

Vacuum tunneling: A new technique for microscopy

The scanning tunneling microscope resolves individual atoms on surfaces by probing the surface electron wavefunctions with the tip of an extremely sharp needle, revealing a new world of steps, terraces and atomic arrays.

Calvin F. Quate

I was introduced to vacuum tunneling high over the Atlantic while flying to London in April 1982. For months prior to that flight I had been fretting about the future work of our microscopy research group at Stanford. We had just completed our work in acoustic microscopy and were looking for new directions. I was considering a variety of problems, such as the building of an x-ray microscope, but nothing would fall into place. I thought that a trip to a conference in London might provide some time to get away and think. On the way to the airport I stopped by my office and picked up the latest issue of this magazine. I think we were over Iceland when I opened it and found a report (PHYSICS TODAY, April 1982, page 21) on a new form of scanning microscopy being developed¹ in Zurich. In London, I changed my travel plans and went to Zurich. It proved to be the start of an adventure for our group, an adventure that still continues, undiminished in excitement.

What I saw in Zurich was a microscope that was very simple yet was able to resolve clearly monatomic steps on the surface of a crystal. The technique is elegant. One positions the tip of an extremely sharp needle so close to the surface of the sample that the wavefunctions of electrons in the tip overlap wavefunctions of electrons in the surface. Applying a small voltage between the probe and the surface then causes electrons to tunnel through the vacu-

um. Because the electron wavefunctions decrease exponentially with distance, the tunneling current is extremely sensitive to the separation of the needle tip and the surface. As a result, when one scans the probe across the sample, surface features as small as atoms show up as variations in the tunneling current.

The details of my first visit to Zurich are still vivid in my memory. I knew nothing of vacuum tunneling but I was convinced that I would recognize a vacuum-tunneling instrument if I saw one. I met three members of the team working on vacuum tunneling: Heinrich Rohrer, with his talent for selecting new fields of research at the appropriate time; Gerd Binnig, with his determination to probe the elusive domain of atoms; and Christoph Gerber, with his large reservoir of good humor and his ability to make things work. I was allowed to look inside a huge book bulging with their accumulated chart recordings. I caught glimpses of a new world, a world of steps and terraces and atomic arrays.

The data that come from scanning-tunneling-microscope images are accurate and distinctive, as one can see in figure 1. The notes on my visit to Zurich read, "Resolution is 4 Å (amazing)." The lateral resolution has since been reduced to 1 Å and it is possible to detect much smaller shifts in the periodic array of atoms. The height corrugations can be determined to within 0.01 Å. This accuracy, which has not been available heretofore, gives theorists a fresh incentive to work on surface structure. The work² of theorists at places ranging from IBM, AT&T Bell Laboratories and Xerox to

the Universidad Autonoma in Madrid and the Università la Sapienza in Rome is indispensable for our understanding of the images.

What I saw during the first few minutes of my visit in Zurich determined the future of our research program at Stanford. I returned home, described the traces on the chart recorder to our graduate students and persuaded one of them, Scott Elrod, to make a mid-course adjustment in his career. He had only the crude sketches that I had carried from Zurich, but with those he was able to build a scanning tunneling microscope. He went on from there to write the first dissertation in the field.

Four generations. The microscope I saw in Zurich was the "second generation" machine. The "first generation" machine, built in 1981, was a complex structure that relied on a superconducting metal bowl. This allowed levitation of the entire system in a magnetic field, to suppress the low-frequency vibrations that are part of the laboratory environment. I wanted to examine this complex for myself, to determine if it was an essential component. But I never saw the superconducting bowl; it seems to have disappeared in the second-generation machine. The new model replaced levitation with eddy-current damping. The simplification in design between the first- and second-generation machines was impressive. The second-generation machine established a pattern that many have followed; it provided us with a good design and sound architecture.

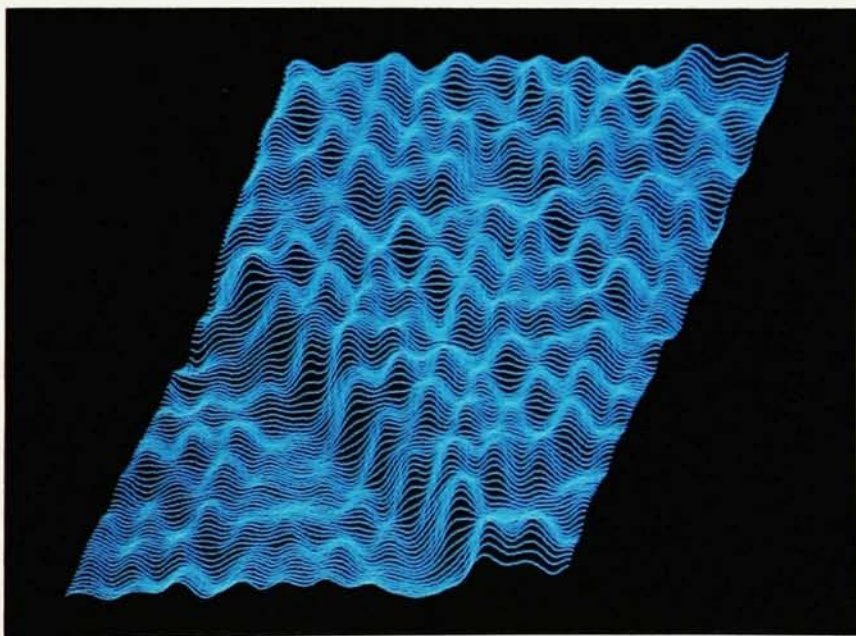
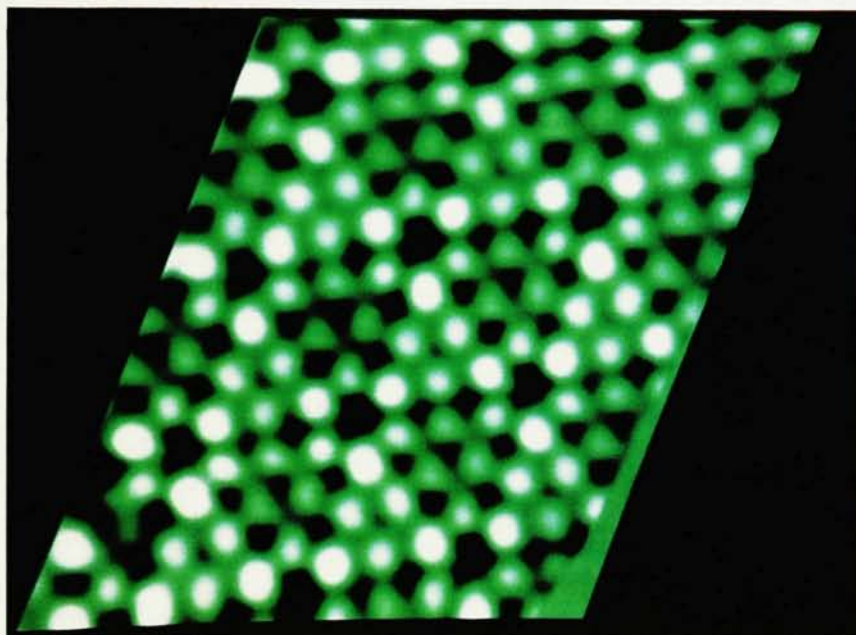
Ironically, had my visit to Zurich been one year later, I would have been deterred by the "third generation"

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Reconstructed silicon surface as seen by the scanning tunneling microscope.

When silicon is heated to 900 °C the surface atoms rearrange themselves into a structure different from that of the bulk atoms. The formation of this new, two-dimensional surface array is called reconstruction. The structure of the reconstructed (111) surface of silicon was known from low-energy electron-diffraction patterns, but the scanning tunneling microscope gave the first direct images of the spatial positions. Top: Image in the form of intensity modulation on a cathode-ray tube. Bottom: The individual traces for another reconstructed silicon surface, showing a step. (Courtesy of Sang-il Park.)

Figure 1



machine.³ In the third generation, the machine's complexity had somehow returned. It was a rather large, tower-like structure made entirely of quartz—to protect against thermal drifts in the position of the probe—and was built in such a way that the damping magnets could be far from the sample—to alleviate concern that stray magnetic fields might disturb other, more conventional measuring techniques. We called this structure the "quartz scaffold." It, too, has disappeared. Its replacement—the "fourth generation" machine—is so small and efficient that it has been dubbed "the pocket microscope."

Beginnings

The scanning tunneling microscope had its beginnings in Frankfurt in 1978, in a conversation between Rohrer and Binnig, who was then a graduate student at Wolfgang Goethe University in Frankfurt. Rohrer was outlining the program on surface science to be established at IBM Zurich. During the discussion, Binnig suggested that vacuum tunneling was the proper tool for the new work. When Binnig arrived in Zurich in November of that year he started immediately to explore new ideas on vacuum tunneling—what a probe might be like, how it might scan the surface.

Binnig wanted to scan surfaces with a fine probe, perhaps a metal whisker, but thermal vibrations worried him. He soon learned that the amplitude of the thermally induced motion would depend on the aspect ratio of the probe. In whiskers that are long and narrow the motion would be intolerable. With short, stubby probes the vibrations

could be tolerated, but how could such stubs probe fine details on a surface? The entry in Binnig's notebook dated 5 January 1979, shown in figure 2, provides the answer. There Binnig notes that the exponential decay of tunneling current between the spherical surface of the tip and the plane surface of the sample is sufficient to confine the

current to a diameter of 45 Å. This must have been the crucial step for all that followed.

In two short years Binnig and Rohrer built the first instrument in Zurich. At 2:00 a.m. on 18 March 1981, the traces on the xy chart recorder showed clear evidence that electrons were tunneling through the vacuum barrier. Some

Lab notes. At the bottom of this page from Gerd Binnig's lab notebook is his 5 January 1979 entry indicating that the current from a tip 1000 Å in diameter is confined to a region only 45 Å in size. The region is so small because the tunneling current between the tip and the sample decreases exponentially as the space between the tip and the sample increases. Later it was found that protrusions on the tip can reduce the tunneling region to less than 10 Å, as figure 3 indicates. Figure 2

weeks later Binnig and Rohrer observed the sharp, repeated steps that replicated the atomic steps from terrace to terrace on their gold sample.

It was not the tunneling current that caught everyone's attention. It was the sharp, repeated steps. Binnig and Rohrer could easily have stumbled and missed these steps. They were difficult to record. In the first instrument the controls were not precise and the tip always touched when they tried to bring it close to the surface of the sample, damaging the surface. Binnig continued, hour after hour, to work with the controls; then suddenly, during the 12th hour, and for no apparent reason, steps appeared on the traces of the chart recorder—steps that were measured in atomic dimensions. Binnig and his group not only recorded the first sharp atomic steps but also saw faint atomic-sized bumps on the lateral terraces. It was much later when they realized what was happening. Differential thermal expansion, introducing relative motion between the various components, moved the tip away from the damaged region onto a smooth untouched region of the gold surface. A small protuberance on their blunt, rough probe was serving as a miniature tip with a very small radius of curvature, as shown in figure 3.

The crew in Zurich must have been startled as they watched those first traces appear on the chart recorder, traces that marked the atomic structure of the gold surface. Their calculations had indicated an expected resolution of 45 Å in the lateral plane. To resolve single atoms, as they were doing, requires a resolution of 2 Å. The difference between 45-Å and 2-Å resolution, attributable to the small protuberance on the tip of their probe, is enormous. The importance of the scanning tunneling microscope—the feature that sets it apart from other instruments—is that it can resolve details in the vicinity of a single atom. If the resolution had been limited to 45 Å the scanning tunneling microscope would have been just one more scanning probe for surface studies. It would

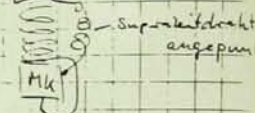
Date and sign every entry. Have every possibly important entry witnessed. Submit an Invention Disclosure of anything possibly new and inventive.

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IBM Technical Notebook

8 83365

22.12.78 Zum Erden der Probe:



3.1.79 Längenfluktuationen

Stab: Länge L , F -Fläche $= F$
 elast. mod. k^*

$$\Delta x = \frac{K}{k^* \cdot F} \Rightarrow K = \frac{k^* \cdot F \cdot \Delta x}{1}$$

$$\text{Energie } E = \frac{1}{2} \frac{k^* \cdot F}{L} (\Delta x)^2$$

$$k^* = 40^{12} \text{ dy} = 10^9 \text{ N}$$

$$\text{für } \Delta x = 0,1 \text{ Å} = 10^{-10} \text{ m} \Rightarrow E = \frac{1}{2} \frac{10^9 \text{ N} \cdot 10^{-10} \text{ m}^2 \cdot 10^{-18} \text{ cm}^2}{1 \text{ cm}^2} = 10^{-19} \text{ Nm} = 10^{-19} \text{ J} \approx 60 \text{ eV} \approx 6 \cdot 10^5$$

$\Rightarrow$ Längenfluktuationen vernachlässigbar!

3.1.79 Wie lang Stab von 100 Å, damit $\Delta x = (x = 0,01 \text{ Å})$ oder $L = 100 \text{ Å}$

Hubwert $L \approx 91 \text{ Å}$

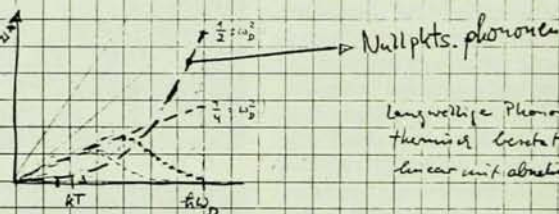
$\Rightarrow$ dünne kurze Fäden + Problem

3.1.79 Nullpts. energie: $U_0 = \frac{1}{2} \frac{k^* \cdot F}{L} (\Delta x)^2$

3.1.79 $\langle u^2 \rangle = \text{effektive Dispersung}$

= Zustandsdichte mal $\langle u^2 \rangle$

Phononen: ω



langwellige Phononen sind im therm. Bereich und verhalten sich linear mit abnehmender Temp.

Mit einer Tunnelstromabhängigkeit von 7 Å und einem Krümmungsradius der Nadel von 1000 Å

$\Rightarrow$ Ortsauflösung $\Delta x = 45 \text{ Å}$

$\Rightarrow$ Mikroskop für Metall (Halbleiter-) Oberflächen

The above understood and witnessed by

Date

and by

Date

not have created the excitement that now surrounds it.

The small protuberances that reduce the area for the tunneling current and lead to the improved resolution in the scanning instrument occur naturally on certain metal surfaces. On tungsten needles the protuberances and the exponential decay of the tunneling current as the tip-to-sample spacing is increased combine to give tips that are in effect less than 10 Å in diameter. These natural tips are often short-lived, but they serve us well while other, more elaborate techniques are being developed.

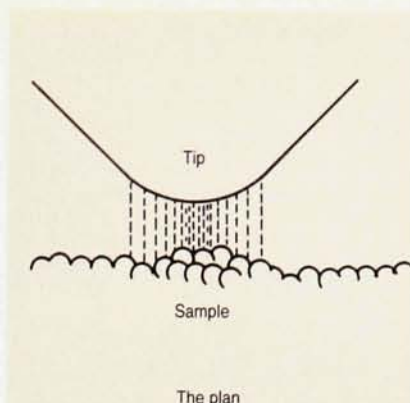
Existing technology. It is intriguing to look back before 1981 to research that hit upon the science and technology used in the vacuum-tunneling microscope but that failed actually to suggest such a device. The possibility of atomic

resolution was not appreciated until members of the group in Zurich carried out their experiments. To do this they had to overcome a number of critical problems—problems that had been solved in a fragmented way by others in laboratories scattered throughout the world. They had to devise a system for controlling the vibrations, but that had been done⁴ before. They had to combine vacuum tunneling with scanning, but others had used scanning. In the late 1970s, Clayton Teague at the National Bureau of Standards used scanning in the "stylus profilometer" to record⁵ three-dimensional images of surfaces with a lateral resolution of 1000 Å. This device measured the profile of a surface by dragging a needle across it. Russell D. Young, also at NBS, used scanning in the "topografiner," a device that scanned surfaces

Sharp tungsten tips. Naturally occurring protuberances reduce the area of the tunneling current, giving the scanning tunneling microscope its atomic resolution. On tungsten needles, the protuberances and the exponential decay of the tunneling current as the tip-to-sample spacing is increased combine to give tips that are in effect less than 10 Å in diameter. The piezoelectric crystal marked z controls the spacing between the tip and the surface under study.

The x and y piezoelectric devices move the tip in a raster pattern across the surface while the tunneling current is monitored and used to create an image. The image is a map of the protrusion of charge density on the surface. The piezoelectric tripod is visible in the photograph on the cover of this issue.

Figure 3



with field-emission electrons and produced images with lateral resolutions of 4000 Å (see Young's article in *PHYSICS TODAY*, November 1971, page 42). Young discussed vacuum tunneling in his *PHYSICS TODAY* article, but he did not pursue the subject in his technical publications. Teague properly demonstrated⁶ vacuum tunneling in his doctoral thesis, but that went unpublished and unnoticed.

The group in Zurich knew that it was possible to view single atoms. That had been done⁷ with the field ion microscope some time ago. But what they could not have known, what they had to discover, was the ease with which one can realize an ultrafine tip. The astonishing first hint of atomic resolution was that the tunneling current was confined to an area small compared with the projected area of the tip of the tungsten needle. Surprisingly, others had also come to this realization. Charles Spindt at SRI International, for example, in his study of field emission from small molybdenum cones concluded⁸ that "the emission from the tip of the cones . . . arises from just one or a few atoms located on the tip." But he did not exploit this for the purpose of imaging.

Field ion microscope

The field ion microscope, the first instrument to achieve atomic resolution, is a non-scanning device that generates images of the atoms on a small plateau at the very tip of a sharp tungsten needle. Both the field ion microscope and the scanning tunneling microscope use sharp tips and tunneling electrons. I have selected three items—the imaging of single atoms, the forming of tips and the "Jason effect"⁹—to illustrate the close relationship between the two instruments.

The field ion microscope has long been used to image single atoms deposited on the atomic plane that forms the apex of the tungsten tip. The images of atomic arrays obtained with the scanning tunneling microscope should come as no surprise when one considers how easily images of single atoms can be

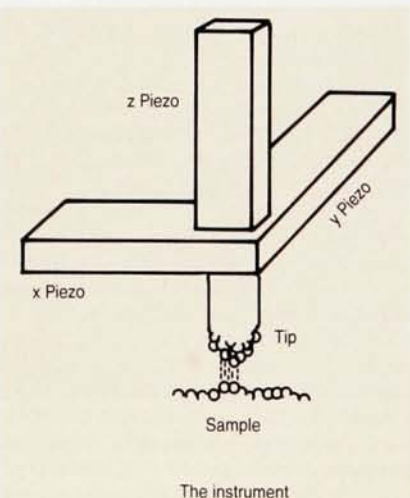
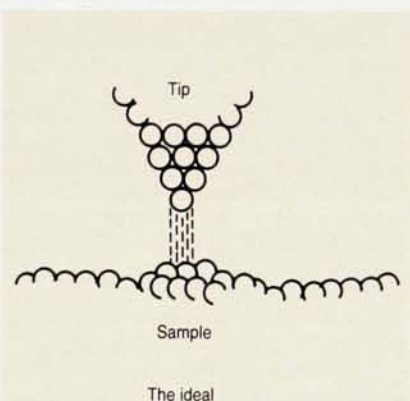
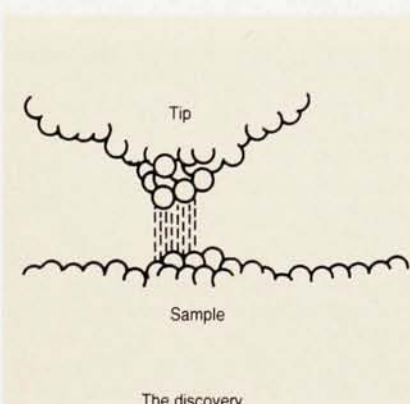
recorded with the field ion microscope.

Tip sharpening is another area where one can discern a relationship between the instruments. The technique for sharpening tips for the field ion microscope is highly developed and is called "field evaporation."¹⁰ In this process a tungsten tip is heated to the temperature where the surface layer of atoms behaves as a liquid. Surface tension in this layer smooths the surface and blunts the extremity of the tip. To circumvent the smoothing one can apply a strong electric field; the atoms then literally evaporate from the surface layer by layer and the tip becomes very sharp.

Hans-Werner Fink at IBM, Zurich, is confident that he can build a stable tip with a single atom at the apex using this technique. Figure 4 shows the result of his first attempt—a tip consisting of a triangle of three, and only three, atoms. Fink should soon achieve his envisioned single-atom tip.

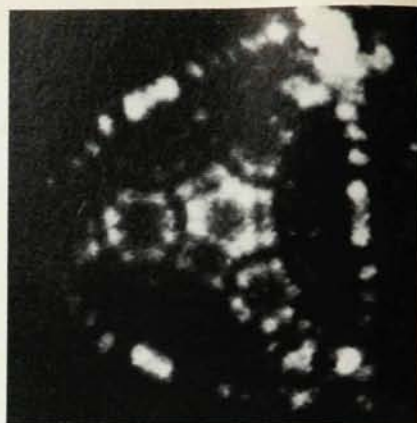
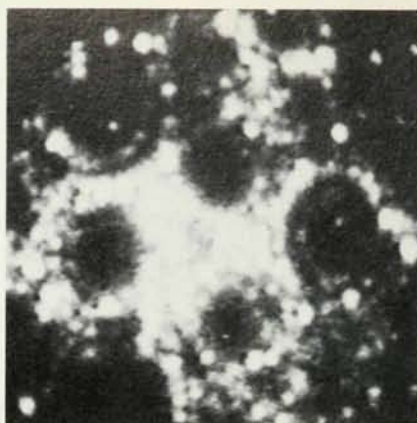
One of the more interesting parallels between the field ion microscope and the scanning tunneling microscope is the Jason effect. In the late 1960s A. J. Jason, in his graduate work with the field ion microscope at the University of Chicago, measured a periodic variation in the energy distribution of ionized atoms leaving the region near the tip. In the field ion microscope, neutral gas atoms encounter high electric fields and are ionized when they approach the tip. The electrons released in this process move from the ionized atom toward the tip, where they are partially reflected. The result is a standing electron wave in the potential well between the ionized atom and the surface of the tip. This standing wave produces the periodic variations measured by Jason.

Similar periodic deviations occur in the energy distribution of electrons emitted from thermionic cathodes, as described¹¹ in a classic paper written almost 40 years ago by Conyers Herring, who was then at Bell Laboratories and is now at Stanford. The emitted electrons leave positive image charges in the surface of the thermionic emit-



Sharpening a tip. These field-ion-microscope images follow a (111) tungsten tip as it is reduced in size through field evaporation. In this process the tip is subjected to a strong electric field of $3 \text{ V/\AA}$ after it has been annealed. Atoms evaporate from the surface, as this sequence shows (left to right), until the final tip (far right) consists of but three atoms. (Courtesy of Hans-Werner Fink.)

Figure 4



ter. These image charges produce a hump, or barrier, in the potential just outside the metallic surface. Electrons leaving the metal surface are partially reflected from this barrier and create the standing waves that produce the periodic variations in the energy distribution.

A similar situation arises in the scanning tunneling microscope when one increases the tip-to-sample spacing. If the spacing is large enough, standing electron waves appear between the sample surface and the tip. These standing waves of charge density produce small, periodic variations in the tunneling current as the voltage on the tip is increased. It would seem that these waves appear whenever there is a free electron in vacuum near a conducting surface. Herring suggests that the effect could be used to study adsorbed layers. My hunch is that the scanning tunneling microscope will prove to be a simple system for implementing his suggestion.

Rapidly developing technology

In the early days of scanning tunneling microscopy most of the results came from Zurich. Other laboratories were exploring the technique, but the quality of their images was uneven. When this situation changed, it changed quickly. It was less than two years ago, at a December 1984 meeting in Cancun, Mexico, that Jene Golovchenko of AT&T Bell Laboratories asked: "Is this science? Can our results be reproduced?" The answer, strongly in the affirmative, came during a July 1985 vacuum-tunneling conference at Oberlech in the Austrian Alps. Every day of that meeting brought new and unexpected reports, ranging from the development of the "pocket microscope" to the use of vacuum tunneling to get detailed answers to questions about the atomic structure of surfaces. Joseph Demuth of IBM in Yorktown Heights, New York, and Golovchenko presented magnificent images of the surface of silicon. By the end of the conference we knew that a powerful new technol-

ogy was available. As Rohrer commented to me: "It's OK now. Everyone seems to be catching on." Indeed, the advances made in 1985 were cited¹² in the Brinkman report as among the most exciting in experimental science since the Bromley report was issued 14 years earlier. The field has developed rapidly: When Binnig began his Oberlech presentation by saying, "At first we didn't realize that it was a microscope," he was thinking back only five years.

Atomic-force microscope. The tunneling microscope, with its requirement for electron current, can be used only to study conducting surfaces. One cannot use it to examine insulators. Binnig recently introduced¹³ a composite device that removes this limitation. He calls it the atomic-force microscope. This microscope features a tip mounted on a small, cantilevered beam. The sample is moved close to the tip and scanned with piezoelectric elements much as is done in the scanning tunneling microscope. The interatomic forces between the tip and the sample deflect the cantilever and this deflection is monitored to determine the force acting on the tip. In the first demonstration of the new device, the tunneling microscope was used to monitor the deflection of the cantilever as the sample was scanned beneath it. The information from the tunneling microscope was used for displaying the image. The resolution was about $30 \text{ \AA}$, but this should soon improve, as several groups are working on new instruments.

Results of research

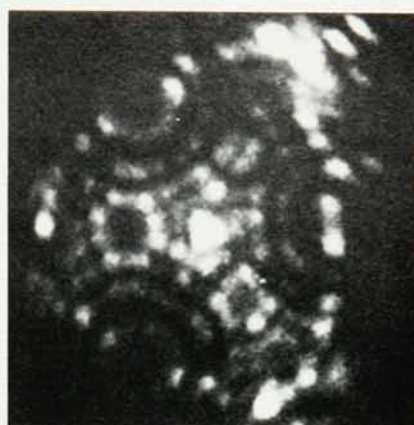
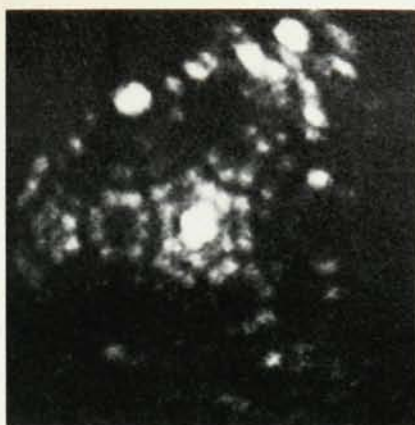
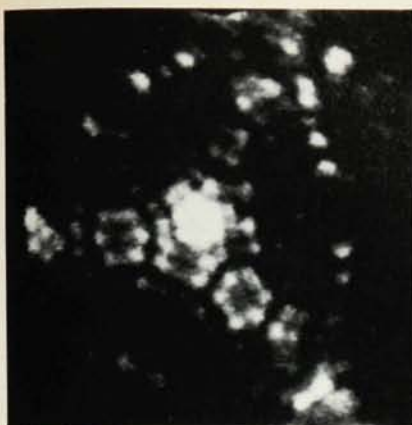
I turn now to some of the problems that investigators have addressed with the scanning tunneling microscope. I begin with graphite, an inert layered structure made up of planes of carbon atoms. The planes are $3.42 \text{ \AA}$ apart and are held together by van der Waals forces. The atoms within the layers are $1.42 \text{ \AA}$ apart and are held together by strong carbon bonds. Graphite is an ideal substrate for the scanning tunnel-

ing microscope because the atomic planes can span more than $1000 \text{ \AA}$ without steps.

With material as flat as graphite it is possible to move the tip over the surface very fast. At Stanford we have demonstrated that the scanning speed can be increased to the point where "real time" imaging is possible. We can record the images directly on videotape. Several groups have shown that it is possible to image materials in air at ambient pressure; ultrahigh vacuum is no longer required. More recently, Paul Hansma and his students at the University of California, Santa Barbara, have shown that the scanning tunneling microscope can produce images of the carbon atoms in graphite when the sample is completely immersed in water. This capability will be important when they begin to image biological molecules in aqueous solution.

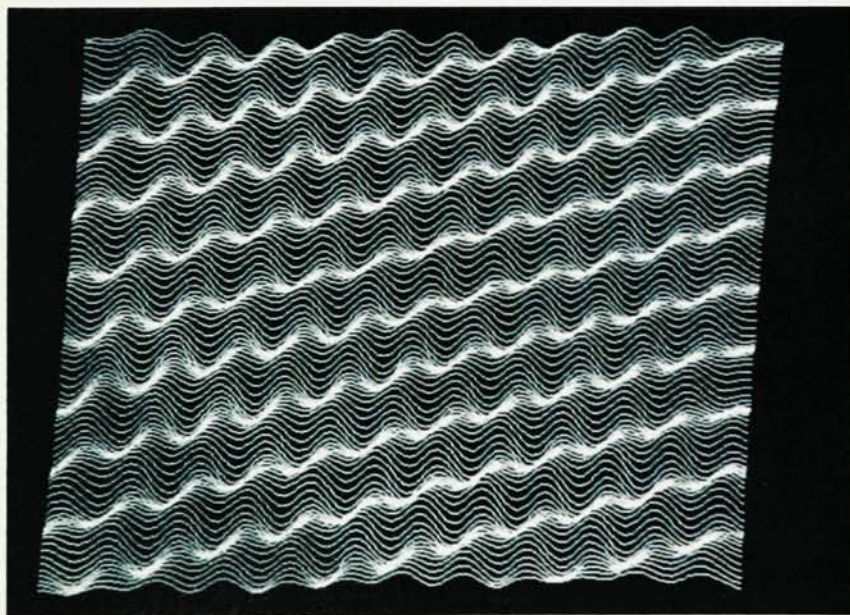
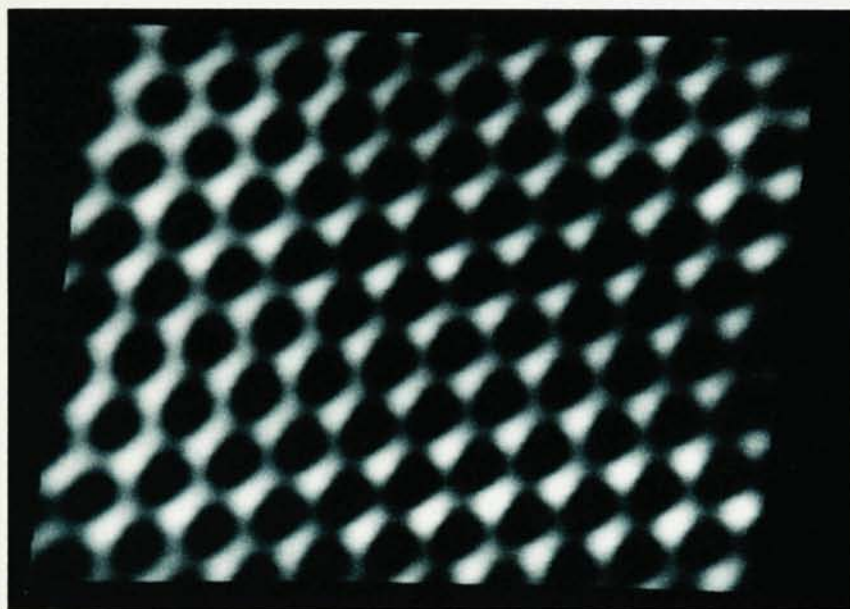
The image in figure 5 shows the basal plane of graphite as it appears on the scanning tunneling microscope operating in air. The most prominent features are the hills and the holes, which form a centered hexagonal array. Some of the atoms in the top two layers are positioned one above the other. Other atoms in the top layer have no counterpart in the next layer down, and the hills, which are areas where the electron wavefunctions extend farthest from the surface, occur at those points. The holes, which are areas where the charge density recedes into the surface by about $1 \text{ \AA}$, occur where the atoms in the second layer have no counterparts in the uppermost layer. In these images the pattern formed by the spatial distribution of the electron wavefunctions is not necessarily a map of the atomic positions. Often the areas of highest charge density coincide with the positions of the atomic nuclei, but there are important cases where this is not true. I will return to this question after I discuss some images of silicon.

Silicon is a technologically important material and its surface will continue to receive a great deal of attention. The



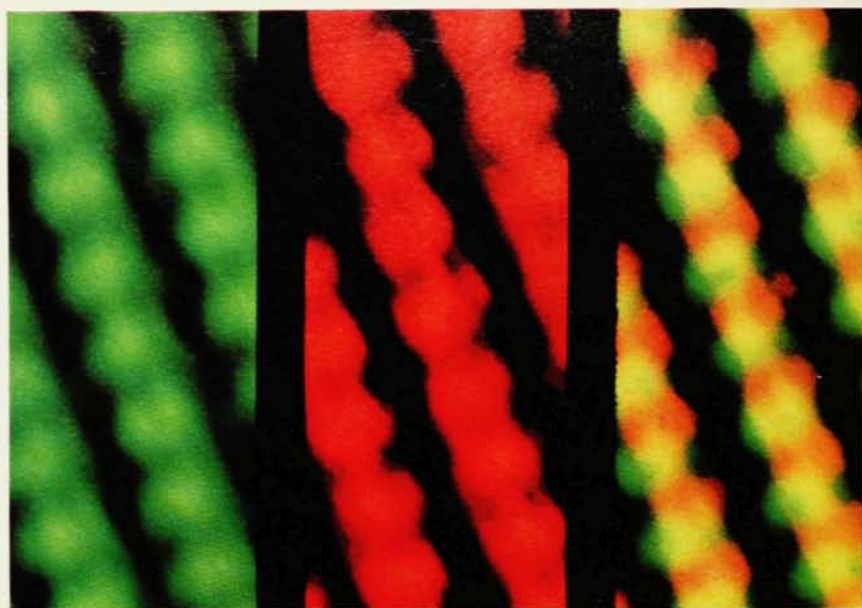
structure of the (111) surface of silicon is more complicated than that of graphite. When the sample is heated above 900 °C, the surface atoms become mobile and the two-dimensional lattice on the surface rearranges in such a way as to minimize the total energy by reducing the number of dangling bonds. The surface is then said to be reconstructed. The reconstruction of the (111) surface of silicon was first observed more than 25 years ago when Jim Lander at Bell Laboratories found 49 additional spots in his low-energy electron-diffraction patterns. (Shuk Y. Tong discusses this in his article in *PHYSICS TODAY*, August 1984, page 50.) The surface undergoes a 7×7 reconstruction; that is, the surface atoms rearrange themselves into a structure with a unit cell whose basis vectors are both 7 times longer than those that describe the bulk material. However, the details of the spatial positions of the atoms in the reconstructed surface eluded Lander. Early in 1983 Binnig published¹⁴ the first scanning-tunneling-microscope image of the reconstructed surface. Many soon realized that this image—now a classic—could provide the missing details. There was a sharp increase in vacuum-tunneling activity throughout the United States and Europe when this image appeared in publication.

Clean surfaces of single crystals consist of terraces and steps. It is well known that the steps play the important role in the various reactions that occur on surfaces. Images from the scanning tunneling microscope can contribute to our understanding of these reactions. Observe, for example, the step on a 7×7 reconstructed (111) surface of silicon in figure 1. This image shows that the reconstruction continues to the very edge of the step. At first this might seem remarkable, but we should realize that it must be this way because the reconstruction actually starts *from* the steps. Russell Becker and Golovchenko of AT&T Bell Laboratories first showed that the scanning tunneling microscope can record these steps with unprecedented



Graphite surface as seen by the scanning tunneling microscope. The bright points in the arrays indicate the positions of those atoms in the uppermost layer that are not directly above atoms in the layer below. These atoms form a centered hexagonal array. Top: Intensity-modulation image. Bottom: Individual traces.

Figure 5



Two surface states. On the (111) surface of cleaved silicon there are two bands of surface states, separated by a gap of 0.45 eV. The lower band lies near the valence band of bulk silicon and is filled. The upper band lies near the center of the bulk gap and is empty. When the sample is biased with -0.7 volts, electrons tunnel into the tip from the filled surface states near the valence-band edge, producing the green image. When the polarity is reversed, electrons tunnel from the tip into the empty surface states in the upper level, producing the red image. The third image, a superposition of the first two, shows both the filled and the unfilled surface states on silicon. The bright spots in the green image occur at points where the red image is dark, and vice versa, illustrating that the scanning tunneling microscope maps charge density, not atomic positions. (Courtesy of Joseph Strosio, Randall Feenstra and Aaron Fein.)

Figure 6

clarity. It is doubtful that this kind of information on the placement of atoms could have been achieved with any other technique.

Surface states. Beyond topography, the scanning tunneling microscope has been used to study surface states on metals and semiconductors. Surface states are states in which the electron wavefunctions are confined to the surface layer. William Kaiser and Robert Jaklevic at the Ford Research Laboratory in Dearborn, Michigan, did some of the first work in this area when they studied the noble metals platinum and gold. These metals are the logical place to start because their surface states have been well characterized with conventional methods. One can use the scanning tunneling microscope to determine the energies of these states by plotting the tunneling current as a function of the voltage on the tip. The locations of the peaks in the derivative of this curve define the energies where the density of states is high. One can record the spatial distribution of a particular surface state by imaging the surface while the voltage on the tip is set for the maximum response to the state under observation.

Randall Feenstra of IBM in Yorktown Heights has in this way recorded the spatial extents of surface states with energies that lie within the band gap of bulk silicon. Feenstra has a facility for cleaving crystals in place and this allows him to study fresh surfaces with the scanning tunneling microscope. Some of his images are quite remarkable. On the (111) surface of cleaved silicon there are two bands of surface states separated by a gap of 0.45 eV. The lower band lies near the valence band of the bulk silicon. That band is filled. The upper band lies near

the center of the bulk gap and is empty. When the sample is biased with a positive voltage, electrons tunnel from the tip into the empty states in the upper level. When the polarity is reversed, electrons tunnel into the tip from the filled surface states near the valence-band edge.

The electron wavefunctions associated with these surface states are standing waves. It turns out that the nodes in the standing wave formed by electrons in the upper level are out of phase with the nodes in the standing wave formed by electrons in the lower level. The electron standing waves are sensed by the scanning tip and the maxima correspond to bright regions in the image. Hence we expect to see a reversal in contrast when the bias on the tip is reversed: The bright regions in the image produced with a positive bias (electrons tunneling into the upper level) should change to dark regions when the bias is reversed (electrons tunneling from the lower level). This is exactly what one sees in the scanning-tunneling-microscope images in figure 6. It is clearly evident that we are measuring the surface charge density, not the topography of atomic positions, because the atomic nuclei are fixed in place at the lattice sites.

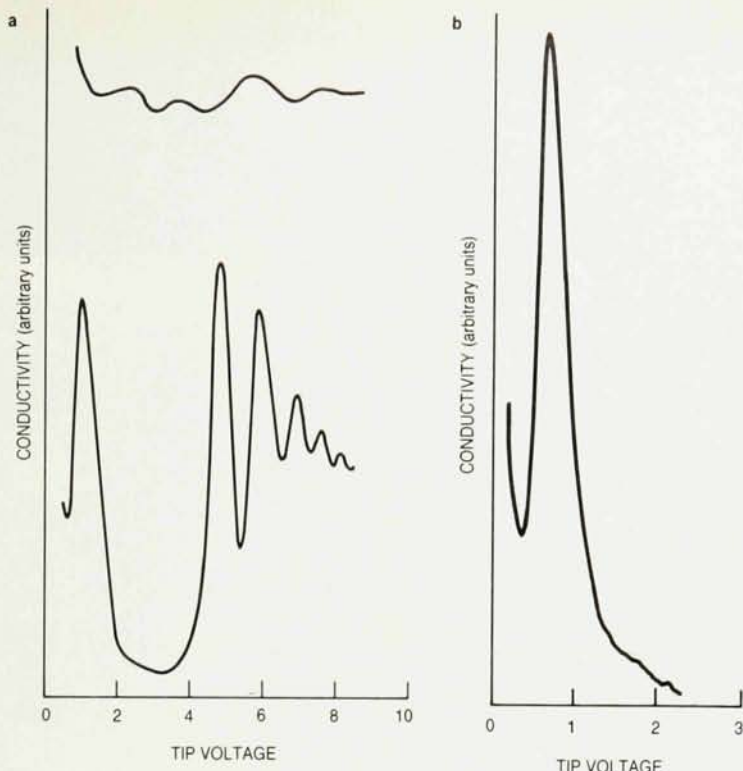
A striking example of surface states in layered structures comes from Frank Salvan of the University of Aix-Marseille II, in Marseilles, France, and his colleagues at the IBM Zurich laboratory. They were interested in the electronic properties of silicon surfaces covered with a monolayer of gold. First they characterized the clean (111) surface of silicon as reconstructed in the 7×7 pattern. They then deposited a monolayer of gold on this reconstructed surface. They varied the gap vol-

tage, monitored the conductivity and observed a strong peak near 1 volt, as figure 7a shows. They assigned this peak to a new surface state because it was not present in the measurement on the clean silicon. It is an easy matter to record spatial variations in this state by scanning the sample with the tip biased to 1 volt. The image in figure 6 illustrates this technique.

Nickel. Binnig's group has used the scanning tunneling microscope to investigate a thin film on a metal substrate, namely nickel oxide on the (100) surface of nickel. They calibrated their system by measuring the conductivity of the surface of clean nickel as a function of the tip voltage, and found nothing unusual. When they moved the tip to an area of the surface covered with a few atomic layers of nickel oxide they observed that the z piezo contracted by 3 Å to maintain a constant current when the tip voltage was held at 1 volt (figure 7b). This change in spacing represents a change in conductivity. Because the tunneling current decreases by about one order of magnitude when the spacing increases by 1 Å, the 3-Å change in spacing indicates a very large increase in conductivity. It is unlikely that this can be attributed to surface states in the nickel oxide. More likely it is associated with some kind of energy-dependent conduction through the thin layer of oxide.

The theory explaining the behavior of nickel oxide has an interesting and controversial history. Nevill Mott mentions¹⁵ this in some of his lectures. He says that "metallic behaviour was predicted. But, in fact, the material is a transparent insulator." The new high-conductivity findings from the scanning tunneling microscope, which disagree with results from some photoe-

Conductivity versus tip voltage for silicon (a) and nickel oxide (b) surfaces. The upper curve in a is for a clean (111) surface of silicon reconstructed in the 7×7 pattern. The lower curve in a is the result of the same measurement after deposition of a monolayer of gold on the silicon surface. The conductivity peak at 1 volt is attributed to an electronic surface state. The conductivity in nickel oxide (b) undergoes a three-order-of-magnitude increase near 0.6 volts. Such a high conductivity is unlikely to be due to a surface state; it is attributed to conduction through the film. (Part a courtesy of Frank Salvan; part b courtesy of Binnig.) Figure 7



mission studies, do not clarify the situation, but rather add to the controversy.

From catalysts to viruses. The work of Jürgen Behm and Wolfgang Hösler of the University of Munich shows the usefulness of tunneling current as a surface probe in a different setting. Behm and Hösler have used the scanning tunneling microscope to study the transformation of the surface of platinum upon exposure to hot ethylene vapor. They chose a region on the platinum surface that was populated with steps. The steps were well separated, so it was possible to distinguish the region near the steps from the flat regions far from the steps. They observed that in the initial stages of exposure to the vapor, carbon atoms were deposited near the steps. As the exposure continued, the carbon atoms extended farther and farther from the steps until they covered the entire terrace. This kind of detail is important in understanding catalytic reactions and illustrates the key role that the scanning tunneling microscope can play.

These examples illustrate the capability of the new technique, but the account is not complete. Robert Coleman and Hansma have used the scanning tunneling microscope at the University of Virginia to observe¹⁶ charge-density waves in TaS_2 at 77 K. The scanning tunneling microscope has also been used at Stanford to study spatial variations in the superconducting energy gap of Nb_3Sn at 6 K. Working on a larger size scale, Nicolas Garcia and his group in Madrid have used the scanning tunneling microscope to study the shapes of viruses and the roughness of their surfaces.

Does the scanning tunneling micro-

scope offer anything beyond the imaging of the electronic structure of surfaces? Perhaps. When we review¹⁷ the history of the scanning electron microscope we learn that it evolved from an imaging device to a system for writing the fine lines in integrated circuits. Some of us believe that the scanning tunneling microscope will evolve in the same way. One day we hope to reach the point where it is possible to manipulate individual atoms or molecules with the tip.

There has already been a start in this direction. Markus Ringger and Hans Gunderodt at the University of Basel, Switzerland, have used the scanning tunneling microscope to write primitive images on a hydrocarbon film with a resolution of 160 Å. Fabian Pease and his student Mark McCord at Stanford have used electron emission from a tungsten tip to develop thin layers of resist. They used a tip potential of less than 10 volts, an energy that is almost within reach of the scanning tunneling microscope. Their work suggests that one day the scanning tunneling microscope will be used to write and read patterns of molecular size.

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