# Atom Tinkerer's Paradise

## Innovations to atom-imaging microscopes create labs on tips

By PETER WEISS

Maybe it was too big—or too small—a leap for his colleagues to fathom. Whatever the reason, the hostility of fellow surface scientists was unvarnished when James K. Gimzewski spoke at a 1985 surface-physics meeting about viewing a single molecule with a new type of instrument—the scanning tunneling microscope.

"They laughed me off the stage. It was new and they hated it," he says.

Microscopists were no more welcoming, says Gimzewski, a physicist at IBM's Zurich Research Laboratory in Rüschlikon, Switzerland, where the scanning tunneling microscope (STM) was invented by his colleagues.

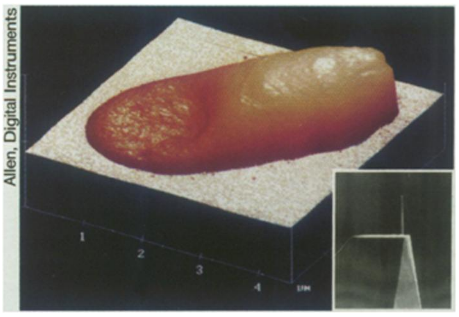
Heinrich Rohrer, who was to share the 1986 Nobel Prize in Physics with IBM colleague Gerd Karl Binnig for his part in the invention, "asked me go to Australia and give a lecture at an international conference on microscopy. All the TEM [transmission electron microscope] guys were shouting and laughing off their heads," Gimzewski recalls.

A dozen years later, these and other pioneers of STM are having the last laugh. The instruments and a host of its offspring, now known collectively as scanning probe microscopes, or SPMs, have become standard equipment in research labs around the globe.

While best known—and most often used—for picturing features as small as single atoms, these atomic probes have acquired a wealth of other talents. Many of the new uses arise from modifications and ingenious tricks devised by determined researchers who regarded the microscopes as an invitation to improvise.

Once skepticism wore off—and the Nobel Prize recognition sank in—scientists realized that an inspiring new terrain had opened up before them. In a world in which atoms could be studied only on average, they had dreamed of seeing and manipulating single atoms and molecules. The ability to touch their objects of study had always been denied to atomic-level scientists—along with the insights and freedom to explore that touching makes possible. Says Binnig, "Atoms are not untouchables anymore."

"What has surprised a lot of people is just how widespread the applications have become," says microscopist Phillip E. Russell of North Carolina State University in Raleigh. Scientists now can use SPMs to measure a wide variety of properties, such as the strength of single chemical bonds. They can also manipulate the atomic world in a growing number of ways—for instance, developing electronic devices made from single molecules and devising new compounds by snipping off atoms.



Allen, Digital Instruments

*Biomedical researchers have adapted atomic force microscopes to measure the volume of sperm heads. They have added a needle (inset), which they tap across the sample to trace contours.*

As Gimzewski puts it, for the atomic and molecular realm, the scanning probe microscope is fast becoming "a laboratory on a tip."

The innovators start from Rohrer and Binnig's basic concepts, now embodied in the two main types of scanning probe microscopes: the STM and the atomic force microscope (AFM). Binnig, Christoph Gerber of IBM, and Calvin F. Quate of Stanford University invented the AFM in 1986.

The STM employs a very fine tip—only one or a few atoms across—connected to a piezoelectric element, a tiny cylinder that lengthens or shortens minutely as the voltage on it changes.

When the probe is within roughly a nanometer of a conductive surface, there is a flow of tunneling current—so-called because the rules of quantum mechanics allow electrons to defy classical physics and penetrate an energy barrier presented by the gap as if they had tunneled through it. The current grows stronger if the tip moves closer.

The instrument is designed so that a measure of the current feeds back to the piezoelectric element. The element adjusts its length to maintain a constant current and thus keep the tip at a constant height, a few angstroms, above the surface. As the tip scans across the surface, it traces a pattern matching the topography below. The landscape shows the shape of atoms but not necessarily their identity.

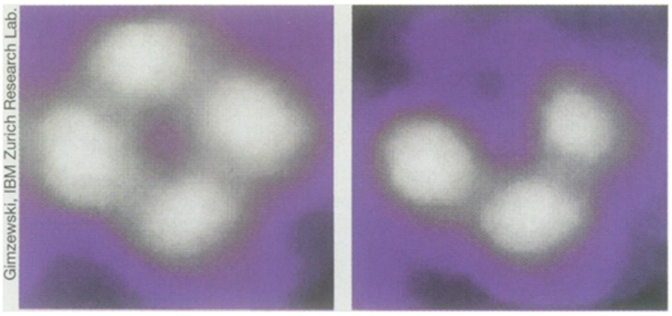
Because the STM can depict only electrically conducting surfaces, its ability to investigate many materials, such as biological samples, is limited. AFMs overcome that restriction. Like the STM, they use an atomically sharp tip, but it is mounted on a cantilever resembling a miniature diving board, which flexes as the various electrostatic forces between the tip and atoms in the sample push or pull. The AFM maps the atomic surface by adjusting the cantilever's height to keep the force on its tip constant.

Many scanning probe microscope innovators have propelled the evolution of the instruments by modifying tips or cantilevers. Some have replaced standard quartz or silicon tips used for imaging with more exotic materials. At Lawrence Berkeley (Calif.) National Laboratory, for instance, a team led by Miquel B. Salmeron uses SPMs with platinum tips to study, on an atomic scale, the catalytic reactions that this metal promotes.

Others have mounted molecules on the tips to interact with the atoms or molecules under study in telling ways. To measure the binding forces within and between single molecules, for example, Hermann E. Gaub and his colleagues at Ludwig-Maximilians University in Munich stick a protein-receptor molecule to an AFM tip. They then bob this tip over a carpet of polymer strands studded with proteins that are mates for the receptor.

By lowering and withdrawing the tip, a technique Gaub calls "fly fishing," the experimenters eventually snag a polymer molecule by the receptor hook. Then they throw the AFM into reverse, using the cantilever not to respond to a force but to exert one, tugging against the bond and measuring the force between hook and fish until molecules deform or break.

Getting creative with cantilevers, Gimzewski and his colleagues conducted a series of experiments in which they made the tiny levers without tips, instead coating the undersides with a layer of material that expands and contracts with temperature, causing the cantilever to bend. Positioning such cantilevers above chemical reactions between atoms on a



Gimzewski, IBM Zurich Research Lab.

*A voltage pulse from a scanning tunneling microscope lops off one lobe of a four-lobed porphyrin molecule (left), transforming it into a new molecule (right).*

surface, the IBM research team was able to measure infinitesimal releases of heat from the reactions.

In another variation of this experiment, they measured humidity by attaching absorbent minerals called zeolites to the end of a tip-free cantilever. As the zeolite absorbs or gives up water, its mass increases or decreases, changing the cantilever's vibration frequency.

Other modifications to the sensing ends of SPMs have made the instruments able to respond to magnetic and electrical fields and flows of ions. Such innovations have proven so useful that whole subgroups of SPMs have sprung up, including magnetic force and magnetic resonance force microscopes, scanning capacitance microscopes, and scanning conducting ion microscopes.

Some researchers have wrung additional performance out of SPMs by expanding the range of conditions under which the instruments work—for example, making machines that operate in extreme cold, maintain extraordinary stability, or make images in the presence of ultrasonic vibrations. Others have combined SPMs with other sorts of sensors, such as optical detectors, to enlarge the instruments' abilities.

At Zhifeng Shao's lab at the University of Virginia School of Medicine in Charlottesville, researchers have built an AFM that works under freezing conditions in which biological molecules become still and relatively stiff, like hard rubber. At room temperature, biomolecules ordinarily wriggle and writhe, making them the bucking broncos of probe microscopy. The sharp tips of SPMs can gouge the often soft surfaces of biological materials, raising questions about the fidelity of images. Using "cryogenic AFM," Shao's team has made extraordinary snapshots of a number of biomolecules.

In the laboratory of Cornell University's Wilson Ho, an STM can detect the vibrational energy of atomic bonds within a single molecule, which provides a way to determine chemical identities. The difficulty has been the need to keep the gap between the tip and the sample so precisely constant that voltage variations induced by atomic vibrations would stand out.

To get the first vibrational readings—from acetylene molecules deposited on copper —Ho and his coworkers doggedly eliminated disturbances. They had calculated that the gap must remain steady to within a thousandth of a nanometer, Ho and his colleagues reported in the June 12 Science. In fact, the machine did 10 times better, says Ho.

Instead of banning vibrations, a research collaboration between the University of Oxford in England and Hewlett-Packard Laboratories in Palo Alto, Calif., has embraced them. In the Aug. 3 Physical Review Letters, a team led by Oxford's Oleg V. Kolosov describes a technique of vibrating a semiconductor sample at 3 megahertz to measure precisely the elasticity of its surface.

The researchers exploit the dual nature of an AFM cantilever: flexible when pushed by a slowly changing force but rigid when the force varies too quickly.

Because the cantilever can't track the oscillations, it stiffly resists them, causing its tip to indent the surface. The cantilever flexes only in response to the slowly varying average contact force. Happily, that average force indicates the surface's softness.

Among researchers pushing to blend SPMs with other types of sensors, Andrew Downes and Mark E. Welland, both of the University of Cambridge in England, have added a light measuring ability. By detecting light emissions from metal atoms stimulated by the STM's tunneling currents, the researchers may have taken a step closer to the long-desired ability to discern an individual atom's chemical identity.

In the May 25 Applied Physics Letters and Aug. 31 Physical Review Letters, the duo described using a sensitive photomultiplier tube and lenses to collect light from a metal sample as it was scanned with the STM tip. They succeeded at distinguishing gold clusters from silver clusters, each just a nanometer across, on the basis of both their emitted light and the voltage across the STM tip at which the emissions began.

In some notable innovations, researchers have left the nuts and bolts of their SPMs untouched, discovering instead novel ways to apply the instruments.

Both Ho and Gimzewski have conducted experiments exploring the mechanical effects of STM tunneling current on molecules. They have shown that current puls-

## Atom-viewing 101: Make STMs at home

For all the sophisticated science that scanning tunneling microscopes (STMs) have spawned, they require surprisingly little technological sophistication to build.

"It's very simple technology," says Phillip E. Russell, a scientist at North Carolina State University in Raleigh who runs the school's scanning-probe-microscopy program. "In my short course, I tell you how to do it with Radio Shack parts." The absence of lenses makes STMs relatively simple. Moreover, remarkably sensitive but widely available piezoelectric elements—common parts of doorbell buzzers and charcoal spark lighters—can give subnanometer control of motion.

High school and even middle school students and their teachers seem to grasp the microscope's concepts, and "they are not afraid of it," says Russell.

One brave builder was in high school when he cobbled together in his bedroom an STM out of Legos and bungee cords. Adam Ezra Cohen of New York built the device for a pittance—about $50, he estimates—and with no microscope-building experience.

Make no mistake. Cohen, now 19, is not your run-of-the-mill home tinkerer. Before graduating high school, he had already compiled a file of more than 140 invention ideas, invented an electrochemical data-storage device and an eye tracker used in neurology research, and won the $40,000 first-place scholarship in the 1997 Science Talent Search (SN: 3/15/97, p. 159). He won the grand prize for both building the STM and devising a way to use it as an "electrochemical paintbrush" that deposits tiny lines of metal on surfaces.

Yet, looking back, Cohen comments that "I don't think this project is too tough for anybody." The key is being willing to devote a lot of time to the task, he says. He worked an hour or two a day for 8 months to build his STM.

Other high schoolers have tackled STM projects, but usually as teams. At the Peddie School in Hightstown, N.J., for instance, a dozen seniors worked through the 1997–1998 school year with their physics teacher Nicholas R. Guilbert to design and build an STM. This spring, however, they donned their caps and gowns without having seen a single atom. Despite the disappointment of not finishing, "we learned an awful lot," Guilbert says. "The whole idea of tunneling gets into the quantum world, which for high school students is a real mystery."

"The almost revolutionary part of this," Russell says, is that "it has opened up imaging and measuring on a small scale to everyone." *—P.W.*

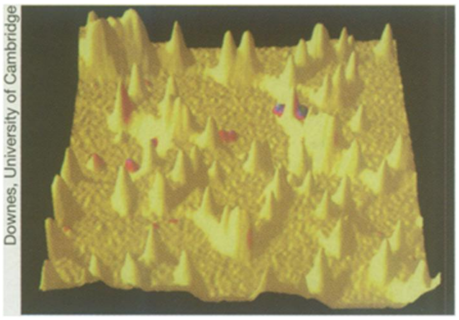
es can cause molecules to rotate, possibly enabling researchers to position individual molecules precisely for a chemical reaction at a particular bond.

Gimzewski has also used an STM as an atomic knife, cleaving an atom off the four-lobed porphyrin molecule. That technique also holds promise for making novel compounds and chemical reactions possible, he says.

Gimzewski and other researchers have used the STM tip to create some of the first ultrasmall electronic devices, using molecules or atoms as circuit components. For instance, by pressing on a $C_{60}$ molecule, also known as a buckyball, with an STM tip, Gimzewski induced it to act as a voltage amplifier, controlled by the current from the STM tip.

A number of experiments in biology have used AFM tips to "feel" changes in the softness of membranes, Binnig says. His research group, for instance, used AFM scans to detect a sudden softening of a cell's walls as a virus penetrated its defenses.

Biology researchers have just begun to recognize that with AFM's ability to map contours comes a new way to measure volumes—of sperm heads, for instance. Michael J. Allen of Digital Instruments in Santa Barbara, Calif., which produces off-the-shelf SPMs, and his colleagues at Lawrence Livermore (Calif.) National Laboratory have used AFM to determine that sperm with abnormal heads, like 25 to 40 percent of human sperm, have no shortage of DNA and other material packed within. These scientists use an unusually long, thin tip and tap it along the surface of the sample instead of dragging it as with a normal tip.


Downes, University of Cambridge

*Microscopists can distinguish metal particles such as silver (red dots) from nonmetals (yellow) by simultaneously measuring light emissions excited by the scanning tunneling microscope probe.*

One yet-to-be-achieved SPM innovation promises what none of the others can—atomic imaging in three dimensions and, perhaps, chemical identification on that scale as well.

Magnetic resonance force microscopy (MRFM) applies the same principles used by hospital magnetic resonance imaging machines, which provide three-dimensional views of internal soft tissues by detecting the spins of quadrillions of atomic nuclei at a time. MRFM, however, aims to locate individual atoms this way, which means detecting the faint magnetic field of a single, spinning nucleus.

A team led by Dan Rugar at IBM Almaden Research Center in San Jose, Calif., is developing extra-long, thin AFM cantilevers with magnetic tips. Their mechanical vibration frequency is expected to change slightly in response to the force from a single electron's magnetic spin. While only a millionth the force typically measured by AFMs, an electron's spin exerts a thousand times more force than the lone nucleus, the researchers' ultimate goal.

"We're quite a ways from the dream of 3-D pictures of molecules," Rugar says. "The electron-spin work is a step toward that."

While seeing individual atoms with MRFM is a distant goal, Michael L. Roukes of the California Institute of Technology in Pasadena says his lab is striving to build a less ambitious MRFM instrument that could be used for examining the magnetized layers within read-write heads in computer hard-disk drives. Although it would not provide resolution at the atomic scale in all directions, it could explore depth with nearly that precision, he says.

Scanning probe microscopes have enabled discovery at the atomic scale. They have also inspired a torrent of toolmaking that has yet to run its course. ☐