Atomic-Resolution TEM Images of Surfaces

The newest electron microscopes that crack the 2-angstrom barrier can resolve atom positions on metal and semiconductor surfaces

Most of the action in such industrially important processes as heterogeneous catalysis, corrosion, and microelectronic circuit fabrication takes place at surfaces. But knowledge of surface structure at the atomic level is frustratingly hard to come by. The silicon from which microcircuit chips are made, for example, is probably the most thoroughly researched material one could name. Yet, scientists who recently attempted a structural analysis of a clean silicon surface had to consider a partial listing of 17 existing models for where the atoms sit before proposing yet another one.

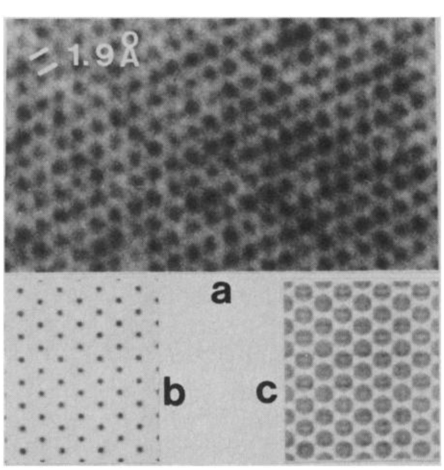
Illustrating the importance researchers attach to having atomic-resolution surface models is the rate at which the newest generation of transmission electron microscopes (TEM's) is making its way into academic and industrial laboratories, despite an almost $1-million price tag and relatively few reports in the literature that substantiate its imaging prowess. According to Robert Sinclair of Stanford University, who is in the process of making a purchase, a dozen or more U.S. laboratories have bought or are buying these high-resolution instruments, which are equally useful for investigating internal interfaces, such as the boundaries between materials.

At the same time, in a series of experiments begun at the University of Cambridge in England and continued at Arizona State University with small gold particles and thin foils, Laurie Marks and David Smith have convincingly demonstrated one way to exploit the new generation electron microscopes for surface structure determinations. A particularly striking feature of the "profile imaging" technique they use is that it takes advantage of the ability of high-resolution instruments to generate images that have a one-to-one correspondence with the actual arrangement of atoms in suitably thin specimens.

Another virtue is the ability to image in real time dynamical structure changes by means of a video-recording system. Last January, for example, at an electron microscopy conference held at Arizona State, Sumio Iijima of the Research and Development Corporation of Japan in Nagoya showed "movies" taken by him and Toshinari Ichihashi tracking with time the motion of surface atoms in small gold particles 20 to 80 angstroms in diameter (*1*). The smaller particles changed shape in a fraction of a second and seemed to have an almost liquid-like quality as they changed. In recent experiments at Arizona State, Smith collaborated with Jan-Olav Bovin and Reine Wallenberg of the University of Lund in Sweden also to record the motion of individual atoms at and just above the surface of tiny gold clusters containing only 55 atoms (*2*).

To those in the field, high-resolution transmission electron microscopy refers to the kind of images obtained when a crystalline material is oriented so that atoms are arrayed in columns parallel to the direction of the electron beam. The magnetic objective lens of the electron microscope collects some (the larger the number the better) of the diffracted beams emerging from the other side of a very thin sample (preferably 100 angstroms or less) and focuses them. Interference between the diffracted beams generates what is termed a lattice image.

Lattice images look like a projection along the direction of the electron beam of the sample's crystal structure, but interpretation is actually much more difficult. Depending on factors that are both fixed (the atomic spacings in the sample and the resolution of the microscope) and to some extent controllable (the thickness of the sample and the focusing conditions in the microscope), for example, black spots in the image may appear at the positions of the columns of atoms (or groups of closely spaced columns), in the tunnels between columns, or at some more arbitrary position. It is generally necessary to make computer simulations of the images expected from model structures, which can be matched with actual images, in order to have any confidence in proposed interpretations of electron micrographs.



A. Ourmazd, AT&T Bell Laboratories

Silicon <111> projection

(a) The experimental atomic-resolution structure image showing atom columns 1.9 angstroms apart. (b) Projection of the silicon diamond cubic crystal structure. (c) Computer simulation of the image expected under optimum focusing conditions in the microscope.

Some years ago, John Cowley of Arizona State proposed the term "structure image" for the restricted set of lattice images that may be directly interpreted, at least up to the resolution of the microscope; that is, black spots do in fact represent the positions of atom columns (or groups of closely spaced atom columns). While the new generation of TEM's can make atomic-resolution structure images of many metals and semiconductors, even when they cannot, they are capable of resolving features about which previous microscopes could provide no useful information.

Consider the case of semiconductors, of which silicon is the most important example. Many semiconductors have a cubic crystal structure in which two atoms are associated with each corner and with each face of the cube, so that each atom has four equally spaced nearest neighbors at the points of a tetrahedron. Only a few orientations of the cube result in neat projected images of columns of atoms with tunnels between them. The main such orientations are those in which the electron beam direction is along an edge of the cube, a diagonal on the cube face, or a diagonal through the cube. To resolve atom columns, the distance between the columns must be greater than the so-called point-to-point resolution of the microscope.

Until recently, this condition held only when the electron beam direction was along the diagonal of a cube face (<110> orientation). Even for this orientation, the resolution was not quite good enough to resolve individual atom columns but only pairs of closely spaced columns in the projection. In silicon, the spacing in the <110> projection between the atoms comprising a pair is 1.4 angstroms, well below the 2.5-angstrom resolution of the electron microscopes available up to now, whereas the spacing between pairs is about 3.1 angstroms.

Earlier this month, Abbas Ourmazd of AT&T Bell Laboratories, Holmdel, New Jersey, Karl Ahlborn of the University of Göttingen in West Germany, and K. Ibeh and Toshikazu Honda of JEOL, Ltd. in Tokyo, published the first structure images of silicon (*3*). The experiments were done on a JEOL 4000EX, which is one of the new generation TEM's and has a point-to-point resolution that is guaranteed by the manufacturer to be at least 1.8 angstroms. While this resolution is not good enough to resolve the atom pairs in the silicon <110> projection, it is just sufficient for atomic resolution images in the cube edge (<100>) and cube diagonal (<111>) projections, where the smallest spacing is 1.9 angstroms.

Taken together the different projections point up another potential advantage of the higher resolution instrument. The atom pairs in the <110> projection are an artifact of the projection. The atoms, all of which are equally spaced in three dimensions, are really farther apart than 1.4 angstroms; it is only in that projection that they appear to be so close and paired. By using one of the mathematical techniques of the type used in x-ray and other medical imaging scanners and known as reconstruction from projections, it is in principle possible to generate a three-dimensional atomic structure from several projections. Several electron microscopists told *Science* that this is one of the most exciting possibilities on the horizon, although there are numerous practical difficulties to be overcome.

Atomic-resolution TEM's did not just spontaneously appear in manufacturers' catalogs but are the result of extensive research projects. For many years, the highest resolution instruments had electron beam energies of 100,000 electron volts (100 keV). Resolution depends on the quality of the magnetic lens (spherical aberration coefficient) and the electron beam energy. Once manufacturers had pushed lens quality as far as it could go, 100-keV instruments were still limited to a point-to-point resolution of about 2.9 angstroms under ideal conditions. The next step was to raise the beam energy to 200 keV, which improved the resolution to 2.3 angstroms at best.

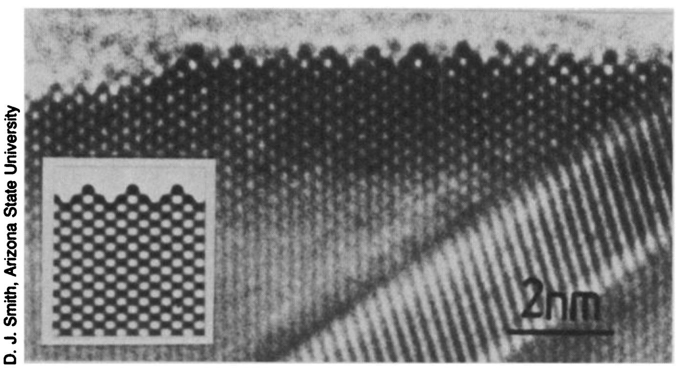
Electron microscopes with beam energies of 1-million electron volts (1 MeV) or higher were in existence at the time, but they were not primarily aimed at achieving ultrahigh resolution. In order to achieve atomic resolution, the electron beam energy must be constant to within a part per million or less, which requires the electronics that supply the accelerating voltage to be equally stable. A similarly rigorous stability requirement holds for mechanical vibrations. These performances are harder to achieve as the beam energy increases.

In the early 1970's, a project began at Cambridge to build a 600-keV electron microscope with sub-2 angstrom resolution. This instrument has been operating for several years, and after some improvements recently reached this goal. An even more ambitious goal was set for scientists and engineers at Hitachi, Ltd. and at JEOL, which won multimillion dollar contracts to develop atomic-resolution 1-MeV electron microscopes for the Tokyo Institute of Technology and the Lawrence Berkeley Laboratory, respectively.

Although the 1-MeV instruments achieved a 1.6-angstrom resolution, they are too large, requiring two-story buildings to house them, and too expensive for most laboratories. Drawing from its experience on the 1-MeV projects, however, JEOL has developed a smaller 400-keV version, the 4000EX, of the larger machine that has atomic resolution and conveniently fits into existing laboratory spaces. Hitachi and the Dutch company, Phillips, are also offering 300-keV electron microscopes with guaranteed point-to-point resolutions of 2 angstroms or less.

It was with the Cambridge instrument that Marks and Smith began their profile-imaging studies of the surfaces of gold particles. The obvious problem with transmission electron microscopy of surfaces is that the electrons spend most of their time in the interior of the sample, so that relatively little of the diffracted intensity represents the surface structure. It is possible, however, to extract surface information because electrons diffracted at the surface travel in different directions from those diffracted in the interior. A particularly elegant example of how to take advantage of this fact is an analysis of a clean silicon surface that was reported last May by Kunio Takayanagi and several co-workers at the Tokyo Institute of Technology (*4*).

In the manner of crystallographers deriving a structure from x-ray diffraction patterns, the Tokyo investigators, who worked with the 1-MeV atomic-resolution microscope, used the positions and intensities of surface diffracted beams to construct a model of the silicon surface, the so-called transmission electron diffraction technique. It would also be possible to use the surface diffracted beams to directly image the surface with atomic resolution, except that it is necessary to block the beams diffracted from the interior. To accomplish this requires narrowing the aperture to accept only a small number of surface diffracted beams, which limits the resolution.



D. J. Smith, Arizona State University

Gold (110) surface

Atoms on metal and semiconductor surfaces often assume structures different from those in the interior. This <110> projection shows in profile the so-called 2 × 1 reconstruction on the (110) surface of a small gold particle.

Profile imaging of surfaces gets around this difficulty by, as the name implies, imaging the edge of a sample, which is parallel to the electron beam, rather than the surface that is normal to it. The method was first applied at Stanford, by Sinclair, Tom Yamashita, and Fernando Ponce, who reported in 1981 that they had observed the motion of atoms along the edge of a thin cadmium telluride specimen (*5*). Motion was inferred from the fact that a sequence of micrographs taken several minutes apart showed some atom-pair columns to have changed position. Cadmium telluride is a semiconductor that has a structure like that of silicon with the difference that each cadmium is surrounded by a tetrahedron of telluriums and each tellurium by a tetrahedron of cadmiums. With the 100-keV electron microscope used, the spots in the <110> projection were therefore cadmium-tellurium pairs, members whose are 1.6 angstroms apart.

The next year, the Stanford researchers collaborated with Smith and several

Cambridge colleagues to make dynamic images with the use of a video recording system on the Cambridge electron microscope. While these experiments demonstrated the motion of various defects, such as dislocations, in the interior of the cadmium telluride, they did not succeed in reproducing images of the motion of surface atoms. Also, for various reasons, the effective resolution in the video images was only about 3 angstroms.

Building on this work, Marks and Smith proceeded to make true structure images of small gold particles, which they reported in 1983 (*6*). The structure of gold is simpler than that of silicon, as there is a single atom associated with each corner and face of a cube (face-centered cubic structure), however, the important crystallographic directions are the same. In the <110> projection, lattice spacings are 2.35 and 2.04 angstroms.

One remarkable outcome of these experiments concerned a particular orientation of the gold surface; namely, the (110) surface, which is the one that would appear if the cubic crystal structure was sliced open by a plane cutting diagonally from one cube edge to the opposite. Three of the most promising new tools for surface structure analysis, scanning tunneling microscopy, grazing-incidence x-ray diffraction, and the profile imaging of Marks and Smith, agreed on the structure of that gold surface, whose atoms adjust their positions to minimize the energy associated with broken chemical bonds. Subsequent studies showed that it was possible to measure quite accurately small atomic displacements connected with the reconstruction, such as a relaxation that pushes the gold atoms outward by about 20 percent, provided that computer simulations of model structure are matched with the actual micrograph.

The most recent dynamic images of the surface atoms on tiny gold particles by Iijima and Ichihashi and by Bovin, Wallenberg, and Smith, which under the heating effect of the electron beam seem not simply to diffuse by hopping along the surface but to form swirling clouds that suck up atoms from one location and deposit them in another, raise the hope of observing in real time with atomic resolution such industrially important processes as the growth of thin layers during the fabrication of microcircuits.

Recently at Stanford, for example, with the aid of a specimen holder whose temperature could be controlled up to several hundred degrees centigrade, Michael Parker and Sinclair have made lower resolution lattice image "movies" of the epitaxial regrowth of an amorphous silicon layer on a crystalline silicon substrate; that is, the amorphous layer near the substrate becomes crystalline when heated (*7*). Such a process may figure prominently in future advanced microcircuits that have ultraminiature transistors lying one atop the other, as well as side by side on a chip, as at present.

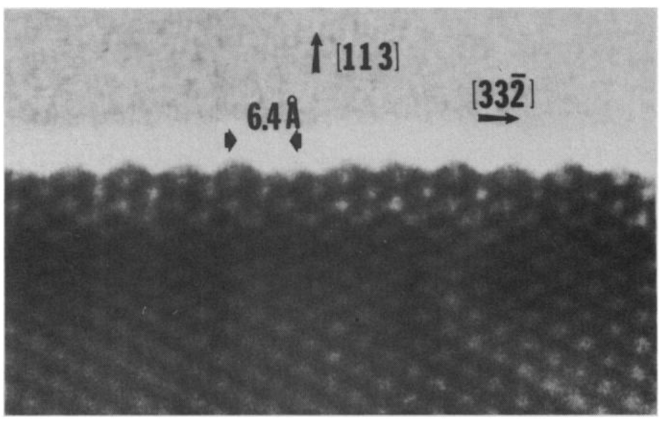
If there is one criticism of the experiments by Marks and Smith with gold particles and foils, it is the lack of an ultrahigh vacuum environment for their specimens. Surface scientists adamantly insist that samples be prepared and cleaned in a vacuum of 10^{-10} torr or better in order to avoid misinterpretations due to uncontrollable and unreproducible contamination. Most electron microscopes do not have vacuums much better than 10^{-6} torr. Because of its chemical inertness, gold resists surface contaminations, which is one reason it was chosen for study.

Nonetheless, there is a trend toward upgrading electron microscopes with better vacuum systems. The improved systems are still not quite what surface scientists would like, but electron microscopes are not naturally compatible with ultrahigh vacuums. The 1-MeV atomic-resolution microscope in Tokyo, for example, is equipped to provide a sample environment characterized by a vacuum close to 10^{-8} torr, and a lower resolution instrument at Bell Labs Murray Hill campus can reach 10^{-9} torr.

With the latter instrument, Murray Gibson, Michael McDonald, and Frank Unterwald have used the profile-imaging method to make lattice images in the <110> projection of silicon surfaces (*8*). The Bell Labs' researchers found that on heating the sample to over 1000°C, the edges of the plate form facets with orientations of the type normally studied by surface scientists [(100), (110), and (111) surfaces] and also one not ordinarily observed, the (113). The reason for this is that surface scientists usually prepare a particular surface in advance by cutting, polishing, and cleaning the one they want to study. On heating, the edge of a thin plate, however, is free to facet with orientations of its choice, usually the ones of lowest energy. The appearance of the (113) surface may mean that surface scientists have been in error in assuming that only the "important" high-symmetry surfaces are worthy of study.

Finally, while the new generation of TEM's makes possible true structure images of metals and semiconductors, it does not follow that the era of computer simulation of images is over. For example, most of the interesting and important problems involve imperfections of one sort or another, which by definition do not involve extensive arrays of well-ordered columns of atoms. As Michael O'Keefe, an electron microscopist working with the 1-MeV atomic-resolution microscope at Berkeley, points out, in these cases computer simulations will always be essential. Another important example comprises materials, such as the zeolites that are currently of so much interest to the petroleum industry for use in heterogeneous catalysts, that cannot be thinned to 100 angstroms or less. Thick samples do not give directly interpretable structure images and hence require computer simulations.

—**Arthur L. Robinson**



J. M. Gibson, AT&T Bell Laboratories

Silicon (113) surface

A <110> profile lattice image shows that atoms on this surface have the same periodicity as in the interior, a 1 × 1 reconstruction that is apparently characterized by the formation of an extra chemical bond between some surface atoms (dimerization).

References

1. S. Iijima and T. Ichihashi, *Jpn. J. Appl. Phys.* **24**, L125 (1985); ______ in preparation.
2. J.-O. Bovin, R. Wallenberg, D. J. Smith, *Nature (London)* **317**, 47 (1985).
3. A. Ourmazd, K. Ahlborn, K. Ibeh, T. Honda, *Appl. Phys. Lett.* **47**, 685 (1985).
4. K. Takayanagi, Y. Tanishiro, M. Takahashi, S. Takahashi, *J. Vac. Sci. Tech. A* **3**, 1502 (1985).
5. R. Sinclair, T. Yamashita, F. A. Ponce, *Nature (London)* **290**, 386 (1981).
6. L. D. Marks and D. J. Smith, *ibid.* **303**, 316 (1983).
7. M. A. Parker and R. Sinclair, in preparation.
8. J. M. Gibson, M. L. McDonald, F. C. Unterwald, in press.