Scanning the Surface

From gold atoms to benzene molecules, the scanning tunneling microscope probes the intricate structure of surfaces

By IVARS PETERSON

"The surface was invented by the devil," said the late physicist Wolfgang Pauli in expressing his frustration with the complexity of surfaces.

Unlike atoms inside a solid, which lie nestled within cocoons of congenial companions, surface atoms stand guard at the frontier between the solid and the rest of the world. They reside in a radically different environment, which means a solid's surface properties differ considerably from those of its interior. That difference has long thwarted attempts at building a precise theoretical and empirical picture of what happens at surfaces.

In the scanning tunneling microscope, researchers now have a surprisingly simple but versatile tool for probing the complexities of surface structures, atom by atom. Already important for investigating the atomic and electronic structure of semiconductor surfaces, the technique reveals contaminants and flaws in the surface structure of materials such as silicon — information that may be valuable for designing faster integrated circuits. Now scanning tunneling microscopy is destined to play an equally important role in studies of the molecular and chemical properties of a wide range of solid surfaces. Surface structure largely determines many crucial properties of materials, including their reactivity, resistance to corrosion and electronic behavior.

"We can observe which surface atoms have reacted and which have not, and determine how the products of the reaction are distributed on the surface," says Phaedon Avouris of the IBM Thomas J. Watson Research Center in Yorktown Heights, N.Y. "This unique capability brings new insight to our understanding of surface chemistry."

The brief time between its invention and its present widespread use demonstrates the microscope's impact. In 1981, the scanning tunneling microscope was a one-of-a-kind scientific instrument. Five years later, its inventors, Gerd K. Binnig and Heinrich Rohrer of IBM's Zurich (Switzerland) Research Laboratory, received the Nobel Prize for their work (SN: 10/25/86, p.262).

Today, more than 100 laboratories worldwide have either built their own versions of the instrument or purchased them from commercial sources. It's difficult to pick up an issue of a journal such as PHYSICAL REVIEW LETTERS without seeing some mention of scanning tunneling microscopy.

In a scanning tunneling microscope, an extremely sharp metal needle, ideally terminating in a single atom, is brought within a few angstroms of the sample's surface. This distance is small enough for electrons to leak, or tunnel, across the gap between sample and needle and generate an electrical current. As the gap between the tip and the sample increases, the current decreases. A scanning mechanism pulls the needle over the sample's surface, constantly adjusting the tip's height to keep the current constant.

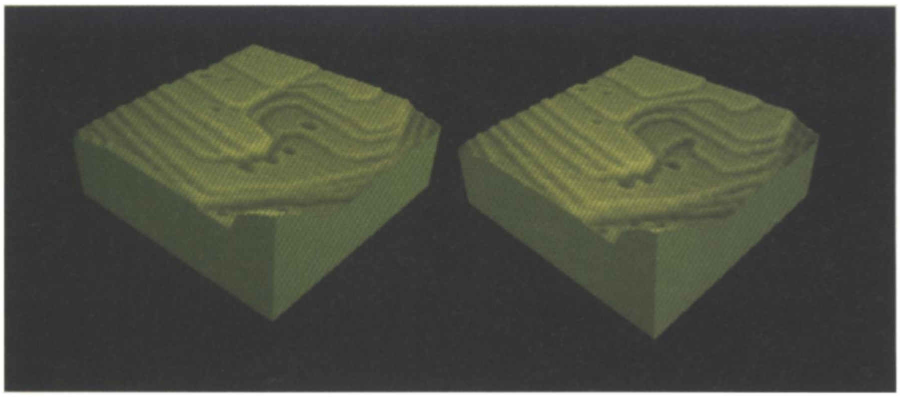
The needle's bobbing journey produces a sketch of the surface's microscopic contours — a kind of topographic map in which the hills and valleys represent arrays of atoms. The instrument is so sensitive to the separation between tip and surface that it can detect differences in height equivalent to one-hundredth of an atomic diameter. The horizontal resolution depends on the needle's sharpness.

Data from a set of scans initially appear as rows of contour lines. Computer processing of that information converts the lines into filled surfaces, rendered in shades of gray as if illuminated by some ethereal light source. Sometimes adding color emphasizes important details or produces an elevation map in which different colors represent different heights.

Interpreting the images is still an art. The microscope doesn't identify what atoms are present. Moreover, the tunneling current observed depends on a number of factors, including the nature of the surface, the needle's geometry and composition, and the electronic properties of both the surface and anything that sits atop it. In addition, the needle itself may sometimes modify the surface, gouging it by pushing aside atoms or molecules.

The microscope works best with substances that readily conduct electrons. For this reason, much early work focused on materials such as silicon, gallium arsenide and graphite (SN: 9/6/86, p.149). On the other hand, many biological materials transfer electrons poorly and can't be examined in a straightforward manner using the scanning tunneling microscope.

When researchers started making images of graphite and gold surfaces in air, the absence of contaminating molecules that were bound to settle on exposed surfaces puzzled them. These molecular visitors seemed invisible to the scanning tunneling microscope.



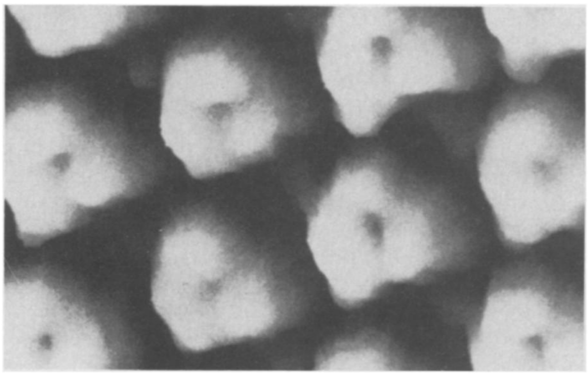
AT&T Bell Labs

In these images of a gold surface, the scanned region is 2,000 by 2,000 angstroms and the terraces are 1 atom high. The two images, separated by 2 minutes in time, show the motion of terrace edges and electrochemically formed pits. During this interval, one of the pits joined with a terrace edge — part of the smoothing process by which the electrochemically roughened surface returns to its original form.

Investigators speculated that perhaps such molecules diffuse along the surface too rapidly to be caught by the microscope. Alternatively, the microscope's needle may physically push molecules aside, or the molecules themselves don't participate in the electron tunneling process. Further studies showed all three mechanisms at work, and researchers soon developed methods for circumventing such problems and capturing images of otherwise elusive visitors.

One recent success was the detection of benzene and carbon monoxide molecules — both highly mobile and electrically insulating — on a clean metal surface. Robert J. Wilson and his colleagues at the IBM Almaden Research Center in San Jose, Calif., got their images by depositing a layer of closely packed benzene and carbon monoxide molecules on a carefully smoothed rhodium surface. The carbon monoxide molecules help wedge the benzene molecules in place to keep them from moving along the surface and blurring the image. Having two different types of molecules packed together in the same array allowed the researchers to study for the first time how strongly different molecules show up in a scanning tunneling microscope image under the same experimental conditions.

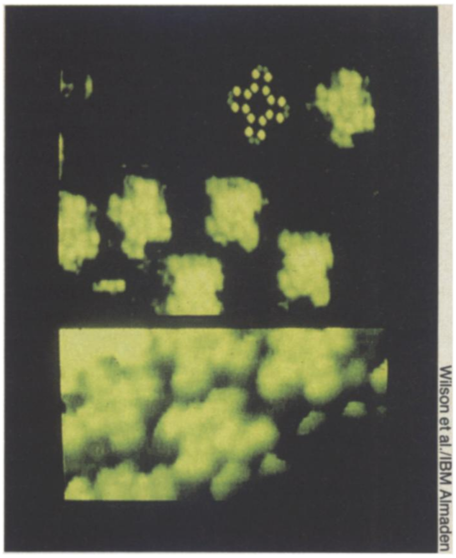
Each ring-shaped cluster represents a single, hexagonal benzene molecule.



IBM Almaden

Images of the structure revealed individual benzene molecules as threefold ring-like features, confirming the traditional picture of benzene molecules as rings of six carbon atoms. The researchers also observed the movement of individual benzene molecules from site to site within disordered regions. Though barely visible, carbon monoxide molecules appeared as very small protrusions between benzene molecules within ordered regions.

Wilson and his colleagues also made the first tunneling-microscope images showing the internal structure of an isolated molecule on a surface to illustrate this technique's potential for observing individual molecules. Earlier experiments had produced detailed images of molecules only in closely packed arrays. In this case, the researchers looked at a distinctively shaped molecule called copper phthalocyanine, a blue pigment, "mounted" atop a metal surface.

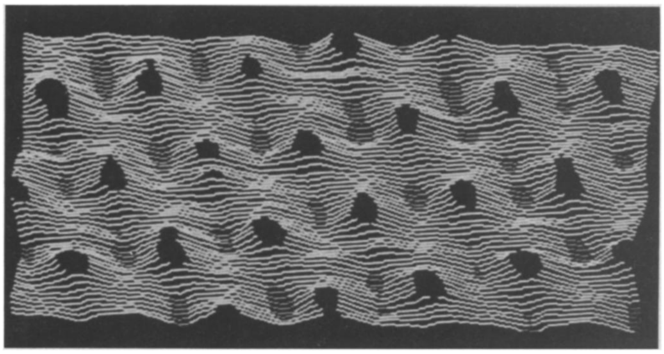


Wilson et al./IBM Almaden

The image above shows the distinctive four-leaf-clover shape of a copper-phthalocyanine molecule lying atop a copper surface. Isolated molecules don't sit on the surface randomly but instead assume one of two possible orientations. The lower half of the picture shows more of the detailed structure of each molecule.

Images of copper phthalocyanine molecules deposited on silicon or graphite surfaces are blurred, indicating that weak bonding or chemical interactions between the molecules and the surface allow the microscope's needle to shift the molecules. In contrast, microscope images of a copper surface clearly reveal the molecule's fourfold symmetry—a pattern resembling a four-leaf clover. Moreover, although the phthalocyanine molecules lie flat, they prefer to rest among the neatly ordered copper atoms in one of two particular orientations. Wilson and his co-workers report their observations in the Jan. 9 PHYSICAL REVIEW LETTERS.

Tycho Sleator and Robert Tycko of AT&T Bell Laboratories in Murray Hill, N.J., were among the first to study in detail individual organic molecules at a crystal surface. They worked with the electrically conducting organic molecule tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ). At low magnification, the researchers saw a terraced surface with steps about 10 angstroms high. Each step appeared to correspond to the addition or subtraction of a single molecular layer. Under a higher magnification, they detected parallel rows of objects, each consisting of a large ball, about 3 angstroms in diameter, with two smaller balls on either side. The researchers interpreted these structures to be the TCNQ parts of the molecules, in which the large ball is a ring of six carbon atoms and the smaller balls are nitrogen atoms.



IBM Thomas J. Watson Research Center

In this scanned image of a graphite surface, the gray "hilltop" areas show the locations of individual carbon atoms.

High-temperature superconductors haven't escaped the probing gaze of the scanning tunneling microscope as scientists seek to demystify their unusual characteristics. Michael D. Kirk and his colleagues at Stanford University studied a superconducting concoction consisting of bismuth, strontium, calcium, copper and oxygen. They found evidence for a complex crystal structure that may play an important role in determining the material's superconducting properties. Their results appear in the Dec. 23 SCIENCE.

Normally, crystals have a regular structure consisting of identical groupings of atoms, called unit cells, that stack together like building blocks. X-ray scattering experiments show that in the bismuth superconductor, the unit cells do not fit together precisely.

By obtaining tunneling-microscope images of the superconductor surface, the researchers discovered that every ninth or tenth row of bismuth atoms is missing from the regularly repeating pattern of atoms in the material. The absence of the bismuth causes nearby oxygen and copper atoms to shift out of their usual positions, distorting some of the unit cells. Because superconducting properties are very sensitive to the positions of copper and oxygen atoms, such distortions may affect the material's superconductivity. Whether the "defect"

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"The startling thing about Biomuse is that you actually can listen to yourself, to your body, make music, and you can quickly learn to manipulate the sound," Lusted remarks. John Chowning, director of Stanford's Center for Computer Research in Music and Acoustics (CCRMA) and a professional trumpet player, quickly learned to produce specific signals just by flicking his finger.

"Being able to switch the sound from a string sound to a glockenspiel sound by changing from visual to nonvisual thought – that was really bizarre," says Lusted, who has the most on-line Biomuse experience to date. "I got good enough at this that I didn't need to close my eyes; I could just think black." In a future generation of Biomuse, the Stanford inventors would like to extract more subtle qualities from brain wave signals so that someone would be able to precisely control the music exclusively with thought. "The idea is to think violin and get violin," Knapp says. "But we're only a billionth of the way there."

At CCRMA on March 23, the scientists staged a demonstration performance of what actually is the second generation of Biomuse systems, though it's the first system that will work in nonlaboratory settings such as stages and therapy rooms. In 1987, only three weeks after Lusted and Knapp discovered their common interest in learning to play the body electric, they had in hand Biomuse I, an awkward-looking gizmo slapped together with parts lying around their laboratories. "It was a back-of-the-envelope mess," Knapp recalls. The electronics were so specialized that only Knapp could program the device. Moreover, it worked only intermittently and in extremely controlled places like laboratories. Anywhere else the input signals would fluctuate wildly, making it impossible for the electronics to make sense of them.

The two scientists since have developed Biomuse II, which they rate as far more stable and reliable. And anyone who has access to MIDI software for a personal computer will be able to program Biomuse II, Knapp says. Representatives from computer companies, electronic instrument companies and other organizations like the Center for Electronic Music attended the March 23 demonstration.

But CCRMA's computer music composers may be among the first to explore Biomuse's artistic possibilities. Instead of using fingers, breath and lips to play instruments, Biomuse "attempts to harness other bodily means of sound control," says CCRMA director Chowning. He expects its primary value for composers to rest in controlling sound features other than notes, things like the localization of sound source, overall loudness and timbre changes. "The ultimate applications probably are not obvious," Chowning adds.

Besides its musical applications, Biomuse technology may help disabled people get jobs by enabling them to control computers without needing fine motor control. "We're looking for alternate means by which patients can work using computer technology, but without needing complicated skills," says Nagler of the Center for Electronic Music. He and the Stanford inventors are considering using EOG signals to allow disabled patients to move the cursor around the screen like an "eye-controlled mouse."

"There are many things we have thought about doing with Biomuse but haven't tried yet," Lusted says. For one, he wants to hook Biomuse up to plants, which have their own brands of bioelectric signals. In animals, transforming bioelectric signals into musical analogs by hooking the animals up with the Biomuse might make for a painless window on their behavior, and would be especially intriguing with highly auditory animals such as dolphins, he suggests. In the world of dance, Biomuse-fitted performers soon might be able to produce sounds that follow their moves as closely as a shadow. "The possibilities are endless," Lusted says. "That makes it hard to decide what to try first." ☐

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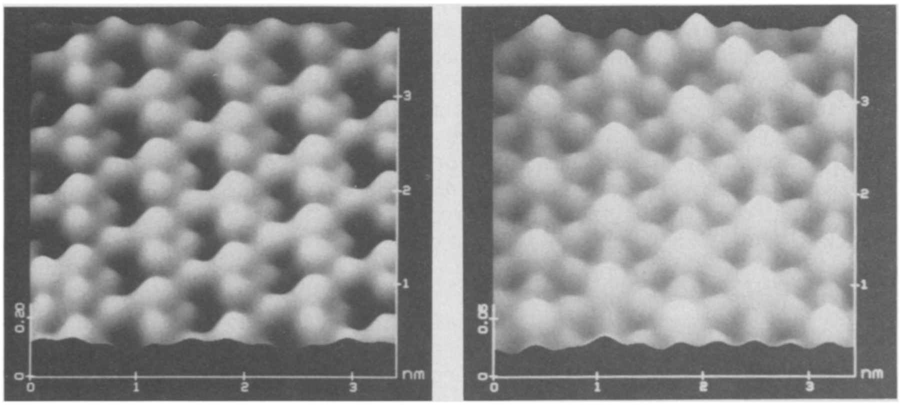
enhances or hinders the material's superconductivity isn't clear yet.

Researchers have also used the scanning tunneling microscope to study the growth, dissolution or rearrangement of crystalline surfaces over the course of electrochemical reactions to gain a more detailed understanding of processes such as corrosion. In the Feb. 20 PHYSICAL REVIEW LETTERS, Dennis J. Trevor and his collaborators at AT&T Bell Laboratories in Murray Hill, N.J., report the results of an investigation of electrochemically induced changes at a gold surface.

The researchers looked at a crystalline gold sample immersed in perchloric acid. In their experiments, they gradually raised, then lowered, the voltage applied to the gold surface, first causing surface gold atoms to react with oxygen, then returning the gold to its pure state. After such a cycle, microscope images of what was originally a smoothly terraced surface reveal pits of various diameters, each usually only one gold atom deep. Within 20 minutes or so, terrace edges shift and pits gradually fuse together and join terrace edges, as gold atoms apparently rearrange themselves to smooth out the surface. The presence of chloride ions seems to speed up the smoothing, or annealing, process.



Schardt et al./SCIENCE

This pair of computer-processed images shows two different arrangements into which iodine atoms can organize themselves on a platinum surface.

Recently, chemist Bruce C. Schardt and his colleagues at Purdue University in West Lafayette, Ind., observed the deposition of iodine on single crystals of platinum in air. They picked out two different packing arrangements into which iodine atoms settle on such a surface.

On the basis of previous studies using other techniques, the researchers did not expect to find two such structures. "This study is a graphic illustration of the value of real-space imaging provided by the [scanning tunneling microscope]," they report in the Feb. 24 SCIENCE. It's also a striking example of the resolution obtainable with such a microscope operating in air.

The number of potential applications for the scanning tunneling microscope keeps growing. Physicists, engineers, chemists and biologists are starting to use this instrument for probing the structure of biologically important molecules such as DNA (SN: 1/28/89, p.53), monitoring the formation of thin films on metals (SN: 1/28/89, p.62) and many other purposes. Industrially, such microscopes guide the manufacture of magnetic recording heads and the production of nickel stampers used to make the tiny depressions carrying the information stored on compact disks.

In the scanning tunneling microscope, Pauli's devilish surfaces may have met their match. ☐