large open circles in the drawing. Resting atop the surface like an adsorbed atom, each adatom repairs three bonds, while adding one new one, for a net reduction of two broken bonds for each of the 12 adatoms shown. However, the bending and stretching of the bonds between the surface and the adatoms undoes much of the good by generating strain energy.

Models for the 7×7 reconstruction incorporating adatoms date back a decade to that of Walter Harrison of Stanford University, but the first solid experimental evidence for their presence appeared in the January 1983 publication by Gerd Binnig, Heinrich Rohrer, Christoph Gerber, and Edmund Weibel of IBM's Zürich Research Laboratory of their scanning tunneling microscopy study of the silicon (111) surface. Scanning tunneling microscopy gives atomic-scale topographic images of surfaces. Prominently displayed were 12 humps that the researchers interpreted as adatoms sitting above the rest of the surface. Even more notable were deep holes at the corners of the unit cell, where the missing atom in the lower half of the double layer comes from (atoms at unit cell corners count only as one-fourth).

In retrospect, summarizes Northrup, it is not surprising that the DAS model should be the correct one, as it has fewer broken bonds than any of its competitors. Calculations of the surface energy of several models for the 7×7 reconstruction just reported at the March meeting of the American Physical Society (APS) by Guo-Xin Qian and D. James Chadi of the Xerox Palo Alto Research Center in fact confirm the low energy of the DAS model.

As for confirming experimental evidence, the strongest may be the scanning tunneling microscopy results also presented at the APS meeting by Ruud Tromp of the IBM York-

town Heights Laboratory (see box).

In a third report at the APS meeting, Ian Robinson of Bell Labs described recent grazing-angle x-ray diffraction experiments carried out by him, Warren Waskiewicz, Paul Fuoss, and Jason Stark of Bell Labs together with Bennett that strongly corroborated the DAS model. Ordinarily, x-ray diffraction has the same problem as transmission electron diffraction; it is not surface-sensitive. However, when the x-ray beam strikes the surface at a grazing angle of 1° or less, the phenomenon of total external reflection prevents the x-rays from penetrating into the interior. Because there are few atoms on the surface to scatter x-rays, the method generally requires the use of a bright synchrotron radiation source.

So far, the investigators have been able to record about 70 diffracted beams, as compared to the approximately 500 the Tokyo group analyzed. However, with this information and a different method of attacking the structure derivation, they could independently deduce the stacking fault and adatom features of the reconstruction. Addition of the dimerization feature improved the fit between the model structure and the experimental data.

Last year, Tromp and Evert van Loenen of the FOM Institute for Atomic and Molecular Physics in Amsterdam analyzed their medium-energy ion-scattering data for the 7×7 reconstructed surface. Particular advantages of ion scattering are that the physics of the scattering is straightforward and that scattering cross sections are well known. Hence, the researchers were able to compare their experimental data with that calculated for numerous proposed models of the 7×7 reconstructed surface. Unfortunately, ion scattering was not sensitive enough to all the features of the surface structure to select just one model, although among the four survivors the DAS model fit best.

An important outcome of this work, however, was the recognition that, in surface reconstructions, more than just the outer layer of atoms are involved in the process of minimizing strain energy. In their calculations, Tromp and van Loenen had to allow atoms to move (relax) in the outer five monolayers to get satisfactory agreement between the simulated and experimental data. In the DAS model, this corresponds to the top two double layers and the adatom layer. ■ **ARTHUR L. ROBINSON**

ADDITIONAL READING

K. Takayanagi, Y. Tanishiro, S. Takahashi, M. Takahashi, "Structure analysis of the silicon (111)-7×7 reconstructed surface by transmission electron diffraction," *Surf. Sci.* **164**, 367 (1985).

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STM Evidence for Silicon (111)

The scanning tunneling microscope (STM) generates topographic images of surfaces with atomic resolution. But, suggestive as the images are, their interpretation is not so straightforward, as reviewed recently in the context of silicon in *Science* by Jene Golovchenko of AT&T Bell Laboratories. The problem is to separate the strictly topographic information (where the atoms are) from that due to the presence of electronic quantum states peculiar to the surface. Tunneling of electrons between these states and the fine wire tip of the STM that scans over the surface can distort the images, for example. However, these effects also provide an opportunity to obtain spatially resolved spectroscopic information about the surface states.

Ruud Tromp, Robert Hamers, and Joseph DeMuth of the IBM Yorktown Heights Laboratory claim to have found a way simultaneously to deal with the problem and exploit the opportunity. At the March meeting of the American Physical Society in Las Vegas, Tromp described how their technique works as applied to the silicon (111) 7×7 reconstructed surface. Their topographic images dramatically confirm the so-called DAS model of the reconstructed surface (see main story), and their spatially resolved tunneling spectra permit the attribution of surface quantum states to specific features of the reconstructed structure.

To deconvolve structural from electronic contributions to STM images, the IBM physicists extended a relatively straightforward method called superposition of atomic charge densities that had been developed for metals by Jerry Tersoff (now at IBM) and Donald Hamann of Bell Labs to calculate what the topographic image of a surface should be. The charge densities reflect only the atomic geometry. By comparison with experimental results on the surfaces of several materials, including silicon, the investigators found that they could distinguish between geometric and electronic features on the basis of the differences in images taken with positive and negative voltages on the sample relative to the STM tip.

Having done this for the 7×7 reconstructed surface, they then compared the observed image taken under positive voltage conditions that exclude electronic contributions peculiar to the surface with images computed by the superposition of atomic potentials method for several model structures, including the DAS model. The agreement between the image calculated from this model and experiment was striking, whereas all other models considered fared poorly. Tersoff told *Science* he was initially surprised the method worked so well but thinks it unlikely that such a close fit could be an artifact.

For spectroscopic information, one measures the tunneling current as a function of the voltage. The IBM researchers devised an electronic technique for obtaining such curves while maintaining the STM tip at a constant distance above the surface (necessary for topographic imaging) and while scanning a surface at the normal rate of about 100 angstroms per second, so that they could obtain topographic and spectroscopic information during the same scan.

From the tunneling spectra averaged over the entire unit cell of the reconstructed silicon surface, they could deduce the energies of several surface quantum states. Moreover, by computer subtraction of images corresponding to voltages just above and just below that at which a particular surface state begins to contribute to the tunneling, they could generate images of the spatial distribution of these states in the unit cell with a resolution of about 3 angstroms. From the distribution of each type of state, the investigators ventured to assign their origin to specific features of the reconstruction.

States identified in this way included broken bonds on the 12 adatoms, broken bonds on the 6 atoms in the upper half of the double layer that are not repaired by adatoms, and back bonds between the adatoms and the surface in the DAS model. As it happens, John Northrup of Arizona State University had been calculating the types of surface quantum states one should expect from the DAS model and reported at Las Vegas that he had found in simplified versions these same three states, whose electronic properties also are in good agreement with those inferred from the large body of photoemission data. ■ **A.L.R.**

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J. A. Golovchenko, "The tunneling microscope: A new look at the atomic world," *Science* **232**, 48 (1986).